Losses of Ca, Mg and SO_4^{2-}-S with Drainage Water at Fertilisation with Different Nitrogen Rates

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Summary

Quantities of Ca, Mg and SO_4^{2-} S leached by drainpipe water from drained Stagnosols of Central Croatia are determined for the period from 1997 to 2004 Ca^{2+}, Mg^{2+} and SO_4^{2-} S concentration in drainage water varied in dependence on the crop type and development stage, on the fertilization, on the quantity and intensity of precipitation, and on the drainage volume. In 8-year average, quantities of Ca, Mg and SO_4^{2-} S leached with drainage water at selected trial treatments with uniform P and K fertilisation and with different nitrogen rates varied from 96.6 to 142.4 kg ha^{-1}, from 46.7 to 69.2 kg ha^{-1} and from 10.6 to 15.2 kg ha^{-1}, respectively.

Key words

subsurface drainage; leaching; Ca; Mg; SO_4^{2-} S

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Introduction

Subsurface drainage is a beneficial water management practice in poorly drained soils but may also contribute to substantial nutrient loads to surface waters. The moist climatic conditions prevailing in Central Croatia predetermine rather significant losses of calcium, magnesium and sulphur by leaching and also theirs negative balance. Sulphur deficiency may become a limiting factor in crop productivity in intensive cropping systems and calcium and magnesium leaching can influence the chemical soil properties. This paper summarises the results of investigations of calcium, magnesium and sulphur migration with drainpipe water in field experiment with different nitrogen fertilization levels carried out from 1997 to 2004 Despite the fact that leaching of Ca, Mg and S with drainpipe water can be connected with fertility of drained soils there is relatively little information in scientific papers that deals with such losses. Saulys and Bastiene (2005) found that from total drainage runoff of cations 87.8% depends on Ca and Mg ions. According to Mengel and Kirkby (1987) average annual leaching from soils in humid climate vary from 200 to 300 kg ha^{-1} of calcium and from 2 to 30 kg ha^{-1} magnesium. Szymczyk and Cymes (2005) studied the effects of precipitation and land use on sodium (Na), calcium (Ca) and magnesium (Mg) outflow from heavy soils via drainage network. Depending on the land use and total precipitation, which influenced soil processes as well as vegetation development, the annual outflow of Na^+, Ca^{2+} and Mg^{2+} from 1 ha of arable lands was 42.6, 287.0 and 31.4 kg, respectively.

Eltun et al. (1996) calculated drainage and surface losses of soil particles, P, K, Mg, Ca, and SO_4^{2-} S. The average annual losses of these variables were 28, 0.32, 7, 12, 159 and 30 kg ha^{-1}, respectively. Plant residues were important sources for loss of P and K, while the loss of Mg, Ca, and S were primarily affected by fertilization. Because of variation in weather factors, there was a great annual variation in nutrient losses, and authors concluded that long term observations are needed in order to obtain reliable data concerning nutrient losses from the various cropping systems. Butkute (2006) studied the concentrations of Ca^{2+} and Mg^{2+} in leachate and their relations with soil pH. The concentrations of Ca^{2+} and Mg^{2+} in leachate differed from 139.67 to 239.33 mg L^{-1} and from 8.13 to 25.00 mg L^{-1} respectively. Soil pH had a strong influence on Ca^{2+} and Mg^{2+} concentrations in the leachate.

Objective of this study is to quantify losses of calcium, magnesium and sulphate via drainage outflow in a field experiment with different nitrogen rates applied for fertilization of grown crops and to define possible influence of fertilization level on loss of selected ions.

Material and methods

A stationary field trial was set up in 1996 on drained Stagnosols in the vicinity of Popovaca. The trial has 10 treatments but only six are taken into consideration in this paper: 1. N_0 PK, 2. N_{100} PK, 3. N_{150} PK, 4. N_{200} PK, 5. N_{250} PK, and 6. N_{300} PK. The trial plot size is 30x130 m (3900 m^2) for each treatment, as conditioned by the drainpipe spacing and their length (130 m). Two drainpipes in their full length are embedded in the area of each fertilizing treatment. The omitted trial treatmens are: 1. check-without fertilization 2. N_{250} PK + Phosphogypsum, 3. N_{250} PK + Zeolite tuff + $CaCO_3$, and 4. black fallow and they are analysed separately. On experimental plots, crops were grown in the following crop sequence: 1995/96, 1998/99 and 2003/04 - maize (*Zea mays*); 1996/97, 1999/2000 and 2002/03 - winter wheat (*Triticum aestivum*); 1997/98 and 2000/01 oilseed rape (*Brassica napus var. oleifera*); 2001/02 and 2004/05 soybean (*Glycine hispida max*.). In the periods with drainage discharge water samples were taken on a daily basis, and average sample was prepared every 5-7 days to be used for chemical analysis of water.

Ca^{2+} and Mg^{2+} content in drainage water was measured by titrimetric EDTA method (Water analysis handbook, HACH, 2nd Edition, p. 327, Chemical Procedures Explained, Appendix A, p. 771) from 1997-2003 and in 2004 by ion chromatography method (HRN EN ISO 14911:2001, Water quality - Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} using ion chromatography - Method for water and waste water) on Dionex ICS-1000 system, analytical column (IonPac CS 16 (5 × 250 mm) at 40°C, Dionex), cation Suppressor [CSRS-ULTRA (4 mm), Dionex] and Conductivity detector (Dionex). The mobile phase consisted of 30 mM MSA (Methanesulfonic acid) passed through the system at 1.50 ml min^{-1}.

SO_4^{2-} content in drainage water have been measured by spectrophotometric method (Water analysis handbook, HACH, 2nd Edition, p. 623, Chemical Procedures Explained, Appendix A, p. 799) in period from 1997 to 2003 and from 2003 by ion chromatography method (HRN EN ISO 10304-1:1998, Water quality - Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions -- Part 1: Method for water with low contamination) on Dionex ICS-1000 system with an analytical column [IonPac AS 17 (4 × 250 mm) at 30°C, Dionex], cation Suppressor [ASRS-ULTRA II (4 mm), Dionex] and Conductivity detector (Dionex). The mobile phase consisted of 10-35-10 mM KOH in gradient work which is provided by eluens generator (EGC-KOH, RFC-30) module with on line preparation of eluens, passed through the system at 1.00 ml min^{-1}.

Table 1. Rainfall features of investigated period

Year	Precipitation, mm												Sum
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
1997	44	55	24	46	73	81	103	63	30	76	127	86	808
1998	65	23	56	59	103	107	121	87	174	120	102	49	1066
1999	36	36	24	112	92	74	80	67	67	47	59	79	773
2000	26	49	72	125	28	48	58	3	82	49	96	79	715
2001	88	4	102	60	35	121	35	44	197	15	78	35	814
2002	16	49	32	135	79	63	90	78	112	67	114	41	876
2003	54	16	8	27	40	29	63	38	91	94	46	7	512
2004	52	40	51	125	67	101	52	54	97	124	58	46	867

Table 2. Drainage efficiency in % of annual precipitation

Treatment	1997	1998	1999	2000	2001	2002	2003	2004	Average
N_0	17.5	27.4	41.6	18.4	33.0	17.9	6.8	24.0	23.3
N_{100}	13.5	23.5	27.4	16.1	26.5	15.2	9.2	18.9	18.8
N_{150}	18.0	32.7	41.0	17.8	40.2	24.1	17.4	29.4	27.6
N_{200}	15.3	24.2	29.9	16.5	29.1	18.3	11.6	21.1	20.8
N_{250}	13.2	23.4	31.2	16.9	28.0	18.9	11.5	20.3	20.4
N_{300}	12.8	17.9	28.9	18.3	28.3	19.6	9.9	20.0	19.5
Average	15.1	24.8	33.3	17.3	30.9	19.0	11.1	22.3	21.7

Results and discussion

Long-term precipitation mean in the area where research is carried out amounts to 865 mm per year, and average annual temperature is 10.7 °C. Rainfall features of investigated period are presented in Table 1. The first discharge used to take water samples from drainpipes occurred in mid November 1997 and the last one at the end of December 2004.

The experimental station soil type is defined as Stagnosols, with A_{ch}+E_{cg} – E_{cg} – B_{tg} sequence of soil horizons. Due to its physical (high content of fine sand, silt and clay) and chemical properties (calcium deficiency, low content of organic matter), this soil type has limited fertility. Because of water stagnation in soil profile drainpipes were installed at the average distance of 20 m. Soil reaction in ploughing layer as well as in the elluvial horizont is acid (pH 4.84), and it is weakly acid in Bg horizont. Total soil nitrogen content in ploughing layer is moderate, humus content is low. Soil content of plant available phosphorus is good, and that of plant available potassium is medium.

Average drainage discharge varied in dependence on precipitation, crop type and growing stage and on nitrogen fertilization. In dry years (2000 and 2003) drainage discharge was low, and differences between different trial treatments were small. In years with average or high precipitation, differences between outflows in different trial treatments were higher and they were also influenced by the crop type and development stage. Drainage efficiency recorded at different years and different trial treatrments is presented in Table 2. Average values varied between 19.5 at treatment with 300 kg ha^{-1} of nitrogen to 27.6 at treatment with 150 of nitrogen per ha. According to some results (Petošić et al., 1998) average drainage discharge coefficient measured in the similar conditions was between 17 and 38%.

Average annual drainage efficiency for all trial treatments range from 11.1% in very dry 2003 to 30.9% in year 2001 Sileika and Guzys (2003) also calculated drainage efficiency for Lithuanian conditions. According to their results in the years with a higher level of precipitation the drainage runoff ranged from 17–39% of the total amount of precipitation. In dry years drainage runoff was 9–20% of the total precipitation amount.

According to the concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}) and sulphate (SO_4^{2-}) in drainage water and the amount of drainage discharge, total loss of these ions is calculated for every year in studied period. Data concerning leaching losses of calcium, magnesium and sulphur for each year in the investigated period and for selected nitrogen fertilisation treatments are presented in figures 1, 2 and 3.

The leached amounts of elements and compounds mainly depend upon drainage runoff intensity and much less on ion concentration in water. Increase in total annual precipitation result with increased leaching of Ca^{2+} and

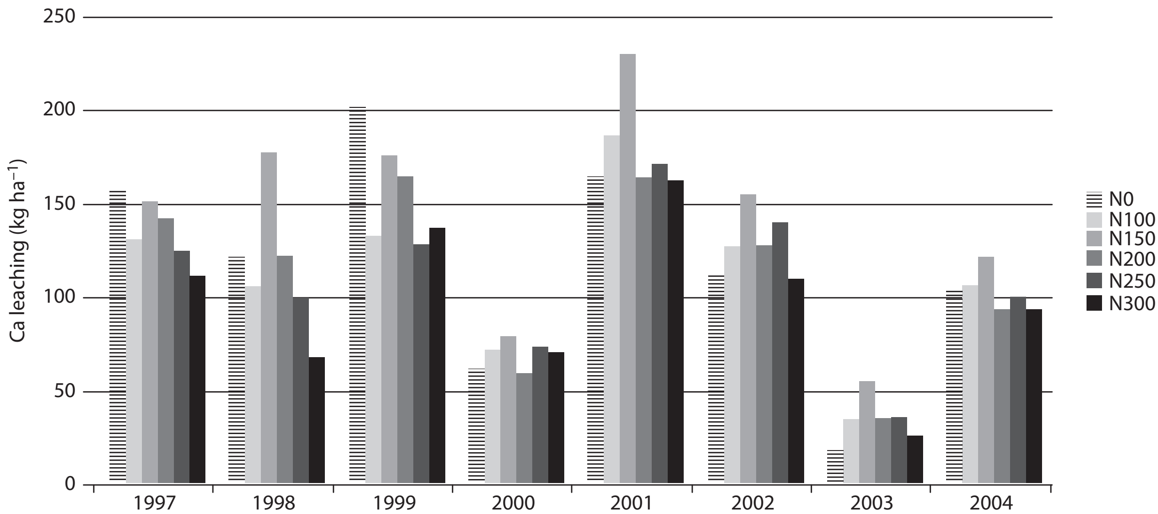

Figure 1. Leaching of Ca^{2+} with drainpipe water per treatments and years, kg ha^{-1}

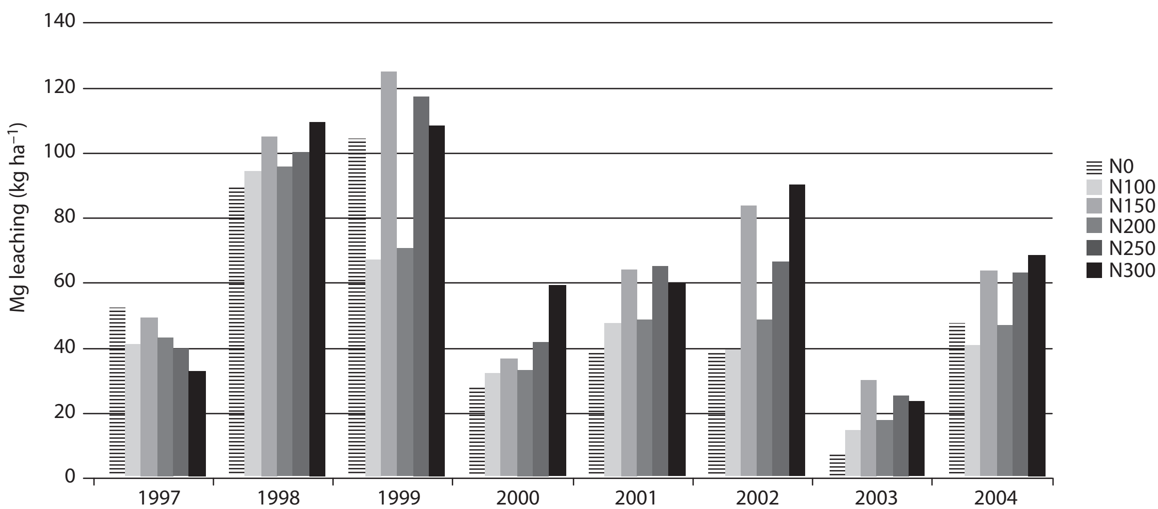

Figure 2. Leaching of Mg^{2+} with drainpipe water per treatments and years, kg ha^{-1}

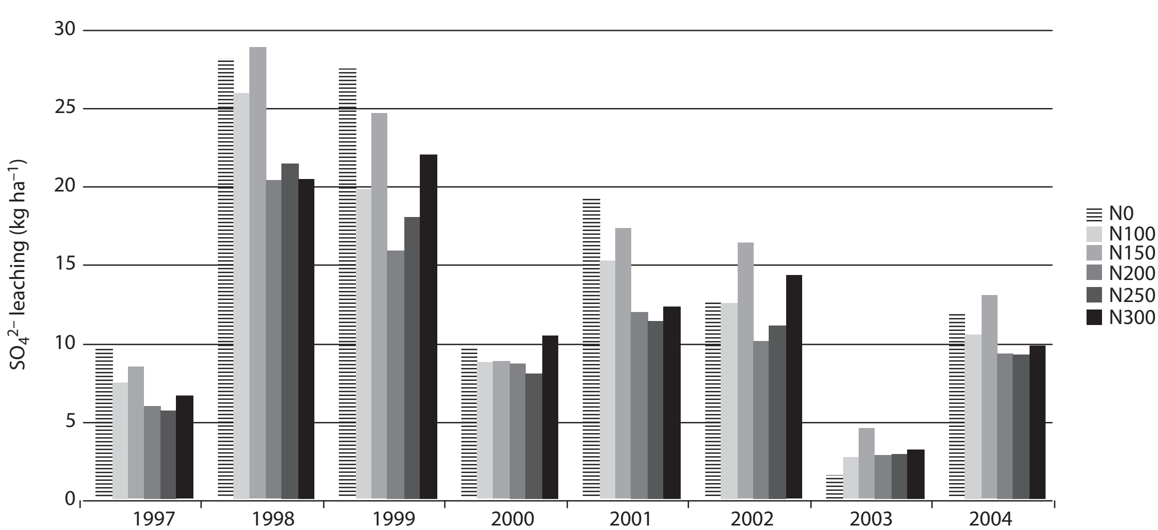

Figure 3. Leaching of SO_4^{2-} S with drainpipe water per treatments and years, kg ha^{-1}

Table 3. Average leaching losses of Ca^{2+}, Mg^{2+} and SO_4^{2-} S for the period 1997-2004 (kg ha^{-1})

Treatment	Ca^{2+} leaching	Mg^{2+} leaching	SO_4^{2-} S leaching
N_0	116.9	50.5	15.0
N_{100}	111.3	46.7	12.8
N_{150}	142.4	69.2	15.2
N_{200}	112.8	50.0	10.6
N_{250}	108.5	64.4	10.9
N_{300}	96.6	68.5	12.3
LSD p 5%	23.5	15.2	2.7
LSD p 1%	31.6	20.3	3.6

Mg^{2+} from soils, as it was found by other authors (Szymczyk and Cymes, 2005, Sileika and Guzys, 2003). The lowest quantities of leached calcium, magnesium and sulphate are recorded in dry 2003.

Average losses of Ca^{2+}, Mg^{2+} and SO_4^{2-} S for the period 1997-2004 are presented in table 3. According to the data on average calcium loss with drainpipe water it can be concluded that nitrogen fertilization at rate of 150 kg ha^{-1} results with significantly highest value of calcium leaching. Statements that higher mineral fertilisation, especially nitrogen fertilisation, induces Ca^{2+} migration and its leaching from the soil, are frequent in the literature. Monaghan et al. (2005) found that N fertilizer application significantly increased losses of nitrate-N and Ca in drainage but had no significant effect on K, Mg, Na, sulfate-S, Cl, and P drainage losses. In opposite to that, Sileika and Guzys (2003) stated that the intensity of agriculture had no influence on Ca^{2+} concentration in drainage water. Taking into account the differences between calcium losses in treatments with different nitrogen fertilisation it is important to stress the complexity of problem. Nitrogen is essential for yield formation, it has influence on water consumption, microbiological activity of soil, and there is no simple explanation for average quantities of leached calcium at different nitrogen fertilisation levels.

Compared to the control treatment magnesium losses were statistically significantly higher at nitrogen fertilisation of 150, 250 and 300 kg ha^{-1}. The range of average magnesium losses in this experiment is from 50.0 to 69.2 kg ha^{-1}. According to some results (Oliveira et al., 2002) no treatment effect was observed for Mg and Ca leaching in the experiment with four doses of N: 0, 30, 60, and 90 kg ha^{-1} of N. The mean mass values for Mg and Ca extrapolated for 1 ha were of 80 and 320 kg ha^{-1}, respectively. Schweiger and Amberger (1979) calculated average losses of Mg in long term lysimeter experiment. Losses were in average 72 kg ha^{-1} in sandy soil and 94 kg ha^{-1} in loam soils. Investigation was carried out in the region with 810 mm of average annual precipitation. Ruszkowska et al. (1988) also quantified leaching of the Ca^{2+}, Mg^{2+}, and SO_4^{2-} in lysimeter experiment. Leaching losses of calcium, magnesium and sulfur were (in kg ha^{-1} per year): 89-120 kg Ca, 6-9 kg Mg, and 36-66 kg S-SO_4 from the loess soil; 49-82 kg Ca, 15-25 kg Mg, and 21-37 kg S-SO_4 from the loamy soil. Ruszkowska et al. (1993) presented the data on the balance of Ca, Mg, and S in relation to soil type, NPK and Mg fertilizer application rates, liming and irrigation in a crop rotation. Annual Ca leaching was 94-180, 18-70 and 94-160 kg ha^{-1} on sandy, loess, and loamy soils, under cropping, and 187, 104 and 222 kg ha^{-1} under fallow. Annual Mg leaching was greatest on the loamy soil, 26-52 kg ha^{-1}, depending on fertilizer application rate. Sulphate leaching was 19-53, 3.7-50 and 49-71 kg ha^{-1} annually on sandy, loess, and loamy soils, respectively.

According to the data from table 3 for average of the years 1997-2004 SO_4^{2-} S leaching via drainage pipes was between 10 and 15 kg SO_4^{2-} S ha^{-1}. Lowest quantity of leached SO_4^{2-} S in this experiment is recorded at nitrogen fertilisation of 200 kg N ha^{-1}. Sulphate leaching was closely related to drainage volume as also found by Eriksen and Askegaard (2000). These values are lower than those reported by Riley et al. (2002). They quantified inputs and outputs of sulfur (S) over a three year period using field lysimeters. Leaching losses of S ranged from 35 kg ha^{-1} to 83 kg ha^{-1}. Eriksen et al. (2002) investigated sulphate leaching and S balances in an organic cereal crop rotation. They found out that sulphate leaching was quantitatively the most important item affecting the S balance, since excess S was lost by leaching.

Conclusion

Trial results point to the following conclusions:

1. Average drainage efficiency varied between 19.5% at treatment with 300 kg ha^{-1} of nitrogen to 27.6% at treatment with 150 of nitrogen per ha. Average annual drainage efficiency for all trial treatments range from 11.1% in very dry 2003 to 30.9% in year 2001.
2. Calcium leaching in drainpipe water varied from 96.6 kg ha^{-1} at the treatment with 300 kg ha^{-1} N up to the 142.4 kg ha^{-1} at the treatment with 150 kg ha^{-1} N and it is significantly highest value of calcium leaching.
3. The average magnesium losses are in the range from 50.0 to 69.2 kg ha^{-1}. Compared to the control treatment, magnesium losses were statistically significantly higher at nitrogen fertilisation levels of 150, 250 and 300 kg N ha^{-1}.
4. SO_4^{2-} S leaching via drainage pipes was between 10 and 15 kg SO_4^{2-} S ha^{-1}. Lowest quantity of leached SO_4^{2-} S is recorded at nitrogen fertilisation of 200 kg N ha^{-1}.

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