The fluctuation of molybdenum content in oilseed rape plants after the application of nitrogen and sulphur fertilizers

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ABSTRACT

The effect of N-S fertilizers on the molybdenum content in oilseed rape plants was investigated in precision field trials. Evaluation was carried out on unfertilized control and two treatments of single fertilizer rates in the first spring fertilizer application, using 100 kg N/ha in AN treatment (nitrochalk) and 100 kg N/ha + 50 kg S/ha in ANS treatment (ammonium nitrate and ammonium sulphate). The results confirmed the significance of sulphur fertilization for the winter oilseed rape plant's cultivation technology, even on fertile soils in the Czech Republic. The control treatment produced a yield of 3.7 t/ha, while in the AN treatment the yield was 49% higher, and the ANS treatment was 60% higher. An antagonistic relationship between the sulphate and molybdenum anions in their absorption by the plants was demonstrated. The molybdenum content in the flowering period of the plants was determined in mg/kg as follows – in the ANS treatment: 0.17 in root, 0.12 in stem, 1.56 in upper leaves, 0.90 in lower leaves, and 1.17 in the flower petals. Higher and statistically more significant molybdenum levels were determined in the AN treatment: 0.21 in the root, 0.19 in the stem, 2.40 in the upper leaves, 1.72 in the lower leaves, and 1.50 mg/kg in the flower petals. The total above-ground biomass of the plants in the flowering period had accumulated molybdenum at 6.06 g/ha in the ANS treatment, and 8.44 g/ha in the AN treatment.

Keywords: molybdenum; sulphur; winter oilseed rape; N-S fertilizers

The total molybdenum concentration averages were approximately 0.2–5 mg/kg in agricultural soils (Scheffer and Schachtaschabel 2002). The Mo fixation in the soil is determined mainly by pH and redox conditions. Strong reduction conditions can give rise to the sulphide – MoS_2. Oxidation conditions can produce MoO_4^{2-}, which is absorbed mainly by the iron and aluminium oxides, and also by organic matter. Under aerobic conditions Mo can occur only as an anion. At pH/H_2O 5 to 6 there is mainly a predominance of MoO_4^{2-} ions. At lower values protoionisation occurs [$HMoO_4^-$ (pK = 4.0) and H_2MoO_4 (pK = 3.6)]. At pH/H_2O < 5 values the polymolybdenum ions, such as $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$ are formed, etc. The concentration of molybdenum in the soil solution is around 2–10 µg Mo/1.

MoO_4^{2-} is transported non-specifically via the plasma membrane by anion carriers, particularly those of phosphates and sulphates (Zimmer and Mendel 1999, Mendel and Hänsch 2002). In long distance transport Mo is easily mobile via xylem as well as phloem of plants. As yet the form in which this element is transported is not known, but its chemical properties indicate that it is most likely the MoO_4^{2-} rather than a complex form (Marschner 1995). By contrast, Tiffin (1992) also cites the form of complexes involved the transport of Mo through the xylem. Heuwinkel et al. (1992) discovered a five-fold increase in concentration of Mo in tomato plants grown under the conditions of phosphorus deficiency. Marschner (1995) hypothesizes that the high content of sulphate anions restricts absorption of molybdenum. Similarly, Murphy et al. (2002) as well as Phillips and Chiy (2002), mention that sulphur fertilizer application significantly reduces the molybdenum content in plants. Experiments by Llamas et al. (2000) indicate that algae have two systems for molybdenum absorption. The significance of molybdenum rests mainly

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in its participation in the oxidation-reduction processes [reduction process of Mo(VI) → Mo(V) → Mo(VI)]. Molybdenum also has a function of a co-factor, i.e. structural and catalytic function, in several enzymes which have been discovered in the higher plants (Zimmer and Mendel 1999, Zdunek-Zastocka and Lips 2003).

Lately, sulphur has often been a limiting element in the nutrition of winter oilseed rape. Application of N-S fertilizers has become a common component of the cultivation technology. However, in a number of field trials this problem has been narrowed down to an issue of nitrogen and sulphur only, without investigating any implications. The aim of the experimental results published here has been to determine the effect of the N-S fertilizers on the contents of macro- and microelements in the winter oilseed rape plants (in this paper we deal only with Mo). Single rates of 100 kg N/ha applied in the form of AN (nitrochalk) and ANS (ammonium nitrate and ammonium sulphate), respectively, have been selected. The overall intensity of fertilizer application was lower than currently practiced in agriculture. Nevertheless, while using such a high single rate is not usual, it is not relatively exceptional either, and in practice it is feasible for the cultivation of winter oilseed rape on heavy soils.

MATERIAL AND METHODS

A precision field trial was set up in Prague-Uhříněves, at the experimental station of the Faculty of Agrobiology, Food and Natural Resources. The following variants were investigated in the trials:

(1) unfertilized control treatment
(2) 100 kg N/ha (a single application of AN: nitrochalk, 27% N) – sidedress the first spring application
(3) 100 kg N/ha + 50 kg S/ha (single application of ANS: ammonium nitrate + ammonium sulphate, 26% N and 13% S) – sidedress the first spring application

The size of the trial plot was 20 m^2. Each treatment had four replicates. The station is situated at 295 metres above the sea level, with average annual temperature of 8.3°C, and annual rainfall reaching 575 mm, of which 380 mm falls during the period between April and September. The level of the subterranean water table is at the depth of 1 metre and is of a permanent character. The favorable water regime is supported by developed illuvial horizons with a relatively good water retaining ability, which influences the stable capacity of moisture that can be utilized by the plants. The soil is represented by luvisol. The ground is a deep top soil (down to 32 cm) and the humus horizon to the depth of 70 cm. The sorption complex is saturated. Chemical analyses of the soils determined the following contents of available nutrients (Mehlich III): 220 mg/kg of potassium, 119 mg/kg of phosporus, and 123 mg/kg of magnesium. The total sulphur content was 850 mg/kg, the S content was 4–7 mg/kg (before the application of fertilizers), and the molybdenum content (Mehlich III extraction) was 1.0 mg/kg. The value of pH/$CaCl_2$ was 6.2.

Winter oilseed rape (Bristol cultivar – two zero variety) was used as a trial crop. This is a typical representative of cultivars with strong branching and low height. It is characterized by very early flowering and it therefore better utilizes moisture during the spring period. The pods are able to assimilate during the period between flowering and harvest periods for up to 5–10 days longer, and this is very positively reflected in the yield formation. The Bristol cultivar has high oil content. Winter wheat was the preceding crop. Apart from the spring application of fertilizers, standard protection of the crop was carried out during the vegetation period. During the vegetation period plant samples were collected (3 plants per trial plot – i.e. 12 plants per treatment). The plant was dissected into individual parts according to the growth period: root, upper leaves, lower leaves, stem, pod, branches, and flower. Following their homogenisation, chemical analyses were carried out for individual replicates.

The total contents of elements in the plant samples were determined in mineral extracts that had been obtained by the method of dry decomposition. The quantities of individual elements were determined by the optical emission spectrometry with induction fixed plasma (ICP – OES, Varian VistaPro, Australia).

RESULTS AND DISCUSSION

The Uhříněves site is very fertile, as indicated by the average yields that have been achieved over three years. The control treatment produced a yield of 3.7 t of seed per hectare, while the AN treatment produced a yield that was 49% higher, and the ANS treatment was 60% higher. During the course of the entire spring vegetation there was a distinct

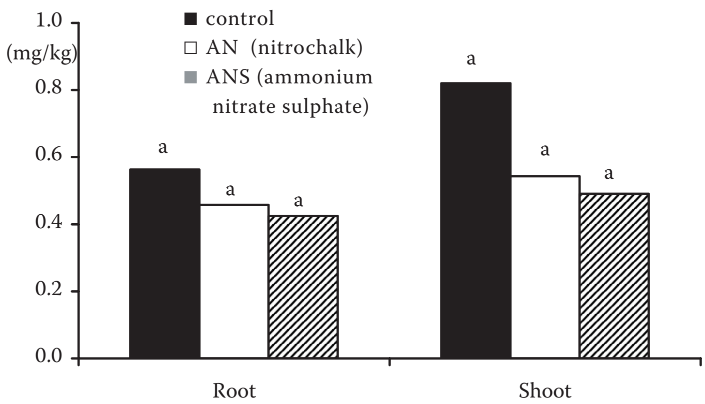

Figure 1. Molybdenum content in plants – vegetation regrowth (the averages marked by the same letter did not significantly differ at α = 0.05 within individual columns)

difference in the intensity of growth between the unfertilized treatment and both fertilized treatments. The achieved results also confirmed the importance of sulphur fertilizers application in the cultivation technology of winter oilseed rape, even on fertile sites. In all three experimental years the yield had always been higher in the ANS treatment. It has been clearly demonstrated that following the application of the ANS fertilizer, the concentration of especially S, Mn, and Zn in plants increased, while the concentration of B did not change significantly (Balík et al. 2005).

The Figures 1–4 show the molybdenum contents in individual parts of the plant during vegetation. The Figure 5 also presents the contents in the seed and straw during the harvest. On the basis of the presented results the lower molybdenum concentration in both fertilized treatments is obvious. In the case of the ANS fertilizer the Mo content is significantly higher. Naturally, the higher increase in biomass, and thus the diluting effect, has also played a role. However, the relatively very low contents in the ANS treatment cannot be explained only by the increase in the biomass. In accordance with the literature data (Stout et al. 1951, Pastricha et al. 1977, Marschner 1995, Zimmer and Mendel 1999), there was also the effect of the antagonistic relationship between the sulphate and molybdenum anions during their absorption by the plant. Chatterjee et al. (1992) therefore recommend an application of sulphate fertilizers in the soils with an extremely high content of Mo so that the absorption of Mo is limited and its excessive accumulation in the plant tissues is limited.

Another cause in the ANS treatment has probably been a distinct reduction in the pH value, especially in the rhizosphere zone, which also increased the sorption of MoO_4^{2-} in the soil, particularly to the iron sesquioxides (Marschner 1995). Furthermore, the molybdic acid is very weak and when pH 6.5 drops to a value of 4.5, its dissociation markedly decreases [$MoO_4^{2-} \rightarrow HMoO_4^- \rightarrow H_2MoO_4$] and polyanions are formed [-tri → hexa-molybdate]. The increased concentration of SO_4^{2-} in the soil solution and the reduced pH value are the cause of the reduced absorption of molybdenum by plants. The statistically significant increase of sulphur in the plants, as well as the increase of Mn and Zn

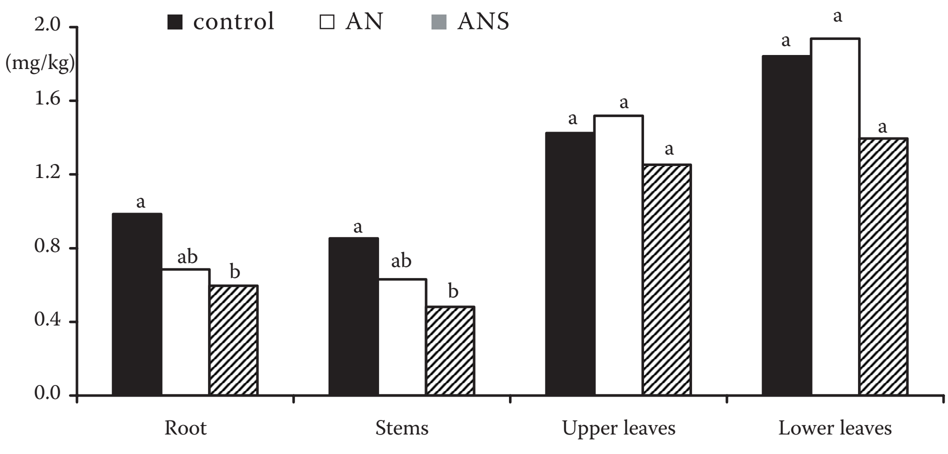

Figure 2. Molybdenum content in plants – budding period

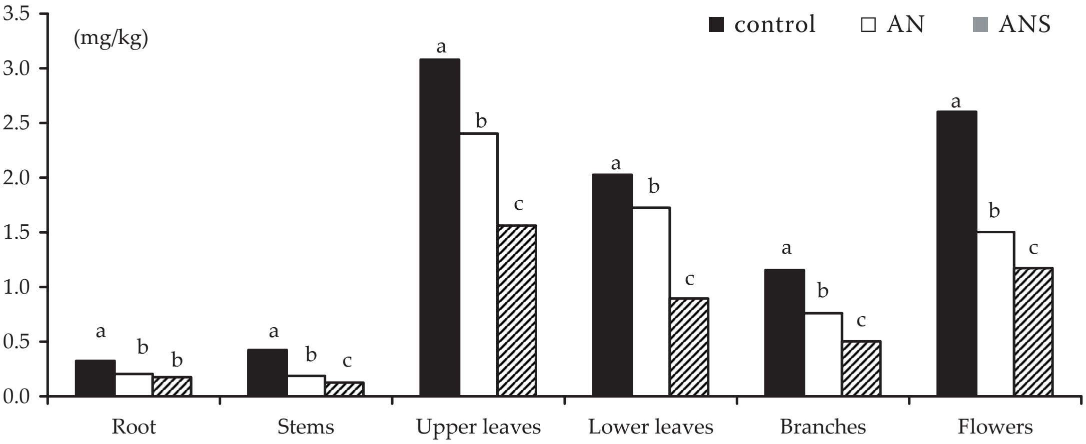

Figure 3. Molybdenum content in plants – flowering period

contents in the plants of winter oilseed rape, in the ANS treatment support this hypothesis (Balík et al. 2005). The obtained results are in perfect agreement with the data of Murphy et al. (2002), who found a reduced concentration of molybdenum in a pasture growth, from 1.85 to 0.87 mg/kg, after the application of sulphur.

The dominant effect of the sulphate anion on the Mo absorption is also indirectly indicated by the results of the mineral sulphur content in the top soil. During the period of elongation growth the S content was 3.9 mg/kg in the AN treatment, 9.2 mg/kg in the ANS treatment, in the flowering period it was 6.3 mg/kg of AN treatment, and 15.2 mg/kg in the ANS treatment, while during the green pod period it was 6.1 mg/kg in the AN treatment and 14.3 mg/kg in the ANS treatment.

The different forms of nitrogen in the investigated fertilizers did not apparently have any effect on the differing Mo absorption in either the AN or ANS variants. As determined by the soil analyses, there was no significant difference in the contents of NH_4^+ and NO_3^- between the topsoil and subsoil 35 days after the application of the fertilizers, which agrees well with the intensive microbial activity in the luvisol at the Uhříněves site. On the basis of our experiments we therefore cannot confirm the conclusions by Hewitt and Gundry (1977) who found very small Mo requirements by the cauliflower plants under nitrogen application in the form of ammonia.

Depending on the plant species and the nitrogen nutrition requirements, the critical level of molybdenum in the leaves fluctuates between 0.1 and 1.0 mg/kg of dry matter (Gupta 1977, Gupta and Lipsett 1981, Marschner 1995). Crucifers, especially cauliflower and cabbage, but also legumes, are crops with a high demand for Mo. Current data on Mo concentration in the plants of winter

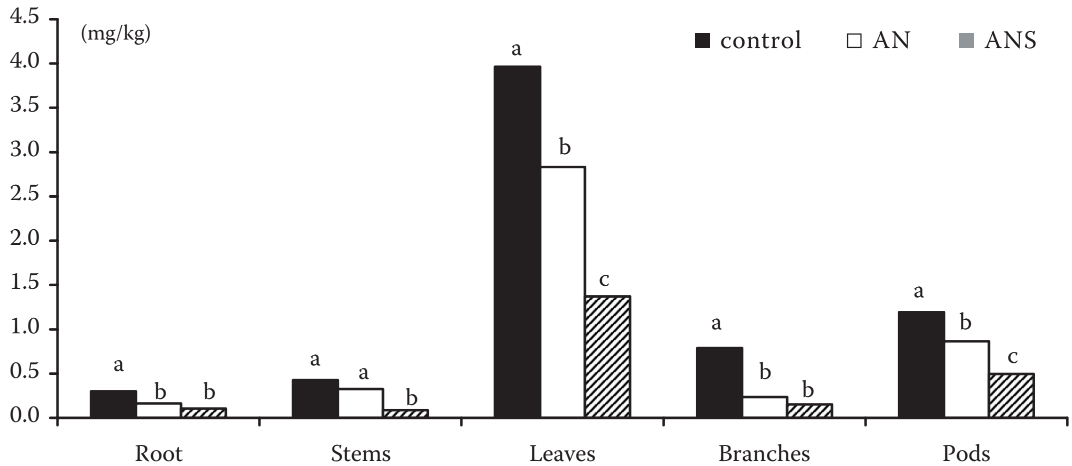

Figure 4. Molybdenum content in plants – green pod period

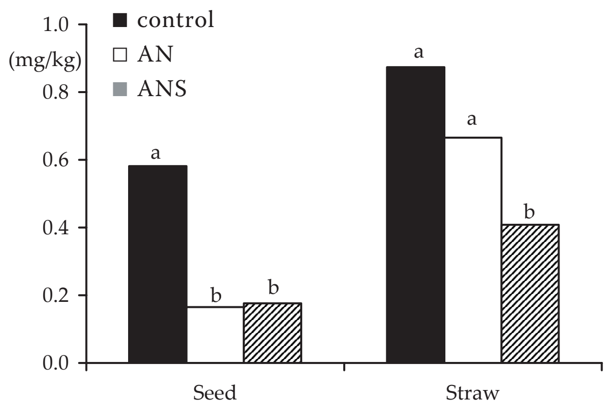

Figure 5. Molybdenum content in plants – harvest

oilseed rape in the Czech Republic are not available. Neuberg (1990) classified the quantity of 0.4 mg/kg or less of Mo in leaves (with the height of growth at 30–40 cm) as low. They considered 0.7 mg/kg as high content. Finck (1997) also presented similar concentration figures. The author lists medium contents in the leaves during the fast elongation period – budding stage – in the range of 0.4–0.8 mg of Mo per kg. All investigated treatments had contents higher than 0.4 mg/kg. The field trials cannot confirm unambiguously into what extent this is really a critical value (< 0.4 mg/kg). Finck and Sauermann (1998) in Germany observed the Mo contents at 37 sites in 1994 at 47 sites in 1995. However, the assumption that following the sodium molybdate application (at 39 g/ha) there would be a statistically significant increase in the seed yield of winter oilseed rape in the growth with Mo content less than 0.4 mg/kg, was not been confirmed.

During the full flowering period the highest Mo concentration is in the upper (younger) leaves. The control treatment had a content of Mo at 3.1 mg/kg. Schröder (1993) also determined similarly high levels of concentration (4.6–4.8 mg/kg) for the flowering period. The Figure 4 indicates that the highest concentrations in the leaves have also been determined during the green pod period. Relatively high concentrations of Mo in the young

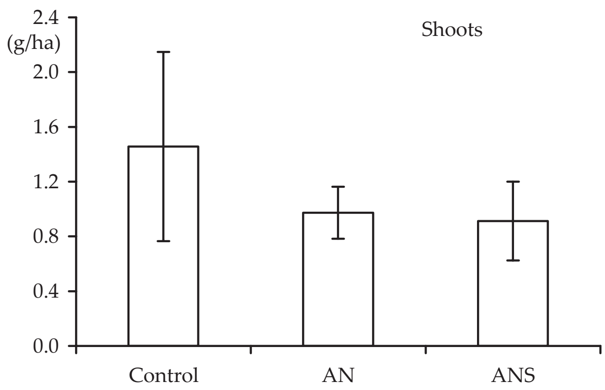

Figure 6. Molybdenum removal by plants – vegetation regrowth

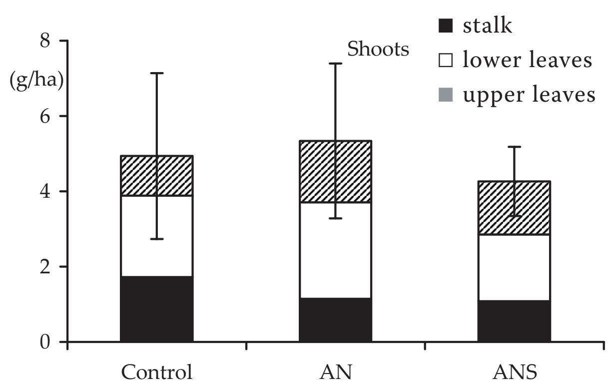

Figure 7. Molybdenum removal by plants – budding period

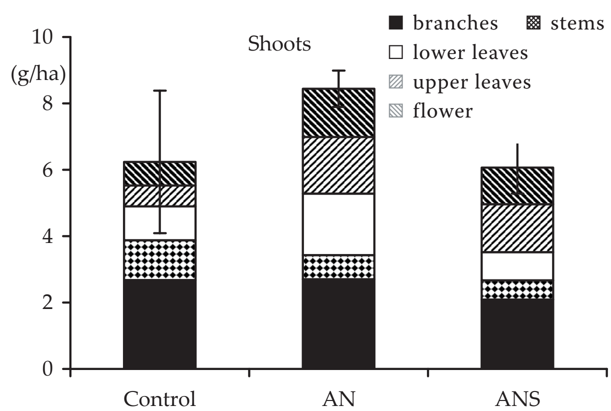

Figure 8. Molybdenum removal by plants – flowering period

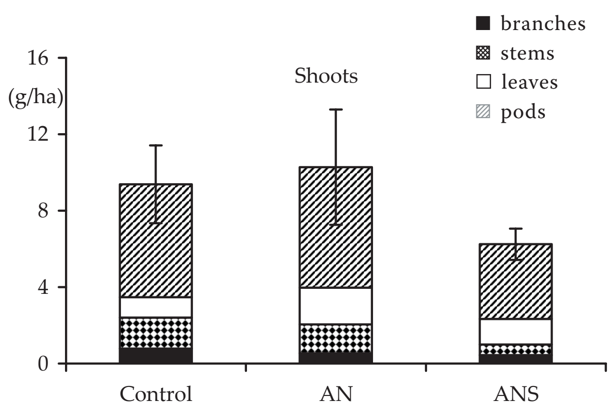

Figure 9. Molybdenum removal by plants – green pod period

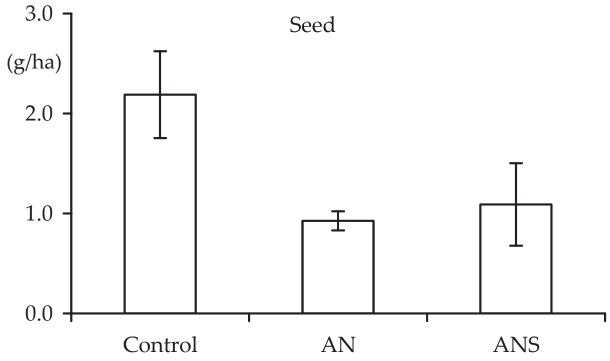

Figure 10. Molybdenum removal by plants – harvest

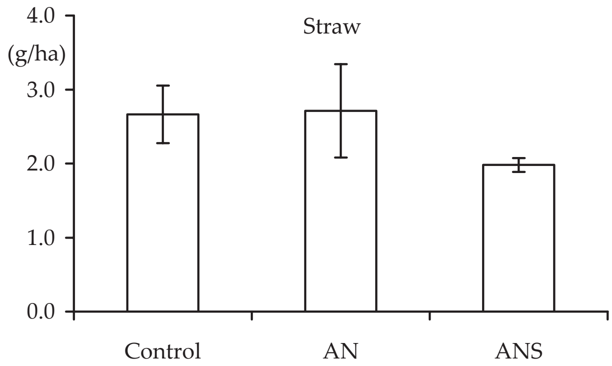

Figure 11. Molybdenum removal by plants – harvest

leaves, flowers and pods suggest a rather high mobility of molybdenum in plants (Gupta and Lipsett 1981). Different Mo contents in the plants during the entire vegetation period is very well reflected in the differences between individual treatments at the time of harvest, which is also in accordance with the findings of Franco and Munns (1981).

The Figures 6–11 document the removal of the investigated element by the above ground biomass. The values of significant deviation are shown for the total removal. They have been calculated for individual data, but they have been left out in order to keep the figures simple and lucid. At the commencement of spring vegetation the roots accumulated 0.23–0.26 g of Mo/ha, and the above ground biomass accumulated 0.97–1.46 g of Mo/ha. During the vegetation period the removed quantity is also increasing. Even though the ANS treatment produced the highest yield of biomass, the total accumulated quantity of Mo is the lowest here, which is due to a distinctly lowest concentration of Mo in the plant tissues. Depending on the variant, the removal during the full flower phase was 6.2–8.4 g Mo/ha, and during the green pod phase it was 6.2–10.3 g/ha. We can therefore conclude that the shown values do not contradict Knittel's (1999) who cites the removal by the above ground biomass of oilseed rape at the level of about 5 g of Mo/ha. At the same time, the seed harvest itself only transports 0.93–2.19 g of Mo/ha out of soil.

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