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Relationship between dissolved organic carbon and calcium and magnesium in soil water phase and their uptake by meadow vegetation

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Abstract

Studies on the effect of dissolved organic carbon (DOC) on the concentration of calcium and magnesium in soil water phase (ground water and soil solution) and on their uptake by plants are less numerous than those on nitrogen and phosphorus. This study was aimed at assessing the relationships between DOC in ground water and soil solution from under meadow on mineral soil and Ca and Mg concentrations and their uptake by plants. Presented studies were performed in the years 2004–2007 on long-term meadow experiments situated in Janki and Laszczki in Masovian Province. Increasing DOC concentrations in soil solutions increased Ca uptake and decreased Mg uptake by plants which was facilitated by decreasing soil acidity. A lack of significant effect of DOC concentration in ground water on Ca and Mg uptake but demonstrated opposite direction of this effect confirms the antagonism in calcium and magnesium behaviour in the environment. Obtained results indicate that mutual relationships among DOC, Ca and Mg in a ground water – soil solution – meadow vegetation system is complex and needs further studies.

Key words: *calcium, dissolved organic carbon, ground water, magnesium, soil solution, uptake by plants*

INTRODUCTION

Dissolved organic carbon is one of important factors affecting the nutrient dynamics in a soil water phase – plant system. As shown by KALBNITZ *et al.* [2000] in their review, dissolved organic matter (DOM) composed of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) plays an important role in carbon, nitrogen and phosphorus biogeochemistry, in pedogenesis and in the transport of pollutants in soils. Rhizosphere, root secretions and microbial decomposition of plant roots are the main source of DOM. These processes release part of total soil carbon (TC) to soil water [KALBNITZ *et al.* 2000; KHALID *et al.* 2007]. Dissolved form of organic matter constitutes only small percent (<1%) of its total content but is extremely mobile and, therefore, is a sensitive indi-

cator of environmental changes in soils and waters [MCDOWELL 2003; SAPEK, BURZYŃSKA 2008; SAPEK, SAPEK 2005; ZSOLNAY 2001]. Apart from soil carbon of various origin, atmospheric particulate matter (PM) contains mineral but also organic components which undergo biochemical processes and are a source of DOM [ANASTASIO 2000; BOR HUNG SHEU 2003; CHIUNG PIN LIU *et al.* 2010]. Atmospheric deposition and organic substances it contains may thus additionally enrich soil waters with DOC.

Studies on the effect of DOC on environmental nutrient cycling pertain mostly to nitrogen and phosphorus [BARBERO 2006; BURZYŃSKA 2004; KALBNITZ *et al.* 2000; KHALID *et al.* 2007]. These elements are present in large amounts in the organic soil fraction (the whole pool of nitrogen, a half of soil phosphorus) [ZAWADZKI (ed.) 1999, after Lityński 1971]. Studies on the effect of DOC on the concentra-

tion of Ca and Mg in soil water phase (ground water and soil solution) and on their uptake by plants are less numerous. They pertain mainly to cation and anion binding from the soil sorption complexes, to formation of dissolved compounds with DOC and to their release from soil [BURZYŃSKA 2004; KALBNITZ *et al.* 2000; SAPEK 2008a; SCHUMAN 2000]. This problem was addressed by e.g. KER and EIMERS [2012] but the authors focussed on the effect of Ca ions in soil water on DOC adsorption by mineral soils. Based on long-term studies (1987–2009), the authors showed that decreasing Ca concentration is accompanied by the increasing concentration of DOC in streams due to its smaller adsorption in mineral soils.

The aim of this study was to assess the relationship between the DOC content in ground water and soil solution from under a meadow on mineral soil and the concentration of calcium and magnesium and the relationship between DOC and the uptake of both elements by plants.

MATERIAL AND METHODS

Determination of DOC in ground water from under long-term meadow experiments set up in 1981/1982 near Falenty on acid mineral soil ($pH_{KCL} = 4.5; 4.3$) in Janki (J) and Laszczki (L) in Masovian Province was made in a three-year period (2004–2006). DOC in soil solution sampled with suction apparatus and porcelain samplers was determined in 2005 and 2007 from four fertilisation objects (Ca_0N_2AN , Ca_2N_2AN , Ca_0N_2CN , Ca_2N_2CN) in Janki. Soil was fertilised with 240 kg of nitrogen (N_2) in a form of ammonium (AN) or calcium (CN) saltpetre and was not limed (Ca_0) or limed once at the beginning of the experiment (Ca_2) with calcium carbonate at a dose according to hydrolytic acidity criterion 2Hh. Soil pH in studied objects was 3.6; 4.3; 5.0 and 6.6, respectively. Detailed description of experiments together with soil and object characteristics is given in SAPEK [2006]. The content of DOC was determined with the colorimetric method using segmental flow analyser Skalar SAN according to producer's instructions [URBANIĄK, SAPEK 2005]. The method was described in SAPEK, BURZYŃSKA [2009].

Ground water was sampled from control wells installed in the buffer zones of two experiments. Mean ground water level in experiment J was at a depth of 120 cm (minimum – 85 cm, maximum – 165 cm) and in experiment L at a depth of 107 cm (minimum 91 cm, maximum – 124 cm) [SAPEK *et al.* 2003]. The method of sampling soil solution with suction apparatus equipped with pore cups was described in SAPEK and PIETRZAK [1996] and PIETRZAK *et al.* [2006]. Calcium and magnesium in ground water and soil solutions were determined with the atomic absorption spectrophotometry and soil pH – in a KCl solution with the potentiometric method.

Analysed relationships between DOC and Ca and Mg concentrations in ground water and soil solution and their uptake by plants pertain to the years when DOC was determined. The abandonment of sward harvesting in experiment L since 2004 restricted the assessment of the effect of DOC on Ca and Mg uptake by plants only to experiment J. As in the case of ground waters, the assessment of DOC effects in soil solutions pertains to experiment J but in four fertilisation objects described above [SAPEK 2006].

RESULTS AND DISCUSSION

RELATIONSHIP BETWEEN DOC IN GROUND WATER AND THE CONCENTRATION AND UPTAKE OF CA AND MG

Ground water in the Janki experiment on soil poorer in organic carbon and silt materials and of lower moisture was characterised by lower concentrations of DOC, Ca and Mg and their marked variability (especially of DOC) compared with ground water from the Laszczki experiment in a three-year study period and in subsequent years. Ground water pH in both experiments was close to neutral, particularly in the Laszczki experiment (Tab. 1, Fig. 1a, 2a).

Table 1. Concentration of dissolved organic carbon (DOC), calcium (Ca) and magnesium (Mg) in ground water under the Janki and Laszczki experiments – mean values from the years 2004–2006

Component	Janki		Laszczki	
	mean $mg \cdot dm^{-3}$	CV%	mean $mg \cdot dm^{-3}$	CV%
DOC	4.91	61.7	7.98	27.1
Ca	74.90	30.4	101.00	16.9
Mg	6.65	53.3	12.40	28.5
pH	6.73	1.8	6.96	0.7

Explanation: CV% – coefficient of variation ($n = 32$).
Source: own study.

In the Janki experiment, increasing concentration of DOC in ground water was accompanied by a significant decrease of both Ca ($r = -0.38^*$) and Mg ($r = -0.55^{**}$) concentrations (Fig. 1b, c). In other words, the smaller was the concentration of Ca and Mg in water (due to sorption of these elements in soil), the weaker DOC was bound in soil and hence the larger was its release to ground water. This relationship for calcium was demonstrated by KER and EIMERS [2012]. In ground water from experiment L, situated on soil richer in organic carbon, Ca and Mg, similar relationship was found only for Mg ($r = -0.46^*$) (Fig. 2c). The concentrations of Ca, despite ground water enrichment in DOC, remained rather stable, which could be an effect of soil richer in Ca (Fig. 2b, Tab. 1).

From among soil waters, ground water is a source of plant nutrients including Ca and Mg [SZPERLIŃSKI 2002; WARCHOŁOWA 1976]. The question is: if and

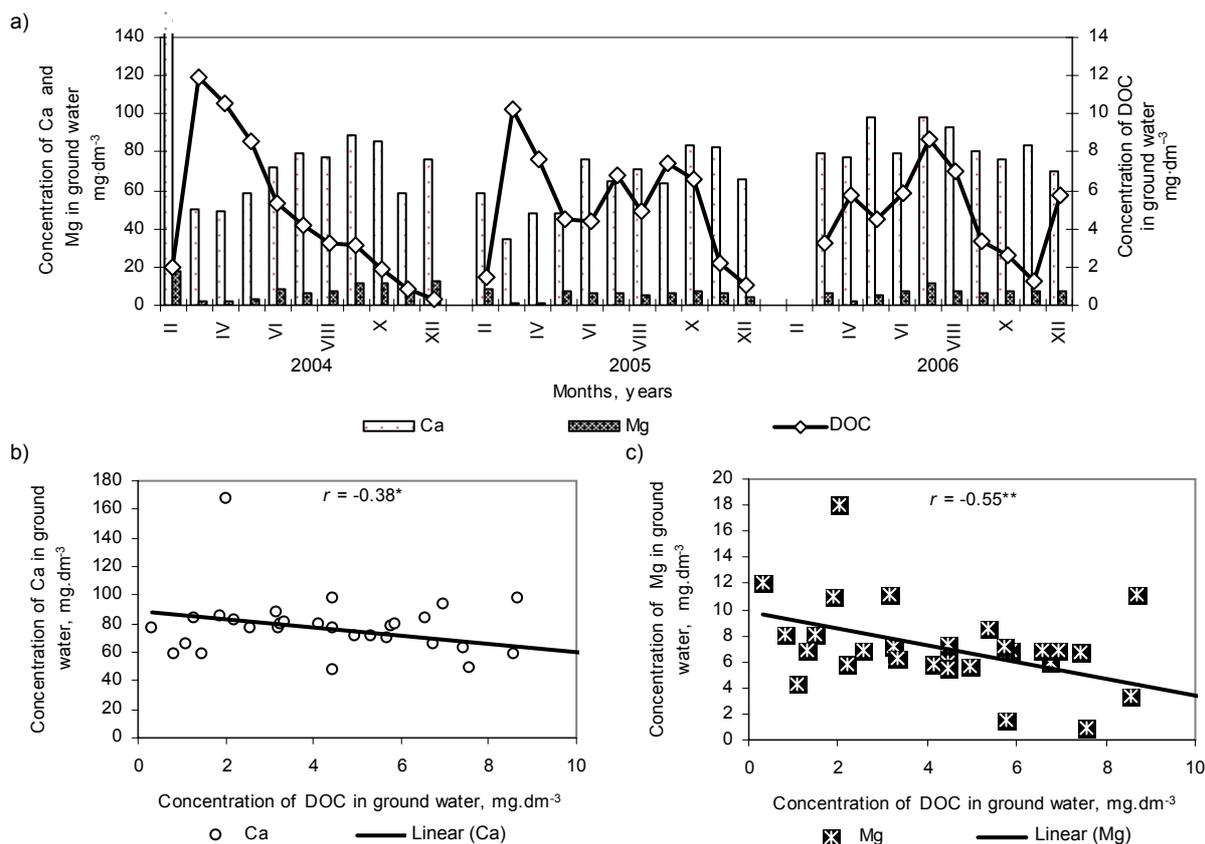


Fig. 1. Changes of the monthly (Jan.–Dec.) concentrations of DOC, Ca and Mg in ground water (a), correlation between the concentrations of DOC and Ca (b) and Mg (c) in Janki experiment in the years 2004–2006; r – coefficients of Pearson linear correlation ($n = 32$); source: own study

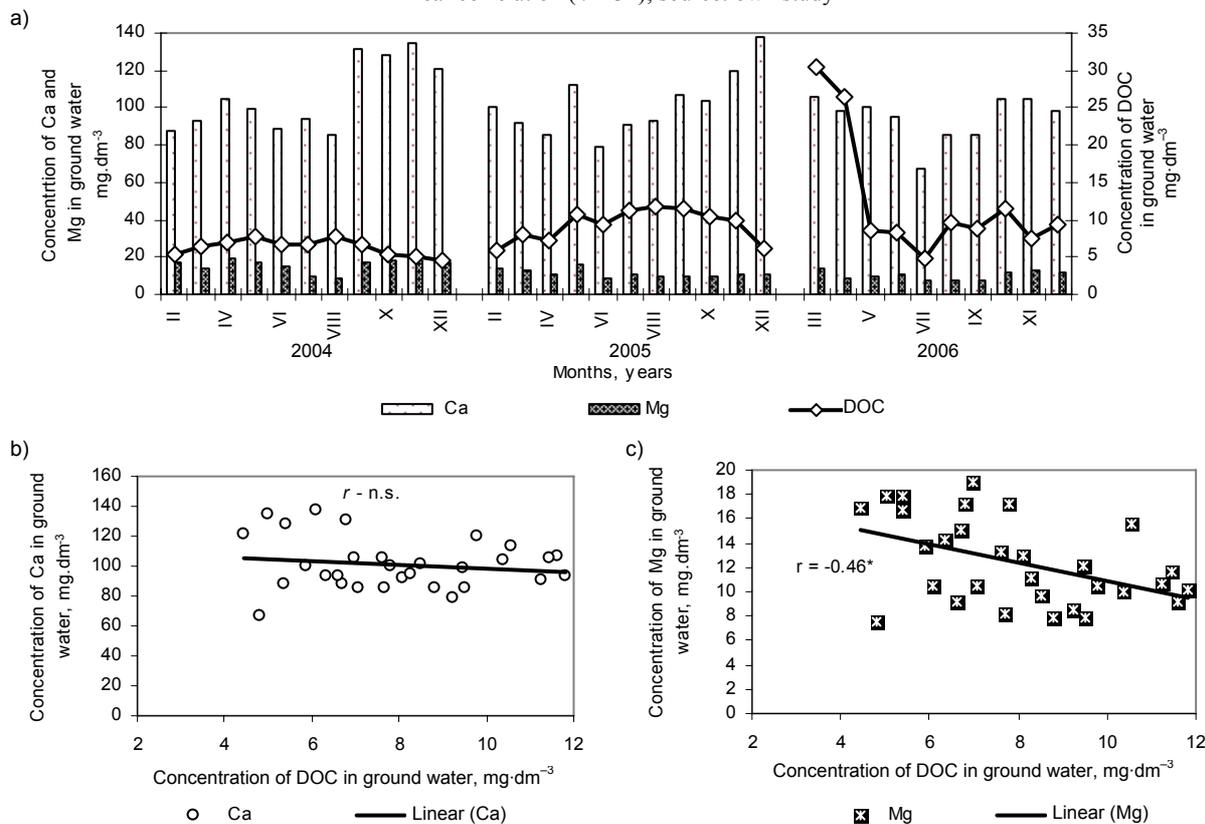


Fig. 2. Changes of the monthly (Jan.–Dec.) concentrations of DOC, Ca and Mg in ground water (a), correlation between the concentrations of DOC and Ca (b) and Mg (c) in Laszczki experiment in the years 2004–2006; r – coefficients of Pearson linear correlation ($n = 33$); source: own study

how the uptake of these nutrients by meadow vegetation depends on DOC concentrations? An assessment of this relationship was based on the uptake of Ca and Mg in three subsequent cuts (I–III) in the Janki experiment. Mean DOC concentration in subsequent years was calculated for months corresponding to the growth periods of subsequent cuts: the 1st cut (April–May), the 2nd cut (June–July) and the 3rd cut (August–September).

During the first growth period, DOC concentration significantly decreased in subsequent study years (2004–2006) regardless of applied nitrogen fertiliser (AN or CN) ($r = -0.95^*$). In the same years, the concentration of DOC significantly increased during the 2nd regrowth period ($r = 0.98^*$) and did not show directional changes in the 3rd regrowth period (Fig. 3a, b). Mean DOC concentrations in ground water in the periods corresponding to subsequent regrowths (I–III)

of meadow sward (6.9, 5.9; 4.8 mg·dm⁻³, respectively) significantly decreased ($r = -1.0^{***}$) in the study years. This could be an effect of weakened microbial activity and of the impact of root system accompanying plant growth [KALBNITZ *et al.* 2002]. Due to different yield in subsequent cuts on meadows fertilised with ammonium nitrate and calcium nitrate (Fig. 3c, d) [SAPEK 2012b], the effect of DOC in ground water on Ca and Mg uptake was assessed with the consideration of fertiliser form. No significant relationship was found between DOC and the uptake of both elements by plants. Opposite trend of Ca and Mg uptake in relation to the concentration of DOC, which may be an effect of different stability of Ca and Mg complexes with DOC, indicates and confirms an antagonistic behaviour of both elements in the environment (Fig. 3c, d) [GORLACH, MAZUR 2002; SZCZERBIŃSKI 2002].

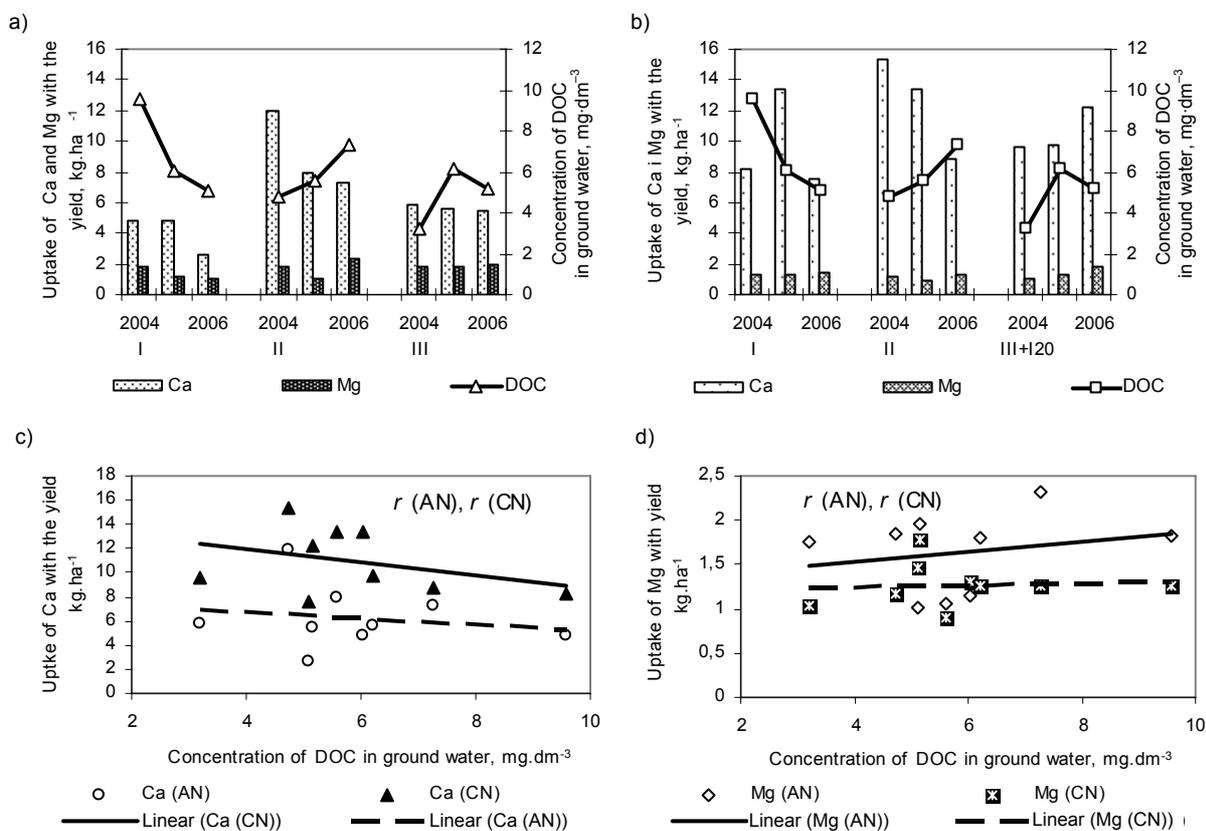


Fig. 3. Concentration of DOC in ground water and Ca and Mg uptake by plants of the three subsequent cuts (I–III) in the years 2004–2006 at fertilisation with ammonium saltpetre AN (a) and calcium saltpetre CN (b); correlation between DOC in ground water and Ca (c) and Mg (d) uptake by plants fertilised with AN and CN; r – coefficients of Pearson linear correlation; source: own study

THE EFFECT OF DOC IN SOIL SOLUTION ON THE CONCENTRATION OF CA AND MG AND THEIR UPTAKE BY PLANTS

Apart from ground water, soil solution is also a source of nutrients for plants [PRUSINKIEWICZ 2011; WARCHALOWA 1976]. Mutual interaction of DOC with Ca and Mg will affect the uptake of these elements by vegetation.

DOC concentration in soil solutions from 4 fertilisation objects increased in the order: Ca₀N₂AN < Ca₂N₂AN < Ca₀N₂CN < Ca₂N₂CN (Tab. 2). Soil pH increased in the same order (pH_{KCl} – 3.6 < 4.3 < 5.0 < 6.6, respectively). Liming applied in the beginning of the experiment acc. to 2Hh stabilised, to a certain degree, the proceeding of soil acidification and the application of calcium nitrate kept soil pH close to the optimum for grasslands [OPITZ VON BOBERFELD

1994; SAPEK 2008b; 2009]. Such pH facilitated the formation of dissolved forms of carbon and calcium whose highest concentrations were noted in soil solution from the object $\text{Ca}_0\text{N}_2\text{CN}$ in soil of $\text{pH}_{\text{KCl}} = 5.0$. Under such conditions, the lowest concentrations of magnesium were recorded (Tab. 2). Mean values calculated for the two study years (2005 and 2007) showed remarkable variability of DOC, Ca and particularly of Mg concentrations in soil solution from the object $\text{Ca}_0\text{N}_2\text{CN}$. The variability resulted from differences in the concentrations of analysed components between years which largely differed in precipitation (529 mm in 2005 and 679.9 mm in 2007) (Tab. 2, Fig. 4a).

No significant relationship was found between the concentration of DOC and those of Ca and Mg in soil solutions. In the object $\text{Ca}_0\text{N}_2\text{AN}$ on most acidic soil ($\text{pH}_{\text{KCl}} = 3.6$), an opposite direction of changes in the concentration of Ca and Mg was again noted with increasing DOC concentrations in soil solution. This was the next confirmation of antagonistic environmental behaviour of Ca and Mg (Fig. 4b, c) [GORLACH, MAZUR 2002]. Differences in the behaviour of the two analysed elements were even more pronounced when the effect of DOC in soil solution on Ca and Mg uptake by plants was compared among four fertilisation objects and particularly – between study years (Fig. 5a). The uptake of Ca and Mg dif-

Table 2. Concentration of dissolved organic carbon (DOC), calcium (Ca) and magnesium (Mg) in soil solutions under the 4 fertilization objects of the Janki experiment – mean values from all results in the year 2005 and 2007

Fertilisation object ¹⁾	Component						
	pH	DOC		Ca		Mg	
		mean $\text{mg}\cdot\text{dm}^{-3}$	CV%	mean $\text{mg}\cdot\text{dm}^{-3}$	CV%	mean $\text{mg}\cdot\text{dm}^{-3}$	CV%
$\text{Ca}_0\text{N}_2\text{AN}$	3.6	10.1	34.3	78.4	52.8	24.0	47.4
$\text{Ca}_2\text{N}_2\text{AN}$	4.3	12.6	42.8	94.8	48.5	33.2	54.1
$\text{Ca}_0\text{N}_2\text{CN}$	5.0	13.1	49.0	127.3	41.5	7.2	93.0
$\text{Ca}_2\text{N}_2\text{CN}$	6.6	15.0	39.7	92.7	55.1	19.7	76.4

¹⁾ Objects fertilized with nitrogen at a dose of $240 \text{ kg N}\cdot\text{ha}^{-1}$ (N_2) in the form of ammonium saltpetre (AN) and calcium saltpetre (CN), not limed (Ca_0) and limed (Ca_2).

Explanation: CV% – coefficient of variation ($n = 27$).

Source: own study.

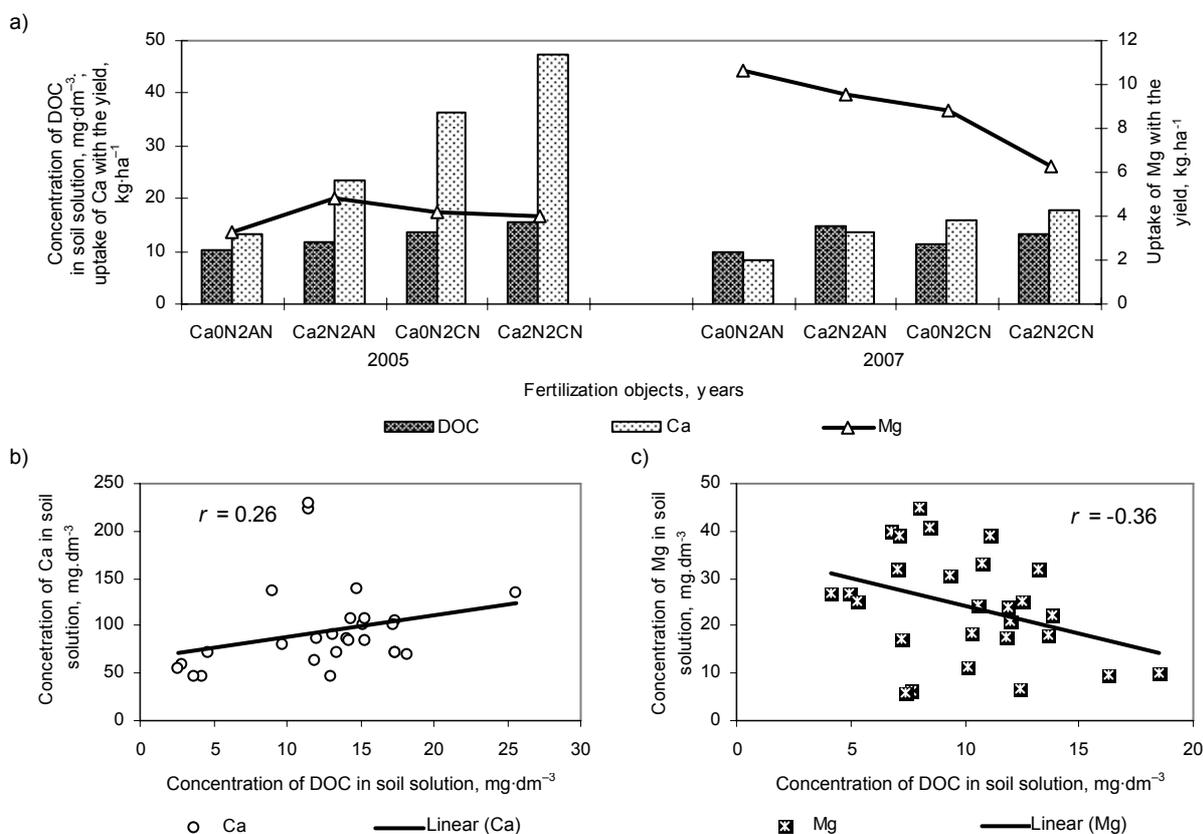


Fig. 4. Concentration of DOC, Ca and Mg in soil solutions from 4 fertilisation objects ($\text{Ca}_0\text{N}_2\text{AN}$, $\text{Ca}_2\text{N}_2\text{AN}$, $\text{Ca}_0\text{N}_2\text{CN}$, $\text{Ca}_2\text{N}_2\text{CN}$) in Janki experiment (a); correlation between the concentrations of DOC and Ca (b) and Mg (c) in the object $\text{Ca}_0\text{N}_2\text{AN}$ in the years 2005 and 2007 ($n = 27$, all determinations); source: own study

ferred between the years of different amount of precipitation [SAPEK 2011]. Ca uptake by plants increased with decreasing soil acidification, especially in the year 2005. Changes in Mg uptake were different, especially in 2007. Mg uptake by plants markedly decreased with soil acidification in particular fertilisation objects (Fig. 5a).

An assessment of the effect of DOC in soil solutions on Ca and Mg uptake by plants in four fertilisation objects and two study years showed significant

positive effect of DOC on Ca uptake and a lack of such an effect for magnesium (Fig. 5b). Due to marked effect of soil pH on studied relationships, the correlations were calculated between soil pH_{KCl} and the concentration of DOC in soil solution and Ca and Mg uptake by plants. The coefficient of Pearson linear correlation was in the first case insignificant, though close to the threshold value ($r_1 = 0.86$; $r_{\text{tab.}} = 0.88$), while two others were significant (Ca) $r_2 = 0.96^{**}$, (Mg) $r_3 = -0.94^*$ (Fig. 5c).

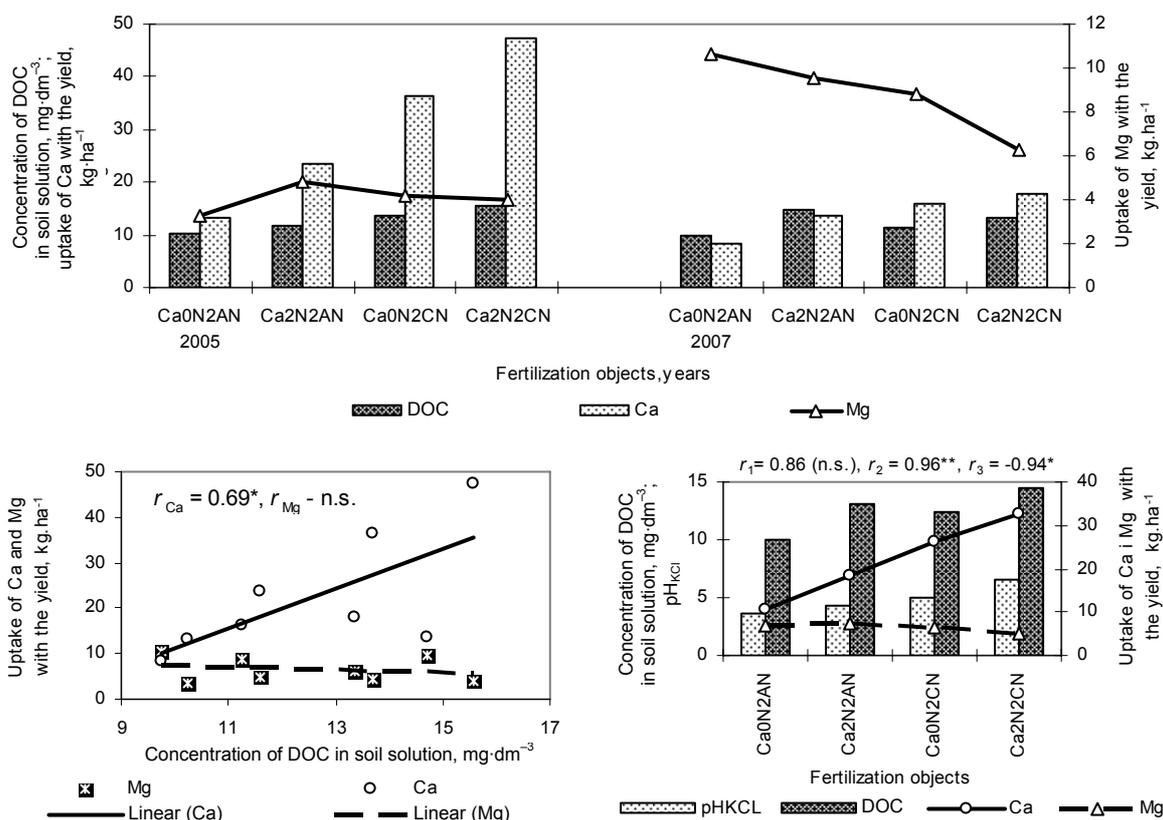


Fig. 5. Concentration of DOC in soil solution and the uptake of Ca and Mg by plants in 4 fertilisation objects ($\text{Ca}_0\text{N}_2\text{AN}$, $\text{Ca}_2\text{N}_2\text{AN}$, $\text{Ca}_0\text{N}_2\text{CN}$, $\text{Ca}_2\text{N}_2\text{CN}$) of Janki experiment (a); correlation between DOC and the uptake of Ca and Mg (mean from 4 objects and the years 2005–2007, $n = 8$) (b); mean for the years 2005 and 2007 soil pH, concentrations of DOC and the uptake of Ca and Mg by plants and their relationships (c); r – coefficient of Pearson linear correlation: $r_{\text{Ca}} - \text{DOC} \times \text{Ca}$, $r_{\text{Mg}} - \text{DOC} \times \text{Mg}$; $r_1 - \text{pH} \times \text{DOC}$, $r_2 - \text{pH} \times \text{Ca}$, $r_3 - \text{pH} \times \text{Mg}$; source: own study

SUMMARY AND CONCLUSIONS

Results of long-term studies on the composition, share and the role dissolved organic matter plays in chemical and biological soil processes underline the need of their continuation in the natural habitat changing due to anthropogenic factors [MCDOWELL 2003]. Discussing results of these studies, MCDOWELL [2003] proposed further directions and questions that still need to be answered. Results presented in this study fell within the scope of these consideration on the changing stream of DOC in a habitat dominated by human activity. Mutual relationships between DOC, Ca and Mg in soil waters and their effect on the uptake of these nutrients by meadow plants are largely determined by soil pH changing due to fertilisation

and de-acidifying measures. Moreover, soil pH affects the availability of relatively weak organic complexes of calcium and magnesium [PRUSINKIEWICZ 2011; SZPERLIŃSKI 2002]. pH-dependent differences in the stability of organic complexes of Ca and Mg resulted in a variable effect of DOC on their concentrations in ground water and soil solution and on their cycling in the environment. Greater stability of calcium than magnesium organic complexes on the one hand and the stronger alkalinity of magnesium on the other make their activity in the ground water – soil solution – vegetation a complex process that needs further studies. Results obtained in this study and observed trends of changes allowed for presenting preliminary conclusions on the effect of dissolved organic matter

on calcium and magnesium concentrations in soil waters and on their uptake by meadow vegetation.

1. Ground water from under grassland in soil poor in organic carbon and clay minerals and of unfavourable moisture was characterised by a low concentration of DOC and by its large variability both seasonally and among study years compared with ground water from under a meadow of favourable soil-water conditions. Under such circumstances, increased DOC concentration in ground water was accompanied by significant decrease of both Ca and Mg concentrations.

2. In ground water from under grassland of soil rich in organic carbon and good physical and water conditions the significant negative effect of DOC was found only for Mg. Ca concentrations were relatively stable.

3. Significant decrease of DOC concentration in ground water during subsequent periods of sward regrowth (I–III) may indicate weakening microbial activity and the effect of plant roots on DOC release from soil during plant growth.

4. No significant effect was found of the DOC concentration in ground water on Ca and Mg uptake by plants. Demonstrated opposite direction of this effect, which suggests different stability of organic complexes of Ca and Mg, confirms the antagonistic environmental behaviour of both elements.

5. Soil pH close to the optimum for grasslands favoured the presence of DOC in soil solution. Increased DOC content was in turn followed by the increased concentration of Ca and decreased concentration of Mg. Remarkable year to year variability of these concentrations could be a result of different amounts of precipitation.

6. The uptake of Ca by plants increased and that of Mg decreased with increasing concentration of DOC in soil solutions. This effect was favoured by decreased soil acidity and again confirms the antagonism between these elements.

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Zależność między rozpuszczalnym węglem organicznym (RWO) w fazie wodnej gleby a stężeniem w niej wapnia i magnezu oraz ich pobraniem z plonem roślinności łąkowej

STRESZCZENIE

Słowa kluczowe: magnez, pobranie z plonem, rozpuszczalny węgiel organiczny, roztwór glebowy, wapń, woda gruntowa

Badania wpływu rozpuszczalnego węgla organicznego (RWO) na stężenie wapnia (Ca) i magnezu (Mg) w fazie wodnej gleby, tj. w wodzie gruntowej i roztworze glebowym, oraz na ich pobieranie przez rośliny są mniej liczne w porównaniu z badaniami azotu i fosforu. Celem pracy była ocena współzależności między stężeniem RWO w wodzie gruntowej i w roztworze glebowym spod łąki na glebie mineralnej oraz stężeniem w nich Ca i Mg, a również zbadanie zależności pobrania wymienionych składników z plonem roślinności od tej formy węgla w wodach glebowych. Prezentowane w pracy badania, obejmujące lata 2004–2007, realizowano na długoletnich doświadczeniach łąkowych usytuowanych w miejscowościach Janki i Laszczki w województwie mazowieckim. Wzajemne relacje RWO oraz Ca i Mg w wodach glebowych i ich oddziaływanie na pobieranie tych dwóch składników pokarmowych przez rośliny łąkowe w znacznym stopniu kształtuje odczyn gleby, zmieniający się w wyniku nawożenia oraz wszystkich zabiegów odkwaszających glebę. Wraz ze zwiększeniem stężenia RWO w roztworach glebowych zwiększało się pobranie Ca, a zmniejszało pobranie Mg z plonem roślin, czemu sprzyjało zmniejszenie kwasowości gleby. Brak istotnego wpływu stężenia RWO w wodzie gruntowej na pobranie z plonem Ca i Mg, lecz wykazany przeciwny kierunek zmian tego wpływu w przypadku obu pierwiastków potwierdza antagonizm w zachowaniu się wapnia i magnezu w środowisku. Uzyskane wyniki badań wskazują, że wzajemne oddziaływanie między RWO oraz Ca i Mg w układzie woda gruntowa–roztwór glebowy–roślinność łąkowa jest złożonym i uwikłanym procesem, wymagającym dalszych badań.