

Concentration of soil CO₂ as an indicator of the decalcification rate after liming treatment**

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A b s t r a c t. This paper presents the results of investigation of decalcification of acid sandy and loamy sand soils by infiltration waters, and potential Ca-leaching after liming treatment. For this purpose, monthly measurements were made of the concentration of CO₂ in the soil air, dissolved inorganic carbon in the soil waters, and their ionic composition. The determined dissolved inorganic carbon ranged from 5.9 to 10.6 mg dm⁻³ and from 9.9 to 16.5 mg dm⁻³ for the sandy and loamy sand soil, respectively. The Ca concentration in soil waters was determined as 5.9-12.4 mg dm⁻³ in sandy soil and 14.2-19.8 mg dm⁻³ in soil loamy sand. The calculated rate of decalcification amounted to 23.0 kg ha⁻¹ year⁻¹ in soil sandy and 19.4 kg ha⁻¹ year⁻¹ in loamy sand soil. The potential Ca-leaching is predicted as 124 kg ha⁻¹ year⁻¹ for S and 87 kg ha⁻¹ year⁻¹ for loamy sand soil. At the treatment level of 3 000 kg ha⁻¹ 4 year⁻¹ of CaO, ~20% of the Ca-fertilizer can be leached after the liming treatment. The results of the CO₂ concentration in the soil air may be useful in estimation of Ca-leaching from soils developed by slightly clayey sands and clayey sands in zones with a moderate climate.

K e y w o r d s: carbon dioxide, soil, water infiltration, decalcification, leaching

INTRODUCTION

The major sources of dissolved inorganic carbon (DIC) in groundwater include soil CO₂ and dissolution of carbonate rocks (Appelo and Postma, 1999; Langmuir, 1997; Stumm and Morgan, 1996). The partial pressure of carbon dioxide in soil air (PCO₂) significantly exceeds that in atmospheric air as result of respiration of soil organisms

(Andrews and Schlesinger 2001; Anthoni *et al.*, 2004; Chirinda *et al.*, 2014; Dudziak and Hałas, 1996; Szaran *et al.*, 2005). Thus, CO₂ diffuses from the soil to the atmosphere. In the global carbon cycle, this component, estimated as 50-60 Gt C year⁻¹ (Houghton, 2007; Prentice *et al.*, 2001), is about 10-fold higher than emission from burning of fossil fuels. A much lower contribution to global carbon cycling is reached by the component related to water cycling. Leaching of dissolved CO_{2(aq)} from the soil to underground waters is estimated at a level of approximately 0.2 Gt C year⁻¹ (Kessler and Harvey, 2001). However, the significance of this circulation is very important because of the role of CO_{2(aq)} in leaching of carbonate minerals, especially calcite, which results in acidification of the environment (Bell and Treshow, 2002; Berner and Berner, 1996; Tian and Niu 2015). In areas under agricultural use, such as in Poland, the processes discussed have a significant influence on the efficient use of land for production purposes (Filipek and Skowrońska, 2013; Hołubowicz-Kliza, 2006).

The compensation of carbonate loss and overall improvement of the properties of soils require application of liming *ie* fertilization with limestone and dolomite base components. Liming contributes to improvement of the availability of macro- and micro-elements for plants and decreases their susceptibility to plant diseases and occurrence of weeds. It also enhances the fertility of acidified soils and leads to immobilization of CO₂. The needs for

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liming in Poland are estimated by chemical and agricultural stations based on the agronomic category of the soil, including grain structure, and the pH value determined in 1 M KCl. Once the soil agronomic category and the demand for liming are determined, the dose of Ca-fertilizers is specified as a quantity of CaO ha⁻¹. Ca-fertilizers are mixtures of powdered limestone, dolomite, and calx CaO (Hołubowicz-Kliza, 2006).

In Poland, the average contribution of acid soils in cultivated land exceeds 50%. In certain areas, this value exceeds 80%. In these areas, the recommended doses of Ca-fertilizers amount to approximately 2 500-3 500 kg ha⁻¹ of CaO for a 4-year period. The applied level of liming, however, is lower, and does not even compensate natural leaching of calcium from the soil; therefore, such treatments do not contribute to the optimization of soil pH values (Hołubowicz-Kliza, 2006).

The level of natural leaching of calcium by infiltrating waters into groundwaters may be used as an indicator of the rate of the decalcification process. The indicator should be considered in planning the levels of liming in areas used for agricultural production. The ongoing climate changes, which result in a longer growing season, will affect the increase in the CO₂ concentration in the soil air and the rate of soil decalcification. Therefore, the evaluation of CO₂ content in the soils exhibiting increased susceptibility to acidification, such as sand and loamy sand, is very important.

MATERIAL AND METHODS

The estimation of Ca-leaching from arable soils to groundwater was performed in a typically agricultural region of the Lublin Upland and Roztocze in SE Poland. Land used for agricultural production in the region constitutes 2/3 of the total area, 50% of which is used as arable land. In the Lublin Upland and Roztocze, approximately 50% of soils are highly acidic (<4.5) or acidic (4.6-5.5), whereas 25% of them are slightly acidic (5.6-6.5) and 25% show pH ~ 7.0 and higher (Tkaczyk and Bednarek, 2011).

The investigation was performed in two testing grounds: in the Lublin Upland – Janówka (N 51°9'7.96", E 23°22'49.52"), basin of the Uherka river and in Roztocze region – Guciów (N 50°34'55.12", E 23°4'20.07"), basin of the Wieprz river. In the Guciów village, the soil developed from slightly clayey sands classified as ps according to the Polish Society of Soil Science (PTGleb., 2008) criteria or S (sand) according to the United States Department of Agriculture (USDA, 2010), whereas the Janówka soil was developed from loamy sands and is classified as LS after USDA (2010), or clayey sands classified as pg according to PTGleb. (2008). The granulometry of soil in Guciów is as follows: sands 84%, dusts 14%, and loams 2%. In Janówka, it is as follows: sands 75%, dusts 21%, and loams 4%. The testing ground in Guciów was under rye cultivation and the field in Janówka under barley cultivation. The crops were

under extensive management. Sandy soils are characterized by good infiltration conditions and therefore high levels of leaching of chemical compounds dispersed throughout the soil. The soil pH index values are in the range of strongly to slightly acid. A majority of such soils occur in the Middle and South Roztocze as well as in vast areas of Pagóry Chełmskie, Kotlina Chodelska, and Wzniesienia Urzędowskie.

The hydro-meteorological conditions have a considerable influence on Ca-leaching from arable soils, particularly the magnitude of meteoric precipitation, air temperature, evaporation rate, and soil permeability. These factors determine the fractionation of the meteoric water between runoff and groundwater recharge. Annual precipitation totals are substantially variable in the study area. The highest precipitation totals occur in Roztocze (650-750 mm). In the Lublin Upland, they range from 550 to above 600 mm. The mean annual total amount of evaporation in the study area amounts to 470-480 mm (Michalczyk and Sposób, 2011); however, over the annum, this value is highly variable. In summer, approximately 70% of precipitation is evaporated. The overlapping of the high precipitation level and evaporation rate in summer limits the groundwater recharge in this season. Conditions favourable for groundwater recharge only exist in the period from September to May. Soil freezing and snow cover usually limit infiltration from December to March. In 2010, the mean annual temperature amounted to 7.4°C (Fig. 1), which is typical of the Lublin Upland.

The total annual precipitation recorded in the Bezek meteorological station (located near Janówka) amounted to 753 mm. In the Guciów station, the value was 960 mm. The precipitation total in 2010 was approximately 30% higher than the multi-annual average. Snow cover persisted from December 2009 to February 2010 and appeared again in December 2010. The evaporation rate was variable in a manner typical of the region. The minimum evaporation rate was recorded in January (4 mm), and the maximum in July (95 mm). In the period from May to October, 420 mm of water evaporated, and almost 550 mm evaporated over the whole year.

In the Lublin Upland and Roztocze, an increase in the groundwater level was recorded from March to June. In the remaining months, the level decreased or was constant (QBG, 2010). An increase in the groundwater level in the period from March to April resulted from thawing of the snow cover, accumulating approximately 150 mm of water. Precipitation in May and September also caused an increase in the groundwater level; therefore, infiltration from the soil to the groundwater table was essential in the months from March to June and in September. In these months, the highest soil moisture (>6%) was recorded. Presumably, in the remaining months, infiltration was strongly limited or

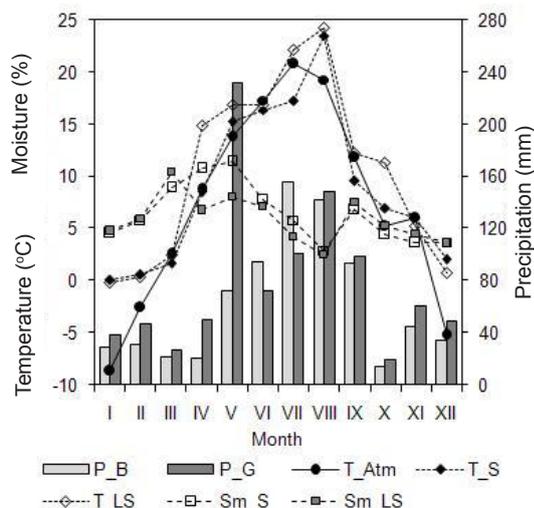


Fig. 1. Results of soil temperature measurements and soil moisture (% w/w) in 2010 (30 cm b.g.l.) on the background of mean air temperature (T_{Atm}) in the Lublin-Radawiec station and monthly precipitation in Guciów (P_G) and Bezek (P_B) near Janówka station (T_S – soil S temperature in Guciów, T_{LS} – soil LS temperature in Janówka, Sm_S – soil S moisture in Guciów, Sm_{LS} – Soil LS moisture in Guciów).

did not occur. The index of underground outflow reached a level of 120 mm in the Lublin Upland, and 120–160 mm in Roztocze (Michalczyk and Sposób, 2011).

Monthly measurements of the CO₂ concentration in the soil air and in the atmosphere were performed in the two selected fields of arable soil. Every three months, air samples were collected from both the soil and atmosphere for $\delta^{13}C$ analysis. The probes for sampling soil air (perforated plastic tubes 1 cm in diameter) were installed permanently. The probes extracted air from a depth of 0.3–0.6 m, below the root layer. Research on spatial diversity of CO₂ in soil air was performed twice in the neighbourhood of the stationary probe, by means of a mobile probe for soil air intake. Control measurements were performed in November 2009 (after installation of the stationary probe) and in July 2010. In the apexes of equilateral triangle with a 10 m side, in the middle of which the stationary probe was installed, the concentration of CO₂ was measured at a depth of 0.3, 0.4, 0.5, and 0.6 m – 12 measurements in total. Significance of the differences between the results of measurements by means of the stationary and mobile probes was checked using the Student t-test for individual samples. The compared mean values in Guciów and Janówka do not show significant differences at $p < 0.05$. Statistical analysis was performed using Statistica software ver. 6.0.

The extraction of soil water was performed by means of a Rhizon soil moisture sampler with a vacuum tube at a depth of 0.3 m. Two samplers were installed in each of the analyzed testing grounds. In the study period, sufficient samples of soil water were only obtained in March, April,

May, June, and September, and the value of the arithmetic mean for 5 analyses was taken for calculation of Ca-leaching from soils by infiltration waters. In the remaining months, an insufficient quantity of water was collected for analysis. The representativeness of the results of the chemical composition of the soil solution was checked on the basis of chemistry research of shallow hypodermic waters in the neighbourhood of the research areas. The Student t-test for two independent samples was used for comparison of DIC and Ca content in the analyzed soil waters and hypodermic waters in porous deposits.

Soil temperature was measured at a depth of 0.3 m in 3 points by means of a Hanna Instrument thermometer with a metal sensor. The result presented the mean value. Three soil samples were also taken from this depth for moisture determination. Laboratory measurements of soil moisture were performed in homogenized samples.

In the laboratory of the Department of Hydrology, Maria Curie-Skłodowska University in Lublin, pH was measured by means of a pH/Conductometer WTW InoLab 1, compatible with a pH electrode Hanna Instrument. Concentrations of anions, cations, and DIC were determined by ion chromatography (Metrohm MIC 3, Switzerland). Anions (sulphates, chlorides, nitrates) were separated by means of a Metrosep A Supp 5-250 column (suppressed, conductivity detection, injection volume 20 μ l). Cations (calcium, magnesium, sodium, potassium) were separated by means of a Metrosep C 2-150 column (non-suppressed, conductivity detection, injection volume 20 μ l). DIC was separated by means of a Transgenomic ICsep ICE-ION-310 column (non-suppressed, conductivity detection, injection volume 20 μ l). The forms of DIC (HCO_3^- , CO_3^{2-} , $CO_{2(aq)}$) were calculated with the application of the hydrochemistry software aqion (<http://www.aqion.de/>).

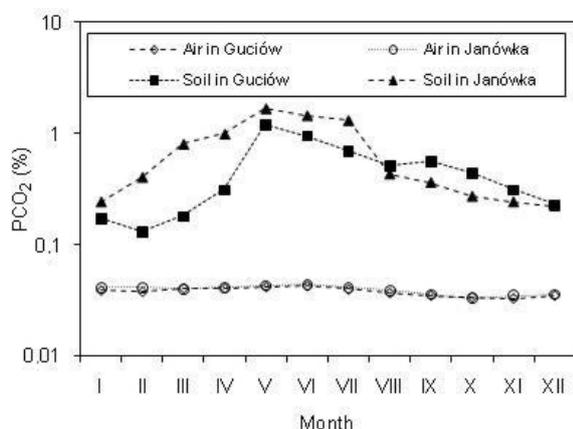
The carbon isotope analysis ($\delta^{13}C$ with respect to the VPDB standard) was performed on CO₂ gas cryogenically separated from ~60 ml air samples. The analysis was performed on a dual inlet and triple collector mass spectrometer at the Mass Spectrometry Laboratory at Maria Curie-Skłodowska University with precision of $\pm 0.06\%$ (standard deviation). Due to the low quantities of water extracted from the soil samples, $\delta^{13}C$ of DIC was not determined.

RESULTS AND DISCUSSION

Meteoric precipitation infiltrating through the soil leaches chemical compounds, which results in a change in the soil chemical composition. Fundamental transformations in the water-atmosphere-soil system result from the shift of the pressure of CO₂ gas (PCO_2) at the air-soil interface (Appelo and Postma, 1997; Langmuir, 1997). Soil PCO_2 is predominantly determined by the respiration of microorganisms and roots of plants (Bieganowski *et al.*, 2013). Seasonal variations of soil temperature and moisture (Fig. 1) adjusted the intensity of these living processes

Table 1. Characteristic values of the CO₂ concentration in atmospheric and soil air (based on monthly measurements in 2010, N=12)

Testing ground		Mean	Median	Standard		Min	Max
				Deviation	Error		
Guciów	Atmospheric air	0.038	0.039	0.003	0.001	0.033	0.043
Janówka		0.039	0.041	0.003	0.001	0.033	0.044
Guciów	Soil air	0.460	0.330	0.330	0.096	0.130	1.200
Janówka		0.830	0.880	0.520	0.154	0.220	1.750

**Fig. 2.** Changes of the CO₂ concentration in atmospheric (A) and soil (S, LS) air (%).

recorded by PCO₂ measurements (Table 1, Fig. 2). Soil temperature at the selected sites varied from 0 to 25°C. It was the lowest in January/February and the highest in July. Soil moisture varied from 2.5 to 10.4% in Guciów and from 3% to more than 11% in Janówka. The highest values were recorded in spring.

The CO₂ concentration in atmospheric air varied from 0.033 to 0.044%. The highest concentration was recorded in the period from January to July (predominantly above 0.04%). From August to December, the value was below 0.04%. The mean results of the CO₂ concentration measurements in soil air in Guciów and Janówka, according to the Student t-test for two independent samples ($p < 0.05$), do not show statistically significant differences ($t = -0.72$, $p = 0.47$).

The recorded PCO₂ in soil shows significantly higher seasonal variation than in atmospheric air. The CO₂ concentration in soil air varied from 0.13 to 1.75%. It was the lowest in winter and the highest in spring and summer during periods of enhanced vegetation. Soil temperature and its moisture have a significant influence on the PCO₂ concentration in the soil (Table 2). The mean results of CO₂ concentration measurements in the air of S and LS soils, according to the Student t-test for two independent samples

($p < 0.05$), show statistically significant differences ($t = -2.08$, $p = 0.049$). This can be an effect of various conditions of production and circulation of CO₂ in the analyzed soils (Dudziak and Hałas, 1996).

The isotopic ratio ¹³C/¹²C of atmospheric CO₂ varied from -8.88 to -10.12‰. In soil, it varied from -20.43 to -24.01‰. The lowest values were recorded in summer. The δ¹³C range observed in soil air suggests that organic matter responsible for CO₂ production is predominantly derived from the plant's photosynthesis according to the C₃ Calvin cycle (Deines, 1980). It also suggests that the investigated soils were not contaminated by oil products (Szarlip *et al.*, 2014). Moreover, these low values clearly demonstrate that the investigated soils are practically carbonate-free, because DIC in carbonate-rich groundwaters of the Lublin Upland and Roztocze have less negative values ranging from -11 to -16 δ¹³C (Staniaszek *et al.*, 1986), and yet the carbon isotope equilibrium between CO₂ and DIC would shift δ¹³C of CO₂ towards less negative values by approximately 9‰ (Szaran, 1997).

The soil waters were acidic and slightly acidic with mineralization (TDS – Total Dissolved Solids) in the range of fresh and ultra-fresh waters (Table 3). These waters had complex hydrochemistry with dominant Ca²⁺, Cl⁻, SO₄²⁻, NO₃⁻ ions and periodic occurrence of HCO₃⁻ and K⁺ ions. Ions, such as Cl⁻, NO₃⁻, SO₄²⁻, K⁺, are mainly of anthropogenic origin related to deposition of atmospheric pollution and agricultural land use.

The values of TDS in soil waters were lower by approximately 15-30% than in shallow hypodermic waters locally found in the neighbourhood of the testing grounds, mainly because of the concentration of ions related to carbonate dissociation (HCO₃⁻ and Ca²⁺). The recorded DIC in these waters varied from 5 mg dm⁻³ to more than 16 mg dm⁻³. Calculations by means of geochemical software aqion showed that CO_{2(aq)} was the dominant form of DIC (Fig. 3). In soil waters in Guciów, CO_{2(aq)} comprised approximately 80% of DIC and in Janówka near 70%. These values and water reaction suggest a low concentration of carbonates in the investigated soils (sometimes lack of carbonates) and their high aggressiveness to carbonate minerals.

Table 2. Correlation matrix between the analyzed soil characteristics, marked correlation coefficients are statistically significant for $p < 0.05$ (N=12)

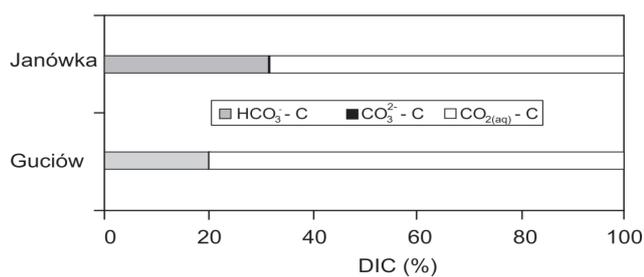
	T_S	T_LS	Sm_S	Sm_LS	S_CO ₂	LS_CO ₂
T_S	1.00	0.97	0.28	0.14	0.79	0.74
T_LS		1.00	0.38	0.27	0.74	0.77
Sm_S			1.00	0.55	0.85	0.66
Sm_LS				1.00	0.30	0.75
S_CO ₂					1.00	0.83
LS_CO ₂						1.00

T_S – S soil temperature, T_LS – LS soil temperature, Sm_S – soil S moisture, Sm_LS – LS soil moisture, S_CO₂ – CO₂ concentration in S soil, LS_CO₂ – CO₂ concentration in LS soil.

Table 3. Physical-chemical composition of soil water (N=5)

Parameter	Soil class					
	Sand			Loamy sand		
	Min-Max	Mean	SD (SE)	Min-Max	Mean	SD (SE)
pH	5.02-5.67	5.44	0.26 (0.12)	5.66-6.35	5.93	0.26 (0.12)
TDS	65-81	72	6.8 (3.0)	91-137	106	19 (8.4)
DIC	5.3-10.6	7.6	1.8 (0.8)	9.9-16.5	11.9	2.6 (1.2)
Cl ⁻	12.3-17.7	15.1	1.9 (0.9)	14.6-21.7	17.6	2.8 (1.2)
SO ₄ ²⁻	9.7-27.6	16.5	6.7 (3.0)	16.7-34.9	20.5	7.3 (3.2)
NO ₃ ⁻ (mg dm ⁻³)	9.8-16.5	14.9	1.4 (0.6)	15.9-23.6	18.8	2.9 (1.3)
Ca ₂ ⁺	5.9-12.4	9.6	2.4 (1.1)	14.2-19.8	17.6	2.1 (0.9)
Mg ₂ ⁺	0.6-1.2	0.9	0.2 (0.1)	0.8-1.7	1.0	0.4 (0.2)
Na ⁺	2.2-4.7	3.6	0.9 (0.4)	4.2-8.7	6.4	1.8 (0.8)
K ⁺	5.2-9.1	7.4	1.6 (0.7)	7.6-15.3	10.6	3.2 (1.4)

SD – standard deviation, SE – standard error.

**Fig. 3.** Weight percentage of basic forms of DIC (HCO₃⁻-C, CO₃²⁻-C, CO_{2(aq)}}-C) occurrence in soil waters.

The saturation indices with respect to the mineral phase of calcite (SI_{calcite}) were negative: below -4 and approximately -3 in Guciów and Janówka, respectively. Such low SI_{calcite} values suggest high potential of dissolution of carbonate minerals.

Ca-leaching from the investigated soils in 2010 was calculated based on the mean concentration of Ca²⁺ in five samples of soil water collected in the period from March to June and in September. The effective infiltration index was assumed to amount to 0.25 soil S and 0.2 soil LS of the annual total precipitation. These values include the range of mean groundwaters outflow in the analyzed area and information about effective infiltration of soils in the area of Poland published in the paper of Witczak and Żurek

Table 4. Ca-leaching from the soil by infiltration waters

Soil class			
Sand		Loamy sand	
Measured value for 960 mm precipitation in 2010	Estimated value for normal precipitation in Roztocze (700 mm)	Measured value for 750 mm precipitation in 2010	Estimated value for normal precipitation in the Lublin Upland (550 mm)
Ca-leaching (kg ha ⁻¹ year ⁻¹)			
23.0	16.8	26.4	19.4

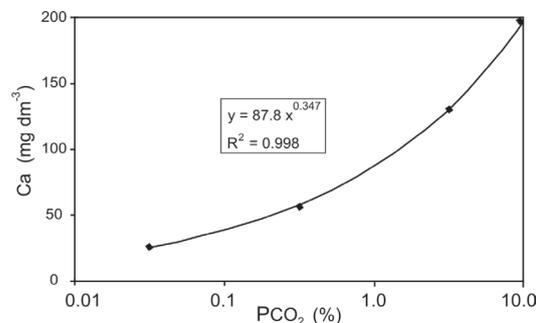
Table 5. Potential concentration of Ca in soil waters after the liming treatment on the background of the Ca concentration in underground (spring) waters draining massive carbonate rocks

Soil class					
Parameter	Sand			Loamy sand	
	Soil water	Groundwater		Soil water	Groundwater
Method of calculation	calculated		mean value for 4 springs	calculated	
	aqion*	Fig. 4		aqion*	Fig. 4
Ca ²⁺ (mg dm ⁻³)	70.8	67.5	77.8	79.0	102.2

Aqion* – geochemical software.

(1994). The decalcification amounted to 23.0 kg Ca ha⁻¹ year⁻¹ in soil S and 26.4 kg Ca ha⁻¹ year⁻¹ in soil LS (Table 4). For normal precipitation in the analyzed areas, values of Ca potential outflow will be lower by approximately 27%. The results of the research are characteristic for arable lands with extensive management, where N fertilising does not exceed 50 kg Ca ha⁻¹ year⁻¹.

The potential Ca²⁺ concentration in soil waters after the liming treatment was calculated with consideration of the following factors: physical-chemical composition, PCO₂ in soil, and SI_{calcite} = 0.0. The adopted SI_{calcite} value for modelling of the process of CaCO₃ dissolving/precipitation results from the fact that its value usually reaches the range ±0.2 in groundwaters circulating in carbonate rocks in the analyzed area. The modelling assumed that dissolving/precipitation of minerals occurred in open system conditions (Appelo and Postma, 1999) and the Ca concentration is only limited by the solubility of CaCO₃ for the treatment with calcite and/or dolomite as well as CaO. These calculations were performed with the application of the geochemical software aqion (Table 5). The software can also be used for the calculation of the concentration of Ca with no data on the ion composition in soil waters, having only the CO₂ content in the soil air. The correlation between PCO₂ in the soil and the concentration of Ca in water determined for the 'pure' H₂O-CO₂-CaCO₃ system was used for that purpose (Fig. 4). The calculations adopted a temperature of 10°C typical of soils in the climate conditions of the moderate zone.

**Fig. 4.** The relationship between PCO₂ in soil and dissolved Ca at a temperature of 10°C calculated with the application of the software (aqion).

The results of the calculations presented in Table 5 show that, after the lime application to the soil, the increase in the Ca concentration in soil S water is 7-fold higher in Guciów and 4-fold higher in Janówka. The findings of the model calculations of the Ca content in soil waters after the lime application were compared to the mean Ca concentration in groundwaters (measured in spring waters draining carbonate rocks). According to the Student t-test for individual samples ($p < 0.05$), the mean concentrations in Guciów and Janówka do not show statistically significant differences ($t = 2.39$, $p = 0.095$, and $t = 2.94$, $p = 0.060$, respectively). These results show that the assumed method for evaluation of the potential Ca concentration on the basis of PCO₂ in soil can be considered as correct.

Table 6. Ca-leaching from soil by infiltration waters and potential leaching after liming treatment

Parameter	Soil class					
	Sand			Loamy sand		
	Estimated value after liming for precipitation					
	600 mm – low	700 mm – normal	960 mm – high	450 mm – low	550 mm – normal	750 mm – high
Ca-leaching (kg ha ⁻¹ year ⁻¹)	106.2	123.9	169.9	71.1	86.9	118.5
Regression equation	Ca-leaching = 0.178 P – 0.46			Ca-leaching = 0.16 P – 1		

Using the results of modelling, the potential level of Ca-leaching from the analyzed soils after the lime application, depending on the total annual precipitation, was calculated to be 124 kg year⁻¹ ha⁻¹ in soil S and 87 kg year⁻¹ ha⁻¹ in soil LS (Table 6). The higher level of potential Ca-leaching from soil S is the result of higher precipitation in the Roztocze region than in the Lublin Upland and better conditions of infiltration in soil S than LS. In lime application at the level of 3000 kg CaO ha⁻¹ over 4 years, it can be leached over 5% of the applied fertilizers in 1 year. In the experimental research, a significant increase in Ca-leaching in arable lands after fertilizing with N was reported. In lysimetric experiments with sandy soil fertilized with NPK, Ca-leaching reached a level of 100-200 kg ha⁻¹ year⁻¹ (Pondel *et al.*, 1991). Somewhat lower values (74-144 kg ha⁻¹ year⁻¹) were recorded by Terelak *et al.* (2000) in the investigations of drained waters flowing from loess and clays.

CONCLUSIONS

1. The values of δ¹³C in soil CO₂ in the range from -20.43 to -24.01‰ indicate their biological origin and carbonate absence in the sand and loamy sand soils.
2. Ca-leaching from soil developed from sandy soil in Roztocze amounted to 23.0 kg ha⁻¹ in 2010.
3. Ca-leaching from soil developed from loamy sands in the Lublin Upland amounted to 26.4 kg ha⁻¹ in 2010.
4. The expected Ca-leaching from sandy soil for normal precipitation in Roztocze (700 mm) is estimated at a level of 124 kg ha⁻¹ year⁻¹.
5. The expected Ca-leaching from loamy sand soil for normal precipitation in the Lublin Upland (550 mm) is estimated at a level of 87 kg ha⁻¹ year⁻¹.
6. After liming treatment with ca. 3000 kg ha⁻¹ 4 year⁻¹ CaO, 16-23% of the applied fertilizer can be leached.
7. This study emphasises the need to consider Ca loss due to water infiltration.
8. The results may be used for estimation of Ca-leaching from soils developed from sand with an admixture of loamy sand and sand in temperate climatic zones.

REFERENCES

- Andrews J.A. and Schlesinger W.H., 2001.** Soil CO₂ dynamics, acidification, and chemical weathering in a temperate forest with experimental CO₂ enrichment. *Global Biogeochemical Cycles*, 15(1), 149-162.
- Anthoni P.M., Knohl A., Rebmann C., Freibauer A., Mund M., Ziegler W., Kolle O., and Schulze E.D., 2004.** Forest and agricultural land-use-dependent CO₂ exchange in Thuringia, Germany. *Global Change Biology*, 10(12), 2005-2019.
- Appelo C.A. and Postma D., 1999.** *Geochemistry, groundwater and pollution.* Balkema, Rotterdam, Brookfield.
- Bell J.N.B. and Treshow M., 2002.** *Air Pollution and Plant Life.* Wiley Press, New York, USA.
- Berner E.K. and Berner R.A., 1996.** *Global Environmental: Water, Air and Geochemical Cycles.* Prentice Hall, Upper Saddle River, NJ, USA.
- Bieganski A., Witkowska-Walczak B., Gliński J., Sokolowska Z., Sławiński C., Brzezińska M., and Włodarczyk T., 2013.** Database of Polish arable mineral soils: a review. *Int. Agrophys.*, 27, 335-350.
- Chirinda N., Plauborg F., Heckrath G., Elsgaard L., Thomsen K.I., and Olesen J., 2014.** Carbon dioxide in arable soil profiles: a comparison of automated and manual measuring system. *Communications Soil Science Plant Analysis*, 45(9), 1278-1291.
- Deines P., 1980.** The isotopic composition of reduced organic carbon. In: *Handbook of Environmental Isotope Geochemistry* (Eds P. Fritz, J.Ch. Fontes). Elsevier, Amsterdam-New York, 329-406.
- Dudziak A. and Hałas S., 1996.** Diurnal cycle of carbon isotope ratio in soil CO₂ in various ecosystems. *Plant Soil*, 183, 291-299.
- Filipek T. and Skowrońska M., 2013.** Current dominant causes and effects of acidification of soils under agricultural use in Poland (in Polish). *Acta Agrophysica*, 20(2), 283-294.
- Holubowicz-Kliza G., 2006.** *Soil liming in Poland* (in Polish). IUNG-PIB Press, Puławy, 1-61.
- Houghton R.A., 2007.** Balancing the global carbon budget. *Annual Review Earth Planetary Sci.*, 35, 313-347.
- Kesler T.J. and Harvey C.S., 2001.** The global flux of CO₂ into groundwater. *Geophysical Research Letters*, 28(2), 279-282.

- Langmuir D., 1997.** Aqueous environmental geochemistry. Prentice Hall, Inc., Simon Schuster/A Viacom Company, Upper Saddle River, NJ, USA.
- Michalczyk Z. and Sposób J., 2011.** Water resources in Poland and their state in Lublin District. Teka Kom. Ochr. Kszt. Środ. Przyr. – OL PAN, 8, 104-111.
- Pondel H., Ruszkowska M., Sykut S., and Terelak H., 1991.** Leaching of fertiliser components from soils based on the research of the Institute of Soil Science and Plant Cultivation (in Polish). Roczn. Glebozn., 42(3/4), 97-107.
- Prentice I.C., Farquhar G.D., Fasham M.J.R., Goulden M.L., Heimann M., Jaramillo V.J., and Wallace D.W., 2001.** The carbon cycle and atmospheric carbon dioxide. In: Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. PTGleb., 2008. Particle size distribution and textural classes of soils and mineral materials – classification of Polish Society of Soil Sciences (in Polish). Soil Sci. Ann., 60(2), 5-16.
- QBG, 2010.** Quarterly bulletin of groundwaters. Polish Hydrogeological Survey. 9(30), 8(29), 8(28), 8(27), 8(26), <http://www.psh.gov.pl>.
- Staniaszek P., Trembaczowski A., Lis J., Szaran J., and Hałas S., 1986.** Variability of the isotope composition of dissolved carbon in the carbonate waters of the Lublin Upland (in Polish). Przegląd Geologiczny, 34(3), 159-163.
- Stumm W. and Morgan J.J., 1996.** Aquatic chemistry: chemical equilibria and rates in natural waters. Wiley Press, New York, USA.
- Szaran J., 1997.** Achievement of carbon isotope equilibrium in the system HCO_3^- -(solution) – CO_2 -(gas). Chemical Geology, 142(1-2), 79-86.
- Szaran J., Dudziak A., Trembaczowski A., Niezgodą H., and Hałas S., 2005.** Diurnal variations of $\delta^{13}\text{C}$ and concentration of atmospheric and soil carbon dioxide in a meadow site. Geological Quarterly, 49(2), 135-144.
- Szarlip P., Stelmach W., Jaromin-Gleń K., Bieganski A., Brzezińska M., Trembaczowski A., Hałas S., and Łagód G., 2014.** Comparison of the dynamics of natural biodegradation of petrol and diesel oil in soil. Desalination Water Treat., 52(19-21), 3690-3697.
- Terelak H., Motowicka-Terelak M., Sadurski W., and Tujaka A., 2000.** Transport of mineral components from cultivated soils to infiltrating waters. State and anthropogenic changes of waters quality (in Polish). University of Łódź Press, 269-276.
- Tian D. and Niu S., 2015.** A global analysis of soil acidification caused by nitrogen addition. Environ. Res. Lett. 10, 024019. doi:10.1088/1748-9326/10/2/024019.
- Tkaczyk P. and Bednarek W., 2011.** Evaluation of soil reaction (pH) in the Lublin Region (in Polish). Acta Agrophysica, 18(1), 173-186.
- USDA, 2010.** Keys to Soil Taxonomy. US Dept. Agriculture, Natural Res. Cons. Serv., Washington, DC, USA.
- Witczak S. and Żurek A., 1994.** Use of soil - agricultural maps in the evaluation of protective role of soil for groundwaters (in Polish). In: Methodological basics of groundwater protection. AGH Press, Kraków, 155-170.