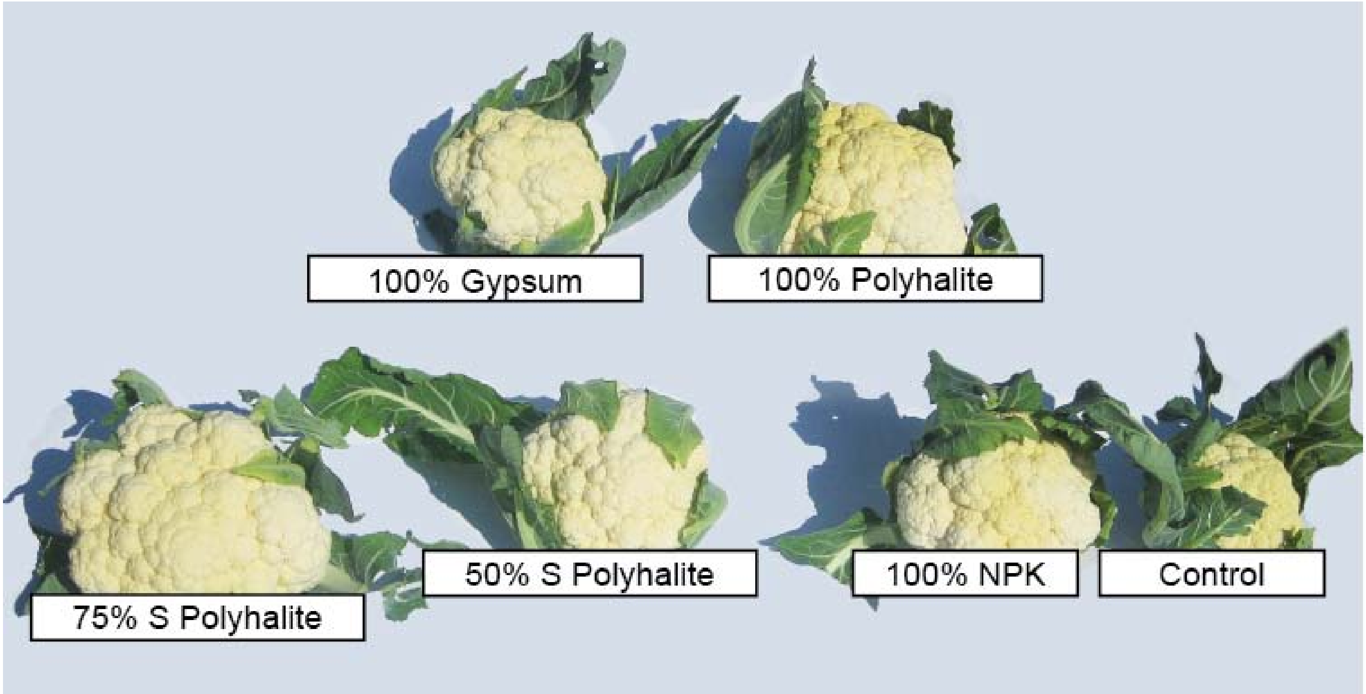
Research Findings



Bioefficacy of Polyhalite Application on Yield and Quality of Cabbage and Cauliflower

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Abstract
Sulfur (S) has been recognized as an important plant macronutrient, associated with high yield and quality, particularly in crops of the Brassica genera. Polyhalite is a natural mineral which occurs in sedimentary marine evaporates, consisting of a hydrated sulfate of potassium (K), calcium (Ca) and magnesium (Mg). The objective of this study was to test the bioefficacy of polyhalite on the performance of two major *Brassica oleracea* cole crops in India, cauliflower and cabbage. Sulfur application gave rise to significantly increased yield and quality of the two crops. Potassium enhanced S uptake, while in turn, S appeared to promote phosphorus (P) and Ca uptake. The highest yields of cabbage and cauliflower, 32.8 and 39.5% more than the control, respectively, were obtained with 100% and 75% of the recommended N-P-K and S doses, respectively, delivered through polyhalite. Possible reasons for the failure of a 100% S dose, either through polyhalite or gypsum, to further increase yield attributes are discussed. More research is required to adjust nitrogen (N) and K fertilization practices where S administration takes place.

Introduction
Sulfur (S) is recognized as the fourth major plant nutrient after nitrogen (N), phosphorus (P) and potassium (K) (Khan *et al.*, 2005), and has been associated with high production goals (Zhao *et al.*, 1999; Hawkesford, 2000; Saito, 2004; Jamal *et al.*, 2010; Kovar and Grant, 2011; Steinfurth *et al.*, 2012). A good response to S application has been reported with respect to crop yield related to the Brassica genera (McGrath and Zhao, 1996; Gironde

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et al., 2014; Tiwari *et al*., 2015), and particularly to cole crops (*Brassica oleracea*) (Susila and Locacsio, 2001).

Brassica oleracea is a major edible crop worldwide that includes several morphologically distinct subtaxa, such as acephala (kale/collards), alboglabra (oriental kale), botrytis (cauliflower), capitata (cabbage), gemmifera (Brussels sprout), gongylodes (kohlrabi), italica (broccoli/calabrese), sabauda (Savoy cabbage) and sabellica (borecole/curly kale), in which the entire shoot is generally harvested (Broadley *et al*., 2008). Over the last three decades, crops in the Brassicaceae have been the focus of intense research based on their human health benefits (Stoewsand, 1995; Björkman *et al*., 2011). Sulfur-containing secondary metabolites, such as glucosinolates and others, have been associated with some anti-cancer activities (Cartea and Velasco, 2008; Sarıkamış, 2009) and with a reduced risk for degenerative diseases, cardiovascular diseases and diabetes (Björkman *et al*., 2011, and references therein). Some S-containing compounds are desired as flavor components in cooked Brassica vegetable products (Schutte and Teranishi, 1974; Engel *et al*., 2002). Glucosinolates contents largely depend on S availability and significantly varies with S fertilization (Falk *et al*., 2007).

Nevertheless, crop responses to S application have been found to also vary widely due to differences in location, soil type, various S-containing compounds in the soil and consequent S availability, crop genotype, environmental conditions and crop management (Björkman *et al*., 2011). Cole crops have a significant S requirement and, where the availability of this mineral is limited, crop yield and quality often decline (McGrath *et al*., 1996; Haneklaus *et al*., 2008). Over the last 20 years, due to strict regulations against industrial S emissions, the yearly global S atmospheric deposition has significantly declined (Kovar and Grant, 2011). During the same time, demands for food production have increased with the growing human population. Subsequently, requirements for S fertilizers have risen dramatically to meet annual crop demands.

Sulfur-deficient plants are typically small and spindly, characterized by interveinal chlorosis of young developing leaves that may become curved and brittle and eventually may fail to grow (Haneklaus *et al*., 2008). The chlorosis is very characteristic in that the veins stand out as a rather blurred, blue-green pattern against a pale green background. On the abaxial (lower) side of the leaf, these dark areas are purple, and this coloration may later spread to the whole leaf. Symptoms tend to develop slowly. In Brussels sprouts, characteristic symptoms include yellowing tops and restricted rooting. Sulfur deficiency is likely to occur in soils that have low levels of organic matter, light-textured sandy soils that have been leached by heavy rainfall or excessive irrigation, soils exhausted by intensive cropping, and soils derived from parent material that is inherently low in S (Jordan and Reisenauer, 1957).

Polysulphate (Cleveland Potash Ltd., UK) is the trade mark of the natural mineral 'polyhalite', which occurs in sedimentary marine evaporates, and consists of a hydrated sulfate of K, calcium (Ca) and magnesium (Mg) with the formula: $K_2Ca_2Mg(SO_4)_4 \cdot 2(H_2O)$. The deposits found in Yorkshire in the UK typically consist of 14% K_2O, 48% SO_3, 6% MgO, and 17% CaO. The S content of gypsum, a common S and Ca supplement alternative, is only 18.6%.

Map 1. Experimental site in India, Karantaka State, at Hessaraghatta, north-west of Bengaluru. *Source:* Google Maps.

The objective of this study was to test the bioefficacy of polyhalite on the performance of two major cole crops (cauliflower and cabbage) in India.

Materials and methods

Field experiments were conducted at the experimental research farm (Block 5) at the Indian Institute of Horticultural Research (IIHR), Hessaraghatta, Bengaluru, Karnataka between October 2013 and March 2014. Cabbage (cv. Tetries) and cauliflower (cv. Unathi) were sown in portrays with fermented coco peat as a rooting medium, and the seedlings were raised in a greenhouse.

The experimental fields were thoroughly ploughed and levelled. Farm yard manure (FYM) was applied at 25 Mg ha^{-1} in the last plough. The recommended dose of fertilizers (RDF) was 150 kg N, 100 kg P_2O_5 and 125 kg K_2O ha^{-1}, and 20 kg S ha^{-1} was also applied as per the treatments. Initial soil samples from the experimental fields were collected before application of FYM and basal doses of fertilizers (Table 1). Transplanting was carried out on 28 October 2013. Appropriate plant protection measures were taken for control of different pest and diseases throughout the cropping period.

The experiments, laid out in a randomized block design with three replicates, included six treatments:

- T_1: Control without S and K fertilization (100% NP only through Urea, DAP).
- T_2: 100% NPK (Urea, DAP, Muriate of Potash (MOP)).
- T_3: 100% NP + 50% S through polyhalite (balanced K through MOP to make 100% K).
- T_4: 100% NP + 75% S through polyhalite (balanced K through MOP to make 100% K).
- T_5: 100% NP + 100% S through polyhalite (balanced K through MOP to make 100% K).
- T_6: 100% NPK (Urea, DAP, MOP) + 100% S through gypsum.

Five plants from each plot were randomly selected periodically (30 and 60 days after transplanting (DAT) and towards harvest)

Table 1. Physico-chemical characteristics of the soil at the experimental site.

Particulars	Value
Particle size analysis (over dry basis)	
Sand (%)	69.6
Silt (%)	9.9
Clay (%)	20.5
Textural class	Sandy clay loam
Soil classification	Typic haplustepts
Chemical properties	
Soil reaction (1:2.5)	6.84
Electrical conductivity (dS m^{-1})	0.125
Organic carbon (g kg^{-1})	11.5
Available nutrients	
Nitrogen (kg ha^{-1})	268.7
Phosphorus (kg ha^{-1})	47.8
Potassium (kg ha^{-1})	298.8
Sulfur (ppm)	16
Exchangeable cations (cmol (p+) kg^{-1})	
Calcium	4.8
Magnesium	0.35
DTPA extractable micronutrients (mg kg^{-1})	
Iron	25
Manganese	9
Zinc	0.8
Copper	2

Photos 1. General view of cabbage (left) and cauliflower (right) experimental fields at Block 5 of IIHR farm. Photos by authors.

and used for growth/biometric observations, such as plant height and number of leaves per plant. Plant height was measured from the base of the plant to the base of the fully opened top leaf.

Crops were harvested after complete maturity, when heads/curds were firm and compact. Yield per plot was expressed in Mg ha^{-1}. Five randomly selected plants from each plot were used to determine shoot and head/curd fresh weight, and head/curd circumference. Crude protein (%), ascorbic acid (mg 100 g^{-1}), and total soluble content (TSS, ºBrix) were determined using a 100 g sample of each plant. Shoot and head/curd samples were weighed, and then dried at 70°C to a constant weight in a hot air oven, thus determining % dry weight and calculated dry matter production. The dried samples were ground and used to determine N, P, K, Ca, Mg, S, and zinc (Zn) contents in the shoot and head/curd samples.

Results

Lacking K and S fertilizers, control plants (T_1) grew and developed significantly slower than plants that received all other treatments (Fig. 1). Cabbage plants grew faster and taller in response to sufficient K application (T_2). Additional S application in the form of polyhalite, up to 75% of the recommended S dose, further enhanced plant growth and development (T_4). The application of the recommended S dose (20 kg ha^{-1}), either as polyhalite (T_5) or gypsum (T_6) brought about some reduction in plant development (Fig. 1). In cauliflower, towards harvest, only T_4 plants were significantly taller, but differences between treatments were more obvious regarding the number of leaves. While T_1 and T_4 possessed the lowest and highest numbers of leaves, respectively, T_2, T_3, and T_6 displayed a similar intermediate number of leaves. Noteworthy is the drop in the number of leaves in T_5 (Fig. 1).

A similar response pattern to K and S application rates and source was found regarding the plant's fresh and dry aboveground biomass, in both cabbage and cauliflower (despite the considerable differences in the absolute figures between the two cultivars). The smallest shoots and heads were produced by the control plants. Sufficient K application caused a significant increase in plant weight. Whereas the 75% S dose (T_4) provided the largest plants,

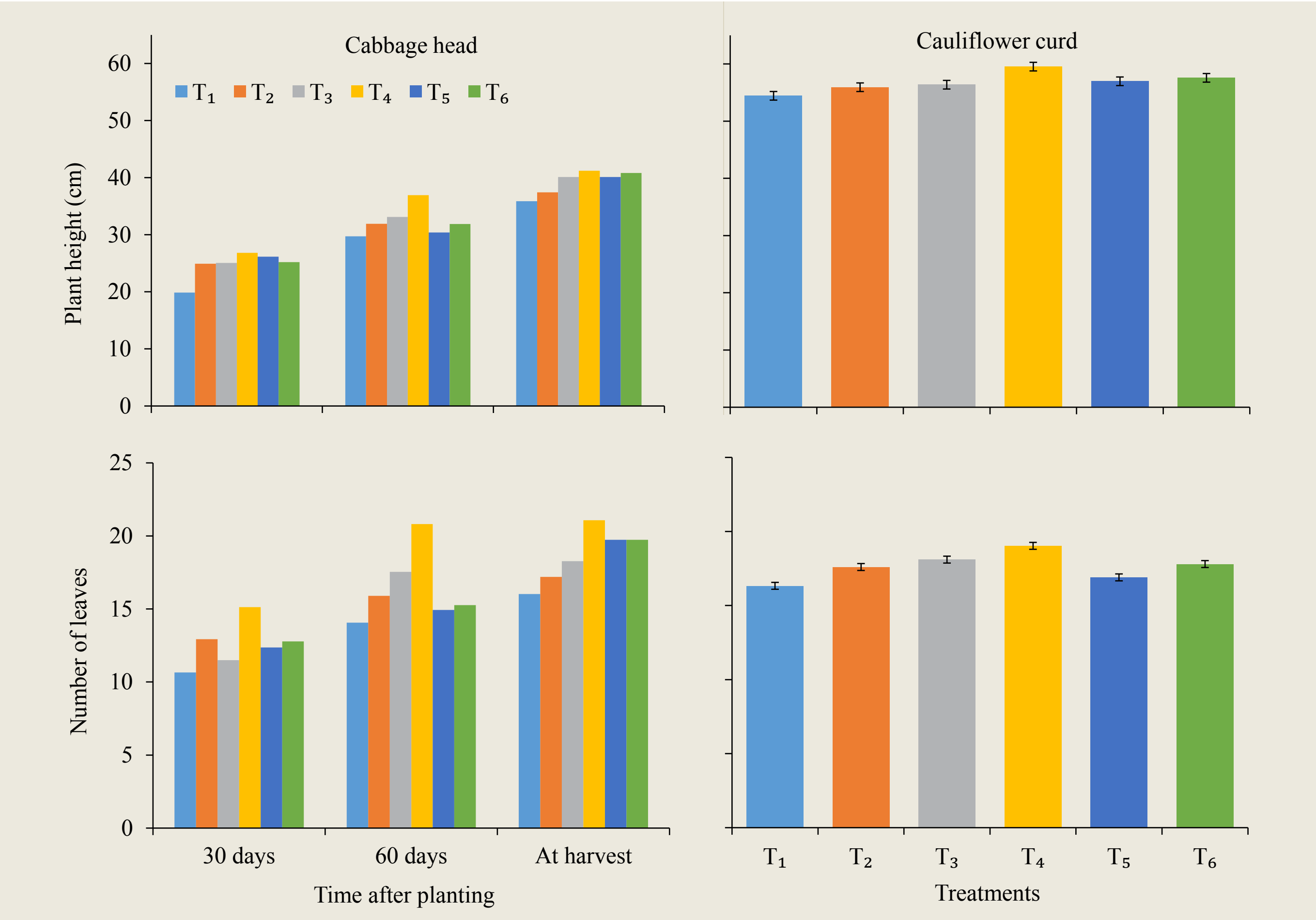

Fig. 1. Effects of K and S application on cabbage height and number of leaves 30 and 60 days after planting and toward harvest (left), and on cauliflower toward harvest (right).

the half S dose (T_3) was not responsive, and the full S doses (T_5, T_6) gave rise to plants that were significantly smaller than those of T_4 (Fig. 2).

T_4 displayed the highest cabbage and cauliflower yields, of 45.7 and 26.1 Mg ha^{-1} respectively, which were significantly different from all other treatments (Fig. 3). The advantage of T_4 was also observed in quality attributes, such as head/curd diameter and compactness at harvest (Fig. 3). T_1 (control, 100% NP, no K and S application) displayed the lowest yields, of 34.4 and 18.7 Mg ha^{-1} for cabbage and cauliflower respectively, which was far below all other treatments. In cabbage, application of sufficient K (T_2) significantly improved yield, head diameter and head compactness, whereas adding 50% S RDF failed to bring about any change. Supplement of 100% S RDF (T_5, T_6) significantly increased yield and some quality attributes, but these remained below the performance of T_4 (Fig. 3). In cauliflower, curd diameter did not respond to the fertilization treatments, excluding T_4. Curd compactness increased significantly with K application but was not affected by further supply of S, excluding T_4 (Fig. 3).

Crude protein content in cabbage heads at harvest, which was significantly lower at T_1 (11.3%), rose to 12.4% in response to sufficient K application dose (T_2), but was not affected further by the addition of S, at any rate or source (Fig. 4). T_4 displayed the highest ascorbic acid (50.8 mg 100 g^{-1}) content at harvest, but it was not significantly different from the other treatments, excluding T_1, which had a far lower concentration of 46 mg 100 g^{-1}. TSS fluctuated considerably among treatments, nevertheless the highest rates were displayed by T_4 and T_6 (Fig. 4).

Although N and P were equally applied in all treatments, considerable differences occurred in their contents in cabbage and cauliflower shoots at harvest (Table 2). T_1 showed the lowest concentrations of these two elements. Nitrogen concentrations increased significantly in T_2, indicating K requirements for N

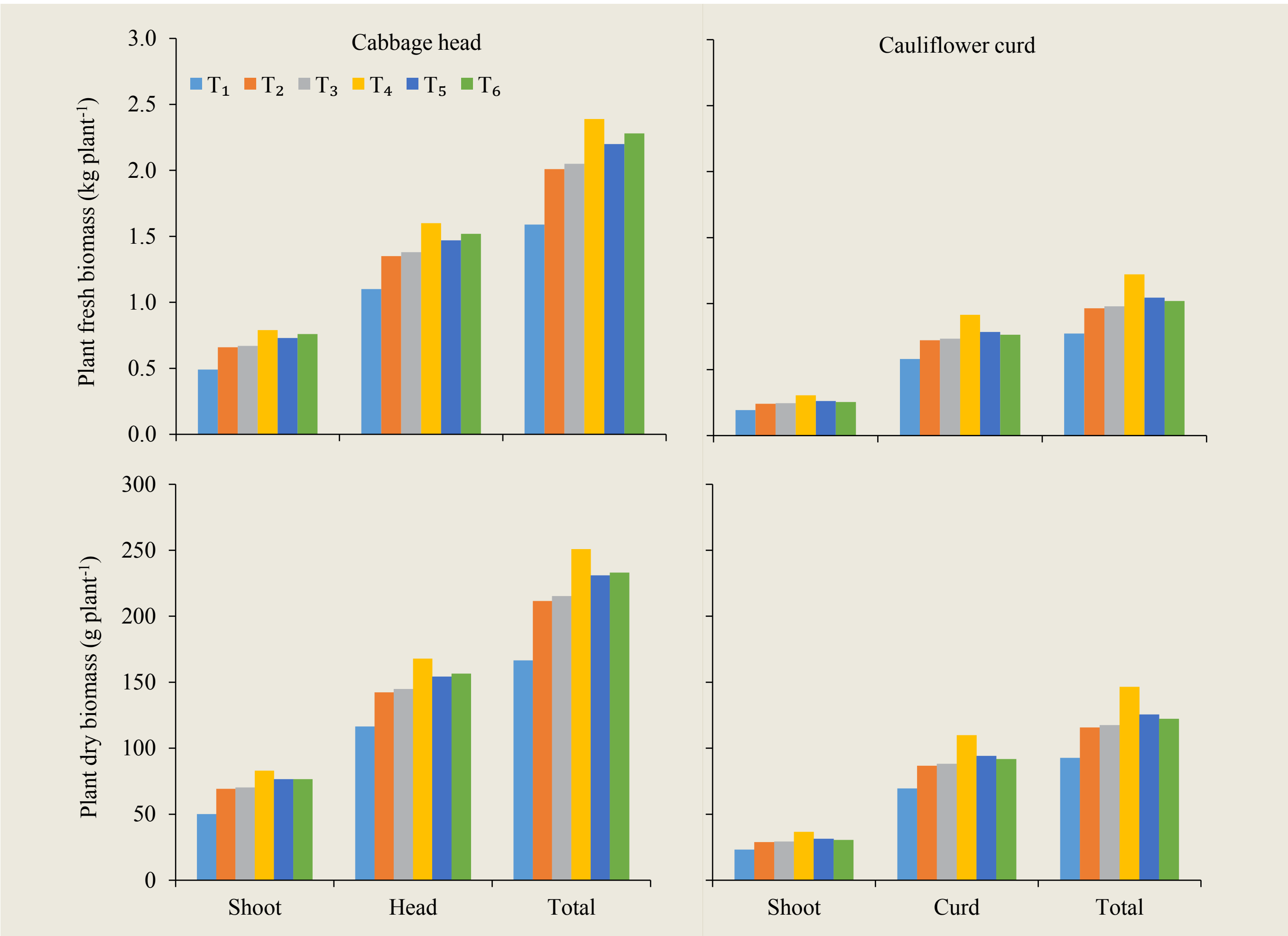

Fig. 2. Effects of K and S application on shoot and head/curd fresh and dry weight of cabbage and cauliflower at harvest.

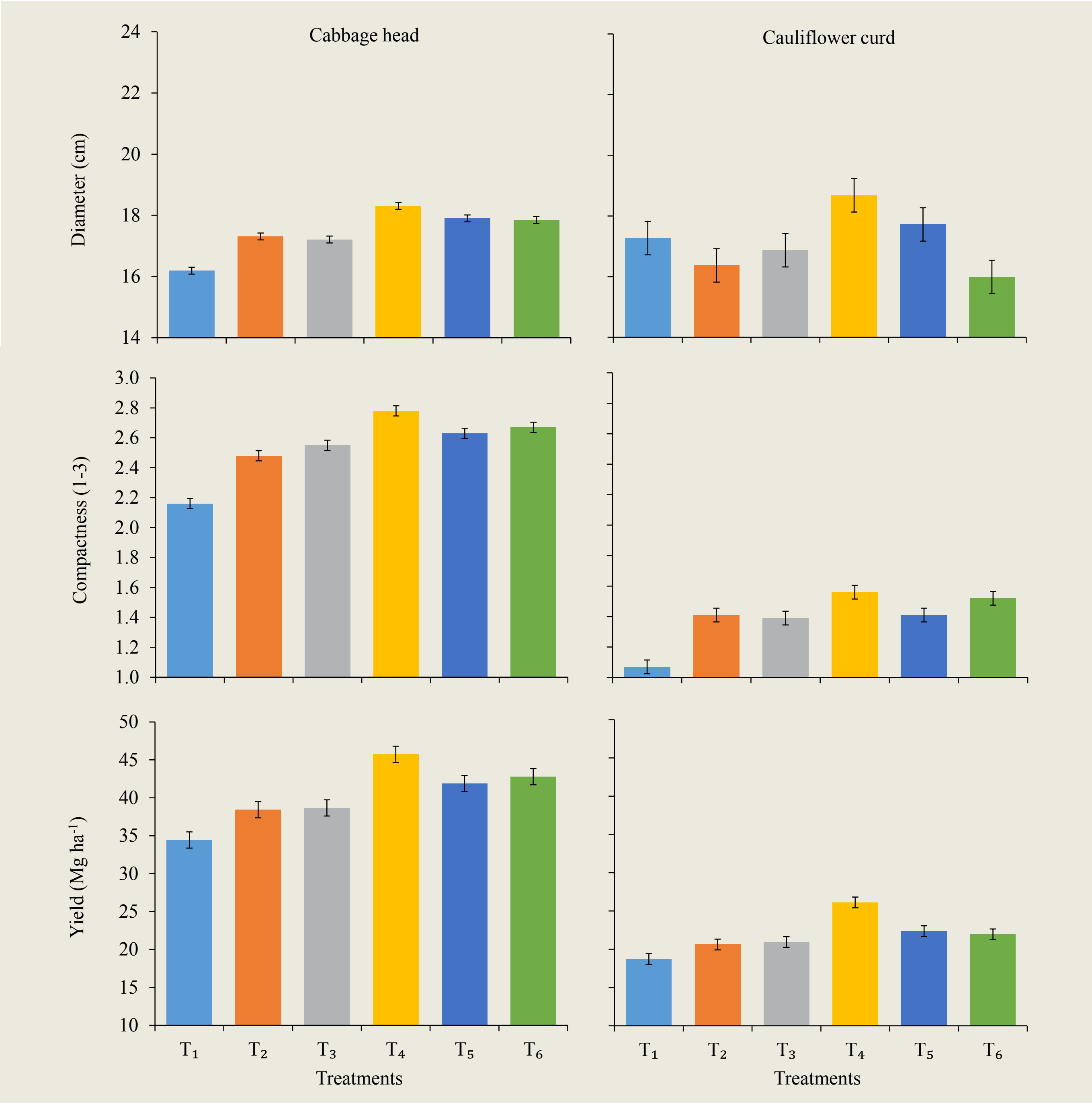

Fig. 3. Effects of K and S application and source on cabbage head (left) and cauliflower curd (right) diameter, compactness, and yield. Bars indicate LSD at P<0.05.

metabolism. No consistent influence of S dose was observed on N concentrations. Nevertheless, S application had some positive impact on P concentrations in the shoots of both crops (T_3-T_6). Nitrogen concentrations in the head or curd were generally lower than in the shoots. In cabbage, K application gave rise to moderate increases in N concentration, with no further effect of S application. In cauliflower, N concentration was somewhat higher in the curds of S-supplied plants.

While a significant increase in P occurred only in T_4 cabbage heads, the concentration of this element in cauliflower curds was significantly higher in all S-supplied plants, with T_4, again, obtaining

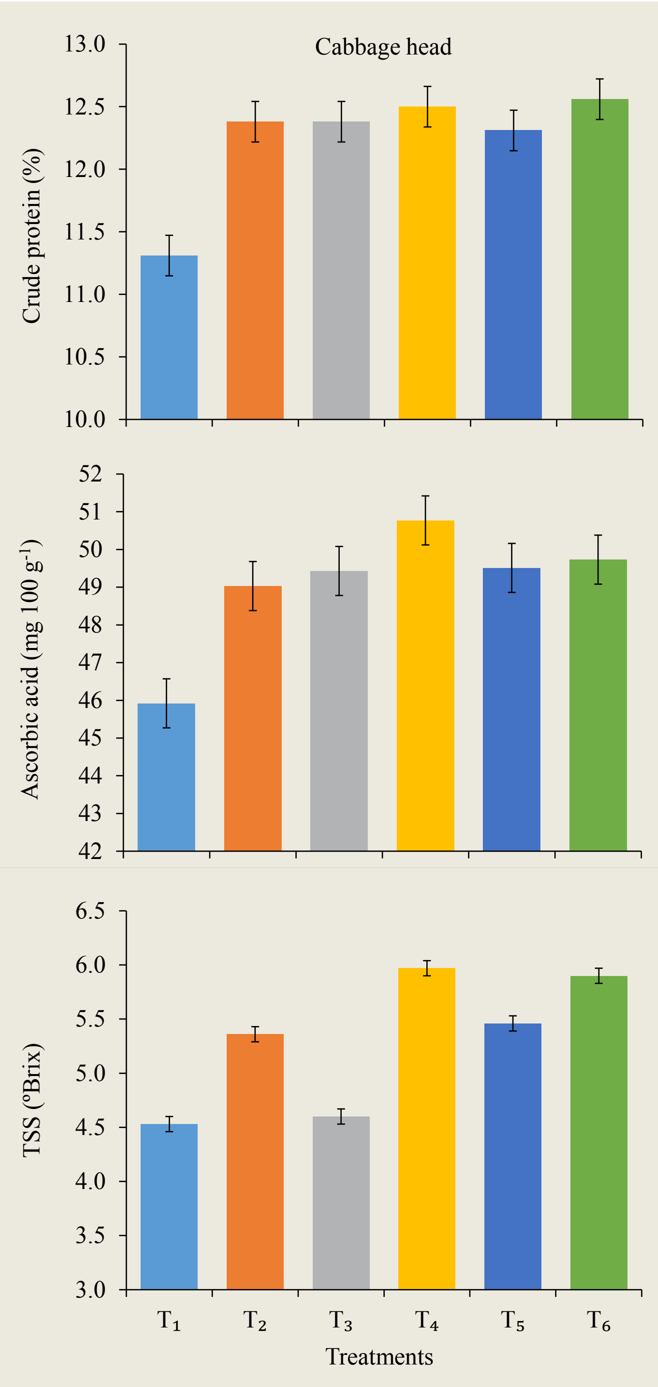

Fig. 4. Effects of K and S application and source on internal quality attributes of cabbage. Bars indicate LSD at P<0.05.

the highest results (Table 2). As expected, T_1 displayed the lowest K concentration, which was slightly increased by supplemented K in treatments T_2-T_6 (Table 2). In the shoots, S application seemed to contribute to further increases in K concentration in both crops. As indicated by treatments T_3-T_6, the rising S dose dramatically increased K concentrations in cabbage heads, whereas this effect was absent in cauliflower curds.

Calcium accumulation in the shoot was considerably influenced by S application dose, particularly in cabbage, where Ca concentrations increased from 2.51 to 4.12%, in T_2 and T_6, respectively (Table 2). This phenomenon was similar but to a lesser extent in cauliflower shoots. In spite of the drastically smaller Ca concentrations in cabbage heads, the enhancing impact of S application remained obvious. In cauliflower curds, which possessed Ca concentrations similar to those of shoots, S effect on Ca accumulation was observed up to 75% S dose (T_4), but declined with further elevations of S. Magnesium concentrations were less affected by the fertilization treatments (Table 2).

Surprisingly, an adequate K dose was enough to increase S concentration in cabbage shoots from 0.75% (T_1) to 1-1.1%; a level that was not further changed by S applied in the form of polyhalite. Gypsum application of 100% S RDF (T_6) did increase S concentration in the shoot (Table 2). On the contrary, S concentration in the cabbage head did respond to elevated S applications up to 75% S RDF (T_4) but slightly decreased with further increase of S. Sulfur concentrations in cauliflower shoots and curds also increased in response to K application in the absence of S supply, but continued to rise with increasing S supplement up to 75% of the S RDF. Further increase in S application dose did not have an impact (Table 2). Zinc concentrations in plants organs fluctuated from 12-23 ppm with no consistent response to fertilizer application.

As a function of the plant's final biomass and nutrient concentration in the plant at harvest, the cumulative nutrient uptake provides an integrative idea of fertilization effects at each treatment (Fig. 5). T_4, which was applied with 100% NPK but only 75% S RDF, obtained the maximum uptake of all measured nutrients. In cabbage, T_4 was followed by T_6 regarding N, K, Ca, and S uptake, whereas the picture in cauliflower was more complex (Fig. 5). In both crops, N uptake benefited significantly from K application, while the response to S was restrained. Phosphorus uptake increased as a result of K application, and continued to rise with S application in cabbage as well as in cauliflower up to 75% S RDF. Potassium uptake was highly responsive to S application in cabbage, but failed to respond in cauliflower, excluding T_4. Calcium uptake, which increased in response to K application in both crops, continued to rise in cabbage with increasing S doses but remained quite constant in cauliflower (again, excluding T_4). A similar Mg uptake profile was shared by the two crops: a significant rise in response to K application and a very modest response to S fertilizers. Sulfur uptake was predominantly affected by K availability, but it also increased due to S supplements (Fig. 5).

Table 2. Effects of K and S application dose and source on nutrient contents (in dry matter) in the shoot and head of cabbage and cauliflower at harvest.

Nutrient	Cabbage						Cauliflower					
	Treatment											
	T_1	T_2	T_3	T_4	T_5	T_6	T_1	T_2	T_3	T_4	T_5	T_6
	Shoot						Shoot					
	% DM											
N	2.75	3.15	3.32	3.16	2.94	3.22	2.14	2.85	2.8	2.98	2.84	2.93
P	0.48	0.48	**0.56**	0.52	0.52	0.52	0.32	0.4	0.42	0.42	0.44	**0.48**
K	3.56	3.68	3.67	**3.92**	3.85	**3.93**	2.33	3.17	2.61	3.04	**3.32**	**3.30**
Ca	1.75	2.51	3.39	**3.92**	3.75	**4.12**	1.04	1.04	1.11	**1.34**	1.18	1.08
Mg	0.20	0.24	0.27	0.28	0.28	**0.30**	0.19	0.23	0.27	0.29	**0.32**	0.24
S	0.75	1.10	1.00	1.10	1.00	**1.47**	0.30	0.48	0.66	**0.86**	0.75	0.71
	ppm											
Zn	12	16	**18**	**18**	**18**	14	16	16	16	**23**	12	13
	Head						Curd					
	% DM											
N	1.77	2.00	2.04	2.00	1.97	**2.16**	0.85	0.93	0.85	0.95	0.98	0.95
P	0.36	0.40	0.44	**0.52**	0.40	0.44	0.32	0.34	0.44	**0.58**	0.50	0.45
K	2.47	2.85	3.38	**3.67**	3.38	3.36	2.93	**3.97**	**3.92**	**3.98**	3.25	3.08
Ca	0.16	0.19	0.20	0.36	0.36	**0.41**	0.90	1.11	1.17	**1.31**	0.96	1.16
Mg	0.21	0.23	0.23	0.23	0.25	0.23	0.23	0.27	0.25	0.25	0.25	0.23
S	0.54	0.66	0.70	**0.90**	0.82	0.83	0.26	0.36	0.46	0.47	0.46	0.51
	ppm											
Zn	17	18	16	17	17	12	14	13	18	12	13	14

Note: Bold numbers represent particularly higher values, while gray represent the lower ones.

Examining the impact of S doses on cabbage and cauliflower, a predominant and consistent effect was obtained from the application of 75% S RDF through polyhalite (with 100% RDF of N and K) administered in T_4, which gave rise to 32.8% and 39.5% increases in the yields of cabbage and cauliflower, respectively, compared to the non-fertilized control (T_1). Generally, no further increase was recorded when the full S RDF was applied, through polyhalite or gypsum; yields even declined (Fig. 3). This result may indicate the existence of one or more factors limiting plant response to additional available S resources.

Nitrogen is known to positively interact with S; in many plant species, elevated availability of S promotes N uptake, and vice versa (McGrath and Zhao, 1996; Abdallah *et al.*, 2010; Jamal *et al.*, 2010). In this study, N was provided as a fixed recommended dose, which might reveal an underestimation of plant requirements when S availability is improved. Nevertheless, the impact of K seems even more interesting; S uptake sharply increased in response to K application, even in the absence of any additional S, but was much less pronounced in response to S application (Fig. 5). This indicates a strong dependency of S uptake and metabolism on K availability. Potassium is the most abundant inorganic cation in plants, comprising up to 10% of a plant's dry weight (Watanabe *et al.*, 2007), and K concentration in the

Discussion

Practically and irrespective of doses, S application improved growth parameters, yield attributes and quality of cabbage and cauliflower. The important role of S fertilization in Brassica crops has been broadly addressed in previous studies (McGrath and Zhao, 1996; Khan *et al.*, 2005; Tiwari *et al.*, 2015), but particular evidence in cole crops, as demonstrated here, is quite rare (Susila and Locascio, 2001).

Photos 2. A T_4 plot (100% NP, 75% S through polyhalite) towards harvest. Photos by authors.

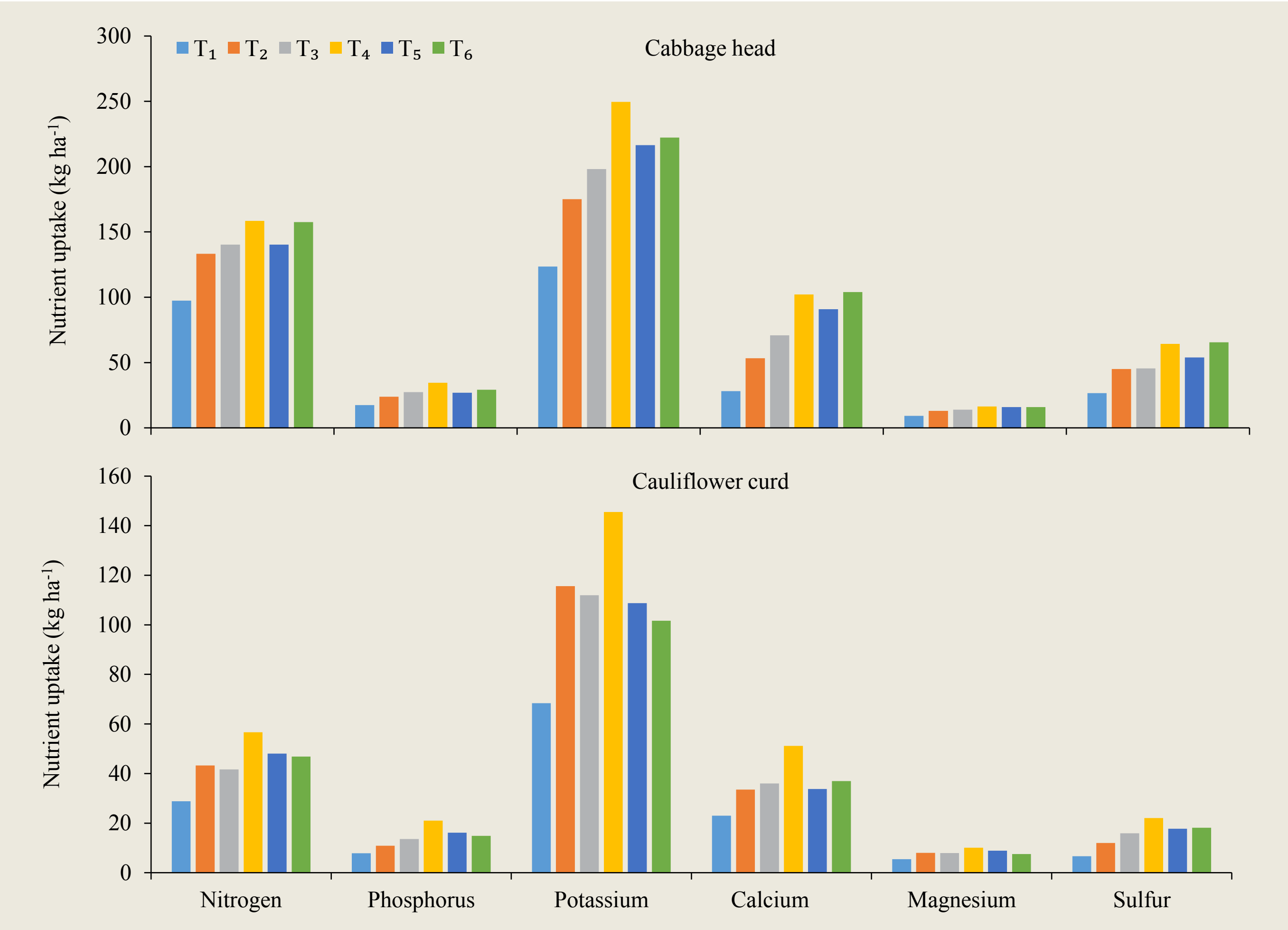

Fig. 5. Cumulative nutrient uptake by cabbage and cauliflower crops, as affected by K and S application dose and source.

shoot is often higher in plants from the Brassicaceae than in those from many other angiosperm families, when grown under comparable conditions (Broadley *et al.*, 2004). While involved in many physiological processes, K impact on plant-water relations, photosynthesis, assimilate transport and enzyme activation can have direct consequences on crop productivity (Marschner, 1995; Pettigrew, 2008; Hochmuth and Hanlon, 2010). Nevertheless, direct relationships or interactions between K and S uptake by plants have not yet been shown elsewhere (White *et al.*, 2010). The results of this study suggest that in cabbage and cauliflower, the recommended K dose was unable to support the exploitation of available S above a certain limit, and instead restricted further growth and development. Alternatively, considerable portions of N and K basal broadcast might have leached away from the rhizosphere, lacking at later stages of plant development. Another possibility is that the recommended S dose (20 kg ha^{-1}) is beyond the peak of the S optimum curve for cole crops. N-P-K fertilization practices, therefore, may require some adjustments when it comes to the practical application of S.

Interestingly, S application significantly promoted the uptake of P and Ca. Phosphorus is essential for plant growth and development. It is a major DNA/RNA keystone and is involved in all energy exchange processes and countless regulatory pathways (Marschner, 1995). The divalent cation Ca^{2+} has structural roles in plant cell walls and membranes, is a counter cation for inorganic and organic anions in the vacuole, and is an intracellular messenger in the cytosol. Calcium uptake is mediated by both symplastic and apoplastic fluxes in the root, while entry and exit of Ca to the symplast is exquisitely controlled by plasma membrane-localized Ca^{2+}-permeable ion channels and Ca^{2+}-ATPases, respectively (Broadley *et al.*, 2008). Evidence, however, of any direct interactions between S and P or Ca uptake is scarce, and therefore requires further investigation.

A comprehensive analysis of polyhalite performance as an S donor, including a full-scale dose comparison with alternative fertilizers, was beyond the scope of the present study. Here, using the full recommended S dose, no significant differences were found between gypsum and polyhalite. However, all yield and quality attributes were inferior to the 75% S dose, delivered through polyhalite. Optimum nutrient availability throughout the growing season is crucial, as their uptake rates are often slower than leaching processes, while plant requirements tend to increase (Hawkesford, 2000; Susila and Locascio, 2001; Abdallah *et al.*, 2010; Hochmuth and Hanlon, 2010; Steinfurth *et al.*, 2012; Girondé *et al.*, 2014). A considerable advantage of polyhalite may therefore be a slow-release pattern of nutrient delivery, including K, which is very mobile in well-watered soils.

In conclusion, S application significantly contributed to increased yield and quality of cabbage and cauliflower. Potassium enhanced S uptake, while in turn, S appeared to promote P and Ca uptake. The highest yields were obtained with a full dose N-P-K and 75% S dose delivered through polyhalite, which ascertained its legitimacy as an S-K-Ca-Mg fertilizer with some slow-release properties. Further research is required to adjust N and K fertilization practices when S is also administered.

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