

APPLICATION OF GEOCHEMICAL INDICES (S : AL; Mg : Al) AND PARTITION COEFFICIENT (K_d) FOR EVALUATING RESPONSE OF CROPS TO ALUMINUM TOXICITY

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Abstract

Field trials were carried out in order to examine the role of some geochemical indices (S : Al; Mg : Al) and partition coefficient (K_d) for evaluating response of crops to aluminum toxicity under acid soil conditions. They were established in 2007/2008 at Gluszyna Lesna (52°14' N and 16°56' E), a 300-hectare agricultural farm near Poznan. Two different crop plants were tested: (i) winter oilseed rape, variety Cabriolet, (ii) maize, variety Anamur. The source of magnesium and sulphur was kieserite ($MgSO_4 \cdot H_2O$) applied at four Mg rates: 0, 25, 50, 100 kg Mg ha⁻¹ in the first decade of November 2007. The results revealed that the values of partition coefficient for magnesium ($K_{d_{Mg}}$) decreased along with a rise in pH, although a reverse trend was observed for the partition coefficient of aluminum $K_{d_{Al}}$. Changes in S : Al indices observed at both sites along with increasing kieserite (Mg) rates suggest that S-SO₄ concentrations in soil may reduce Al toxicity. The introduction of S-SO₄ to soil may be intended to meet plant's nutritional requirements and, simultaneously, react with exchangeable aluminum (Al_{ex}) in order to mitigate its phytotoxicity. On the other hand, the incorporated magnesium (Mg^{2+}) was expected to exchange with Al^{3+} ions in the soil cation exchange complex (CEC). The values of Mg : Al indices decreased with raising kieserite rates at the oilseed rape site. Changes of Mg : Al indices observed under extremely acid soil conditions (maize site) along with increasing kieserite (Mg) rates suggest that Mg : Al cannot be treated as a direct index describing the $Mg_{ex} - Al_{ex}$ interaction, especially at 25 and 50 kg Mg ha⁻¹ rates. The values of S : Al and Mg : Al indices were lower at the maize site than at the oilseed rape site because of large amounts of Al_{ex} concentrated in soil solution (amounts of Al_{ex} on the maize site were ca 3-fold higher than those determined at the oilseed rape site).

Key words: winter oilseed rape, maize, aluminum toxicity, soil acidity, S:Al and Mg:Al indices, partition coefficient (K_d).

ZASTOSOWANIE GEOCHEMICZNYCH WSKAŹNIKÓW (S:Al; Mg:Al) ORAZ WSPÓLCZYNNIKA PODZIAŁU (K_d) DO OCENY REAKCJI ROŚLIN UPRAWNYCH NA TOKSYCZNOŚĆ GLINU

Abstrakt

Doświadczenie założono, aby zbadać rolę niektórych wskaźników geochemicznych (S:Al oraz Mg:Al) oraz współczynnika podziału (K_d) w ocenie reakcji roślin uprawnych na toksyczność glinu w warunkach zakwaszenia gleby. Polowe doświadczenia przeprowadzono w sezonie wegetacyjnym 2007/2008 w gospodarstwie rolnym o powierzchni 300 ha, w Głuszynie Leśnej (52⁰14, N and 16⁰56, E) k. Poznania. Doświadczenia obejmowały dwie rośliny uprawne: rzepak ozimy i kukurydzę oraz cztery dawki magnezu: 0, 25, 50 i 100 kg Mg ha⁻¹ zastosowane w postaci kizerytu (MgSO₄·H₂O), w pierwszej dekadzie listopada 2007. Wykazano, iż współczynnik podziału dla magnezu ($K_{d_{Mg}}$) zmniejszał się wraz ze wzrostem pH gleby, natomiast odwrotny trend zaobserwowano w przypadku współczynnika podziału dla glinu ($K_{d_{Al}}$). Zmiany wskaźników S/Al, obserwowane na obu stanowiskach, sugerują, że zawartość S-SO₄ w glebie może redukować toksyczność glinu. Zastosowany S-SO₄ służył zarówno do zaspokojenia potrzeb pokarmowych rośliny względem siarki, jak i do neutralizowania glinu wymiennego (Al_{wym}), aby ograniczyć jego fitotoksyczność. Z drugiej strony wprowadzenie do gleby magnezu (Mg²⁺), poza żywieniowym aspektem, może powodować wypieranie jonów Al³⁺ z glebowego kompleksu sorpcyjnego (KS). Na stanowisku z rzepakiem ozimym wartości wskaźnika Mg/Al malały wraz z rosnącymi dawkami kizerytu. Zmiany wartości wskaźnika Mg:Al, zachodzące wraz z rosnącymi dawkami kizerytu (Mg) na stanowisku z kukurydzą (skrajnie kwaśne warunki zakwaszenia gleby), wskazują, iż wskaźnik Mg:Al nie może być traktowany jako bezpośredni czynnik opisujący współdziałanie Mg – Al, szczególnie dla dawek 25 i 50 kg Mg ha⁻¹. Wartości wskaźników S:Al i Mg:Al były zdecydowanie niższe na stanowisku z kukurydzą w porównaniu ze stanowiskiem z rzepakiem ozimym. Wynikało to z bardzo dużej zawartości Al_{wym} w roztworze glebowym (zawartość Al_{wym} na stanowisku z kukurydzą była 3-krotnie wyższa niż na stanowisku z rzepakiem ozimym).

Słowa kluczowe: rzepak ozimy, kukurydza, toksyczność glinu, zakwaszenie gleb, wskaźniki S:Al oraz Mg:Al, współczynnik podziału (K_d).

INTRODUCTION

Soil acidity is a major growth-limiting factor for plants, both worldwide and in Poland. Poor plant growth on acid soil has been linked to monomeric aluminum (Al³⁺) toxicity (KINRAIDE 1993, BARCELO et al. 1996, KIDD, PROCTOR 2001), which usually occurs at pH < 5.0 or, more precisely, at pH < 4.7. Less phytotoxic forms, Al(OH)²⁺, Al(OH)₂⁺, are expected at pH between 5.0 and 6.5, when conditions suitable for mitigating aluminum phytotoxicity appear (LINDSAY 1979). Due to excess of aluminum cation excess, crops, which have a smaller and shallower root system, are unable to take up sufficient amounts of many nutrients in order to cover their nutritional needs (SZATANIK-KŁOC, JÓZEFACIUK 2002, GRZEBISZ et al. 2005).

The present state of knowledge concerning the mitigation of aluminum toxicity assumes an implementation of a practical procedure, i.e., liming (GRZEBISZ et al. 2006). However, a question arises about some other alternative methods aimed at inducing crop plants' response to aluminum toxicity under acid soil conditions. This problem can be solved if relationships between some macronutrients, for example sulphur (S), magnesium (Mg), and aluminum cation (Al^{3+}) in acid soil will be considered. It is assumed that both macronutrients (S and Mg) are intended to alleviate aluminum toxicity and hence ensure a high nutrient efficiency of crop plants grown under acid soil conditions.

Sulphur (S), occurring in the soil solution as SO_4^{2-} anions, may precipitate Al^{3+} ions present in the soil solution (SKUBISZEWSKA, DIATTA 2008), whereas magnesium as Mg^{2+} cation in the soil solution can exchange with Al^{3+} ions in the soil cation exchange complex. Moreover, magnesium may exhibit a great capacity for decreasing Al^{3+} accumulation in plant root apoplast (GRZEBISZ, HARDTER 2006) owing to the antagonistic effect of Mg – Al ions in acid soil.

Metals ions, including aluminum and magnesium, exhibit different affinity with naturally occurring adsorbents and the reactions between these metal ions and adsorbents are observed to be reversible as related, among others, to soil pH and their content in soils. The magnitude of this process is generally estimated by chemical tests as well as speciation studies. The ratio of Al and Mg in the solid phase to that in solution at equilibrium is defined as partition coefficient K_d , which is reported as Me_{ads} / Me_{sol} where, Me_{ads} – adsorbed/retained Al or Mg and Me_{sol} – their concentrations in solution (DIATTA et al. 2003, 2004). High values of partition coefficients are believed to indicate that Al and Mg have been retained by the soil solid phase through sorption reactions, while low values imply that most of Al and Mg are partitioned to the ambient soil solution, where they are potentially prone to transport and biological or geochemical reactions. The mechanisms involved are related to several physical and chemical soil properties, of which soil reaction (pH), organic matter, clay and silt contents are most often indicated as the ones which control dynamic processes of metal geochemistry.

It was assumed that partition coefficients for aluminum and magnesium ($K_{d_{Al}}$, $K_{d_{Mg}}$) may play an important role in understanding the relationship between aluminum (Al) and magnesium (Mg) concentrations in the soil solid phase and the soil solution. Furthermore, $K_{d_{Al}}$, $K_{d_{Mg}}$ status in soil as well as the relationship with pH are expected to provide useful agrochemical tool for evaluating crop plants response to soil acidification.

The aim of the present study was to report the geochemical characteristics of some indices i.e., S : Al; Mg : Al and partition coefficient (K_d), in the assessment of crops' response to aluminum toxicity under acid soil conditions.

MATERIAL AND METHODS

1. Characteristics of experimental field, designs and agrochemical soil properties

a) Field trials and soil sampling

Field trials were established in 2007/2008 at Gluszyna Lesna (52°14' N and 16°56' E), a 300-hectare agricultural farm, near Poznan. Soils under these trials belong to the agronomical category covering the range from class IV to V. Two different crops were tested: (i) winter oilseed rape, variety Cabriolet, and (ii) maize variety Anamur. The source of magnesium and sulphur was kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) applied at four Mg rates: 0, 25, 50, 100 kg Mg ha⁻¹ in the first decade of November 2007. Soil samples were collected at the depths 0-20 cm and 20-40 cm as follows: (i) initial samples – just before kieserite application, both for oilseed rape and maize site, (ii) in spring – at the plant regrowth phase for winter oilseed rape, (iii) during the flowering phase for maize.

b) Soils chemical analysis

Prior to chemical analyses, soil samples were air-dried at room temperature for 4 days, crushed to pass through a 1.0 mm screen and stored in plastic bags before chemical analyses. The pH was determined potentiometrically (*w/v*, 1:5) according to the Polish Standard (1994) in 1.0 mole KCl dm⁻³. Cation exchange capacity (CEC) was obtained by summation of 1 mole KCl dm⁻³ extractable acidity and exchangeable alkaline cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) extracted by 1 mole $\text{CH}_3\text{COONH}_4$ dm⁻³ (pH 7.0), as described by THOMAS (1982). These elements were determined by the FASS method (Varian Spectra AA – 250 Plus).

Exchangeable aluminium was determined according Sokolov's method (MOCEK et al, 2000) by using 1 mole KCl for displacing Al ions. The recovered extracts were divided into two aliquots, of which one was directly titrated for determining the concentrations of H and Al, whereas the second one was titrated after Al precipitation with NaF. Exchangeable Al was obtained from the difference between these chemical tests. Sulphur was assessed by the turbidimetric method based on the extraction of S-SO₄ compounds by 2% CH₃COOH and further precipitation S-SO₄ with a 20% BaCl₂ solution (SPARKS 1996). Sulphur concentrations were determined by using Specord 40 AnalytikJena equipment. All analyses were performed in duplications.

2. Characteristics of geochemical indices and partition coefficient

In this study, the following indices have been suggested for estimating Al, Mg and S geochemical changes as induced by oilseed rape and maize growth.

$$Kd_{Al} = \frac{Al_{total} (mg\ kg^{-1})}{Al_{ex} (mg\ dm^{-3})} \quad (1)$$

$$Kd_{Mg} = \frac{Mg_{total} (mg\ kg^{-1})}{Mg_{ex} (mg\ dm^{-3})} \quad (2)$$

$$S : Al = \frac{S - SO_4 (mg\ kg^{-1})}{Al_{ex} (mg\ kg^{-1})} \quad (3)$$

$$Mg : Al = \frac{Mg_{ex} (mg\ kg^{-1})}{Al_{ex} (mg\ kg^{-1})} \quad (4)$$

where:

- Kd_{Al} – aluminum partition coefficient, ($dm^3\ kg^{-1}$);
- Kd_{Mg} – magnesium partition coefficient, ($dm^3\ kg^{-1}$);
- $S : Al$ – index expressing the relationship between $S-SO_4$ and Al_{ex} (mass ratio basis);
- $Mg : Al$ – index expressing the relationship between Mg_{ex} and Al_{ex} (mass ratio basis);
- Al_{ex} – exchangeable aluminum ($mg\ kg^{-1}$);
- Mg_{ex} – exchangeable magnesium ($mg\ kg^{-1}$).

Additional estimation of potential aluminum phytotoxicity was undertaken as reported below (DIATTA et al. 2009):

- | | |
|--|-------------------|
| < 36.0 $mg\ Al_{ex}\ kg^{-1}$ soil, | slight effect |
| 36.0 – 45.0 $mg\ Al_{ex}\ kg^{-1}$ soil, | negative effect |
| > 45.0 $mg\ Al_{ex}\ kg^{-1}$ soil, | phytotoxic effect |

Indices as well as partition coefficients were represented graphically using EXCEL[®] spreadsheets.

RESULTS AND DISCUSSION

1. Soil chemical properties

The chemical properties reported in Table 1 showed that before establishment of the trials, soils under oilseed rape were acid (pH 4.65-4.70) while the maize site contained extremely acid soils (pH 3.70-3.75) (GRZEBISZ et al. 2005, STRZEMSKI et al. 1973), irrespective of the sampling depth. The amounts

Table 1

Selected chemical soil properties of oilseed rape and maize sites before the field trial
(mean, $n = 16$)

Plant	Soil layer (cm)	pH _{KCl}	Al _{ex}	S-SO ₄	Mg _{ex}	Ca _{ex}	K _{ex}	Al _{tot} (%)
					(mol dm ⁻³ CH ₃ COONH ₄)			
					mg kg ⁻¹			
Oilseed rape	0-20	4.70	38.67	14.93	35.06	228.18	130.66	2.1
	20-40	4.65	49.60	16.06	59.06	269.24	145.34	2.4
Maize	0-20	3.75	150.03	19.68	46.84	207.12	72.11	1.8
	20-40	3.70	120.45	19.05	46.50	194.94	58.65	1.7

of exchangeable aluminum (Al_{ex}) at the maize site varied within the range 120.45-150.03 mg kg⁻¹ and were *ca* 3-fold higher than those determined at the oilseed rape site (38.67-49.60 mg kg⁻¹). These amounts fluctuated within the *negative* (oilseed rape site) and *phytotoxic* (maize site) effect range of Al_{ex}, which means that phototoxicity most probably did occur, mainly under acid conditions. Both soils (under oilseed rape and under maize) were characterized by the sulphur (S-SO₄) content of 14.93-19.68 mg kg⁻¹ and similar levels of exchangeable magnesium (Mg_{ex}) at both sites. The agrochemical properties of the sites were in general less favorable (mainly pH) to oilseed rape and maize yields, but suitable for verifying the geochemical-based indices (S/Al; Mg/Al) and partition coefficient (Kd_{Al}; Kd_{Mg}) concept.

2. Aluminum (Kd_{Al}) and magnesium (Kd_{Mg}) partition coefficients

The partition coefficient (K_d) expresses the relationship between an element contained in the soil solid phase and its concentration in the soil solution. Higher Kd_{Al} values imply that when more Al is retained (immobilized) in the soil solid phase, Al concentration in the soil solution is lower, and *vice versa*. The same applies to Kd_{Mg}, although high levels of Mg concentrations in the soil solution are most frequently expected to be caused by agrochemical practice. The geochemical characteristics of these parameters are closely linked with pH changes. From the data found in the scientific literature, it may be concluded that aluminum generates protons (H⁺), unlike magnesium generating hydroxide anions (OH⁻). These geochemical features were outlined by relating the respective partition coefficients to soil pH, as illustrated in Figures 1 and 2.

The above capacity to generate H⁺ and OH⁻ is expressed on the basis of a (moles H⁺ or OH⁻ produced by Al³⁺ and Mg²⁺, respectively), which is a product of the linear coefficient value ($y = ax + b$, where: $y = K_d$; $x = \text{pH}$; $b = \text{moles of negative charges produced by soil}$).

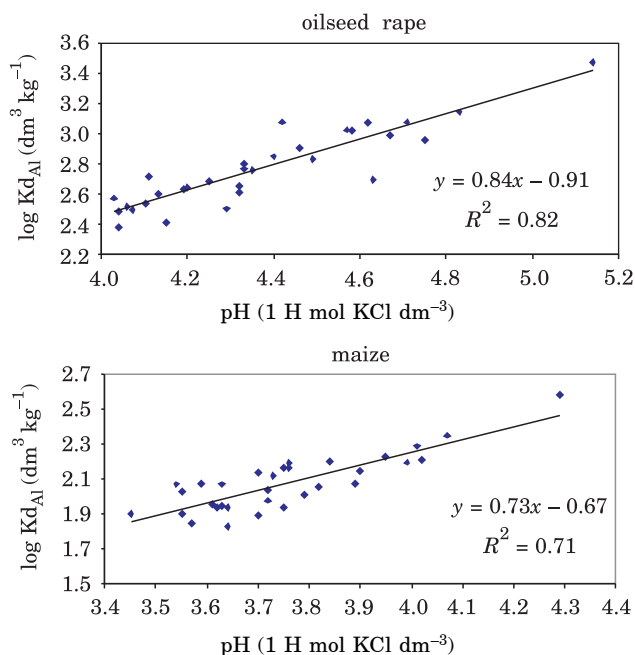


Fig. 1. Relationship between partition coefficient for aluminum ($\log K_{d_{Al}}$) and soil pH at the oilseed rape site during the regrowth and at the maize site during the flowering stages (0-40 cm depth)

The linear relationship between $K_{d_{Al}}$ and soil pH for both sites suggests more intensive generation of hydrogen ions (H^+) by Al^{3+} along with an increasing pH value (Figure 1). Aluminum (Al^{3+}) starts to produce more H^+ in order to decrease soil pH through H^+ soil acidification. The proton generation capacity index (a_H) reached 0.84 and 0.73 moles H^+ per mole Al^{3+} for the oilseed rape and maize sites, respectively. This is particularly important in terms of Al proton generation capacity in soils. The reported values indicate that for the acid site (i.e. oilseed rape), more protons are required to decrease the soil pH in order to ensure more Al activity. This action was not necessary at the maize site, characterized by extremely acid conditions. Higher Al concentrations were found within the pH range 4.0-4.7, and this corresponded to aluminum partition coefficients ($K_{d_{Al}}$) varying from 2.4-3.0 $dm^3 kg^{-1}$ at the oilseed rape site.

At the maize site, the highest concentration of Al_{ex} varied in the pH range 3.55-3.85, and this corresponded to partition coefficients ($K_{d_{Al}}$) of 1.8-2.2 $dm^3 kg^{-1}$. The lower values of ($K_{d_{Al}}$) at the maize site as compared to the oilseed rape site are attributable to the extremely high amounts of exchangeable aluminum (Al_{ex}) – Table 1. The values of coefficients of determination (R^2) at both sites are high (0.82 and 0.71, respectively for oilseed rape and maize sites). This means that relationships between partition coefficients for Al ($K_{d_{Al}}$) and soil pH demonstrated a fairly strong dependence.

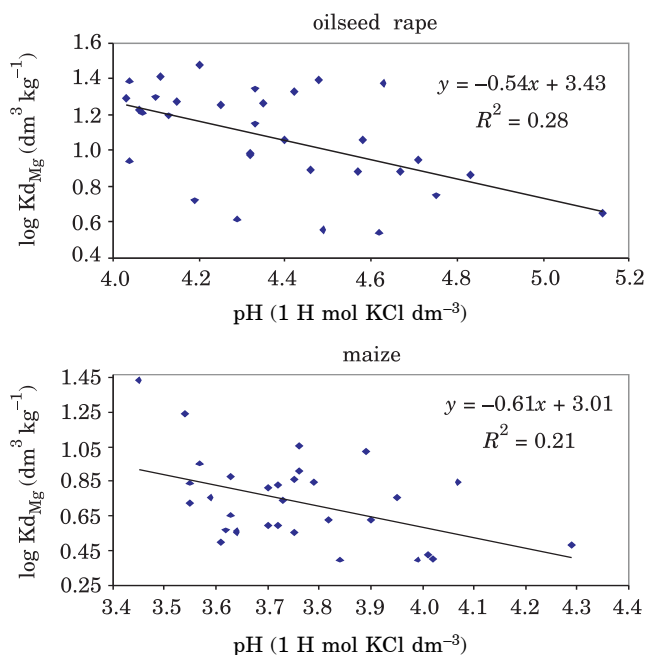


Fig. 2. Relationship between partition coefficient for magnesium ($\log Kd_{Mg}$) and soil pH at the oilseed rape site during the regrowth and the maize site during the flowering stages (0-40 cm depth)

Relationships between the partition coefficient for Mg (Kd_{Mg}) and soil pH at the oilseed rape and maize sites are illustrated in Figure 2. Most interesting is the occurrence of a reverse trend observed for Kd_{Mg} as compared to Kd_{Al} . Magnesium generated lower amounts of hydroxide anions (OH^-) along with a pH raise and the overall geochemical reaction is expected to overcome aluminum-induced soil acidification. This is directly related to the rise in Mg concentrations in the soil solution, which further leads to a decrease in the Kd_{Mg} values. This assumption is supported by low Kd_{Mg} values in the range from 0.30 to 1.05 $\text{dm}^3 \text{ kg}^{-1}$, just half of the values of Kd_{Al} (maize site). The same pattern was observed at oilseed rape site with Kd_{Mg} values varying from 0.80 to 1.40 $\text{dm}^3 \text{ kg}^{-1}$, i.e., also half the value of Kd_{Al} (at oilseed rape site).

Hydroxide anion generation capacity (a_{OH^-}) varied from -0.54 to -0.61 moles OH^- per mole Mg^{2+} for the oilseed rape and maize sites respectively, confirming a decrease in OH^- ion generation by Mg^{2+} along with a pH increase. This situation is reverse to the one reported for the Al proton generation capacity in soils. It means that acid conditions strengthen OH^- production in contrast to slightly alkaline or alkaline soils.

3. Sulphur and magnesium versus aluminum: S : Al, Mg : Al geochemical indices

Figure 3 illustrates changes related to S : Al indices, accordingly to kieserite (Mg) rates during the oilseed rape regrowth and maize flowering stages. The values of S : Al decreased generally at the depth 20-40 cm, as compared to 0-20 cm, irrespective of Mg rates and type of site. This finding may be attributed to high concentration of Al in the subsoil (20-40 cm). The occurrence of high Al concentration under such conditions (Table 1) seems to be expected since, based on a diagram of Al dissolution as described by LINDSAY (1979), monomeric Al forms (i.e., Al^{3+}) appear mostly at $\text{pH} < 4.7$. Such approaches have been reported by WALKER et al. (1990) and confirmed by DIJKSTRA and FITZHUGH (2003) in different soil ecosystems. Changes of S : Al indices as observed at both sites along with increasing kieserite (Mg) rates suggest that the S-SO_4 concentration in soil may reduce Al toxicity. The introduction of S-SO_4 to soil may be intended to satisfy plants' nutritional requirements and, simultaneously, cause a reaction with exchangeable aluminum (Al_{ex}) in order to mitigate its phytotoxicity. The results caused by 50 and 100 kg Mg ha^{-1} rates at the oilseed rape site made it more evident that large amounts of S-SO_4 have reacted with Al_{ex} . This may be attributed to

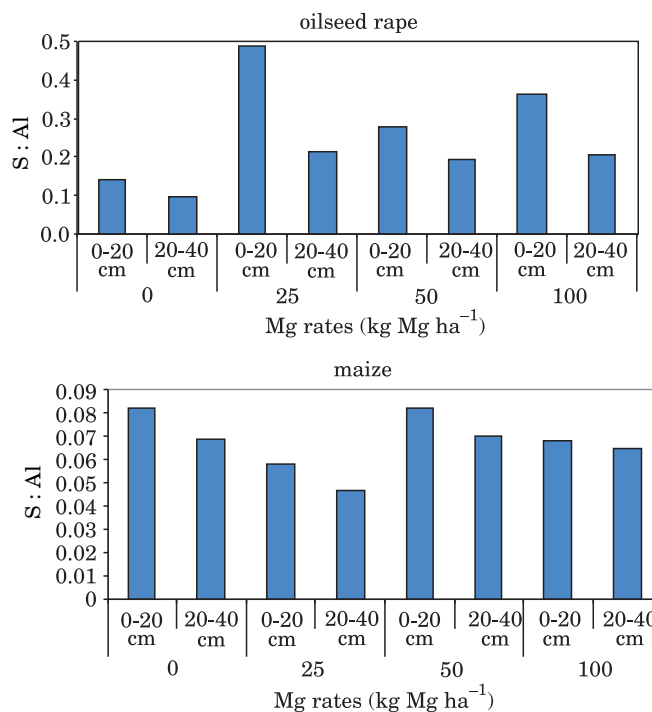


Fig. 3. Changes in S : Al indices at two depths, 0-20 cm and 20-40 cm, under oilseed rape (regrowth stage) and maize (flowering stage) receiving four Mg rates (kg ha^{-1}) as kieserite

the low S : Al values in these treatments, as compared to the ones with 25 kg Mg ha⁻¹. The same trend was observed at the maize site, but only for the 100 kg Mg ha⁻¹ treatment, where S : Al indices were lower as compared to the 50 kg Mg ha⁻¹ rate. With respect to the oilseed rape site, values of S : Al mostly varied within the range from 0.10 to 0.30. It was only the control treatment that was characterized by an S : Al value below 0.10. The low content of S-SO₄ has prevented the S-SO₄ – Al_{ex} reaction. At the maize site, S : Al indices may be divided as follows:

S : Al < 0.045 – the S-SO₄ – Al_{ex} reaction limited due to large amounts of Al_{ex},

S : Al > 0.045 – interaction between S-SO₄ and Al_{ex} more efficient because of relatively low amounts of Al_{ex}.

Changes of Mg : Al indices as influenced by kieserite application on the oilseed rape and maize sites are illustrated by Figure 4. The Mg : Al values were the most interesting as they were decreasing along with the rising kieserite rates applied on the oilseed rape site. The introduction of magne-

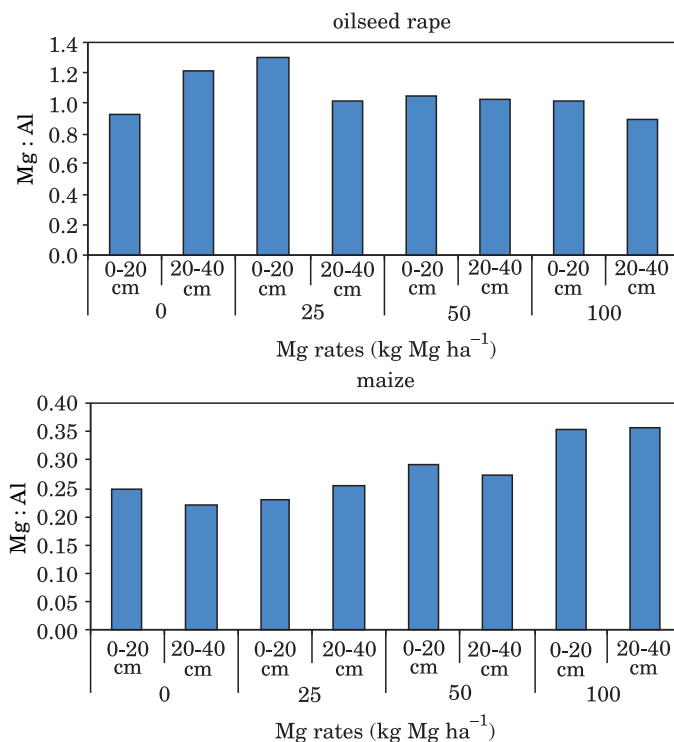


Fig. 4. Changes of Mg : Al indices at two depths, 0-20 cm and 20-40 cm, under oilseed rape (regrowth stage) and maize (flowering stage) receiving four Mg rates (kg ha⁻¹) as kieserite

sium Mg^{2+} , in addition to nutritional purposes, is intended for an exchange of Mg^{2+} with Al^{3+} ions in the soil cation exchange complex (CEC), especially when total Al content is considered (Table 1).

The Mg:Al indices at the maize site proved to be reverse to the ones observed at the oilseed rape site, i.e. the Mg:Al values increased along with the rising kieserite rates. This particular finding may be attributed to a smaller and shallower root system, which was unable to efficiently take up magnesium in order to cover maize's nutritional requirements affected by Al^{3+} toxicity. Changes in the Mg:Al indices observed under extremely acid soil conditions (the maize site) along with increasing kieserite (Mg) rates suggest that Mg:Al may not be the only index describing the $Mg_{ex} - Al_{ex}$ interaction, especially at 25 and 50 $Mg\ ha^{-1}$.

The values of Mg:Al were almost identical at both depths (0-20, 20-40 cm), irrespective of the site. A reverse pattern was observed for the S:Al indices, where values of the S:Al ratio generally decreased at the depth 20-40 cm, as compared to 0-20 cm, irrespective of Mg rates and site characteristics.

Generally, values of the S:Al and Mg:Al indices were lower at the maize site than at the oilseed rape plot due to the high levels of Al_{ex} (the amounts of Al_{ex} at the maize site were *ca* 3-fold higher than those determined at the oilseed rape site).

CONCLUSIONS

1. Values of the partition coefficient for aluminum (Kd_{Al}) rose along with a pH increase, irrespective of the site. At higher Kd_{Al} , more Al was retained in the soil solid phase and less in the soil solution.

2. Magnesium partition coefficients (Kd_{Mg}) decreased with a pH rise (a reverse trend than that of Kd_{Al}). Magnesium generated fewer hydroxide anions (OH^-) along with a pH growth. OH^- groups are expected to overcome aluminum-based soil acidification.

3. Changes of the S:Al indices observed at both sites with increasing kieserite (Mg) rates suggest that the S- SO_4 concentration in soil may have reduced Al toxicity. The introduction of S- SO_4 to soil is intended to meet plants' nutritional requirements and simultaneously react with exchangeable aluminum (Al_{ex}) in order to mitigate its phytotoxicity.

4. Changes in the Mg:Al indices observed under extremely acid soil conditions (the maize site) imply that Mg:Al may not be the only index describing the $Mg_{ex} - Al_{ex}$ interaction, especially at 25 and 50 $Mg\ ha^{-1}$ rates.

5. Values of the S:Al and Mg:Al indices were lower at the maize site, as compared to the oilseed rape site, due to high levels of Al_{ex} (amounts of Al_{ex} at the maize site were *ca* 3-fold higher than at the oilseed rape site).

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