

**Thesis of doctoral (PhD) dissertation**

**APPLICATION OF A NEW SOIL ANALYTICAL METHOD IN SITE-SPECIFIC  
NUTRIENT MANAGEMENT**

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Debrecen, 2016

## **Introduction**

An essential element of site-specific management is to measure soil properties. One of the most important parts of site-specific management is nutrient management.

While some of the site characteristics can be constant in a farm level, the heterogeneity of the soil properties is high regarding different fields, and even in the same field.

Site-specific nutrient-management has a 100 year-old history in Hungary. Some pioneer of the fertilization experiments: Cserhádi Sándor (Cserhádi and Kosutány, 1887; Cserhádi, 1900), Sigmund Elek (Sigmund, 1904; 1930). Even in this time it was evident that agricultural soils are different in terms of fertility, and it should be taking into account during the planning of fertilization. The national fertilization advisory system was founded in 1979 and since nowadays it affects the nutrient management practice.

Calculation methods and factors were modified during the last years, but the extraction methods did not changed, however Hungarian scientists, in accordance with the international trends, studied the development and adaptation of new soil measurement methods.

Researchers of the Agricultural University of Debrecen started to study the well-known 0,01 M  $\text{CaCl}_2$  method in 1990. The advantages of this method are: the concentration of the salt solution is similar like the soil solution, therefore solubility is nearly the same; multielemental, therefore the macro elements and easily oxidizable organic nitrogen could be also measured; suspension could be easily filtered.

The aim of my study was to compare the conventional methods with the 0,01 M  $\text{CaCl}_2$  method and to measure the influence of soil- and agronomical factors on this relationship in a representative dataset and in long-term experiments.

I also aimed to prepare recommendations for the extension of soil measurement methods, and for site-specific nutrient management.

## **Materials and methods**

### ***Soil Information and Monitoring System***

The concept of the Soil Information and Monitoring System (SIMS) was developed in 1991 by the Institute of Soil Science and Agricultural Chemistry of the Hungarian Academy of Science. Soil sampling was started in 1992. The aim of the system was the evaluation and monitoring of the Hungarian soil conditions. Sampling sites characterize the chemical and physical properties of the Hungarian soils. From the 1236 sampling sites 865 are located in agricultural land. I measured soil samples from 629 sampling sites collected in 2004. I received the physical and chemical characteristics, AL-P, -K and soil type of these soils from the SIMS dataset.

### ***Long-term experiment of Karcag***

The long-term fertilization and crop rotation experiment is located in the Research Institute of Karcag of the University of Debrecen. The experiment was set up according to the guidelines National Fertilization Long-term Experiments in 1965, in split-plot arrangement and in four replications.

The B17 experiment is a wheat-corn-corn-wheat biculture and NPK long-term fertilization experiment. The treatments are presented in the 1. table. The nitrogen fertilizer was ammonium-nitrate in split application (50-50%, autumn-spring). Phosphorous and potassium was applied in autumn. For the 1<sup>st</sup> and 3<sup>rd</sup> replications lime was applied in the 20<sup>th</sup> (14,5 t ha<sup>-1</sup>) and 32<sup>nd</sup> (11 t ha<sup>-1</sup>) of the experiment. The primary tillage was plowing.

The experimental soil is meadow chernozem (FAO: Luvic Phaeosem), saline in the deeper layers. The depth of the humus containing layer is 90 cm. Humus content is 2,5-2,9%, therefore the N-supply is medium. According to the AL-P and -K the P- and K-supply capacity of the soil is very weak and good, respectively (Buzás et al., 1979). The KCl-pH is 5-5,5. Soil texture is clay-loam, and the limit of plasticity is 47.

**1. table:** NPK treatments of the B17 experiment of Karcag (kg NPK ha<sup>-1</sup>) (1971-)

Treatments	1971-1987			1987-		
	N	P	K	N	P	K*
N <sub>0</sub> P <sub>0</sub> K <sub>0</sub>	-	-	-	-	-	-
N <sub>1</sub> P <sub>0</sub> K <sub>0</sub>	50	-	-	100	-	-
N <sub>1</sub> P <sub>1</sub> K <sub>0</sub>	50	22	-	100	26	-
N <sub>1</sub> P <sub>2</sub> K <sub>0</sub>	50	44	-	100	52	-
N <sub>2</sub> P <sub>0</sub> K <sub>0</sub>	100	-	-	150	-	-
N <sub>2</sub> P <sub>1</sub> K <sub>0</sub>	100	22	-	150	26	-
N <sub>2</sub> P <sub>2</sub> K <sub>0</sub>	100	44	-	150	52	-
N <sub>3</sub> P <sub>0</sub> K <sub>0</sub>	150	-	-	200	-	-
N <sub>3</sub> P <sub>1</sub> K <sub>0</sub>	150	22	-	200	26	-
N <sub>3</sub> P <sub>2</sub> K <sub>0</sub>	150	44	-	200	52	-
N <sub>1</sub> P <sub>0</sub> K <sub>1</sub>	50	-	83	100	-	83/166
N <sub>1</sub> P <sub>1</sub> K <sub>1</sub>	50	22	83	100	26	83/166
N <sub>1</sub> P <sub>2</sub> K <sub>1</sub>	50	44	83	100	52	83/166
N <sub>2</sub> P <sub>0</sub> K <sub>1</sub>	100	-	83	150	-	83/166
N <sub>2</sub> P <sub>1</sub> K <sub>1</sub>	100	22	83	150	26	83/166
N <sub>2</sub> P <sub>2</sub> K <sub>1</sub>	100	44	83	150	52	83/166
N <sub>3</sub> P <sub>0</sub> K <sub>1</sub>	150	-	83	200	-	83/166
N <sub>3</sub> P <sub>1</sub> K <sub>1</sub>	150	22	83	200	26	83/166
N <sub>3</sub> P <sub>2</sub> K <sub>1</sub>	150	44	83	200	52	83/166
N <sub>4</sub> P <sub>3</sub> K <sub>2</sub>	200	65	83	250	79	83/207

\* Remark: 83 kg K/ha for winter wheat 166 /207 kg K/ha for corn

Soil sampling was made in each year (2007-2009) after harvest. I received the CEC values of the soils for the 2007 year and the AL-P and -K for the 2007 and 2008 years from the researchers of the Institute. Winter wheat was seeded in 2007-2008 and corn was planted in 2009-2010.

### *Long-term experiment of Hajdúböszörmény*

The NPK fertilization and plant density experiment was set up by Dr. Sárvári Mihály in Hajdúböszörmény.

The 3-factorial experiment has three replications in strip design. The plots of two varieties, PR38A79 (FAO 300) and PR37Y12 (FAO 390), from the 8 corn hybrid existing in the experiment, were sampled. The NPK treatments are presented in the 2<sup>nd</sup> table.

**2. Table:** NPK treatments of the long-term experiment of Hajdúböszörmény  
(kg NPK ha<sup>-1</sup>) (1989-)

Treatments	N	P	K
N <sub>0</sub> P <sub>0</sub> K <sub>0</sub>	0	0	0
N <sub>40</sub> P <sub>11</sub> K <sub>25</sub>	40	10.9	24.9
N <sub>80</sub> P <sub>22</sub> K <sub>50</sub>	80	21.8	49.8
N <sub>120</sub> P <sub>33</sub> K <sub>75</sub>	120	32.7	74.7
N <sub>160</sub> P <sub>44</sub> K <sub>100</sub>	160	43.6	99.6
N <sub>200</sub> P <sub>55</sub> K <sub>125</sub>	200	54.5	124.5

Fertilization was made in spring, and plant residue was mixed into the soil. The primary tillage was plowing.

The experimental soil was meadow (FAO: Luvic Phaeosem). The humus containing layer is 50 cm deep. According to the humus content (3,5%) the N-supply is good. According to the AL-P and -K contents of the soil the P- and K-supply capacity are weak and very weak, respectively (BUZÁS et al., 1979). The pH of the soil in KCl is 6,1. Soil texture is clay and the limit of plasticity is 54. The average depth of water table is. The soil sampling was made in 2010 spring, before fertilization and planting.

### *Analytical methods*

Soil measurements were made on the chemical laboratory of the Department of Agrochemistry and Soil Science, University of Debrecen.

*Soil preparation:* After soil sampling we stored the samples in plastic bags, than air dried them. After sieving (<2mm) we stored samples in paper bags.

*0,01 M CaCl<sub>2</sub> method:* 0,01 M CaCl<sub>2</sub> soil extraction was made according to Houba et al. (2000). 5 g of prepared soil was shaken with 50 ml of solution for 2 hours.

After 10 minutes of centrifugation (2500 rpm) (MLW T54, NDK) we collected the supernatant solution for further analysis. N- and P-content was measured by a Continuous Flow Analyzer (Scalar SAN<sup>PLUS</sup>SYSTEM, Scalar, Breda, the Netherlands). Total N content was determined after UV-destruction. Total N contains the inorganic fractions (NO<sub>3</sub>-N + NH<sub>4</sub>-N) and the easily extractable organic N fraction (N<sub>org</sub>). N<sub>org</sub> is the difference of total N and inorganic N.

K content was measured after filtering and the precipitation of Ca by oxalic acid by a UNICAM-SP95B (Pye Unicam Ltd., Cambridge, England) spectrophotometer.

### *Calculation of nutrient balance*

I calculated the nutrient-balance of the long-term experiments. The agronomical nutrient balance was calculated by the difference of the plant nutrient uptake and nutrient content of the fertilizers, that doesn't take into account other inputs or outputs. Agronomic balance shows if fertilization could cover the plant uptake.

Nutrient mobilization and other inputs (nutrient content of seed, atmospheric deposition, N-fixation of microbes) could be take into account in the net nutrient balance by the nutrient uptake of plants in the control treatment (Németh, 1995).

### *Statistical analysis*

For the statistical analysis I used the SPSS 13. program. Normality test was performed by Kolmogorov Smirnov test and graphical methods. Outliers were filtered by box-plot graph. Extreme outliers were excluded from further analysis.

Relationship between different extraction methods was measured by correlation and regression analysis.

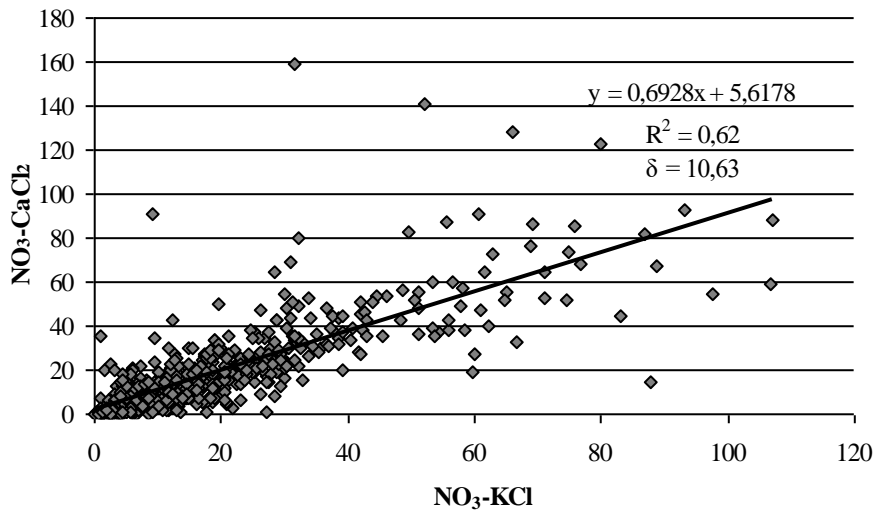
In long-term experiments the effect of treatments was measured by One-Way ANOVA and General Linear Model. Post-hoc analysis was performed by Duncan test.

The relationship between  $N_{org}$  (dependent variable) and the most important physical and chemical soil characteristics was studied by PLS regression (Esposito Vinzi et al., 2010). With this method we create latent variables (components) which are related with the explanatory variables. Components that explains more than 1% of the variance of  $N_{org}$  are included into the model.

## Results

### *Soil Information and Monitoring System*

The relationship between the  $\text{NO}_3\text{-N}$  contents extracted by 0,01 M  $\text{CaCl}_2$  and 1 M  $\text{KCl}$  is shown on the Figure 1. The correlation was close on the studied dataset ( $r=0,79$ ).



**Figure 1:** Relationship between  $\text{CaCl}_2\text{-NO}_3\text{-N}$  and  $\text{KCl-NO}_3\text{-N}$  ( $\text{mg kg}^{-1}$ ) ( $n=632$ )

Remark: Correlation is significant in the  $P \leq 0.001$  significance level  
 $\delta$  – Standard error of the estimate

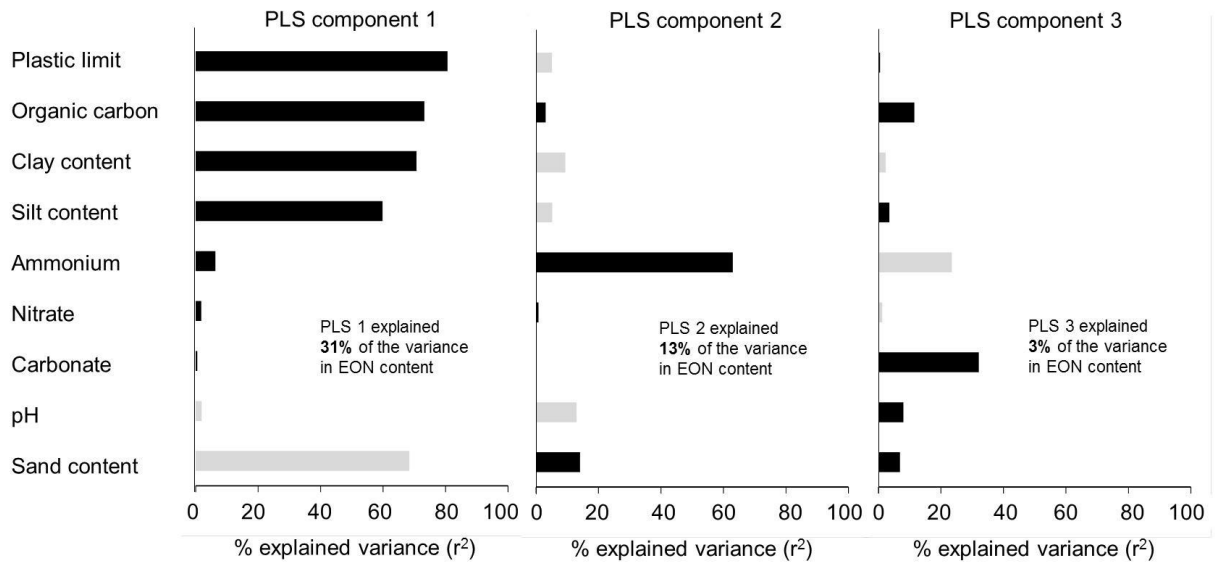
In spite of the methodological differences – including soil:extractant ratio, concentration, extraction time –  $\text{NO}_3\text{-N}$  extracted by different methods are in the same order of magnitude.

To investigate the role of 0.01 M  $\text{CaCl}_2$  extractable organic N it is important to know the factors influencing the amount of  $\text{CaCl}_2\text{-N}_{\text{org}}$ . Among factors discussed in the literature the effect of soil properties could be studied on the SIMS dataset.

There was a medium correlation between  $\text{CaCl}_2\text{-N}_{\text{org}}$  and humus content ( $r = 0.59$ ), weak correlation between  $\text{CaCl}_2\text{-N}_{\text{org}}$  and limit of plasticity ( $r = 0.49$ ), clay, silt and sand contents ( $0.26 < r < 0.40$ ).

There were significant correlations between explanatory variables, therefore PLS regression was performed to eliminate this effect. 47% of the variance of  $\text{CaCl}_2\text{-N}_{\text{org}}$

could be explained by the components. The relationship between the soil properties and the components is presented in Figure 2.



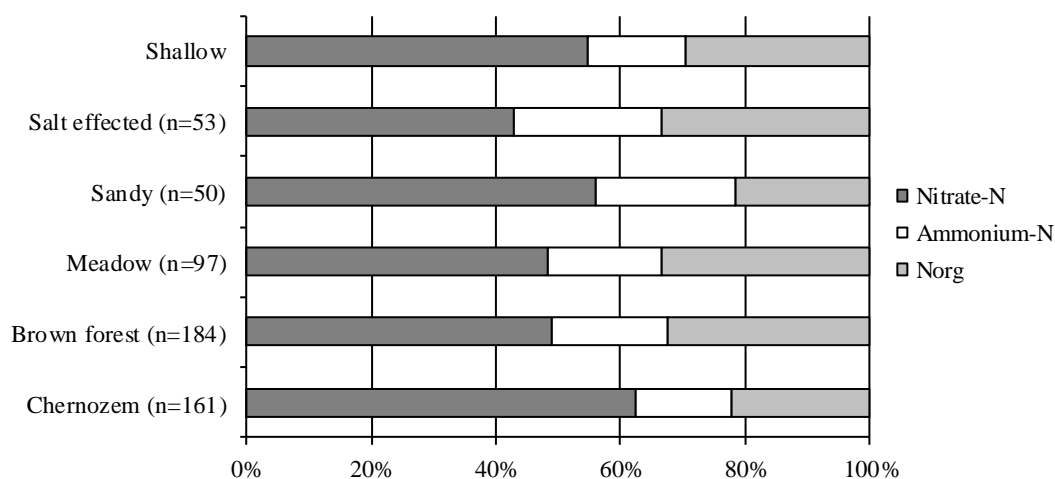
**Figure 2.** Explained variance for all variables in the model of extractable organic N, which explained 47% of the variation in EON.

Remark: Bars with the same color are positively related to each other within the component (black bars are positively correlated with EON, grey ones are negatively correlated with EON).

The most important soil properties affected  $\text{CaCl}_2\text{-N}_{\text{org}}$  fraction were soil texture related factors (clay, silt, loam-content and limit of plasticity) and humus content. There were a negative correlation with sand content and positive with silt, clay, plastic limit and humus. This result suggests that mineralization circumstances affects  $\text{CaCl}_2\text{-N}_{\text{org}}$  fraction.

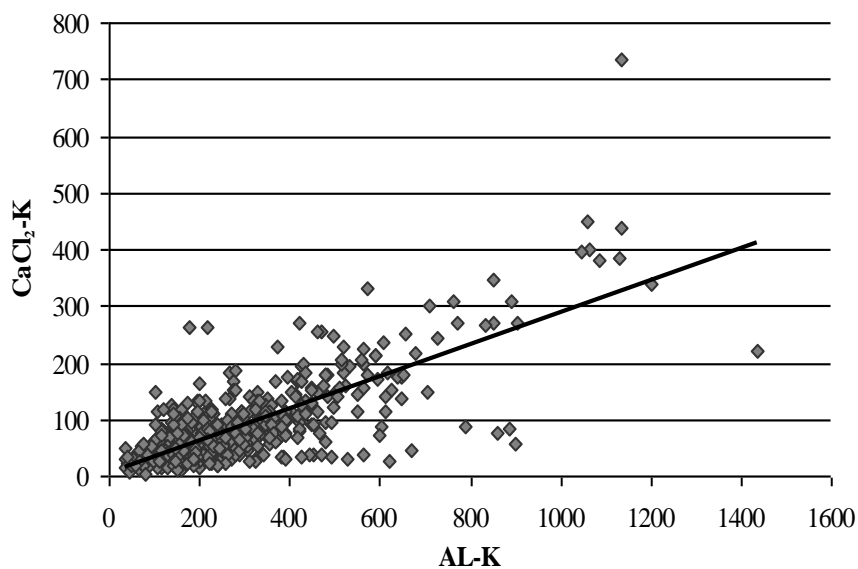
Ratios of the different N fractions on different soil types are presented in Figure 3. The total  $\text{CaCl}_2$ -extractable N contains  $\text{NO}_3\text{-N}$ . The ratio of  $\text{CaCl}_2\text{-N}_{\text{org}}$  (20-33%) was between the  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ , which suggests that extractable organic N couldn't be neglected in plant nutrition. The ratio of  $\text{CaCl}_2\text{-N}_{\text{org}}$  was 33% on meadow soils.





**Figure 3:** Ratios of CaCl<sub>2</sub>-N fractions on different soil types

The relationship between K contents extracted by the conventional AL method and 0,01 M CaCl<sub>2</sub> is presented on Figure 4. The K content extracted by the AL, which is a stronger extractant was on average three times higher than that of CaCl<sub>2</sub>.



**Figure 4:** Relationship between AL-K and CaCl<sub>2</sub>-K

The regression equation between the K contents extracted by different methods:

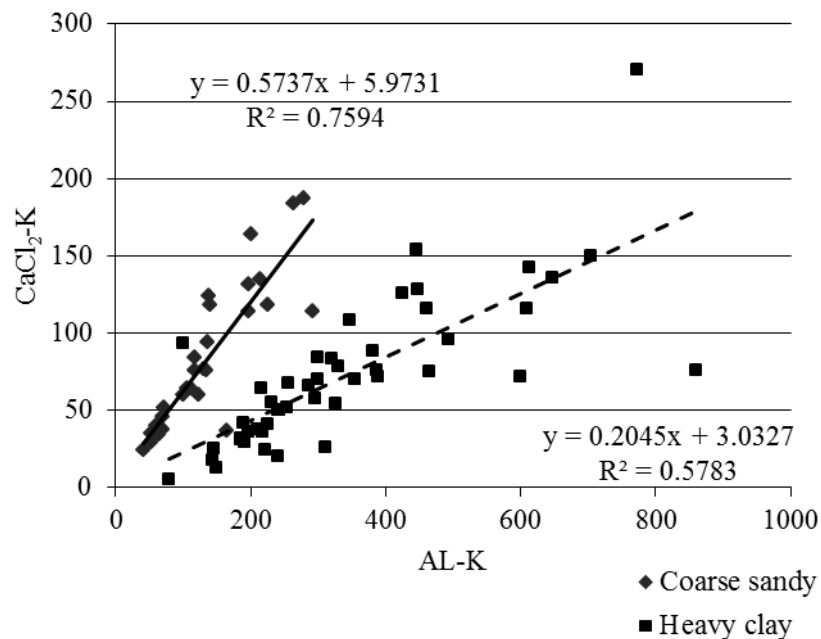
$$Y (\text{CaCl}_2\text{-K}) = 0.282 \text{ AL-K} + 5.42 \quad R^2 = 0.58 \quad \delta = 51.2$$

Soil physical and chemical properties have a different effect on the extractable K. Soils were divided into soil texture classes based on limit of plasticity. The average K contents and the ratios of K extracted by different methods are presented in Table 3. While soil texture affected AL-K the 0,01 M CaCl<sub>2</sub>-K was constant.

**Table 3: The amount and the ratio of AL and 0,01 M CaCl<sub>2</sub>-extracted K (mg kg<sup>-1</sup>) as a function of soil texture**

Soil texture	N	CaCl <sub>2</sub> -K (mg kg <sup>-1</sup> )			AL-K (mg kg <sup>-1</sup> )			AL-K/CaCl <sub>2</sub> -K
		average	min.	max.	average	min.	max.	
Coarse sand	48	83.1	24	187	151	37	527	1.8
Sand	51	74.3	12	230	162	36	439	2.2
Sandy loam	107	78.4	9	440	238	41	1136	3.0
Loam	146	87.8	11	400	291	50	1200	3.3
Clay loam	149	87	15	450	313	65	1438	3.6
Clay	86	88.1	15	736	332	58	1135	3.8
Heavy clay	45	72.6	5	270	340	78	860	4.7
Total	629	83.2	-	-	276	-	-	3.3

It is a well-known fact that in case of the same exchangeable K there is more K in the soil solution of a sandy soil than that of a clay soil. Exchangeable K usually increase by the increasing clay content, but the soluble K doesn't follow this tendency. The reason of this fact is that clay soils fix K more than light-textured soils. The regression on coarse sand and heavy clay soils can describe the differences (Figure 5). We can see that the same CaCl<sub>2</sub>-K results in a relatively lower AL-K on the heavy clay soil than that of on a sandy soil, therefore it can be concluded that CaCl<sub>2</sub>-K is mainly related to easily available K and AL-K related to the amount of K reserves.



**Figure 5:** Relationship between AL-K and CaCl<sub>2</sub>-K (mg kg<sup>-1</sup>) on coarse sand and heavy clay soils

The relationship between pH and K contents are presented in Table 4. 0.01 M CaCl<sub>2</sub>-K was constant but the AL-K increased as a function of pH.

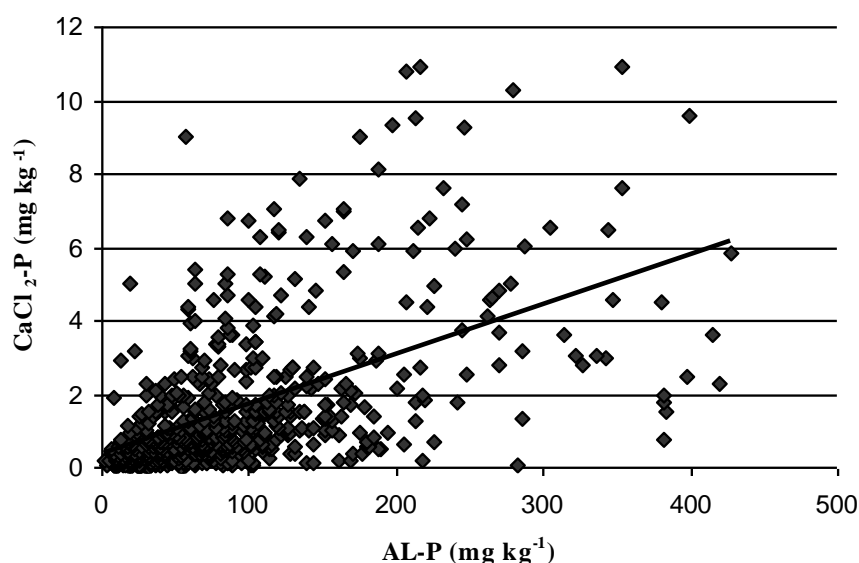
**Table 4:** The amount and ratio of AL- and 0,01 M CaCl<sub>2</sub>-K (mg kg<sup>-1</sup>) as a function of pH

pH <sub>KCl</sub>	N	CaCl <sub>2</sub> -K (mg kg <sup>-1</sup> )			AL-K (mg kg <sup>-1</sup> )			AL-K/ CaCl <sub>2</sub> -K
		average	min.	max.	average	min.	max.	
Very acidic	69	83.1	24	255	151.2	40	518	1.8
Acidic	109	74.3	18	398	161.7	70	1046	2.2
Slightly acidic	147	78.4	5	385	238	37	1200	3
Neutral	123	87.8	14	345	290.6	36	1438	3.3
Slightly alkaline	181	87	9	736	312.9	37	1136	3.6
Total	629	83.2	-	-	275.9	-	-	3.3

A huge difference was found between the amounts of CaCl<sub>2</sub>-P and AL-P (Figure 6).

CaCl<sub>2</sub>-P was less than 2% of AL-P. The regression equation was the following:

$$Y (\text{CaCl}_2\text{-P}) = 0.0137 \text{ AL-P} + 0.3478 \quad R^2 = 0.31 \quad \delta = 1.71$$



**Figure 6:** Regression between AL-P and CaCl<sub>2</sub>-P (n = 622)

CaCl<sub>2</sub>- and AL-P contents of soils as a function of carbonate content are demonstrated on Table 5. CaCl<sub>2</sub>-P decreased as a function of increasing carbonate content, which is in accordance with the solubility of phosphate compounds. In contrast, the amount of AL-P was bigger on soils with high carbonate content. The ratio of AL-P and CaCl<sub>2</sub>-P increased as a function of increasing carbonate content. It can be explained by the acidic characteristic of AL, which allows to soluble P-reserves, like Ca-phosphates.

**Table 5:** CaCl<sub>2</sub>-P and AL-P contents and ratios of AL-P and CaCl<sub>2</sub>-P as a function of carbonate content

Carbonate content	N	CaCl <sub>2</sub> -P (mg kg <sup>-1</sup> )			AL-P (mg kg <sup>-1</sup> )			AL/CaCl <sub>2</sub>
		average	min.	max.	average	min.	max.	
No carbonate	302	1.86 <sup>a*</sup>	0.01	18.5	68 <sup>a</sup>	1.3	510	37
Less carbonate	148	1.69 <sup>a</sup>	0.05	11.0	110 <sup>bc</sup>	8.7	470	65
Medium carbonate	142	1.31 <sup>a</sup>	0.01	6.8	130 <sup>c</sup>	7.4	420	99
High carbonate	30	0.69 <sup>b</sup>	0.05	6.8	96 <sup>b</sup>	19.2	227	141
Total	622	1.64			94			57

\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

### *Long-term experiment of Karcag*

The 0.01 M CaCl<sub>2</sub> extractable NO<sub>3</sub>-N, NH<sub>4</sub>-N, N<sub>org</sub> contents and total N in 2007-2009 are presented in Table 6.

**Table 6:** Effect of long-term N fertilization on 0.01 M CaCl<sub>2</sub> extractable N fractions in the long-term experiment of Karcag B17. (2007-2009)

Treatments (kg N ha <sup>-1</sup> )	NO <sub>3</sub> -N (mg kg <sup>-1</sup> )	SD*	NH <sub>4</sub> -N (mg kg <sup>-1</sup> )	SD*	N <sub>org</sub> (mg kg <sup>-1</sup> )	SD*	N <sub>total</sub> (mg kg <sup>-1</sup> )	SD*
2007								
N <sub>0</sub>	4.5	a	2.16	a	2.82	a	9.5	a
N <sub>100</sub>	8.7	b	3.47	b	3.08	a	15.3	b
N <sub>150</sub>	13.6	c	4.56	b	3.06	a	21.3	c
N <sub>200</sub>	22.8	d	4.33	b	3.38	b	30.5	d
N <sub>250</sub>	34.7	e	6.08	ab	4.47	c	45.2	e
Average	15.5		4.12		3.22		22.8	
2008								
N <sub>0</sub>	4	a	3.16	a	4.62	a	11.8	a
N <sub>100</sub>	7.7	b	6.11	a	5.26	ab	19.1	b
N <sub>150</sub>	9.7	bc	5.23	a	5.22	ab	20.2	b
N <sub>200</sub>	11.7	c	6.22	a	5.78	b	23.7	bc
N <sub>250</sub>	13.1	c	6.43	a	7.27	c	26.8	c
Average	9.6		5.75		5.47		20.8	
2009								
N <sub>0</sub>	6.2	a	1.47	a	4.48	a	12.2	a
N <sub>100</sub>	11.2	ab	2.31	a	3.59	a	17.1	ab
N <sub>150</sub>	15	bc	2.18	a	3.98	a	21.2	ab
N <sub>200</sub>	19.6	cd	3.3	a	4	a	26.9	bc
N <sub>250</sub>	23	d	4.68	a	4.67	a	32.4	c
Average	15.2		2.65		3.93		21.8	
2007-2009 (average)								
N <sub>0</sub>	4.9	a	2.26	a	3.98	a	11.1	a
N <sub>100</sub>	9.2	b	3.96	a	3.97	a	17.1	b
N <sub>150</sub>	12.8	b	3.99	a	4.09	a	20.9	b
N <sub>200</sub>	18.0	c	4.62	a	4.39	a	27.0	c
N <sub>250</sub>	23.6	d	5.73	a	5.47	b	34.8	d
Average	13.4		4.17		4.21		21.8	

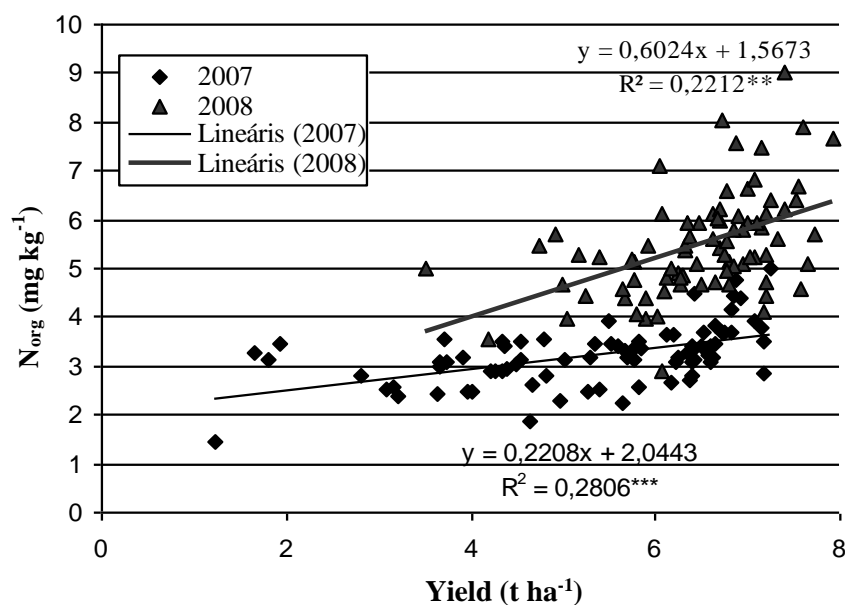
\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

In 2007, 2008 and 2009 each N rate increased significantly the amounts of NO<sub>3</sub>-N and N<sub>total</sub> fractions, however there were smaller differences between the NO<sub>3</sub>-N and

$N_{\text{total}}$  contents of different treatments in 2008 and 2009. The highest  $\text{NO}_3\text{-N}$  content was detectable in 2007, which could be explained by the drought in 2007 April. This is the period of intensive tillering and stem extension, therefore drought stress in this stage decreased N-uptake dramatically.

The amounts of  $N_{\text{org}}$  fraction were significantly affected by N-fertilization in 2007 and 2008, which could be explained by the indirect effects of fertilization. N fertilization increases the root development and intensive rooting increases microbiological activity as well. The indirect effect of N-fertilization proven by the significant relationship between winter wheat yield and  $N_{\text{org}}$  in 2007 ( $r=0.53$ ) and in 2008 ( $r=0.47$ ). Regression was studied between the yield and  $N_{\text{org}}$  because yield is strongly related to total biomass production (Figure 7).

The relationship between corn yield in 2009 and  $N_{\text{org}}$  could not be proven. The straw was harvested in the experiment, therefore the different results could be explained by the different rooting and depth of active root zone of the winter wheat and corn. However the total biomass/root production of corn is usually higher, winter wheat roots are mainly concentrated in the upper soil layer. The active root system and the increased microbial activity in the shallow soil layer increased the easily extractable organic N, which was sampled and measured during this study.



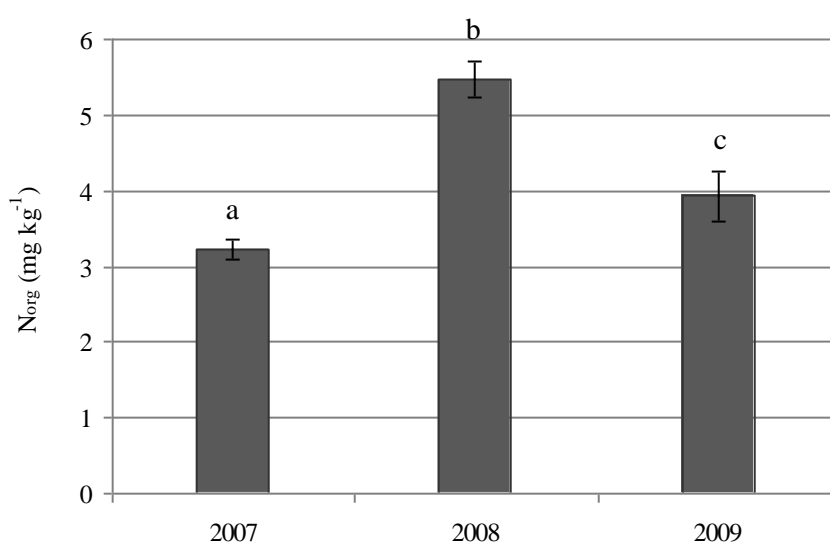
**Figure 7:** Relationship between the yield of winter wheat and  $N_{\text{org}}$  content after harvest (n=160) (2007, 2008)

\*\* Correlation is significant in the P=0,01 significance level

\*\*\* Correlation is significant in the P=0,001 significance level

Earlier measurements proved that the growing season affects  $N_{org}$  fraction, which could be explained by the effects of precipitation and temperature on biomass production and microbiological activity. Seasonal changes of  $N_{org}$  could be detected in the long-term experiment of Karcag (Figure 8). Average  $N_{org}$  contents of the different years were significantly different. The average  $N_{org}$  content of 2008 was 70% higher than that of in 2007.

It can be concluded that in a given growing site seasonal effect is the most important factor influencing  $N_{org}$ .



**Figure 8:** Average  $N_{org}$  content in 2007-2009

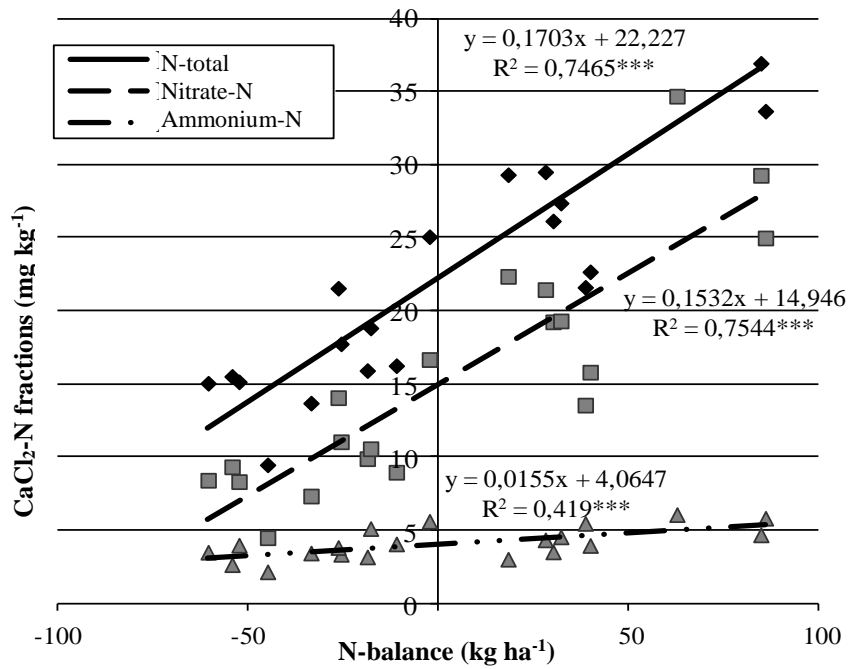
Error bars represents the confidence interval (P=5%)

\*Significant difference: Averages signed with the same letter didn't differ on the  $p \leq 5\%$  significance level

Relationship between agronomic N balance and  $CaCl_2$ -N fractions was studied by regression analysis (Figure 9, 10, 11). In 2007 there was close correlation between agronomic N balance,  $CaCl_2$ - $N_{total}$  and  $NO_3$ -N ( $r=0.86$ ;  $r=0.87$ ), while medium correlation was found between N balance and  $NH_4$ -N ( $r=0.65$ ).

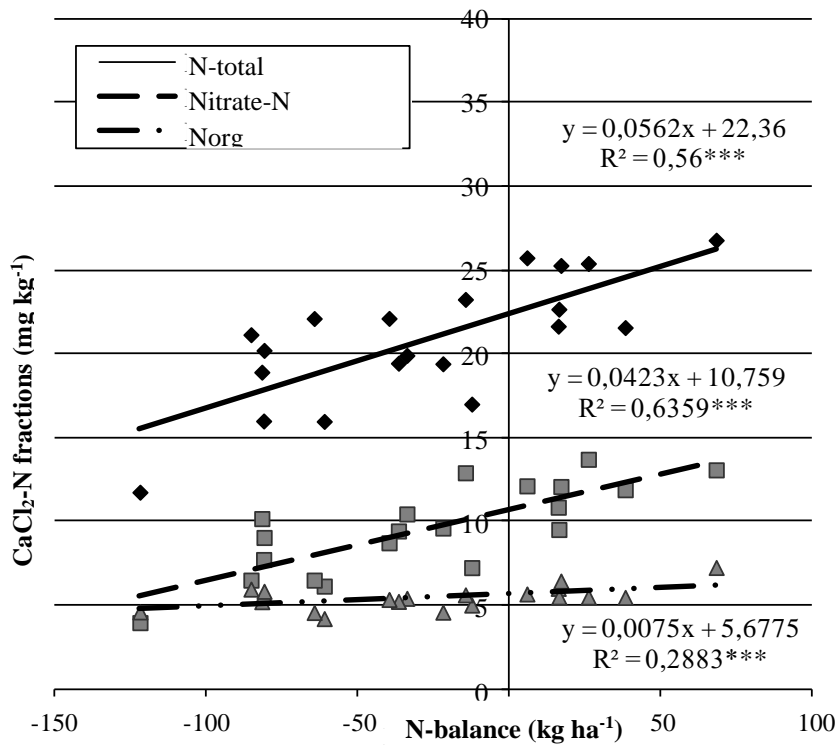
$CaCl_2$ - $N_{total}$  and  $NO_3$ -N were closely related to N balance in 2008 as well ( $r=0.75$ ;  $r=0.8$ ), but the steepness of the curve was lower. In 2008  $N_{org}$  and N balance were also related ( $r=0.54$ ).

There were significant, close relationship between N balance,  $CaCl_2$ - $N_{total}$  and  $NO_3$ -N in 2009 ( $r=0.93$ ;  $r=0.93$ ).



**Figure 9:** Relationship between CaCl<sub>2</sub>-N fractions and agronomic N balance (n=20; 2007)

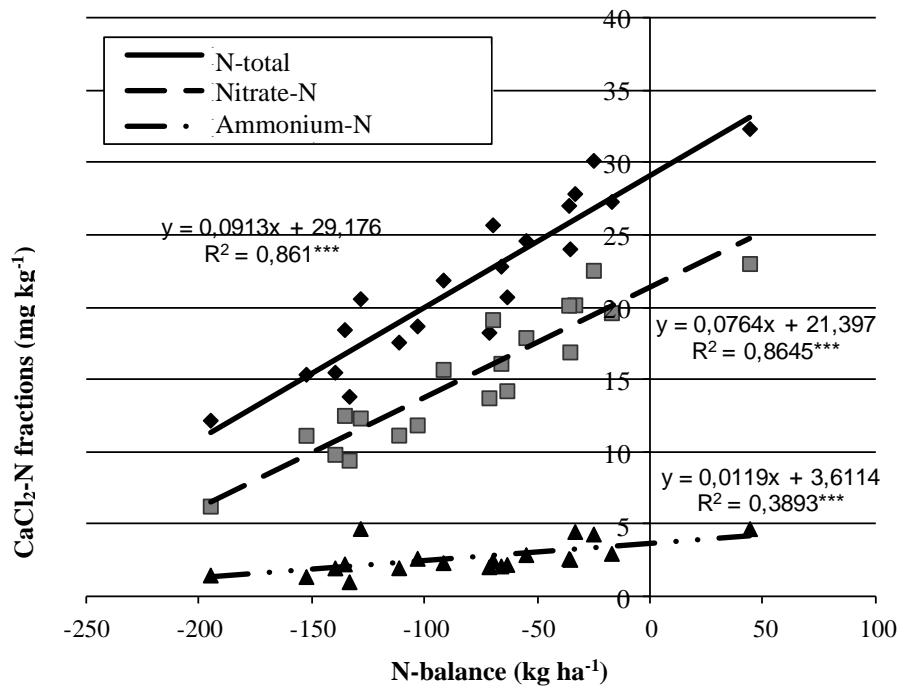
\*\*\* Correlation is significant in the P=0.001 significance level



**Figure 10:** Relationship between CaCl<sub>2</sub>-N fractions and agronomic N balance (n=20; 2008)

\*\*\* Correlation is significant in the P=0.001 significance level





**Figure 11:** Relationship between CaCl<sub>2</sub>-N fractions and agronomic N balance (n=20; 2009)

\*\*\* Correlation is significant in the P=0.001 significance level

The close relationship between CaCl<sub>2</sub>-N<sub>total</sub> and agronomic N balance prove that the decreasing or increasing of soil N reserves causes the decrease or increase in the amount of CaCl<sub>2</sub>-N<sub>total</sub>, while the regression equations were different in each year. However soil properties are constant, the seasonal effects causes significant differences between years.

Average amounts of CaCl<sub>2</sub>-P and AL-P in each year are demonstrated in Table 8. It can be concluded that AL-P increased consequently an an effect of increasing P fertilizer rates, CaCl<sub>2</sub>-P only increased as an effect of higher P rates.

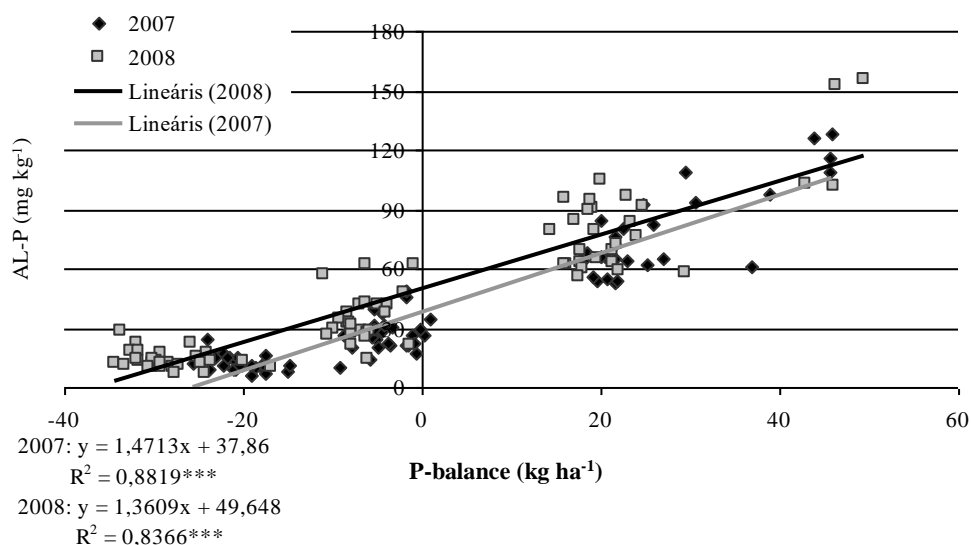
**Table 8:** Effect of long-term P-fertilization on the amounts of 0.01 M CaCl<sub>2</sub> and AL extractable P, yield and agronomic P balance in the long-term experiment of Karcag (2007-2009)

Treatments (kg P ha <sup>-1</sup> )	Yield (t ha <sup>-1</sup> )	P balance** (kg ha <sup>-1</sup> )	CaCl <sub>2</sub> -P (mg kg <sup>-1</sup> )	SD*	AL-P (mg kg <sup>-1</sup> )	SD*	AL-P/CaCl <sub>2</sub> -P
2007 (winter wheat)							
P <sub>0</sub>	3.8	-18.4	1.04	a	13.8	a	13
P <sub>22</sub>	6.1	-3.3	1.10	a	35.6	b	32
P <sub>44</sub>	6.0	23.6	1.57	b	76.0	c	48
P <sub>66</sub>	6.9	45.2	4.27	c	127.9	d	30
Average	5.3		1.38		44.7		32
2008 (winter wheat)							
P <sub>0</sub>	5.9	-28.4	0.96	a	12.8	a	13
P <sub>22</sub>	6.8	-6.5	0.95	a	29.5	b	31
P <sub>44</sub>	6.8	19.9	1.67	b	71.2	c	43
P <sub>66</sub>	6.7	46.2	5.65	c	119.7	d	21
Average	6.5		1.40		40.7		29
2009 (corn)							
P <sub>0</sub>	9.0	-50.9	0.97	a			
P <sub>22</sub>	9.5	-27.6	0.93	a			
P <sub>44</sub>	9.2	0.4	1.31	b			
P <sub>66</sub>	8.2	31.8	2.23	c			
Average	9.1		1.12				
2007-2009							
P <sub>0</sub>		-97.7	1.04	a			
P <sub>22</sub>		-37.4	1.10	a			
P <sub>44</sub>		43.9	1.57	b			
P <sub>66</sub>		123.1	4.27	c			
Average			1.38				

\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

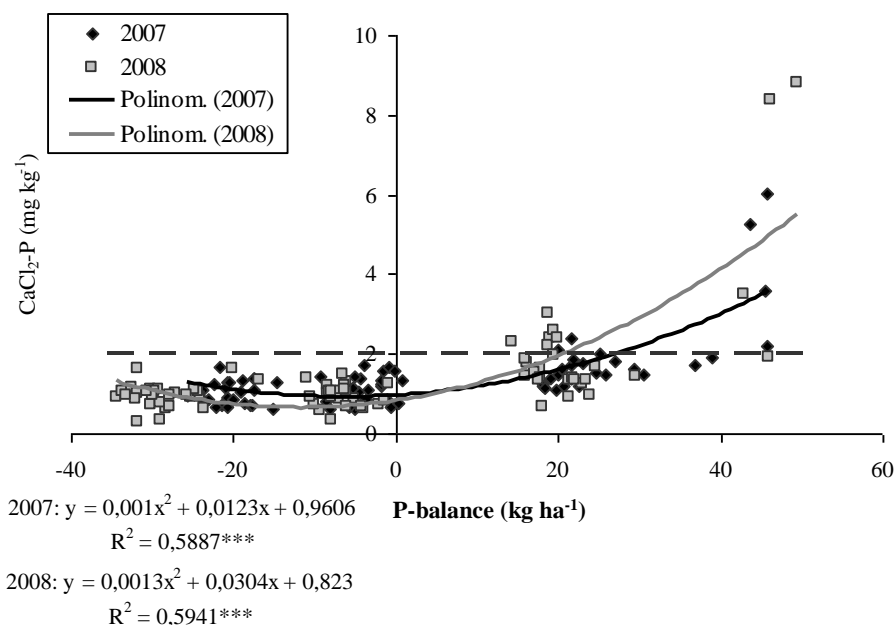
\*\* Agronomic P balance: difference of the P fertilizer rate and plant P uptake

Relationship between the agronomic P balance and P extracted by CaCl<sub>2</sub> and AL was measured by regression analysis (Figure 12, 13, 14). There was a close significant relationship between AL-P and P balance ( $r_{2007}=0.94$ ;  $r_{2008}=0.92$ ). The relationship was linear, and proved that AL-P is closely related to the changes in P reserves.



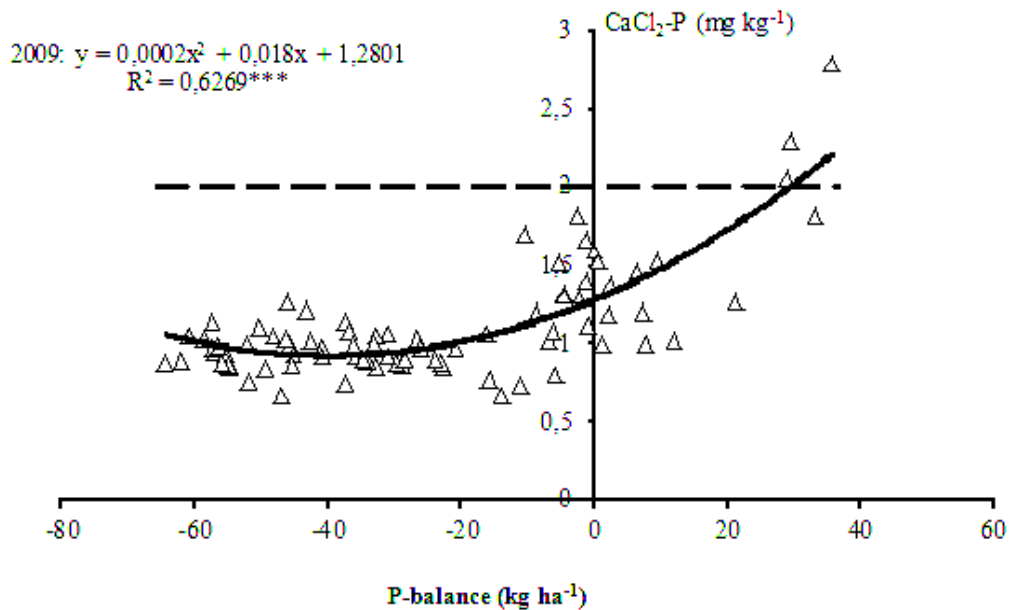
**Figure 12:** Relationship between AL-P and agronomic P balance (n=80; 2007-2009)  
 \*\*\* Correlation is significant in the P=0.001 significance level

The relationship between P balance and  $\text{CaCl}_2\text{-P}$  was non-linear ( $r_{2007}=0.77$ ;  $r_{2008}=0.77$ ;  $r_{2009}=0.79$ ) and significant (Figure 13, 14), but the correlation was less close than in case of AL-P.



**Figure 13:** Relationship between  $\text{CaCl}_2\text{-P}$  and agronomic P balance (n=80; 2007, 2008), and preliminary P-limits according to Jaszberenyi and Loch (2001) (2 mg  $\text{kg}^{-1}$ )  
 \*\*\* Correlation is significant in the P=0.001 significance level

In 2009 the P balance was mainly negative as an effect of high corn nutrient uptake. In accordance with the negative P balance CaCl<sub>2</sub>-P amount was low (Figure 16).



**Figure 14:** Relationship between CaCl<sub>2</sub>-P and agronomic P balance (n=80; 2009), and preliminary P-limits according to Jaszberenyi and Loch (2001) (2 mg kg<sup>-1</sup>)  
 \*\*\* Correlation is significant in the P=0.001 significance level

Two replications of the experiment were treated by CaCO<sub>3</sub>, therefore the effect of liming, K fertilization and the interaction of them could be measured. Both factors (P≤0.001) and the interaction (P≤0.05) affected the amount of CaCl<sub>2</sub>-K and only K fertilization affected the amount of AL-K (P≤0.001). The amounts and ratio of CaCl<sub>2</sub>-K and AL-K are represented in Table 9.

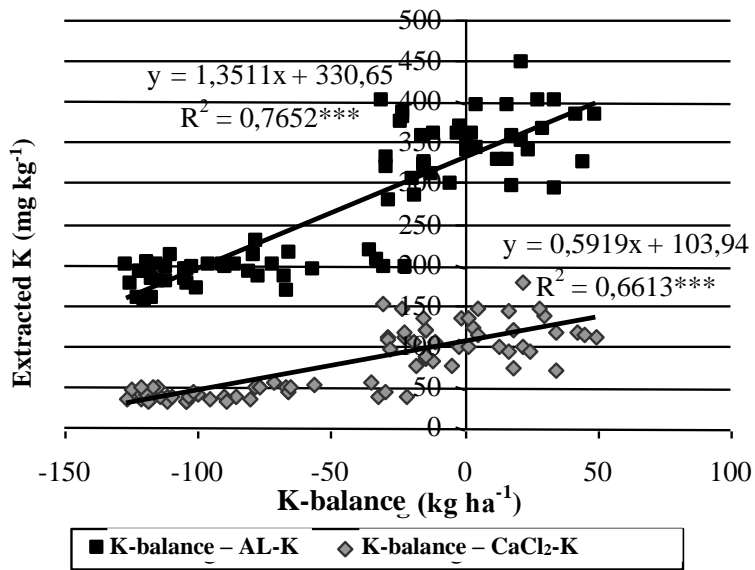
**Table 9:** Effect of long-term K-fertilization on the amounts of 0.01 M CaCl<sub>2</sub> and AL extractable K, yield and agronomic K balance in the long-term experiment of Karcag (2007-2009)

Treatments (kg K ha <sup>-1</sup> ; liming)	Yield (t ha <sup>-1</sup> )	K balance** (kg ha <sup>-1</sup> )	CaCl <sub>2</sub> -K (mg kg <sup>-1</sup> )	SD*	AL-K (mg kg <sup>-1</sup> )	SD*	AL-K/CaCl <sub>2</sub> -K
2007 (búza)							
K <sub>0</sub>	5.2	-77.3	46	a	182	a	4.0
K <sub>0</sub> + liming	5.3	-78.5	37	b	197	a	5.3
K <sub>83</sub>	5.7	-1.4	129	c	356	b	2.7
K <sub>83</sub> + liming	5.2	4.7	95	d	339	b	3.6
Average	5.3		77		269		3.5
2008 (búza)							
K <sub>0</sub>	6.8	-101.5	57	a	198	a	3.5
K <sub>0</sub> + liming	6.1	-91.2	45	a	199	a	4.4
K <sub>83</sub>	6.8	-19.0	150	b	357	b	2.4
K <sub>83</sub> + liming	6.2	-9.6	117	c	333	b	2.8
Average	6.5		92		272		3.0
2009 (kukorica)							
K <sub>0</sub>	9.2	-167.0	52	a			
K <sub>0</sub> + liming	9.8	-178.3	42	b			
K <sub>166</sub>	8.2	-66.5	98	c			
K <sub>166</sub> + liming	9.5	-90.3	75	d			
Average	9.2		66				
2007-2009							
K <sub>0</sub>		-115.3	51	a			
K <sub>0</sub> + liming		-116.0	41	b			
K <sub>83/166</sub>		-29.0	126	c			
K <sub>83/166</sub> + liming		-31.7	96	d			
Average			78				

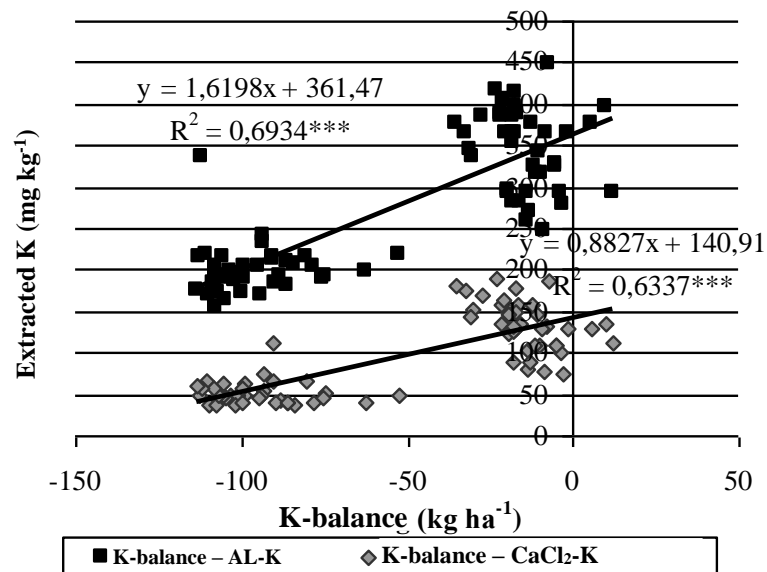
\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

\*\* Agronomic K balance: difference of the K fertilizer rate and plant K uptake

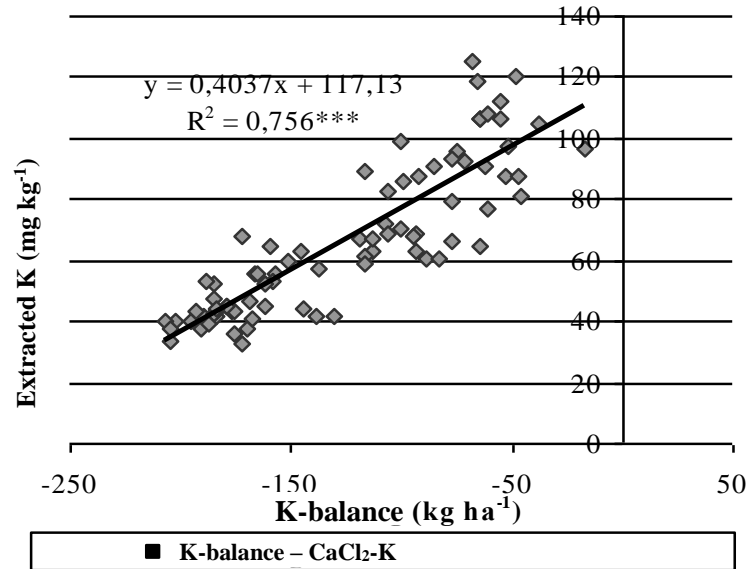
Relationship between K balance, CaCl<sub>2</sub>-K and AL-K are presented in Figure 15, 16 and 17. There was significant close correlation between CaCl<sub>2</sub>-K, AL-K and agronomic K balance. Both methods indicated well the changes in K reserves.



**Figure 15:** Relationship between agronomic K balance, CaCl<sub>2</sub>-K and AL-K (2007)  
 \*\*\* Correlation is significant in the P=0.001 significance level



**Figure 16:** Relationship between agronomic K balance, CaCl<sub>2</sub>-K and AL-K (2008)  
 \*\*\* Correlation is significant in the P=0.001 significance level



**Figure 17:** Relationship between agronomic K balance, CaCl<sub>2</sub>-K and AL-K (2009)  
 \*\*\* Correlation is significant in the P=0.001 significance level

### *Long-term experiment of Hajdúböszörmény*

Average amounts of 0.01 M CaCl<sub>2</sub> extractable N fractions of the different NPK treatments are shown on Table 10. Average inorganic N fraction was less than that of in the Karcag experiment, while yields in the same year were higher. Only the highest N rate could increase CaCl<sub>2</sub>-N<sub>total</sub>.

Agronomic N balances are also presented on the Table. The N balance was negative in each treatment.

**Table 10:** Effect of fertilization on CaCl<sub>2</sub> extractable N fractions (n=24; 2010)

Treatments	Yield (t ha <sup>-1</sup> )	N balance (kg ha <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> -N		NH <sub>4</sub> <sup>+</sup> -N		N <sub>org</sub>		N <sub>total</sub>	
			SD*	SD*	SD*	SD*	SD*	SD*		
N <sub>0</sub> P <sub>0</sub> K <sub>0</sub>	5.1	-120	3.31	a	0.99	a	6.46	a	10.76	a
N <sub>40</sub> P <sub>11</sub> K <sub>25</sub>	9.4	-206	3.86	a	2.03	a	6.14	a	12.04	a
N <sub>80</sub> P <sub>22</sub> K <sub>50</sub>	9.9	-172	3.93	a	1.47	a	5.97	a	11.37	a
N <sub>120</sub> P <sub>33</sub> K <sub>75</sub>	10.1	-133	4.18	a	2.00	a	6.29	a	12.47	a
N <sub>160</sub> P <sub>44</sub> K <sub>100</sub>	9.9	-84	4.01	a	1.20	a	6.05	a	11.25	a
N <sub>200</sub> P <sub>55</sub> K <sub>125</sub>	10.1	-55	7.06	b	3.66	b	6.89	a	17.60	b
<b>Average</b>			4.39		1.89		6.30		12.58	

\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

\*\* Agronomic N balance: difference of the N fertilizer rate and plant N uptake

The amounts of CaCl<sub>2</sub>-P, AL-P and the agronomic P balance are presented in Table 11. Long-term fertilization didn't increase CaCl<sub>2</sub>-P and AL-P increased only as an

effect of highest rate. P balance was negative in each treatment, which could be explained by the high yields. The CaCl<sub>2</sub>-P contents of the experimental soil were compared to the preliminary P limits according to Jászberényi and Loch (2001). The preliminary limit value on clay and pH 6-7 soils is between 0,5 and 1 mg kg<sup>-1</sup>. The amount of CaCl<sub>2</sub>-P was higher than the limit value suggesting that phosphorous is not a limiting factor in the studied experiment.

**Table 11:** Effect of fertilization on CaCl<sub>2</sub>- and AL-P (n=24, 2010.)

Treatments	P balance (kg ha <sup>-1</sup> )	CaCl <sub>2</sub> -P	SD*	AL-P	SD*
		(mg kg <sup>-1</sup> )			
N <sub>0</sub> P <sub>0</sub> K <sub>0</sub>	-62	0.71	a	55.3	ab
N <sub>40</sub> P <sub>11</sub> K <sub>25</sub>	-118	1.68	a	31.5	a
N <sub>80</sub> P <sub>22</sub> K <sub>50</sub>	-111	0.95	a	35.8	a
N <sub>120</sub> P <sub>33</sub> K <sub>75</sub>	-101	1.14	a	53.1	ab
N <sub>160</sub> P <sub>44</sub> K <sub>100</sub>	-87	0.77	a	62.8	ab
N <sub>200</sub> P <sub>55</sub> K <sub>125</sub>	-82	1.37	a	84.4	b
<b>Average</b>	-94	1.10		53.8	

\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

\*\* Agronomic P balance: difference of the P fertilizer rate and plant P uptake

The average CaCl<sub>2</sub>-K and AL-K amounts and agronomic K balance are presented in Table 12. As an effect of highest fertilizer rate both K fractions increased significantly.

I compared CaCl<sub>2</sub>-K values to the preliminary K limit values determined by Jászberényi et al (1999) on the basis of long-term experiments. For clay soils they suggested the 50-60 mg kg<sup>-1</sup> value. The amount of CaCl<sub>2</sub>-K didn't reach this value in the experiment. According to the AL-K value the K-supply capacity of the soil is weak. The weak K-supply of the soil and smectite-dominated clay mineral composition explains low CaCl<sub>2</sub>-K values.



**Table 12:** Effect of fertilization on CaCl<sub>2</sub>- and AL-K (n=24, 2010.)

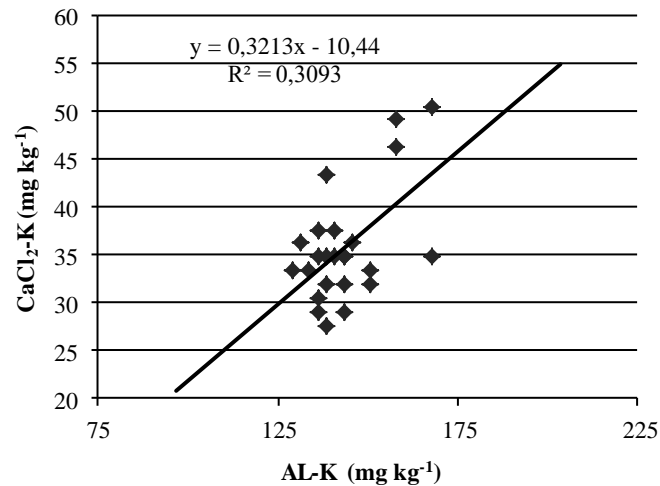
Treatments (kg NPK ha <sup>-1</sup> )	K balance** (kg ha <sup>-1</sup> )	CaCl <sub>2</sub> -K (mg kg <sup>-1</sup> )	SD*	AL-K (mg kg <sup>-1</sup> )	SD*	AL-K/ CaCl <sub>2</sub> -K
N <sub>0</sub> P <sub>0</sub> K <sub>0</sub>	-106	30.8	a	138.6	ab	4.5
N <sub>40</sub> P <sub>11</sub> K <sub>25</sub>	-191	37.3	a	140.4	ab	3.8
N <sub>80</sub> P <sub>22</sub> K <sub>50</sub>	-172	33.3	a	135.0	a	4.1
N <sub>120</sub> P <sub>33</sub> K <sub>75</sub>	-148	35.1	a	142.2	ab	4.1
N <sub>160</sub> P <sub>44</sub> K <sub>100</sub>	-115	32.6	a	149.5	bc	4.6
N <sub>200</sub> P <sub>55</sub> K <sub>125</sub>	-99	45.2	b	156.2	c	3.5
<b>Average</b>	-139	35.7		143.7		4.0

\*Significant difference: Averages signed with the same letter didn't differ on the p≤5% significance level

\*\* Agronomic K balance: difference of the K fertilizer rate and plant K uptake

Correlation between AL- and 0.01 M CaCl<sub>2</sub>-K was presented on Figure 18. Correlation was linear and medium (r=0.56). In the experiment of Karcag I found a close correlation between the different K fractions (r=0.93-0.95). These results could be explained with the differences between the clay mineral compositions of the two soils. While the soil of Hajdúböszörmény experiment is clay, and it has high K reserves, the dominated clay mineral is smectite, which fixate K. In the soils of Karcag experiment dominated clay mineral is illite, which has a good K-supply.

The ratio of AL-K and CaCl<sub>2</sub>-K was 4.

**Figure 18:** Regression between CaCl<sub>2</sub>-K and AL-K (n=24; 2010.)

## **New and novel scientific results**

1. According to the results it could be stated that 0.01 M CaCl<sub>2</sub> extracted P- and K- contents couldn't be calculated from the AL-P and -K contents with regression analysis.
2. It can be concluded that 0.01 M CaCl<sub>2</sub>-N<sub>total</sub> fraction was mainly related to fertilization.
3. It was demonstrated that the amount of CaCl<sub>2</sub>-N<sub>org</sub> was between the NO<sub>3</sub>-N and NH<sub>4</sub>-N fractions, on control soils it was 33% of the CaCl<sub>2</sub>-N<sub>total</sub> fraction, therefore the amount of CaCl<sub>2</sub>-N<sub>org</sub> couldn't be neglected in N-supply.
4. According to the results of a representative dataset and long-term experiments CaCl<sub>2</sub>-N<sub>org</sub> fraction was mainly related to soil texture and soil organic matter content and in a given soil it could be modified by seasonal effects, fertilization and crop rotation.

## **Practical scientific results**

1. It can be concluded that  $\text{CaCl}_2\text{-N}_{\text{total}}$  fraction is closely related to fertilization and agronomic N balance, therefore this parameter could be a useful tool to the determination of side dressing and topdressing N rates.
2. According to the results, 0.01 M  $\text{CaCl}_2$  method is able to detect the environmentally harmful surplus P content of soil.
3. In contrast with the AL-K, the amount of  $\text{CaCl}_2\text{-K}$  is not related to soil texture or the pH of soil, therefore 0.01 M  $\text{CaCl}_2$  could be a complementary method besides AL for the determination of K-supply of soils.

## Publications in the topic of the thesis

### Scientific papers in Hungarian reviewed journals in foreign language

- Berta-Szabó, E., Zsigrai, Gy., Szabó, A., Loch, J. (2010): Effects of long-term K fertilization and liming on the extractable and exchangeable K contents of a Haplic Phaeosem soil. *Agrártudományi Közlemények/Acta Agraria Debreceniensis*. 141–145. Debrecen. ISSN: 1588–8363.
- Berényi, S., Bertáné Szabó, E., Pepó, P., Loch, J. (2011): Effect of fertilization and irrigation on N fractions determined in 0.01 M calcium chloride on lowland pseudomycelial chernozem. *Agrokémia és Talajtan, 60. Supplementum*, 191-202.
- Bertáné Szabó E., Sipos P., Kovács B., András D., Győri Z. (2012): Recent Results to the Evaluation of the Long-Term Effects of Metal Pollution in Tisza River. *Acta Phytopathologica et Entomologica Hungarica*, 47./2. 355-362.

### Scientific papers in Hungarian reviewed journals

- Bertáné Szabó E., Berényi S., Loch J. (2009): A 0,01 M kalcium-klorid és Baker–Amacher kivonószerek alkalmazásának lehetőségei a növények számára hasznosítható kálium meghatározásában. *Agrártudományi Közlemények*, 36. 7-15.
- Bertáné Szabó E., Berényi S., Loch J. (2009): A 0,01 M CaCl<sub>2</sub>, a Baker–Amacher és az ammónium-laktát-ecetsav (AL) kivonószerekben oldható K-tartalom összehasonlítása. *Agrokémia és Talajtan*, 58./1. 45-56.
- Berényi S., Bertáné Szabó E., Pepó P., Loch J. (2009): A trágyázás és öntözés tartamhatása a 0,01 M kalcium-kloridban oldható N-frakciókra alföldi mészlepedékes csernozjom talajon. *Agrokémia és Talajtan*, 58./2. 251-264.
- Bertáné Szabó, E., Loch, J., Zsigrai, Gy., Blaskó, L. (2010): Effects of long-term fertilization on the yield of winter wheat and N forms on Luvic Phaeosem soil determined in 0.01 M CaCl<sub>2</sub>. *Agrokémia és Talajtan*, 59./1. 135-144.
- Bertáné Szabó E. (2010): Tartam trágyázás hatása a különböző kivonószerekkel mérhető foszfor tartalom változására réti csernozjom talajon. *Agrártudományi Közlemények*, 41. 7-11.

### Scientific papers in reviewed journals in foreign language

- Loch, J., Bertáné Szabó, E., Pirkó, B. (2009): Nitrogen advisory fertilizer system and monitoring in Hungary. *Fertilizers and Fertilization*, 37. 59-72.
- Bertáné Szabó, E., Loch, J., Pirkó, B. (2009): Experiences with the determination of nitrogen by 0,01 M CaCl<sub>2</sub> extractant in Hungarian soils and long-term experiments. *Fertilizers and Fertilization*, 37. 182-194.
- Bertáné Szabó, E., Berényi, S., Erdeiné Kremper, R., Balláné Kovács, A., Loch J. (2009): The effect of fertilization and irrigation on the change of NO<sub>3</sub>-N determined in 0.01 M CaCl<sub>2</sub> of the soil profile. *Analele Universităţii din Oradea, Fascicula: Protecția Mediului*, 14. 25-31.
- Bertáné Szabó, E., Kremper, R., Loch, J. (2010): Possibilities of the determination of plant available soil potassium content. *Fertilizers and Fertilization*, 40. 34-44.

Bertáné Szabó, E., Győri, Z., Kremper, R., Zsigrai Gy., Loch, J. (2014.): *Assessment of Environmentally Harmful Nitrogen Surplus by 0.01 M Calcium Chloride Soil Extractant in Long-Term Experiments. Communications in Soil Science and Plant Analysis*, 45. 1453-1463.

Reviewed conference proceedings in foreign language:

Bertáné Szabó, E., Berényi, S., Erdeiné Kremper, R., Balláné Kovács, A., Loch J. (2009): *The effect of fertilization and irrigation on the change of NO<sub>3</sub>-N determined in 0.01 M CaCl<sub>2</sub> of the soil profile. Poster on the International Symposium „Risk factors for environment and food safety” & „natural resources and sustainable development”, Oradea, Romania. Abstract Book. 30-37.*

Bertáné Szabó E., Berényi S., Győri Z., Kremper R., Loch J. (2011): *Assessment of environmentally harmful N surplus by 0.01 M CaCl<sub>2</sub> soil extractant in long-term experiments. Poster on the 12th International Symposium on Soil and Plant Analysis. Abstract Book. 61.*

Bertáné Szabó E., Fekete I., Sipos P., Andrási D., Győri Z., Kovács B. (2012): *Long-term effects of contamination from mining accidents on the contents of Zn, Cu, Pb and Cd in a floodplain soil of the river Tisza (Hungary). Poster on the 9th International Symposium on Environmental Geochemistry. Abstract Book. 207-208. ISBN: 978-972-789-365-2.*

Győri Z., Boros N., Bertáné Szabó E., Sipos P. (2012): *Long term effect of metal pollution in the catchment area of Tisza River. 8th International Soil Science Congress on "Land Degradation and Challenges in Sustainable Soil Management" Proceedings Book. 228-232.*

Reviewed conference proceeding in Hungarian language:

Berényi S., Szabó E., Kremper R., Loch J. (2008): *A talaj kálium ellátottságának vizsgálata módosított Baker-Amacher és 0,01 M CaCl<sub>2</sub> egyensúlyi kivonószerek alkalmazásával. Talajvédelem, Különszám. Talajtani Vándorgyűlés Nyíregyháza, Szerk.: Simon László, Talajvédelmi Alapítvány, Bessenyei György Könyvkiadó, Nyíregyháza. 369.-374.*

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