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## Soil formation on mafic rocks of north Galicia, Spain. 4. Charge characteristics

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**Abstract.** Point of net zero charge was lower in a serpentinite soil than in a pyrigarnite soil, resulting in a net negative charge in the former and a net positive charge at soil pH in the latter. PZNC is strongly raised by high free-iron contents, while pH-dependent (CEC) is more strongly related to organic matter than to sesquioxides. At soil pH, positive charge of sesquioxides and negative charge of organic matter approximately compensated each other, and much of the remaining negative charge was due to contribution of layer lattice clays.

**Key-words:** mafic rocks, charge characteristics, CEC, PZNC

**Introduction.** Exchange properties of soils on mafic rocks are to a large extent determined by iron compounds and organic matter. In 11 soils described from north-west Spain (Van den Born & Buurman, 1985), total iron (as % (w/w) Fe<sub>2</sub>O<sub>3</sub>) makes up 12-34 % of the fine earth fraction in serpentinite soils, 4-52 % in soils on chloritized amphibolite, and 7-11 % in pyrigarnite soils, while dithionite-extractable iron

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(as weight % Fe) is 4-22 %, 2-34 % and 2-5 %, respectively. Combined with strongly varying contents and composition of clay, and varying contents of organic matter, contrasts with respect to CEC and Point of Zero Net Charge (PZNC) should be expected.

**Materials and methods.** Charge characteristics of Ah and Bw horizons of profiles E (serpentinite) and T (pyrigarnite) were measured in detail. In all samples, three values for exchange properties were obtained.

1. Sum of bases and extractable acidity (SCat) was determined in 1 mol/l BaCl<sub>2</sub> extract, in which also the pH was measured (pH<sub>1</sub>). In most cases, pH<sub>1</sub> was close to the pH-KCl of the samples and SCat is therefore an indication of the exchange capacity at soil-pH;

2. After saturation with Ba, an excess MgSO<sub>4</sub> was added to the Ba-saturated sample. The Mg remaining in solution was back-titrated and during the titration the pH was recorded. This provides a CEC value at a pH higher than that of SCat (pH<sub>2</sub> and CEC<sub>2</sub>);

3. CEC at a buffered pH of 8 was determined by the method of Bascomb (1964), which is another CEC value. The two values for CEC and SCat give an impression of the pH dependence of the CEC. The two CEC values are obtained by the same method and can be compared without reservation; comparison with SCat meets with some restrictions. The contribution of the clay fraction to the CEC was calculated from the XRFS-analysed Ba content of Ba-saturated clay separates after removal of free sesquioxides. Ba being virtually absent in the parent rock, adsorbed Ba is a measure of the CEC of the clay fraction at pH around 5 (the pH of the Ba-clay suspension before centrifuging). For PZNC determinations 4g portions of an oven-dry fine-earth sample were equilibrated with 20 ml aqueous solutions containing different amounts of KOH (up to 3 ml 0.1 mol/l) or HCl (up to 8 ml 0.1 mol/l). Equilibration lasted five days, after which the various pHs were measured and plotted against the amount of acid or base added. Subsequently, 1 ml KCl solution, 2 mol/l, was added to each sample to bring the salt concentration to 0.1 mol/l, and pHs were measured after shaking for three hours and plotted in the same graph. Subsequently, 5.7 ml KCl solution, 2 mol/l, was added to each solution to bring the salt concentration to 0.5 mol/l. Again pHs were measured after five hours shaking, and plotted. The titration curves before and after a specific KCl-addition intersect if the net amount of protons that is expelled from the double layers of clay and organic matter (the CEC components) equals the net amount of protons taken up by the surface of positively charged sesquioxides (the AEC components). Therefore, the pH of the intersection point must be lower than the PZNC of the sesquioxide(s), and it decreases with a greater number of relocated protons and with smaller amounts of sesquioxides. The number of relocated protons in its turn, is a function of the combined titration curves at different KCl concentrations of the pure clay and the pure organic matter; it increases with their amounts in the system. The centre of the intersection points of the curves was read as the PZNC of the system.

Table 1. Selected chemical properties of horizons of profiles E and T (fine earth).

Horizon	pH-KCl	pH-H <sub>2</sub> O	Org C	Clay	Al <sub>d</sub>	Fe <sub>d</sub>	Al <sub>p</sub>	Fe <sub>p</sub>	C <sub>p</sub>	PZNC	Exchange properties						
											pH <sub>1</sub>	SCat	pH <sub>2</sub>	CEC <sub>2</sub>	CEC	CEC contr. pH8	CEC clay
<i>Profile E</i>																	
Ah2	4.3	4.5	8.0	28	0.8	21.8	0.3	4.5	3.4	3.9	4.2	102	5.2	112	391	570	161
Bw	5.2	5.6	1.0	26	0.1	11.8	0.0	0.4	0.5	3.5	5.7	151	6.4	180	260	644	169
<i>Profile T</i>																	
Ah	4.4	4.0	9.1	19	1.5	5.0	1.1	1.8	4.5	4.6	4.4	117	5.6	110	430	448	83
Bw	4.5	4.3	1.6	18	1.1	3.5	1.0	0.9	1.5	4.7	4.7	38	5.8	5	223	249	44

d = dithionite extraction; p = pyrophosphate extraction; pH<sub>1</sub> = pH of cation extract; pH<sub>2</sub> = pH of CEC<sub>2</sub> determination; contr. clay = clay percentage × CEC of clay fraction. CEC and SCat values in mmol/kg; contents in weight percentages.

**Results.** Relevant chemical data of the four horizons for which the PZNC was determined are given in Table 1.

In accordance with theoretical considerations, pH-KCl is lower than pH-H<sub>2</sub>O if soil pH is above PZNC (profile E), and higher than pH-H<sub>2</sub>O if soil pH is below PZNC (profile T).

In profile E, PZNC of the Ah is higher than that of the Bw. Clay contents, and also the contribution of the clay fraction to the CEC being similar, we may conclude that the negative shift in PZNC due to a greater organic carbon content (7 % more in Ah) is less than the positive shift due to a greater sesquioxide content (10 % more Fe<sub>d</sub> and 0.7 % more Al<sub>d</sub> in Ah).

In profile T, the PZNCs are considerably higher. Here, a difference of 7.5 % C has slightly more influence than the difference in sesquioxide content (1.5 %). In this profile, a greater fraction of sesquioxides, especially Al, is bound in organic complexes. The high PZNCs will be partly due to high kaolinite and gibbsite contents in the clay fraction. CEC shows a strong pH dependence. Like in other profiles the calculated contribution of the clay fraction is sometimes higher than SCat, which indicates that in the untreated sample part of the clay charge is blocked by sesquioxides. In three samples of Table 1, the clay contribution is of the same order of magnitude as SCat. This indicates that at pH 5 an amount of negative charge equivalent to the contribution of organic matter is blocked by sesquioxides. In the Ah of profile E, however, SCat is considerably lower than the clay contribution, which may be explained by the very high Fe<sub>d</sub> content of this horizon.

In all profiles investigated, samples with high organic matter contents have a steeper rise in CEC with pH than samples with high sesquioxide contents. Samples with similar organic matter contents (3-3.5 %) and varying sesquioxide contents (14-33 % Fe<sub>d</sub>) had a similar increase of CEC with pH and it was not possible to specify the effect of sesquioxides.

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## Heterogeneity of Dutch rainfall

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**Abstract.** Rainfall data for the Netherlands have been used to investigate aspects of heterogeneity of rainfall, in particular local differences in rainfall levels, time trends in rainfall, and local differences in rainfall trend. The possible effect of urbanization and industrialization on the distribution of rainfall has also been studied. Consideration has been given to whether local differences in rainfall justify a partition of the Netherlands into regions. Finally, the degree of areal reduction in hydrological design based on variation of rainfall in time and space has been investigated. *Key-words:* rainfall, trend, local differences, urban precipitation enhancement, kriging, areal reduction factor.

**Trends in rainfall.** The rainfall characteristics used in the investigation of homogeneity in time and space are total annual rainfall and annual frequencies of exceedance during the summer or the winter period of certain threshold values (1, 15 and 25 mm) of daily rainfall. Time trends in these rainfall characteristics averaged over the Netherlands have been estimated. For the period 1951-1979, the time trend is negative for the summer period; for the period 1906-1979, the time trend is posi-