Concentrations of copper, zinc and manganese in the roots, straw and oil cake of white mustard (*Sinapis alba* L.) and Indian mustard (*Brassica juncea* (L.) Czern. et Coss.) depending on sulphur fertilization

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ABSTRACT

The purpose of this experiment was to determine the influence of the soil application of sulphur (S) on concentrations of micronutrients in the root residues, straw and oil cake of white and Indian mustard. The plant material for chemical analyses originated from a controlled field experiment conducted in experimental fields at the University of Warmia and Mazury in Olsztyn, Poland (2006–2008). In both white and Indian mustard, the richest source of Cu (7.2; 7.0 mg/kg dry matter (DM)) and Zn (64.6; 55.3 mg/kg DM) was the oil cake from mustard seeds. Regarding Mn, both white and Indian mustard accumulated the highest content of this element in roots (48.2; 50.8 mg/kg DM), less in oil cake (31.9; 35.5 mg/kg DM) and the least Mn was determined in straw of both species (24.0; 17.1 mg/kg DM). The application of sulphur caused a significant increase in the concentration of Zn and Mn in white mustard roots. The content of micronutrients in roots of Indian mustard was not differentiated significantly by S fertilization. The application of sulphur caused a significant decrease in the content of Mn in white mustard straw and Cu in Indian mustard straw. The content of micronutrients in white mustard oil cake and Indian mustard oil cake was not significantly changed by S fertilization.

Keywords: oilseed crops; S fertilization; post-harvest biomass; micronutrients content

On a macro-scale, winter rape is a major oil-producing crop in Europe. However, diverse soil conditions, agrarian structure and climate exclude the cultivation of this oil species from some parts of the continent. In north and central eastern Europe, spring oil crops, including species from the family Brassicaceae which are the best adapted to the European climate, are gaining more and more economic importance. Noteworthy is the role that oil plants can play in agricultural ecosystems exposed to strong anthropogenic pressure. There, Brassicaceae can produce a beneficial effect: directly, by their post-harvest residues affecting the soil environment, or indirectly, by influencing the yield volume and quality of the subsequent crop. Oil plants in the family Brassicaceae seem to be an attractive option as preceding crops in a rotation system because of the high biological value of post-harvest root fragments left in soil. Another reason is their appreciable fertilizing potential. Relatively copious microelement fertilization of cruciferous plants (in response to their large demand, especially for boron, manganese, copper or molybdenum) means that their root residues in soil and straw are an important source of micronutrients in soil. On plant production farms, they are often the major supply of soil micronutrients (Szczebiot and Ojczyk 2002).

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What distinguishes oil plants from other crops is their high demand for sulphur. On the other hand, sulphur (S) fertilization of plants in the family Brassicaceae may have an essential effect on the use value of produced biomass. Obviously, S fertilization of plants most strongly impairs the nutritive value of non-fat seed residues due to an elevated biosynthesis of glucosinolates, especially the ones with alkene complexes (Ahmad and Abdin 2000, Chandel et al. 2003, Hassan et al. 2007, Jankowski et al. 2008, Gerendás et al. 2009). Equally important for the quality of biomass obtained from sulphurphilic plants is that soil application of sulphur can largely modify the soil reaction and microbial activity. As a result, some elements, including micronutrients, may accumulate in plant tissues in higher amounts (Salt et al. 1995, Chlopecka et al. 1996, Blaylock et al. 1997, Chaignon et al. 2002, Cui et al. 2004). Thus, S fertilization can affect the fertilizer value of post-harvest residues from plants in the family of Brassicaceae (root residues and straw) as well as change the quality of oil cake from seeds of these plants.

The objective of this study was to determine the content of Cu, Zn and Mn in root residues, straw and oil cake from white and Indian mustard grown under different S fertilization regimes.

MATERIAL AND METHODS

A field experiment was conducted at the Experimental Station in Bałcyny (53°35'49''N, 19°51'20.3''E), which belongs to the University of Warmia and Mazury in Olsztyn, Poland. The field experiment was run in a three-year cycle of trials (2006–2008). The experiment comprised the following variables:
– the crop: white mustard and Indian mustard;
– dose of S fertilizer applied to soil: (+S) white mustard 40 kg/ha; Indian mustard 25 kg/ha; (–S) – no S fertilization.

The experiment was designed according to the random block method (split-plot) with 3 replications. The size of a plot for harvest was 18 m^2. Each year, the experiment was set up on grey-brown podzolic soil with the texture of clay developed from light loam. The preceding crop for mustard plants was spring barley grown after spring wheat (the 1st and 2nd cycle of experiments) or after winter wheat (the 3rd cycle). The content of macro- and micronutrients in the arable soil horizon before sowing the plants is specified in Table 1.

The pre-sowing fertilization consisted of 70 kg N/ha, 17 kg P/ha and 100 kg K/ha (white mustard) or 70 kg N/ha, 13 kg P/ha and 66 kg K/ha (Indian mustard). In addition, a second dose of nitrogen in the amount of 30 kg/ha was applied at the early budding stage of white mustard (BBCH 50). Phosphorus was applied to soil in the form of triple superphosphate; potassium – as high percentage (60%) potassium salt; nitrogen – as ammonium nitrate (–S treatments) or ammonium sulphate and ammonium nitrate (+S treatments). Sulphur was applied together with the pre-sowing dose of nitrogen. The NPK or NPKS fertilization levels were determined according to expected seed yields of white and Indian mustard, predicted from the multi-annual yields of these crops in the same area. It is worth noticing that the application of sulphur to Indian as well to white mustard did not significantly affect pH value of soil plough layer (0–30 cm).

The organic carbon content of soil was determined according to the research protocol of the Chemical and Agricultural Research Laboratory, by the modified Kurmies' method. The available nutrient content and soil pH were determined in the plough layer, in accordance with the Polish Standards. The soil pH was determined with an electronic pH-meter with 20°C temperature compensation in deionized water and in 1 mol/L KCl in the 5:1 ratio. Available phosphorus and potassium were extracted in calcium lactate solution (the Egner-Riehms method) and then phosphorus was determined by colorimetry (the vanadium-

Table 1. Soil conditions

Specification	2006	2007	2008
Organic carbon content of soil (%)	1.47	1.75	1.57
Soil reaction (1 mol/L KCl)	6.39	6.08	6.05
Content of available nutrients in soil (mg/kg)			
P	107	85	143
K	104	133	104
Mg	103	85	51
SO_4^{2-}-S	25	10	10
Cu	4.4	2.7	2.8
Zn	23.1	11.1	10.9
Mn	230	180	235
Content of nutrients in soil (mg/kg)			
S_{tot}	163	140	144

molybdenum method) and potassium – by spectrophotometry (the AES method). Magnesium was extracted in 0.01 mol/L $CaCl_2$ and determined by spectrophotometry with the AAS method. The content of micronutrients (copper, zinc and manganese) in soil was determined in extracts obtained with 1 mol/L HCl by atomic absorption spectrometry (AAS) method. Total sulphur was determined by the Butters-Cheney's method, while sulfate sulphur was assessed by the Bardsley and Lancaster's method, extracting soil with acetate buffer. Sulphur in solutions obtained as described above was determined by nephelometry.

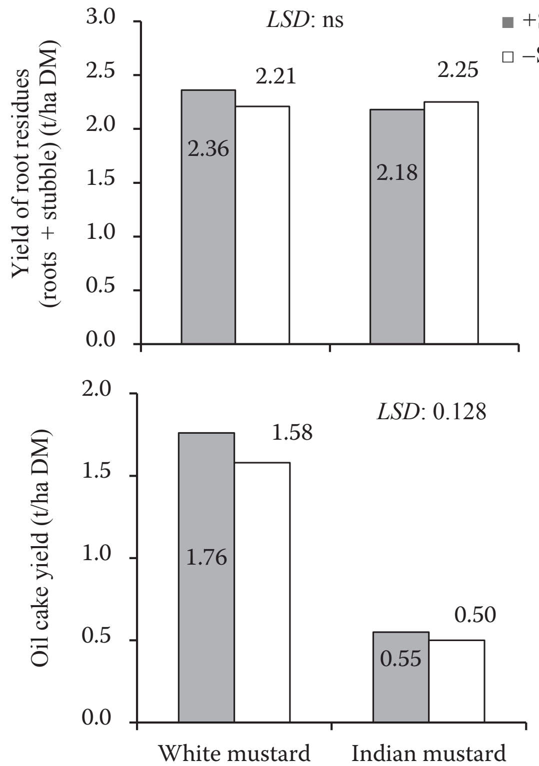
Concentrations of Cu, Zn and Mn were determined in the dry matter of root residues (roots + stubble), straw and oil cake from white and Indian mustard. The determinations were performed each year on plants from each plot. Material for chemical analyses was collected immediately after harvest. Roots with some soil were sampled (from an area of about 400 cm^2) into a steel cylinder 22.57 cm in diameter inserted to the depth of 30 cm. Next, each sample was rinsed with water on a 1 mm mesh sieve. Dried roots and stubble, straw and oil cake samples were ground in a laboratory mill. The concentrations of Cu, Zn and Mn were determined by atomic absorption spectrometry in mineralized samples (5000 g of plant material in a 1:4 mixture of chloric (VII) and nitric acids).

The results of chemical analyses were submitted to the analysis of variance (ANOVA) in line with the assumed methodology of the experiment. The means from treatments were compared using the Duncan's test. The *LSD* was set at 5% error.

RESULTS AND DISCUSSION

Sulphur fertilization had no significant effect on the yields of root residues and straw in white and Indian mustard. Sulphur application to soil resulted in a significant decrease in the yield of white mustard oil cake per ha, and it had no significant effect on the yield of Indian mustard oil cake (Figure 1).

Szczebiot and Ojczyk (2002) found that roots of white and Indian mustard contained Zn (110 and 123 mg/kg dry matter (DM)) and Mn (124 and 91 mg/kg DM). The concentration of Cu in roots of both mustard species was similar and typically 2- and 3-fold lower than that of Zn or Mn. In the current experiment, white and Indian mustard roots were a better source of Mn (48 and 51 mg/kg DM) than of Zn (29 and 23 mg/kg DM) (Figure 2). The content of Cu in roots was on a statistically similar level in both mustard species (content of Cu in roots was lower than that of Zn and Mn by 10- and 8-fold in white mustard and by 14- and



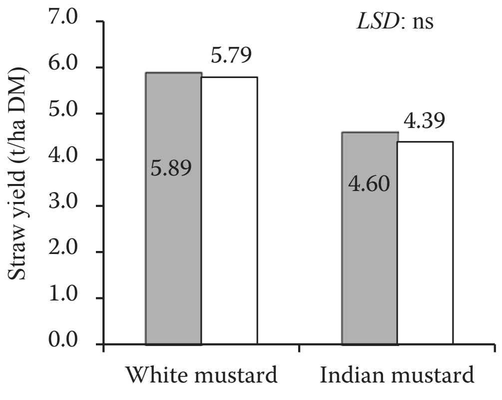


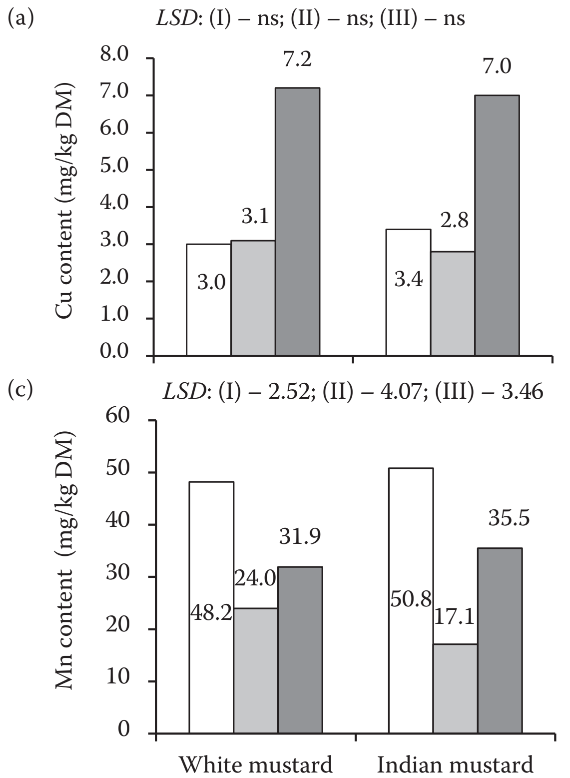
Figure 1. Effect of sulphur (S) fertilization on the biomass yield of white and Indian mustard (2006–2008). DM – dry matter; ns – non-significant differences

15-fold in Indian mustard, respectively). Szczebiot and Ojczyk (2002) showed that among the analyzed oil crops, spring oilseed rape accumulated the highest amount of Zn (148 mg/kg DM) in roots and stubble; the accumulation of Zn was moderately high in roots of Indian mustard (123 mg/kg DM), whereas white mustard accumulated the least Zn in roots (110 mg/kg DM). On the other hand, roots of white mustard contained about 33 mg/kg DM more Mn than roots of Indian mustard. This study demonstrated a reverse relationship between the concentrations of Zn and Mn in the roots of both mustard species (Figure 2). White mustard roots contained more Zn than Indian mustard roots. In contrast, Indian mustard roots were a better source of Mn (i.e. contained more of this micronutrient) than white mustard roots.

Above all, white mustard straw contained large amounts of Zn and Mn (53 and 21–59 mg/kg DM) (Jakubus 2006, Chandra et al. 2009). The concentrations of Cu, Pb and Ni in white mustard straw did not exceed 2–3 mg/kg DM (Jakubus 2006). In our trials, white mustard contained about 3.1 mg Cu, 36 mg Zn and 48 mg Mn in 1 kg of dry matter of straw (Figure 2). The content of Cu in Indian mustard straw was similar, but the concentrations of Zn and Mn were significantly lower than in white mustard straw. Consequently, Indian mustard straw was potentially a worse source of micronutrients supplied to soil than white mustard, which coincides with the results reported by Jakubus (2006) and Chandra et al. (2009).

Bell et al. (1999) demonstrated that the non-fat residue of Indian mustard seeds contained about 48–55 mg Zn/kg DM and 45–51 mg Mn/kg DM. Copper is one of those elements which appear in low (4.3–6.1 mg/kg DM) concentrations in oil cake from oil plants (Banaszkiewicz 1998, Bell et al. 1999, Kalembasa and Adamiak 2010). In our experiment, of the three determined micronutrients, white mustard oil cake and Indian mustard oil cake contained most Zn (64.6 and 55.3 mg/kg DM), less Mn (31.9 and 35.5 mg/kg DM) and the least of Cu (7.2 and 7.0 mg/kg DM) (Figure 2). The content of Cu in oil cake from the two mustards was on a statistically similar level. The content of Zn was significantly higher in white mustard oil cake than in Indian mustard oil cake. In contrast, Indian mustard oil cake was richer in Mn than white mustard oil cake. It is worthwhile to note that among the three types of biomass analyzed in our experiment, oil cake contained more Cu and Zn than roots or straw, irrespective of the mustard species. However, Mn was determined in higher quantities in roots of both mustard species (Figure 2).

At present, sulphur has become an obvious ingredient of fertilizers supplied under oil crops from



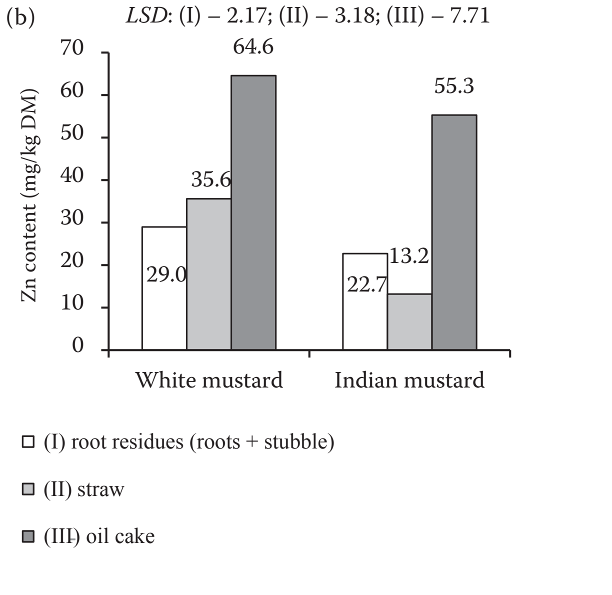
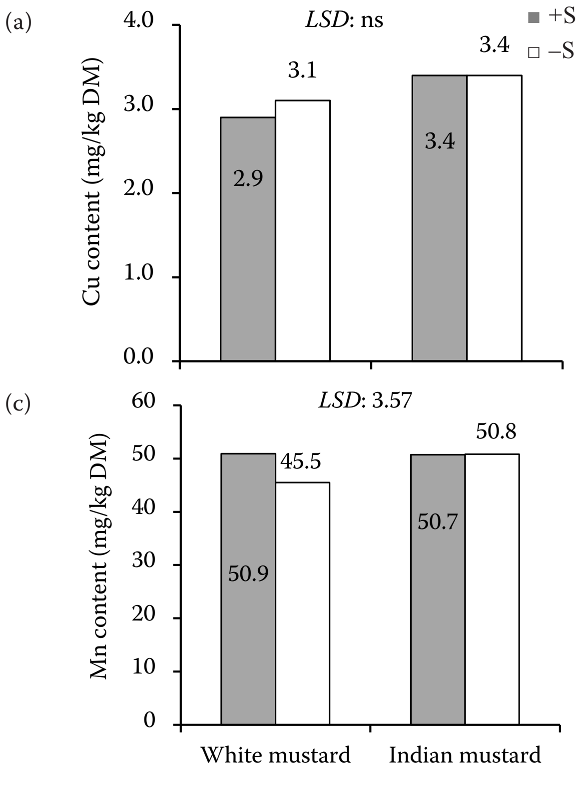


Figure 2. Content of Cu (a), Zn (b) and Mn (c) in the root residues, straw and oil cake of white and Indian mustard (2006–2008). DM – dry matter; ns – non-significant differences

the family of Brassicaceae. There are a few reasons, such as the high loss of sulphur from soil, increasing popularity of cruciferous plants (especially oilseed rape) and significantly reduced atmospheric emission of this element by industries. On the other hand, while sulphur has a strong acidifying effect, the reduction of soil pH is one of the ways to improve the bioavailability of some micronutrients (Salt et al. 1995, Chlopecka et al. 1996, Blaylock et al. 1997). Higher Cu mobility, particularly in soil contaminated by this element, is observed as the soil becomes more acid in reaction (Tyler and Olsson 2001, Chaignon et al. 2002). Kayser et al. (2000), who used $NaNO_3$ for extracting Cd and Zn from soil, found that 35-fold and 8-fold more of these elements, respectively, could be extracted when the soil pH was lowered from 7.2 to 6.9. Cui et al. (2004) discovered that an increase in the concentration of sulphur (from 0 to 160 mmol/kg of soil) caused a 1.8- and 2.4-fold increase in the concentrations of lead and Zn in Indian mustard roots (in treatments without EDTA). Similarly, Kulczycki (2004a,b) reported an increase in the concentrations of Cu (0.4 mg/kg DM), Zn (10 mg/kg DM) and Fe (7 mg/kg DM) in biomass of white mustard after S fertilization (0, 1, 2, 3 g S per pot containing 5 kg of soil). A study by Balík et al. (2006, 2007) showed that S fertilization in a dose of 50 kg/ha in a controlled plot experiment induced a tendency towards an increasing concentration of Mo (Balík et al. 2006) and lower Cu (Balík et al. 2007) in winter oilseed rape. Regarding molybdenum, a higher concentration of SO_4^{2-} in soil and lower soil pH may have led to an inferior uptake of this element by plants (Balík et al. 2006). It is worth noticing that quite frequently the crop itself may largely affect the mobility of micronutrients in soil because of some changes in its rhizosphere. The chemical conditions in the root zone might be completely different from those in the remaining soil and can therefore cause significant changes in the chemical parameters of soil, leading to subsequent modifications of the bioavailability of trace elements in soil (Hinsinger 2001). Chaignon et al. (2002) demonstrated that tomato plants were much more sensitive to toxic concentrations of Cu in soil than oilseed rape. In very acid soils, rapeseed plants could increase the pH in their rhizosphere much higher than tomato plants. The data illustrated in Figures 3–5 imply that the pre-sowing application of sulphur caused a significant increase in the content of Zn (by *ca* 4.6 mg/kg DM) and Mn (by *ca* 5.4 mg/kg DM) in white mustard root residues (Figures 3b,c). Sulphur fertilization of Indian mustard did not differentiate significantly the concentrations of the three micronutrients (Cu, Zn and Mn) in root residues (Figures 3a–c). Sulphur fertilization did not differentiate the content of



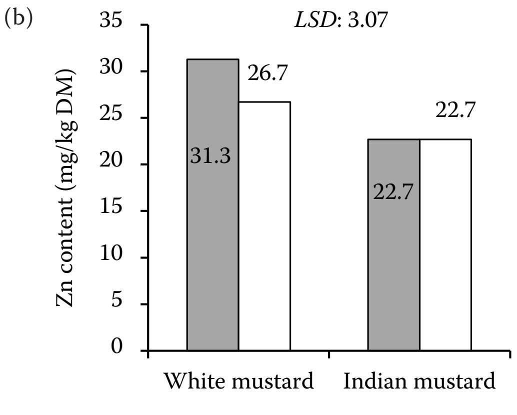


Figure 3. Effect of sulphur (S) fertilization on the content of Cu (a), Zn (b) and Mn (c) in the root residues (roots + stubble) of white and Indian mustard (2006–2008). DM – dry matter; ns – non-significant differences

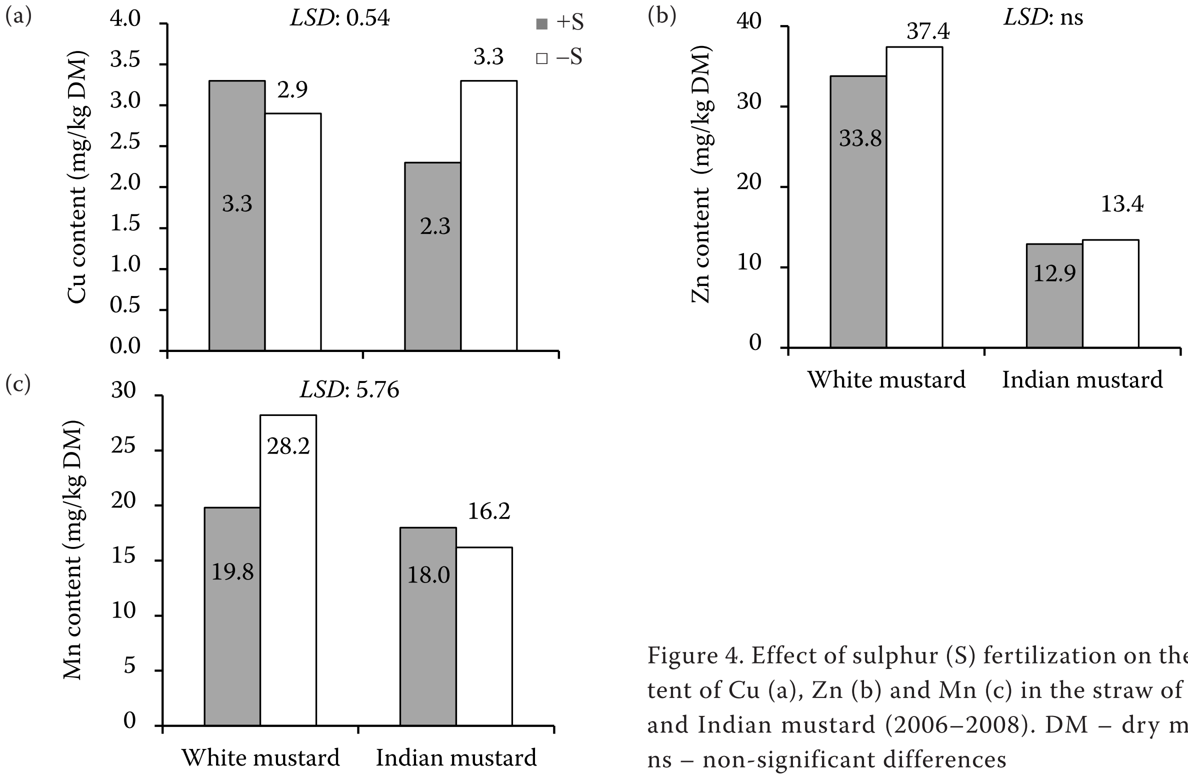


Figure 4. Effect of sulphur (S) fertilization on the content of Cu (a), Zn (b) and Mn (c) in the straw of white and Indian mustard (2006–2008). DM – dry matter; ns – non-significant differences

Cu or Zn in white mustard straw (Figures 4a,b). In turn, the concentration of Mn in white mustard straw decreased significantly (8.4 mg/kg DM, by about 30%) due to pre-sowing sulphur fertilization (Figure 4c). It can be suspected that a decrease in the Mn content of white mustard straw in response to S fertilization may have been induced by the drought which occurred during the plant development critical stage (budding). A particularly strong decrease in the Mn content of white mustard straw under the influence of S fertilization was observed in the 3rd cycle of the

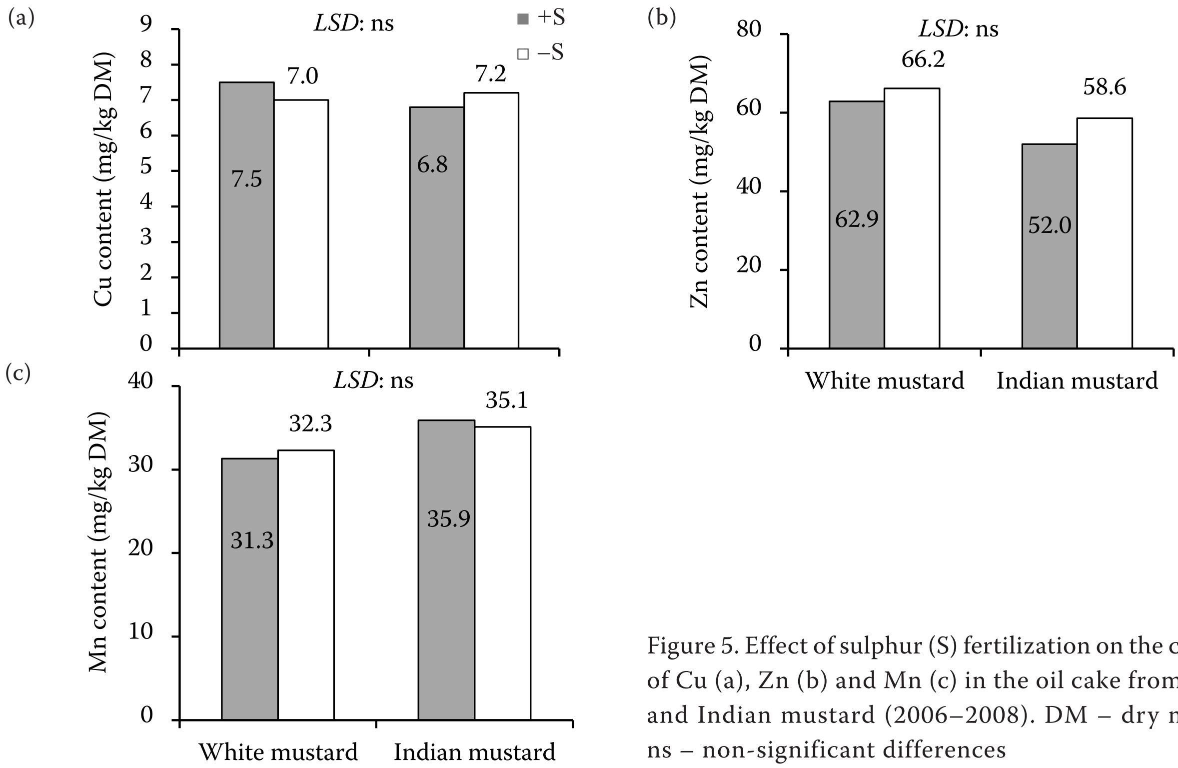


Figure 5. Effect of sulphur (S) fertilization on the content of Cu (a), Zn (b) and Mn (c) in the oil cake from white and Indian mustard (2006–2008). DM – dry matter; ns – non-significant differences

experiment, when the average value of the hydrodynamic index designed by Sielianinov was 0.6 at budding was. Sulphur fertilization, especially when soil moisture was low, can lead to a marked decrease in the Mn uptake by plants (Grzebisz 2008). The value of the Sielianinov's index during the budding stage of Indian mustard was much better (1.4). Sulphur fertilization of Indian mustard caused a significant decrease (1.0 mg/kg DM, by about 30%) of the Cu concentration in straw (Figure 4a). In turn, a significant depression in the Cu content in Indian mustard straw in response to S fertilization was especially evident in the 2nd and 3rd research cycle. In these plant growing seasons, the experiment was set up on soils with lower Cu available abundance than in the 1st cycle. Moreover, during the second and third research cycle, the stem elongation and budding stages in Indian mustard took place under good water supply conditions (K = 2.1 and 1.4) for this species. Good water supply may result in a weaker development of the root system. A weaker root system, at a lower Cu supply in soil and soil S fertilization, can be responsible for a lower Cu uptake by plants (Grzebisz 2008). White mustard grows a much stronger root system than Indian mustard (regardless of the climate). Kluczycki (2004a), who fertilized white mustard with S, noticed a small increase in the Cu content in the whole post-harvest biomass. The content of the other two elements (Zn and Mn) in Indian mustard straw was not significantly changed by S fertilization (Figures 4b,c). The content of the three micronutrients in oil cake from both mustard species was not significantly differentiated by S fertilization (Figures 5a–c). However, it is interesting to notice a clear (although not significant statistically) tendency towards decreasing concentrations of Cu and Zn in Indian mustard oil cake in response to S fertilization (Figures 5a,b). In contrast, S fertilization under white mustard plants triggered an evident increase in the content of Cu as well as a decrease in the content of Zn in oil cake from its seeds (Figures 5a,b).

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