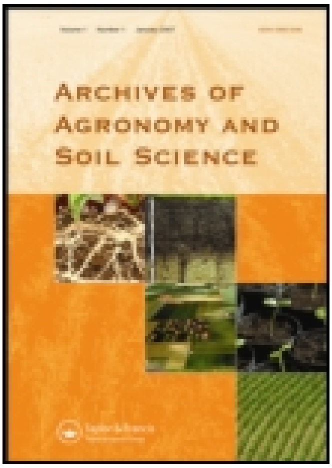


Archives of Agronomy and Soil Science
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gags20

# Waste silicate minerals as potassium sources: a greenhouse study on spring barley

Mikulá[scheck] Madaras [a], Markéta Mayerová [a], Martin Kulhánek [b], Magdalena Koubová [c] & Miloš Faltus [d]

[a] Crop Research Institute, Prague, Czech Republic
[b] Czech Agricultural University, Prague, Czech Republic
[c] Czech Geological Survey, Prague, Czech Republic
[d] F. F. Servis s.r.o., Prague, Czech Republic

Accepted author version posted online: 27 Feb 2012.Published online: 30 Mar 2012.

*Archives of Agronomy and Soil Science*
Vol. 59, No. 5, May 2013, 671–683



# Waste silicate minerals as potassium sources: a greenhouse study on spring barley

Mikuláš Madaras[a]*, Markéta Mayerová[a], Martin Kulhánek[b], Magdalena Koubová[c] and Miloš Faltus[d]

[a]*Crop Research Institute, Prague, Czech Republic;* [b]*Czech Agricultural University, Prague, Czech Republic;* [c]*Czech Geological Survey, Prague, Czech Republic;* [d]*F. F. Servis s.r.o., Prague, Czech Republic*

(*Received 9 September 2011; final version received 11 February 2012*)

After 1989, the use of potassium (K) mineral fertilizers in the Czech Republic dropped from $\sim$55 kg K ha$^{-1}$ to a mean rate of $\sim$6.5 kg in the last decade. In order to test alternative solutions for K fertilization, the trioctahedral mica mineral zinnwaldite (8% K), orthoclase (10% K) and waste mica from Cínovec (Krušné Hory Mts/Erzgebirge, Czech Republic), consisting primarily of zinnwaldite, were applied as the only K sources for spring barley. The minerals were treated in three different types of high-energy mills under different working conditions. Application rates in the range 139–820 mg K kg$^{-1}$ were tested in quartz sand cultures. In all treatments, plant growth, total plant biomass and the K content in the plant tissues increased in the order zinnwaldite > waste mica > orthoclase. K fractionation and K plant uptake were significantly influenced by the milling method used. The effect of 195 mg K kg$^{-1}$ as zinnwaldite on K uptake from K-depleted soils was positive; however, it was smaller than in sand cultures because of the relatively high content of non-exchangeable K in the soils. Direct use of waste mica as a K fertilizer is limited by the increased fluorine and heavy metal content.

**Keywords:** potassium; fertilizers; waste processing; silicate minerals; high-energy milling



## Introduction

Fertilization of agricultural soils by mineral potassium (K) fertilizers in the Czech Republic had declined dramatically over the last two decades. Annual application rates of $\sim$55 kg of mineral K ha$^{-1}$, supported by state policy, declined to $\sim$6.5 kg K ha$^{-1}$ within a few years after 1989 (economic/political system change) and has remained at this level through the last decade, with an extreme minimum in 2009 of 0.25 kg K ha$^{-1}$ (Agriculture 2010).

Crushed K-bearing silicate rocks represent an alternative to K fertilizers. They are far more abundant than soluble K salts (van Straaten 2002), and use of local sources of these rocks can decrease the cost of materials and transport, compensating for their lower K content. Many studies have demonstrated yield increases due to the

*Corresponding author. Email: madaras@vurv.cz

ISSN 0365-0340 print/ISSN 1476-3567 online

http://dx.doi.org/10.1080/03650340.2012.667079
http://www.tandfonline.com

use of milled K-bearing rocks (e.g. Manning 2010; Karimi et al. 2011). In some cases, the lower solubility of the silicate K minerals and the slow K release can be viewed as an advantage (Bakken et al. 1997). Moreover, dissolution can be enhanced by the milling method used (Priyono and Gilkes 2008).

Natural K silicate minerals, which can be used as alternative K fertilizers, include feldspars, phyllosilicates (a mineral group of micas, e.g. phlogopite, biotite, muscovite and glauconite), hydromica (mixed-layered minerals) and the feldspathoids leucite and nepheline. K-bearing minerals are common in the geological units within the Czech Republic. K minerals, especially micas, are often constituents of geological post-processing wastes. For example, large deposits of mica minerals (several Mt) are located as waste following Sn–W ore treatment in sludge beds in the Krušné Hory Mts (Erzgebirge, Czech Republic) (Štemprok et al. 2003). This mica-rich fine-grained waste contains zinnwaldite, which is a trioctahedral Li-containing mica (with structural and weathering characteristics, as well as a K content close to that of biotite). Mica can easily be separated from this mineral waste via magnetic separation (Botula et al. 2005) or flotation (Samková 2009), depending on the Fe content. As for other K-bearing materials capable of being utilized as fertilizers, fine-grained sludges and discarded minerals rich in feldspars are produced by rock processing, however, they are often only considered as waste.

The aim of our research was: (1) to study the effects of K release from mica minerals and orthoclase upon spring barley grown in a sand culture, (2) to investigate the effects of various milling conditions on K release from zinnwaldite, and (3) to compare the effects of KCl fertilizer and zinnwaldite on spring barley cropped in K-depleted soils.

## Materials and methods

For the experiments, zinnwaldite and K-feldspar were obtained from Krupka, situated in the eastern part of the Krušné Hory Mts. The zinnwaldite was collected from the monomineral side zone in the 5th of May Gallery, situated in the greisenized kersantite in the exocontact of the Preisselberg granite cupola (Štemprok et al. 2003). From the zinnwaldite material, well-developed mica crystals and aggregates only were selected and washed before further processing. The feldspar was collected at dumps of pegmatite galleries belonging to the Knötel granite. The waste mica was obtained from a sludge bed near Cínovec, where the waste material had been deposited after Sn–W (tin–wolfram) mining (Botula et al. 2005).

The identities of the minerals were determined using both their total chemical composition and X-ray diffraction (XRD) patterns (CuK $\alpha$ radiation with the powder diffractometer Philips X'Pert System, with a graphite monochromator). The major oxides (Table 1) were determined using total digestion with mineral acids (HF-$HClO_4$) and/or the sintering of the sample and subsequent chemical analysis, according to Potts (1995). The accompanying components with the zinnwaldite (several wt%) were comprised of Fe oxides and kaolinite. The feldspar materials mainly consisted of orthoclase (73%), less of albite (19%), a small amount of quartz (6%), as well as other minerals (kaolinite, mixed-layered silicates, mica). The waste mica (consisting predominantly of zinnwaldite) was separated from the waste material by magnetic separation.

The minerals were milled using three types of laboratory mills under different conditions (Table 2). The particle size distribution was analysed by the

Table 1. Chemical composition of minerals used as K fertilizers in the sand culture experiment.

| | Zinnwaldite | Waste mica | Orthoclase |
|---|---|---|---|
| $SiO_2$ | 43.84 | 46.86 | 64.92 |
| $TiO_2$ | 0.02 | 0.05 | 0.01 |
| $Al_2O_3$ | 20.90 | 20.24 | 18.06 |
| $Fe_2O_3$ | 2.25 | 1.66 | 0.56 |
| FeO | 12.16 | 9.17 | 0.60 |
| MnO | 0.80 | 1.32 | 0.02 |
| MgO | 0.04 | 0.04 | 0.07 |
| CaO | 0.37 | 0.25 | 0.12 |
| $Na_2O$ | 0.12 | 0.12 | 2.22 |
| $K_2O$ | 9.87 | 9.56 | 11.97 |
| $P_2O_5$ | 0.01 | 0.01 | 0.03 |
| $H_2O$ | 2.99 | 2.19 | 0.49 |
| $CO_2$ | 0.32 | 0.22 | 0.14 |
| $Li_2O$ | 2.64 | 3.52 | 0.02 |
| $Rb_2O$ | 1.22 | 1.34 | 0.40 |
| Sum | 97.55 | 96.55 | 99.63 |
| $F^-$ (calculated) | 2.45 | 3.45 | – |
| Cd[a] | – | $<1$ | – |
| Hg[a] | – | $<1$ | – |
| Pb[a] | – | 80 | – |
| As[a] | – | 31 | – |
| Cr[a] | – | 56 | – |

Note: Values for oxides and fluorine are given as % total mass. Values for heavy metals in the waste mica from Cínovec are given in mg $kg^{-1}$. [a]Based on the published analysis of zinnwaldite from Cínovec (Govindaraju 1994).

sedimentation method. For the pot experiments, the minerals were treated with a two-rotor mill using two successive milling procedures.

### *K fractionation*

The water-soluble K ($K_{H2O}$) was determined after shaking of 1 g of mineral in demineralized water (1:50 w/v) for 30 min. Ammonium-acetate soluble K ($K_{NH4OAc}$) was determined in 1 M $NH_4OAc$ (shaking for 1 h, 1:50 w/v) and acid-soluble K ($K_{HCl}$) in 1 M HCl, incubated for 20 h at 50°C. Potassium in extracts was analysed by inductively coupled plasma–atomic emission spectrophotometry (ICP–AES). Exchangeable K ($K_{ex}$) was calculated as the difference between $K_{NH4OAc}$ and $K_{H2O}$; non-exchangeable K ($K_{non\text{-}ex}$) was calculated as the difference between $K_{HCl}$ and $K_{NH4OAc}$. In this article, we use the term plant-available K ($K_{avail}$) for the sum of $K_{H2O}$, $K_{ex}$ and $K_{non\text{-}ex}$, and the term structural K for the difference between the total K (HF-$HClO_4$ digested) and $K_{avail}$.

### *Sand culture experiments*

Four spring barley plants (var. *Prestige*) were grown in plastic pots filled with 1750 g of fine quartz sand. The purity of the sand was checked by XRD. The sand contained 7 mg $K_{HCl}$ $kg^{-1}$.

The experiment consisted of eight treatments in four replications (Table 3). The minerals were applied at two application rates (A and B $= 5 \times$ A); these were

Table 2. Milling conditions used for processing of the K-bearing minerals.

| Treatment | Equipment | Frequency | Number of milling procedures | Time | Type of mill |
|---|---|---|---|---|---|
| Two-rotor mill A | Two 170-mm rotors revolving in opposite directions, each with five concentric rows of impact bits | 12 000 r.p.m. | 1 | Continuous | Laboratory Disintegrator DESI – 11 (Desintegraator Tootmise OÜ, Estonian Republic) |
| Two-rotor mill B | Two 170-mm rotors revolving in opposite directions, each with five concentric rows of impact bits | 12 000 r.p.m. | 2 | Continuous | |
| One-rotor mill | 110-mm rotor with eight impact bits | 16 800 r.p.m. | 1 | Continuous | Fritsch Pulverisette 14 (Fritsch GmbH, Germany) |
| Disc mill A | Steel grinding jar 200 mL, one steel ring and one inner cylinder | 930 r.p.m. | 1 | 2 min | Vibratory disc mill VM-4 (OPS Přerov, Czechoslovakia) |
| Disc mill B | Steel grinding jar 200 mL, one steel ring and one inner cylinder | 930 r.p.m. | 1 | 10 min | |

homogeneously mixed into the sand. The pots were placed in a greenhouse at 25°C under electric lights. The plants were irrigated each second day by K-free Hoagland solution to keep the water content at approximately field capacity. After the third week, the chlorophyll content, as Soil Plant Analysis Development (SPAD) index, was measured by a SPAD 502 Minolta meter. After 6 weeks, the plants were harvested and dried until of constant weight. The roots were carefully taken out, and a ~2 mm layer of the adhering sand ('rooting zone') was analysed separately to the bulk substrate. The plant biomass was mineralized by microwave digestion, and the K content was analysed by ICP–AES.

The experimental testing of the effects of different milling conditions on K availability was similarly implemented. The zinnwaldite was treated as listed in Table 2, and then mixed into the sand at the application rate of 287 mg K $pot^{-1}$.

### *Soil pot experiment*

The soils (Table 4) were taken from the control plots of a long-term fertilization experiment in Hněvčeves (loam) and Kostelec nad Orlicí (sandy loam), which had not received any K fertilizers since 1979. The plastic pots were filled with 4 kg of dry and sieved soil. Three treatments in four replications were set up for each soil: (1) control (NP), (2) NPK (400 mg K as KCl $pot^{-1}$, 100 mg K $kg^{-1}$) and (3)



Table 3. Treatments of the sand culture experiment. The K-bearing minerals were applied at two application rates (A and B = 5 × A).

| Treatment | K added per pot (mg) | Application ratio (w/w – K-bearing mineral to quartz sand) |
|---|---|---|
| Control | 0 | – |
| KCl | 24 | – |
| Zinnwaldite A | 287 | 1 : 500 |
| Waste mica A | 277 | 1 : 500 |
| Orthoclase A | 243 | 1 : 715 |
| Zinnwaldite B | 1435 | 1 : 100 |
| Waste mica B | 1385 | 1 : 100 |
| Orthoclase B | 1220 | 1 : 143 |

Table 4. Properties of soils used in the experiment.

| | Kostelec | Hněvčeves |
|---|---|---|
| Soil classification | Haplic Luvisol on loess | Haplic Luvisol on loess |
| Soil texture | sandy loam | loam |
| $pH_{KCl}$ | 5.1 | 5.8 |
| Soil organic carbon | 1.1 | 1.55 |
| Available P | 85 | 38 |
| $K_{ex}$ | 50 | 78 |
| $K_{non\text{-}ex}$ | 475 | 765 |
| $K_{aqua\ regia}$ | 3 200 | 3 400 |

Note: Values for organic carbon are given in %, values for the available phosphorus and potassium fractions are given in mg $kg^{-1}$. $K_{ex}$, exchangeable K; $K_{non\text{-}ex}$, non-exchangeable K; $K_{aqua\ regia}$, aqua regia-extractable K.

NP + zinnwaldite (780 mg K as zinnwaldite $pot^{-1}$, 195 mg K $kg^{-1}$). Twenty plants of spring barley were grown until milk-wax ripeness.

The data were evaluated by Statgraphic Centurion XVI software using both the analysis of variance (ANOVA) and *t*-test.

## Results

### *Sand culture experiment*

Addition of the milled minerals had positively affected the growth of spring barley when compared with K-free control (Table 5). Both application rates led to significant increases of plant biomass and to better overall growth of the plants, which was indicated by both the SPAD index and by better offshooting. The addition of milled minerals had increased the K content in plant biomass. The effects on the total biomass and K-content were in the order zinnwaldite > waste mica > orthoclase.

Biomass production at a lower zinnwaldite application rate (287 mg K $pot^{-1}$) was at the level of the KCl treatment (24 mg K $pot^{-1}$); even though the content of K in the biomass was only about one third that of the KCl treatment. This means that the KCl treatment was over-supplied with K; however, without any further positive effects on plant growth. Therefore, the addition of 287 mg K $pot^{-1}$ (186 mg K $kg^{-1}$) as zinnwaldite was sufficient to supply K in the early stages of plant growth. Higher K mineral application rates led to an approximately twofold increase in the K concentration in the biomass, as well as a several-fold increase of the total K uptake (Figure 1). At a yet higher application rate of zinnwaldite (1435 mg $pot^{-1}$), the biomass was 30% higher than at KCl treatment, but the K concentration in the aboveground biomass was 27% lower. This points out that it was not only the K nutrition, but also some other factors, which had contributed to the barley growth.

In the rooting zone, significant changes were detected in the contents of $K_{NH4OAc}$ and $K_{non\text{-}ex}$ (Figure 2). In all treatments, the $K_{NH4OAc}$ in the rooting zone was higher than in the rootless substrate; this was more pronounced at lower application rates. The rooting zone was depleted in $K_{non\text{-}ex}$ at lower rates; at higher application rates the differences were not significant. $K_{avail}$ in the substrate adjacent to the roots decreased by 12–29%. The balance calculations demonstrated that the net $K_{avail}$. decrease in the rooting zone roughly corresponded to the K uptake by the plants.

### *Effects of the milling method*

The milling method influenced both the distribution of particle size fractions of the materials and the K pools (Table 6). The high-speed one-rotor mill was more effective than the two-rotor mill. Double-milling and prolonged milling times transformed an additional 3% of the structural K to more available forms, and increased the content of finer fractions in the milled material. A five times longer milling time in a vibratory mill led to a significant recomposition between the $K_{non\text{-}ex}$ and $K_{ex}$.

The K uptake by barley plants was closely correlated with $K_{ex}$ and $K_{NH4OAc}$ in the milled materials ($r^2 = 0.996$ and 0.991, respectively). According to the differences between the K uptake and the storage of K in the $K_{ex}$ and $K_{H2O}$ pools, a significant portion of the K was also taken up from the non-exchangeable form.

Table 5. Results of the pot experiment with spring barley grown for 6 weeks in sand cultures with addition of potassium in the form of KCl and milled K-bearing minerals (average of four replications; standard deviation in parentheses).

| | Control | KCl | Zinnwaldite A | Waste mica A | Orthoclase A | Zinnwaldite B | Waste mica B | Orthoclase B | F test value |
|---|---|---|---|---|---|---|---|---|---|
| K application rate (mg pot$^{-1}$) | 0 | 24 | 287 | 277 | 243 | 1435 | 1385 | 1220 | |
| Aboveground biomass (g pot$^{-1}$) | $0.48^{a}$ (0.02) | $0.92^{c}$ (0.24) | $0.98^{c}$ (0.05) | $0.71^{ab}$ (0.04) | $0.63^{b}$ (0.06) | $1.30^{d}$ (0.19) | $1.09^{c}$ (0.07) | $0.95^{c}$ (0.23) | 13.7 |
| Total biomass (g pot$^{-1}$) | $0.67^{a}$ (0.01) | $1.52^{cd}$ (0.17) | $1.46^{de}$ (0.07) | $1.13^{bc}$ (0.07) | $1.07^{b}$ (0.17) | $1.98^{e}$ (0.13) | $1.63^{f}$ (0.05) | $1.48^{de}$ (0.29) | 19.7 |
| SPAD index | $20.4^{a}$ (1.27) | $26.7^{b}$ (1.42) | $30.7^{bc}$ (1.96) | $27.9^{ab}$ (1.81) | $31.6^{c}$ (3.55) | $33.5^{c}$ (2.17) | $31.7^{c}$ (2.30) | $31.6^{c}$ (2.44) | 14.4 |
| Offshoots | $0^{a}$ | $1^{ab}$ | $1^{ab}$ | $0^{a}$ | $1^{ab}$ | $5^{b}$ | $2^{c}$ | $1^{ab}$ | 7.5 |
| K in aboveground biomass (%) | $0.44^{a}$ (0.02) | $1.92^{b}$ (0.47) | $0.68^{a}$ (0.02) | $0.63^{a}$ (0.01) | $0.58^{a}$(0.01) | $1.40^{c}$ (0.07) | $1.27^{c}$ (0.07) | $1.00^{d}$ (0.11) | 33.7 |

Note: Different letters indicate values that are significantly different ($p = 0.01$). SPAD index, Soil Plant Analysis Development index measured using a Minolta SPAD 502 meter.

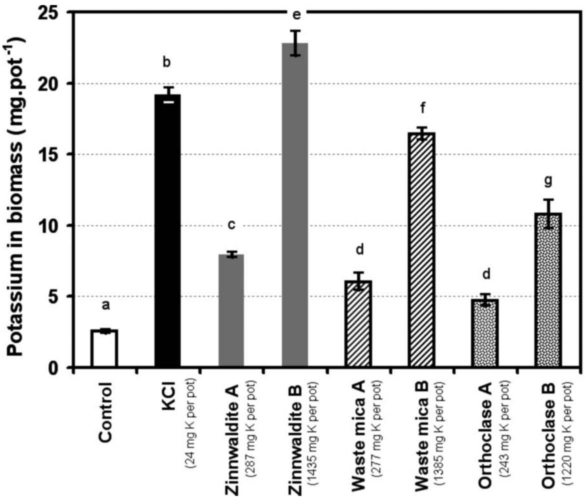


Figure 1. Total K uptake by spring barley plants fertilized by zinnwaldite, waste mica and orthoclase at two application rates (A and B = 5 × A) in sand culture experiments. Bars show ± standard deviation. Different letters indicate values which were significantly different ($N = 4$, $p = 0.01$).

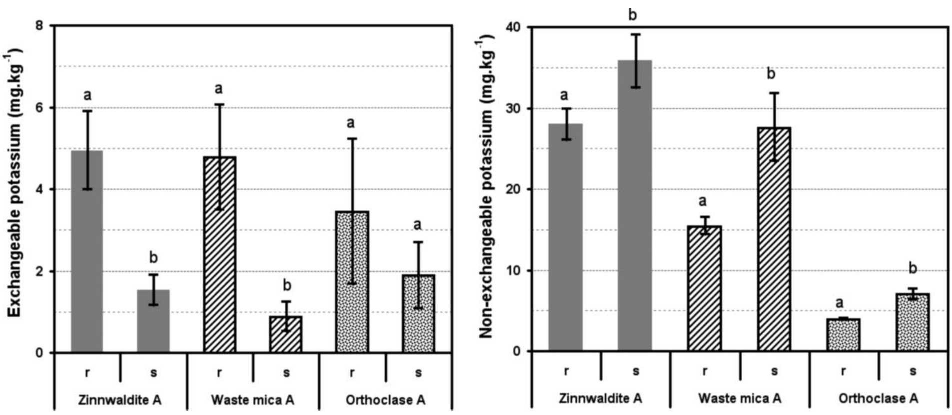


Figure 2. Contents of exchangeable and nonexchangeable K around roots (r) and in free rootless substrate (s), in sand culture experiments fertilized by zinnwaldite (287 mg K pot$^{-1}$), waste mica (277 mg K pot$^{-1}$) and orthoclase (243 mg K pot$^{-1}$). Bars show ± standard deviation. Different letters indicate statistically significant differences between the rooting zone and the rootless substrate of a particular treatment ($N = 4$, $p = 0.01$).

### *Soil pot experiment*

The addition of KCl to both soils had positive effects on K uptake; confirming that both soils, even though they have moderate $K_{non\text{-}ex}$ reserves (Table 4), had a decreased ability to supply K for plants. In the case of both loamy and sandy-loamy Luvisols, the addition of KCl at the rate of 100 mg K kg$^{-1}$ increased the K concentration in plant biomass by 62% and 98%, respectively ($p < 0.001$) as well as increasing, on average, the biomass production by 20%; therefore, the addition of KCl led to an approximate two-fold increase of K uptake per pot (Figure 3).

Table 6. The effects of different milling conditions on particle size distribution, potassium fractionation and K uptake by spring barley in a sand culture experiment (average per pot; standard deviation in parentheses).

| Milling conditions | Size fractions <0.002 mm (%) | 0.002–0.063 mm (%) | > 0.063 mm (%) | $K_{structural}$ (mg pot$^{-1}$) | $K_{non\text{-}ex}$ | $K_{ex}$ | $K_{H2O}$ | $K_{avail}$ | K plant uptake |
|---|---|---|---|---|---|---|---|---|---|
| Control (sand) | – | – | 100 | – | 12 | 0 | 0 | 12 | 2.7$^{a}$ |
| Two-rotor mill A (one milling cycle) | 5.3 | 64.0 | 30.7 | 266 | 18.7 | 1.3 | 0.7 | 20.7 | 5.7$^{b}$ (0.76) |
| Two-rotor mill B (two milling cycles) | 7.7 | 82.1 | 10.2 | 257 | 25.0 | 3.7 | 0.9 | 29.6 | 7.9$^{c}$ (0.41) |
| One rotor mill | 8.6 | 89.1 | 2.3 | 252 | 29.8 | 3.5 | 1.1 | 32.3 | 8.2$^{c}$ (0.66) |
| Disc mill A (2-min milling) | 10.6 | 70.4 | 19.0 | 254 | 28.0 | 2.8 | 2.2 | 33 | 7.5$^{c}$ (0.30) |
| Disc mill B (10-min milling) | 14.9 | 75.2 | 9.9 | 248 | 15.9 | 16.5 | 6.5 | 38.9 | 18.2$^{d}$ (1.21) |

Note: Different letters indicate values that were significantly different ($N = 4$, $p = 0.01$). $K_{structural}$, structural K; $K_{non\text{-}ex}$, non-exchangeable K; $K_{ex}$, exchangeable K; $K_{H2O}$, water-soluble K; $K_{avail}$, plant-available K (sum of $K_{non\text{-}ex}$, $K_{ex}$ and $K_{H2O}$).

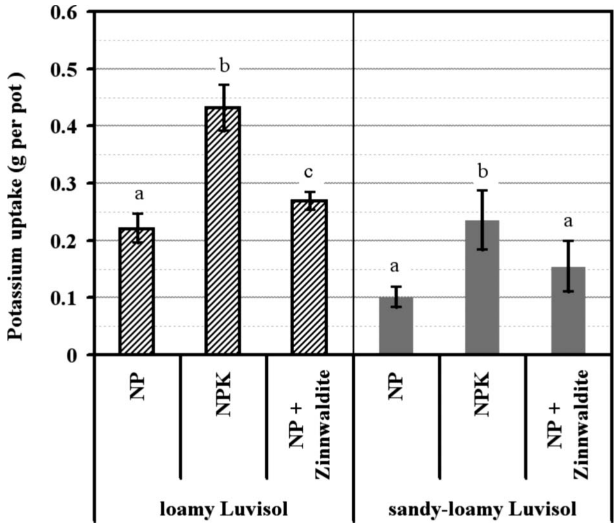


Figure 3. Potassium uptake of the aboveground biomass of spring barley grown on K-depleted soils in a pot experiment, treated with KCl (400 mg K $pot^{-1}$) and zinnwaldite (780 mg K $pot^{-1}$). Bars show $\pm$ standard deviation. The different letters mark statistically significant differences between the treatments of a particular soil ($N = 4$, $p = 0.05$).

The K concentration in plant biomass after zinnwaldite application (195 mg $kg^{-1}$) increased by 15% in loamy Luvisol ($p = 0.066$). In sandy-loamy Luvisol, addition of zinnwaldite increased the biomass production by 59% ($p = 0.056$). The application of zinnwaldite increased the K uptake in loamy Luvisol by 22% ($p = 0.035$), and in sandy-loamy Luvisol by 53% ($p = 0.06$) (Figure 3).

The vitality of the plants grown on sandy-loamy Luvisol was much worse, compared with the loamy Luvisol, which may also account for the lower level of statistical significance.

## Discussion

### *Availability of K from minerals*

Trioctahedral micas are among the most important sources of K in mineral soils. The different availabilities of K from the two mica materials can be explained by the differences in their $Fe^{2+}$ content, as higher $Fe^{2+}$ content is known to promote weathering and also enhance K release (Huang 2005). Higher $F^-$ and $Li^+$ contents are also known to contribute to retention of $K^+$ by the mica structure (Leonard and Weed 1970). Availability of K from orthoclase was usually found to be much lower than from the micas (e.g. Fraps 1921), because the rate of K release is very slow compared with the micas (McLean and Watson 1985). Bakken et al. (1997) found K from orthoclase virtually unavailable for Italian ryegrass. However, Sanz Scovino and Rowell (1988) reported that crops took up $\sim$10% of the feldspar's K during a 14-month period; further, that feldspar application appeared to be valuable, especially in soils with low cation exchange capacity.

Lower plant responses upon zinnwaldite application to the soils arose from the fact that the soils naturally contained non-exchangeable K. With the application of zinnwaldite, $K_{avail}$. increased by 3% for loamy Luvisol, and 5% for sandy-loamy Luvisol. The effect of zinnwaldite addition would probably better manifest itself in soils of much lower $K_{avail}$.

### *Effects of the milling method*

Potassium availability from silicate K minerals can be substantially altered by the milling conditions. By high-energy milling, Priyono and Gilkes (2008) increased the agronomic effectiveness of gneiss to the level of that of potassium sulfate. The K concentration in the plant biomass is a function of plant-available K in the soil (Hejcman et al. 2010). The correlation between $K_{ex}$ and K uptake by spring barley is very close (Matula 2009), which explains why the highest K uptake was observed in mica treated by prolonged vibratory milling. However, $K_{non\text{-}ex}$ also contributes to the K uptake, and its depletion is observed in the immediate vicinity of root surfaces (Moritsuka et al. 2004).

The aim of the milling optimization was to transform the structural K into more available forms, which was only partially achieved. The best method, the 10-min vibratory milling, transformed only an additional 3% of the total K to $K_{avail}$, compared to the 2-min milling. The economy of the additional time and energy was obviously low. More milling cycles in a two-rotor mill, in combination with higher rotor speeds and better geometry of the impact bits, might be a more promising way for processing the micaceous K-bearing materials.

### *Environmental risks*

The use of minerals as fertilizers increases the risk of environmental contamination and toxicity caused by the release of associated elements (e.g. Fe and Al toxicity, Karimi et al. 2011). In low-phosphate mineral fertilizers, current Czech law (Regulation of the Ministry of Agriculture of the Czech Republic on the requirements on fertilizers, 474/2000, Law Digest) defines the limits of the elemental contents within fertilizers: Pb (10 mg $kg^{-1}$), Hg (1 mg $kg^{-1}$), As (10 mg $kg^{-1}$), Cd (1 mg $kg^{-1}$) and Cr (50 mg $kg^{-1}$). Because of the elevated Pb, As and Cr contents (Table 1), the waste mica cannot be used directly as a fertilizer. For Pb, the limits for Ca-containing as well as for organo-mineral fertilizers are higher (30 and 100 mg $kg^{-1}$, respectively); therefore, the waste mica would be used as a constituent part of a multi-component fertilizer, where the content of critical elements in the final product would be lower.

Current Czech law does not define the limit for fluorine (F), which is potentially harmful (Fuge 1988). F is naturally present in micas, amphiboles and apatites; in soils, it usually occurs in the range of 200–400 mg $kg^{-1}$. An application of 250 kg K $ha^{-1}$ of waste mica would increase soil F by $\sim$25 mg $kg^{-1}$. However, the fluorine content in micas of the Krušné Hory Mts. is variable (1.5–5.0%, Rieder 1970); therefore, selection of low F-materials or prospecting in other sludge beds would be preferable before commercial use.

## Conclusions

Our research has shown that potassium-bearing waste mica and orthoclase were both able to release available K to spring barley; even when they were applied at relatively small rates. The significant effects of zinnwaldite application should be expected, especially when applied to soils of a low $K_{non\text{-}ex}$ content. The availability of K from the minerals can be increased by the optimization of the milling conditions, which should be focused upon in the transformation of structural K into more available forms. The mica from the Cínovec sludge deposit is an example of how older geological wastes might be reutilized. However, the fluorine and heavy metal content limits its direct usage. More testing regarding the environmental risks would be necessary before any decision to use the waste mica from Cínovec for fertilizer production.

## Acknowledgements

This study was supported by the Ministry of Agriculture of the Czech Republic, Project No. QI91C118. The authors are grateful to Ilja Knésl for performing the mineral analyses; to Marie Trčková for help in designing the sand culture experiments, and to two anonymous referees for their valuable comments on the manuscript.



## References

Agriculture. 2010. Prague: Ministry of Agriculture of the Czech Republic.
Bakken AK, Gautneb H, Myhr K. 1997. The potential of crushed rocks and mine tailings as slow-releasing K fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. Nutr Cycl Agroecosys. 47:41–48.
Botula J, Rucký P, Řepka V. 2005. Extraction of zinnwaldite from mining and processing wastes. Trans VŠB – Technical University of Ostrava, Geol Ser. 51(2):9–16.
Fraps GS. 1921. Availability of potash in some soil-forming minerals (bulletin no. 284). College Station (TX): Texas Agricultural Experiment Station.
Fuge R. 1988. Sources of halogens in the environment, influences on human and animal health. Environ Geochem Hlth. 10(2):51–61.
Govindaraju K. 1994. 1994 compilation of working values and sample description for 383 geostandards. Geostandard Newslett. 18:1–158.
Hejcman M, Száková J, Schellberg J, Tlustoš P. 2010. The Rengen grassland experiment: relationship between soil and biomass chemical properties, amount of elements applied, and their uptake. Plant Soil. 333:163–179.
Huang PM. 2005. Chemistry of potassium in soils. In: Tabatabai MA, Sparks DL, editors. Chemical processes in soils. Madison (WI): SSSA.
Karimi E, Abdolzadeh A, Sadeghipour HR, Aminei A. 2011. The potential of glauconitic sandstone as a potassium fertilizer for olive plants. Arch Agron Soil Sci. DOI:10.1080/03650340.2011.557369.
Leonard RA, Weed SB. 1970. Mica weathering rates as related to mica type and composition. Clay Clay Miner. 18:187–195.
Manning DAC. 2010. Mineral sources of potassium for plant nutrition. A review. Agron Sustain Dev. 30:281–294.
Matula J. 2009. A relationship between multi-nutrient soil tests (Mehlich 3, ammonium acetate, and water extraction) and bioavailability of nutrients from soils for barley. Plant Soil Environ. 55(4):173–180.
McLean EO, Watson ME. 1985. Soil measurements of plant-available potassium. In: Munson RD, editor. Potassium in agriculture. Madison (WI): ASA, CAAS and SSSA.
Moritsuka N, Yanai J, Kosaki T. 2004. Possible processes releasing nonexchangeable K from the rhizosphere of maize. Plant Soil. 258:261–268.
Priyono J, Gilkes RJ. 2008. High-energy milling improves the effectiveness of silicate rock fertilizers: a glasshouse assessment. Commun Soil Sci Plan. 39:358–369.
Potts PJ. 1995. A handbook of silicate rock analysis. London: Blackie.
Rieder M. 1970. Chemical composition and physical properties of lithium-iron micas from the Krušné Hory Mts. (Erzgebirge). Part A: chemical composition. Contr Mineral Petrol. 27:131–158.

Samková R. 2009. Recovering lithium mica from the waste after mining Sn–W ores through the use of flotation. GeoSci Eng. 55(1):33–37.

Sanz Scovino JI, Rowell DL. 1988. The use of feldspars as potassium fertilizers in the savannah of Colombia. Nutr Cycl Agroecosys. 17:71–83.

Štemprok M, Holub FV, Novák JK. 2003. Multiple magmatic pulses of the eastern volcano-plutonic complex, Krušné hory/Erzgebirge batholith, and their phosphorus contents. Bull Geosci. 78(3):277–296.

van Straaten P. 2002. Rocks for crops: agrominerals of sub-Saharan Africa. Nairobi (Kenya): International Centre for Research in Agroforestry.