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CALCIUM AND MAGNESIUM IN ATMOSPHERIC PRECIPITATION, GROUNDWATER AND THE SOIL SOLUTION IN LONG-TERM MEADOW EXPERIMENTS

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Abstract

At present, atmospheric precipitation is considered a cause of environmental pollution. Less attention is paid to nutrients in rainfall that might supply plant requirements. Hence, there is a need to assess relationships between rainfall, groundwater and the soil solution in the context of their mineral content (including magnesium and calcium) essential for soil fertility as well as proper plant growth and development. Such an attempt was made based on long-term meadow experiments run in the vicinity of the village Falenty, the Province of Mazowsze (*województwo mazowieckie*). The relationships between the Ca and Mg content in wet precipitations in Falenty, and in groundwater and the soil solution under long-term meadow experiments were evaluated. Moreover, concentrations and loads of these elements were compared between wet precipitation, groundwater and the soil solution. The positive effect of rainfall Ca and Mg on soil water is differentiated by the significant variability of both concentrations and loads of Ca in precipitation. The fact that Ca binds more strongly to soil than Mg may result in the lack of a positive effect of Ca on the soil solution. The beneficial influence of Ca concentrations on soil solutions depend on the acid reaction of soil. No such relationship was observed for Mg. This confirms the influence of differences in soil pH, soil abundance and different solubility of the two elements on the chemical composition of soil waters.

Key words: atmospheric precipitation, calcium, groundwater, long-term meadow experiment, magnesium, relationship, soil solution.

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WAPŃ I MAGNEZ W OPADZIE ATMOSFERYCZNYM, WODZIE GRUNTOWEJ I ROZTWORZE GLEBOWYM W DŁUGOLETNICH DOŚWIADCZENIACH ŁĄKOWYCH

Abstrakt

Obecnie szczególną uwagę zwraca się na opad atmosferyczny, jako jedną z możliwych przyczyn zanieczyszczenia środowiska. Natomiast znacznie mniejszą poświęca się zawartości w nim składników pokarmowych uzupełniających potrzeby roślin. Skłania to do próby oceny wzajemnych powiązań między opadem, wodą gruntową i roztworem glebowym w aspekcie zawartości w nim składników mineralnych, w tym wapnia i magnezu, niezbędnych dla żyzności gleby oraz rozwoju i wzrostu roślin. Oceny dokonano w warunkach rejonu Falent, w województwie mazowieckim, na przykładzie długoletnich doświadczeń łąkowych. Badano i oceniono zależności między Ca i Mg w mokrym opadzie z Falent oraz w fazie wodnej gleby – wodzie gruntowej i roztworach glebowych spod doświadczeń łąkowych. Ponadto oszacowano oddziaływanie stężenia, a także ładunku tych składników między mokrym opadem, wodą gruntową i roztworem glebowym. Dodatnie oddziaływanie Ca i Mg zawartych w opadzie na wody glebowe różnicuje znaczna zmienność zarówno stężenia, jak i ładunku Ca w opadzie. Natomiast silniejsze w porównaniu z Mg wiązanie Ca przez glebę może skutkować brakiem wpływu tego składnika z opadu na jego stężenie w roztworze glebowym. Dodatni wpływ stężenia Ca w wodzie gruntowej na jego stężenie w roztworach glebowych warunkuje kwaśny odczyn gleby. W przypadku Mg nie obserwowano takiej zależności. Potwierdza to wpływ różnic odczynu, zasobności gleb oraz różnej rozpuszczalności związków omawianych składników na skład chemiczny wód glebowych.

Słowa kluczowe: długoletnie doświadczenia łąkowe, magnez, opad atmosferyczny, roztwór glebowy, wapń, woda gruntowa.

INTRODUCTION

Our care of the environment, justified and reasonable, now turns people's attention to atmospheric precipitation as a potential source of pollution. This problem was discussed for example in a review by Sapek (2011), which dealt with nitrogen, and in another article by Sapek and Sapek (2011), concerned with phosphorus. Calcium and magnesium are contained in atmospheric precipitation, both wet like rain and snow, and dry such as dew, fog, cloud drops and aerosols (Van Loon, Duffy 2007). The main source of these elements in the atmosphere is the dispersion of soil and fragments of biological matter, wherefrom both elements are dissolved in the atmospheric water (Rubio et al. 2008, Tsukuda et al. 2006). Apart from industrial regions with excessive alkaline dust emissions, calcium and magnesium surplus is a rare problem, while the shortage of these elements is a much more common issue (Sapek, Sapek 2011). The presence of both elements in atmospheric precipitation is a factor aiding neutralization of acid rains. The content of calcium and magnesium in wet precipitation as well as their presence in particulate matter contained in dry deposits determine the pH of acid rain (Schroeder 1989, Anstasio 2000, Fisak et al. 2002, Hlawliczka et al. 2002). Rainfall is often seen as a source of water, but much less attention is paid to its content of nutrients, which supply plants' demands. Atmospheric precipitation may be an important source of nutrients provided they are deficient in natural ecosystems (Schlesinger et al. 1982, Arianoutsou 1989, Chadwick et al. 1999, Kacorzyk et al. 2012). As a source of calcium and magnesium, which control its pH, rainfall may play a significant role in maintaining the fertility of natural meadow ecosystems.

Precipitation is the main source of water to the liquid phase of soil, comprising groundwater and the soil solution, which is the milieu for plant nutrition. The availability of calcium and magnesium, which ensures good plant growth, depends *inter alia* on the ca and Mn concentrations in groundwater and particularly in the soil solution (Prusińkiewicz 2011, Szperliński 2002).

Atmospheric precipitation is an additional source of plant nutrients, although its exact contribution depends on relationships between rainwater, groundwater and the soil solution. Another factor to be considered is the mineral composition of deposition. Sapek, Kalińska and Nawalany (2006) tried to assess the effect of mineral components in atmospheric precipitation on their content in groundwater. They evaluated the relationship between the ionic composition of wet deposition and groundwater, which should be viewed in the context of the antagonistic behaviour between calcium and magnesium in the environment (Gorlach, Mazur 2002). The content of minerals in groundwater and in surface waters also depends on the type of soil and its use. Positive relations between concentrations of magnesium, potassium and sodium have been observed in waters from agricultural areas (Cymes, Szymczyk 2005, Orzepowski, Pulikowski 2008). An important factor in the cycling of nutrients, including Ca and Mg, in the water phase is the presence of particulate matter (PM) and organic compounds in atmospheric precipitation (Anastasio 2000, Hlawliczka et al. 2002, Schroeder 1989). The above considerations have inspired the current assessment of relationships between calcium and magnesium in the water phase (groundwater and soil solution) of soil covered with grassland.

In brief, the aim was to assess changes in the content of calcium and magnesium during the year as well as their mutual relationships in wet precipitation falling in the village Falenty and in the groundwater and soil solution under long-term meadow experiments. Another objective was to evaluate relationships between ca and Mn concentrations and loads in wet precipitation and the water phase of soil.

MATERIAL AND METHODS

Atmospheric precipitation samples collected in Falenty represented wet deposition, i.e. rain and snow (Sapek 2011). Samples were collected on a meadow maintained as a long-term experiment at the Experimental Station of the Institute of Technology and Life Science in Falenty, 13 km south of Warsaw. The description of the sampling apparatus and protocol can be found in Sapek et al. (2003). The atmospheric precipitation data were obtained from a meteorological station set near the experimental site in Falenty (Sapek and Nawalany 2006). Both experiments were located 2 and 3 km from the meteorological station and precipitation sampling site. Groundwater samples were collected from soil under long-term meadow experiments set up in 1981/1982 on acid (pH_{KCL} – 4.5; 4.3) mineral soil in Janki (J) and Laszczki (L), situated 2 km south from meteorological station. A map showing the exact location of all experimental sites was attached to the former paper (Sapek 2006).

In 1981 and 1982, two long-term meadow experiments were set up according to the random blocks method with four replications. The aim of these trials was to assess the impact of single liming on soil acidity, nutrient dynamics and yields from meadows; another goal was to study the mineralization of nitrogen and phosphor compounds during successive years. The experimental fields and a regulated stream were used to investigate the groundwater, soil solution and surface water chemistry (Sapek, Sapek 2011). Soils differed in pH, content of organic carbon content (J – 19, L – 38 g kg^{-1}), Ca (J – 1.44, L – 2.58 g kg^{-1}), Mg (J – 0.47, L – 0.89 g kg^{-1}), particles <0.02 mm (J – 18.4, L – 22.4%) and moisture (J – 22.1, L – 26.7% vol.).

Groundwater was collected from control wells installed in strips of land separating the experiments from surroundings. The mean groundwater depth was 120 cm in experiment J (max. 85 cm, min. 156 cm) and 107 cm (max. 91 cm, min.124 cm) in experiment L (Sapek et al. 2003). Moreover, water was sampled from a nearby stream flowing from springs near the village Laszczki (Rossa, 2003). Soil solutions originated from the experiment in Janki, where suction apparatuses were installed in four fertilisation objects of the experiment: Ca_0N_2AN, Ca_2N_2AN, Ca_0N_2CN, Ca_2N_2CN, i.e. from soil fertilised with 240 kg N supplied as ammonium saltpetre (AN) and calcium saltpetre (CN), not limed (Ca_0) or limed (Ca_2) once at the onset of the experiment with calcium carbonate in an amount according to the hydrolytic acidity 2 Hh. Details of the sampling method with suction apparatuses fitted with porcelain cups and the calculations of component outwash from soil are given in Sapek and Pietrzak (1996) and Pietrzak, Urbaniak and Sapek (2006). A precise description of the experiments, including characteristics of fertilisation variants, is presented in Sapek and Nawalany (2006). Calcium and magnesium concentrations in samples of precipitation, groundwater and the soil solution were determined with atomic absorption spectrophotometry, while pH was measured in KCl by potentiometry (Sapek, Sapek 1997). The results of concentrations of the analyzed components cover the following periods: 1988-2007 for wet precipitation, 1995-2007 for groundwater and 1996-2007 (excluding 1999 and 2004) for the soil solution. Samples of wet precipitation were collected from subsequent rainfalls provided the volume was sufficient for chemical analyse. The sampling of the other types of water kinds produced an annual average of 23 samples of groundwater, 9 samples of surface water from the stream, from 4 to 7 samples of the soil solution in 1996-1997, and from 15 to 31 soil solution samples in 2000-2002. Mean values of determinations from the above years of investigations as well as variability coefficients were calculated.

The collected data on wet precipitation, groundwater and the soil solution were numerous and diverse, which is why nonparametric correlations of the Spearman's rank order and adequate coefficients r_s were calculated. The Pearson's linear correlation coefficient (r) was used to evaluate changes in the wet precipitation volume.

RESULTS AND DISCUSSION

Concentrations and loads of calcium and magnesium; mutual relationships between precipitation and the soil water phase

Precipitation. In 1988-2007, the average calcium concentration in wet precipitation was 3.24 mg dm^{-3} and that of magnesium 0.64 mg dm^{-3}, both with a similar range of variability: 23.1 and 23.4%, respectively. The concentrations of both elements were similar to the mean concentrations in rainfall calculated from various literature data (Ca – 3.44 mg dm^{-3}, Mg – 0.81 mg dm^{-3}) (Sapek, Sapek 2011). The rainfall pH was acidic and rather stable over the years (mean pH – 5.2 at a variability coefficient of 6.9%). The mean annual precipitation was 544 mm, varying within 13% (Table 1). Changes in the annual precipitation in 1988-2007 showed a statistically significant increasing trend (r = 0.56*) – Figure 1*a*. The dynamics of calcium and magnesium is illustrated by changes in the annual concentrations and their direction. Fluctuations of the Ca and Mg concentrations over the years translated into non-significant values of the Spearman's rang correlation coefficients (Ca – r_{s1} = 0.14, Mg – r_{s1} = 0.15), although the increasing Ca and Mg concentrations were accompanied by their higher loads (Ca – r_{s3} = 0.54**, Mg – r_{s3} = 0.51*) – Figure 1*b*,*c*. Moreover, as concentrations of Ca in atmospheric precipitation increased, so did the Mg levels (r_s = 0.46*) – Figure 1*d*.

The mean annual calcium loads (17.4 kg ha^{-1}) delivered with wet precipitation to the soil surface in 1988-2007 showed high variability (CV= 42.0%), especially compared with much smaller loads of magnesium: 2.5 kg ha^{-1} (CV = 21.2%) – Table 2. The latter resembled the mean loads of Mg (3.4 kg ha^{-1}) calculated from a reviewed publication (Sapek, Sapek 2011). However, loads of calcium in Falenty were much higher than the mean value (8.2 kg ha^{-1}), calculated from the same source as magnesium. Unlike the high changeability of Ca loads, the loads of magnesium significantly increased with time (r_{s2} = 0.52*) – Figure1*c*. the absence of a significant relationship between loads of the two elements, Ca and Mg, might be the result of the aforementioned changes (r_s ns) – Figure1*e*.

Table 1

Mean pH and concentrations of calcium and magnesium in wet precipitation from Falenty and in groundwater and the soil solutions

Sample type	Sampling site/experiment	Fertilisation object	Years	pH***		Ca (mg dm^{-3})		Mg (mg dm^{-3})	
				mean	CV (%)	mean	CV (%)	mean	CV (%)
Precipitation*	Falenty		1988-2007	5.2	6.9	3.24	23.1	0.64	23.4
Ground water	Janki		1995-2007	7.5	4.6	64.2	17.8	6.34	21.1
Ground water	Laszczki		-„-	7.6	3.7	95.1	18.4	13.3	14.7
Stream water	stream** (Janki)		-„-	7.42	4.2	62.5	16.2	9.77	24.8
Stream water	stream** (Laszczki)		-„-	7.52	3.6	63.4	14.7	9.74	23.3
Soil solution	Janki	Ca_0N_2AN	1996-2007	8.01	2.9	74.8	20.7	17.5	53.1
Soil solution	Janki	Ca_2N_2AN	-„-	8.01	3.3	94.9	16.0	25.8	43.0
Soil solution	Janki	Ca_0N_2CN	-„-	7.96	6.2	87.8	37.1	17.7	52.0
Soil solution	Janki	Ca_2N_2CN	-„-	8.13	3.0	71.8	38.7	31.8	53.5

* Mean annual precipitation from the studied period = 544 mm (CV = 13%);

** Stream delivering water from springs in the field; Ca_0N_2AN, Ca_2N_2AN, Ca_0N_2CN, Ca_2N_2CN – soil objects fertilised with 240 kg nitrogen (N_2) in the form of ammonium saltpetre (AN) or calcium saltpetre (CN), not limed (Ca_0) or limed (Ca_2) according to hydrolytic acidity criterion 2 Hh;

*** pH of soil solutions - mean from 1997-2002

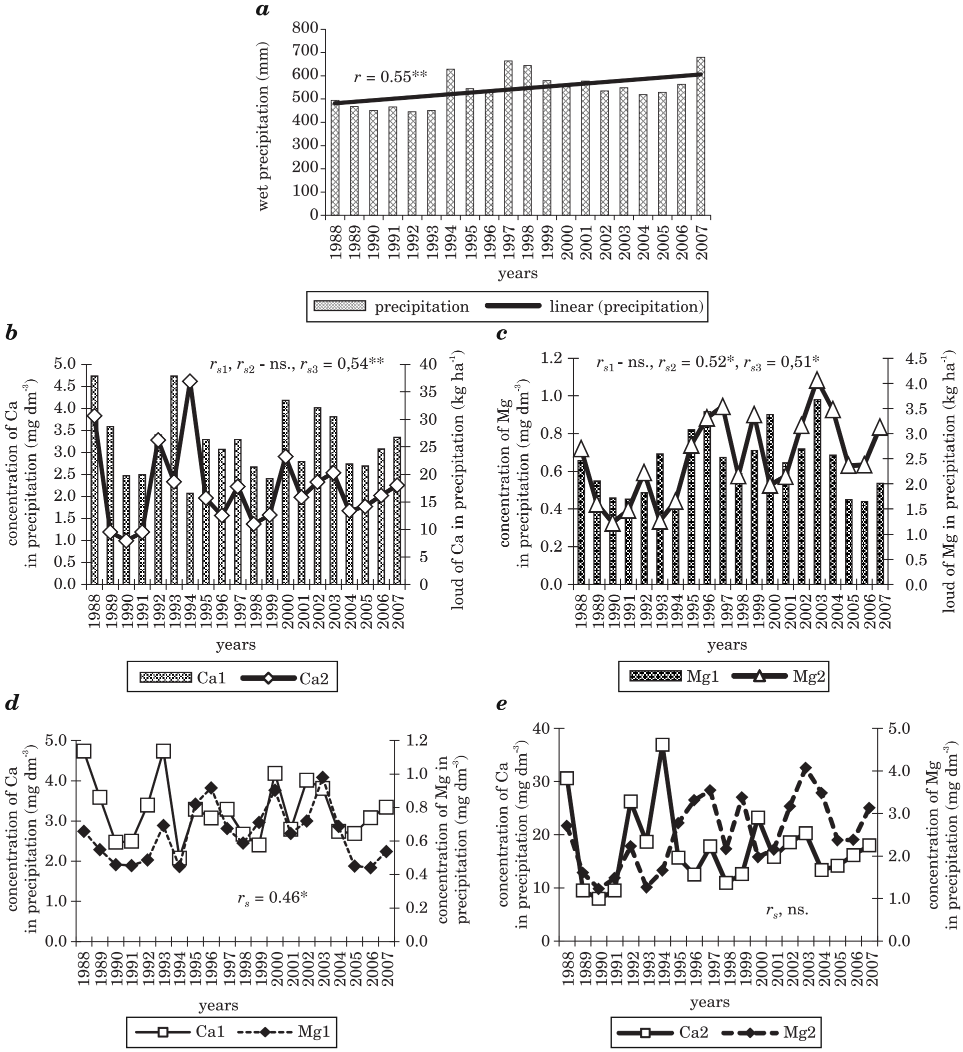

Fig. 1. Annual precipitation in Falenty and the concentration and load of calcium (Ca_1 , Ca_2 and magnesium (Mg_1, Mg_2) in wet precipitation in 1995-2007 – relationships between precipitation volume – *a*, concentration – *b*, as well load – *c*, and years; relationships between concentration and load of calcium (Ca_1 x Ca_2) and magnesium (Mg_1 x Mg_2), concentration of calcium and magnesium (Ca_1 x Mg_1) – *d*, and their load (Ca_2 x Mg_2) – *e*, in wet precipitation; *r* – Pearson's linear correlation coefficient, r_s, r_{s1}, r_{s2} , r_{s3} – spearman's rank order correlation coefficients

Groundwater. Groundwater from the experiment in Laszczki was richer in calcium (95.2 mg dm^{-3}) than groundwater from experiment in Janki (64.2 mg dm^{-3}), with similar variability of element concentrations in both waters (c. 18%) during the study. Groundwater in the former site showed twice as much magnesium, weakly alkaline pH (7.6) and better stability

Table 2

Mean loads of calcium and magnesium introduced with wet precipitation on the soil surface in Falenty and mean calcium and magnesium leaching from soil to soil solution in the Janki experiment

Sample type	Sampling site/ experiment	Fertilisation object	Years	Ca (kg ha^{-1})		Mg (kg ha^{-1})	
				mean	CV (%)	mean	CV (%)
Precipitation	Falenty		1988-2007	17.4	42.0	2.50	21.2
Soil solution	Janki	Ca_0N_2AN	2000-2003	13.4	45.5	1.85	35.7
Soil solution	Janki	Ca_2N_2AN	-„-	13.6	60.3	2.38	73.5
Soil solution	Janki	Ca_0N_2CN	-„-	14.5	52.4	2.94	81.0
Soil solution	Janki	Ca_2N_2CN	-„-	10.7	63.6	5.40	70.6

Ca_0N_2AN, Ca_2N_2AN, Ca_0N_2CN, Ca_2N_2CN – as in Table 1

of both parameters compared to the other location (Table 1). The dynamics of changes in the concentrations showed a time-dependent increasing trend for Ca and decreasing one for Mg in both experimental locations. Thus, the Ca concentrations in groundwater in experiment J significantly increased during the study (r_{s1}(J) = 0,53*) – Figure 2*a*,*b*. Since 2004, the meadow in Lszczki has not been harvested, which encouraged the author to analyse concentrations of Ca and Mg in 2004-2007. Despite the lack of statistical significance, there was a clear tendency for decreasing Ca and Mg concentrations in groundwater from this experiment (Figure 2*b*,*d*). No correlations between the concentrations of the analysed elements were found in groundwater from both experiments (Figure 2*c*,*d*). The mean calcium concentrations determined in 1995-2007 in the stream which delivers water to fields and meadows in both Janki and Laszczki were similar to their concentrations in groundwater from Janki. Concentrations of magnesium (9.75 mg dm^{-3}) in the stream water were intermediate to Mg concentrations in groundwater from two experiments (Table 1).

Soil solutions. Soil solutions from the experiment in Janki contained more calcium and magnesium than groundwater, which was reflected in their mean concentrations from the years 1996-2007. The pH of the soil solutions from four different fertilisation treatments was close to 8.0, despite the big differences in the soil pH (pH_{KCl} 3.6-6.6) and differentiated Mg and Ca concentrations in the soil solution (Tables 1, 3). The highest mean Ca concentration (94.9 mg dm^{-3}) was found in the solution from very acidic soil (pH_{KCl} = 4.3) fertilised with acid-forming ammonium saltpetre but limed once at the onset of the experiment in 1981 (variant Ca_2N_2AN) – Tables 1, 3. This confirms re-acidification, that is higher soil acidification after liming, also demonstrated in earlier studies (Sapek 2009). Most magnesium (31.8 mg dm^{-3}) was contained in soil solutions under soil with nearly neutral pH (pH_{KCl} = 6.6) from the treatment limed and fertilised with calcium saltpetre (Ca_2N_2CN), which indicates that mg was more intensively leached than

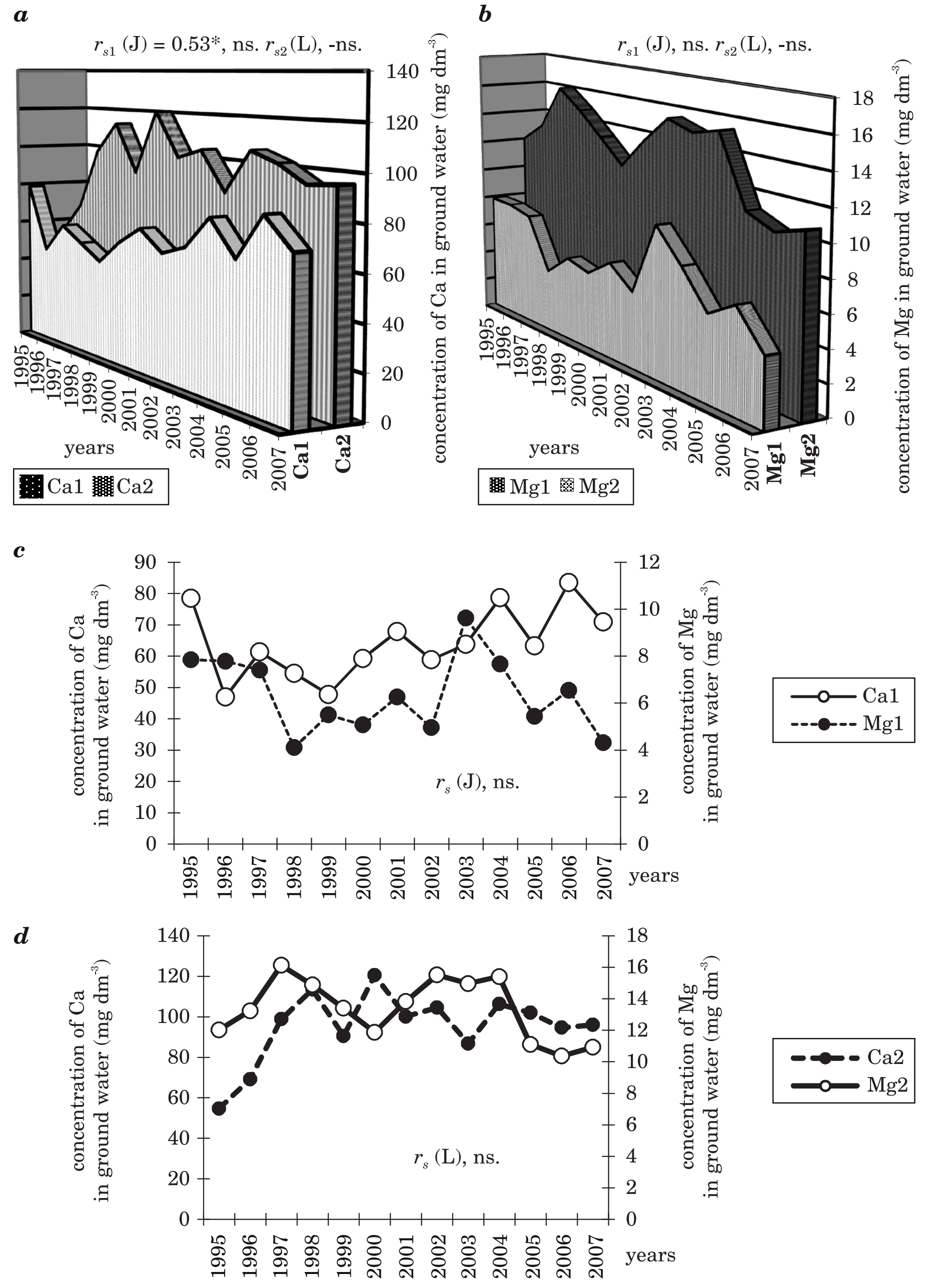

Fig. 2. Concentrations of calcium – *a*, and magnesium – *b*, in groundwater from the experiments in Janki (J) and Laszczki (L) in 1995-2007 – relationships between concentration and years; relationships between the concentration of calcium and magnesium in groundwater from experiment J (Ca_1-Mg_1) – *c*, and experiment L (Ca_2-Mg_2) – *d*; r_s, r_{s1}, r_{s2} – spearman's rank order correlation coefficients

Table 3

Mean pH_{KCl} in the 0-10 cm soil layer from four objects in the meadow experiment in Janki (1995-2007)

Value	pH_{KCl} of soil from fertilisation objects			
	Ca_0N_2AN	Ca_2N_2AN	Ca_0N_2CN	Ca_2N_2CN
Mean	3.6	4.3	5.0	6.6
Coefficient of variability, CV (%)	5.1	11.67	12.0	3.6

Ca_0N_2AN, Ca_2N_2AN, Ca_0N_2CN, Ca_2N_2CN – as in Table 1

Ca (Gliński 1999). The remarkable variability of elemental concentrations (CV%), especially magnesium, in soil solutions from particular fertilisation objects can be explained by different soil reaction and by the different uptake of these nutrients by plants (Tables 1, 3, Figure 3*a*,*b*). The effect of Ca and Mg uptake by plants on their content in the soil solution has been dealt with in another paper (Sapek, 2011).

The Ca concentrations in the soil solutions showed just a tendency to increase in consecutive years, which originated from their great variability (Figure 3*a*). Concentrations of Mg in the solution from soils fertilised with calcium nitrate (Ca_0N_2CN, Ca_2N_2CN) were significantly decreasing in years (r_{s3} = -0.68*, r_{s4} = -0.83**) – Figure 3*b*. A comparison between the Ca and Mg concentrations in the soil solution from soils with an extreme pH showed a significant decrease in the Mg concentrations and an increase in the Ca content (r_{s4} = -0.83**) in the soil solution from acidic (Ca_0N_2AN) and neutral soil (Ca_2N_2CN) (Figure 3c and d), but only in the case of neutral soil a decrease in the Mg concentrations was significant;y correlated with the increase in the Ca concentrations (r_s = -0.68*) – Figure 3*c*,*d*. A further decrease in soil pH in the following fertilisation treatments was accompanied by a higher amount of leached Mg, but not Ca, which is demonstrated by the trend lines (Tables 2, 3, Figure 4*a*,*b*). The changes confirm the antagonistic behaviour between these elements in the environment (Gorlach, Mazur 2002).

The smallest loads of Ca (13.4 kg ha^{-1}) and Mg (1.85 kg ha^{-1}) were leached from very acidic soil (pH_{KCl} = 3.6) of the variant Ca_0N_2AN, which is certainly attributable partly to their uptake by plants from soil, which was very poor in these elements. The high variability of Ca and Mg loads (compared to their concentrations) among particular fertilisation objects in the subsequent years was probably an effect of the less available information, but also of the differentiated Ca and Mg uptake by plants (Sapek 2011) – Tables 1, 2.

Impact of calcium and magnesium concentrations and loads in wet precipitation on the soil water phase

The results on concentrations and loads of the two elements in wet precipitation and their concentrations in groundwater and the soil solutions did not enable the author to assess their relationships in 1995-2007. Due to

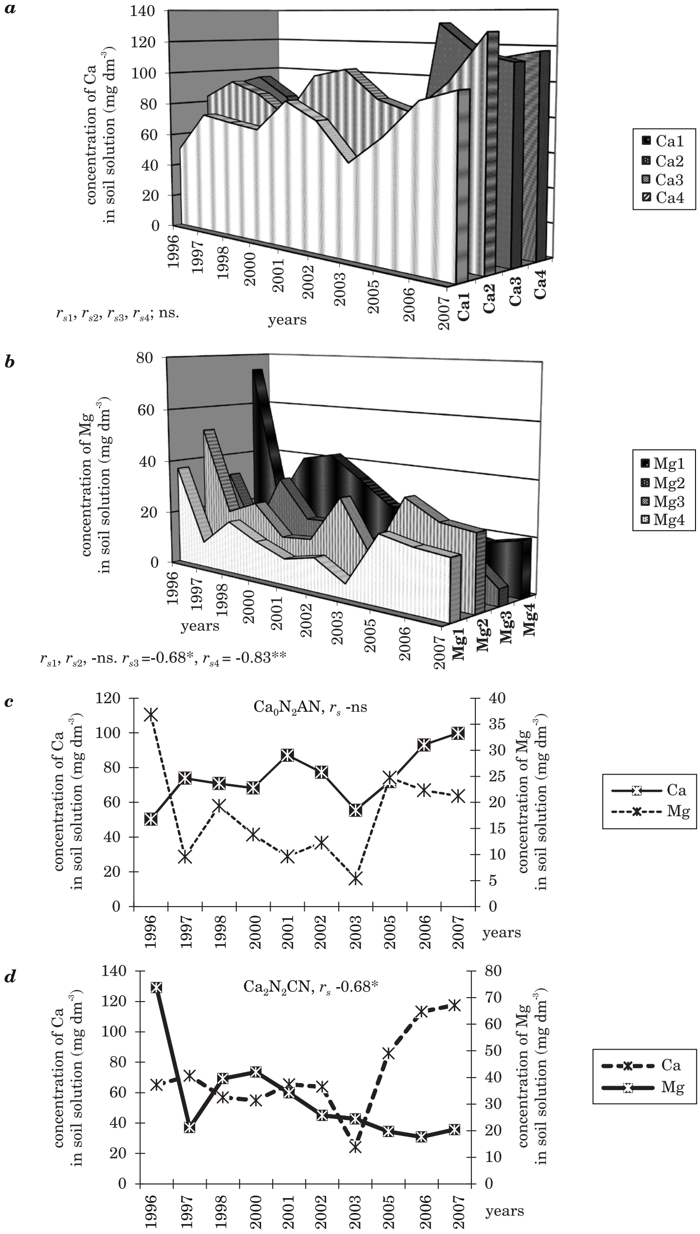

Fig. 3. Changes in the concentration of calcium (Ca_1, Ca_2, Ca_3, Ca_4) – *a*, and magnesium (Mg_1, Mg_2, Mg_3, Mg_4) – *b*, in soil solutions from 1-4 fertilisation objects (Ca_0N_2AN, Ca_2N_2AN, Ca_0N_2CN, Ca_2N_2CN) in the Janki experiment in 1996-2007 – relationships between concentration on 104 objects and years; relationships between the concentration of calcium and magnesium in solutions from the objects Ca_0N_2AN – *c*, and Ca_2N_2CN – *d*; r_s, r_{s1}, r_{s2}, r_{s3}, r_{s4} – spearman's rank order correlation coefficients

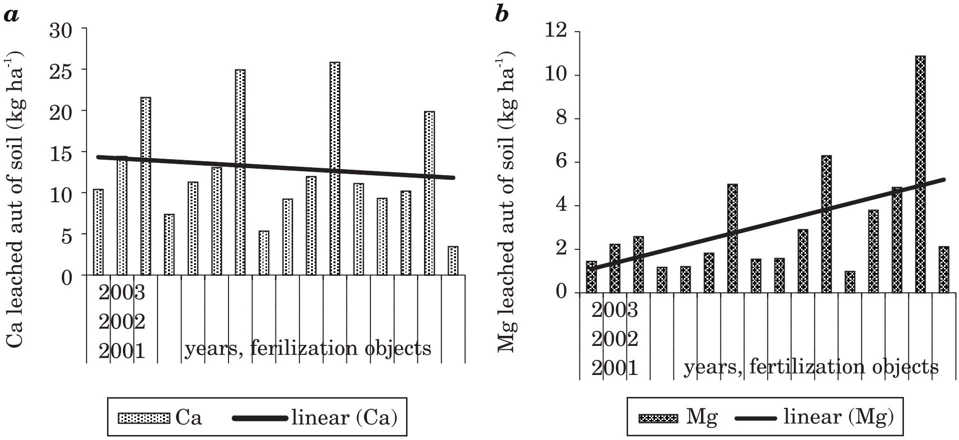

Fig. 4. Changes of calcium – *a,* and magnesium – *b*, loads released from soil to soil solutions on 4 fertilisation objects: Ca_0N_2AN, Ca_2N_2AN, Ca_0N_2CN, Ca_2N_2CN in the Janki experiment in 2000-2003

the insufficient number of data on Ca and Mg loads leached from soil to the soil solution (2000-2003) the relationships of these parameters with other variables were not analysed (Tables 1, 2).

Precipitation – groundwater. The concept of precipitation as a source of plant nutrients inspired the author to continue similar investigations, previously performed on the relationship between Ca and Mg concentrations in groundwater from meadow experiments, in water from a nearby stream and their loads delivered on the surface of land (Sapek et al. 2005). The Spearman's rank order correlations showed both positive and significant impact of Ca from precipitation on concentrations of this element in groundwater under less fertile and calcium poor soil from experiment J (r_{s1} = 0.67**). Similar effects were determined in water from the regulated stream (r_{s3} = 0.77**). No such influence was observed in groundwater under Ca richer soil from experiment L (r_{s2} ns.) – Figure 5*a*. Moreover, bigger loads of Mg in precipitation enriched groundwater with this element in both experiments (r_{s1} = 0.81**, r_{s2} = 0.80**). Besides, in such conditions, their concentrations in the stream water in experiment L increased significantly (r_{s3} = 0.90**) – Figure 5*b*. A positive impact of the Ca and Mg concentrations in precipitation on their levels in groundwater was verified.

Precipitation – the soil solution. The presence of Ca and Mg in wet precipitation has no significant relationship with the Ca concentrations in the soil solution from soils with the extreme pH, i.e. from 3.6 to 6.6, particularly the latter one (Table 3, Figure 6*a*). Changes in the Ca concentrations in 1996-2007 showed some tendency towards a decrease in the soil, although the content of calcium in precipitation increased between 1996 and 2007 (Figure 6*a*). That could have been caused by Ca binding to soil particles

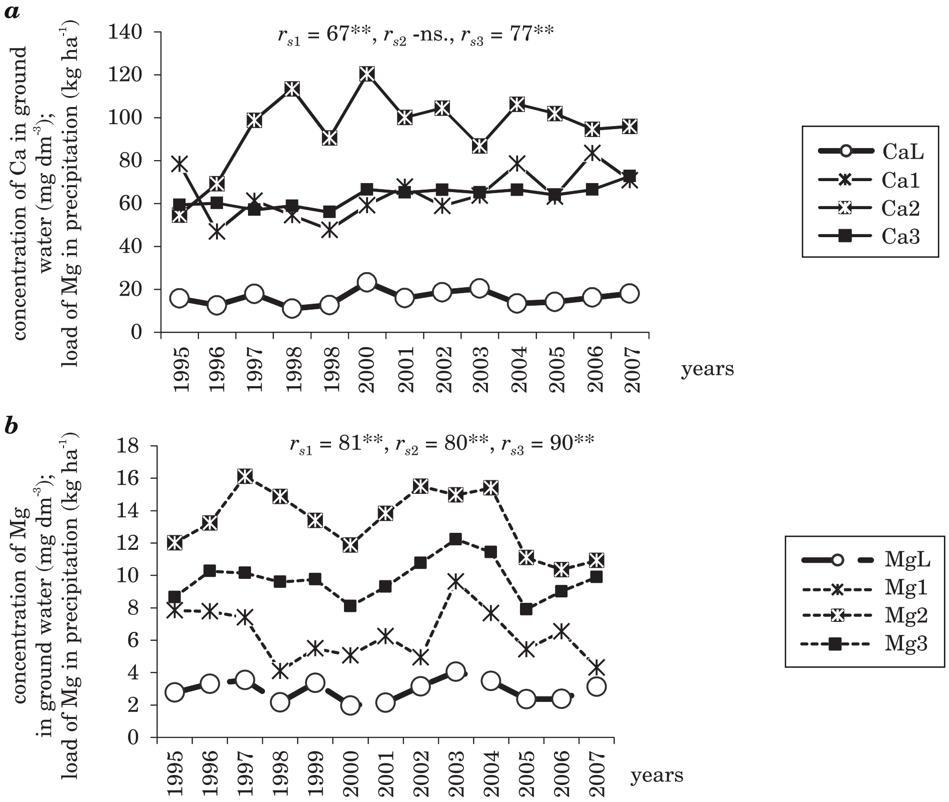

Fig. 5. Concentrations of calcium and magnesium in groundwater from experiment in Janki (Ca$_1$, Mg$_1$) and Laszczki (Ca$_2$, Mg$_2$) and in water from the stream (Ca$_3$, Mg$_3$), as well as loads of calcium (Ca$_L$) and magnesium (Mg$_L$) in precipitation in 1995-2007; relationships between calcium – *a*, and magnesium – *b*, in groundwater and loads in precipitation; r_{s1}, r_{s2}, r_{s3}, – spearman's rank order correlation coefficients

more readily Mg, and by the soil sorption capacity (GLIŃSKI, 1999), as manifested by an increase of Ca concentrations in precipitation being accompanied by higher Mg concentrations in the soil solution (r_{s2} = 0.68*) – Figure 6*b*. Changes in Mg loads in wet precipitation had no impact on Ca concentrations in the soil solution.

Groundwater – the soil solution. Calcium concentrations in groundwater were related to Ca concentrations in the soil solution (r_{s1} = 0,70*), but only from the acid soil (pH$_{KCl}$ - 3.6) in the Ca$_0$N$_2$AN variant, where the leaching of this element was more intensive (SAPEK 2011) – Figure 7*a*. No such relation was assessed in the case of Mg (Figure 7*b*).

Chemical composition of the soil water phase (soil water), originating from the infiltration of precipitated waters, depends on the chemical composition of precipitation, its intensity and the rate of infiltration downwards

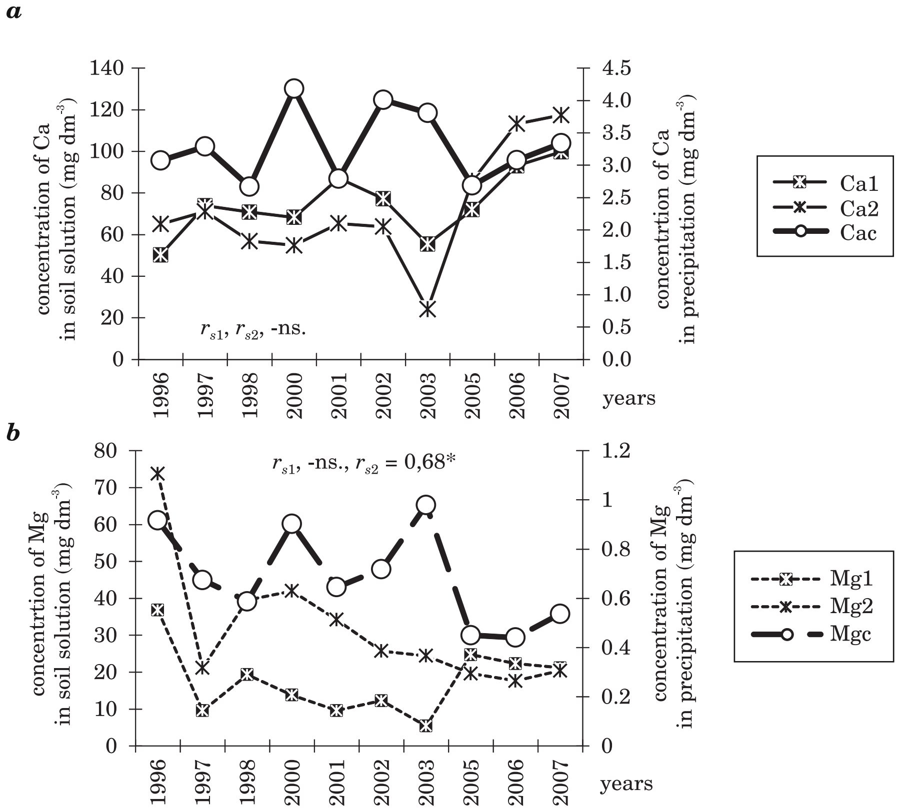

Fig. 6. Relationships between calcium and magnesium concentration in soil solution from the fertilisation objects Ca_0N_2AN (Ca_1, Mg_1) and Ca_2N_2CN (Ca_2, Mg_2) in the Janki experiment and concentration of calcium (Ca_c) – *a*, and magnesium (Mg_c) – *b*, in precipitation; r_{s1}, r_{s2} – spearman's rank order correlation coefficients

the soil profile, but it is also conditioned by soil properties, chiefly chemical characteristic and grain size structure (KATZ 1989, RACZYK 2008). The effect of soil properties on Ca and Mg concentrations in groundwater were confirmed by the substantial Ca and Mg enrichment of groundwater from the experiment in Laszczki, carried out on soil which was more compact and richer in organic carbon than soil from the experiment in Janki. CYMES and SZYMCZYK (2005) also found that the type of soil and its use are the most important factors differentiating concentrations of Ca and Mg. Due to their depth (on average 107-120 cm), the groundwater resources analysed herein may be perceived as soil-ground water. Therefore, their chemical composition largely depends on atmospheric precipitation and particularly on its Ca and Mg content (SZPERLIŃSKI 2002). Concentrations and loads of Ca and Mg in wet precipitation around Falenty made the pH of rainfall acidic (pH = 5.2), quite close to the pH = 5.63, which is typical of non-polluted precipitations (Zwoliński 1996). For comparison, the mean annual pH of atmospheric precipitation near Olsztyn was 4.47-4.87 (Szwejkowski et al. 2007). The environs of Falenty may be considered rural, as there are no large industrial companies nearby. On the other hand, the village lies in the vicinity of a large urban agglomeration (Warsaw) and near a motorway, which leads to the enrichment of wet precipitation in both acidifying components and in particulate matter containing calcium and magnesium. Calcium compounds are invariably less soluble, which is why - despite their greater abundance - their effect on soil and soil solutions may be more complex and less visible than that of magnesium (Hawliczka et al. 2003). In the conditions med during the current investigation, a positive and significant relation between concentrations of soluble forms Ca and Mg in precipitation, and the lack of a significant increase of Ca loads, unlike Mg loads, support the conclusions proposed by Hawliczka et al. (2003) about the effect of forms of both ele-

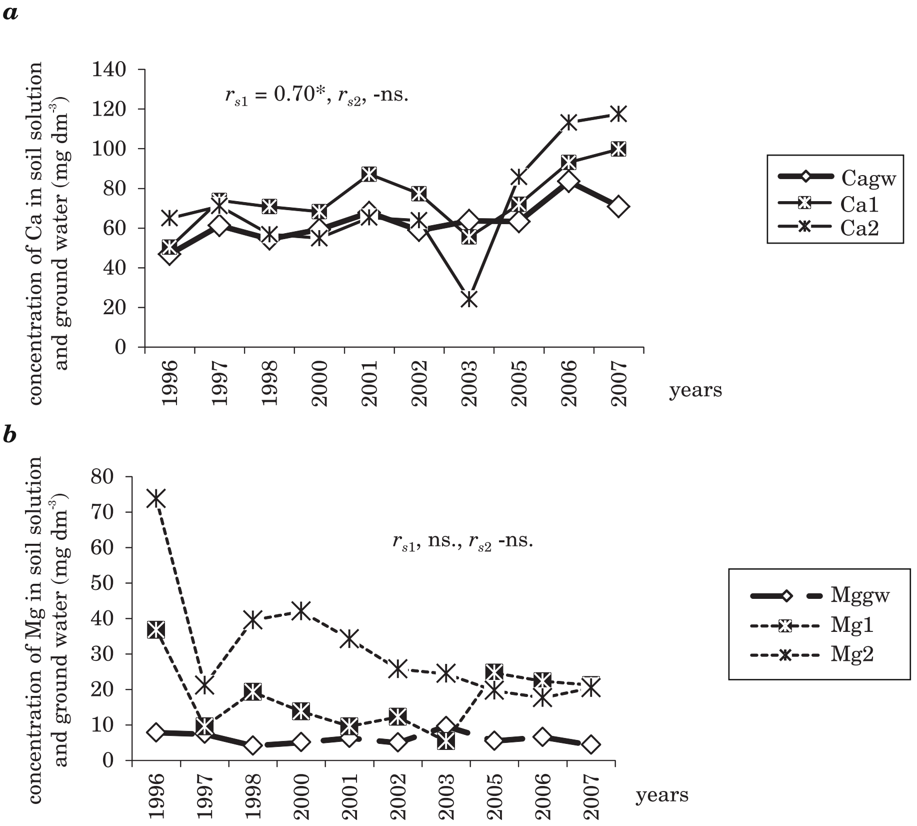

Fig.7. Relationships between the concentration of calcium – *a*, and magnesium – *b*, from objects: in soil solution Ca_0N_2AN (Ca_1, Mg_1) and Ca_2N_2CN (Ca_2, Mg_2) and concentration of calcium (Ca_{gw}) and magnesium (Mg_{gw}) in groundwater in the Janki experiment; r_{s1}, r_{s2} – spearman's rank order correlation coefficients

ments on their environmental cycling. The present determinations of Ca and Mg in the stream water imply that the soil properties from the experiments and agro-technical treatments had no effect on concentrations of either of the elements. As shown in SAPEK et al. (2003), these concentrations largely depend on the runoff from nearby fields and crops.

Precipitation permeating downwards the soil profile affects both groundwater and the soil solution. Concentrations of Ca and Mg measured in the soil solutions are higher than in groundwater from the same experiment, which is also caused by the method of their acquisition and sampling depth (LIGĘZA, SMAL 2004). In theseinvestigations, samplers collecting the soil solutions were installed 10 cm below the ground. Calcium or magnesium leached from this layer did not travel to deeper soil layers, neither was it adsorbed or diluted. However, the said concentrations were affected by the uptake by plants, for which the soil solution is one of the main mineral resources (PRUSIŃKIEWICZ 2011, SAPEK 2011). Differences in concentrations of minerals, including Ca and Mg, in the soil solutions collected from the fertilisation treatments with extremely different soil pH confirmed the effect of type of soil and its use, suggested for example by LIGĘZA and SMAL (2004).

CONCLUSIONS

1. Increase in calcium concentrations in wet precipitation in and around Falenty was accompanied by higher concentrations of magnesium, although no such correlation was were observed for their loads.

2. Concentrations of calcium in groundwater from soil under experimental meadows increased in the subsequent years, but only in the case of soil richer in calcium and magnesium as well as organic carbon.

3. Concentrations of magnesium were deceasing in the soil solution from objects fertilised with calcium nitrate, but increasing in the soil solution from soils of neutral pH.

4. Amounts of magnesium transferred from soil to the soil solution increased at a pH ranging from 3.6 to 6.6, but analogous quantities of calcium remained constant.

5. Increase in calcium loads in precipitation resulted in its higher concentrations in groundwater from soil poor in calcium and organic carbon as well as in water from the stream. No such effect was detected for magnesium.

6. Increase in magnesium concentrations in precipitation lead to its higher concentrations in the soil solution from soils with the pH close to 7.

7. Increase in calcium concentrations in groundwater from soils with low pH was accompanied by higher calcium concentrations in the soil solution from acid soil. The absence of such relationships in the case of magnesium could have been due to the difference in solubility of both compounds.

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