

## Leaching of plant nutrients from cultivated soils

### II Leaching of anions

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**Abstract.** Leaching of anions from three soil samples (sand, fine sand and sandy clay) representing the plough layer was studied in a lysimeter experiment under conditions corresponding to the fallow. The effect of fertilization and that of acid irrigation solution on the amounts of anions washed out was also studied.

The extraction of anions from different soils seems to correspond to that of cations: the coarser the soil, the higher the nutrient losses. This was valid for nitrate and sulfate, but the amounts of phosphate extracted were insignificant. The sum of the anion equivalents leached was lower than the respective sum of cations in all the leachates indicating that a part of the cations was leached as bicarbonate.

The physical properties of the soil regulating the infiltration of water affect the movement of anions bonded non-specifically. The anions in pores of soil aggregates seem to be protected against leaching to a certain degree. However, the biological value of an anion is an important factor. It seems that microbiological processes may decrease the leaching losses of nitrate.

### Introduction

The sorption mechanism largely determines the liability of an ion to leaching. Anions adsorbed specifically form a coordination complex on the surface of the adsorbing material (HINGSTON, POSNER and QUIRK 1972) and are difficult to wash out. Anions retained unspecifically are in the diffusive part of the surface electric double layer separated at least by one water molecule from the surface of the particle (HINGSTON, ATKINSON, POSNER and QUIRK 1968) and are liable to leaching. Obviously, the movement of ions like these in the soil is to a great degree determined by the same factors that regulate the movement of the water in the soil. Chemical properties of the soils and microbiological activity may also be of importance. It has been noted, for example, that in contrast to the cation exchange capacity, the sorption capacity of the anions increases with increasing acidity (WIKLANDER 1964).

The purpose of this study was to investigate the leaching of native and applied nitrate, sulfate and phosphate anions in different soils, and to compare the effect of water and diluted acid on it.

## Materials and methods

The lysimeter experiment was carried out under greenhouse conditions with three crushed, unsieved soil samples: sand, fine sand and sandy clay soil. Their properties and the experimental design are presented in the previous work (HARTIKAINEN 1978). One half of the lysimeters received the following amounts of nutrients per 1.7 l of soil: 100 mg N as  $\text{KNO}_3$ , 100 mg S as  $\text{MgSO}_4 \cdot 7 \text{ H}_2\text{O}$  and 50 mg P as  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .

The solutions percolated during twentyfour hours were measured and analysed for nitrate by using a specific electrode (Orion Ionanalyzer meter). The average amounts of the total leachates collected were: 1330 ml from the sand, 1370 ml from the fine and 1363 ml from the sandy clay soil.

Sulfate was determined turbidimetrically as  $\text{BaSO}_4$  (KORKMAN 1973). Gum arabic was used for the stabilization of the suspension. The measurement of the transmission of the sample was done by a »Lange J» colorimeter with a blue filter.

Phosphate was analysed by the molybdenblue method by using ascorbic acid as the reductant (ANON. 1969).

## Results

The sums of the different anions leached by five percolations are presented in Table 1 with 95 per cent confidence limits. The leaching of nitrate and sulfate from the three soil samples differed strikingly. The cumulative curves in Figure 1 describe the losses of fertilizer nitrogen from the lysimeters during the experimental period. All the nitrate added in the chemicals was washed out from the sand soil sample. Its leaching from the fine sand soil was statistically significant only on the third irrigation treatment and the nitrogen losses were lower than in the sandy clay soil sample.

Irrigation with the acid solution enhanced the extraction of nitrate, especially in the fine sand sample (Figure 1), in which it increased the nitrogen losses almost threefold.

The leaching of fertilizer sulfate was practically complete in coarser soils, but in the clay soil sample water extracted only low amounts of this anion.

The analytical results from the leaching of phosphate remained somewhat questionable. Turbidity of the leachate interfered with the colorimetric measurements and caused a great variation between the analytical data. The results of the clay soil sample indicating an exceptionally high leaching may to a large degree be due to the suspended clay, from which the acidic reagents may dissolve phosphate during the phosphorus analysis (e.g. LEE 1969). The effect of fertilization was statistically significant only in the fine sand soil, but it was the reverse to the effect on the other anions studied: the amounts of phosphorus washed out by water were higher in the unfertilized lysimeters than in the fertilized ones. Besides microbial processes this may be due to the increase in the salt concentration in the soil solution reducing the solubility of phosphates held by aluminium and iron compounds. Futher, it is possible that the leachate from fertilized lysimeters was not so turbid as that from unfertilized ones.

Table 1. Total leaching of anions by infiltrating solution mg/l soil.

Irrigation solution	Salts added	$\text{NO}_3\text{-N}$	$\text{SO}_4\text{-S}$	$\text{PO}_4\text{-P}^*$
<i>Sand</i>				
$\text{H}_2\text{O}$	0	44.1 ± 25.7	59.4 ± 10.5	0.03 ± 0.01
	+	104.2 ± 11.7	114.6 ± 11.9	0.02 ± 0.01
$\text{H}_2\text{SO}_4$	0	48.1 ± 11.3		0.02 ± 0.01
	+	110.2 ± 14.7		0.02 ± 0.00
<i>Fine sand</i>				
$\text{H}_2\text{O}$	0	3.4 ± 2.6	83.5 ± 7.9	0.03 ± 0.00
	+	7.7 ± 5.1	149.8 ± 58.2	0.02 ± 0.01
$\text{H}_2\text{SO}_4$	0	8.0 ± 19.8		0.03 ± 0.02
	+	19.3 ± 15.5		0.02 ± 0.00
<i>Sandy clay</i>				
$\text{H}_2\text{O}$	0	8.3 ± 2.5	22.0 ± 6.1	0.34 ± 0.06
	+	27.5 ± 16.0	41.5 ± 11.4	0.23 ± 0.07
$\text{H}_2\text{SO}_4$	0	6.0 ± 3.4		0.78 ± 1.13
	+	31.9 ± 12.5		0.54 ± 0.49

\*Four percolations only.

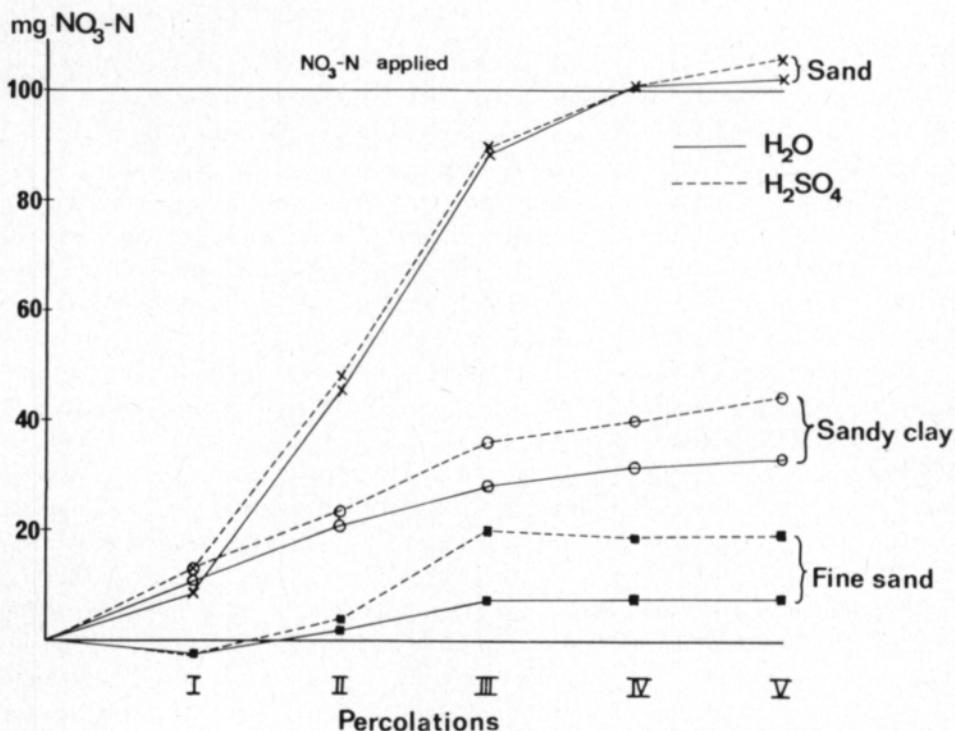


Figure 1. Leaching of fertilizer nitrogen form different soil samples.

Cations and anions are likely to be washed out in equivalent amounts. Comparing the sums of leached anion equivalents to the respective sums of the basic cations calculated from the analytical data from the previous work (HARTIKAINEN 1978) it was found that the amounts of anions were always

considerably lower than those of the cations. The chloride content was less than 1 meq in all the lysimeters and can be neglected. The portions of anion equivalents from the corresponding amounts of cations are presented in percentages in Table 2. The losses of phosphorus were so low that they were not taken into account. Thus, the percentages indicate the portions of cations washed out as nitrate or sulfate. The rest of the cations was obviously leached mainly as bicarbonate.

Table 2. The leaching of anions as percentage of the corresponding leaching of cations.\*

Irrigation solution	Salts added	Sand	Fine sand	Sandy clay
$H_2O$	0	39.9 <sup>b</sup>	31.3 <sup>a</sup>	57.8 <sup>de</sup>
	+	48.9 <sup>e</sup>	48.1 <sup>e</sup>	62.3 <sup>ef</sup>
$H_2SO_4$	0	53.2 <sup>cd</sup>	47.6 <sup>e</sup>	68.2 <sup>f</sup>
	+	51.4 <sup>cd</sup>	49.2 <sup>e</sup>	76.0 <sup>g</sup>

\*Means followed by a common letter do not differ at  $P = 0.05$ .

The relative amount of »bicarbonate» seems to be most significant in fine sand soil. This is in accordance with the high content of organic matter of the sample. Correspondingly it seems that the amount was lowest in the sandy clay sample poor in organic matter.

## Discussion

The liability of anions to leaching is determined, in addition to the sorption mechanism of the ion, also by properties of the soil material. In different soils it seems to correspond to the behaviour of cations (cf. HARTIKAINEN 1978): leaching losses were lowest in the clay soil and showed a tendency to increase when soil material became coarser. However, phosphate makes a striking exception; the amounts washed out from the columns of sand and fine sand soils were at most about one tenth of the losses from the clay soil sample. The phosphorus probably was fixed in the suspended eroded solid material and was not dissolved in the leachate. Thus it was not immediately biologically available. The model experiment proves that those properties of a soil which limit the leaching, may enhance the liability to erosion.

According to HINGSTON, POSNER and QUIRK (1972) sulfate and phosphate anions are adsorbed by specific bonding forming a coordination complex to the surface of sorbing material. Phosphate has often been found to decrease the retention of sulfate. KAMPRAHT, NELSON and FITTS (1956) consider that this results from the sorption mechanism of the same kind. But ENSMINGER (1954) supposes that it is caused by the sorption on same compounds. In this lysimeter experiment, however, these anions behaved in different ways. Added sulfate was leached effectively, particularly from the coarser soil samples, phosphate not at all. Thus it seems that the stability of the possible coordination complex formed is a critical factor determining the leaching of anions of this kind. Furthermore, GEBHARDT and COLEMAN (1974) suppose, contrary to HINGSTON et al., that sulfate is adsorbed non-specifically as counterion opposing

positively charged sites on oxide surfaces. However, they presume that the adsorption reaction involves a ligand exchange rather than simple ion-ion interaction.

Nitrate bonding non-specifically was easily leached from the sand soil sample, very pervious to water. Analytical results of the fine sand soil suggest that the aggregate structure of the sample obviously decreased the loss of this nutrient. Nitrate ions found in pores of the aggregates are known to be protected against leaching (CUNNINGHAM and COOKE 1958, WEBSTER and GASSER 1959).

However, it seems that the physical properties of a soil do not alone control the movement of the anion. There may have been microbial activity in the fine sand sample rich in organic matter, which possibly decreased the nitrogen losses by denitrification or microbiological immobilization. This supposition is supported by the fact that irrigation with the acid solution enhanced the extraction of nitrate, especially in this sample, increasing the nitrogen losses by almost threefold. This may be due to the fact that the microbial immobilization was reduced by the drastic change of the environmental circumstances in the acid treatment.

In addition to the microbial activity of a soil the biological value of the anion is an important factor. Obviously, the movement of a chloride ion is largely determined only by the physical characteristics of the soil. However, although nitrate is adsorbed in the soil by non-specific bonding, sulfate ions may somewhat promote its movement by exchange reactions.

Irrigation with the acid solution significantly decreased the leaching of »bicarbonate» from the unfertilized soil columns. This obviously resulted from the diminished production of carbon dioxide due to increased acidity reducing the microbial activity. Further it can be caused by the increase in the electrolyte concentration lowering the solubility of carbon dioxide. The increase of concentration in soil solution may to a certain extent explain the observation that the fertilization decreased the amount of »bicarbonate» washed out by water from the columns of sand and fine sand soils.

The results of this work are in accordance with the conclusion presented by GÄCHTER and FURRER (1972) that the liability to leaching diminishes in proportion to the relative amount of finer soils. Differing results obtained in practical studies (e.g. VIRO 1953, SÄRKKÄ 1971) are apparently caused by the fact that with an increasing portion of the finer soils the potential loading from the watershed rises accordingly. Effects of the factors connected with the soil material remained unsolved in the studies mentioned above because the relative amount of cultivated soils and finer soils, the location of settlements with a sewage system and the closeness of houses and livestock are highly correlative with each other.

It should also be taken into consideration in an evaluation of the results from the lysimeter experiment that the amount of the irrigation solution was equal to a very heavy or prolonged rain. Furthermore, it should be borne in mind that the trial was carried out in conditions corresponding to the fallow. Thus it yields no information, as to the degree the growing plant lowering the soil moisture and taking up nutrients influences the leaching.

## REFERENCES:

- ANON. 1969. Juoma- ja talousveden tutkimusmenetelmät. Elintarviketutkijain seura. 169 p. Helsinki.
- CUNNINGHAM, R. K. & COOKE, G. W. 1958. Soil nitrogen. 2. Changes in levels of inorganic nitrogen in a clay-loam soil caused by fertilizer additions, by leaching and uptake by grass. *J. Sci. Fd Agric.* 9: 317—324.
- ENSMINGER, L. E. 1954. Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Sci. Soc. Amer. Proc.* 18: 259—263.
- GEBHARDT, H. & COLEMAN, N. T. 1974. Anion adsorption by allophanic tropical soils: Sulfate adsorption. *Soil Sci. Soc. Amer. Proc.* 38: 259—262.
- GÄCHTER, R. & FURRER, O. J. 1972. Der Beitrag der Landwirtschaft zur Eutrophierung der Gewässer in der Schweiz. 1. Ergebnisse von direkten Messungen im Einzugsgebiet verschiedener Vorflüter. *Schweiz. Z. Hydrol.* 34: 41—70.
- HARTIKAINEN, H. 1978. Leaching of plant nutrients from cultivated soils. 1. Leaching of cations. *J. Scient. Agric. Soc. Finl.* 50: 263—269.
- HINGSTON, F. J., ATKINSON, R. J., POSNER, A. M. & QUIRK, J. P. 1968. Specific adsorption of anions on goethite. *Trans. 9th Int. Congr. Soil Sci. Adelaide.* 1: 669—677.
- , POSNER, A. M. & QUIRK, J. P. 1972. Anion adsorption by goethite and gibbsite. 1. The role of the proton in determining adsorption envelopes. *J. Soil Sci.* 23: 177—192.
- KAMPRAHT, E. J., NELSON, W. L. & FITTS, J. W. 1956. The effect of pH, sulfate and phosphate concentrations on the adsorption of sulfate by soils. *Soil Sci. Soc. Amer. Proc.* 20: 463—466.
- KORKMAN, J. 1973. Sulfur status in Finnish cultivated soils. *J. Scient. Agric. Soc. Finl.* 45: 121—215.
- LEE, G. F. 1969. Analytical chemistry of plant nutrients. In Eutrophication; causes, consequences, correctives. p. 646—658. Washington.
- SÄRKÄ, M. 1971. Kasvinravinteiden huuhtoutuminen maaperästä Suomessa. *Kemian Teollisuus* 5: 367—377.
- WEBSTER, R. & GASSER, J. K. R. 1959. Soil nitrogen. 5. Leaching of nitrate from soils in laboratory experiments. *J. Sci. Fd Agric.* 10: 584—588.
- WIKLANDER, L. 1964. Cation and anion exchange phenomena. In Chemistry of the soil, ed. Bear. p. 161—205. London.
- VIRO, P. 1953. Loss of nutrients and the natural nutrients balance of the soil in Finland. *Comm. Inst. For. Fenn.* 42. 1.: 1—45.

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## SELOSTUS

### Kasvinravinteiden huuhtoutumisesta viljelysmaista

#### 2. Anionien huuhtoutuminen

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Lysimetrikokeessa tutkiitti anionien huuhtoutumista hiekk-, hieta- ja savimaan muokkauskerroksesta kesantoa vastaanissa olosuhteissa. Happaman kastelulioksen vaikutusta selvitettiin käyttämällä 0.025 M  $\text{H}_2\text{SO}_4$ -liuosta.

Nitraatin ja sulfaatin uuttuminen oli sitä voimakkaampaa, mitä karkeampaa maa oli, mutta fosfaatti huuhtoutui kaikista koejäsenistä erittäin vähän. Läpivaluneiden liosten anionien ekvivalenttisumma oli aina pienempi kuin vastaava kationisumma, minkä katsottiin viittaan siihen, että osa kationeista huuhtoutui bikarbonaattina.

Veden liikkeitä maassa sätelevät fysikaaliset tekijät vaikuttavat epäspesifisesti pidättyniiden anionien liikkumiseen. Murujen huokosiu joutuneet anionit ovat ilmeisesti jossain määrin turvassa huuhtoutumiselta. Mutta näyttää myös siltä, että mikrobiologiset prosessit voivat vähentää biologisesti arvokkaiden anionien, kuten nitraatin, huuhtoutumista.