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## Impact of organic and mineral fertilising on aluminium mobility and extractability in two temperate Cambisols

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**Abstract:** Different fertilisation systems cause changes in the content of mobile aluminium (Al) forms in the soil as a result of soil pH changes. Long-term stationary fertilisation experiments established in 1996 at 2 sites were evaluated. Experiments consisted of unfertilised control treatment and 6 other treatments, combining mineral fertilisation with the application of farmyard manure, sewage sludge and straw. To record the changes in mobile Al forms, we used 5 extraction procedures with agents: water,  $\text{CaCl}_2$ , KCl,  $\text{CaCl}_2/\text{DTPA}$  (CAT) and Mehlich 3 solutions. At treatment nitrogen (N) + straw, topsoil acidification was observed, resulting in the increased content of mobile Al. At treatments with mineral fertilisation (N, NPK), increased content of mobile forms of Al was recorded. Application of cattle manure and sewage sludge helped to stabilise the soil pH and reduce mobile Al forms. The close correlation between the methods determining the exchangeable Al ( $\text{CaCl}_2$  and KCl solutions) was observed; however, KCl extraction was more favourable in soils of low Al extractability, as the amount of extracted Al was 3–4 times higher. Positive correlations were determined between Al extracted by Mehlich 3 solution and the content of exchangeable Al. The less frequently used CAT method also turned out to be perspective for mobile Al determination. Furthermore, aluminium content determined in Mehlich 3 extract was compared with mobile phosphorus amounts in  $\text{H}_2\text{O}$ , CAT and Mehlich 3, respectively. All three investigated phosphorus forms showed significantly negative correlations with Al.

**Keywords:** soil pH; mobile forms of Al; exchangeable aluminium;  $\text{CaCl}_2/\text{DTPA}$  (CAT) method; Mehlich 3

Increased soil acidity accelerates solubility of aluminium (Al) compounds, which is a primary source of toxicity to plants at  $\text{pH} < 5.5$  (Parker et al. 1989). Special attention thus must be paid to exchangeable aluminium (Drábek et al. 2005) as the dynamic balance is set up between exchangeable and soil solution aluminium.  $\text{Al}^{3+}$  in soil solution is hydrolysed, which results in acidification of the soil environment as well as worsening of plant growth conditions. The content of exchangeable aluminium usually shows a negative correlation with pH values (Vieira et al. 2008).

Increased content of mobile aluminium in soil often results in yield reduction (Kamprath 1984, Johnson et al. 1997). Valle et al. (2009) determined a significant decrease of wheat grain yields as a consequence of the increase of exchangeable aluminium content from  $0.2 \text{ mmol}_+/\text{kg}$  to  $5.1 \text{ mmol}_+/\text{kg}$ .

Moore and Edwards (2005), using the gradually increasing nitrogen (N) doses (from 65 up to 260 kg N/ha/year) reported an exponential growth of exchangeable aluminium from  $1.0 \text{ mg Al/kg}$  (2<sup>nd</sup> year) up to  $100 \text{ mg Al/kg}$  (7<sup>th</sup> year of trials). Similarly, Bouman et al. (1995) determined a significant increase of exchangeable Al and hydrogen (H) at gradually increasing N fertilisation using urea and ammonium nitrate (45–180 kg N/ha/year). Schroder et al. (2011) recorded the effective cation exchange capacity saturation with aluminium ( $\text{Al}_{\text{SAT}}$ ) of 33.9% after intensive ammonium nitrate fertilisation (274 kg N/ha/year), whereas at the dose of 34 kg N/ha/year it was only 16.4%. Compared to that, the unfertilised control showed the ratio of only 1.09%. Johnson et al. (1997) observed that the  $\text{Al}_{\text{SAT}}$  content nearing to 16% might induce phytotoxicity in plants. The mathematical

model presented by Schroder et al. (2011) suggests that each percent of  $Al_{SAT}$  decreased the wheat yield on average by 2.8%. Al toxicity manifested in some years by the purple colouring of wheat leaves and a poor root system. Similarly, Wise (2002) recorded a decrease of winter wheat yields at increased aluminium content in the cation exchange complex. Wen et al. (2014) reported increased pH values and soil organic matter content at treatments with long-term (22 years) manure fertilisation, accompanied by the occurrence of amorphous nanominerals such as allophane and imogolite. Both these phenomena led to the transformation of exchangeable aluminium into stable forms. Soil nanominerals allophane and imogolite can sorb much more organic compounds than bulk soil minerals, mainly due to their high level of hydration, large surface and stable surface charge (Mikutta et al. 2006); these processes may contribute to organic matter protection and accumulation.

The results of recent complex observations of agrochemical properties of soils in the Czech Republic show that almost 25.2% of arable soils have  $pH_{CaCl_2}$  lower than 5.5 (Smatanová and Sušil 2017). Arable soils acidification can be attributed to intensive mineral nitrogen fertilisation, insufficient organic fertilisation and significantly reduced liming.

The aims of this paper are (1) to determine the impacts of different fertilisation systems on changes in the content of mobile aluminium forms in soils; (2) to compare different methods for soil Al determination, and (3) to investigate the influence of increased soil acidity and Al mobility on soil phosphorus pools.

## MATERIAL AND METHODS

Five field trials were established in 1996 at the experimental bases of the Czech University of Life Sciences Prague in different soil-climatic conditions (Vašák 2016). Potential for changes in soil aluminium behaviour due to low soil pH showed only two of five locations – B and C. Because of that, only these locations are evaluated in this manuscript (Table 1).

Within these trials, three crops were rotated in the following order: potatoes, winter wheat and spring barley. Each year, all of the crops were grown. The size of the experimental plots was 60 m<sup>2</sup>; each treatment was 4 times replicated. The trial included seven treatments: (1) no fertilisation (control); (2) sewage sludge (SS1); (3) farmyard manure (FYM1); (4) half dose of farmyard manure + N in mineral nitrogen

fertiliser (FYM1/2); (5) mineral nitrogen fertiliser (N); (6) NPK in mineral fertiliser (NPK); (7) spring barley straw + N in mineral nitrogen fertiliser (N + St) (Table 2). Organic fertilisers, farmyard manure, sewage sludge and straw, were always applied in autumn (October) to potatoes. Mineral phosphorus and potassium fertilisers were applied to each crop in autumn; mineral nitrogen fertilisers in the form of calcium ammonium nitrate were applied to potatoes and spring barley in spring, before crop establishment. In the case of winter wheat, the dose of nitrogen was divided in half, with the first half applied at BBCH 21, the second at BBCH 31–32. The content of nitrogen was 140 kg N/ha for wheat and 70 kg N/ha for spring barley; FYM1/2 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 level of 30 kg P/ha (triple superphosphate) and potassium at a level of 100 kg K/ha (60% potassium salt).

## Analytical procedures and statistical evaluation

$pH_{CaCl_2}$ . ISO 10390 (1994) was used to determine  $pH_{CaCl_2}$  values.

**Water extraction ( $Al_{H_2O}$ ).** Water extraction ( $Al_{H_2O}$ ) was performed, according to Luscombe et al. (1979).

Table 1. Basic description of investigated locations

Location	B	C
GPS coordinates	49°33'16"N 15°21'2"E	49°33'23"N 14°58'39"E
Altitude (m a.s.l.)	525	610
Mean annual temperature (°C)	7.0	7.7
Mean annual precipitation (mm)	665	666
Soil type	Stagnic Cambisol	
Soil texture	sandy loam	
Clay (%) (< 0.002 mm)	5.8	3.2
Silt (%) (0.002–0.05 mm)	43.6	37.1
Sand (%) (0.05–2 mm)	50.6	59.7
Bulk density (g/cm <sup>3</sup> )	1.4	1.3
$C_{org}$ (%)	1.4	1.3
$pH_{CaCl_2}$	5.1	5.3
CEC (mmol <sub>+</sub> /kg)	90	45

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

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Table 2. Experimental design (all nutrients doses are in kg/ha per 3 years)

Treatment	Nitrogen		
	potatoes/maize	wheat	barley
Control	–	–	–
SS1	330 <sup>1</sup>	0	0
FYM1	330 <sup>1</sup>	0	0
FYM1/2	165	115	50
N	120	140	70
NPK <sup>2</sup>	120	140	70
N + St	120 + St	140	70

<sup>1</sup>Total dose of nitrogen applied in organic fertiliser; Average yearly dose based on the analysis of farmyard manure and of sewage sludge. <sup>2</sup>Applied as follows: N – calcium ammonium nitrate (27% N), P – triple superphosphate (21% P), K – potassium chloride (50% K); FYM – farmyard manure – average doses of fresh FYM were as follows: B – 59.45 t/ha per 3 years (13.42 t of dry mass/ha per 3 years; 2.459% N in dry mass); C – 68.97 t/ha per 3 years (19.32 t of dry mass/ha per 3 years; 1.708% N in dry mass) SS and FYM were applied seven times; straw was applied six times. SS1 – sewage sludge – average doses of fresh sewage sludge were following: 30.18 t/ha over 3 years (9.383 t/ha over 3 years of dry mass). Straw was applied in doses of 5 t/ha over 3 years: 28 kg N – B; 35.5 kg N – C

**Calcium chloride soil extraction ( $\text{Al}_{\text{CaCl}_2}$ ).** The content of  $\text{Al}_{\text{CaCl}_2}$  was determined, according to Novozamsky et al. (1993).

**$\text{CaCl}_2$ /DTPA (CAT) extraction** (CSN EN 13651, 2002). 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  $\text{CaCl}_2$  and 0.002 mol/L DTPA). Solution was shaken for 1 h on horizontal shaker.

**Potassium chloride extraction ( $\text{Al}_{\text{KCl}}$ ).** Exchangeable aluminium was extracted in 1.0 mol/L KCl (Bertsch and Bloom 1996).

**Mehlich 3 extraction ( $\text{Al}_{\text{M3}}$ ).** Procedures were followed according to those reported previously (Mehlich 1984).

To determine the relationships between Al and P, phosphorus content was measured together with Al content in water extract, CAT and Mehlich 3 to obtain  $\text{P}_{\text{H}_2\text{O}}$ ,  $\text{P}_{\text{CAT}}$  and  $\text{P}_{\text{M3}}$ , respectively.

**Determining of different Al fractions.** The concentrations of Al and P in all of the above mentioned extracts, as well as concentrations of Na, K, Ca, Mg and Mn in  $\text{NH}_4\text{OAc}$  were determined using optical emission spectroscopy with inductively coupled plasma (ICP-OES) with axial plasma configuration, Varian, VistaPro, equipped with an autosampler SPS-5 (Agilent Technologies, Mulgrave, Australia).

Aluminium saturation was calculated according to Johnson et al. (1997) using the following equation:

$$\text{Al}_{\text{SAT}}(\%) = \left( \frac{\text{Al}_{\text{KCl}}}{\text{ECEC}} \right) \times 100$$

Where:  $\text{Al}_{\text{KCl}}$  – exchangeable Al ( $\text{cmol}_+/\text{kg}$ ); ECEC – effective cation exchange capacity, which is the sum of exchangeable  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$  determined in 1 mol/L  $\text{NH}_4\text{OAc}$  at pH 7.0 ( $\text{cmol}_+/\text{L}$ ) plus exchangeable  $\text{Al}^{3+}$  ( $\text{cmol}_+/\text{kg}$ ).

**Statistical analysis.** The results were assessed using analysis of variance (ANOVA) with the Fisher LSD (least significant difference) post-hoc test. To evaluate the obtained results, the Statistica software (StatSoft Inc. 2015) was used.

## RESULTS AND DISCUSSION

The changes of  $\text{pH}_{\text{CaCl}_2}$  at individual treatments are given in Table 3. The values obtained in 1996 (before the establishment of the trial) and in 2017 (after the barley harvest) were compared. Application of manure positively affected soil  $\text{pH}_{\text{CaCl}_2}$ . The application of sewage sludge had a slightly positive effect on  $\text{pH}_{\text{CaCl}_2}$ . With the N + straw treatment, there was a clear tendency to topsoil acidification. The presented results further show a clear negative effect of mineral fertilisation alone (N, NPK).

Table 3. Changes of  $\text{pH}_{\text{CaCl}_2}$  during the period of 1996/2017

Site	Control	SS1	FYM1	FYM1/2	N	NPK	N + St
B	–0.25 <sup>b</sup>	–0.10 <sup>bc</sup>	0.14 <sup>d</sup>	0.00 <sup>c</sup>	–0.31 <sup>a</sup>	–0.15 <sup>b</sup>	–0.35 <sup>a</sup>
C	–0.22 <sup>b</sup>	–0.05 <sup>bc</sup>	0.16 <sup>c</sup>	–0.06 <sup>bc</sup>	–0.20 <sup>b</sup>	–0.43 <sup>a</sup>	–0.47 <sup>a</sup>

Different letters in the row mean significant difference ( $P \leq 0.05$ ) among fertilising treatments. Control – no fertilisation; SS1 – sewage sludge; FYM1 – farmyard manure; FYM1/2 – half dose of farmyard manure + N in mineral nitrogen fertiliser; N – mineral nitrogen fertiliser; NPK – NPK in mineral fertiliser; St – spring barley straw

Table 4. Aluminium (Al) content in different extraction solutions (mg Al/kg)

Site	Control	SS1	FYM1	FYM1/2	N	NPK	N + St
<b>Al<sub>H<sub>2</sub>O</sub></b>							
B	41 <sup>a</sup>	44 <sup>a</sup>	42 <sup>a</sup>	44 <sup>a</sup>	43 <sup>a</sup>	42 <sup>a</sup>	43 <sup>a</sup>
C	21 <sup>ab</sup>	18 <sup>ab</sup>	19 <sup>ab</sup>	20 <sup>ab</sup>	20 <sup>ab</sup>	22 <sup>b</sup>	19 <sup>a</sup>
<b>Al<sub>CAT</sub></b>							
B	247 <sup>ab</sup>	237 <sup>ab</sup>	229 <sup>a</sup>	241 <sup>ab</sup>	232 <sup>ab</sup>	288 <sup>c</sup>	252 <sup>b</sup>
C	209 <sup>ab</sup>	192 <sup>a</sup>	176 <sup>a</sup>	237 <sup>b</sup>	263 <sup>c</sup>	262 <sup>bc</sup>	253 <sup>bc</sup>
<b>Al<sub>M3</sub></b>							
B	1051 <sup>ab</sup>	1069 <sup>ab</sup>	1033 <sup>a</sup>	1058 <sup>ab</sup>	1068 <sup>ab</sup>	1097 <sup>b</sup>	1077 <sup>b</sup>
C	950 <sup>a</sup>	938 <sup>a</sup>	921 <sup>a</sup>	935 <sup>a</sup>	994 <sup>a</sup>	1017 <sup>a</sup>	1030 <sup>a</sup>
<b>Al<sub>CaCl<sub>2</sub></sub></b>							
B	1.2 <sup>ab</sup>	0.8 <sup>a</sup>	1.2 <sup>ab</sup>	1.0 <sup>ab</sup>	1.4 <sup>b</sup>	1.5 <sup>ab</sup>	1.2 <sup>ab</sup>
C	1.6 <sup>ab</sup>	1.2 <sup>a</sup>	1.6 <sup>a</sup>	1.7 <sup>ab</sup>	3.1 <sup>ab</sup>	3.0 <sup>b</sup>	2.9 <sup>b</sup>

Different letters in the row mean significant difference ( $P \leq 0.05$ ) among fertilising treatments. Control – no fertilisation; SS1 – sewage sludge; FYM1 – farmyard manure; FYM1/2 – half dose of farmyard manure + N in mineral nitrogen fertiliser; N – mineral nitrogen fertiliser; NPK – NPK in mineral fertiliser; St – spring barley straw; Al<sub>H<sub>2</sub>O</sub> – water extraction; Al<sub>CAT</sub> – CAT extraction; Al<sub>M3</sub> – Mehlich 3 extraction; Al<sub>CaCl<sub>2</sub></sub> – calcium chloride soil extraction

### Extraction procedures

**Water-soluble (Al<sub>H<sub>2</sub>O</sub>) and exchangeable aluminium (Al<sub>KCl</sub>, Al<sub>CaCl<sub>2</sub></sub>).** In Table 4 are given the Al<sub>H<sub>2</sub>O</sub> contents. The differences among fertilising treatments were not statistically significant. On the other hand, water as an extract released a significant amount of Al, which was 42.7 mg Al/kg at location B and 19.9 mg Al/kg at location C, respectively. It is from 9 to 36 times higher Al content compared to CaCl<sub>2</sub> extraction.

The content of exchangeable Al was determined using 1 mol/L KCl, which is a commonly used method nowadays (Drábek et al. 2005), as well as using 0.01 mol/L CaCl<sub>2</sub>, previously evaluated by Johnson et al. (1997) (Table 4). Compared to 0.01 mol/L CaCl<sub>2</sub>,

Al extracted by 1 mol/L KCl was more effective, as the amount of extracted aluminium was 3–4 times higher. It is a positive feature, especially in soils of pH<sub>CaCl<sub>2</sub></sub> < 5.5, where the amount of extractable Al is usually low. Higher extraction strength of the KCl agent results from a higher concentration of replacing cation (K<sup>+</sup>) and consequently from higher acidity caused by H<sup>+</sup> released from exchange sites to the solution. On the other hand, a very tight correlation was determined between both methods (Table 5), which suggests that both of them may be used. Extraction in 0.01 mol/L CaCl<sub>2</sub> solution is closer to real conditions at site at a given time (Novozamsky et al. 1993). In our trials, the content of exchangeable aluminium (Al<sub>KCl</sub>) did not reach over 20 mg Al/kg (site B) and 11 mg Al/kg (site C). These concentrations are low and should not be toxic for plants. Valle et al. (2009) reported a significant decrease of wheat grain yields, at the content of exchangeable Al above 5.1 mmol<sub>+</sub>/kg (i.e. 45.9 mg Al/kg). Similarly, low contents (1.04 mmol<sub>+</sub>/kg) as in our observations were analysed by Norton et al. (2018) at soils of pH 5.5.

To assess aluminium toxicity, aluminium saturation (Al<sub>SAT</sub>) of the effective cation exchange capacity (CEC) was calculated (Johnson et al. 1997). In our trials, the content of Al<sub>SAT</sub> was always < 3% – i.e. very low Al saturation level (Table 6). Kamprath (1984) stated that at Al<sub>SAT</sub> lower than 10%, the wheat yield was not affected. Johnson et al. (1997) published the limit level of Al<sub>SAT</sub> lower than 16%. Higher saturation resulted in phytotoxicity of wheat plants grown in Oklahoma (USA) soils. Moreover, using the Al<sub>SAT</sub> criterion, growth and yield of plants in our trials were not negatively influenced by the content of toxic aluminium forms.

**CAT method.** Results of CaCl<sub>2</sub>/DTPA extraction (CAT) are shown in Table 4. It is a method frequently used for determination of available forms of nutrients in substrates (Dubský et al. 2019). The acid character of CAT solution, as well as DTPA chelating effects, result in a strong extraction effect of this agent. Out of all the tested methods used in these localities, CAT showed

Table 5. Pearson correlation coefficient values for different extraction solutions

	Al <sub>CAT</sub> /Al <sub>M3</sub>	Al <sub>H<sub>2</sub>O</sub> /Al <sub>M3</sub>	Al <sub>CAT</sub> /Al <sub>H<sub>2</sub>O</sub>	Al <sub>KCl</sub> /Al <sub>CaCl<sub>2</sub></sub>	Al <sub>KCl</sub> /Al <sub>M3</sub>	Al <sub>KCl</sub> /Al <sub>CAT</sub>	Al <sub>KCl</sub> /Al <sub>H<sub>2</sub>O</sub>
B	0.806***	−0.118	0.023	0.759***	0.792***	0.713***	−0.469**
C	−0.018	−0.402*	0.514**	0.901***	0.746***	0.810***	−0.134

\* $P < 0.05$ ; \*\* $P < 0.01$ ; \*\*\* $P < 0.001$ ; Al<sub>CAT</sub> – CAT extraction; Al<sub>M3</sub> – Mehlich 3 extraction; Al<sub>H<sub>2</sub>O</sub> – water extraction; Al<sub>KCl</sub> – potassium chloride extraction



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Table 6. Saturation of effective cation exchange capacity (%) by aluminium

Site	Control	SS1	FYM1	FYM1/2	N	NPK	N + St
B	0.50 <sup>b</sup>	0.21 <sup>a</sup>	0.24 <sup>a</sup>	0.60 <sup>abc</sup>	0.79 <sup>bc</sup>	3.04 <sup>d</sup>	1.09 <sup>c</sup>
C	0.40 <sup>b</sup>	0.00 <sup>a</sup>	0.00 <sup>a</sup>	0.09 <sup>ab</sup>	1.10 <sup>b</sup>	1.10 <sup>b</sup>	2.43 <sup>c</sup>

Different letters in the row mean significant difference ( $P \leq 0.05$ ) among fertilising treatments. Control – no fertilisation; SS1 – sewage sludge; FYM1 – farmyard manure; FYM1/2 – half dose of farmyard manure + N in mineral nitrogen fertiliser; N – mineral nitrogen fertiliser; NPK – NPK in mineral fertiliser; St – spring barley straw

the tightest correlation with the  $\text{pH}_{\text{CaCl}_2}$  value changes caused by different fertilisation systems (Figure 1). In our trials, the CAT method mostly showed significant negative correlations with mobile phosphorus in soils (Table 7). A negative relationship between the content of soil mobile aluminium forms and phosphorus was also described by Sims and Vadas (2005).

**Mehlich 3 method ( $\text{Al}_{\text{M3}}$ ).** No tight correlations between the changes in pH values and  $\text{Al}_{\text{M3}}$  content were determined. The possible potential of using this method is demonstrated by positive correlations with exchangeable aluminium ( $\text{Al}_{\text{KCl}}$ ) (Table 5). Mehlich 3 procedure stands for a "robust" method, having prob-

ably a limited power in case of aluminium. Both organically and inorganically sorbed aluminium was determined. Nevertheless, the advantage is its potential to determine a range of nutrients; using the analytical method with the ICP measurement, data on mobile aluminium may be obtained easily, too. This procedure is suitable mainly at soils with  $\text{pH}_{\text{CaCl}_2} < 5.5$ . Compared to the method of non-crystalline Al determination using the ammonium oxalate, the advantage of Mehlich 3 is a significantly shorter exposition time. Our experiments also revealed a negative correlation between the  $\text{Al}_{\text{M3}}$  content and mobile phosphorus ( $\text{P}_{\text{H}_2\text{O}}$ ,  $\text{P}_{\text{CAT}}$ ,  $\text{P}_{\text{M3}}$ ) (Table 7), which indirectly confirms the hypothesis that  $\text{Al}_{\text{M3}}$  may be used to predict the P sorption capacity in soils (Fernández Marcos et al. 1998).

According to Fernández Marcos et al. (1998), as to determining mobile non-crystalline aluminium, Mehlich 3 results are equal to those of ammonium oxalate ( $\text{Al}_{\text{O}}$ ). Also, Sen Tran et al. (1990) reported a very good correlation with oxalate ( $\text{Al}_{\text{O}}$ ). At high  $\text{Al}_{\text{O}}$  concentrations, this relation is no more linear. Decreased Mehlich 3 extract sensitivity to non-crys-

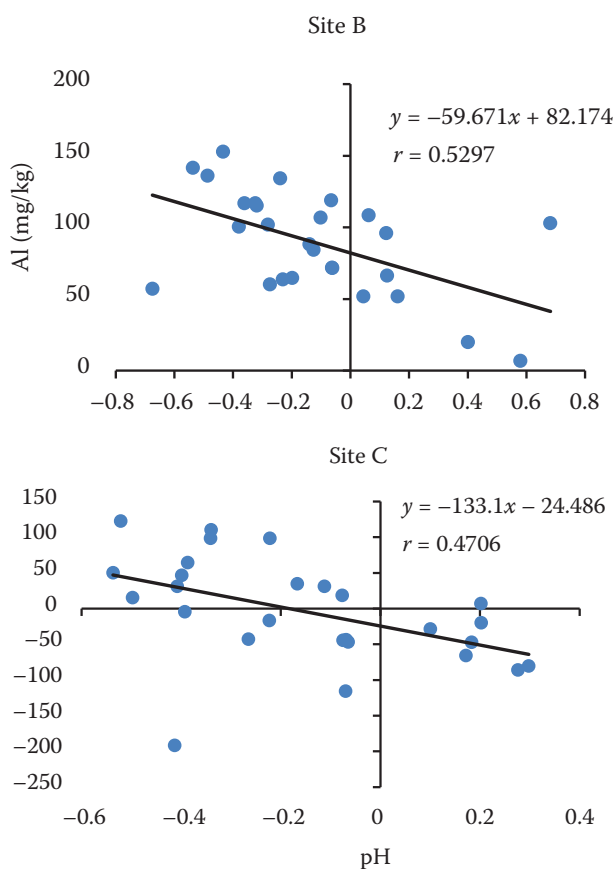


Figure 1. Changes of  $\text{Al}_{\text{CAT}}$  in accordance with changes of  $\text{pH}_{\text{CaCl}_2}$

Table 7. Pearson correlation coefficients for content of aluminium (Al) and phosphorus (P)

Site	$\text{P}_{\text{H}_2\text{O}}$	$\text{P}_{\text{CAT}}$	$\text{P}_{\text{M3}}$
$\text{Al}_{\text{M3}}$			
B	-0.370**	-0.353**	-0.389**
C	-0.291*	-0.204	-0.061
$\text{Al}_{\text{CAT}}$			
B	-0.529***	-0.522***	-0.562***
C	-0.602***	-0.554***	-0.678***
$\text{Al}_{\text{KCl}}$			
B	-0.465**	0.191	-0.468**
C	-0.555***	-0.502***	-0.509***

\* $P < 0.05$ ; \*\* $P < 0.01$ ; \*\*\* $P < 0.001$ ;  $\text{Al}_{\text{M3}}/\text{P}_{\text{M3}}$  – Mehlich 3 extraction;  $\text{Al}_{\text{CAT}}/\text{P}_{\text{CAT}}$  – CAT extraction;  $\text{Al}_{\text{KCl}}$  – potassium chloride extraction;  $\text{P}_{\text{H}_2\text{O}}$  – water extraction

talline aluminium at high  $Al_o$  concentrations may be caused by low fluorine concentration (0.015 mol/L) and further by the short time of extraction (only 5 min). Fernández Marcos et al. (1998) assumed that the Mehlich 3 method is suitable for determining mobile aluminium in a wide range of soils. The authors further confirmed the hypothesis that  $Al_{M3}$  might be successfully used for prediction of phosphorus sorption capacity in soils. Similar results about the use of the Mehlich 3 method for assessment of changes in the content of mobile aluminium were published in the study of Monterroso et al. (1999); the authors also reported a significant  $Al_{M3}$  correlation with the content of non-crystalline aluminium.

### Effect of the fertilisation systems

The evaluation of individual extraction agents does not allow drawing unequivocal and conclusive decrease of mobile aluminium forms at treatments using cattle manure and sewage sludges (Table 4). Significantly conclusive results, however, arise from the values of aluminium saturation of the sorption complex ( $Al_{SAT}$ ). Our previous research (Balík et al. 2018) prove the increase of the total organic carbon in topsoil ( $C_{org}$ ), microbial biomass carbon ( $C_{mic}$ ) as well as easily-extractable carbon ( $C_{DOC}$ ) at these two treatments. We suppose that these factors contributed to a decrease in the  $Al_{SAT}$  values, which means reduced aluminium mobility. Similarly, Wen et al. (2014) in long-term experiments with manure amendment determined a decrease of the  $Al_{SAT}$  values and an increased ratio of the amorphous aluminium. The content of amorphous Al significantly correlated with the organic carbon content in topsoil. As described by Rutkowska et al. (2015), long-term manure application decreased the exchangeable aluminium content at the NPK treatment by 15% and the NP treatment by 30%. Application of organic substances has a positive impact on the immobilisation of toxic Al ions, thanks to the production of stable organo-mineral complexes (Qin et al. 2010). Also, increased production of soil nanominerals (allophane, imoglite) after the manure application may be a novel mechanism to reduce soil acidification (Mikutta et al. 2006). Similarly, Tao et al. (2019) reported a significant decrease of exchangeable aluminium in long-term experiments with manure application.

Mineral fertilisation alone resulted in a tendency of topsoil acidification and higher aluminium mobility.

Especially the  $Al_{SAT}$  ratio increased. This weaker acidification process than expected may be explained by two factors: (a) average N fertilisation intensity (120 kg N/ha/year); (b) form of N fertiliser used (calcium ammonium nitrate). Still, the process of acidification ( $pH_{CaCl_2}$ ) and increase of aluminium mobility ( $Al_{H_2O}$ ,  $Al_{CAT}$ ,  $Al_{M3}$ ,  $Al_{KCl}$ ) is evident in all analyses carried out, which is in good agreement with many literature sources (Bouman et al. 1995, Moore and Edwards 2005, Schroder et al. 2011, Rutkowska et al. 2015).

Interestingly, N + straw treatment resulted in acidification of soil and increased aluminium mobility; it was evident mainly from the  $Al_{SAT}$  ratio. It is well known that aluminium has a high affinity to organic substances and may form permanent bonds with various organic fractions. Their stability depends on the type of organic substance and the number of hydroxyl and phenolic groups directly bound to aluminium (Parker 2005). It is probable that straw, mainly at site C, does not contribute to increased stability of the organo-mineral complex and it is mineralised quickly after application. In contrast to our results, Qina et al. (2010) reported an increase in soil pH and a decrease of water-soluble and exchangeable aluminium after rice straw application for 12 years.

A close correlation between the methods determining the exchangeable aluminium ( $Al_{CaCl_2}$  and  $Al_{KCl}$ ) was observed; however, KCl extraction appeared more favourable. The less frequently used CAT method turned out to be more perspective for mobile aluminium determination and has several advantages: (i) good reaction to changes of mobile Al forms related to changes of soil pH values; (ii) positive correlations with exchangeable sorbed Al and *vice versa* (iii) negative correlation with mobile P forms; (iv) determined Al contents in common soils did not fall below the ICP detection level. A very good tool to express the ongoing acidification processes and the content of mobile aluminium forms is effective cation exchange capacity saturation with aluminium. The content of mobile and exchangeable aluminium forms, as supposed, showed a negative correlation with mobile P. Application of cattle manure and sewage sludges helped stabilise the soil pH and reduce mobile forms of aluminium. At treatment N + straw, topsoil acidification and increased aluminium mobility were observed, resulting mainly in the increased content of mobile  $Al_{SAT}$ . At treatments with mineral fertilisation (N, NPK), a tendency to increased content of mobile forms of aluminium was observed.

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