

<https://doi.org/10.17221/109/2019-PSE>

Balance of potassium in two long-term field experiments with different fertilization treatments

JIRÍ BALÍK*, JINDŘICH ČERNÝ, MARTIN KULHÁNEK, ONDŘEJ SEDLÁŘ, PAVEL SURAN

Faculty of Agrobiological, Food and Natural Resources, Czech University of Life Sciences Prague, Prague, Czech Republic

*Corresponding author: balik@af.czu.cz

Citation: Balík J., Černý J., Kulháněk M., Sedlár O., Suran P. (2019): Balance of potassium in two long-term field experiments with different fertilization treatments. *Plant Soil Environ*, 65: 225–232.

Abstract: Balance of potassium (K) was observed in long-term stationary field experiments (21 years) at two sites with different soil and climatic conditions (Luvisol, Cambisol). The following crops were rotated within the trial: potatoes–winter wheat–spring barley. All three crops were grown each year. The trial comprised 6 treatments: (1) no fertilization; (2) farmyard manure; (3) half dose of farmyard manure + nitrogen (N) in mineral nitrogen fertilizers; (4) mineral nitrogen fertilizers; (5) NPK in mineral fertilizers; (6) straw of spring barley + N in mineral nitrogen fertilizers. The recovery rate of potassium from farmyard manure by crops was 24–26%, from mineral fertilizers it was 27–52%. Different fertilization intensities were manifested by significant differences in the content of exchangeable K in soil. Changes in non-exchangeable K (K_{ne}) were recorded only at the Luvisol site (850 mg K_{ne} /kg), but not at the Cambisol site (3000 mg K_{ne} /kg). The maximum negative balance (–2376 kg K/ha/21 years) was recorded at the mineral nitrogen fertilization treatment.

Keywords: farmyard manure; mineral fertilizers; potatoes; wheat, barley; bioavailable K; non-exchangeable K

The total potassium (K) content in soils is in the range 0.01% to 4% and usually oscillates around ca 1%. To determine the optimum content of bioavailable K in soil, various methods may be used. In past, it was especially the Egner-Riehm method (Egner et al. 1960). In the Czech Republic, the official method for agricultural soils analyses nowadays is the Mehlich 3 method (Mehlich 1984, Madaras and Lipavský 2009, Schroder et al. 2009, Kulháněk et al. 2014, Madaras and Koubová 2015). Binner et al. (2017) used the $CaCl_2$ /DTPA (CAT) extraction to determine the optimum content of bioavailable K in soil; yet, this method is suitable mostly for garden substrates analyses. To determine exchangeable potassium (K_{ex}), 1 mol/L ammonium acetate solution was used (Blake et al. 1999, Liu et al. 2010, Madaras et al. 2014). However, plants do not uptake only potassium from the soil solution and exchangeable K. They are able to absorb also some part of the non-

exchangeable K (K_{ne}) (Hinsinger and Jaillard 1993). In the plant rhizosphere, a zone poor in K is formed. As a consequence, plants excrete H^+ to the rhizosphere (Steingrobe and Claasen 2000), which results in release of non-exchangeable K. To determine non-exchangeable K, boiling 1 mol/L HNO_3 extraction is often used followed by subtracting of NH_4OAc -determined $K_{(ex)}$ from the obtained values (Srinivasarao et al. 2014, Das et al. 2018, Kitagawa et al. 2018). As reported by Liu and Bates (1990), the content of non-exchangeable K provides good information about the amount of plant-available K. A significant positive correlation with fixed ammonium ion strongly supports the hypothesis that non-exchangeable K is bound mainly at boundaries of the clay minerals of the 2:1 types, mica and vermiculite (Brouder 2011). The fact that a significant correlation was not determined between the content of non-exchangeable K and clay particles supports

Supported by the European Regional Development Fund – Project NutRisk Centre, Project No. CZ.02.1.01/0.0/0.0/16_019/0000845.

the hypothesis that the clay mineral type is more important than the total content of clay particles (Kitagawa et al. 2018). The authors further suggest determining not only exchangeable K but also non-exchangeable K, which enables a complex view of the potassium issue, especially at insufficient K fertilization (risk management) and resulting K deficit in agricultural soils.

The aim of this study is to determine the potassium balance and related changes in soils at different fertilization treatments. Long-term field experiments were carried out at two different sites. The crop rotation used in the experiment corresponds well with the intensive farming systems used in the Czech Republic (CR). This research is also important from the viewpoint of the long-term sustainable soil management in CR, with respect to the fact that annual potassium doses in mineral fertilizers for more than 20 years have been only 5–6 kg K/ha agricultural soil.

MATERIAL AND METHODS

The trials were established in 1996 at two sites with different soil-climatic conditions: Hněvčeves and Humpolec (Table 1). Within the trials, three crops were rotated in the following order: potatoes, winter wheat, spring barley. Each year all of the crops were grown. The trial comprised 6 treatments: (1) no fertilization (control); (2) farmyard manure (FYM 1); (3) half dose of farmyard manure + nitrogen (N) in mineral nitrogen fertilizers (FYM 1/2); (4) mineral nitrogen fertilizers (N); (5) NPK in mineral fertilizers (NPK); (6) straw of spring barley + N in mineral nitrogen fertilizers (N + ST) (Černý et al. 2010). Organic fertilizers – farmyard manure and straw (ST) were always applied in autumn (October) to potatoes. Mineral phosphorus and potassium fertilizers were applied to each crop in autumn; mineral nitrogen fertilizers were applied to potatoes and spring barley in spring prior to the crop establishment. In the case of winter wheat, the nitrogen dose was divided into halves, the first one was applied at BBCH 21, the second one at BBCH 31–32. The application rate of mineral nitrogen was 140 kg N/ha for wheat and 70 kg N/ha for spring barley; at FYM 1/2 treatment, N was applied at the rate of 115 kg N/ha for wheat and 50 kg N/ha for barley. The NPK treatment of winter wheat and spring barley included phosphorus at a rate of 30 kg P/ha (triple super phosphate) and potassium at a rate of 100 kg K/ha (60% potassium salt). At the other treatments, the dosage of phospho-

rus (P) and K depended on the content of nutrients in the applied organic fertilizers (Table 2).

Soil analyses were always proceeded with air-dried soil samples (≤ 2 mm; 0–30 cm depth; four replications). For the purposes of this manuscript, soil samples taken up in the year 1996 were analysed in detail (autumn, before experiment establishing) and at the end of 7th crop rotation, shortly after plant harvest in 2017. The data evaluated here are based only on the results of the soils taken up from the plots with spring barley.

All plants were harvested after reaching the maturity stage every year of the experiment to get the yield data. Samples of barley and wheat grain and straw as well as potato tubers were dried at 40°C and subsequently proceeded with dry decomposition (Mader et al. 1998). The potassium content was measured due to the atomic adsorption spectrometry (AA280FS, Agilent Technologies, Mulgrave, Australia).

CaCl₂/DTPA (CAT) extraction (CSN EN 13651, 2001). For this procedure, 3.00 g of soil sample was weighed into 50 mL tubes. To all samples was applied 30 mL solution of 0.01 mol/L CaCl₂ and 0.01 mol/L 0.002 diethylenetriaminepentaacetic acid (DTPA). The solution was shaken for 1 h on a horizontal shaker. Extracts were filtered and measured on the optical emission spectrometer with inductive coupled plasma (ICP-OES, Agilent Technologies 700, Victoria, Australia).

Table 1. Characteristics of experimental fields

	Hněvčeves	Humpolec
Location	50°18'46"N, 15°43'3"E	49°33'16"N, 15°21'2"E
Altitude (m a.s.l.)	265	525
Mean annual temperature (°C)	8.2	7.0
Mean annual precipitation (mm)	573	665
Soil type	Haplic Luvisol on loess	Stagnic Cambisol on paragneiss
Soil texture	Clay loam	Sandy loam
Clay (%) (< 0.002 mm)	4.4	5.8
Silt (%) (0.002–0.05 mm)	77.0	43.6
Sand (%) (0.05–2 mm)	18.7	50.6
Bulk density (g/cm ³)	1.50	1.40
C _{org} (%)	1.06	1.38
pH _{CaCl2}	5.9	5.1
CEC (mmol ₊ /kg)	116	90

CEC – cation exchange capacity; C_{org} – organic carbon

<https://doi.org/10.17221/109/2019-PSE>

Table 2. Application rates of nutrients (kg/ha)

Treatment	Potatoes					Wheat					Barley					Σ (3-year cycle)				
	N	P		K		N	P		K		N	P		K		N	P		K	
		Hn	Hu	Hn	Hu		Hn	Hu	Hn	Hu		Hn	Hu	Hn	Hu		Hn	Hu	Hn	Hu
Control	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
FYM 1	330 ¹	90 ²	108 ²	382 ²	308 ²	0	0	0	0	0	0	0	0	0	0	330	90	108	382	320
FYM 1/2	165 ¹	45 ²	54 ²	191 ²	160 ²	115	0	0	0	0	50	0	0	0	0	330	45	54	191	160
N	120	0	0	0	0	140	0	0	0	0	70	0	0	0	0	330	–	–	–	–
NPK ³	120	30	30	100	100	140	30	30	70	70	70	30	30	100	100	330	90	90	270	270
N + St	120 ⁴	3.6 ⁵	3.9 ⁵	47 ⁵	56 ⁵	140	0	0	0	0	70	0	0	0	0	330 ⁴	3.6	3.9	47	56

¹Nitrogen as the total nitrogen in organic fertilizers; ²Average yearly dose depends on the nutrient content in organic fertilizers; ³Mineral fertilizers: N – calcium ammonium nitrate (27% N); P – triple super phosphate (21% P); K potassium chloride (50% K); ⁴120 kg mineral N + straw (23 kg N – Hn; 22 kg N – Hu); ⁵Straw. *Average doses of fresh farmyard manure: Hněvčeves – 63.0 t/ha/3 year (13.4 t of dry mass/ha/3 years; 2.462% N in dry mass); Humpolec – 59.45 t/ha/3 years (13.42 t of dry mass/ha/3 years; 2.459% N in dry mass). Hn – Hněvčeves; Hu – Humpolec; FYM – farmyard manure; St – straw

Mehlich 3 extraction (Mehlich 1984). The amount of 3.00 g of soil sample was extracted with 30 mL solution of 0.02 mol/L CH₃COOH, 0.25 mol/L NH₄NO₃, 0.015 mol/L NH₄F, 0.013 mol/L HNO₃, 0.001 mol/L ethylenediaminetetraacetic acid (EDTA). The solution was shaken for 5 min on a horizontal shaker and subsequently filtered. Potassium content in extracts was measured by the ICP-OES.

Ammonium acetate extraction (hereinafter NH₄OAc) was realized due to modified procedure by Haby et al. (1990). Soil samples (3.00 g) were extracted with 30 mL 1 mol/L ammonium acetate solution at pH 7.00. The soil solution slurry was shaken for 2 h, and the solution was separated from the solid by centrifugation. The addition of excess NH₄⁺ to the soil displaces the rapid exchangeable potassium from the exchange sites of the soil particles. The concentrations of K were subsequently analysed by the ICP-OES.

Boiling HNO₃ extraction (Helmke and Sparks 2000) was following: 2.5 g of finely ground soil sample was heated with 25 mL of 1 mol/L HNO₃ in an Erlenmeyer flask on a hot plate for 10 min after boiling started. After cooling for 5 min, the sample was filtrated and the extract was diluted to 100 mL with 0.1 mol/L HNO₃. The K concentration of the extract solution was determined by the ICP-OES.

Statistical analysis. The results were assessed using the ANOVA statistical analysis. To evaluate the obtained results, the Statistica programme (StatSoft Inc. 2015, Tulsa, USA) was used.

RESULTS AND DISCUSSION

Potassium balance. Table 3 shows the inputs and outputs at individual variants. It is a summary done for the period of 21 years. The outputs are determined

Table 3. The balance of potassium (kg K/ha/21 years) for the period 1996–2017

Site		Control	FYM 1	FYM 1/2	N	NPK	N + St
Hněvčeves	K input	0	2674	1337	0	1890	282
	crop uptake	1124	1818	1830	1744	2111	2037
	balance	–1124	856	–493	–1744	–221	–1755
Humpolec	K input	0	2240	1120	0	1890	336
	crop uptake	1663	2192	2452	2376	2178	1893
	balance	–1663	48	–1332	–2376	–288	–1557

FYM – farmyard manure; St – straw

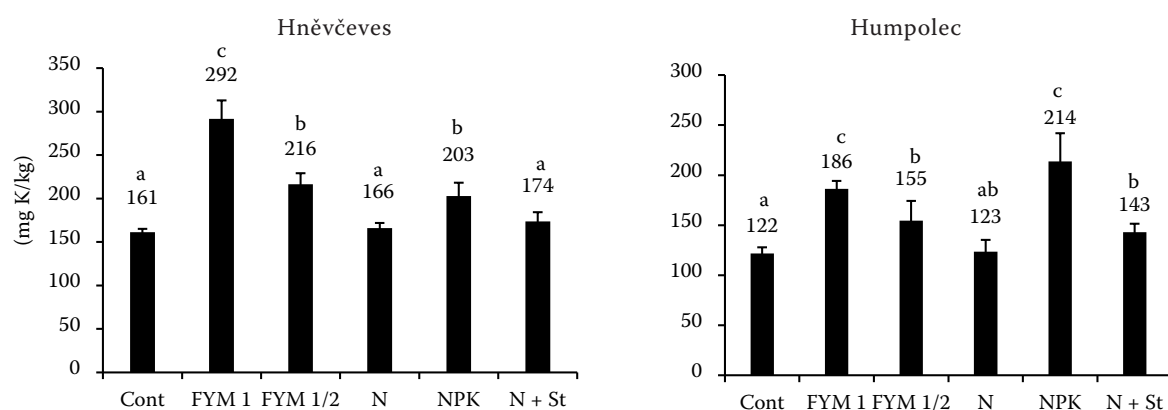


Figure 1. Potassium content in the plough layer (mg K/kg, method Mehlich 3). Cont – control; FYM – farmyard manure; St – straw

by yields and K content in plants. At the Hněvčeves site, higher yields of cereals were recorded (grain: wheat – 7.07 t dry matter/ha; barley – 4.54 t dry matter/ha) compared to the Humpolec site (grain: wheat – 6.29 t dry matter/ha, barley – 3.83 t dry matter/ha). Higher yields of potatoes were recorded at the Humpolec site (7.82 t dry matter/ha) than at the Hněvčeves site (7.40 t dry matter/ha). The contents of potassium in wheat grain (0.46–0.48% K) and barley (0.37–0.38% K) were identical at both sites. Significantly greater differences were obtained in the K content in straw: (Hněvčeves: wheat 0.88% K, barley 0.98% K; Humpolec: wheat 1.03% K, barley 1.18% K); and differences were recorded for K content in potato tubers (Hněvčeves: 1.84% K, Humpolec: 2.15% K). Even though the contents of bioavailable potassium in soil at the Humpolec site were lower, reported K uptake by plants was higher – by 348 kg K/ha on average for all variants and the period of 21 years. This difference was probably caused by higher potato yield and also by higher precipitation

and its regular distribution throughout the vegetation period, which might have a positive influence on the K uptake. Table 3 shows the positive balance (inputs minus outputs) only at the variant fertilized with manure. The highest negative balance (–2376 kg K/ha) was obtained at fertilization with mineral nitrogen at the Humpolec site. Negative balance was calculated also for the NPK fertilization, with average application dose of 90 kg K/ha/year. Neither regular straw incorporation influenced the K balance. The utilization of K from manure at the Hněvčeves site was 26%, at the Humpolec site it was 24%. In case of the NPK fertilization it was 52% (Hněvčeves) and 27% (Humpolec). There is a clear tendency to higher K utilization at soils with higher sorption capacity, which complies with the results of Blake et al. (1999). Higher K utilization at mineral fertilization may be caused by lower dose of K applied compared to manure treatments. At lower application doses, their utilisation is generally better. Blake et al. (1999) did not determine significant differences in K bal-

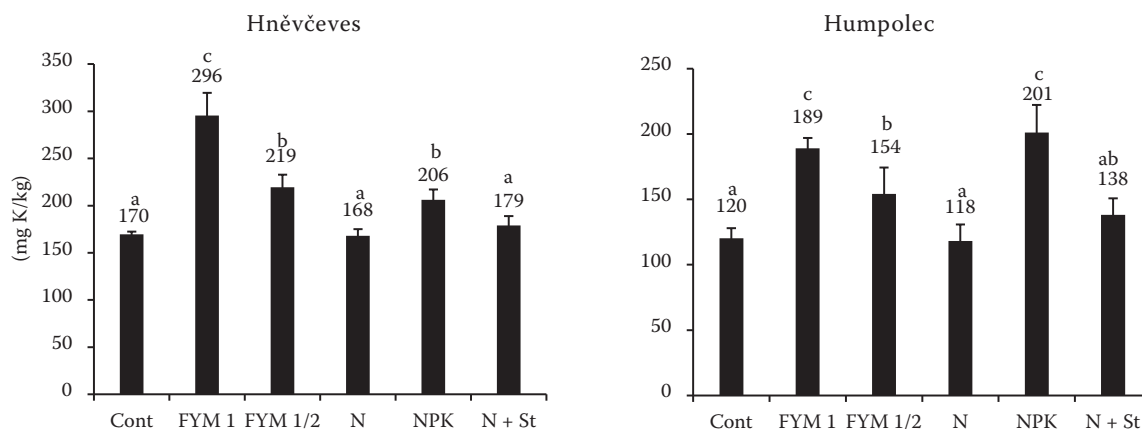


Figure 2. Content of exchangeable potassium in the plough layer (mg K/kg). Cont – control; FYM – farmyard manure; St – straw

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Table 4. Saturation of potassium in cation exchange capacity (%)

	Hněvčeves	Humpolec
Contol	3.76	3.42
FYM 1	6.54	5.38
FYM 1/2	4.84	4.39
N	3.71	3.36
NPK	4.55	5.73
N + ST	3.96	3.93
Average	4.56	4.37

FYM – farmyard manure; St – straw

ance between the manure-supplied K and mineral fertilization. These authors explain this as a result of K not strongly sorbed in manure.

Content of bioavailable K. Results obtained using the Mehlich 3 extraction agent are given in Figure 1. At both sites, statistically significant differences were recorded among individual variants, in compliance with the K fertilization intensity. At the Hněvčeves site, the average value of all treatments reached 200 mg K/kg, i.e. by 31% more compared to the Humpolec site – 157 mg K/kg. As to the official assessment of K pool in the plough layer in the CR for loamy soils, it is ranked in the category ‘satisfactory pool’ or ‘good pool’ – based on the variant (Smatanová and Sušil 2018). It may be presumed that even in the control variant the yields were not influenced by the lack of N.

As shown in Figure 2, manure application resulted in a significant increase of the exchangeable K content. Liu et al. (2010) reported similar results in the long-term experiments. Significantly lowest contents

were obtained at variants without K fertilization. Comparison of both sites shows significantly higher content (by 34.6%) at the Hněvčeves site (with average values of 206 mg K/kg) than in Humpolec (153 mg K/kg). If the values are recalculated to the level of saturation of the sorption complex with potassium, this parameter almost does not differ for the two sites – it is 4.56% in Hněvčeves and 4.37% in Humpolec (Table 4); it is given by the differences between the total values of the cation exchangeable capacity (Hněvčeves: 116 mmol₊/kg, Humpolec: 90 mmol₊/kg). The content > 3.50% cation exchange capacity (CEC) is considered as satisfactory for these soils. Comparison of the K values at both extraction agents (Mehlich 3/ NH₄OAc) shows certain similarity. For the Hněvčeves location, the Pearson’s correlation coefficient between the K contents determined with Mehlich 3 and NH₄OAc was 0.989 at the significance level $P < 0.001$; for the Humpolec location it was 0.958. The relationship between K in ammonium acetate and Mehlich 3 is: $y = 0.974x + 7.6145$, $R^2 = 0.9772$ (Hněvčeves), $y = 0.9505x + 5.6757$, $R^2 = 0.9815$ (Humpolec). It is thus probable that mainly exchangeable potassium is released at the Mehlich 3 extraction. High agreement of these methods is, to a certain extent, given by the fact that the study evaluates corresponding long-term field trials. At ordinary agricultural soils, the agreement would probably be lower.

CAT extraction revealed significantly lower K content compared to other extraction methods (Figure 3). The average content for all variants was 110 mg K/kg at the Hněvčeves site and 120 mg K/kg at the Humpolec site. It is interesting that the ratio of the values (Hněvčeves/Humpolec) is opposite compared to the Mehlich 3 and NH₄OAc methods, which is probably caused by different character of clay parti-

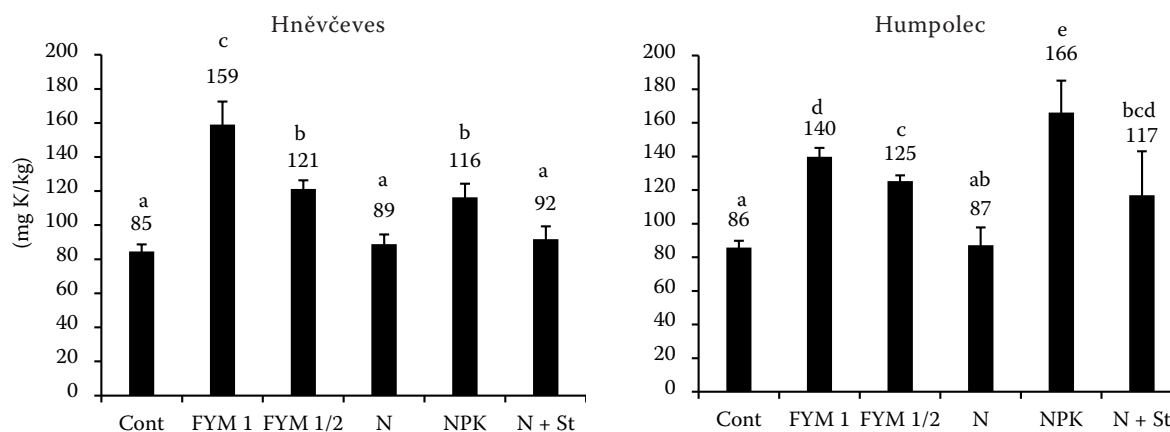


Figure 3. Potassium content in the plough layer (mg K/kg; CaCl₂/DTPA extraction). Cont – control; FYM – farmyard manure; St – straw

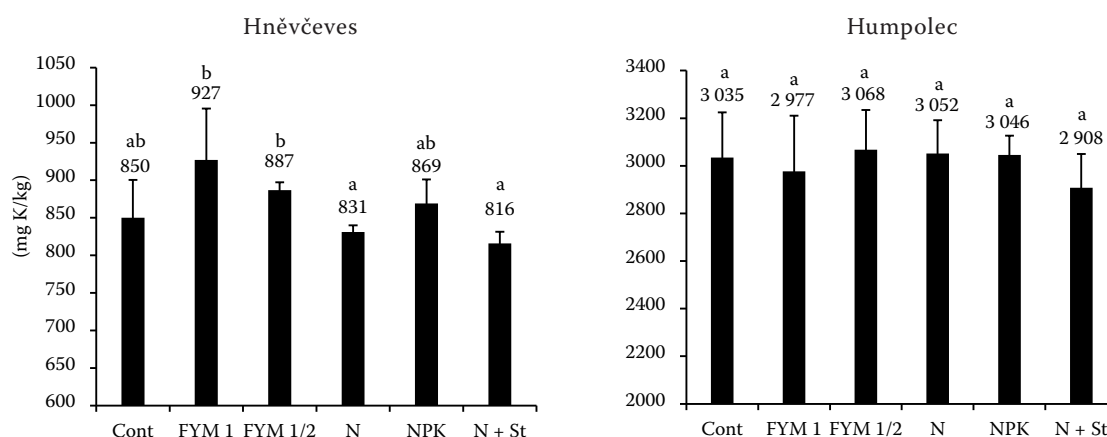


Figure 4. Content of non-exchangeable potassium in the plough layer (mg K/kg). Cont – control; FYM – farm-yard manure; St – straw

cles at the two sites. Binner et al. (2017) stated that this method was sensitive at variants with added clay sorbents of the smectite type.

Content of non-exchangeable K. Contents of non-exchangeable potassium are shown in Figure 4. Both sites significantly differ; contents were in the range of 816 to 927 mg K/kg at the Hněvčeves site in contrast to the interval 2908–3068 mg K/kg at the Humpolec site. There is a significant influence of the soil-forming materials. Parent material of Cambisol (Humpolec) is paragneiss; in the process of material changes (weathering) potassium is released in significant amounts. On the contrary, Luvisol (Hněvčeves) on loess has markedly lower potential to release K. Blake et al. (1999) observed the changes in the content of non-exchangeable K at long-term field trials sites. The highest contents were reported for Bad Lauchstadt: 1810–2196 mg K/ha, whereas lower contents were reported for Rothamsted: 650–1442 mg K/ha. This corresponds with the range recorded at the Hněvčeves site. High contents approaching 3000 mg K/kg were published by Øgaard and Krogstad (2005) for selected soils in Norway. Figure 4 shows that completely different fertilization for the period of 21 years did not have a significant impact on the changes of non-exchangeable K at the Humpolec site, not even at variants unfertilized with K in the long term. At comparison of K amount obtained at harvest (1663–2376 kg K/ha) and the content of non-exchangeable K in the plough layer (ca 12 500–12 800 kg K/ha) it is clear that the effect of fertilization on the changes in the non-exchangeable K may not have been manifested.

At the Hněvčeves site, a significant tendency to decrease the non-exchangeable K content was ob-

served at the variants without K fertilization. The content of non-exchangeable K in the plough layer was ca 3600–3800 kg/ha, which is comparable with the K values at harvest (1124–2111 kg K/ha). Moreover, non-exchangeable K was also important for replenishing plant-available K in soil at this site. A decrease of the non-exchangeable K in the long-term trials at the unfertilized variants compared to the manure application was reported also by Blake et al. (1999) and Srinivasarao et al. (2014). Furthermore, it must be stressed that not all of the non-exchangeable K may be used by plants, as it is released continuously during many years, as was reported by Moritsuka et al. (2002). Non-exchangeable K release depends on many factors, such as K concentration in soil solution, concentration of other cations and pH value (Wang et al. 2011).

Table 5 summarizes the results of individual tested methods related to the boiling HNO_3 extraction. At the Hněvčeves site, the average content of 1069 mg K/ha was obtained, whereas at the Humpolec site it was 3167 mg K/kg. The ratio of non-exchangeable K at Luvisol (Hněvčeves) was 80.9%, as compared to

Table 5. Comparison of the extraction ability of four methods for potassium (K) determination (expressed in % of the K content extracted by boiling 1 mol/L HNO_3)

Site	M3	CAT	K_{ex}	K_{ne}	HNO_3
Hněvčeves	18.8	10.1	19.1	80.9	100.0
Humpolec	4.9	3.7	4.8	95.2	100.0

100% Hněvčeves 1069 mg K/ha; 100% Humpolec 3167 mg K/ha; M3 – Mehlich 3; CAT – $\text{CaCl}_2/\text{DTPA}$ extraction; K_{ex} – exchangeable K; K_{ne} – non-exchangeable K

<https://doi.org/10.17221/109/2019-PSE>

Table 6. The changes of potassium content (kg/ha) in the plough layer of soils after 21 years of experiment

	Site	Control	FYM 1	FYM 1/2	N	NPK	N + ST
Mehlich 3	Hněvčeves	–297	–28	–129	–221	94	–180
	Humpolec	–273	–80	–97	–332	–190	–164
K _{ex}	Hněvčeves	–233	128	–48	–205	5	–275
	Humpolec	–311	–137	–154	–420	–84	–244
CAT	Hněvčeves	–185	108	–27	–122	–5	–207
	Humpolec	–126	25	42	–189	88	4

FYM – farmyard manure; St – straw; K_{ex} – exchangeable K; CAT – CaCl₂/DTPA extraction

Cambisol (Humpolec) with 95.2%. The comparison of the Mehlich 3 and NH₄OAc methods shows that their extraction strength is similar. The values obtained using the CAT extraction were only 60–65% compared to the previous methods.

Changes in K in 1996/2017. The archive samples from 1996 were analysed (for each parcel individually) and the results were compared with the 2017 analysis. The differences in the potassium content in the plough layer (kg K/ha) are reported in Table 6. K amount in the plough layer decreased in all the unfertilized variants. The highest decrease is recorded at variant with mineral N fertilization. The comparison of negative values in the potassium balance (Table 3) and changes in Table 6 shows that the values in Table 6 are lower compared to the balance only. It can be explained by continuous mobilisation of potassium from the non-exchangeable bonds and further also by not considering the K content in the subsoil, which is also a significant potassium source for plants.

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Received on February 22, 2019

Accepted on March 12, 2019

Published online on April 2, 2019