Chapter 6

Sulfur status of Chinese soils and response of Chinese cabbage to sulfur fertilization in the Beijing area

Abstract

During recent years sulfur deficiency has become a major problem in agricultural crops throughout China, due to an imbalance of sulfur in relation to N, P and K in the fertilizers. One-fourth of the tested Chinese soils appeared to be sulfur deficient. Pot experiments at locations in the Beijing area showed that shoot biomass production of Chinese cabbage was significantly enhanced upon sulfur fertilization of the soil. A level of fertilization of 15 to 30 kg S ha\(^{-1}\) was sufficient to get optimum yield. However, the level of fertilization in other regions in China might have to be adjusted to the level of local atmospheric sulfur deposition.

Introduction

Sulfur is the fourth major nutrient after N, P and K for agricultural crops and is essential for growth and physiological functioning of plants. Sulfur is needed for the synthesis of the amino acids cysteine and methionine, which are of great significance in the structure, conformation and function of proteins and enzymes. Furthermore, it is incorporated into several other metabolites, as thiols (glutathione), sulfolipids and secondary sulfur compounds (alliins, glucosinolates, phytochelatins), which play an important role in the physiology of plants and in the protection and adaptation of plants against stress and pests (De Kok et al., this issue). Sulfur fertilization is not always optimal, which might negatively affect both crop yield and quality. It has been recognized that currently sulfur deficiency is one of the major plant nutrient stresses in crops throughout the world (Schnug, 1991; McGrath and Zhao, 1996; Schnug and Haneklaus, 1998; Zhao et al., 1999). In China sulfur deficiency has also become apparent and now occurs frequently (Wang et al., 2001; Cui and Wang, 2003; Zhao et al., 2003; Li and Liu, 2004; Meng et al., 2004). The use of high yielding varieties, increased cultivation intensity, and an overall improvement of cultural management practices has resulted in a sustained increase in crop production in the last decades. This had led to increased removal of nutrients from agricultural ecosystems. The sulfur input to soil has decreased due to the use of low sulfur-containing fertilizers. In the past fertilizers such as ammonium sulfate, single superphosphate, potassium sulfate and farmyard manure were used. At present these fertilizers are often replaced by low sulfur or sulfur-free fertilizers such as complex fertilizers (like N15P15K15), DAP (diammonium phosphate) and urea. For example, the share of ammonium sulfate production in the total nitrogen fertilizers production in China dropped from 100% in the 1950s to 44.9% in the 1960s, 6% in the 1970s and 0.7% in the 1990s. The N/S ratio in the fertilizers used in China increased from 1.0 in
1960 to 8.8 in 1990 (Liu, 1995). Recently, China has improved the balance of N, P and K in fertilizers, however, the importance of S and other micronutrients is often ignored. As a consequence in several regions, sulfur has become a limiting factor for optimal yield and quality of crops. In order to get insight into the sulfur status of Chinese agricultural soils, more than 18,000 samples from all over the country and about 900 samples from the Beijing and Tianjin areas were analyzed.

Chinese cabbage is a common and widely grown vegetable throughout the country, especially in northern China, since it has a high yield and relatively short growing period. For instance, winter Chinese cabbage usually has a yield of 100-120 ton ha$^{-1}$ in the Beijing and Tianjin areas. With the current high production levels, an adequate supply of nutrients must be available for optimum plant growth and production. However, Chinese farmers tend to apply more nitrogen fertilizer than is needed for optimal yield, whereas often insufficient phosphate and potassium are applied. In addition, the significance of the secondary nutrients and micronutrients are ignored, resulting in loss of potential yield and income from production of this vegetable. Responses to sulfur fertilization were reported for some leaf vegetables and Chinese cabbage in China (Chen et al., 2000; Liu et al., 2003).

In general, Chinese cabbage is grown in the vicinity of cities and here yield and quality might be negatively affected by air pollution (Zheng et al., 1996). Coal is still the principal source of energy in China and its combustion results in high levels of the air pollutants SO$_2$, NO$_x$, and acid rain. The impact of acid deposition on agricultural crops and forests in southern China has been reviewed by Feng (2000). Despite the potential toxicity of sulfurous air pollutants they also may contribute to the plants’ sulfur fertilization. For instance, one of the primary causes of sulfur deficiency in North America and Western Europe is attributed to the ongoing reduction of atmospheric sulfur deposits as the consequence of strict regulations on industrial sulfur emissions (Schnug, 1991; McGrath et al., 1996). This is supported by laboratory experiments, which have shown that dependent on the atmospheric level and the pedospheric sulfur supply of plants, SO$_2$ may act as both toxin and nutrient (De Kok et al., 1998, 2000; De Kok and Tausz, 2001; Yang et al., 2003). It remains to be questioned to what extent SO$_2$ pollution in the vicinity of Chinese cities is toxic or contributes to sulfur fertilization of Chinese cabbage. The current paper presents results of pilot experiments with two cultivars of Chinese cabbage, which were grown in pots with local soil with and without additional sulfur fertilization at two sites in the Beijing area.

**Material and methods**

**Soil testing**

ASI Soil Analysis Methods (PPI/PPIC Beijing Office, 1992; Portch and Hunter, 2003) for available soil sulfur test was adopted. Available soil sulfur was extracted by 0.08 M calcium phosphate and measured by the turbidimetric procedure for SO$_4^{2-}$-S in the PPIC-CAAS Corporative Soil and Plant Analysis Laboratory. If the level of available soil
When sulfur is lower than 12 mg l⁻¹, the soils are considered to be sulfur deficient. Soils containing sulfur levels ranging from 12 to 24 mg l⁻¹ are potentially sulfur deficient. At these soil sulfur levels supplemental sulfur fertilization is required to obtain optimal crop yield and quality. If available sulfur is higher than 24 mg l⁻¹, the soils are considered to be sulfur sufficient.

Response of Chinese cabbage to sulfur fertilization at two sites in the Beijing area

Two experimental sites were selected; one at central Beijing inside the 3rd Ring Road (site A) and one at the outskirts of Beijing outside the 6th Ring Road (site B). The data of atmospheric SO₂ concentrations in Beijing were provided by the Beijing Environmental Protection Bureau and were also measured by the national standard method (GB/T 15262: Ambient air – Determination of sulfur dioxide – Formaldehyde absorbing – Pararosaniline spectrophotometry).

For the experiments a fluviogenic soil was taken from Changping County, Beijing; it is the main soil type in the Beijing and Tianjin areas. The soil was air-dried for a few days and sieved through a 2 mm screen. Available nutrients and adsorption characteristics were determined by ASI Soil Analysis Methods. From the obtained data it was evident that the soil had a high pH, high levels of plant available Ca, Mg and Cu and low levels of plant available N, P, K, S, Fe, Mn and Zn (Table 1). Two cultivars of Chinese cabbage (Brassica pekinensis, cv. Kasumi F1, Nickerson-Zwaan, the Netherlands and cv. Beijing 3, China) were used in the experiments.

In the summer of 2002 the response of Chinese cabbage to sulfur fertilization was tested at the two experimental sites. Plants were fertilized with nutrients at levels more than adequate for maximum growth but much less than those considered to be toxic or out of balance with other plant nutrients and conditions. The levels of the various nutrients were added to the soil according to “a Systematic Approach to Soil Fertility Evaluation and Improvement”, and were based on soil test results and sorption studies (data not shown). The nutrients were added as follows: 50 mg N l⁻¹ soil, 234 mg K l⁻¹ soil, 55 mg P l⁻¹ soil, 0.4 mg B l⁻¹ soil, 20 mg Fe l⁻¹ soil, 28 mg Mn l⁻¹ soil, 5 mg Zn l⁻¹ soil and 66 mg S l⁻¹ soil. The latter represents an equivalent to a level of sulfur fertilization of approx. 130 kg ha⁻¹ and is referred to in the Fig. 3 as +S. In part of the pots no sulfur was added; referred to as -S. The nutrients were added as a solution and mixed thoroughly with the soil. The soil was watered to field capacity and 15-20 seeds were sown in each pot (with 800 ml air-dried soil), and then thinned to 4 plants per pot after emergence. All treatments were irrigated by a system of capillary irrigation (1.5 g NH₄NO₃ per 5 liters of de-ionized water) at the bottom of the pot in order to maintain a soil moist content close to field capacity. The plants in pots were placed under a plastic transparent foil in order to provide protection against heavy rainfall in summer. After 20 days the first harvest of the plants was carried out and two plants in the diagonal corner in each pot were harvested. The second harvest was carried out after 28 days.

In the summer of 2003 the response of Chinese cabbage to various levels of sulfur fertilization was tested at one of the experimental sites (site A). The same cultivars of Chinese cabbage were used. The same soil as used in the first experiment and the basal nutrients at the optimum levels were added, except S (see above). Sulfur was applied as
K₂SO₄ at levels of 0, 15, 30, 60, 90 and 120 kg S ha⁻¹ which was calculated by 20 cm cultivated layer and 1.2 g cm⁻³ soil bulk density of this soil (so the applied rate was 0.0, 6.3 12.5, 25.0, 37.5, 50.0 mg S kg⁻¹ soil in the pot experiments). The soil was watered to field capacity and 20 seeds were sown in each pot (containing 1 kg air-dried soil) and thinned to 2 plants per pot after emergence. During the experiment period all pots were watered with the same amount (50-100 ml) of NH₄NO₃ solution (2.0 g NH₄NO₃ per 5 liters of deionized water) every day. There were 5 replicates in each treatment of the 6 fertilization levels of sulfur. The pots were put under a plastic shed, which provided the plants protection against heavy rainfall in summer. The plants were harvested after 28 days.

Table 1. Levels of available nutrients in fluviogenic soil from Changping County, Beijing, China and the critical levels for the different nutrients.

<table>
<thead>
<tr>
<th>pH</th>
<th>Organic matter (%)</th>
<th>Nutrients (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil test results</td>
<td>8.1 1.09</td>
<td>Ca 2204 Mg 244 K 53 N 12 P 15 S 0.5 B 0.46 Cu 2.5 Fe 8.0 Mn 4.1 Zn 1.7</td>
</tr>
<tr>
<td>Critical levels</td>
<td>400 121</td>
<td>Ca 78 Mg 50 K 12 N 12 P 0.20 S 1.0 Fe 10 Mn 5.0 Zn 2.0</td>
</tr>
</tbody>
</table>

The fresh and dry (80 °C, 24 hours) weight of shoots was measured after harvest. Total nitrogen was determined with the Kjeldahl method according to Barneix et al. (1988). Analysis of the total S content was carried out as described by Durenkamp and De Kok (2002). Sulfate was determined after HPLC separation according to Tausz et al. (1996). The content of P, K, Zn, Mn, Fe, Ca and Mg of the shoots were determined after H₂SO₄-H₂O₂ digestion (Lu, 1999).

Results and discussion

The status of available soil sulfur

During recent years a total of 18,183 soil samples from China (and 923 samples from Beijing and Tianjin) were analyzed. From the data on available soil sulfur it is obvious that 24% (27% in Beijing and Tianjin) of the soils tested were S deficient, with available sulfur levels less than 12 mg l⁻¹ (the critical level), while 18% (14% in Beijing and Tianjin) of the soils contained available sulfur levels ranging from 12 to 24 mg l⁻¹, which might be considered to be potentially sulfur deficient (Table 2). The data demonstrated that sulfur deficiency of soils is a widespread problem in China and that in these areas additional sulfur fertilization is required for optimal crop yield and quality.
Table 2. The status of available sulfur (mg l\(^{-1}\)) in the selected soil.

<table>
<thead>
<tr>
<th></th>
<th>Min.</th>
<th>Mean</th>
<th>Max.</th>
<th>&lt;12</th>
<th>12-24</th>
<th>24-48</th>
<th>&gt;48</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>0</td>
<td>40</td>
<td>820</td>
<td>24</td>
<td>18</td>
<td>28</td>
<td>30</td>
<td>18,183</td>
</tr>
<tr>
<td>Beijing and Tianjin</td>
<td>0</td>
<td>55</td>
<td>262</td>
<td>27</td>
<td>14</td>
<td>16</td>
<td>43</td>
<td>923</td>
</tr>
</tbody>
</table>

\textbf{SO}_2\textit{ pollution levels in Beijing}

The atmospheric SO\(_2\) concentration in Beijing has substantially decreased during recent years. This can be ascribed to the great effort to reduce air pollution levels in the city. The change in use of coal to natural gas as energy source and a stricter regulation of pollutant emissions have resulted in a strong decrease of SO\(_2\) emission over the period of 1998 to 2002 (Fig. 1). The natural gas supply in the city was more than 1.8 billion m\(^3\) in 2002, which was about 6 times higher than in 1998. The use of high quality and low-sulfur coals was 8 million ton in 2002, which was 4-fold higher than in 1998. SO\(_2\) annual mean concentration has decreased from 120 µg m\(^{-3}\) in 1998 to 67 µg m\(^{-3}\) in 2002. During 2002 and 2003, the atmospheric SO\(_2\) levels were monitored at the experimental sites during the experimental period and the daily mean concentrations in Beijing are shown in Table 3 and Fig. 2. SO\(_2\) concentrations in Beijing in the summer time were about 20 µg m\(^{-3}\).

Table 3. SO\(_2\) concentrations at two experimental sites in the Beijing area in 2002. SO\(_2\) concentration was measured every day at site A and twice a week at site B during the experiment period (for information on sites see Material and methods).

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>17</td>
<td>2-34</td>
</tr>
<tr>
<td>Site B</td>
<td>17</td>
<td>9-32</td>
</tr>
</tbody>
</table>

\textbf{Impact of sulfur fertilization on Chinese cabbage}

Sulfur fertilization of the fluviogenic soil from the Beijing and Tianjin areas had a substantial impact on Chinese cabbage and resulted in a significant increase of the shoot fresh weight production of two cultivars of Chinese cabbage (Fig. 3). The fresh weight of the shoot of Beijing 3 was significantly higher upon sulfur fertilization at both harvests. However, an increase in shoot weight of Kasumi F1 upon sulfur fertilization was only observed at day 28. This indicated that the local cultivar Beijing 3 had a higher sulfur demand than Kasumi F1 (Fig. 3). There were no differences in plant growth within the same treatment for either harvesting day or experimental site.
Sulfur fertilization resulted in an increase of the total sulfur, which was mainly due to a higher sulfate content of the plants (Fig. 3). The organic sulfur content was also increased upon sulfur fertilization for both harvests at the different sites.

![Energy supply and SO\textsubscript{2} concentration change in recent years. Data from Beijing Environment Monitoring Station.](image1)

![SO\textsubscript{2} concentrations (daily mean) in Beijing during the experimental period. Data from Beijing Environment Monitoring Station.](image2)

Sulfur fertilization only slightly increased total nitrogen content of Beijing 3 for both harvests, whereas that of Kasumi F1 was hardly affected (Fig. 3). The N/S ratio in non-sulfur fertilized plants was much higher than that of the sulfur-fertilized plants in both cultivars especially after 28 days when shoot growth was reduced (Fig. 3). The ratio of N/S was between 15 to 20 in the sulfur-fertilized plants.

Upon 28 days of sulfur fertilization the levels of other plant nutrients in shoots were also affected (Table 4). The levels of P, K, Fe, Mg, Zn, Ca and Mn in shoots of Chinese
cabbage cv. Kasumi F1 were slightly enhanced upon sulfur fertilization. In cv. Beijing 3 sulfur fertilization only resulted in an enhancement of the levels of K, Zn, Mn.

Table 4. Effect of sulfur fertilization on P, K, Ca, Mg, Fe, Zn and Mn content of shoots of two cultivars of Chinese cabbage. Plants were grown at site A for 28 days. Data represent the mean of 3 measurements with 8 plants in each (± SD). Different letters (a, b) indicate significant differences at p ≤ 0.05 between different treatments.

<table>
<thead>
<tr>
<th></th>
<th>P (%)</th>
<th>K (%)</th>
<th>Ca (%)</th>
<th>Mg (%)</th>
<th>Fe (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
<th>Mn (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-S</td>
<td>0.42±0.04a</td>
<td>2.67±0.22a</td>
<td>2.9±0.2a</td>
<td>0.33±0.0a</td>
<td>294±53a</td>
<td>47±7a</td>
<td>51±4a</td>
</tr>
<tr>
<td>+S</td>
<td>0.39±0.06a</td>
<td>3.81±0.5b</td>
<td>2.5±0.2a</td>
<td>0.34±0.0a</td>
<td>302±21a</td>
<td>64±13b</td>
<td>72±13b</td>
</tr>
<tr>
<td>Kasumi F1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-S</td>
<td>0.42±0.01a</td>
<td>2.48±0.05a</td>
<td>2.8±0.1a</td>
<td>0.32±0.0a</td>
<td>293±53a</td>
<td>40±6a</td>
<td>45±8a</td>
</tr>
<tr>
<td>+S</td>
<td>0.53±0.05b</td>
<td>3.32±0.1b</td>
<td>3.2±0.2b</td>
<td>0.38±0.0b</td>
<td>376±60b</td>
<td>65±10b</td>
<td>65±6b</td>
</tr>
</tbody>
</table>

Optimizing of sulfur fertilization for Chinese cabbage

It was evident from the previous results that the levels of sulfur in the fluviogenic soil from Beijing and Tianjin were not sufficient for optimal growth of Chinese cabbage. In order to assess optimal sulfur fertilization plants were grown on soil fertilized with 0, 30, 60, 90 and 120 kg S ha⁻¹ (Fig. 4). The shoot fresh weight increased by 50% when 30 kg S ha⁻¹ sulfur fertilizer was applied for Beijing 3 and was not further affected at higher levels of sulfur fertilization. There were no differences in shoot biomass production at 30, 60, 90 and 120 kg S ha⁻¹. For Kasumi F1, sulfur fertilization at 15 kg ha⁻¹ was sufficient for optimal shoot biomass production.

Sulfur fertilization resulted in a slight increase of the total S content in both cultivars of Chinese cabbage and an increase of the total N content in Beijing 3 (Fig. 4). As a consequence the N/S ratio of shoots of Kasumi F1 decreased from 38 in the non-fertilized to 29 in the fertilized plants (Fig. 4). Likewise, the N/S ratio of Beijing 3 decreased from 29 to 24. It has been suggested that the N/S ratio could be used as a diagnostic tool to determine plant sulfur deficiency, based on an assumed direct interaction between nitrogen and sulfur assimilation in plants (Zhao et al., 1996; Thomas et al., 2000; Blake-Kalff et al., 2002; Randall et al., 2003). However, one should be cautious in the use of the N/S ratio for sulfur diagnosis, since it may also be strongly affected by the level of nitrogen fertilization. A high N/S ratio could be due to the oversupply of nitrogen even though sulfur was sufficient. For instance, the two experiments showed different N/S ratios in sulfur-sufficient plants. It was 15-20 for both cultivars in the first year, while it was 24-25 for Beijing 3 and 29 for Kasumi F1 in the second year, since the level of nitrogen fertilization was somewhat higher.
Fig. 3. Response of growth, sulfur and nitrogen metabolites of two cultivars of Chinese cabbage to sulfur fertilization at two sites in the Beijing area. Plants were grown in the fluviogenic soil for 20 and 28 days at site A (open bars) and site B (dotted bar, see Material and methods). Without sulfur fertilization (-S) and with 66 mg SO₄²⁻·L⁻¹ soil (+S). The fresh weight of shoots (g) represents the mean of 12 measurements with 2 plants in each (± SD). Total S, total N, and sulfate content (µmol g⁻¹ DW) of the shoot represent the mean of 3 measurements with 8 plants in each (±SD) at day 20 and the mean of 4 measurements with 6 plants in each (± SD) at day 28. The organic sulfur content was derived by subtracting the sulfate content from that of the total S content. Different letters indicate significant differences at p ≤ 0.05 between (+S) and (-S) treatments.
Fig. 4. Effect of different levels of sulfur fertilization on growth, total S, total N and N/S ratio of two cultivars of Chinese cabbage. Sulfur was applied as K₂SO₄ at levels of 0, 15, 30, 60, 90 and 120 kg S ha⁻¹ which was calculated by 20 cm cultivated layer and 1.2 g cm⁻³ soil bulk density of this soil (so the applied rate was 0.0, 6.3 12.5, 25.0, 37.5, 50.0 mg S kg⁻¹ soil in the pot experiments, see Material and methods). Data of the fresh weight of shoot represent the mean of 5 measurements with 2 plants in each (± SD). Total S and total N content of the shoot represent the mean of 3 measurements with 2 plants in each (± SD). Different letters indicate significant differences at p ≤ 0.05 between different treatments.

The total S and total N contents of non-sulfur fertilized plants were higher in the second year (Fig. 4) than in the first year (Fig. 3). This may be ascribed to the different irrigating regimes of the pots. During the first year plants in pots were irrigated by a system of capillary irrigation (irrigation water contained 1.5 g NH₄NO₃ per 5 liters of de-
ionized water) and the water content of the soil was maintained close to “field capacity”. During the second year pots were watered daily with 50-100 ml irrigation water containing 2.0 g NH₄NO₃ per 5 liters of de-ionized water. As a consequence there was more variation in the soil water content. There is no doubt that plants are able to utilize foliarily absorbed sulfurous air pollutants as a sulfur source for growth (De Kok et al., 1998, 2000; De Kok and Tausz, 2001; Yang et al., 2003). It has been demonstrated that levels of ≥ 0.06 µl l⁻¹ SO₂ (≈150 µg m⁻³ SO₂) are sufficient to cover the sulfur need of Chinese cabbage for growth (Yang et al., 2003). It remains to be questioned to what extent atmospheric SO₂ deposition has contributed to the sulfur fertilization of Chinese cabbage at the different sites in the Beijing area, although the ambient SO₂ levels were relatively low (Table 3).

Conclusions

Sulfur fertilization of soils is necessary to obtain optimal yield in various areas in China. For instance the present data showed that in the Beijing area a level of sulfur fertilization of 15-30 kg S ha⁻¹ was needed to get optimal biomass production of Chinese cabbage. However, the level of fertilization in other regions in China might have to be adjusted to the level of local atmospheric sulfur deposition.

References


