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Leaching of chemical elements under some anthropogenic impacts on Fluvisols

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Abstract

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The aim of the study was to estimate the effect of long-term fertilizer application on the content and leaching of chemical elements with lysimetric water after maize grown as monoculture.

The pilot site is Tsalapitsa village (near town of Plovdiv) in Southern Bulgaria. The experimental design included one control variant and two variants with fertilizer $-(N_{100}P_{75}; N_{200}P_{150} \text{ kg.ha}^{-1})$ on Fluvisols. The investigation has been carried out in 2019 year. The field plots were equipped with Ebermeir lysimeters at 50 and 100 cm depth from the surface of the soil. Lysimetric water samples are taken several times a year depending on the amount of infiltrate.

Experimental data shows that the lysimetric water after maize growth could be defined as calcium-hydrocarbonate composition. The reaction of the lysimetric water is neutral and tendency of decreasing of pH values was observed as a result of the long-term use of fertilizers. The ions of calcium, nitrates, sulphates and bicarbonates are prevalent and the content of magnesium, potassium, sodium and chloride are low. The research shows that the highest content and leaching of nitrate nitrogen with lysimetric water (18.8 kg.ha⁻¹) were obtained under variant (N₂₀₀P₁₅₀). The highest calcium losses (42.0 kg.ha⁻¹) are observed under the same treatment from 0-100 cm soil layer.

The different fertilized rates and type of land use are among the factors that influenced elements leaching and losses.

The obtained results show that the relative order of migration of the elements has the following form: Ca > S > N > Mg > Cl > Na > K.

Keywords: chemical elements; fertilizer rates; leaching; order of migration

Introduction

In recent years, the question of the impact of anthropogenic loading on the quality of the environment has been increasingly raised. Authors indicate the need to developing of new criteria and standards for setting acceptable limits for impacts on agroecosystems. According to Stoicheva et al. (2006), Zhao et al. (2010), Piccini et al. (2016) and Singh et al. (2018) the liquid phase in soil is an important diagnostic parameter and it can be used to give information on an early prognosis of the possible change that may occur. However, from an ecological point of view, the impact of the strength of anthropogenic load with nitrogen fertilizers can be assessed based on the established conditions for migration of chemical elements under one-meter soil layer.

Many studies (Stoicheva et al., 2003; Oenema et al., 2005; Cameron et al., 2008; Müller et al., 2015; Simeonova et al., 2017) have documented that the chemical composition of the lysimetric water depends on the nature and of solid phase of soils and climatic condition, as well as on different anthropogenic impacts (fertilization, irrigation, applying of herbicides, cultivation, the crop we grow and etc.). Saghat-

elyan et al., (2013) indicates that the lysimetric filtrate can to estimated of elements mobility in the soil and pollution of infiltration waters inflowing to ground and surface waters.

The aim of the study was to estimate the effect of longterm fertilizer application on the content and leaching of chemical elements with lysimetric water after maize grown as monoculture.

Materials and Methods

The area of this study is located in South Bulgaria $(24^{\circ}35'\text{E}; 42^{\circ}14'\text{N} \text{ and } 180 \text{ m}$ above the sea-level), near the town of Plovdiv, Bulgaria, in the village of Tsalapitsa. The region belongs to the transition subzone between Moderate and Mediterranean Continental Climates zones (Levicharska, 1991). The region is characterized by the following mean annual climatic data: rainfall in the 2018 is 507 mm, while in the first half of 2019 – 230 mm. The average rainfall for this region of 500-540 mm. Mean annual air temperature for this region is 12.2°C.

The soil on which the experiment was set up is classified as Fluvisols. The soil profile has coarse texture and low water holding capacity (14.99%). The arable horizon has the following mean characteristics: light texture, low clay content (18.6%), bulk density between 1.54 and 1.66 g.cm⁻³, pH_{H20} is 6.0, total nitrogen - 0.111 %, humus content - 1.23%, and cation exchange capacity - 22.4 cmol.100 g⁻¹.

The field experiment started in 1972 with maize in grown as a monoculture under irrigation. The lysimeters are installed on the following variants: non-treated plots N_0P_0 (B₁) the yield depended mainly of natural nitrogen sources; optimal treatment $N_{200}P_{150}$ (B₃) was compared for full compensation of the nitrogen uptake; treatment with $N_{100}P_{75}$ (B₅) kg.ha⁻¹ a deficit of nitrogen fertilization. After maize grown, to estimate the fertilizer after-effect, in 2019 year spring barley was grown with no fertilizer application.

The field plots were equipped with Ebermeir lysimeters (Stoichev, 1974) collecting water from a depth of 50 and 100 cm layers from the surface of the soil. Lysimetric water samples are taken several times a year depending of the amount of infiltrate. The pH values and chemical composition (K⁺, Na⁺, Ca²⁺, Mg²⁺, NO₃⁻N, HCO₃⁻, Cl⁻, SO₄⁻²⁻) of lysimetric water are determined using the laboratory methods of analysis described in Arinushkina (1970) and Page et al. (1982).

Results and Discussion

Changes of environment and applied agricultural practices have an impact of agricultural production. Some studies (Giorgi et al., 2004; Backlund et al., 2008; Myers et al., 2017) shows that the climate change is increasingly important and that the climatic factors have a significant impact and puts the functioning of agroecosystems at high levels of biotic and abiotic stress (Jones & Thornton 2003; Tapiador & Sánchez 2008; Hawkins & Sutton, 2011). Changes in temperatures, precipitation patterns, absorption and uptake of nutrients by the crops etc., have a significant impact on agriculture. They also have a significant impact on the drainage and the chemical elements uptake of the soil profile which has been established and in our previous studies (Simeonova et al., 2015; 2017).

The results for 2019 (Figure 1) show that in the experiment (after maize growing) the drained water quantity varied between 17.31 and 44.23 dm³ respectively for the two layers 50 and 100 cm.



Fig. 1. Average volume of lysimetric waters (dm³), Tsalapitsa, 2019

The changes occurred in the solid phase of the soil under the influence of fertilization are also reflected in the chemical composition of the lysimetric water. As it is shown (Figure 2) the pH values varies from 7.05 to 7.55, the observed trend of pH values decreasing is the result of the long-term fertilization of maize. Some authors (Stoichev et al., 1986; Ganev, 1992; Atanassova et al., 2013) in their studies indicate that long-time mineral fertilization it is possible to cause acidification of the soil layer in this type of soil, increase in manganese and aluminum exchange forms and decrease of the amount of exchange calcium and magnesium, which are indicative of permanent changes in the soil solid phase.

Chemical composition of lysimetric water

The obtained data for the chemical composition of the lysimetric water are from the winter-spring months of 2019. During this period, are created conditions for the humidifi-



Fig. 2. pH values of lysimetric water, Tsalapitsa, 2019

cation and migration of chemical elements with a runoff, as providing information on the position of the elements after the cultivation of maize at different variants of fertilization.

The results showed (Table 1) that the highest potassium content in the lysimetric water was obtained under the variant $B_5 (N_{100}P_{75})$ -3.37 mg.l⁻¹ and the lowest (2.03 mg.l⁻¹) at the $B_3 (N_{200}P_{150})$ variant from 1m soil layer.

The sodium content in the water is highest from the $N_{200}P_{150}$ (B₃₎ treatment (21.96-17.98 mg.l⁻¹) at both depths respectively, while in the other variants the values are close (Table 1).

Anthropogenic loading has an impact on the content of some elements, such as calcium, whose concentration increases with increasing fertilizer levels (Table 1). The highest levels of calcium and magnesium were found in the lysimetric water obtained from the $N_{200}P_{150}(B_3)$ variant (84-106 mg.l⁻¹) was calculated for full compensation of the nitrogen uptake with the yield, and respectively from 22 to 26.50 mg.l⁻¹ for magnesium. According to Stiocheva et al. (2001) the fact could be considered as an indicator for an increase of the velocity of the weathering of the soil minerals. However, in the present situation these processes are the limits of the soil capacity to compensate the acidifying agents in the soil solution, an evidence for which is the neutral reaction of the drainage flow. It is found that the calcium content corresponds to that of nitrate nitrogen (Table 1).

Data show that after maize cultivation, the waters obtained of the non-treated variant N_0P_0 (B₁) have the lowest nitrate nitrogen contents (6.45-14.0 mg.l⁻¹). The lysimetric water from active root zone of the B₃ ($N_{200}P_{150}$) variant has a nitrate contents about 2-3 times the higher compared to the non-fertilized variant – N_0P_0 . It was found that nitrogen values varied significantly, especially in the 0-50 cm layer.

The content of hydrocarbonates in the drainage runoff decreases in the fertilized variants and reaches the lowest value in the variant $B_3 (N_{200}P_{150}) - 61.54 - 87.53 \text{ mg.l}^{-1}$ (Table 1). The values of chlorine in the lysimetric water has very low variation $(19.0 - 26.25 \text{ mg.l}^{-1})$, where the differences between the untreated and fertilized variants are negligible. It has been found that the sulphates content of lysimetric water ranges from 51.0 to 86.0 mg l⁻¹ at variant $B_3 (N_{200}P_{150})$.

Some studies (White & Blum, 1995) shows that the climate change have great impact on pedogenic weathering of minerals. In a study by Atanassov et al. (1985) ionic composition of the leachate depends except by on the natural conditions – geology and hydrology of the land, soil type and climatic conditions, the form and amount of fertilizer used as well as by the processes of weathering. In this context, the

Table 1. Chemical composition of lysimetric water (mg.l⁻¹), Tsalapitsa, 2019

Elements, mg.l ⁻¹	Depth, 0-50 cm						Depth, 0-100 cm					
	B ₁ N P	B ₅	B ₃	mean	+/-SD	Cv, %	B ₁ N P	B ₅	B ₃	mean	+/-SD	Cv, %
	1°0 ¹ 0	¹ N ₁₀₀ 1 75	¹ N ₂₀₀ ¹ 150				1 N 0 1	¹ N ₁₀₀ 1 ₇₅	¹ N ₂₀₀ ¹ 150			
рН	7.50	7.45	7.30	7.45	0.13	2	7.25	7.10	7.05	7.15	0.10	1
K+	2.63	3.37	2.14	2.71	0.62	21	3.27	2.58	2.03	2.65	0.63	23
Na+	11.09	14.67	21.96	15.91	5.54	35	12.72	13.04	17.98	14.58	2.95	20
Ca ²⁺	46.00	79.80	84.80	70.07	20.96	30	54.80	74.80	106.30	78.63	25.96	33
Mg^{2+}	11.00	19.80	22.50	17.77	6.01	34	15.65	17.37	26.65	19.89	5.91	30
N-NO ₃₋	6.45	32.17	34.00	24.21	15.40	64	14.00	29.70	47.75	30.48	16.88	55
HCO ₃ -	130.66	104.34	61.54	107.5	21.79	20	122.14	95.21	87.53	92.96	30.36	18
Cl-	20.35	19.00	23.10	20.82	2.09	10	26.25	25.50	21.80	24.52	2.38	9
S042-	51.00	58.00	79.00	62.67	14.57	23	63.50	67.00	86.00	72.23	12.03	17

water could be regarded as "filtrates" of weathering. Therefore, it is necessary to comparing the values of the mineral composition of Fluvisols with ionic composition of the received lysimetric water where it is possible to determine the impact of the anthropogenic loading on the direction of the processes of the pedogenic weathering. The molecular ratios between SiO, and alkaline and alkaline earth elements calculated respectively for water (L) and soil (R) are used, which can give idea for geochemical type of weathering of the mineral part of the soil. After their calculation, they are found to have values for L = 0.08 and R = 7.89 respectively, i.e R > L, which is typical for most Bulgarian soils and refers to the sialytic type of weathering. At the weathering of the mineral part of the studied soil, the calcium cations are exported intensively to the soil profile, magnesium and sodium with much less intensity.

According to Saghatelyan et al. (2013) landscape – geochemical research and the study of leaching of chemical elements with lysimetric water can be successfully used to evaluate and predict of the states of the ecosystems and to conduct groundwater monitoring.

Output of chemical elements via leaching

Fluvisols are coarse textured soils, with significant spatial heterogeneity and great variety in the arrangement of alluvial materials. This determines a high amount of drainage aeration pores and conditions for fast water movement downward the profile. In this situation, it is possible migration of chemical elements and unutilized nitrogen by crops with the water out of soil root zone and reaching to the ground water level. The amount of elements leached out of the top one-

■ K+ 🗵 Na+ 🗆 Ca2+ 🗉 Mg2+ 🖾 N-NO3- 🖬 HCO3- 🖾 Cl- 📾 S042-

meter soil profile was derived from the volume and elements concentration of lysimetric water.

The data show that the highest nitrate nitrogen losses are found in the lysimetric water under $B_3 (N_{200}P_{150})$ variant, whose absolute value reaches 18.80 kg.ha⁻¹ at a depth of 0-100 cm (Figure 3). Almost the whole amount of N leached was in nitrates. In all cases, fertilization had led to increasing of N losses. The calcium is among the cations with the highest water migration rate that influenced from intensive land use. Its high concentration in lysimetric water and migration mobility determines the significant losses of this element outside the one-meter soil layer.

Very good correlation was found between the N rates and Ca²⁺ losses (R²= 0.917, y = 16.25x – 9.566). Calcium leaching increased with increasing of N leaching rates. Similar to nitrogen, the highest calcium leached with the lysimetric water of the same B₃ (N₂₀₀P₁₅₀) variant, reaching to 38.7 kg.ha⁻¹ at 0-50 cm and up to 42.0 kg.ha⁻¹ for the layer 0-100 cm, and for magnesium – 10.5 kg.ha⁻¹ (Figure 3). Leaching of K⁺ and Na⁺ was not significantly affected by fertilizer inputs. The position of these elements depends on their distribution between the geochemical and biological circles rather than the water migration. The lysimetric waters received from B₃ (N₂₀₀P₁₅₀) variant have the highest sulphates leaching 34.9 kg.ha⁻¹ (0-50 cm).

When comparing the values of the migration of the chemical elements with the lysimetric water of the treatment variants the following relative order can be obtained:

Ca > S > N > Mg > Cl > Na > K

Similar is situation is the non-treatment variant of migration. As can see from a relative order the migration of



■ K+ ⊠ Na+ □ Ca2+ ■ Mg2+ ⊠ N-NO3- ■ HCO3- ⊠ Cl- ■ S042kg.ha⁻¹

Fig. 3. Leaching of chemical elements (kg.ha⁻¹) with lysimetric water of Fluvisols, Tsalapitsa, 2019

chemical elements, calcium is the most mobile element, while potassium is the lowest. The place of the other elements may change depending on the depth and the type of soil, crops grown, etc.

Conclusions

It is found that the most sensitive to long-term fertilizer application are the nitrates, calcium, magnesium, sulphates and pH values. Long-term application of fertilizers in maize grouwing under irrigation, is a precondition for appearance of a changes in the soil lysimetric water.

The obtained results show that the nitrate nitrogen leaching varies between 2.4 and 18.8 kg.ha⁻¹ for the 0-100 cm layer, with the highest losses with lysimetric water were registered under variant ($N_{200}P_{150}$). The highest calcium losses (42.0 kg.ha⁻¹) is observed under the same treatment from 0-100 cm soil layer.

The data show that the relative orders of migration of the elements of the different variants have the following form: Ca > S > N > Mg > Cl > Na > K.

Although fertilization has an impact on the rate of water migration of some elements, it does not significantly change the general order of geochemical mobility.

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