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INFLUENCE OF SOIL-TEXTURE ON NITRATE LEACHING FROM SMALL-SCALE LYSIMETERS TOWARD GROUNDWATER IN VARIOUS ENVIRONMENTS

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Abstract: The purpose of the present paper is to test the existence of significant differences concerning the effluent needed to remove the equivalent of an amount of 200 kg N ha^{-1} applied fertilizer containing NO_3^- and to quantify the nitrate leached per mm of effluent for three different soil textures: sandy, sandy-loamy and loamy-clayey. The experiment was performed on undisturbed soils sampled in small-scale lysimeters, 0.3 m in diameter and 1.0 m height. NH_4NO_3 fertilizer granules were applied as a batch solution with a concentration of 6.26 g L^{-1}. Water was applied by a drip irrigation system in the lysimeters. Below the bottom outlets, glass containers were placed to periodically collect the effluent for chemical analyses and volume determinations. Soil texture and clay type determined the nitrate leaching pattern. Distinctly significantly more nitrates were leached out per mm of water from sandy- than from loamy soils. Swell-shrink clayey soils are almost impermeable and have a low risk in groundwater contamination with nitrate. If climate change continues and extreme rainfall events occur, nitrate leaching could be even greater within the region containing permeable sandy soils. To minimize nitrate leaching, sprinkling or drip irrigation, no-till cropping systems and split-fertilizer application should be applied.

Keywords: undisturbed-soils, soil processes, sand, sandy-loam, loamy-clay

1. INTRODUCTION

Modern agriculture needs fertilizer application to obtain high yield. Soil nitrogen, as nitrate or ammonium in mineral form, is one of the most important macro-elements for crops. Large nitrate amounts are annually lost below the root zone of the soil profile from agricultural fields (Nielsen & Jensen 1990), contributing to terrestrial and coastal eutrophication, polluting freshwater, endangering biodiversity, etc. (Sutton et al., 2011; Erisman et al., 2013). Among the important N losses from agricultural fields are ammonia (NH_3) volatilization, emissions of N_2O to the air, NO_3^- leaching to groundwater and surface water, and also ammonium (NH_4^+) losses (Davidson & Kanter 2014). At the continent level, the EU has reported no significant improvement in water quality in the affected regions (EU 2015). Additionally, Musacchio et al., (2019) showed that despite the 1991 Nitrate Directive (ND; 91/676/EEC, EU Commission. 1991) most regions in northern Italy present steady or increasing nitrate concentrations, even in previously and supposedly resilient aquifers.

Studies on large soil plots have been performed in oceanic-climate countries like England, showing a high risk of leaching (Addiscott 1991; Catt 1991). Many models using, among others, physical and chemical soil properties and experimental data, have been created to estimate such losses. For instance, Schroeck et al., (2019) have recently explored the fate of reactive nitrogen from present agricultural production practices on arable and grassland soils by using the soil modeling tool LandscapeDNDC to quantify the nitrogen distributed into the atmosphere, hydrosphere and the crops.

The amount of nitrate leached out from the soils toward groundwater or surface waters mainly depends on the soil nitrate content, soil texture, soil water dynamics and groundwater depth (Loch This is not cited in text1983; Knox & Moody 1991; Zhou et al., 2010; Zhao et al., 2010; Kurunc et al., 2011; De Waele et al., 2017; Hansen et al., 2019; Vogeler et al., 2019). NO_3^- concentrations over 50mgL^{-1} in drinking water might cause methaemoglobinaemia, specifically in infants (WHO 2007). Farmers usually reduce nitrate leaching losses during the growing season by fitting split fertilizer applications to the crop demand. The most serious leaching risk in many temperate-climate countries is during the cold and wet periods, generally in autumn, winter and early spring, when the soils are either bare or have small developed crops, and when the soil water content (SWC) is between field capacity (FC) and saturation. Such situations could intensify in the future due to climate change.

A river catchment is generally complex, consisting of a variety of relief forms, sloped hills, flat platforms or plains, soils, land uses, vegetation types and crops. Particle-size distribution of the soils is also important for soil permeability magnitude that determines leaching (Canarache 1990). Lăcătușu et al., (2019) recently reported groundwater and surface water pollution in a river catchment of Southern Romania, specifically in and around the built-up areas of villages. The groundwater beneath can be affected by pollution with fertilizers, particularly nitrate, or other pollutants. It is therefore useful to know how the fertilizers and pollutants move into various-textured soils and subsequently into the subsoil toward groundwater.

Large field plots are representative for large-scale experiments, but are too diverse for soil homogeneity and are also difficult to isolate hydrologically. For this reason, small-plots or undisturbed large soil columns or mini-lysimeters of various-textured soils, having the advantage of a proper control of the experimental factors, are also used to investigate leaching losses of nitrate, phosphorous and other substances. In particular, soil columns were increasingly used to study the movement of pollutants into the soils and their leachate. Thus, Zhao et al., (2009), Li et al., (2013) and Vanden Nest et al., (2014) reported data on total phosphorous leaching under unsaturated conditions.

Even if many investigations have been carried out to explain fertilizers' leaching from the soils, there is still a need to clarify some aspects related to the influence of particle-size distribution, permeability, air porosity and depth to the groundwater, on nitrate movement into the soils. For instance, it is difficult to estimate the amount of nitrate leached from the soil depth where the plants have their main rooting system as a function of precipitation for various-textured soils, and this literature gap needs to be reduced.

The purpose of the present paper is to test the existence of significant differences concerning the effluent needed to remove the equivalent of a high amount of applied fertilizer containing NO_3^- and to quantify the nitrate leached per mm of effluent (precipitation), for three different soil textures: sandy, sandy-loamy and loamy-clayey when the soils are wet and the leaching risk is high. Another objective is to determine leaching characteristics out of the 0-1 m depth soils, such as leaching start, maximum concentration and leaching end, for these three textures to find out measures to recommend for limiting such losses in the exposed environments.

2. MATERIAL AND METHODS

2.1. The natural site conditions

The region of study is situated in the southern part of Romania, which has a temperate-continental climate, a Dfb class after Köppen-Geiger climate classification (Geiger 1961). The mean annual temperatures are between 10.5 and 11.0°C and the annual precipitation between 500 and 600 mm, with 180-200 mm occurring during the October through March period combined with lower reference evapotranspiration, and about 320-400 mm during the growing season (April through September); there is a general trend of rising temperature, reference evapotranspiration and crop evapotranspiration for the studied area (Paltineanu et al., 2002, 2011, 2012; Paltineanu & Chitu 2019).

There is a large diversity of soil textures in Romania, where the loamy texture and assimilated textures are prevalent with more than 11 million ha (48%), followed by moderate-fine texture with more than 8 million ha (34%), and coarse texture with cca. 1 million ha (5%), the rest being occupied by different mixed textures in the soil profiles (ICPA Bucharest Archive). Such soils are also largely present in other parts of the world (Jones et al., 2010).

Three different soil types have been selected for this study: i) a chernic-argic phaeozem, FZce-ar (as Luvic-chernic Phaeozem after IUSS WG-WRB, 2015*) from Draganesti village, Teleorman county, situated at 44.09337°N, 25.54698°E, with an altitude of 89 m above sea level and possessing a clayey-loamy texture in the topsoil and a loamy-clayey one in the subsoil with strong swell-shrink properties (Paltineanu et al., 2020a), ii) a cambic chernozem, CZca (Haplic Chernozem*) from Grindu village, Ialomita county, 44.790°N and 26.939°E, and 62 m altitude, with a loamy texture in the topsoil and a sandy-loamy one in the subsoil, and iii) a sandy-textured eutric psamosol, PSeu (Eutric Arenosol*) showing a high permeability, 43.779°N, 24.2078°E and altitude of 61 m, from Potelu-Ianca village, Olt county. The soils are classified according to the Romanian Soil Taxonomy (Florea & Munteanu 2012) and also to IUSS WG-WRB, 2015*.

Soil samples were collected from the soil profile horizons in bags and sent to the Institute's laboratory to determine particle-size distribution and chemical analyses (pH-in 1:2.5 water suspension using SR 7184-13:2001 PTL04, organic carbon content STAS 7184/21-82 PTL12, total nitrogen content using Kjeldahl method STAS 7184/2-85 PTL09, NO_3^--N potentiometric PT46, NH_4^+-N by distillation PT47, and other current analyses after Florea et al., (1987). Undisturbed samples were taken in metal rings, 5 cm diameter and 5 cm height, to determine bulk density (BD) and saturated hydraulic conductivity (Ks) using the standardized methods published by Dumitru et al., (2009).

The 1-m depth weighted-average clay content (<0.002 mm) was 20.2% kg kg^{-1} (with a maximum of 30% in the topsoil) in the case of CZca, 47.4% kg kg^{-1} (with a maximum 49.0% in the Bt horizon, prevailing swell-shrink features) for FZce-ar, and 0.51% kg kg^{-1} (a maximum 0.7% in the topsoil, and a sand content of 97%) for PSeu.

There was a compacted hardpan soil horizon just below the Ap layer in two out of the three studied soils, showing higher BD values: 1.85 kg dm^{-3} in the case of CZca and 1.56 kg dm^{-3} in the case of FZce-ar, while the PSeu soil had a relatively homogeneous profile compactness (BD=1.50-1.60 kg dm^{-3}). The weighted-mean BD value over the 1.0 m depth was 1.58 kg dm^{-3} for CZca, 1.40 kg dm^{-3} for FZce-ar, and 1.56 kg dm^{-3} for PSeu.

The soil clay content and the BD values induced specific Ks values for these soils (Hillel 1980; Canarache 1990, Paltineanu et al., 2016). Thus, Ks was minimum in either the hardpan horizon (5.05 mm h^{-1}) of CZca or the rich-in-clay Bt horizon of FZce-ar (0.17 mm h^{-1}), and was excessively high in the PSeu soil (78-247 mm h^{-1}). The Ks weighted-harmonic means over 1 m depth were as much as 17.04 mm h^{-1} for CZca, 2.44 mm h^{-1} for FZce-ar and 201.5 mm h^{-1} for PSeu. Air porosity, calculated as difference between total porosity and FC, ranged between 23.9 and 25.5% (24.6% weighted average) in the case of PSeu, between 13.7 and 19.7% (15.9% weighted average) for CZca, and between 2.0 and 20.0% (7.6% weighted average) for FZce-ar. More details on the soil physical properties of these soils can be found in a previous paper (Paltineanu et al., 2020b).

The pH of the investigated soils present increasing values, from slightly acid (5.0-5.6) in the topsoil to neutral and slightly alkaline (7.0-8.4) values in the subsoil for CZca and FZce-ar, while pH shows a narrow range, from 6.2 to 7.0, for PSeu (Table 1).

The soil organic carbon content (OC) also decreases gradually from topsoil to subsoil, with the highest values in FZce-ar, while the total nitrogen content, the NO_3^--N content and NH_4^+-N content show a similar pattern for CZca and FZce-ar, and are more homogeneously distributed with depth in PSeu (Table 1).

2.2. Sampling of small-scale lysimeters

Stainless steel small-scale lysimeters, 1 m in length and 0.3 m in diameter, were gradually inserted in the previously wetted soils that were close to FC, by hitting with a heavy sledge hammer (10 kg mass) in a thick circular metal ring laid over the lysimeters until the lysimeters reached cca. 0.05-0.10 m depth. The soil around the lysimeter was continuously removed in order to minimize friction. Following insertion, a pit was dug around the lysimeters to facilitate handling, and the soil was cut off at the lysimeter bottom. Both lysimeter extremities were isolated using double-layer plastic sheets tied with ropes. Four lysimeters were sampled from the CZca area at Grindu, three lysimeters from the FZce-ar area at Draganesti, and three lysimeters from the sandy soil area at Potelu-Ianca.

The lysimeters were then transported into the Institute's laboratory and laid each one over a circular stainless-steel holder provided with a drainage system consisting of two layers. One of these layers has 1-cm height coarse and fine sand at the intimate contact with the soil, and the other one is a 4-cm height gravel layer 3-7 mm sized, below the sand. Under the drainage system there is a stainless-steel sieve over a tap-outlet device to collect the effluent. The manipulation of the 120-140 kg soil lysimeters was carried out by using a mobile indoor crane and two fastening belts to hold and move them. Details of lysimeters' sampling and permeability determination can be read in a previous paper (Paltineanu et al., 2020b).

2.3. Conditioning the soil lysimeters for fertilizer and water application

The soil was removed from the top of the lysimeters on a 15-mm depth to allow application of the fertilizer and water. Over the FC-wetted soil, NH_4NO_3 fertilizer granules were applied as a batch solution having a concentration of 6.26 g L^{-1} and corresponding to an application of 200 kg N ha^{-1}, i.e. 4.04 g of NH_4NO_3 $lysimeter^{-1}$. The NO_3^- fraction is 0.775 from the entire fertilizer amount, i.e. 3.131 g $lysimeter^{-1}$. The value of 200 kg N ha^{-1} is close to the limit of 170 kg ha^{-1} $year^{-1}$ of nitrogen from organic manure as recommended by EU Nitrate Directive (ND; 91/676/EEC). After the first water applications, the removed soil was gradually put back in the lysimeters.

Table 1. Some of the main soil chemical properties for the CZca, FZce-ar and PSeu soils. Note that OC is organic carbon, N is nitrogen, while symbol ♠ shows the weighted-arithmetic mean for the 0-1 m lysimeters' depth, and ♠♠ shows the weighted-antilog mean for pH

Soil type	Horizon	Depth	pH	OC content	Total N content	NO_3^--N content	NH_4^+-N content
	Symbol	cm	units	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
CZca	Ap	0-17	5.63	1.55	1422	37.93	14.14
	Ap hard	17-29	6.27	1.41	1337	12.33	3.29
	Am	29-42	6.50	1.44	1485	7.53	1.99
	A/B	42-54	6.65	1.20	1158	7.23	2.00
	Bv1	54-72	6.84	0.93	958	5.70	1.99
	Bv2	72-89	7.00	0.79	863	5.00	1.33
	B/C	89-109	8.40	0.59	800	5.32	2.03
	Mean♠	**0-100**	**6.24♠♠**	**1.13**	**1141**	**12.24**	**4.11**
FZce-ar	Am1	0-10	5.05	2.69	2530	111.1	9.0
	Am2	10-23	5.55	2.14	1768	32.5	2.0
	AB	23-51	6.57	2.00	1514	15.7	7.0
	Bt1	51-93	6.89	1.31	1059	24.2	3.0
	Bt2	93-118	7.02	1.00	836	18.4	2.0
	Mean♠	**0-100**	**5.86♠♠**	**1.73**	**1410**	**31.2**	**4.5**
PSeu	Ao	0-31	6.20	0.76	1478	4.98	1.89
	Cn1	31-52	6.55	0.79	1423	4.50	0.63
	Cn2	52-84	6.80	0.48	1590	4.21	1.92
	Cn3	84-106	6.94	0.31	1444	4.21	0.65
	Mean♠	**0-100**	**6.49♠♠**	**0.60**	**1498**	**4.51**	**1.44**

The tap water used during the experiment had a nitrate concentration of 5-8 mg L^{-1}, being substantially lower than the 25 mg L^{-1} "concern threshold" (Eurostat 2012; Musacchio et al., 2019), and an electro-conductivity (EC) value of 271-328 (µS cm^{-1}), while pH only varied between 7.61 and 7.88. Water was applied by a specific drip irrigation system with an emitter discharge of 2 L h^{-1} (28.2 mm h^{-1}) for half an hour daily over the topsoil in the lysimeters. Each soil lysimeter was provided with a distribution pipe, a tap and an emitter to strictly control water application. Below the bottom outlets of the soil lysimeters considered as being the main part of the root zone for many plants, 2-L volume glass containers were placed in order to periodically collect the effluent for chemical analyses and volume determinations. NO_3^- concentration (potentiometric method, PT 114), pH (PT 101) and electro-conductivity (EC, PT 102) were determined in the effluent in the Institute's laboratory after the standardized methods in this country (Florea et al., 1987). As isotope tracing was not used, exact determination of N origin in the effluent was not possible with a high accuracy; consequently, we used the term of leached fertilizer equivalent. Water was applied until the equivalent of total amount of the applied fertilizer was calculated as being leached out of the soil. The air temperature in the laboratory was between 10 and 15°C during the 2019-2020 autumn-winter experiment.

The data was processed by help of usual statistical procedures, i.e. Student t-test to establish significant differences between two means and also for the significance of the correlation coefficients.

3. RESULTS

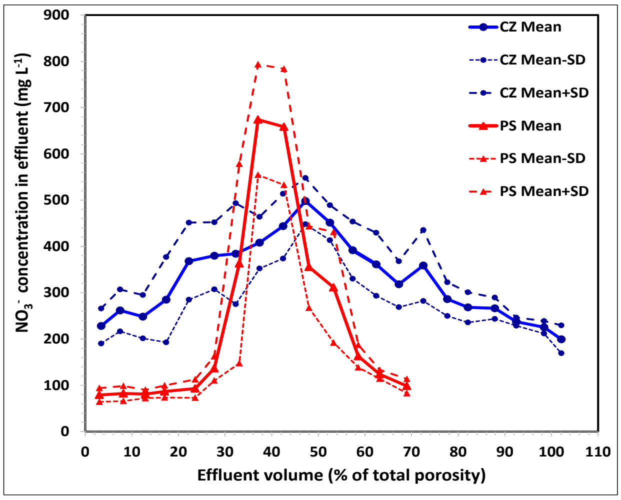
3.1. Dynamics of the NO_3^- concentration and electro-conductivity (EC) depending on the effluent volume

The NO_3^- breakthrough curves calculated for 5%-step effluent classes framed by their standard deviation values are shown in Figure 1a for CZca and PSeu soil types. There was no leachate from the FZce-ar soil lysimeters. The effluent was expressed as percent from the total porosity of the lysimeter soil. The graph curves are slightly asymmetrical.

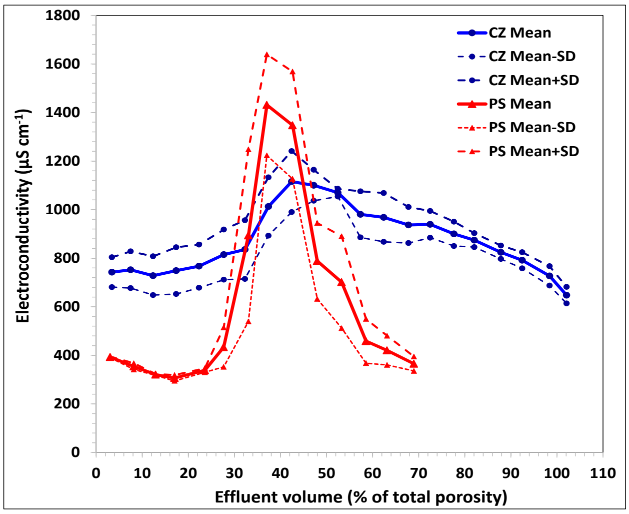
For CZca, the NO_3^- concentration means start increasing relatively gradually from the 200-250 mg L^{-1} at an effluent volume less than 10%, and this essentially comes from the soil prior to fertilizer application, up to a 500 mg L^{-1} (8.16% as relative concentration from the initial solution of 6.26 g L^{-1}) peak at an effluent volume of about 45%.

The descendent part of the graph practically reaches values close to the starting NO_3^-

concentration means at an effluent volume of 97%. Standard deviation graph lines are more distanced from one another in the ascending part of the graph than in its descending part. In the case of PSeu, the graph has a higher peak and a shorter range. Fig. 1b shows a similar graph for EC.



a)



b)

Figure 1. Dynamics of the NO_3^- concentration (a) and electro-conductivity-EC (b), mean values framed by standard deviations for 5% classes, depending on the effluent volume for CZca and PSeu soil types

These two properties are highly significantly (R=0.939, p≤0.001) correlated after a direct linear relationship, Figure 2, showing that the EC variation mainly occurred due to the nitrate variation for both investigated permeable soils, PSeu and CZca.

3.2. Correlations between some leaching characteristics

Figure 3 shows the relationship between the steady-state effluent rate and the effluent needed for the total removal of the equivalent applied nitrate in the CZca and PSeu lysimeters studied. This relationship is linear, inverse and distinctly significant (R=-0.92, p ≤ 0.01). The CZca data are in the left-up area of the graph, while the PSeu data are in the right-down area.

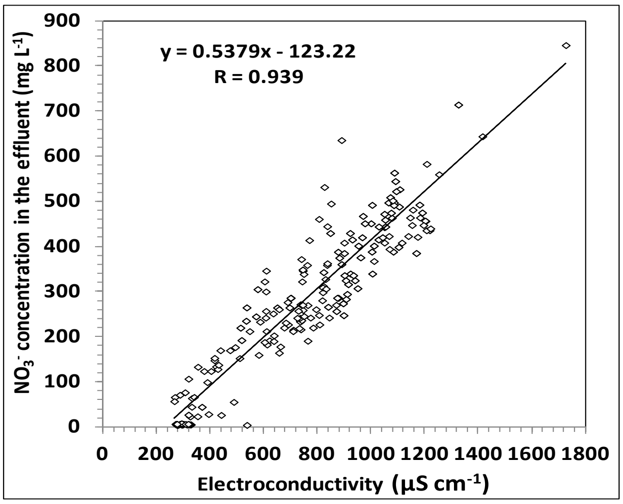


Figure 2. The linear relationship between NO_3^- concentration and electro-conductivity (EC) of the effluent leached from the two soil types, CZca and PSeu

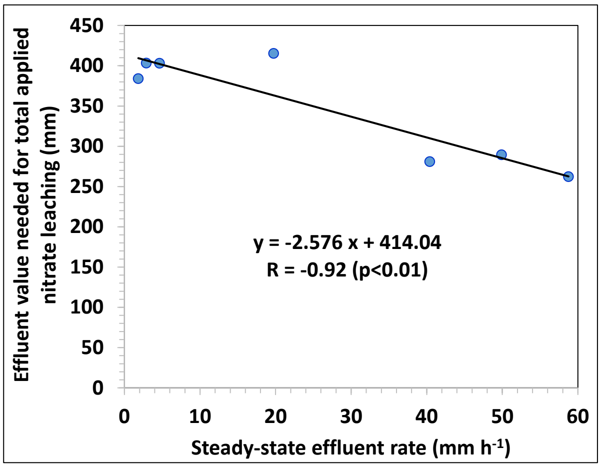


Figure 3. Relationship between the steady-state effluent rate and the effluent needed for the equivalent of total applied nitrate leachate in the CZca and PSeu lysimeters studied

There is also a moving-average relationship between the effluent leached and the equivalent of the applied nitrate removal from the soil lysimeters, Figure 4. The pattern of nitrate leaching is typical for each soil texture studied for both CZca and PSeu soils. The removal of the equivalent of the applied nitrate fertilizer has a shorter range for the sandy soils (PSeu) and a larger range for the mid-textured soils (CZca). These relationships might help in estimating nitrate leaching losses beyond the root systems.

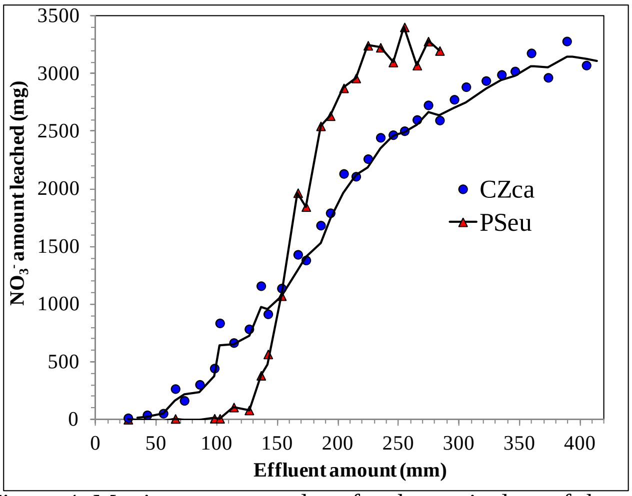


Figure 4. Moving average values for the equivalent of the applied nitrate fertilizer removed by leaching and the effluent amount as 10-mm classes for the investigated sandy- and sandy-loamy textured soils

3.3. Differences between the studied soil types concerning nitrate leaching

Table 2 synthesizes the differences between the studied soil types concerning nitrate leaching. The effluent volume at the start of fertilizer NO_3^- leaching depends, in addition to the conductive soil properties, by the antecedent SWC. Although the FC of sandy soils is very low, infiltration mainly occurs through soil macropores that were roughly assimilated here with air porosity. The water (effluent) needed to start the applied nitrate leaching from the lysimeters was highly significantly greater in PSeu lysimeters (25.5%, i.e. 105 mm) than in CZca lysimeters (16.5%, i.e. 69 mm), probably because the fertilizer was mainly stored in a more stable form in micropores.

The average NO_3^- leaching end in the case of CZca soil occurred when the cumulative effluent reached around 97% of the total porosity, and this was 402 mm of effluent volume, representing about 70-75% from the annual precipitation in the Grindu region.

In the case of FZce-ar there was no leaching out of the 1.0 m deep soil lysimeter. For PSeu the end of leaching to remove the equivalent of applied nitrate was at 67% of the total porosity, i.e. 278 mm, or about 55% from the annual precipitation in the Potelu-Ianca region. According to the above figures, the effluent amount needed by PSeu is highly significantly lower than the one needed by CZca to remove the entire applied NO_3^- fertilizer (Table 2).

At the end of NO_3^- solute leaching from the CZca soil lysimeters, the cumulative mean of this anion was 3.07 ± 0.30 g per lysimeter, and this value is very close to the initial 200 kg ha^{-1} NO_3^- amount from the NH_4NO_3 fertilizer application, i.e. 3.13 g nitrate per soil lysimeter that was applied at the start of the nitrate leaching experiment. In the case of PSeu, these figures were also very close, i.e. 3.2 ± 0.2 g nitrate per lysimeter. Table 2 also shows the total NO_3^- leached per mm of effluent for each soil type. As expected, distinctly significantly more nitrates (11.6 mg mm^{-1}) were leached out per mm of effluent from the highly permeable PSeu soil than from the mid permeable CZca soil (7.65 mg mm^{-1}). The maximum relative nitrate concentration versus the initial concentration (6.26 g L^{-1}) was 8.2% for CZca and significantly higher, i.e. 11.2% for PSeu, while the effluent volume when this maximum occurred was 45% from the total porosity (cca. 190 mm) for CZca and 40% (165 mm) for PSeu.

4. DISCUSSION

The solute flow in the soil lysimeters generally occurred at a SWC situated between FC and saturation. Under a continuous descendent and unsaturated flux that can usually exist in the cold and wet season, the leaching of nutrients depends on the steady-state infiltration rate, which is the higher flow rate occurred in the lysimeter soil with continuous water application (Paltineanu et al., 2020b). The concentration of nitrates in the soil solution and groundwater is a result of the soil hydraulic conductivity, soil texture and porosity and the physical properties of the geological deposits underneath (Knox & Moody 1991; Lacatusu et al., 2019; Hansen et al., 2019). Groundwater generally flows along large areas, and the described situation of this study only refers to the in-situ nitrate fertilizer movement into the soils.

As Figs. 1 and 4 show, soil physical properties, mainly soil texture and Ks, determine the effluent concentration pattern, and this means shorter and taller graphs for sandy-textured soils, mid graphs for sandy-loamy textured ones and no effluent for heavy-clay, swell-shrink soils. During the whole experimental period the effluent had a higher nitrate concentration than the EU limit of 50 mg L^{-1}. This flow pattern determines the risk of in-situ pollution of groundwater for the regions where permeable soil exists.

Within the studied soils, the spatial variability was relatively high, not only between the soil types but also between soil lysimeters within the same type, particularly for CZca soils. Each soil lysimeter has its own conductive properties. A correlation was found between the steady-state effluent rate, as a measure of soil permeability of the lysimeters, and the effluent needed to remove the equivalent of total applied nitrate in the case of permeable soils. This relationship was inversely and distinctly significant, meaning lower effluent amounts needed to remove the nitrate for high-permeability soils.

Table 2. Characteristics of the effluent containing NO_3^- during leaching from lysimeters within the two investigated soils of different textures and physical properties;

Lysimeter number per soil type	SS♣ effluent rate (mm h^{-1})	Effluent volume at the start and end of fertilizer NO_3^- leaching (% of soil total porosity)			NO_3^- leached at the end of leaching		Maximum NO_3^- relative♣♣ concentration occurred at effluent volume	
		At start (%)	At end (%)	At end (mm)	(total, mg)	mg mm^{-1} effluent	(%)	of (%)
CZca								
1	2.9	16.9	97.2	403.48	2694	6.68	8.71	43.3
2	19.74	17.2	100.1	415.36	3322	8.00	6.91	54.0
3	1.83	14.9	92.6	384.18	2976	7.75	8.02	37.0
4	4.64	17.0	97.2	403.26	3305	8.20	9.01	46.7
Mean± SD	7.28 ± 8.4	16.5^{bbb} ± 1.07	96.8 ± 3.1	401.6^{aaa} ±12.9	3074 ± 299.3	7.65^{bb} ± 0.68	8.16^{b} ± 0.93	45.3 ± 7.1
PSeu								
8	58.76	27.5	63.4	262.4	3286	12.52	13.61	41.2
9	49.9	24.7	70.0	289.6	2883	9.96	10.29	36.6
10	40.4	24.4	67.9	281.1	3426	12.19	9.64	42.2
Mean± SD	49.7± 9.2	25.5^{aaa}± 1.7	67.1± 3.4	277.7^{bbb} ±13.9	3199± 282	11.6^{aa} ± 1.4	11.2^{a} ± 2.1	40.0 ± 3.0

Symbols used: ♣is steady-state rate previously determined (Paltineanu et al. 2020), ♣♣shows the effluent concentration related to the initial concentration of the applied solution, which was 6262 NO_3^- mg L^{-1}, and different superscript letters (^{a},^{b}) in the same lysimeter show significant differences for the probability (p) ≤ 0.05, while the associated symbols ^{aa},^{bb} and ^{aaa},^{bbb} in the same lysimeters show distinctly significant (p ≤ 0.01) and highly significant (p ≤ 0.001) differences, respectively, in this order of magnitude, according to Student's t-test with n_1+n_2-2 degrees of freedom.

The differences between the soil types with various textures concerning nitrate leaching are shown in Table 2. The highest probability to remove the entire applied 200 kg ha^{-1} NO_3^- fertilizer is for the sandy soils in the Potelu-Ianca region, because there is a need of only 280 mm of effluent (precipitation), versus 400 mm for the mid-textured CZca soils from the Grindu region, while for the swell-shrink soils the leaching risk is very low, occurring only when the soils are dry and cracked (Paltineanu 2001).

Distinctly significantly more nitrates were leached out per mm of effluent and implicitly per mm of precipitation, under conditions similar to the wet season with predominantly descendent solute flux, from the highly permeable PSeu soil than from the mid-permeable CZca soil. Accordingly, significant differences with higher values were found for the maximum relative nitrate concentration for PSeu versus CZca. Apart from these two soil types and textures, the swell-shrink soils showed a totally different behavior, practically impermeable when wet. These clayey soils are substantially different from other clayey and more permeable soils, such as those described by Catt (1991). Consequently, both soil texture and clay type are important in estimating nitrate leaching. For swell-shrink soils the risk of leaching in the cold and wet period of autumn-winter-early spring is very low, but there is a risk of runoff when combined with certain landscape properties, such as recently reported Singh et al., (2020). Furthermore, such low permeable soils manifest severe waterlogging and surface gleyzation within the Bt soil horizon if the mean annual precipitation is higher (generally over 600 mm), as in the northern part of Southern Romania. Combined with other landscape characteristics, such as the depth of groundwater, physical and chemical properties of the geological deposits, slope, land use, etc., soil texture is a main factor regarding groundwater pollution, with sandy soils presenting the highest risk and heavy-clay soils, the lowest risk.

From the soil texture point of view, our results are in agreement with the findings of other authors, e.g. Donner et al., (2004) and Hansen et al., (2019), who showed that coarse-textured soils, with higher hydraulic conductivity and low water storing capacity, are generally prone to nitrate leaching. Donner et al., (2004) have concluded that there is a lower probability for nitrate leaching losses from clay-textured soils. Other scientists have reported different results. For instance Vinten et al., (1994) found non-significant differences for nitrate leaching from sandy versus clay-loamy textured soils in the first years of study due to a certain travel time. Notwithstanding, even in clayey-textured soils nitrate leaching can occur to a lower extent through macropores (Li & Ghodrati 1994; Kurunc et al., 2011) and through cracks and macropores in dry, cracked heavy-clay, swell-shrink soils (Paltineanu 2001).

A river catchment environment is generally complex in geology, relief, slope, soils, land uses, etc. The most permeable soils can generate hot spots with increased nitrate concentration of groundwater. Such spots have been reported relatively by Kurunc et al., (2011) who have noted that the hot spots coincided with high water table, high sand content, and irrigated intensive crops. According to Donner et al., (2004), considerable amounts of nitrates transported to the southern seaside in the Gulf of Mexico originate from hot spots in the further North American Corn Belt. Lacatusu et al., (2019) recently found high nitrate concentration in the deep groundwater of a regional river catchment in Southern Romania, the Glavacioc River, particularly in the built-up areas. The soils of this river catchment are mainly fine-textured, low-permeable soils, and the following question arises: from where does this groundwater pollution come? Is it in-situ, or ex-situ and flowing across, or were those hot spot locations polluted exclusively through an inadequate use of domestic wells nearby?

Hess et al., (2020) and Zheng et al., (2020) reported, among others, increased nitrate leaching in groundwater with increasing precipitation and fertilizer application depending on land use. The results from the present study advance this line of thinking by finding a direct relationship between the amounts of precipitation, assimilated with the effluent volume, and the leachate equivalent of entire nitrate fertilizer usually applied for a whole year (Fig. 4). Another new finding of the present study is that the maximum relative nitrate concentration of the effluent under a continuous water supply was significantly higher in the case of the sandy PSeu soils versus the CZca soils, but at non-significantly different effluent volumes of 40 (165 mm) to 45% (190 mm) in the permeable PSeu and CZca soils.

If climate change continues as reported in some papers for the region (Paltineanu et al., 2011, 2012: Paltineanu & Chitu 2019) and extreme rainfall events occur, particularly as pulsed precipitation, then nitrate losses could be even more severe within the region containing permeable soils. Even if alternative dry and rainy years occur, nitrate accumulated in soils during the drought periods could be leached in the following wet years, as reported by Zhou et al., (2010).

As pointed out, the results of this study show the higher potential risk of nitrate leaching below the rooting system of many field crops or fruit trees from the sandy and loamy textured soils as well as a lower risk from the clay-textured soils. These findings can have practical consequences for EU Nitrate Directive, which could be detailed by taking into account the soils` texture combined with the hydraulic conductivity in its recommendations. Thus, the low-permeable clayey-textured soils could be excepted from the maximum NH_4NO_3 annual rate application for the in-situ risk of groundwater pollution. However, where the relief conditions are favorable for runoff, there is an increased risk for surface water pollution.

To minimize nitrate leaching losses within the soils discussed, irrigation should be applied by using the most economical methods (sprinkling or drip irrigation, according to the land use), split-fertilizer application and no-till cropping systems, as Hess et al., (2020) emphasized the positive role of the no-till cropping systems in the U.S. Midwest.

Because this study was carried out within soils with various textures and other soil properties, the findings obtained here might be used everywhere in regions showing a high risk of nitrate leaching. Further experiments using ^{15}N should be carried out for a higher precision in determining the exact origin of the nitrate lost below the root system of crops or natural vegetation.

5. CONCLUSIONS

Soil texture and clay type determine the nitrate leaching pattern. A significantly lower effluent - precipitation amount (cca. 280 mm) is needed for sandy soils (PSeu) to lose the equivalent of the entire applied fertilizer amount (200 kg N ha^{-1} annually) versus the loamy and sandy-loamy soils (CZca) during a predominantly wet season; accordingly, the risk of groundwater pollution with nitrate is substantially higher for sandy soils.

Distinctly significantly more nitrates were leached out per mm of effluent (precipitation) during a simulated wet season, when there is a predominantly descendent solute flux, from the highly permeable PSeu soil than from the mid-permeable CZca soil.

The maximum relative nitrate concentration of the effluent under a continuous water supply occurred at significantly greater values in the case of the sandy PSeu soils versus the CZca soils, but at non-significantly different effluent volumes of 165 mm to 190 mm in the permeable PSeu and CZca soils.

Clay type is very important for soil permeability and nitrate leaching; clayey soils with strong swell-shrink properties have a low risk in groundwater contamination with nitrate at saturated conditions, and the EU Nitrates Directive could recommend different nitrogen fertilizer amounts depending on soil permeability. However, where the relief conditions are favorable for runoff, there is an increased risk for surface water pollution.

Future studies, preferably using NO_3^- markers and lysimeters with larger diameters, such as to contain more large pores and cracks, should be carried out on soils possessing intermediate textures to better characterize nitrate leaching for a wider range of soils.

If the climate change continues and extreme rainfall events occur, then nitrate leaching losses could be even greater within the regions containing permeable sandy or sandy-loamy soils.

To minimize nitrate leaching losses within the soils discussed in this study some measures should be applied, such as sprinkling or drip irrigation, no-till cropping systems, split-fertilizer application according to crop development and mean rainfall amount.

Because this study was carried out within soils with various textures, the obtained findings might be used everywhere in regions showing a high risk of nitrate leaching.

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