The effect of long-term fertilization on the sulphur content in soil and in the mountain meadow sward (Czarny Potok)

M. Kopeć, K. Gondek

Agricultural University in Cracow, Poland

ABSTRACT

The influence of long-term regular mineral fertilization on the soil environment considering the total sulphur and the sulphur balance in the habitat of the permanent mountain meadow was investigated. The experimental field (set up in 1968) is situated at Czarny Potok (20°8' E, 49°4' N) in the central part of the Polish Carpathian. With completed annual NPK fertilisation 1.8 kg S.ha⁻¹ was introduced into the soil. The highest sulphur amount was found in the 0–10 cm horizon and this value slightly exceeded the content considered as natural. The sulphur content in the sward from Czarny Potok was lower than the mean sulphur content calculated in Poland for grasses (0.21% S). In the case of full NPK fertilisation the amount of removed sulphur ranged from 11.4 to 14.0 kg S.ha⁻¹. The mean sulphur leaching into the soil profile from surface of 1 ha can be estimated from 1.1 to 3.7 kg S.ha⁻¹.

Keywords: sulphur content; mineral fertilization; soil; permanent mountain meadow

In Poland, there are regions with a visible deficiency of sulphur as well as its surplus. These differences result from the effect of local sources of SO, emission. SO, emission in the region of the Polish Carpathian is directly connected with the industrial regions in the West (the Śląsk province –16.8% SO, of emission in Poland) and less industrialized regions in the east (the Małopolska province – 4.45% of emission in Poland and the Podkarpacie province – 1.5% of SO, emission in Poland). Total emission in Poland in 1999 amounted to 1.719 mln t it means 55 kg SO₂.ha⁻¹. Undoubtedly SO₂ emission over long distances is the problem concerning the whole country. An increase of the mean sulphur content in the humic layer of Polish soils observed during the last 20 years is also something to worry about (Motowicka-Terelak and Terelak 2000). The authors of these findings proved that until 1970 comparative studies showed that together with the increasing variability the total S content increased by 174 mg.kg⁻¹ in mineral soils and by 380 mg.kg⁻¹ in organic soils. This matter is important considering the intensification of agricultural production and phytotoxic effect of sulphur on the environment. The effect of sulphur on plants is direct and indirect, for example, by soil degradation. It is assumed that grasses need slightly less sulphur than phosphorus, for *Papilionaceae* this demand is about the same and Cruciferous need more phosphorus than sulphur. However, due to the differences in yields, for rape and maize the amount of sulphur removed from soil with the yields is significant (30–40 kg S.ha⁻¹). On average, together with the yield of 100 kg of hay dry mass it is removed approximately 0.20 kg S.ha⁻¹. Determination of the sulphur content, considering its dynamics in the environment, is important regarding the period of its deficiency and surplus (Leigh and Johnston 1994). Rational management will have to be based on balance of this element with other nutrients particular with nitrogen. The

aim of the study is to answer the question if long-term regular mineral fertilization influenced the soil environment considering the total sulphur content and what the sulphur balance is in the habitat of the permanent mountain meadow.

MATERIAL AND METHODS

The experimental field is situated at Czarny Potok near Krynica, PL (20°8' E, 49°4' N) about 720 m a.s.l. at the foot of Jaworzyna Krynicka in the central part of the Polish Carpathian on a land slope 7° and NNE aspect. The experiment was set up in 1968 on a natural mountain meadow of moor mat-grass (Nardus stricta L.) and red fescue (Festuca rubra L.) type with the great share of dicotyledonous plants. The experimental brown acid soil was developed from Magura sandstone, with granulometric composition of light loam (40% of 1–0.1 mm fraction; 37% of 0.1-0.2 mm and 23% of > 0.02 mm fraction) with three characteristic genetic horizons: sod AhA (0-20 cm), browning ABbr (21–46 cm) and matrix BbrC (47–75 cm). The experiment was set up with the randomised block method in five replications including eight fertilised objects (Table 1). In the 7th and 8th year, as well as in the 26th and 27th year of the experiment consecutive effects of mineral fertilisers were investigated. During the first break in fertilisation the cultivation measures were limited to cutting and harvesting the sward yields. During the second break in mineral fertilisation, the sward was grazed by sheep after the amount of harvested yield had been assessed (1 m²) in the 1st and 2nd cut.

In the initial period of the experiment until 1974, silicophosphate and 40% potassium salt were used, whereas triple superphosphate and 60% potassium salt were applied after the first break in fertilisation. Since the autumn

Table 1. The scheme of fertilizing in the static experiment in Czarny Potok (2000)

Fertilising objects	Nutrient rate (kg.ha ⁻¹ .year ⁻¹)			Nitrogen form	S amount introduced with fertilisers (kg.ha ⁻¹ .year ⁻¹)	Share of grasses (%)	
	P	K	N		(1.8.1.1.1.1)	0Ca	+Ca
PK	39.24	124.5	_		1.7	78	79
PK + N1an	39.24	124.5	90	ammonium nitrate	1.7	79	85
PK + N2an	39.24	124.5	180	ammonium nitrate	1.8	93	95
PK + N1u	39.24	124.5	90	urea	1.7	88	90
PK + N2u	39.24	124.5	180	urea	1.7	94	93
N	_	_	90	ammonium nitrate	0.05	82	84
P	39.24	_	_		1.6	81	78
0	_	_	_		_	73	72

in 1985 and with the same level of fertilisation, the experiment has been conducted in two series: unlimed and limed (1985, 1995). In the 18^{th} year a half of each plot (21 m²) was limed with lime containing 80.1% CaCO $_3$ according to the value equal to a half of soil hydrolytic acidity of each fertilised plot. Liming with calcium carbonate in a dose equal to the whole value of hydrolytic acidity in the soil of each fertilised plot was repeated in the 28^{th} experimental year.

The vegetation period in the experimental area lasts from April to September (150–190 days). Average yearly precipitation over the 1968–1997 period for the experiment at locality (measured at the Krynica meteorological station) was 820.1 mm and 538 mm for the six-month period (April–September), i.e. the time assumed as vegetation period. The amount of precipitation in the region during the year and through April-September did not fluctuate much (respectively variability V% = 17.7 and 20.8). The quantity of precipitation in April-September constitutes about 2/3 of yearly total precipitation. Eight times average monthly temperature in April in the experimental area, measured during 30 years (1968-1997), was lower than 5°C. Average yearly temperature was 5.7°C and average for vegetation period was 11.7°C. Variability of mean monthly temperature during the discussed period was slight, it exceeded 20% only for April, whereas for May and September it was about 10%. Results presented in this paper refer to the studies conducted in 2000. Yields of sward green mass were determined twice a year: the first cut was harvested on the 3rd of June, whereas the second cut mainly on the 10th of September.

In the autumn after the second cut, soil for analyses was sampled from three layers 0–10 cm, 10–20 cm and 20–45 cm. In the experiment objects there were lysimeters with the surface 444.6 cm² placed at the depth of 45 cm. Filtrate was collected three times: in spring, after the first cut and the second cut. Total sulphur in plants and in soil was determined with the ICP after earlier mineralisation with nitric acid and magnesium nitrate whereas in lysimeter water directly on ICP (Zbíral 1999). Total nitrogen in plants was determined with the Kjeldahl method.

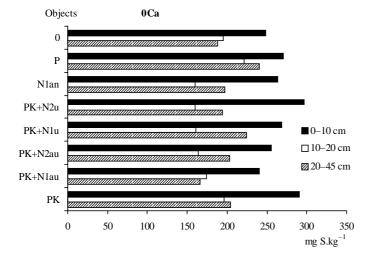
Samples for analyses were prepared as weighted means from five replications of each fertilised objects. The analysis results were assumed as reliable if the determination error from two replications did not exceed 5%.

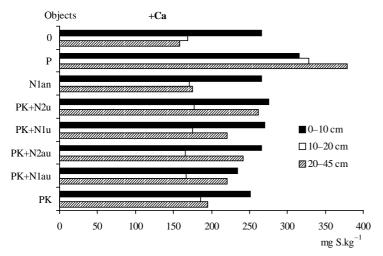
RESULTS AND DISCUSSION

Changes in share of species in the sward resulting from fertilisation are confirmed by many authors in short and long-term experiments (Gorlach and Curyło 1990, Leigh and Johnston 1994, Jeźikova and Lihan 1997). Changes in the share of leading species during 30 years in the object without fertilisation were slight. The share of two species Festuca rubra L. and Nardus stricta L. was all the time at the same level of 50%. Mineral fertilisation applied in Czarny Potok caused significant changes in the botanical composition already in the first three years of the experiment (Kopeć 2002). Such a visible reaction of sward species to fertilisation is typical particularly of poor communities. Unilateral fertilisation with ammonium nitrate and complete fertilisation increased the share of grasses in the yield eliminating the share of dicotyledonous particularly Papilionaceae. As a result of combined fertilisation with nitrogen, phosphorus and potassium rapid decline in the share of Nardus stricta L. was observed. In the third decade of systematic fertilisation with ammonium nitrate Nardus stricta L. share amounted to 60%.

Nitrogen fertilisation applied against a background of PK for both doses 90 and 180 kg N.ha⁻¹ increased *Holcus mollis* L. share in the sward. The speed of this process depended mainly on the nitrogen rate. After 10-year application of 180 kg N (irrespective of the form) in the mountain condition monoculture of this species was maintained. Despite a systematic increase in *Holcus mollis* L. share in the sward with the dose 90 kg N.ha⁻¹ against the background of PK fertilisation there was a significant difference in the speed of this species increase in comparison to the dose of 180 kg N.ha⁻¹ against the background of PK fertilisation.

Figure. 1. Sulphur content in three soil horizons (mg.kg⁻¹) in treatments with and without liming

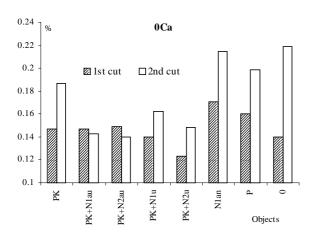




Favourable floristic composition was obtained for NPK fertilisation with the dose of 90 kg N.ha⁻¹. Fertilisation in this rate caused occurrence of valuable grasses as *Poa pratensis* L. and *Phleum pratense* L. and considerable increase in *Festuca pratensis* Huds share.

First liming after 18 years of the experiment had the biggest influence on changes in the sward floristic composition in the objects with incomplete fertilisation. The sward on the NPK objects in particular with the dose of

180 kg N.ha⁻¹ did not respond to liming at all. The effect of liming was the most visible in the first four years after this treatment. Since the 5th year differences in the sward composition between limed and unlimed objects started to decrease. In the experiment in Czarny Potok liming repeated twice caused significant changes including an increase in the share of favourable species in the sward. The biggest effect was observed on the objects with reduced mineral fertilisation while the lowest on the objects



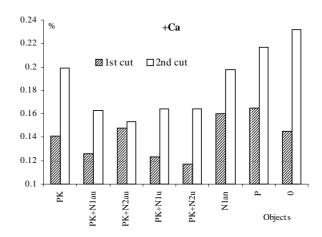


Figure 2. Sulphur content in sward (%) grown on limed and nonlimed treatments

Table 2. Amount of sulphur removed with the sward and weight ratio of N to S

Fertilising objects		S amoun	t removed	with yield (k	N/S					
	0Ca			+Ca			0Ca		+Ca	
	1st cut	2 nd cut	total	1st cut	2 nd cut	total	1st cut	2 nd cut	1st cut	2 nd cut
PK	3.5	6.4	9.9	2.9	4.7	7.6	12.4	13.2	11.4	12.2
PK + N1an	5.3	6.1	11.4	5.4	7.6	13.0	11.9	14.9	13.7	11.6
PK + N2an	5.8	7.4	13.2	6.9	7.1	14.0	13.8	14.1	11.9	13.4
PK + N1u	4.3	9.4	13.7	5.4	6.4	11.8	12.8	12.8	10.9	11.5
PK + N2u	4.4	8.1	12.5	6.3	7.5	13.8	17.6	15.3	15.9	12.4
N	2.8	6.0	9.8	3.1	5.7	8.8	11.7	10.9	13.5	11.6
P	1.7	5.9	7.6	2.4	3.5	5.9	9.8	11.4	8.6	8.7
0	1.5	4.1	5.6	2.1	4.0	6.1	10.8	11.0	10.8	9.1

with full NPK fertilisation. The sward reacted to liming in a similar way as in other long-term experiments, for example, in Rothamsted (Tilman et al. 1994) (the share of *Papilionaceae* and valuable grasses increased in the sward of objects without nitrogen and with small nitrogen doses). Festuca pratensis Huds, Poa pratensis L. and Dactylis glomerata L. expanded and replaced mainly Nardus stricta L. and Holcus mollis L. As a result of liming Holcus mollis L. share decreased, on average, twice over particularly in the case of the sward fertilised with a higher nitrogen dose where reaction to the first liming was slight. Three years after the second fertilization Holcus mollis L. share, occurring in monoculture, decreased to 45-50%. The results of the experiment in Czarny Potok confirmed the findings of the other authors stating that dynamic of changes in species share in the sward varies greatly in course of time and liming on the objects causes only a slight (by a few per cent) increase in the Papilionaceae share. Alchemia vulgaris L. and Heracleum sphonddium L. are among herbs, which increased their share after liming in the experiment in Czarny Potok. Detailed information about botanical composition is presented by Kopeć (2002).

In the fertilizers used in the experiment the sulphur content was very low (lower than 0.06% of total S) except for triple superphosphate in which the sulphur content amounted to 1.8%. With completed NPK fertilisation 1.8 kg S.ha⁻¹ was introduced into the soil together with the fertilizers (Table 1). In the region where the experiment was set up the SO_2 emission decreased due to modernisation of the gas installation near Krynica in the early nineties. The mean concentration of sulphur dioxide in Krynica in 2000 amounted to 3 μ g SO_2 .m⁻³ and this value was 10 times lower than the quota (Anonymous 1999a). Criteria of limits on the total sulphur content in soil state four classes according to the agronomic category and the organic matter content. The total sulphur content in soil lower than 200 mg.kg⁻¹ is considered as a natural sulphur content (class 0). In the region of the experiment 72% of soils belonged to this class and 22% to the class with the increased sulphur content (Anonymous 1999b).

The sulphur content in the soil from the experiment varied according to the horizon (Figure 1). The highest sulphur amount was found in the 0–10 cm horizon and this value slightly exceeded the content considered as natural. Deeper into the soil profile the sulphur content decreased and in most objects increased again in the 20–45 cm horizon. In the object without fertilization this dependence was not observed and the sulphur content did not vary in the horizons below 0–10 cm. Results confirm the finding reported by Motowicka-Terelak and Terelak (1998) and Lükewille et al. (1995) stating that the

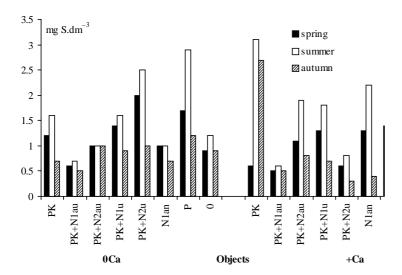


Figure 3. Sulphur content leached $(mg.dm^{-3})$ in three periods of the year

Table 3. Exchangeable aluminium in soil (Al_{exch}.cmol.kg⁻¹ soil)

Fertilising objects		0Ca		+Ca			
	0-10 cm	10-20 cm	20–45 cm	0-10 cm	10-20 cm	20-45 cm	
PK	1.38	1.96	1.26	0.05	0.07	0.20	
PK + N1an	1.24	1.55	1.08	0.09	0.21	0.55	
PK + N2an	1.67	2.80	1.17	0.03	0.22	0.66	
PK + N1u	1.50	1.84	1.36	0.04	0.09	0.36	
PK + N2u	1.99	2.76	1.84	0.07	0.21	0.95	
N	0.89	2.26	1.12	0.06	0.06	0.12	
P	0.39	0.69	0.48	0.06	0.11	0.50	
0	0.27	0.56	0.63	0.07	0.09	0.10	

upper horizons contain more sulphur than horizons lying deeper what results from the dependence between the humus and sulphur content in soil and ambient concentration of sulphur compounds in the last 20 years. The sulphur content in the meadow sward differed in the fertilized objects and cuts (Figure 2). On the whole, a higher sulphur content in the sward of studied objects was found in the second cut (from 0.14 to 0.23%S) than in the first cut (from 0.12 to 0.17% S) with the exception of the objects fertilised with ammonium nitrate against the PK background in series without liming. The highest sulphur content was found in the sward of the second cut in the objects without fertilisation while the lowest in objects with full NPK fertilisation. Differences in the sulphur content in the sward of limed and unlimed treatments were small. Overall, the higher sulphur content was characteristic for the second sward cut. The sulphur content in the sward from Czarny Potok was lower than the mean sulphur content calculated in Poland for grasses (0.21% S). The latter was reported by Motowicka-Terelak and Terelak (2000). The higher sulphur content was closely correlated with the low dry matter yields obtained from the objects with incomplete fertilization. The sum of sulphur removed with yields from the objects (Table 2) with incomplete fertilisation amounts to 10 kg S.ha⁻¹ and in the object without fertilization 5.6–6.1 kg S.ha⁻¹. In the case of full NPK fertilisation the amount of removed sulphur ranged from 11.4 to 14.0 kg $S.ha^{\text{--}1}$ in all combinations and both fertilizing series. A higher amount of taken sulphur in the second cut was connected with the draught, which reduced the yield of the 1st cut. The Sperman correlation coefficient (for 16 cases of first cut) showing the dependence between the sulphur content and yield amounted to -0.52 and for the second cut -0.89.

The ratio of nitrogen to sulphur is often considered as an index of the sulphur content. In case of grain crops the value 15 is considered as correct. In the meadow sward in Czarny Potok (Table 2) the value N:S ranged from 8.6 to 17.6 and lower values were characteristic for the sward fertilised unilaterally with phosphorus (8.6–11.4) and the sward not fertilized (9.1–11) The dose of 180 kg N.ha⁻¹ + PK in comparison to 90 kg N.ha⁻¹ + PK increased this value, however not in all cases. Values presented in the table imply low utilization of fertiliser nitrogen. The ratio of

these elements in soil is considered equally important and its changes connected with the high dynamics of these elements cause disturbance in physiological processes in plants and a yield reduction. The sulphur content in analysed samples of lysimeter water ranged greatly according to a sampling date and the object. Precipitation during studies differed. Monthly average precipitation in winter amounted to 122 mm, from the beginning of vegetation to 1st cut, 101 mm and between cuts, 165 mm. A low amount of eluate collected after the 1st cut was connected with the drought in June 2000. The highest sulphur amounts in filtrate were found (Figure 3) in samples collected in summer on the 70th day after fertilization with triple superphosphate while the lowest in samples collected after the 2nd cut, after the period of intensive sward growth. Liming favoured sulphur leaching but the leaching process depended on yields and on the sulphur uptake by the sward in particular objects. Lower yields in the object fertilised with phosphorus and potassium in limed series in comparison with series without liming favoured sulphur leaching into the soil profile. The amount of lysimeter water during the whole year collected in particular objects ranged from 7.4 to 11.5 dm³ per lysimeter. The sulphur leaching into the soil profile from surface of 1 ha can be estimated at 1.1 to 3.7 kg S.ha⁻¹. On average, for all objects in series without liming leaching amounted to 2.06 kg S.ha⁻¹ and was lower than the average leaching in series with liming by 0.44 kg.ha⁻¹.

Estimated values are very low and are connected with slight sulphur amounts introduced with fertilisers, with very low industrialisation in this region and low wet and dry sulphur precipitation. Retention of sulphates in soil is connected with the reaction of precipitation of sulphate ions with aluminium (Table 3). An increase in the acid soil reaction causes hydration of absorbed sulphates, hence after liming sulphur availability for plants increases, but leaching of SO₄²-ions increase as well. Together with the change in the soil reaction biomass of soil microorganisms also changes (Paul and Clark 1998). Liming favours sulphur release, among other things, by accelerating the decomposition of organic compounds, leading to sulphur release and its change into soluble sulphates. Analysis of Spermann correlation proved the negative correlation between the sulphur content in the sward of

the second cut and the exchangeable aluminium content in the 0-10 cm horizon of the soil from series without liming (R = -0.78, p < 0.02). There was not any significant correlation between the exchangeable aluminium content and the sulphur content in the soil or in the filtrate. In conditions of the experiment in Czarny Potok there was a slight tendency for an increase in the sulphur content in the deeper horizon due to liming of the objects fertilized with NPK and significant increase in the sulphur content in the objects unilaterally fertilised with phosphorus. Sulphur release because of liming caused changes, mainly an increase in the sulphur content of sward particularly in the second cut. At the same time, there was a correlation between the sulphur content in soil and yields. An increase in the sulphur content in the soil in the objects fertilised with phosphorus in series with liming was connected with the lower yields and with the lower sulphur uptake in comparison with the same object in series without liming.

Leaching of sulphate sulphur does not depend on the fertilisation level or type, and the way of soil utilization. On average, 80–100 kg S-SO₄ from ha is leached yearly in lysimeter conditions in three typical Polish soils. However, the sulphur content in loam was 30–50 times higher than the content found in Czarny Potok. Heneklaus et al. (2000) stated a much wider range of leached sulphur: 40–80 kg.ha⁻¹, and according to them this occurrence is associated with many factors: climate, soil agronomic category, surface configuration, fertilization, plant yield or the way of fodder acquisition in case of grasslands. Heneklaus at al. (2000) mentioned experiments in which 10–20% of 43 kg S.ha⁻¹ of sulphur applied with fertilizers on the pasture in New Zealand in autumn was leached.

REFERENCES

Anonymous (1999a): Ocena stanu zanieczyszczenia gleb województwa małopolskiego metalami ciężkimi i siarką. WIOŚ Krakow, Bibl. Monit., Środo.

- Anonymous (1999b): Raport o stanie środowiska w 1998 roku na obszarze województwa małopolskiego. WIOŚ Krakow, Bibl. Monit., Środo.
- Gorlach E., Curyło T. (1990): Reakcja runi łąkowej na wapnowanie w warunkach wieloletniego zróżnicowanego nawożenia mineralnego. Rocz. Gleb., *41*: 161–177.
- Heneklaus S., Bloem E., Schnug E. (2000): Sulphur in agroecosystems. Folia Univ. Agric. Stetin., Agric., 204: 17–31.
- Jeżikova O., Lihan E. (1997): Dlhodobe hnojenie aluviálnej luky pri dvoch pomeroch N:P:K. Poľnohospodárstvo, *43*: 303–317.
- Kopeć M. (2002): Causes of mountain meadow soil chemical degradation in long-term fertiliser experiment. Rostl. Výr., 48: 159–166.
- Leigh R., Johnston A. (1994): Long-term experiments in agricultural and ecological sciences. CAB Int., Wallingford, UK.
- Lükewille A., Malessa V., Alewell Ch. (1995): Measured and modelled retenton of inorganic sulfur in soils and subsoils (Harz Mountains, Germany). Wat., Air Soil Pollut., 85: 683–688.
- Motowicka-Terelak T., Terelak H. (1998): Siarka w glebach Polski – stan i zagrożenie. PIOŚ Warszawa, Bibl. Monit. Środo.
- Motowicka-Terelak T., Terelak H. (2000): Siarka w glebach i roślinach Polski. Folia Univ. Agric. Stetin., Agric., 204: 7–16.
- Paul E.A., Clark F.E. (1998): Soil microbiology and biochemistry. Acad. Press Inc. Polish ed. Mikrobiol. Bioch. Gleb. Wyd. Uniw. M. Curie-Skłodowska, Lublin.
- Tilman D., Dodd M., Poulton P., Johnston A., Crawley M. (1994): The park grass experiment: Insights from the most long-term ecological study. Long-term experiments in agricultural and ecological sciences. CAB Int., Wallingford, UK: 287–303.
- Zbíral J. (1999): Comparison of some extraction methods for determination of sulphur in soils of the Czech Republic. Rostl. Výr., *45*: 439–444.

Received on November 1, 2001

ABSTRAKT

Vliv dlouhodobé aplikace minerálních hnojiv na obsah síry v půdě a v píci trvalé horské louky (Czarny Potok)

Byl ověřován vliv dlouhodobé aplikace minerálních hnojiv na celkový obsah síry v půdě a na její obsah a bilanci v píci trvalé horské louky. Pokusný pozemek byl založen v roce 1968 v lokalitě Czarny Potok (20°8' E, 49°4' N) v centrální části polských Karpat. Plným každoročním hnojením pozemků (NPK) se minerálními hnojivy dodávalo ročně 1,8 kg S.ha⁻¹. Nejvyšší obsah síry byl zjištěn v půdním profilu (0–10 cm), a ten pouze mírně překračoval průměrný obsah síry běžně se vyskytující v přírodě. Obsah síry v píci sklizené na pokusné lokalitě byl nižší než průměrný obsah síry zjištěný v travách v Polsku (0,21 % S). V případě plného hnojení NPK se pohyboval celkový odběr síry v intervalu od 11,4 do 14,0 kg S.ha⁻¹. Množství síry vyplavené z 1 ha sledovaných porostů kolísalo od 1,1 do 3,7 kg S.ha⁻¹.

Klíčová slova: obsah síry; minerální hnojení; půda; trvalá horská louka

Corresponding author:

Dr. hab. Michał Kopeć, University of Agriculture, Department of Agriculture Chemistry, A. Mickiewicza 21, 31-120, Kraków, Poland, rrkopec@cyf-kr.edu.pl