# Leaching of plant nutrients from cultivated soils

## I Leaching of cations

HELINÄ HARTIKAINEN

University of Helsinki, Department of Agricultural Chemistry, 00710 Helsinki 71

**Abstract.** Leaching of native and added basic cations was studied in a lysimeter experiment. The trial was carried out with three surface soil samples: sand, fine sand and sandy clay. The effect of the acidic precipitation on the leaching losses was studied by using 0.025 M sulfuric acid as irrigation solution.

The cation concentration in the leachate seemed to be determined by the CEC of the soil sample. The relative and absolute leaching losses were lowest in the sandy clay and highest in the sand soil. Five percolations extracted most abundantly calcium and least abundantly sodium, the losses of magnesium and potassium were of about the same magnitude. In regard to cation reserves of the soils the relative amounts leached usually followed the sequence:  $Na > Mg \approx Ca > K$ .

Fertilization seemed to promote the leaching of cations, especially that of soil calcium. Water extracted 10 to 37 % of added magnesium, but only 2 to 6 % of added potassium due to the effective retention. The acid in the irrigation water increased the losses of all cations studied, most drastically the losses of divalent ones.

### Introduction

Studies concerning the leaching of cations from soil are scarce, especially in Finland. According to VIRO (1953), the quality of inorganic matter in watercourses is determined by the bedrock of the watershed, but the concentration of this matter depends on the type of the soil. On the basis of a correlation analysis he claims that the bulk of inorganic material in river waters is derived from clay soils. His study covered the whole of Finland, but this relation did not exist in the northern parts of the country, where the concentrations were too high compared with the area of cultivated clay soils. It is obvious that the analytical results also include nutrients fixed in the eroded solid soil material. Thus it is not proved that the leaching, i.e. the movement of cations in the solution, would be significant particularly in clay soils.

The aim of the present study was to compare the leaching intensities of native and added cations in different soils and to simulate the effect of increased rainfall acidity. This was carried out by a lysimeter experiment in greenhouse.

Table 1. Characteristics of the experimental soils.

	Sand	Fine sand	Sandy clay
pH (CaCl <sub>2</sub> )	5.4	5.0	6.0
Org. C %	2.9	6.8	3.3
Exch. Na me/100 g	0.07	0.15	0.20
» K »	0.34	0.50	1.65
» Mg »	0.48	1.00	4.12
» Ca »	7.40	11.78	17.27
CEC at pH 7.0	17.23	28.97	31.11

#### Materials and methods

The three mineral soil samples used in the model experiment were collected from the neighbourhood of Helsinki. They represented the plough layer of cultivated soils of different texture. The soils are characterized by data in Table 1. Soil pH was measured by Beckman pH-meter in a 0.01 M CaCl<sub>2</sub> suspension in the ratio of 1 to 2.5 and exchangeable cations were extracted with 1 M NH<sub>4</sub>OAc solution (pH 7.0).

The lysimeters were constructed from hard plastic sewage tubes (diameter 84 mm, height 36 cm). The bottom of each tube was closed with a stopper, in to which 86 holes (diameter 3.5 mm) were drilled. The tubes were greased very thinly with vaseline. On the bottom of each lysimeter was placed 270 g of washed coarse sand and the air dried and crushed, but unsieved, soil samples were added as small portions:  $1\,900\,\mathrm{g}$  of sand soil,  $1\,600\,\mathrm{g}$  of fine sand and  $1\,900\,\mathrm{g}$  of sandy clay. After the soils in the columns had been moistened by capillary suction they were incubated at about field capacity for seven days at  $+15^{\circ}$  C.

In one half of the lysimeters the following amounts of chemicals per 1.7 l of soil were placed to the depth of one centimeter: 279.1 mg K (7.1 meq) as  $KNO_3$ , 32.3 mg Ca (1.6 meq) as  $Ca(H_2PO_4)_2 \cdot H_2O$ , 75 mg Mg (6.2 meq) as MgSO<sub>4</sub>· 7 H<sub>2</sub>O.

During the experimental period of eight months the lysimeters were surface irrigated five times with a total amount of 1 500 ml of distilled water or 0.025 M sulfuric acid solution corresponding to a total precipitation of 265 mm. The trial was carried out with four replicates.

One day after every irrigation the percolated solutions collected in to plastic bottles were measured and analysed for potassium and sodium (EEL flame photometer), calcium and magnesium (Perkin Elmer 290 atomic absorption spectrophotometer).

### Results

The average amounts of the total leachates collected were: 1330 ml from the sand, 1 370 ml from the fine sand and 1 363 ml from the sandy clay soil. The sums of the different cations washed out by the five percolations are presented in Table 2 with 95 per cent confidence limits.

Table 2. Total leaching of cations by percolating solution (mg/l soil).

Irrigation solution	Salts added	Na	K	Mg	Ca
Sand					
H <sub>2</sub> O	0	$8.0 \pm 0.2$	19.9 ± 2.5	$14.6 \pm 2.8$	286 ± 59
	+	$9.4 \pm 0.3$	$30.4 \pm 3.8$	$25.8 \pm 1.6$	$525 \pm 47$
H <sub>2</sub> SO <sub>4</sub>	0	$10.6\pm1.0$	$43.6 \pm 2.6$	45.7 ± 2.9	$975 \pm 226$
	+	$12.3\pm0.7$	$50.9 \pm 5.7$	$61.8 \pm 4.4$	$1239 \pm 17$
Fine sand					
Н,О	0	$8.1\pm0.6$	$16.8 \pm 1.5$	$18.3 \pm 2.1$	$299 \pm 33$
	+	$9.5\pm1.2$	$20.0 \pm 0.8$	$22.5 \pm 2.6$	$370 \pm 16$
H <sub>2</sub> SO <sub>4</sub>	0	$10.6 \pm 2.0$	$25.8 \pm 6.7$	$39.6 \pm 22.5$	$693 \pm 158$
	+	$12.3 \pm 1.4$	$31.2 \pm 2.8$	$51.9 \pm 5.6$	859 ± 97
Sandy clay					
H,O	0	$5.7 \pm 0.5$	$7.8 \pm 0.3$	$8.0 \pm 1.1$	56 ± 15
	+	$6.9 \pm 1.5$	$11.7 \pm 2.5$	$18.9 \pm 3.1$	$125 \pm 31$
H <sub>2</sub> SO <sub>4</sub>	0	$11.5 \pm 2.9$	$28.8 \pm 5.5$	$62.1 \pm 12.7$	$659 \pm 127$
	+	$12.4\pm1.5$	$42.1 \pm 21.5$	$76.3 \pm 4.5$	$671 \pm 57$

As expected, water extracted lower amounts of cations than the acid solution. Leaching of all cations studied tended to be higher from the coarser soils than from the clay soil sample. Losses of calcium were most significant and those of sodium the lowest.

Because the soil samples markedly differed from each other in their nutrient reserves, the absolute amounts washed out do not characterize their liability to leaching. The amount of exchangeable cations extracted with 1 M NH<sub>4</sub>OAc (pH 7) was chosen for the basis of mutual comparison of the samples. To this value the amount of fertilizer cations was added.

As shown in Table 3, water extracted relatively most effectively sodium, although the absolute losses were low (cf. Table 2). The amounts of cations washed out from the unfertilized lysimeters mainly followed the sequence Na > Mg > Ca > K, but the addition of salts made the portion of calcium greater than that of magnesium. The content of potassium in the percolated solution was in all soil samples and in all treatments the lowest as compared to the native exchangeable and added resources in the soils indicating the ability of this nutrient to resist the leaching.

The relative amounts of exchangeable cations in unfertilized soil columns mainly corresponded to those in the leachates after irrigation with water (Table 4). Thus it seems that the type of the soil largely determines also the cation composition in the leachate.

The differences between the amounts of cations washed out from the fertilized and unfertilized lysimeters indicate the losses of added cations (Table 5). These data also show the effective sorption of potassium. Salt addition usually seemed to intensify the leaching of native calcium from soil. The acid treatment generally increased the losses of added nutrients, except the loss of calcium from the sandy clay and that of potassium from the sand soil sample.

Table 3. Leaching of basic cations in different soil samples expressed in percentage of the sum of the native exchangeable and added cations.

Irrigation solution Sa	alts added	Na	K	Mg	Ca
Sand					
H <sub>2</sub> O	0	42.1	13.5	22.6	17.2
	+	49.5	9.6	23.7	31.3
H <sub>2</sub> SO <sub>4</sub>	0	55.7	29.6	70.5	58.8
	+	65.0	16.3	56.7	73.9
Fine sand					
H <sub>2</sub> O	0	25.4	9.0	15.1	13.5
	+	29.6	5.7	13.6	16.5
H <sub>2</sub> SO <sub>4</sub>	0	33.3	13.9	32.6	31.2
	+	38.4	8.9	31.3	38.4
Sandy clay					
H <sub>2</sub> O	0	10.9	1.7	1.4	1.5
	+	13.2	1.9	3.2	3.2
H <sub>2</sub> SO <sub>4</sub>	0	21.8	6.3	11.1	17.0
	+	23.6	6.7	12.7	17.3

Table 4. The relative amounts of the exchangeable basic cations in soil columns and cation composition in percolated solution per cent of sum of cations.

		Na	K	Mg	Ca	
	Sand					
	soil	0.9	4.1	5.8	89.3	
	leachate	2.1	3.1	7.4	87.4	
	Fine sand					
	soil	1.1	3.8	7.5	87.7	
	leachate	2.1	2.5	8.8	86.7	
	Sandy clay					
	soil	0.9	4.6	18.2	76.3	
	leachate	6.5	5.0	16.8	71.8	

Table 5. Leaching of the added cations (%).

Irrigation solution	K	Mg	Ca	
Sand				
H <sub>2</sub> O	6.4	25	1258	
H <sub>2</sub> SO <sub>4</sub>		37	1390	
Fine sand				
H <sub>2</sub> O	1.9	10	374	
H <sub>2</sub> SO <sub>4</sub>	3.3	28	874	
Sandy clay				
H <sub>2</sub> O	2.4	25	363	
H <sub>2</sub> SO <sub>4</sub>		32	63	

#### Discussion

The liability of cations to leaching from different soils seems to depend on the cation exchange capacity of the sample; the relative losses were highest in the sand soil and lowest in the sandy clay sample rich in nutrients. The content of exchangeable magnesium e.g. was low in the sand and fine sand soil (0.48 and 1.00 meq/100 g respectively) in relation to the clay soil sample (4.10 meq/100 g). Considering the relative leaching the differences between the soils were reversed. It seems that the leaching of cations is not as marked from the clay soil as from the cultivated coarser soils. The opposite results presented by Viro (1953) are thus likely to be due to analysis of river water including eroded solid material.

The type of the soil also seems to determine the cation composition in the leachate. It is likely that seepage water from a clay soil is more diluted but contains relatively more magnesium than seepage water from coarser soils, because our clay soils are quite rich in exchangeable magnesium (KAILA 1973).

In a survey published by WIKLANDER (1970), the differences between the cation composition in the plough layer and that in drainage water were much larger than in this study. The ratio of relative concentrations of sodium and potassium in water was about eight times higher than that in the respective soil. In the present material the corresponding ratio in the sand soil was three-fold and in the clay soil sixfold. If the soil columns had been longer, it is likely that the ratio of sodium to potassium would be larger in the percolated solution due to effective sorption of potassium. It is possible that the retention of calcium increases the content of magnesium in drainage water. Thus the cation exchange may quite significantly regulate the leaching of cations.

Calcium was the main cation leached owing to the fertilization, except in the clay soil sample washed by acid solution. Also the relative amount of magnesium was higher than that of the univalent ions. The effect of the salt addition promoting the leaching of divalent cations may be increased by the increase in concentration of the soil solution. This alters the cation exchange equilibrium so that the ratio of divalent ions to univalent ones on the exchange surface decreases (Wiklander 1964).

The chemicals applied did not contain sodium. This means that all the sodium leached derived from the native resources of the soils. The increase in the leaching of this cation owing to the fertilization was statistically significant, except in the clay soil sample. This probably results from the displacement of strongly hydrated sodium ions on the surfaces of soil particles by fertilizer cations. Water extracted this element a somewhat greater extent from the coarse soils than from the clay soil sample with a high CEC. The behaviour of sodium accords with the observation that in Quarternary deposits the alkali metals indicate contamination of ground water caused by agricultural settlement (LAHERMO 1970).

The acidic irrigation water increased the leaching of cations to a somewhat greater degree from the clay soil with high pH and large CEC than from the coarser soil samples, though the absolute amounts of the respective ions leached are of the same order or even lower in the clay soil. This is in accordance with

the observation that the sensitivity of soils to acid precipitation increases with the exchange capacity and the base saturation. Futher, below pH 5-5.5 the adsorption energy of hydrogen ion is small, while above this pH level it increases strongly leading to a greater replacing efficiency for base cations (Wiklander 1973/1974). It may also, to some extent, be caused by the unequal percolation of water in lysimeters filled with clay soil. This supposition is supported by the fact that the amounts of cations washed out by the acid solution increased in the clay soil immediately in the beginning of the experiment whereas in the coarser soils the effect did not appear until after the second or third irrigation treatment.

The loss of magnesium from the clay soil sample increased, due to the acid treatment, four to eightfold as compared to water extraction, evidently as a consequence of the release of nonexchangeable magnesium: the fine particle size fractions in Finnish clay soils are known to contain nonexchangeable, acid extractable magnesium in abundance (Kaila and Ryti 1968). Saturation of the soil with exchangeable hydrogen considerably increases the release of nonexchangeable magnesium to the exchangeable or soluble form (Wiklander and Koutler-Andersson 1963). This kind of chemical weathering took place also in other soil samples. It seemed to become more effective towards the end of the experimental period, since the cation concentrations in later leachates somewhat increased.

In field conditions leaching tsudies are usually made by analysing drainage or stream waters. Because the water has passed a thick soil layer before getting in the drainage system, it is likely that its cation composition is determined by cation exchange processes in the deeper soil layers. The initial process in leaching of nutrients is the movement of ions out from plant root zone. Thus the nutrients are practically no longer obtainable to plants, even if they do not yet get into drainage or brook water. This means that an analysis like this cannot alone give any reliable information about the effect of leaching processes on the cation composition in the plough layer.

#### REFERENCES

- KAILA, A. 1973. Calcium, magnesium and potassium in mineral soils from the southern half of Finland. J. Scient. Agric. Soc. Finl. 45: 254-261.
  - & RYTI, R. 1968. Calcium, magnesium and potassium in clay, silt and fine sand fractions of some Finnish soils. J. Scient. Agric. Soc. Finl. 40: 1-13.
- LAHERMO, P. 1970. Chemical geology of ground and surface waters in Finnish Lapland. Bull. Comm. geol. Finlande 242.
- WIKLANDER, L. 1964. Cation and anion exchange phenomena. In Chemistry of the soil, ed. Bear. p. 161-205. London.
  - 1970. Utlakning av näringsämnen. 1. Halten i dräneringsvatten. Grundförbättring 23: 117-141.
  - 1973/1974. The acidification of soil by acid precipitation. Grundförbättring 26: 155-164.
  - & KOUTLER-ANDERSSON, E. 1963. Influence of exchangeable ions on release of mineralbound ions. Soil Sci. 95: 9-15.
- Viro, P. 1953. Loss of nutrients and the natural nutrient balance of the soil in Finland. Comm. Inst. For. Fenn. 42.1.: 1-45.

Ms received June 13, 1978.

## Kasvinravinteiden huuhtoutumisesta viljelysmaista

### 1. Kationien huuhtoutuminen

HELINÄ HARTIKAINEN

Yliopiston maanviljelyskemian laitos, Viikki, 00710 Helsinki 71

Lysimetrikokeessa seurattiin sekä luontaisten että lannoitteena lisättyjen emäskationien huuhtoutumista hiekasta, hiedasta ja hietasavesta. Lisäksi selvitettiin happaman kasteluliuoksen  $(0.025 \text{ M} \text{ H}_2\text{SO}_4)$  vaikutusta huuhtoutumistappioihin.

Maanäytteen KVK näytti vaikuttavan läpivaluneen liuoksen kationikonsentraatioon. Suhteelliset ja absoluuttiset huuhtoutumat olivat pienimmät hietasavessa ja suurimmat hiekassa. Tutkituista kationeista uuttui eniten kalsiumia ja vähiten natriumia. Magnesiumin ja kaliumin määrät olivat samaa suuruusluokkaa. Maanäytteiden kationireserveihin nähden suhteellinen huuhtoutuminen seurasi yleensä järjestystä:  $Na > Mg \approx Ca > K$ .

Kationien uuttuminen lisääntyi lannoituksen seurauksena ja kohdistui voimakkaimmin maan kalsiumiin. Tehokas pidättyminen vähensi kaliumin määrää läpivaluneessa liuoksessa. Hapan kasteluliuos edisti huuhtoutumista voimakkaimmin savinäytteessä.