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PROEFSTATION VOOR TUINBOUW ONDER GLAS, NAALDWIJK

Stamboeknr.: 3163

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ONDER GLAS TE NAALDWIJK

Survey of analysis figures in the 1:2 volume extract of soil samples
taken between Aug. 1980 and Febr. 1981

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Intern Rapport nr. 9.

februari 1982

2243444

Introduction.

The Research Station at Naaldwijk changed the units of elemental determinations for the routine soil test results from milliequivalents to millimols to be in keeping with the International Standard of Units. The change in units to millimol was made in August 1980. From August 1980 to January 1981 225 sample analysis results were selected at random from samples sent into the routine soil analysis laboratory. The samples varied in location of origin in the Netherlands and therefore there was also variation in soil type and in type of crop grown. The samples were analyzed by the 1:2 volume extract method described by Sonneveld and v.d. Ende (1971). The pH, electrical conductivity (EC), ammonium (NH₄), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), nitrate (NO₃), chloride (Cl), sulfate (SO₄), bicarbonate (HCO₃), and phosphate (P) levels were determined in the extract. The sum of cations (CA) and sum of anions (AN) were calculated by addition of all cations and anions respectively, and expressed as milliequivalent per liter extract. For P 1 mmol was taken to be 1 milliequivalent.

The median, range and upper and lower quadrant values obtained from the soil analysis results (n = 225).

Table 1.

Determination	median	range	lower quartile	upper quartile
NH ₄ (mmol/l)	0.10	0.00- 1.00	0.10	0.10
K	1.80	0.00- 4.60	1.10	2.30
Na	3.20	0.40- 7.70	2.50	4.10
Ca	3.50	0.40-13.00	2.60	4.60
Mg	1.20	0.10- 4.30	0.90	1.60
NO ₃	2.40	0.10- 8.70	1.20	3.40
Cl	2.60	0.30- 6.10	1.80	3.50
SO ₄	3.60	0.00-12.00	2.40	4.90
HCO ₃	0.50	0.00- 1.70	0.30	0.70
P	0.12	0.00- 0.60	0.08	0.17
AN (meq/l)	1.30	0.15- 3.34	1.02	1.69
CA (meq/l)	1.46	0.30- 4.49	1.17	1.89
EC (mS/cm)	1.37	0.35- 3.54	1.11	1.70
pH	6.90	5.80- 7.80	6.70	7.20

The (EC) was expressed as mS/cm at 25°C, and the elements were expressed as mmol/liter. Information about soil type, crop grown, collection day and location of the samples were recorded, but were later shown to have no influence of the results.

Results and Discussion.

The median, range and median spread values found are presented in table 1. The median values were reported rather than sample mean to minimize the effect of extreme values. As shown, the Na, K, Ca, NO₃, Cl, SO₄ and Mg ions were present in relatively high concentrations, while NH₄, HCO₃ and P were present in relatively low concentrations. The correlation coefficients of the ion determinations with EC are presented in table 2.

Table 2. The correlation coefficients for the relationship between the determinations and EC (n = 225)

NH ₄	r = 0.348 ⁺⁺	NO ₃	r = 0.512 ⁺⁺
K	r = 0.729 ⁺⁺	Cl	r = 0.756 ⁺⁺
Na	r = 0.780 ⁺⁺	SO ₄	r = 0.913 ⁺⁺
Ca	r = 0.937 ⁺⁺	HCO ₃	r = 0.082
Mg	r = 0.910	P	r = 0.112

As expected the ions present in higher concentrations showed higher correlations with the EC. All of the ions gave a positive correlation with EC except P and the HCO_3 ions. The determinations were correlated with each other and the higher correlations found are presented in table 3.

Table 3. The regression equations and correlation coefficients for the relationship between determinations (n = 225)

$$\begin{aligned} \text{Na} &= 0.898 \text{ Cl} + 0.84 & r &= 0.907^{++} \\ \text{Ca} &= 1.048 \text{ SO}_4 - 0.12 & r &= 0.925^{++} \\ \text{SO}_4 &= 3.044 \text{ Mg} - 0.15 & r &= 0.885^{++} \end{aligned}$$

The correlations between pH and the determinations were also studied. The HCO_3 ion gave the highest correlation while the other determinations gave low correlation coefficient values. The relationship between pH and HCO_3 was:

$$\text{pH} = 0.320 x - 1.72 \quad r = 0.419^{++}$$

The pH HCO_3 and pH relationship was also studied, but did not give better results.

The sum of cations (CA) and sum of anions (AN) were highly correlated with each other and with EC and are presented in table 4.

Table 4. The regression equations and correlation coefficients for the relationship between the sum of ions and EC (n=225).

$$\begin{aligned} \text{AN} &= 1.082 \quad \text{CA} + 0.08 & r &= 0.982^{++} \\ \text{EC} &= 0.832 \quad \text{AN} + 0.27 & r &= 0.970^{++} \\ \text{EC} &= 0.764 \quad \text{CA} + 0.23 & r &= 0.982^{++} \end{aligned}$$

The relationship between conductivity (EC) and (CA) is presented in figure 1. The relationship between CA and AN totals showed an 8.2% difference in their overall sums:

$$\text{AN} = 1.082 \text{ CA} + 0.08$$

This difference in anion and cation sums for soil analysis is higher than that obtained by Sonneveld and v. Dijk (1977) in the same laboratory. Their research obtained the following relationship between cation and anion sums:

$$\text{CA} = 1.007 \text{ AN} - 0.22$$

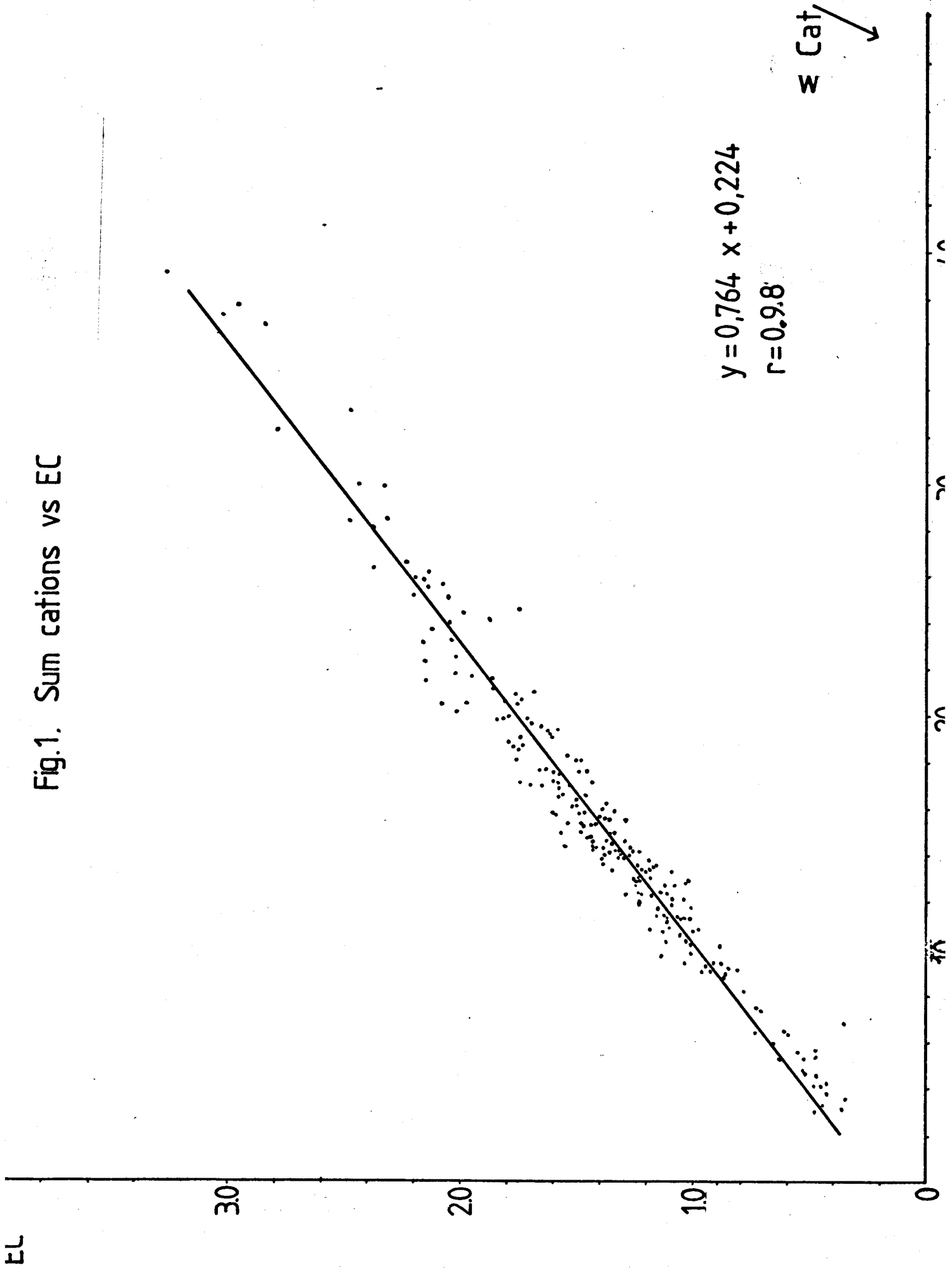
To determine the possible cause for the difference in CA and AN totals the individual determinations were correlated with the absolute differences in ion sums $[\text{CA} - \text{AN}]$. The correlation coefficients are presented in table 5.

Table 5.

The correlation coefficients for the relationship between the determinations and $[\text{CA} - \text{AN}]$.

$$\begin{array}{ll} \text{NH}_4 & r = 0.606^{++} & \text{NO}_3 & r = 0.009 \\ \text{K} & r = 0.239^{++} & \text{Cl} & r = 0.394^{++} \\ \text{Na} & r = 0.392^{++} & \text{SO}_4 & r = 0.367^{++} \\ \text{Ca} & r = 0.559^{++} & \text{HCO}_3 & r = 0.257^{++} \\ \text{Mg} & r = 0.433^{++} & \text{P} & r = -0.280^{++} \end{array}$$

Fig.1. Sum cations vs EC



As expected the level of absolute difference between CA - AN increased as the ion content level increased according to the equation $y = ax + b$ where y = the absolute difference, x = ion determination and a and b are constants. The determinations exhibited a positive correlation with [CA - AN] with the exception of P. The P ion content levels were too low to give a good correlation with the ion totals. The low correlation between NO_3 and [CA - AN] is not explained. The HCO_3 and NH_4 ions gave higher correlation coefficient values with [CA - AN] than with (EC). This is an indication that one or both of these ions may have influenced the imbalance in ion sums. To look further at the data the individual ion determinations were correlated with the relative difference between the ion sums. It was expected that the determinations would show a negative relationship with the relative difference between [CA - AN] according to the equation $y = a + \frac{b}{x}$ where $y = \frac{\text{CA}-\text{AN}}{\text{CA}}$ x = ion determination, and $a + b =$ constants. The results of the determinations are given in table 6.

Table 6. The correlation coefficients for the relationship between the ion determinations and $\frac{\text{CA}-\text{AN}}{\text{CA}}$. (n= 225)

NH_4	$r = 0.304$	NO_3	$r = - 0.308$
K	$r = - 0.243$	Cl	$r = - 0.182$
Na	$r = - 0.224$	SO_4	$r = - 0.341$
Ca	$r = - 0.182$	HCO_3	$r = 0.306$
Ma	$r = - 0.207$	P	$r = - 0.176$

The determinations exhibit correlation coefficients of approximately 18 - 34% and give negative correlations as expected with the exception of NH_4 and HCO_3 . This is a further indication that the NH_4 and HCO_3 ion determinations influenced the ion balance.

Conclusion.

The determinations were correlated with each other and the close correlations found were presented in this paper. The pH was correlated with all the determinations and EC. The HCO_3 ion gave the only close correlation coefficient with pH. The logarithm of HCO_3 was also studied, but not shown to improve the correlation with pH.

The sum of cations and sum of anions were highly correlated with each other and with electrical conductivity as expected. There was however an imbalance of 8% in the cation and anion totals and an effort was made in this paper to determine if one or more of the determinations was influencing the ion totals. The NH_4 and HCO_3 ions were shown to be more highly correlated with the absolute difference between the ion totals than with electrical conductivity. These two ions also exhibited a positive correlation with the relative difference between the ion totals.

It would appear from these relationships that NH_4 and HCO_3 were influencing the balance between the cation and anion sums.

Literature

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