
The Influence of Mineral NPK Fertilizer Rates and Their Ratio on Potassium Dynamics in Soil: Data from a Long-Term Agricultural Plant Fertilization Experiment

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Article

The Influence of Mineral NPK Fertilizer Rates and Their Ratio on Potassium Dynamics in Soil: Data from a Long-Term Agricultural Plant Fertilization Experiment

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Abstract: A fertilisation experiment with aim to determine the effect of different potassium fertiliser rates and their interaction with nitrogen and phosphorus on field rotation productivity, potassium balance, fertiliser utilization and changes in content of potassium in soil was carried out in Lithuania between 1971 and 2020. The multi-factorial scheme with 45-treatment plots, where seven (including zero) rates of nitrogen, phosphorus and potassium fertilisers were studied. The experimental treatments during the study period included winter wheat, spring wheat, spring barley, sugar beet, spring rapeseed, annual and perennial grasses. It was found that potassium fertilisers was the most effective on agricultural crops when used in combination with other major plant nutrients – nitrogen and phosphorus. The balance of potassium (K_2O) in soil, when nitrogen and phosphorus fertilisers were applied together, to compensate for potassium removal, when applying low nitrogen (N) 72 kg ha^{-1} and phosphorus (P_2O_5) 64 kg ha^{-1} fertiliser rates, 128 kg ha^{-1} of potassium fertilisers is required. When using high nitrogen 180 kg ha^{-1} and phosphorus 160 kg ha^{-1} fertiliser rates, 160 kg ha^{-1} of potassium is needed. The highest potassium uptake, reaching 51.6%, was achieved when plants had been fertilised with nitrogen 108 kg ha^{-1} , phosphorus 96 kg ha^{-1} , and potassium 96 kg ha^{-1} . When fertilising with potassium fertilisers alone, the content of plant available K_2O content in the soil increased, while fertilisation with nitrogen and phosphorus combined it's decreased, except in the plots where the plants had been fertilised with potassium fertiliser at rates of 128 kg ha^{-1} and higher. Due to the influence of fertilizers, the amount of non-exchangeable potassium in the soil also increased, but relatively less compared to the amount of available potassium content.

Keywords: potassium fertilizers; nutrient interaction; metabolizable energy; balance; soil

1. Introduction

Potassium is one of the main plant nutrients, along with nitrogen and phosphorus. It influences many physiological processes affecting plant growth, yield and its quality, as well as plant resistance to pathogens, frost, heat and drought, pesticides and heavy metals [1,2]. Moreover, potassium is almost as important as nitrogen for plant nutrition and its impact on crop yields in low-potassium soils is no less than that of nitrogen and phosphorus [3,4]. Potassium deficiency in agricultural crops reduces yield, quality and stress tolerance [5,6]. This is particularly important in recent times, as droughts and heat stresses due to climate change are expected to have a negative impact on the yield of agricultural crops [7]. However, potassium fertiliser use is significantly lower worldwide compared to nitrogen and phosphorus, which imbalances the relationship between these nutrients in soil and plants [2,8]. The interaction of nitrogen with potassium and/or phosphorus leads to improved root development and other plant functions that influence yield and its quality [9,10]. Phosphorus and potassium fertilisers have a significant impact on the efficiency of nitrogen fertilisers, as well as on phosphorus and potassium dynamics in soil, leading to an increase in the efficiency of nitrogen and phosphorus fertiliser use [4,11,12]. Improved nitrogen uptake also reduces nitrate

pollution [13]. On the other hand, the effectiveness of potassium fertilisers on agricultural crops also depends on their nutrition with other nutrients, especially nitrogen and phosphorus [12,14]. Furthermore, it has been noted that balanced application of nitrogen, phosphorus and potassium fertilisers to agricultural crops results in a five to ten times more efficient uptake of fertilisers compared to applying nitrogen fertilisers alone [12].

Potassium reserves in the soil are high, however, not all of them are readily available to plants [7]. Most of potassium, 90–98%, is found in soil minerals such as feldspar and mica, and only a small fraction of potassium in this form is available to plants. Another source of soil potassium is non-exchangeable potassium, which accounts for up to 10% of the total potassium content. Non-exchangeable potassium is found in 2:1 clay minerals and is not much taken up by plants. The third source of soil potassium is potassium directly taken up by plants (1–2 %), which is present in the exchangeable form and in soil solution [15,16]. Currently, due to the reduced use of potassium fertilisers, potassium uptake by plants is decreasing [17]. The main causes of soil potassium deficiency are the removal of potassium with crop yields, losses due to leaching and soil erosion, and inefficient use of potassium fertilisers [8,18,19].

The demand for mineral potassium fertilisers is increasing rapidly in developing and populous countries, as well as in some developed countries [7,20]. For example, a quarter of China's agricultural land is low in potassium [2,18,19,21]. In India, on average, potassium inputs from fertilisers are as much as 3–5 times lower compared to its accumulation in the yield of agricultural crops, and the inputs of this nutrient for plant growth are about seven times less than nitrogen and three times less than phosphorus [22]. As noted by other sources [2,23], potassium is the main yield-limiting factor in as much as 72% of India's agricultural land. The potassium balance in soil is also affected by unbalanced application of nitrogen, phosphorus and potassium fertilisers, straw removal, as well as recent introduction of higher-yielding crop varieties [24,25].

In Lithuania, 16.8% of soils had low potassium content ($<100 \text{ mg kg}^{-1}$) in 1995–2006 [26]. However, in some countries, such as Germany and Switzerland, more potassium is incorporated into soil with fertiliser than is taken up by plants [27,28]. However, potassium fertiliser resources are limited and non-renewable worldwide, and need to be used efficiently [8,29].

Achieving stable and high crop yields, maintaining adequate nutrient levels in soil and reducing potassium leaching requires sufficient attention to the potassium balance in soil [17,30]. Fertilisation recommendations for agricultural crops are usually based on studies of the exchangeable potassium content in the topsoil, as the effectiveness of potassium fertilisers for agricultural crops depends on the content of this element in soil [2]. However, the effect of potassium fertilisers on agricultural crops depends not only on the exchangeable potassium but also on the concentration of non-exchangeable potassium in soil, as well as on soil texture, cation exchange capacity, soil moisture, presence of other plant nutrients in soil, and the type of crop [15,22,31]. In addition, soil potassium content is influenced by soil forming rock, weathering intensity, application of organic and mineral fertilisers, leaching, erosion and potassium export with crop yield [8]. Potassium is most commonly deficient in acidic sandy soils, as well as in waterlogged and saline soils [15].

The effects of fertilisation on crop yields and soil nutrient balance are more objectively assessed by using the results of long-term fertilisation experiments on agricultural crops [17,32,33].

Can be hypothesized, that potassium fertilizers have a greater influence on the productivity of field crop rotation, if they are used together with nitrogen and phosphorus fertilizers. As a result, the absorption of potash fertilizers will improve, so there will be less potash accumulation in the soil, compared to fertilizing agricultural plants with potash fertilizers only.

Therefore, the aim of this work was to determine the long-term influence of different potassium fertiliser rates and their interaction with nitrogen and phosphorus on field rotation productivity, potassium balance, fertiliser utilization and changes in content of potassium in soil.

2. Results

2.1. Field crops productivity

The effectiveness of potassium fertiliser on the productivity of field rotation significantly depended not only on the rate of potassium fertiliser, but also on the nitrogen and phosphorus nutrition of the crop. This can be seen in [Table 1], as applying the average annual fertilisation rates of 96 and 192 kg ha⁻¹ K₂O, but without nitrogen and phosphorus fertiliser, did not lead to a statistically significant increase in the amount of metabolisable energy when comparing the above fertiliser rates with each other. However, there was a significant increase of 16.3 and 17.4 %, respectively, in the metabolisable energy of those rates compared with 40.3 GJ ha⁻¹ obtained in the unfertilised plots. In contrast, fertilisation with 96 and 192 kg ha⁻¹ K₂O in combination with nitrogen and phosphorus fertilisers (N₁₀₈P₉₆) resulted in a significant increase in the amount of metabolisable energy of up to 98.7 and 107.9 %, respectively, compared with the unfertilised plots.

Table 1. Effect of mineral fertiliser rates and its combinations on the productivity of agricultural crops in terms of average annual metabolizable energy.

| Average annual fertilization rate kg ha ⁻¹ | | | | | | | | |
|---|-------------------------------|------------------|----------|----------|-----------|------------|----------|-----------|
| N | P ₂ O ₅ | K ₂ O | | | | | | |
| | | 0 | 32 | 64 | 96 | 128 | 160 | 192 |
| Average annual metabolizable energy GJ ha ⁻¹ | | | | | | | | |
| 0 | 0 | 40.3a* | | | 46.9b | | | 47.3b |
| | 96 | 49.1bc | | | 53.6cdef | | | 54.8def |
| | 192 | 51.5bcde | | | 53.6cdef | | | 55.3defg |
| 36 | 32 | | 61.8hijk | | | | 65.7jkl | |
| | 160 | | 66.6klmn | | | | 68.7lmno | |
| 72 | 64 | | | 72.2nop | | 75.8pqr | | |
| | 128 | | | 74.1opq | | 77.6pqrs | | |
| 108 | 0 | 50.1bcd | | | 58.3fghi | | | 64.4jkl |
| | 96 | 63.2ijkl | | | 80.1rstu | | | 82.8stuvw |
| | 192 | 65.6jkl | | | 82.6stuvw | | | 84.1tuvw |
| 144 | 64 | | | 78.2qrst | | 81.6rstuvw | | |
| | 128 | | | 80.4rstu | | 85.5uvw | | |
| 180 | 32 | | 71.8mnop | | | | 77.2pqrs | |
| | 160 | | 76.4pqr | | | | 85.4uvw | |
| 216 | 0 | 57.0efgh | | | 64.1jkl | | | 60.6ghij |
| | 96 | 65.8jkl | | | 82.5stuvw | | | 85.2uvw |
| | 192 | 65.9jklm | | | 83.1stuvw | | | 87.3w |

Note: * – significant differences were established between the data lettered a, b, c, d, e, f and etc. at 5% probability level ($p \leq 0.05$).

Fertilisation with potassium and phosphorus fertilisers significantly increased the efficiency of nitrogen fertiliser. Fertilising agricultural crops with 216 kg ha⁻¹ nitrogen, but not with phosphorus and potassium, resulted in an average annual production of 57.0 GJ ha⁻¹ of metabolisable energy over the study period. Fertilisation with N₂₁₆P₀K₉₆ showed a 12.4 % increase in metabolisable energy when compared to plots fertilised with nitrogen fertiliser (N₂₁₆P₀K₀) alone. However, the highest increase

in metabolisable energy over the study period of 53.2% was obtained when agricultural crops were fertilised annually with the maximum fertiliser rate (N₂₁₆P₁₉₂K₁₉₂) compared to those fertilised with nitrogen only at a rate of 216 kg ha⁻¹ but without phosphorus and potassium fertilisers. The studies show that there was no reliable reduction in metabolisable energy when agricultural crops were also fertilised annually with lower fertiliser rates of 108 kg ha⁻¹ of nitrogen, 96 kg ha⁻¹ of phosphorus (P₂O₅) and 96 kg ha⁻¹ of potassium (K₂O).

Statistical correlation analysis of the results showed a very strong correlation (R=0.94; p ≤ 0.05) between the metabolisable energy content in GJ ha⁻¹ and NPK fertiliser rates and their interaction [Table 2].

Table 2. Dependence of the metabolic energy (GJ ha⁻¹) on NPK fertiliser rates (kg ha⁻¹) and their interaction.

| Equation $y=a_0+a_1N+a_2P+a_3K+a_4N^2+a_5P^2+a_6K^2+a_7NP+a_8NK+a_9PK$ parameters | | | | | | | | | | R |
|---|------------------|------------------|------------------|------------------|------------------|------------------|----------------|----------------|----------------|--------|
| a ₀ | a ₁ | a ₂ | a ₃ | a ₄ | a ₅ | a ₆ | a ₇ | a ₈ | a ₉ | |
| 39,8 | 0.24* | 0.19* | 0.13* | -0.00085* | -0.00081* | -0.00059* | 0.00022 | 0.00023 | 0.00016 | 0.94* |
| P | | | | | | | | | | |
| | < a ₁ | < a ₂ | < a ₃ | < a ₄ | < a ₅ | < a ₆ | 0.0020 | 0.0016 | 0.046 | ≤ 0.05 |

Note: * – correlation statistically significant at the 95% probability level (p ≤ 0.05).

Metabolisable energy content of the rotation statistically significantly depended on the rates of nitrogen, phosphorus and potassium fertilisers, and significant relation not obtained between those nutrients.

2.2. Potassium accumulation and balance in agricultural crop yields

Potassium accumulation in the yields of agricultural crops depended on the rates of potassium fertiliser, as well as on their fertilisation with nitrogen and phosphorus [Table 3]. On average, annual fertilisation of agricultural crops with 96 and 192 kg ha⁻¹ K₂O, but without nitrogen and phosphorus fertilisation, resulted in an increase in potassium accumulation in the yield by 37.5 and 51.8 %, respectively, compared to the potassium-unfertilised plots. In contrast, the average annual fertilisation of agricultural crops with all the major plant nutrients (N₁₀₈P₉₆K₉₆) increased potassium accumulation in the crop yield by 121.4%.

Table 3. Effect of long-term fertilisation on potassium accumulation in crop yields and its balance in the soil.

| Average annual fertilization rate kg ha ⁻¹ | | | | | | | | |
|--|-------------------------------|------------------|-----------|-------------|-------------|-----------|------------|-----------|
| N | P ₂ O ₅ | K ₂ O | | | | | | |
| | | 0 | 32 | 64 | 96 | 128 | 160 | 192 |
| Potassium (K ₂ O) accumulation in agricultural crops yields kg ha ⁻¹ / Balance kg ha ⁻¹ | | | | | | | | |
| 0 | 0 | 56a*/-56 | | | 77cd/18 | | | 85de/105 |
| | 96 | 63ab/-63 | | | 86de/9 | | | 103ghi/87 |
| | 192 | 72bc/-72 | | | 90ef/5 | | | 100fg/90 |
| 36 | 32 | | 86de/-54 | | | | 110ghij/50 | |
| | 160 | | 102gh/-70 | | | | 118jkl/42 | |
| 72 | 64 | | | 104ghi/-40 | | 125lmn/3 | | |
| | 128 | | | 114ijkl/-50 | | 143op/-15 | | |
| 108 | 0 | 78cd/-78 | | | 113hijk/-18 | | | 132mno/58 |

| | | | | | | | | |
|-----|-----|----------|-------------|------------|-------------|-----------|----------|-----------|
| | 96 | 83de/-83 | | | 124klmn/-29 | | | 158qr/32 |
| | 192 | 90ef/-90 | | | 133mno/-38 | | | 165rst/25 |
| 144 | 64 | | | 122klm/-57 | | 150pq/-22 | | |
| | 128 | | | 125lmn/-61 | | 153pq/-25 | | |
| 180 | 32 | | 113hijk/-81 | | | | 135no/27 | |
| | 160 | | 116jkl/-84 | | | | 161qr/-1 | |
| 216 | 0 | 84de/-84 | | | 119jkl/-24 | | | 138o/52 |
| | 96 | 84de/-84 | | | 133mno/-38 | | | 152pq/38 |
| | 192 | 89ef/-89 | | | 133mno/-38 | | | 176t/14 |

Note: * – significant differences were established between the data lettered a, b, c, d, e, f and etc. at 5% probability level ($p \leq 0.05$).

The highest potassium accumulation in agricultural crops was obtained when fertilised with the maximum rates of nitrogen, phosphorus and potassium fertilisers ($N_{216}P_{192}K_{192}$). That resulted in a 214.3% increase in potassium accumulation in the crop yield compared to plots not fertilised with mineral fertilisers.

Potassium accumulation in crop yields was strongly and significantly ($R=0.96$; $p \leq 0.05$) influenced by nitrogen, phosphorus and potassium fertiliser rates, also by nitrogen and potassium interaction [Table 4]. Nitrogen fertiliser had the greatest effect on potassium accumulation in the yield of agricultural crops, followed by potassium fertiliser to a lesser extent and phosphorus fertiliser to the least extent.

Table 4. Dependence of potassium (K_2O) accumulation ($kg\ ha^{-1}$) in agricultural crop yields on NPK fertiliser rates ($kg\ ha^{-1}$) and their interaction.

| Equations $y=a_0+a_1N+a_2P+a_3K+a_4N^2+a_5P^2+a_6K^2+a_7NP+a_8NK+a_9PK^*$ parameters | | | | | | | | | | R |
|--|-------|-------|-------|----------|---------|----------|--------|---------|--------|-------------|
| a_0 | a_1 | a_2 | a_3 | a_4 | a_5 | a_6 | a_7 | a_8 | a_9 | |
| 55,0 | 0.46* | 0.14* | 0.31* | -0.0017* | -0.0005 | -0.0009* | 0.0001 | 0.0009* | 0.0005 | 0.96* |
| p | | | | | | | | | | |
| | < a1 | < a2 | < a3 | < a4 | 0.018 | < a6 | 0.494 | < a8 | 0.0017 | ≤ 0.05 |

Note: * – correlation statistically significant at the 95% probability level ($p \leq 0.05$).

Without potassium fertiliser, regardless of whether the plants were fertilised with nitrogen and phosphorus fertilisers or not, the annual balance of this element was negative, ranging from 56 to 90 $kg\ ha^{-1}$ [Table 3]. In contrast, a positive potassium balance was obtained when the plants were fertilised with a potassium fertiliser rate of 96 $kg\ ha^{-1}$ but without nitrogen and phosphorus fertilisers. When the crops were fertilised with the above-mentioned rate of potassium and 108 $kg\ ha^{-1}$ of nitrogen fertiliser, a negative potassium balance was obtained, due to the higher yields produced. The effect of phosphorus fertiliser on the potassium balance was less significant compared to nitrogen. When agricultural crops were fertilised with 216 $kg\ ha^{-1}$ of nitrogen and 192 $kg\ ha^{-1}$ of potassium, and when phosphorus was not used or applied at rates of 96 and 192 $kg\ ha^{-1}$, the amount of potassium incorporated into the soil was 52, 38 and 14 $kg\ ha^{-1}$ more than the amount of potassium accumulated by the crop yield, respectively. Annual fertilisation of agricultural crops with high rates of 192 $kg\ ha^{-1}$ K_2O resulted in a positive potassium balance in the soil, however, the combined application of nitrogen and phosphorus fertilisers resulted in a less significant potassium balance.

2.3. Uptake of potassium from fertilisers

The uptake of potassium from mineral fertiliser depended on the application of potassium and nitrogen, and to a lesser extent on the application of phosphorus [Table 5]. When potassium was

applied to agricultural crops at fertiliser rates of 96 and 192 kg ha⁻¹ without nitrogen and phosphorus, the uptake of potassium from the fertiliser was only 22.1 and 15.2 %.

Table 5. Effect of mineral fertiliser rates and it's combinations on the uptake of potassium fertiliser.

| Average annual fertiliser rate kg ha ⁻¹ | | | | |
|--|-------------------------------|------------------|------|------|
| N | P ₂ O ₅ | K ₂ O | | |
| | | 0 | 96 | 192 |
| Uptake of potassium from fertiliser % | | | | |
| 0 | 0 | – | 22.1 | 15.2 |
| | 96 | – | 24.2 | 21.0 |
| | 192 | – | 18.9 | 14.7 |
| 108 | 0 | – | 36.8 | 28.4 |
| | 96 | – | 43.1 | 39.6 |
| | 192 | – | 45.3 | 39.5 |
| 216 | 0 | – | 36.8 | 28.4 |
| | 96 | – | 51.6 | 35.8 |
| | 192 | – | 46.3 | 45.8 |

In contrast, the best uptake of potassium fertiliser by the plants (51.6 %) was obtained when fertilised at N₁₀₈P₉₆K₉₆. Increasing the average annual rate of potassium fertiliser to 192 kg ha⁻¹ reduced its uptake, but not uniformly, and more potassium was taken up when the crops had not been fertilised with nitrogen and phosphorus fertilisers, or when fertilised at lower rates. Potassium uptake by agricultural crops at high rates of nitrogen and phosphorus (N₂₁₆P₁₉₂) was almost the same at the 96 and 192 kg ha⁻¹ K₂O fertiliser rates, i.e. 46.3 and 45.8 %, respectively.

2.4. Accumulation of potassium in soil

The plant available potassium (K₂O) content in the soil, as significantly determined by the Egner-Riehm-Domingo method and used as a reference in Lithuania, varied over a wide range of 183–630 kg ha⁻¹ in the plots after 50 years of experimentation, or the maximum difference accounted for 3.4 times [Table 6]. In the plots not fertilised with potassium fertiliser in 2020, the plant available K₂O content was about 105–138 kg ha⁻¹ lower than in 1971. The increase in plant available K₂O was limited to the soil of plots where the plants had been under-fertilised with nitrogen and phosphorus fertilisers and where they had received at least 96 kg ha⁻¹ of potassium each year.

Table 6. Effect of mineral fertiliser rates and combinations on soil potassium levels.

| Average annual fertilization rate kg ha ⁻¹ | | | | | | | | |
|---|-------------------------------|------------------------|----|----|---------------------|-----|-----|---------------------|
| N | P ₂ O ₅ | K ₂ O | | | | | | |
| | | 0 | 32 | 64 | 96 | 128 | 160 | 192 |
| Soil potassium A–L / non-exchangeable kg ha ⁻¹ | | | | | | | | |
| 0 | 0 | 222cdef*/ 8583abc | | | 426nop/ 9699def | | | 576t/ 9774f |
| | 96 | 231defg/ 8889abcdef | | | 363kl/ 9327bcdef | | | 630u/ 9195abcdef |

| | | | | | | | | |
|-----|-----|------------------------|------------|------------|----------------------|-----------|----------|----------------------|
| | 192 | 198abc/ 8277ab | | | 402mn/ 9318bcdef | | | 567st/ 9333cdef |
| 36 | 32 | | 264h/ – | | | | 561st/ – | |
| | 160 | | 246efgh/ – | | | | 549st/ – | |
| 72 | 64 | | | 267h/ – | | 420no/ – | | |
| | 128 | | | 261gh/ – | | 474qr/ – | | |
| 108 | 0 | 219bcde/ 9621cdef | | | 402mn/ 8943abcdef | | | 456pq/ 9534cdef |
| | 96 | 192ab/ 8268a | | | 366kl/ 9354cdef | | | 450opq/ 9675def |
| | 192 | 183a/ 9207abcdef | | | 330ij/ 9255abcdef | | | 573st/ 9507cdef |
| 144 | 64 | | | 252fgh/ – | | 432nop/ – | | |
| | 128 | | | 225cdef/ – | | 366kl/ – | | |
| 180 | 32 | | 240efgh/ – | | | | 420no/ – | |
| | 160 | | 192ab/ – | | | | 492r/ – | |
| 216 | 0 | 189a/ 8916abcdef | | | 384lm/ 9306bcdef | | | 543s/ 9627cdef |
| | 96 | 183a/ 8667abcdef | | | 342jk/ 9033abcdef | | | 501r/ 9234abcdef |
| | 192 | 204abcd/ 9066abcdef | | | 306i/ 8604abcd | | | 426nop/ 9294bcdef |

Note: before the experiment was set up in 1971, the average amount of available K₂O in the soil was 327 ± kg ha⁻¹; X – significant differences were established between the data lettered a, b, c, d, e, f and etc. at 5% probability level. (p ≤ 0.05).

When fertilising the agricultural crops with nitrogen fertiliser at rates of 72 kg ha⁻¹ and above on average annually, along with phosphorus fertiliser, the plant available K₂O content in the soil decreased in most of the treatment plots, except for those where the crops had been fertilised with potassium fertiliser at rates of 128 kg ha⁻¹ and above.

After 50 years of experimentation, we also conducted tests on the 0–20 cm soil layer to assess soil non-exchangeable potassium using a more potent extractant, 1N HNO₃ [Table 6]. This method allowed us to detect potassium not only in the exchangeable form, but also in clay particles. The potassium content in that extract varied between 8268 and 9774 kg ha⁻¹ in the experimental plots, which was 13–45 times higher than plant available K₂O measured by the A-L method. The maximum difference in the content of soil non-exchangeable potassium found, depending on NPK fertilisation, was only 1890 kg ha⁻¹ or 18% of the maximum content. The increase in non-exchangeable potassium found in the soil was also influenced by higher rates of potassium fertiliser but the influence of nitrogen and phosphorus fertilizers was less regular.

The regression analysis of the data revealed a very strong correlation (R=0.93; p<0.05) between the plant available K₂O content in the soil determined by the A-L method and the nitrogen, phosphorus and potassium fertiliser rates and no relation on their ratios [Table 7]. The multinomial regression parameters show that the application of potassium fertilisers resulted in a significant increase of plant available K₂O content in the soil, as determined by the A-L method, while the application of nitrogen and phosphorus fertilisers its led to a decrease.

Table 7. Dependence of soil potassium content (kg ha⁻¹) on NPK fertilization rates and their interaction.

| Equation $y=a_0+a_1N+a_2P+a_3K+a_4N^2+a_5P^2+a_6K^2+a_7NP+a_8NK+a_9PK$ parameters | | | | | | | | | | R |
|---|------------------|------------------|------------------|------------------|------------------|----------------|----------------|----------------|----------------|--------|
| a ₀ | a ₁ | a ₂ | a ₃ | a ₄ | a ₅ | a ₆ | a ₇ | a ₈ | a ₉ | |
| Plant available K ₂ O | | | | | | | | | | |
| 227,8 | -0.49* | -0.29* | 1.96* | 0.002* | 0.001* | -0.00012 | -0.0008 | -0.002 | 0.0007 | 0.93* |
| P | | | | | | | | | | |
| | < a ₁ | < a ₂ | < a ₃ | < a ₄ | < a ₅ | 0.351 | 0.912 | 0.252 | 0.0051 | < 0.05 |
| Non-exchangeable K ₂ O | | | | | | | | | | |
| 8901 | 2.95* | -4.24* | 5.56* | -0.012 | 0.015 | -0.0061 | 0.0019 | -0.0084 | -0.0021 | 0.68* |
| P | | | | | | | | | | |
| | <a ₁ | <a ₂ | <a ₃ | 0.323 | 0.324 | 0.695 | 0.841 | 0.394 | 0.849 | < 0.05 |

Note: * – correlation statistically significant at the 95% probability level ($p \leq 0.05$).

The correlation analysis showed a medium tight, but statistically significant relationship ($R=0.68$; $p \leq 0.05$) between the content of soil non-exchangeable potassium and the rates of nitrogen, phosphorus and potassium fertilisers.

3. Discussion

In the long-term (50-year) study, the application of potassium fertiliser was most effective on soils with low plant available K₂O content when used in combination with other main plant nutrients – nitrogen and phosphorus. The average annual crop metabolisable energy (GJ ha⁻¹) within the crop rotation was strongly ($R = 0.97^*$) dependent on the NPK fertiliser rates and their interaction. According to other authors, the interaction of nitrogen, phosphorus and potassium fertilisers improved crop growth and yield, while the effectiveness of the interaction between nutrient elements depended on their relative content in soil [12,14]. Studies in three long-term fertilisation experiments on agricultural crops in Rothamsted, Bad Lauchstädt and Skierniewice also showed that the effectiveness of potassium fertilisers decreased when plants experienced deficiencies in nitrogen, phosphorus and magnesium [34]. Studies in China showed that the most effective rate of potassium fertiliser applied to agricultural crops was 120 kg ha⁻¹, which increased maize and winter wheat yields by 16.7 and 25.1% respectively [33]. It is also noted that potassium, like phosphorus, is very important for nitrogen uptake by agricultural plants. The balanced application of these fertilisers to agricultural crops resulted in a sixfold increase in root mass compared to plants solely fertilised with nitrogen fertiliser [12].

In our study, the fertilisation of agricultural crops with nitrogen fertiliser (N₁₀₈P₀K₀) alone resulted in a 24.3% increase in metabolisable energy content, and fertilisation with all three plant nutrients (N₁₀₈P₆K₉₆) resulted in a 98.8% increase in metabolisable energy content compared to unfertilised plots. Balanced fertilisation of agricultural crops resulted in higher crop yields, which in turn resulted in higher potassium accumulation. However, the high amounts of potassium that are removed from the soil pose a problem in the production of agricultural crops. This is especially true as straw has recently been used more and more for thermal energy production, and in such cases, it does not return to the soil [35]. As Smill [18] points out, globally only 35% of potassium exported with cereal crop yields is compensated for with fertilisers, while other authors [36] have reported that only 10% of the potassium balance in the soil is compensated for. The negative soil potassium balance has been identified as a serious problem for food production at both the regional and global level [37]. To address this problem partially, cereal straw should be left and ploughed in more often and potassium fertilisers should be used more efficiently, according to the recommendations that have been developed [8,38]. According to our research, when straw and other agricultural crop by-

products are removed from the field, an average of about 160 kg ha⁻¹ of potassium (K₂O) should be applied annually to stabilise the plant available K₂O content in the soil.

The efficiency of potassium fertiliser use is reflected in its uptake.

It has been estimated that from 1961 to 2015, only 19% of potassium from fertiliser was taken up by cereals and, food crops [8]. However, in our study, potassium uptake from fertiliser was significantly higher, at 51.6%, when agricultural crops were fertilised using a balanced fertiliser combination of 216 kg ha⁻¹ of nitrogen and 96 kg ha⁻¹ of P₂O₅ and K₂O each. This indicates that there is still significant room for improvement in the efficiency of potassium fertiliser use worldwide. Moreover, similar results on potassium fertiliser uptake have been obtained by researchers in other countries. Long-term fertilisation experiments carried out in Rothamsted (UK), Bad Lauchstädt (Germany) and Skierniewice (Poland) have estimated potassium uptake from fertilisers to be between 44% and 62%, depending on the cation exchange capacity and the amount of clay in soil [34]. In the Czech Republic, two long-term fertilisation experiments on agricultural crops showed that the uptake of potassium from mineral fertilisers ranged from 27% to 52% [39].

Potassium fertilisers are more efficiently absorbed by agricultural crops when fertilised at optimal rates. Our study showed that an increase in the average rate of potassium fertiliser from 96 to 192 kg ha⁻¹ K₂O resulted in a decrease in potassium uptake of 51.6% to 45.8%. Similar patterns were found in a long-term (8 years) fertilisation experiment in China, where annual application of 48 kg ha⁻¹ of potassium resulted in 39.5% uptake by plants. However, when the rate of potassium fertiliser application was increased to 156 kg ha⁻¹, the uptake of potassium decreased to 16.4% [33]. The efficiency of potassium fertiliser use can be improved by taking into account the plant available K₂O content in the soil when fertilising, as studies in the USA have shown that it is not economically viable to fertilise agricultural crops with potassium fertilisers if the plant available K₂O content in the soil is above the average, as they already have sufficient soil reserves of this plant nutrient [40].

Fertiliser application rates, balance and uptake of potassium from fertilisers influence the changes in the amount of this element in the soil. Plots not fertilised with potassium, but fertilised with nitrogen and phosphorus, show a greater decrease in plant available K₂O compared to unfertilised plots. These trends have been observed in our long-term experiment, and studies in France have shown that in unfertilised plots, the decrease in plant available K₂O in the soil over a 25-year period is small and is due to the release of potassium from other forms. However, that decrease was lower than indicated by the potassium balance calculation [41]. Other researchers in long-term fertilisation experiments found that plant available K₂O levels in unfertilised plots decreased over 21 study years, but perhaps due to potassium being released from the non-exchangeable form, these changes did not always accurately reflect the balance of potassium in soil [39]. In a long-term crop fertilisation experiment in Rothamsted, UK, changes in soil potassium levels did not correlate with the balance of this plant nutrient [42]. Similar results were obtained in our study, with an increase in plant available K₂O in soil in plots also did not always match the balance of this element. In addition, as a result of long-term fertilization, there is an increase not only in the mobile but also in the non-exchangeable potassium content in the soil. Potassium in this form is in dynamic equilibrium with plant available potassium and potassium in the soil solution and is therefore also important in plant nutrition [43].

4. Materials and Methods

4.1. Location and Climate conditions

The experiment was carried out for 50 years (1971-2020) in central Lithuania at Skėmiai (Latitude 55.574616, Longitude 23.750375), 95 m above sea level. Soil: sandy loam Epicalcari-Endocalcari-Endohypogleyic Luvisol (WRB, 2015). Its physical and agrochemical characteristics are presented in [Table 8].

Table 8. Soil properties of the experimental field in the 0-20 cm layer.

| Study indicators | Values±SD |
|---|-----------|
| Clay particles (< 0,002 mm) % | 14.1±0.65 |
| Silt (0,002–0,05 mm) % | 31.2±2.17 |
| Sand (0,05–2 mm) % | 54.7±2.72 |
| Bulk density g cm ² | 1.50±0.16 |
| C _{org} % | 1.58±0.14 |
| Effective exchange cation capacity me kg ⁻¹ | 130±4.60 |
| pH _{KCl} | 7.2±0.56 |
| Available P ₂ O ₅ kg ha ⁻¹ | 171±5.50 |
| Available K ₂ O kg ha ⁻¹ | 327±11.1 |
| Total K ₂ O % | 2.73±0.10 |

Note: data prior to the test installation in 1971.

Most of Lithuania has a temperate (boreal) climate, with the average temperature in the coldest month below -3 °C and that of the hottest month below 22 °C. There is sufficient rainfall in all seasons, with snow cover in winter. The country has a warm season of 230–250 days and a growing season of 185–196 days [44]. In Lithuania, 32% of precipitation is converted into runoff and the rest (68%) is returned to the atmosphere through evaporation processes [45].

Between 1971 and 2020, the average annual air temperature in the experimental area located in Central Lithuania was 7.1 °C, and the average annual precipitation was 572 mm.

4.2. Experimental design and its details

The research was carried out according to a 45-treatment multi-factor design (Π3) developed by V. Peregudov, in which seven (including zero) rates of nitrogen, phosphorus and potassium fertilisers were investigated [46]. The design consisted of three designs: A 27-treatment 3×3×3 design, in which three (0, 3 and 6) nitrogen, phosphorus and potassium fertiliser rates were studied; 8-treatment design of 2 × 2 × 2, with two (1 and 5) nitrogen, phosphorus and potassium fertiliser rates, supplemented by the central design treatment 333 (9 treatments in total); and an 8-treatment design of 2×2×2, with two (2 and 4) nitrogen, phosphorus and potassium fertiliser rates, supplemented by the central design treatment 333 (9 treatments in total). Here, hundreds indicate nitrogen, tens indicate phosphorus and ones indicate potassium fertiliser rates, where on average over the experimental period 1 rate N=36, P₂O₅=32, K₂O =32 kg ha⁻¹. The treatments were arranged with two replicates. The specific NPK rates are given in the results tables, where the abbreviations used are: N₀, N₁₀₈, N₂₁₆ – 0, 108 and 216 kg ha⁻¹ of nitrogen (N) applied annually, respectively; P₀, P₉₆, P₁₉₂ – 0, 96 and 192 kg ha⁻¹ of phosphorus (P₂O₅) applied annually, respectively; and K₀, K₉₆, K₁₉₂ – 0, 96 and 192 kg ha⁻¹ of potassium (K₂O) applied annually, respectively. The total size of the experimental plot was 6×9 m. The fertilisers used were ammonium nitrate, granular superphosphate and potassium chloride crystals.

During different periods of the experiment, the following crops were grown: 10 years of winter wheat, 2 years of spring wheat, 10 years of spring barley, 6 years of sugar beet, 4 years of spring oilseed rape, 10 years of annual forage legumes and 8 years of perennial grasses.

4.3. Sampling and Methods of Chemical Analysis

Soil samples for general soil characterisation of the experimental area were taken prior to the setting up of the experiment in spring 1971, and for the determination of available potassium (K₂O) from each field in autumn 2020, after the spring barley harvest. Samples were taken from the 0-20 cm soil layer with a 1.5 cm diameter drill, with 15 punctures per pooled sample per field. Soil analyses were carried out on air-dry samples after screening the soil through a 2 mm sieve.

The concentration of available potassium (K_2O) in soil was determined by the Egner-Riem-Domingo (A-L) method [47]. Soil available K_2O were extracted using 1:20 (wt vol⁻¹) soil suspension of ammonium lactate-acetic acid extractant (pH 3.7). The suspension was shaken for 4 h. Mobile K_2O was determined using flame emission spectroscopy with a flame photometer Scherwood M410.

Soil exchangeable and non-exchangeable potassium content in soil was determined using the 1 mol l⁻¹ hot nitric acid HNO_3 extraction method [48]. The finely ground soil was gently heated with nitric acid (HNO_3) in an Erlenmeyer flask for 15 minutes from the start of boiling. The cooled sample was filtered and the extract was diluted to 100 ml with 0.1 mol l⁻¹ HNO_3 . The K concentration of the extract solution was determined by an atomic absorption spectrometer Analyst 200. The amount of non-exchangeable potassium in the soil was calculated from the amount of potassium dissolved in the 0.1 mol l⁻¹ HNO_3 minus the amount of this element obtained by the A-L method.

According to the soil bulk density, potassium content in the soil, the resulting mg kg⁻¹ was converted to kg ha⁻¹.

The determination of soil pH was performed using 1:5 (vol vol⁻¹) soil suspension in 1 M KCl.

Organic carbon (C_{org}) according to ISO 10694:1995, dry combustion with total carbon analyser Liqui TOC II.

Potassium (K) in plants. The samples were burned in a muffle for 6–8 h at a temperature of 550 degrees. After that, after adding nitric acid, it was evaporated to dryness for 1 h. It was further treated with 20 % HCl, again heated to dryness and washed with distilled water. Potassium content was determined using a flame photometer JENWAY PFP7.

4.4. Calculations and data analysis

The average yield of agricultural crops over the entire 50-year study period was calculated in terms of the energy value of the yield, using the average values of data from analyses carried out in Lithuania for individual crops [49].

The potassium balance in soil (B) is calculated using the formula: $B \text{ kg ha}^{-1} = T - D$, where T is the amount of potassium (K_2O) applied to the soil with fertiliser in kg ha⁻¹; D is the amount of potassium (K_2O) accumulated in the crop and removed from the field in kg ha⁻¹.

The harvest of the main and secondary crops has been removed from the field. Potassium losses due to leaching were not included in the balance sheet calculation.

The uptake of potassium from mineral fertilisers (UK %) was calculated using the formula:

$UK\% = \frac{K-N}{F} \times 100$, where F is the potassium (K_2O) fertiliser rate (kg ha⁻¹); K-N is the amount of potassium (K_2O) accumulated in the plants (kg ha⁻¹) in potassium-fertilised and in unfertilised plots, respectively.

Statistical significance of the experimental data was assessed using *Duncan's Multiple Range test*; significant differences were established between the data lettered a, b, c, d, e, f and etc. at 5 % probability level ($P \leq 0.05$). Mean and their ratios as well as standard deviations (SD) were calculated using software *Microsoft Office Excel 2010*. To determine the strength and nature of the relationship between the variables, correlation and regression data analysis was performed using software *STATISTICA 7* [50,51].

5. Conclusions

In the long-term (50-year) mineral NPK fertilization experiment, the yield of agricultural crops, potassium balance, potassium use efficiency and potassium content in soil depended not only on potassium fertilisation, but also on its interaction with nitrogen and phosphorus. The balance of potassium in soil was positive when agricultural crops had been fertilised with potassium fertilisers only. However, when nitrogen and phosphorus fertilisers were applied together, to compensate for potassium removal, when applying low nitrogen 72 kg ha⁻¹ and phosphorus 64 kg ha⁻¹ fertiliser rates, 128 kg ha⁻¹ of potassium fertilisers is required. When using high nitrogen 180 kg ha⁻¹ and phosphorus 160 kg ha⁻¹ fertiliser rates, 160 kg ha⁻¹ of potassium is needed. The highest potassium uptake, reaching 51.6%, was achieved when plants had been fertilised with nitrogen 108 kg ha⁻¹, phosphorus 96 kg ha⁻¹

¹, and potassium 96 kg ha⁻¹. When fertilizing with potassium fertilisers alone, the content of plant available K₂O content in the soil increased, while fertilisation with nitrogen and phosphorus combined it's decreased, except in the plots where the plants had been fertilised with potassium fertiliser at rates of 128 kg ha⁻¹ and higher. Due to the influence of fertilizers, the amount of non-exchangeable potassium in the soil also increased, but relatively less compared to the amount of available potassium.

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