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FERTILIZERS` LEACHING FROM THE ROOT SYSTEM ZONE – A POTENTIAL ENVIRONMENTAL RISK FOR GROUNDWATER POLLUTION IN COARSE AND MEDIUM-TEXTURED SOILS

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Abstract: The objectives of the paper are to test if the nitrogen (mineral and organic), phosphorous and potassium fertilizers commonly used in field crops penetrate deep into the soils, and find out their leaching characteristics in the case of different-textured soils, in order to assess the potential environmental risk and recommend measures for limiting such losses. Three soil types were studied in undisturbed micro-lysimeters: sandy-textured Eutric Arenosol, AR-eu, loamy-textured Haplic Chernozem, CH-ha, and clayey-textured, swell-shrink Luvic-Chernic Phaeozem, PH-ch-lv. Two fertilizer applications containing amide N, as well as P_2O_5 and K_2O were applied. Then distilled water was applied daily according to the infiltration rate simulating a wet season, and the effluent was collected. Soil texture and soil hydraulic properties determined the pattern of effluent concentration for all chemicals. K leaching losses from the root system zone of the soils presented the highest means, followed by N losses, while the lowest losses were found for P. Significant differences between the soils were found. Because various soil textures were studied with this experiment, the results might be used in similar environments from many countries. If global warming with extreme rain events continues, then fertilizer leaching losses could increase. To minimize nutrient leaching losses some measures are recommended. Further research should be focused on larger soil-texture diversity and cropped soils.

Keywords: phosphorous; potassium; total nitrogen; different textures, environmental risk

1. INTRODUCTION

Fertilizers are used today for a high and competitive production in many crops (Durukan et al., 2020; Kakar et al., 2020). Nitrogen, phosphorous and potassium are among the most important macro-elements for crops. Crops do not generally use the entire fertilizers applied to soil, and some amounts are leached beyond the depth of the crop root system, especially nitrate. The most severe risk of leaching is in the wet periods, generally in autumn and spring seasons, when the crops are less developed or the soils are bare. To a lesser extent than nitrate, other fertilizers such as potassium and phosphorous compounds are also lost by leaching and runoff from the field.

Small plots, lysimeters or undisturbed large soil columns are generally used in studying fertilizer leaching. Some decades ago, Singh et al., (1984) reported a different behavior of soil texture and soil moisture content regarding urea movement into soil columns, concluding that the greater the water application the deeper urea penetration into the soils. In dry sandy-loam soils urea peaks were noted with water front, but in sandy soil the wetting front moved faster and the urea peaks remained behind. The authors also observed a non-reacting behavior of urea, similar to Cl^- anion concerning its movement with soil-water before it is hydrolyzed. Anami et al., (2008) have studied the effect of swine-derived wastewater in Brazil and have found out that “the potential for contamination of underground water by nitrate ions is high, in contrast to what occurs with phosphate ions that presented low potential of contamination due to their high reactivity”. Experimenting on soil columns, Antil et al., (2009) emphasized the effect of soil water content and water application on the urea amount and urea-derived NH_4^+ in the soils and reported a decreasing trend of these substances with depth, irrespective of water application rates. Soil columns have also been recently used to investigate leaching of phosphorous fertilizers from soils (Djodjic et al., 2004; Zhao et al., 2009; Andersson et al., 2013; Chatain et al., 2013; Li et al., 2013; Vanden Nest et al., 2014), and potassium fertilizers as well (Alfaro et al., 2006; Kolahchi & Jalali, 2007).

Many of these studies were done using disturbed soil columns which do not have the same porosity and conductive properties of natural soils. There is therefore a need to expand leaching studies, particularly concerning the influence of particle-size distribution and soil permeability on total nitrogen, phosphorous and potassium movement into the soils beyond the rooting depth of crops.

The objectives of the present experiment are to: a) test if the nutrients commonly used in field crops penetrate deep in the soils, and b) find out the leaching characteristics of total nitrogen (including NO_3-N, NH_4-N, and organic N), phosphorous and potassium fertilizers in the case of three different-textured soils: sandy, loamy and loamy-clayey, when the soils are wet and leaching is high, in order to assess the potential environmental risk and recommend some measures for limiting such losses.

2. MATERIAL AND METHODS

2.1. The environmental conditions of the experimental site

The experimental site is located in southern Romania, and is characterized by a temperate-continental climate, with 10.5-11.0°C mean annual temperatures and 500-600 mm annual precipitation. There is a general trend of warming climate for the studied area as reported by Chitu & Paltineanu (2019) and Paltineanu et al., (2002, 2011, 2020a).

The landscape complexity of Romania is considerable, as there is a large soil textures` diversity where the loamy texture is prevalent, followed by moderate-fine texture and coarse texture (ICPA Bucharest Archive). According to Jones et al., (2010), similar textured soils are largely scattered in various parts of the world.

For this study, three different-textured soil types (according to IUSS WG-WRB 2015) have been chosen: i) a sandy-textured, highly permeable Eutric Arenosol, AR-eu located at 43.779°N, 24.2078°E and 61 m above sea level (a.s.l.), ii) a loamy, moderately permeable Haplic Chernozem, CH-ha (44.790°N and 26.939°E, 62 m a.s.l.), and iii) a loamy-clayey, slowly-permeable textured Luvic-chernic Phaeozem, PH-ch-lv, with strong swell-shrink properties (44.09337°N, 25.54698°E, and 89 m a.s.l.).

From the soil profiles described above, disturbed soil samples were taken from various parts of the soil horizons to collect average horizon samples in order to determine particle-size distribution and some chemical analyses (pH-in 1:2.5 water suspension using SR 7184-13:2001 PTL04 method, total nitrogen content (Nt) using Kjeldahl method STAS 7184/2-85 PTL09, NO_3^--N potentiometric PT46, NH_4^+-N by distillation PT47, mobile forms of phosphorous (P_{AL}) and potassium (K_{AL}) as plant available extracted in ammonium acetate-lactate using STAS 7184/19-82 PTL19 and STAS 7184/18-80 PTL 22 methods), respectively, and other current analyses described by Florea et al., (1987). Bulk density (BD), total porosity (TP) and saturated hydraulic conductivity (Ks) were also determined using the standardized methods presented by Dumitru et al. (2009).

Particle-size distribution differed substantially between the three soil types. For the 0-1 m depth representing the main part of the rooting system (Paltineanu et al., 2017) for most of the grown crops in the region, the weighted-average clay content (<0.002 mm particle size) was 5.1% (while the sand content was 97%) for AR-eu soil type, 20% for CH-ha, and 47.4% (with a maximum 49.0% in the Bt horizon) for PH-ch-lv.

The soil conductive properties shown here by Ks essentially depend on clay content and bulk density (BD) (Paltineanu et al., 2016). Ks showed excessively high values in the AR-eu soil (78-247 mm h^{-1}) and minimum values in the hardpan Ap horizon of CH-ha (5.05 mm h^{-1}) and especially in the rich-in-clay Bt horizon (0.17 mm h^{-1}) of PH-ch-lv soil type. The Ks weighted-harmonic means over 1 m depth were 201.5 mm h^{-1} in AR-eu, 17.04 mm h^{-1} in CH-ha, and 2.44 mm h^{-1} in PH-ch-lv soil types; however, water infiltration and leaching losses are mainly governed by the slowest permeability values within the soil profiles (Hillel, 1980).

The soil pH ranged from 6.2 to 7.0 within AR-eu soil type, and from slightly acid (5.0-5.6) in the topsoil to neutral and slightly alkaline (7.0-8.4) values in the subsoil of CH-ha and PH-ch-lv types

(Table 1). Nt content had a similar pattern for CH-ha and PH-ch-lv soil types, and was lower in AR-eu (Table 1). The mobile, plant available forms of P and K, P_{AL} and K_{AL}, also decreased with depth and were the highest in PH-ch-lv, followed by CH-ha, and the lowest values for AR-eu. Some of the soil physical and chemical properties were previously described by Paltineanu et al., (2020b).

The sampling of micro-lysimeters, 0.3 m in diameter and 1 m in length, was previously reported by Paltineanu et al. (2020b) and Domnariu et al., (2020). Three undisturbed-soil lysimeters were used as replicates for AR-eu and PH-ch-lv, and four for CH-ha soil.

2.2. Application of fertilizer and water over the micro-lysimeters

Before nutrient application, water was applied over the soils to help them adjust as much as possible to natural soil conditions. Above the wetted soil, a 10-8-8 rich-in-NPK liquid fertilizer was first applied in lysimeters. The fertilizer consisted of an amount of 10% amide N from urea (CH_4N_2O), 8% P_2O_5 as HPO_4^{-2} and $H_2PO_4^-$, and 8% K_2O as a phosphate compound. The fertilizer also contained 0.92% of HCO_3^- and 0.36% of Cl^-. The fertilizer solution amount dissolved in 0.5 L of water was applied as much as 14.14 g per lysimeter, resulting in a 28.2 g NPK L^{-1} concentration. This application was equivalent to an amount of 200 kg N ha^{-1}, an amount of 160 kg P ha^{-1} and 160 kg K ha^{-1}, respectively According to the 10-8-8 NPK fertilizer ratio the solution consisted of 1.41 g N $lysimeter^{-1}$, 1.13 g P $lysimeter^{-1}$ and 1.13 g K $lysimeter^{-1}$. Up to 1 L of distilled water (14.15 mm depth) was generally applied daily over the lysimeters' soil during the experiment according to the soil infiltration rate.

Glass recipients were placed below the bottom outlets of the soil lysimeters to periodically collect the effluent for chemical concentration and volume determinations. P and K extractable in water, pH (method symbol PT101), total nitrogen (Nt), Kjeldahl method, and electro-conductivity (EC) as well as conductometric residue (method PT102) were determined from the effluent in the Institute's laboratory after the methods standardized by Florea et al., (1987).

A second fertilizer application, similar to the first one, doubled the initial amount of fertilizers applied over the soils and was made when the EC values reached approximately the initial effluent values in most of the lysimeters, and this occurred after about an effluent volume leached of cca. 116±25.2% from total porosity (TP), and the watering cycle continued similarly, also collecting the effluent.

On a few occasions during the experiment, soluble salts (methods PT103-110 for carbonates, bicarbonates, sulfates, chlorides, phosphates, calcium, magnesium, potassium) were also determined to find out the prevailing anions and cations as well as the mineral residue leached.

At the end of leaching experiment, soil samples were taken in four replicates for each 0.1 m depth using an Eijkelkamp auger down to the lysimeter bottom. Then they were combined for the same depths in each lysimeter, resulting in 10 soil samples for each lysimeter. The mass values of total N, mobile P_{AL} and mobile K_{AL} in the lysimeters' soils were calculated by multiplying the chemical analytic results with the dry soil mass resulted from bulk density and soil volume for each 0.1 m lysimeter increment, and we then obtained profiles` values. The sums of the amount of each fertilizer applied plus the initial soil state content equivalent were compared with the sums of the leached fertilizers and the final soil state content equivalent for each lysimeter and soil type.

Because no isotope tracing was used in this experiment, the exact determination of P, N and K origin in the effluent, both from the fertilizer and the soil, was not possible and the term of equivalent was used instead for the leached fertilizer.

Water was applied until an effluent equivalent of about 139-310 % of soil total porosity, or 575-1288 mm of precipitation for the permeable AR-eu and CH-ha soils, depending on soil permeability of each lysimeter, was leached out of the 1 m soil depth investigated. Nevertheless, only 10% of total porosity (42 mm) could be applied in the slowly-permeable PH-ch-lv soil-type lysimeters. During the experiment the air temperature in the lab ranged between 10 and 15°C.

The data obtained from the experimental work have been processed by using Microsoft Excel, SPSS14 and specific statistical procedures such as Student t-test, and the symbols of the specific significant differences are: * for the probability p<0.050, ** for p<0.010, *** for p<0.001, and ns for not significant.

3. RESULTS

3.1. Dynamics of pH and electro-conductivity (EC) as a function of the effluent volume

The pH and EC values versus the effluent volume for all micro-lysimeters where there was leaching during the experiment, i.e. AR-eu and CH-ha because PH-ch-lv soil was impermeable when wet, are depicted in Figure 1.

Table 1. The main soil chemical properties for the investigated CH-ha, PH-ch-lv and AR-eu soil types

Soil type	Horizon	Depth	pH	Total N content	P_{AL} content	K_{AL} content
	Symbol	cm	units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
CH-ha	Ap	0-17	5.63	1422	69.2	171.0
	Ap hard	17-29	6.27	1337	33.0	176.9
	Am	29-42	6.50	1485	18.0	123.7
	A/B	42-54	6.65	1158	15.0	98.1
	Bv1	54-72	6.84	958	29.6	78.4
	Bv2	72-89	7.00	863	14.7	66.6
	B/C	89-109	8.40	800	3.5	50.8
	Mean♠	**0-100**	**6.24♠♠**	**1141**	**28.1**	**109.2**
PH-ch-lv	Am1	0-10	5.05	2465	75.0	288.9
	Am2	10-23	5.55	1765	62.7	173.1
	AB	23-51	6.57	1510	9.7	159.0
	Bt1	51-93	6.89	1095	16.8	141.5
	Bt2	93-118	7.02	835	6.4	122.6
	Mean♠	**0-100**	**5.86♠♠**	**1402**	**25.8**	**162.4**
AR-eu	Ao	0-31	6.20	811	15.0	49.2
	Cn1	31-52	6.55	833	11.3	43.5
	Cn2	52-84	6.80	603	10.0	41.6
	Cn3	84-106	6.94	477	18.7	41.6
	Mean♠	**0-100**	**6.49♠♠**	**692**	**13.2**	**44.3**

Note: P_{AL} and K_{AL} are the mobile, plant available forms of K and P, respectively, while symbol ♠ shows the weighted-arithmetic mean for the 0-1 m lysimeters' depth, and and ♠♠ shows the weighted-antilog mean for pH (some properties were included from Domnariu et al., 2020)

The pH values varied between 7.44 and 8.52, with a mean of 8.16±0.15 for CH-ha, and between 6.89 and 8.52, with a mean of 7.74±0.18 for AR-eu soils. CH-ha mean is significantly ($p<0.050$) higher than AR-eu mean. Figure 1 shows that there were some local peaks in the pH dynamics, for instance around of 50 and 150-250% of effluent volume for AR-eu soil, and around 70-80 and 170-180% of effluent volume for CH-ha. However, there were important differences between lysimeters, even within the same soil type.

EC values of both leached soils, AR-eu and CH-ha, varied within some more precise patterns. The mean values for the entire effluent volume range were 633.6±127 µS cm^{-1} for CH-ha soil type, with 326/869 µS cm^{-1} as minimum/maximum values, and 467.4±239 µS cm^{-1} for AR-eu, with 144/1038 µS cm^{-1} as minimum/maximum values, respectively. Even if the AR-eu mean was about 74% from the CH-ha mean, they were not significantly different due to the scattered data. There were two peaks for each soil type, at cca. 70-80% and 170-180% of effluent volume for AR-eu, and at about 100% and 180-220% of effluent volume for CH-ha, Figure 1. The peaks for both pH and EC roughly coincide with the mid-interval values of effluent-volume between nutrient applications.

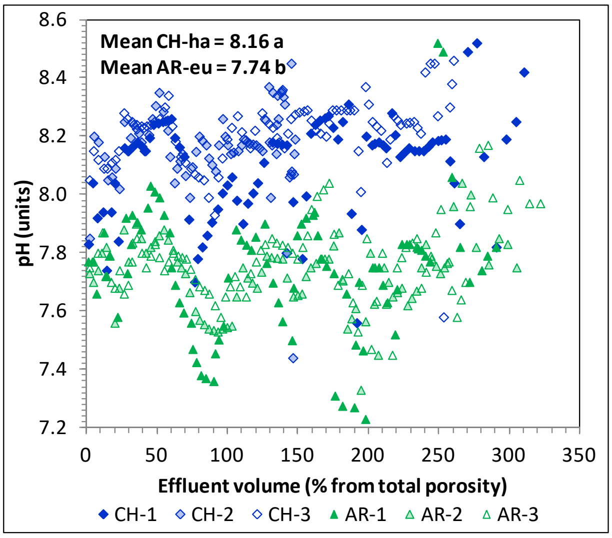
3.2. Concentrations of P, K and N depending on effluent volume

Concentrations of P, K and N depending on effluent volume are depicted in figures 2 and 3. There are significant ($p<0.050$) differences between CH-ha and AR-eu soil types concerning the means of P (0.22 mg L^{-1}) and K (3.16 mg L^{-1}) concentrations for the whole effluent volume range, Figure 2. In the case of CH-ha soil type, P and K concentrations show a saw-tooth pattern with very low values, generally <0.5 mg L^{-1} for P and <2.0 mg L^{-1} for K, while in the case of AR-eu soil type the above concentrations present some peak values that are consistent with EC values presented above.

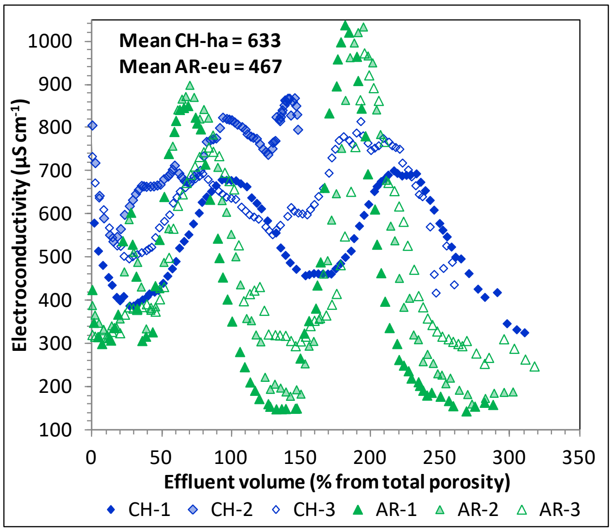
N concentration was also generally higher for AR-eu for the entire effluent volume range, with a mean of 6.7 mg L^{-1} versus 4.25 mg L^{-1} found for CH-ha soil type, yet the difference was not significant (Fig. 3). There were some local peaks for N concentrations versus the effluent volume and large differences among the micro-lysimeters within the same soil types.

3.3. Total nutrients leached from the soils

The comparison between the total nutrients leached after the entire water applied from the two soil types, AR and CH where there was leaching, is shown in Figure 4.



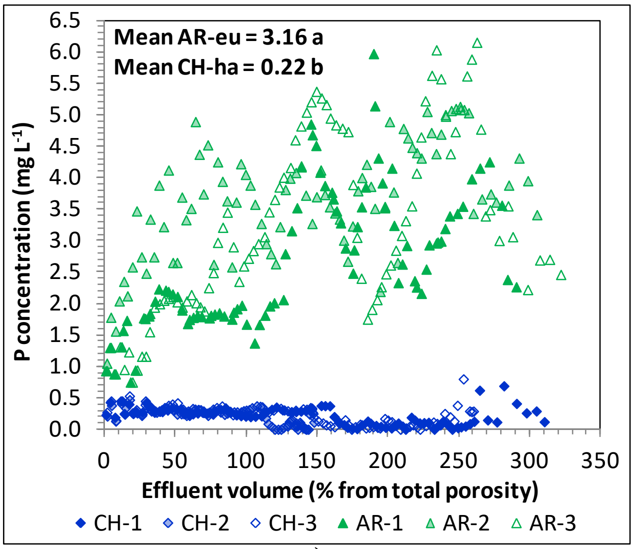
a)



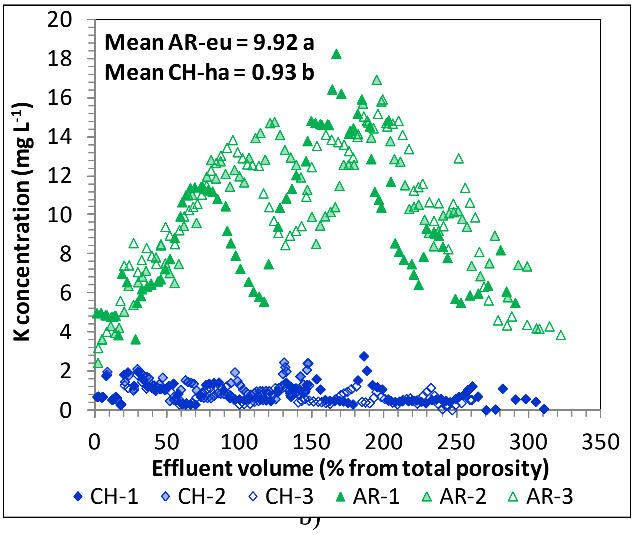
b)

Figure 1. The pH (a) and EC (b) values versus the effluent volume for all micro-lysimeters where there was leaching (CH-1, CH-2, CH-3, and AR-1, AR-2 and AR-3) during the experiment; legend indices 1 to 3 show the number of lysimeters for each soil type

The leached P was highly significantly ($p<0.001$) greater (17.7 times) for AR-eu (267.4 mg) than CH-ha (15.1 mg) soil type. A similar ratio (13.9 times) occurred for K leached from these soil types, where the leached K was as much as 830.5 mg in the case of AR-eu and only 59.6 mg for CH-ha, these differences being also highly ($p<0.001$) significant. However, the N difference between AR-eu (555.3 mg) and CH-ha (288.5 mg) was only significant ($p<0.050$) due to data scattering, and their ratio was 1.9.



a)



b)

Figure 2. The concentration values of P (a) and K (b) versus the effluent volume for all micro-lysimeters where there was leaching (CH-1, CH-2, CH-3, and AR-1, AR-2 and AR-3) during the experiment

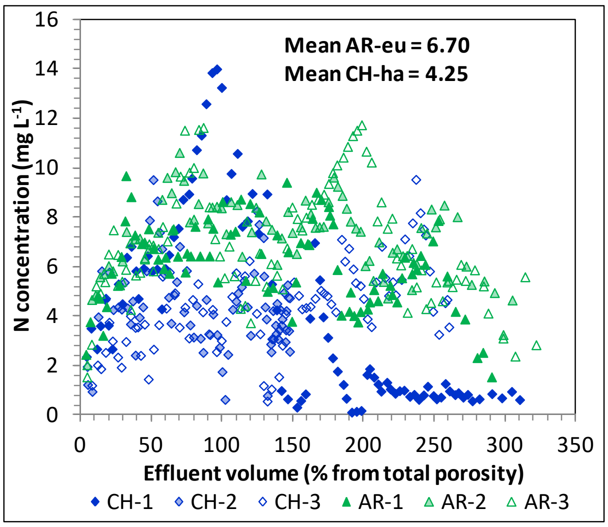


Figure 3. The N concentration values versus the effluent volume for all micro-lysimeters where there was leaching (CH-1 to CH-3, and AR-1 to AR-3) during the experiment

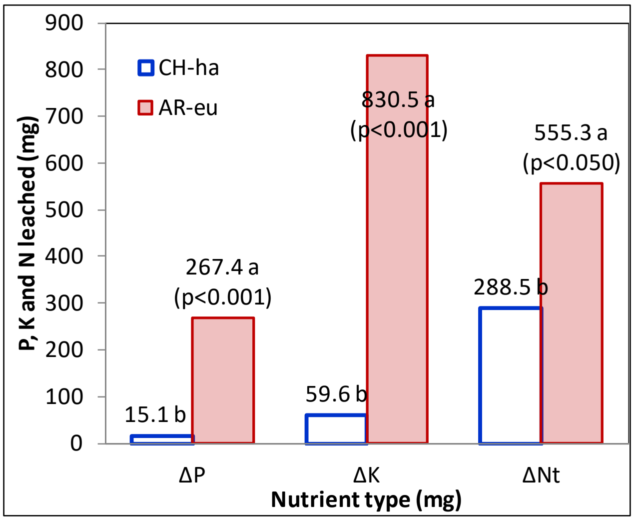


Figure 4. Comparison between the total nutrients leached from the two soil types, AR and CH, where there was leaching, respectively, with significant differences for each nutrient amount between the soil types

3.4. Correlations between electrical conductivity and K and N concentrations

There were direct correlations between EC and K and N concentrations only in the case of AR-eu soil type, for the entire range of the effluent volume, Figure 5. The coefficients of correlation were highly significant ($p<0.001$). The relationships between EC and K concentration showed a higher slope (0.0073) versus the relationships between EC and N (0.0028).

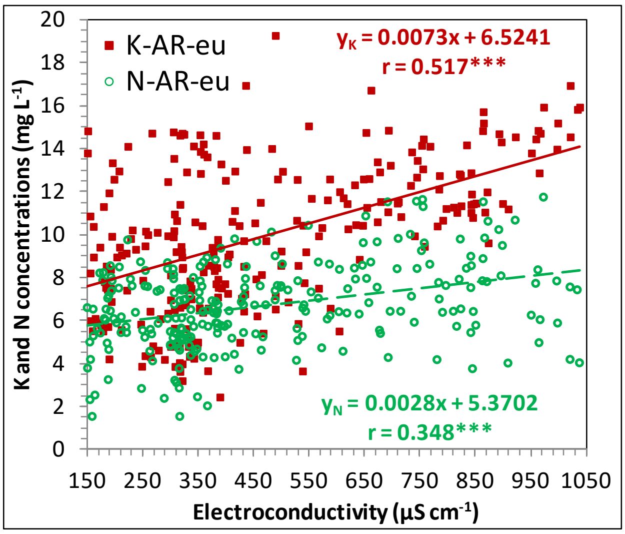


Figure 5. Relationships between EC and K and N concentrations in the solutions leached from the AR-eu soil type during the experiment

3.5. Comparisons between some chemicals leached from the AR-eu and CH-ha soil types

Table 2 shows that HCO_3^-, SO_4^{-2} and Cl^- anions prevailed in the effluent that was periodically collected along the leaching experiment from the micro-lysimeters, after various effluent volumes, as well as Ca^{+2} followed by Mg^{+2} and Na^+ cations, with very low N and K^+ water content values.

For all sampling occasions, significant differences of various levels for the analyzed components were found between the CH-ha and AR-eu soils studied, mainly for CO_3^{-2}, HCO_3^- and mineral residue (Res.), with the highest values in the case of CH-ha. The behavior of K^+ cation was inversely related. Cl^- was always higher for CH-ha versus AR-eu, sometimes significantly, Ca^{+2} was also higher in the same soil, except once, while there was no clear trend for Mg^{+2} and Na^+. Among the nutrients analyzed, N and K^+ always showed the highest values in the sandy textured soil, AR-eu.

3.6. Comparison between the beginning and the end of leaching experiment for pH and the studied nutrients from the soils

This comparison is depicted in tables 3, as final data, and 4 as differences between the final (Table 3) and initial (Table 1) data. The soil pH values show vary small average changes between these two soil states, 0.18 units for CH-ha mean and 0.05 units for AR-eu soil mean; only PH-ch-lv had a larger mean difference, 0.40 units (Table 4).

Table 4 also shows that total soil N content was generally moved (negative values) from the upper soil horizons toward the lower ones. P_{AL} soil contents decreased from both CH-ha and PH-ha-lv soil types, and were almost unchanged as mean values for AR-eu soil. There was a substantial increase in K_{AL} soil content for CH-ha and PH-ch-lv soil types and only a slight increase for AR-eu soil type.

Comparing the initial soil N, P, K content values plus the applied fertilizer values versus their final soil content values plus their leached values for each soil type (Figure 6), it was noted that for all studied soil types the first values were close to the latter ones. The differences between the final soil content values plus its leached amount and the initial soil content values plus the applied fertilizer, for each chemical element, were not significant in the case of N, all soil types; in the case of K, there were not significant differences for CH-ha soil type, but there were significant ($p<0.050$) differences, even if with close values, for AR-eu and PH-ch-lv, with an inverse trend. It is only in the case of P where the initial plus the applied values were systematically and significantly higher than the final soil content plus the leached amount.

Table 2. The pH (units), anions and cations as well as total nitrogen (N) and mineral residue (Res.) (mg dm^{-3}) analyzed from the solutions leached and collected periodically from the micro-lysimeters for CH-ha and AR-eu soils, the figures in italics show an inverse trend of the mean values)

Soil type/ Lysimeter	pH	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	N	Res.
	At effluent volume of 16.8±1.41 (% from total porosity)										
CH-ha	8.04	12.5	157.4	47.4	39.1	83.4	9.2	7.2	0.5	1.3	358
AR-eu	7.86	0.00	53.2	45.3	34.1	42.4	4.8	6.4	4.1	1.6	192
Significance	ns	***	***	ns	*	**	***	ns	***	ns	***
	At effluent volume of 61.4±8.3 (% from total porosity)										
CH-ha	8.19	8.85	180.2	40.4	40.5	102.4	9.8	5.4	0.5	0.8	389
AR-eu	7.66	0.00	48.2	59.4	25.8	98.5	13.8	12.2	10.4	6.9	275
Significance	***	***	***	ns	ns	ns	ns	*	***	**	**
	At effluent volume of 111.2±23.6 (% from total porosity)										
CH-ha	8.25	12.8	146.7	85.9	37.9	91.0	19.6	5.1	1.6	2.3	403
AR-eu	7.88	0.00	55.6	46.2	18.1	26.7	7.2	9.8	7.6	6.4	178
Significance	**	**	***	*	***	***	ns	*	***	*	***
	At effluent volume of 164.4±39.7 (% from total porosity) after the second nutrient application										
CH-ha	8.20	7.4	187.1	20.3	21.4	118.1	13.0	5.7	1.4	3.9	378
AR-eu	7.42	0.00	40.3	21.2	19.3	119.7	20.1	4.1	3.6	5.4	234
Significance	**	*	***	ns	ns	ns	*	ns	*	ns	***
	Overall means										
CH-ha	8.2	10.4	167.8	48.5	34.7	98.7	12.9	5.9	1.0	3.3	382
AR-eu	7.7	0.0	48.0	42.3	22.5	77.3	12.8	8.4	6.9	5.8	224

Table 3. The soil chemical properties after leaching for the investigated CH-ha, AR-eu and PH-ch-lv soils

Soil type	Horizon	Depth	pH	Total N content	P_{AL} content	K_{AL} content
	Symbol	cm	units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
CH-ha	Ap	0-17	5.82	1424.6	54.9	212.7
	Ap hard	17-29	6.04	1340.1	27.3	193.5
	Am	29-42	6.20	1309.2	15.1	167.4
	A/B	42-54	6.41	1150.1	11.3	123.7
	Bv1	54-72	6.55	1096.4	14.1	105.9
	Bv2	72-89	6.78	961.4	11.0	92.1
	B/C	89-109	7.43	838.1	8.7	80.5
	Mean♠	**0-100**	**6.42♠♠**	**1164.2**	**0.12**	139.6
PH-ch-lv	Am1	0-10	5.75	2041.7	74.47	363.7
	Am2	10-23	5.75	1728.8	40.76	218.9
	AB	23-51	6.13	1613.5	14.82	182.6
	Bt1	51-93	6.67	1285.7	2.36	184.8
	Bt2	93-118	6.91	1080.8	0.00	179.4
	Mean♠	**0-100**	**6.31♠♠**	**1496.3**	**17.89**	**206.1**
AR-eu	Ao	0-31	5.84	1089.0	18.6	66.1
	Cn1	31-52	6.48	672.5	15.3	49.1
	Cn2	52-84	7.07	570.9	10.6	35.5
	Cn3	84-106	7.08	557.3	11.0	29.9
	Mean♠	**0-100**	**6.54♠♠**	**750.7**	**14.1**	**46.9**

Note: The symbols have the same meaning as in Table 1

Table 4. Differences in the soil chemical properties, final values minus initial values, for the investigated CH-ha, AR-eu and PH-ch-lv soil types

Soil type	Horizon	Depth	pH	Total N content	P_{AL} content	K_{AL} content
	Symbol	cm	units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
CH-ha	Ap	0-17	0.19	2.63	-14.35	41.73
	Ap hard	17-29	-0.23	3.13	-5.75	16.60
	Am	29-42	-0.30	-175.81	-2.88	43.69
	A/B	42-54	-0.24	-7.87	-3.67	25.56
	Bv1	54-72	-0.29	138.39	-15.53	27.54
	Bv2	72-89	-0.22	98.45	-3.72	25.47
	B/C	89-109	-0.97	38.14	5.18	29.67
	Mean	0-100	0.18	23.20	-27.98	30.36
PH-ch-lv	Am1	0-10	0.73	-423.34	-0.53	74.81
	Am2	10-23	0.16	-36.21	-21.94	45.82
	AB	23-51	-0.42	103.46	5.12	23.56
	Bt1	51-93	-0.23	190.71	-14.44	43.27
	Bt2	93-118	-0.14	245.78	-6.40	56.84
	Mean	0-100	0.40	94.33	-7.91	43.71
AR-eu	Ao	0-31	-0.36	277.97	3.55	16.88
	Cn1	31-52	-0.07	-160.55	3.98	5.60
	Cn2	52-84	0.27	-32.02	0.64	-6.11
	Cn3	84-106	0.14	80.25	-7.70	-11.74
	Mean	0-100	0.05	58.67	0.93	2.63

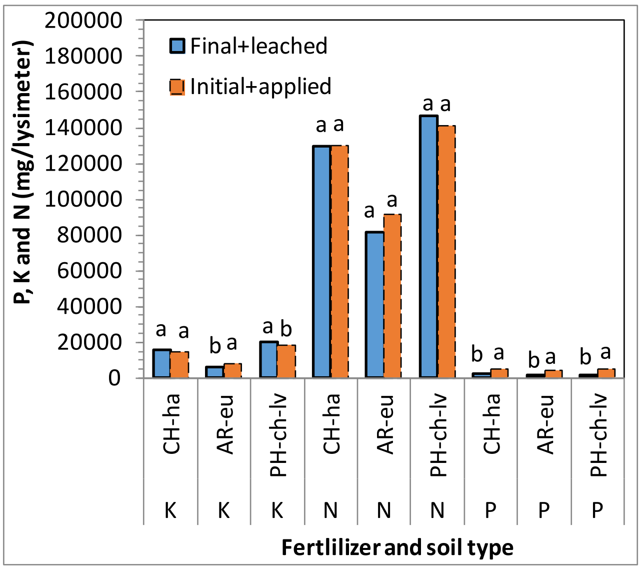


Figure 6. Comparison between the sum of the amount of fertilizers applied plus the initial soil state content and the sum of the leached fertilizer and the final soil state content for each lysimeter and soil type; different letters in the graph show significant differences between the initial state and final state for each chemical studied

4. DISCUSSION

The effluent contained nutrients leached from the studied soils and the applied fertilizers as well.

After fertilizer applications and continuous water supply, movement of fertilizers were expected to present a delay versus water movement, as Singh et al., (1984) reported that even in highly-permeable sandy soils the water front moved faster than the urea peak. In initially wet soils, as there is also the case here, the urea moving front did not coincide with the wetting front, following infiltration and after redistribution, and urea behaved as a non-reacting ion like Cl^- with respect to its movement with soil-water before it is hydrolyzed (Singh et al., 1984). The graph shapes of figs. 1-3 from our study show therefore such pattern, with initial low fertilizer contents.

Dynamics of solute pH and EC depending on the effluent volume was influenced by the nutrient application occasions, with the peaks approximately coinciding with the mid-interval effluent volumes between nutrient applications (Figure 1).

Soil texture and hydraulic conductivity were essential for the pattern of effluent concentration for all the considered aspects. For instance, EC showed thinner and taller peaks (Fig. 1) for the highly permeable AR-eu soil type versus the moderately-permeable CH-ha soil type, while there was no leaching from the swell-shrink, heavy-clay, slowly-permeable PH-ch-lv soil. EC was higher within CH-ha soils versus AR-eu soils, but not significantly different, most probably being determined by the soil chemical composition (Table 1). Indeed, most anions and cations participating to EC values were mostly leached from the more fertile CH-ha soil as shown in Table 2.

Unlike EC, pH variations of the effluent occurred within a narrower range, with significantly higher values for CH-ha versus AR-eu ones, even if both the initial and final soil pH values (Tables 1 and 3) were not too much different between these soil types. This difference probably occurred due to a quicker leaching of the chemicals influencing pH within AR-eu soil, with a substantially higher permeability, than CH-ha soil, and probably due to the difference in the buffering capacity of the soils. As Gould et al., (1986) reported, the rapid hydrolysis of urea in the soil can produce high soil pH values and high ammonium ion concentrations. It is not known yet why pH increased in the PH-ha-lv soil type, where there was no leaching. Nevertheless, this aspect remains to be better investigated through further experiments.

Significant differences between CH-ha and AR-eu soil types were found for the concentrations of P, K and N depending on effluent volume (figures 2 and 3), with higher values for AR-eu soil. From all these agrochemicals leached below the 1.0 m lysimeter depth, K presented the highest mean values, and at the same time K was also stored in CH-ha and PH-ha-lv soil types, especially in the latter, due to the lack of leaching for PH-ha-lv. This is probably a consequence of K_{AL} release in the soil solution from the total K content of the soil matrix. Substantial K leaching losses were also reported by Erickson et al., (2005) and Kolahchi & Jalali (2007) for sandy soils, as our results also showed, while Alfaro et al., (2006) noted higher preferential flow losses from clayey soils versus sandy soils, but these losses occurred under different soil water conditions than ours. Kolahchi & Jalali (2007) also found out that in sandy soils with lower buffer capacity and in which K^+ does not interact strongly with the soil matrix, the application of K^+ fertilizers increases K^+ concentration in the soil solution, especially if the crops are irrigated with water containing higher concentrations of Ca^{2+} and other cations.

Total N leaching losses, consisting of NO_3-N, NH_4-N and organic N, followed in size, and these were also generally confirmed by N transfer from the upper toward the deeper soil horizons (Tables 3 and 4). The chemical balance shown in Figure 6 also indicates non-significant N differences between the final- and the initial states of the combined fertilizer-soil-solution system in the overwhelmingly wet environment of this experiment. These results also fall within the experimental errors.

Among the agrochemicals studied, the lowest leaching losses were found for P, even if there was a significant decrease in the final soil P_{AL} content, probably due to some chemical reactions of P immobilization in the topsoil with acid pH values, where the fertilizers were applied. The total soil P content was not determined. Similarly, Jalali & Jalali (2017) identified only a small class of soils having a high risk of P leaching. However, P leaching losses might be important though cracks or macropores in dry swell-shrink soils as earlier reported Paltineanu (2001), Djodjic et al., (2004), and Andersson et al., (2013).

For the two fertilizer applications of a total of 400 kg N ha^{-1}, 320 kg P ha^{-1} and 320 kg K ha^{-1}, highly significant ($p<0.001$) larger P amounts were leached out per 100 mm of effluent during the simulated wet season conditions studied, with a continuously descendent leaching flux, from AR-eu soil type (21.1 mg/100 mm of effluent) than from the CH-ha soil type (1.55 mg/100 mm of effluent) and PH-ch-lv soil type (0 mg). There were also highly significant differences in the same manner for the other two chemicals, K and N, with 65.6 mg/100 mm of effluent for AR-eu versus 6.28 mg/100 mm of effluent for CH-ha in the K case, and with 43.8 mg/100 mm effluent versus 29.4 mg/100 mm of effluent in the N case for these two soil types. It is worth to mention that the N fertilizer applied to the investigated soils did not contain NO_3-N, and the nitrate part from the total N leached came from the soils.

Due to the different permeability values among the studied soils, there were also significant differences for the leaching losses of all these nutrients between AR-eu and CH-ha soil types, and between these two soil types and the swell-shrink PH-ch-lv soil type. Domnariu et al., (2020) examined NO_3^- leaching from soil lysimeters and also found significant differences concerning the nitrate leached for similar textured soils.

The spatial variability among the studied soils was relatively high, between the soil types themselves as expected, and also between soil micro-lysimeters within the same soil type acting as a noise.

The leaching losses of K and N were higher, particularly K losses (Fig. 4). Only for the soil presenting the highest permeability, i.e. AR-eu, K and N concentrations correlated with EC (Fig. 5), and this means that K and N participated to a greater extent to EC in the effluent, and that these soil types showed again the highest pollution risk with agrochemicals from the nutrients investigated.

The potential for contamination of underground water by various ions is high, particularly for nitrate, in contrast to what occurs with phosphate ions that presented low potential of contamination due to their high reactivity (Anami et al., 2008). Our results also showed a very low mobility of P leaching, irrespective of soil texture, and the lowest losses beyond 1.0 m depth, consistent with the conclusions of Anami et al., (2008).

The concentration of agrochemicals derived from the soils themselves and the applied fertilizers in the groundwater is a function of soil texture, combined with soil structure, determining the magnitude of hydraulic conductivity, porosity and other in-situ soil physical and chemical properties. Landscape characteristics such as slope and land use, which were not investigated here, can substantially contribute to nutrients` leaching and runoff. The concentration also depends on the fertilizer amounts applied by farmers at the land surface. Knox & Moody (1991) and Lacatusu et al., (2019) have also explained that leaching is also closely linked to the depth to groundwater and to the geological deposits below. While heavy-clay soils present the lowest pollution risk with agro-chemicals, sandy soils present the highest risk.

The findings presented in Table 2 are consistent with the groundwater composition reported by some scientists, meaning that what is leached from the soil profile could be found deeper in the subsoil and in the groundwater as well. Thus, in the southern part of Romania, Lacatusu et al., (2019) found mean water contents that were higher in anions such as HCO_3^- , NO_3^- , SO_4^{-2} and Cl^-; the water content values in cations were lower in comparison, due to their specificity of being electrically attracted and retained by the soil colloids, prevailing Ca^{+2}, Mg^{+2} followed by Na^+. Notwithstanding, only a lower K^+ water content was still found in the groundwater.

Comparing the soil textures studied in this experiment, our results are also consistent with, for instance, those of Donner et al., (2004), who reported that highly-permeable coarse textured soils are generally prone to leaching, as opposed to the clay-textured soils and as was stressed by Li & Ghodrati (1994) and Kurunc et al., (2011). The last authors as well as Paltineanu (2001) emphasized that only the rare macropores and soil cracks are permeable in the heavy-clay soils. Even if the heavy-clayey soils are almost impermeable when wet, groundwater beneath can be polluted with fertilizers, as found by Lacatusu et al., (2019) in a river catchment in southern Romania, specifically in the built-up areas of some villages. The question is whether the groundwater was polluted in-situ or ex-situ.

The values regarding nutrient losses from the present study show that fertilizer leaching increases with effluent volume and consequently with precipitation. This finding is in agreement with the conclusions of Hess et al. (2020) and Zheng et al. (2020), who reported that leaching to groundwater also depends on land use. Additionally, Hess et al. (2020) stressed the positive role of the no-till cropping systems in the U.S.

Nutrient leaching should also be concerning in the context of climate change. If global warming with extreme events, especially with increased precipitation storms, continues in the region, as forecasted by Paltineanu et al., (2011, 2020a), then fertilizer leaching losses could increase within the regions with highly permeable sandy-textured or moderately-permeable loamy-textured soils. Another way to lose fertilizers from the fields is through runoff during severe storms, mainly from sloped areas, and this risk is bigger for swell-shrink waterlogging soils during the wet season; these losses might result in river eutrophication.

The results of this experiment emphasize the different behavior of various textured soils when wet, and the proportion of the leaching losses. They also show the higher potential risk of nutrient leaching below the crop rooting system from the sandy and loamy textured soils anywhere in the world; at the same time they suggest the lower pollution risk of the clayey-textured soils. Additionally, leaching losses could affect crop production costs and might present a pollution risk for nutrients, mainly with K and N.

In order to minimize nutrient leaching losses, sprinkling or drip irrigation, according to land use, and no-till cropping systems whereby crop residue is left on the soil surface are recommended, as well as split-fertilizer application, because these measures help retain both water and nutrients in the shallower part of the soils.

Further research should be focused on larger soil-texture diversity, cropped soils, biochar application and simultaneous determination of as many as possible substances leached, including cations and anions.

5. CONCLUSIONS

The flow of effluent containing nutrients leached from soils and fertilizers in the micro-lysimeters was a predominantly descendent, solute flux that essentially occurred between the soil water content corresponding to the range between field capacity and saturation. The results emphasize the different behavior of various textured soils when wet, and the proportion of the leaching losses, as a novelty. Soil texture and hydraulic conductivity were essential for the pattern of effluent concentration for all the chemicals studied.

The dynamics of solute pH and EC was influenced by the nutrient application occasions, with the peaks approximately coinciding with the mid-interval effluent volumes between nutrient applications.

Among the agrochemicals studied, K leaching losses presented the highest mean values, followed by N losses (including all N types), while the lowest leaching losses were found for P. It is worth to mention that the N fertilizer applied to the investigated soils did not contain NO_3-N, and the nitrate part from the total N leached came from the soils.

Significant differences between CH-ha and AR-eu soil types were found for the effluent concentrations in P, K and N depending on effluent volume, with the highest values for AR-eu soil type.

Highly significant larger P amounts were leached out per 100 mm of effluent during the simulated wet season conditions studied from the highly permeable AR-eu soil type than from the moderately-permeable CH-ha soil type and the slowly-permeable PH-ch-lv soil type. Similarly, there were also highly significant differences for K and N leaching losses between AR-eu and CH-ha soil types. These losses might reach the groundwater, depending on the subsoil and geological deposits below.

The mass balance between the final soil content plus the leached amount and the initial soil content plus the applied amount for each chemical studied showed that these differences were generally small, underlying a correct quantification in spite of not using isotopic markers.

The different soil textures studied with this experiment let us evaluate that the results might be also used in similar environments from many neighbor countries.

If the global warming with extreme storms continues, then fertilizer leaching losses could be increased within the regions with highly permeable sandy-textured or moderately-permeable loamy-textured soils anywhere worldwide; at the same time the results stress the lower pollution risk of the swell-shrink clayey-textured soils when wet. On the other hand, these losses could affect the crop production costs.

In order to minimize nutrient leaching losses, adequate irrigation methods should be employed in addition to split-fertilizer applications.

Further research should be focused on larger soil-texture diversity, cropped soils, biochar application and an increased number of leached chemicals analyzed.

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