Int. Agrophysics, 2005, 19, 91-97

INTERNATIONAL
Agrophysics
www.ipan.lublin.pl/int-agrophysics

Effect of the change of accompanying cation of mineral nitrogen fertilizers on soil physical properties

H.H. Becher

Institute of Soil Science, Department of Ecology, Weihenstephan Center of Life and Food Sciences, Technical University of Munich, D-85350 Freising, Germany

Received August 23, 2004; accepted December 23, 2004

A b s t r a c t. In 1932, a nitrogen fertilizer trial was initiated on a loamy Oxyaquic Eutrochrept near Munich (Germany). After 45 years, the sodium nitrate plots showed a much stronger slaking of the soil surface compared to the calcium nitrate plots in 1976. Sampling of the experimental plots to 1 m depth in order to determine bulk density, saturated hydraulic conductivity, soil moisture characteristic, slaking resistance and exchangeable cations was only possible after termination of the experiment in 1998. Comparison of the laboratory results of both plots showed increased contents of exchangeable Na, but no decrease of exchangeable Ca for the sodium nitrate plots. Bulk density at depths >50 cm increased and the slaking resistance decreased on those plots. The other soil structural properties determined were not significantly affected. The reason behind these unexpected findings is the change from sodium nitrate to calcium nitrate + cattle salt as the sodium nitrate fertilizer in 1984, 15 years prior to sampling. The resulting additional supply of Ca^{2+} was able to remediate the formerly visible deterioration of the soil structure by Na^{+}. The adverse structural effects of an unfavourable fertilizer type (based on monovalent cations) can therefore be reversed by a change to a more appropriate type (based on bivalent cations, preferentially Ca^{2+}).

K e y w o r d s: slaking, structural properties, loamy soil, Na and Ca as cations

INTRODUCTION

The adverse effects of high salt concentration and/or high sodium contents, measured as exchangeable sodium percentage (ESP) or sodium adsorption ratio (SAR), are well-known. Among them, the most prominent ones are the decrease of aggregate stability and/or the increase of clay dispersion leading to surface sealing (Ben-Hur, 1991; Levy *et al.*, 1991; Little *et al.*, 1992; So and Aylmore, 1993; Regea *et al.*, 1997) or hardsetting (Gusli *et al.*, 1994a; 1994b). Soil surface sealing reduces water infiltration and thus not only enhances soil erosion by water (Keren and Singer, 1988; Ben-Hur, 1991; Shainberg and Levy, 1992; Le Bissonnais *et al.*, 1993), but also hinders the emergence of seedlings (Uppenkamp, 1986). These phenomena are especially pronounced in Mediterranean areas, which is evidenced by several reviews (Shainberg, 1985; Shainberg and Levy, 1992) and a series of studies on salt-affected soils, recently published in special issue of the Australian Journal of Soil Research (39(6) 2001). Under humid-temperate climate, the adverse effects of high Na^{+} levels in soils are restricted to marine soils of coastal regions (Müller, 1959; 1964; Kuntze, 1965; Schroeder and Brümmer, 1969; Brümmer *et al.*, 1971).

During his studies on soil erosion by water, Martin (1988) demonstrated that a surplus of K^{+} as the dominant monovalent cation as a result of pronounced K fertilization also decreased aggregate stability, thereby increasing soil slaking and surface sealing, even in inland areas. Shainberg *et al.* (1987) and Levy and Watt (1990) found a similar effect of K^{+}, which was however less pronounced compared to that of Na^{+}.

These findings imply that the permanent use of sodium-rich fertilizers may also be unfavourable for the structural properties of soils under humid-temperate climate. The adverse effects of long-term use of sodium nitrate ($NaNO_3$), as compared to calcium nitrate ($Ca(NO_3)_2$) as nitrogen fertilizer, were clearly visible on bare trial plots in early spring and late autumn (Fig. 1), *eg* in 1976, of a field trial established as early as 1932 within the Weihenstephan campus area of the Technical University of Munich, Germany. The light colour of the ploughed soil surface in Fig. 1a belonged to the plot fertilized with sodium nitrate. The two close-ups show that the surface of the sodium

Corresponding author's e-mail: becher@wzw.tum.de

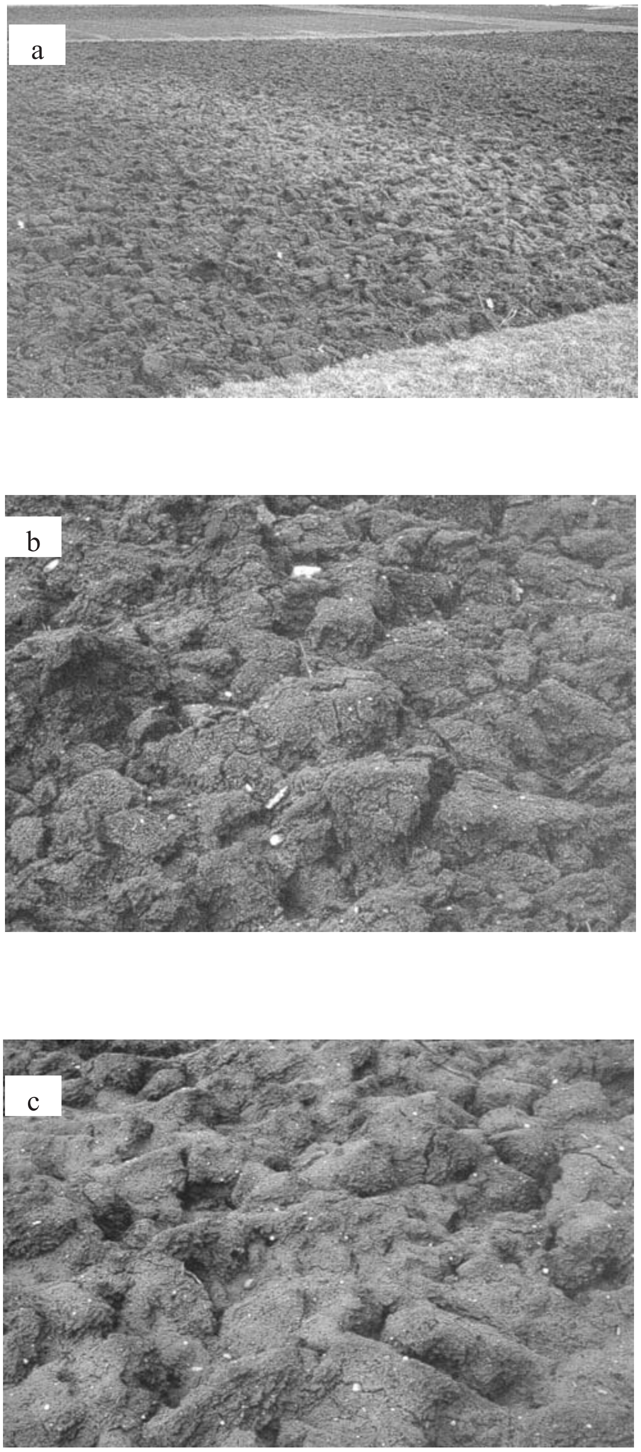

Fig. 1. Soil surface conditions during the field trial on nitrogen fertilizer types carried out since 1932 by the Institute of Plant Nutrition, Technical University, Munich. The pictures were taken in spring, 1976, and show an overview across one part of the trial area (a), a close-up of the calcium nitrate plot (b), and a close-up of the sodium nitrate plot (c).

nitrate plot (Fig. 1c) was much more slaked compared to the calcium nitrate plot (Fig. 1b). The visual assessment of the slaking after Boekel (1976) yielded 7 for the calcium nitrate plot and 5.5 for the sodium nitrate plot. At that time, sampling of the trial plots down to about 1 m depth was not possible without endangering the trial. When construction activities resulted in the termination of the trial in late 1998, sampling was finally performed in the spring of 1999. The results of determinations of selected soil physical and soil chemical properties are reported and discussed in this paper. The main objectives were to test whether (i) this visual finding and rating can be confirmed by results of soil physical determinations, and (ii) the structural differences are restricted to the topsoil layer.

MATERIAL AND METHODS

As mentioned above, the field trial was established as early as 1932 within the campus area Weihenstephan (Freising) of the Technical University of Munich, Upper Bavaria, Germany. Seven different types of nitrogen fertilizers were applied to plots of 50 m^2 (3.33×15 m) each, including 4 replicates for all of the treatments. All the plots were managed according to common agricultural practice, including (i) ploughing in late summer or autumn and secondary tillage in spring, or (ii) ploughing in spring, if necessary, followed by secondary tillage. The long duration of the trial saw a lot of technical progress in agriculture, and the management of the trial plots subsequently also changed with time.

The soils at the trial site have been classified as weakly Oxyaquic Eutrochrepts, developed from loess, overlying Tertiary fine sands. In March 1999 two soil pits were established down to at least 1 m, one of which was situated on a plot fertilized with calcium nitrate ($Ca(NO_3)_2$) (calcium nitrate plot), and the other one on a sodium nitrate ($NaNO_3$) (sodium nitrate plot) treated plot. 15 undisturbed core samples (365 cm^3; 8.8 in $\phi \times$ 6 cm) and disturbed samples were taken out of each discernible horizon, resulting in 5 horizons for the calcium nitrate plot and 4 horizons for the sodium nitrate plot which were adjacent to each other.

Saturated hydraulic conductivity was determined on 12 core samples following Hartge (1966). Bulk density and soil water characteristic were performed after Hartge (1965), using the 3 remaining core samples of each horizon. The water characteristic determination was in so far modified that always the same subsample of about 10 cm^3 up to water tensions of 1.5 MPa was used. To avoid loss of soil material during transfer of the subsamples between the balance and the membrane, each subsample was supported by a highly permeable paper filter of adequate size. From these data, the pore size distributions were calculated.

After crushing and sieving the air-dried disturbed samples to 2 mm, about 50 g of the 1-2 mm fraction were separated to determine the slaking resistance of small soil aggregates, using the modified procedure of Becher and Kainz (1983). In contrast to the procedure described by these authors, the amount of water entering the sample was monitored, but not the water leaving the sample. The idea behind this method is that increasing amounts of percolated water reflect increased stability of the aggregates, which is equivalent to decreased proneness for slaking. Grain size distribution, pH, C_{org}, and exchangeable cations were determined using the standard procedures described by Schlichting *et al*. (1995).

RESULTS

The two profiles showed no strong differences with respect to texture (Table 1). pH, C_{org}, K^+_{exch}, Mg^{2+}_{exch}, and even Ca^{2+}_{exch} do also not reflect the different treatments of the two plots. Only the content of Na^+_{exch} was higher for the sodium nitrate plot. The structural parameters – bulk density (ρ_b) and saturated hydraulic conductivity (k_s, geometric mean) indicated that the content of Na^+_{exch} may have affected soil structure at depths >50 cm. Pore size distributions as reflected by water retention at field water capacity (FWC) and permanent wilting point (PWP), show typical values for weakly waterlogged Eutrochrepts and were not affected by the fertilizer type. This is also demonstrated by the soil water characteristics (Fig. 2). The differences in pore volumes of the upper horizons may have been caused by the very last soil tillage.

All aggregate samples (1-2 mm) showed the same general course of the percolation volume y (ml) with time x (s) (Fig. 3), which was best fitted by using Eq. (1):

$$y = a + b\sqrt{x} + cx \quad (1)$$

where: the intercept a represents the water volume necessary for filling the system as well as the inter-aggregate pores, the regression coefficient b describes the initial change in percolation volume with time caused by disruption and slaking of the aggregates when water enters the single aggregates, the regression coefficient c reflects the subsequent change with time due to the abrasion of fine particles off the aggregates and their translocation by the percolating water. The cumulative percolation volumes of replicates of some samples varied only slightly (Fig. 3a), whereas those of replicates of some other samples varied considerably (Fig. 3b), indicating that soil heterogeneity may have existed even at the level of small aggregates

T a b l e 1. Properties of the soil samples taken in 1999 from a long-term nitrogen fertilizer field trial, which was started in 1932 by the Institute of Plant Nutrition, Technical University, Munich

	Plots with								
	Calcium nitrate					Sodium nitrate			
Horizon	A_p	IIB_{v1}	IIB_{v2}	IIB_{gv3}	$IIIB_{gv4}$	A_p	IIB_{v1}	IIB_{v2}	$IIIB_{gv3}$
Depth (cm)	0-28	28-40	40-60	60-75	75->100	0-28	28-50	50-80	80->100
pH	6.27	6.29	6.23	6.23	6.25	6.41	6.32	6.44	6.40
C_{org} (% mass)	0.87	0.36	0.27	0.18	0.21	1.08	0.36	0.24	0.21
Clay (% mass)	23	20	19	17	25	22	21	18	23
Silt (% mass)	45	22	19	22	55	45	20	23	48
Sand (% mass)	32	58	63	61	19	33	59	58	30
Na^+_{exch} (cmol kg^{-1})	0.07	0.09	0.10	0.08	0.10	0.14	0.36	0.29	0.37
K^+_{exch} (cmol kg^{-1})	0.41	0.24	0.21	0.19	0.20	0.43	0.22	0.20	0.22
Ca^{2+}_{exch} (cmol kg^{-1})	10.70	10.74	9.32	8.29	10.77	10.25	10.55	8.51	9.12
Mg^{2+}_{exch} (cmol kg^{-1})	0.02	0.02	0.02	0.02	0.04	0.02	0.02	0.03	0.04
ESP (%)	0.6	0.8	1.0	0.9	0.9	1.3	3.2	3.2	3.8
ECP (%)	95.5	96.8	96.6	96.6	96.9	94.6	94.6	94.2	93.5
M^+/M^{2+} (-)	0.045	0.031	0.033	0.032	0.028	0.056	0.055	0.057	0.064
ρ_b (g cm^{-3})	1.65	1.64	1.62	1.68	n.d.	1.69	1.64	1.73	1.75
k_s 10^{-3} (cm s^{-1})	1.18	1.28	1.27	3.87	n.d.	1.12	3.27	6.84	1.10
P (% vol.)	41	42	47	47	n.d.	39	48	47	47
FWC (% vol.)	32	30	27	28	n.d.	32	31	27	29
PWP (% vol.)	21	18	18	19	n.d.	23	19	16	17
PV (ml)	17.1	30.8	29.0	13.3	2.5	14.5	26.6	11.1	3.3

Horizons according to German Soil Survey Manual (Anonymous, 1994); ESP – exchangeable sodium percentage, ECP – exchangeable calcium percentage, M^+/M^{2+} – ratio of mono- to bivalent cations, ρ_b – bulk density, k_s – geometric mean of saturated hydraulic conductivity, P – pore volume, FWC – field water capacity, PWP – permanent wilting point, PV – percolated volume of water within 10 min after subtraction of volume for filling the system; n.d. – not determined, exch – exchangeable.

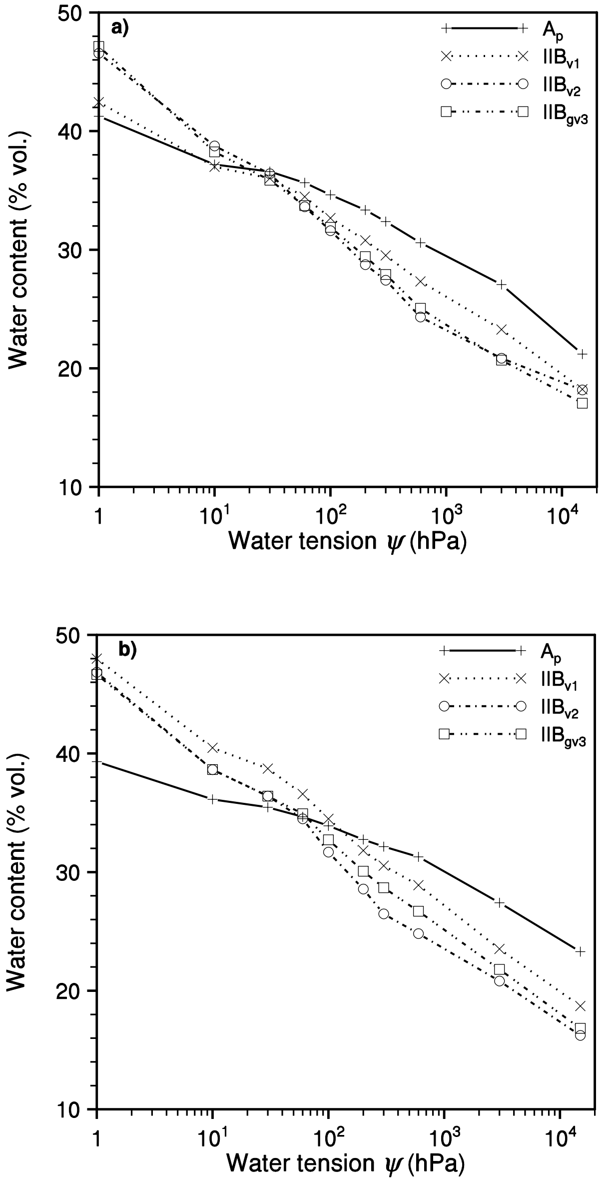

Fig. 2. Soil moisture characteristics for the calcium nitrate (a) and the sodium nitrate plots (b).

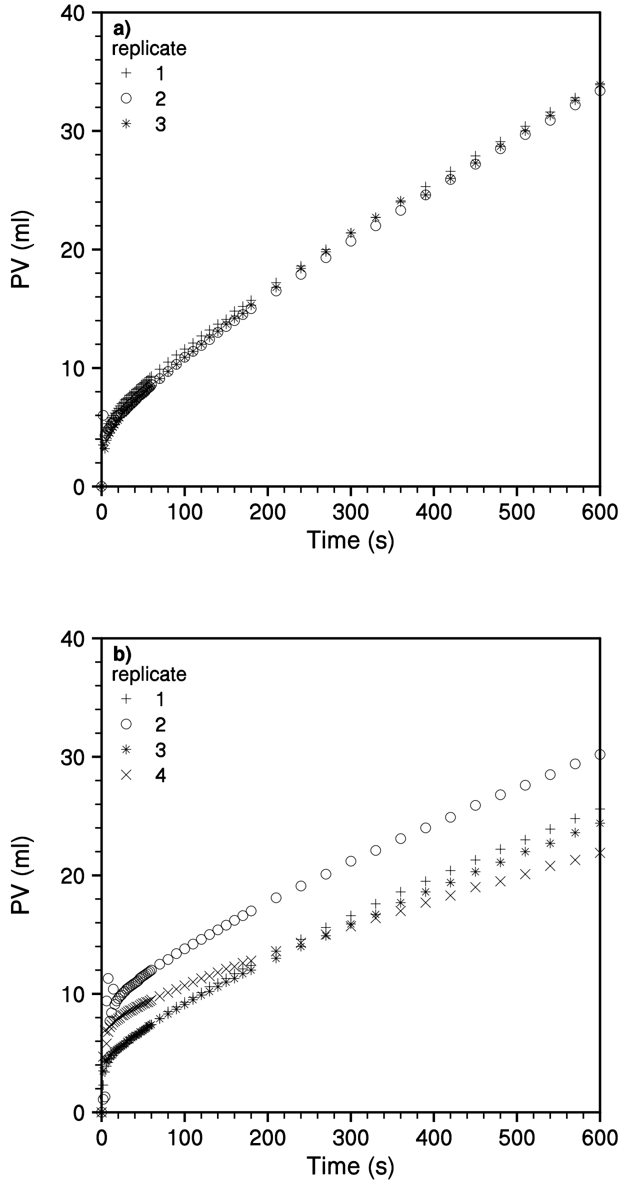

Fig. 3. Cumulative water volumes percolated (PV) within 10 min through replicate aggregate (1-2 mm) samples, samples with minor variation (a) and samples with large variation (b).

(1-2 mm). The differences shown were neither affected by horizon nor by the type of fertilizer. Nevertheless, mean cumulative curves were calculated which showed that the resistance against slaking of the aggregates from IIB_{v1} horizons was much stronger than those from A_p and the underlying IIB_{v2} and IIB_g horizons (Fig. 4). At first glance, the samples from the sodium nitrate plot (Fig. 4b) seemed to be stronger (it means less slaking) than those from the calcium nitrate plot (Fig. 4a). After subtraction of the water volume entering and filling up the system and inter-aggregate pores (roughly intercept *a*), however, the aggregates from the calcium nitrate plot turned out to be stronger because of higher final percolation volumes (Table 1).

DISCUSSION

The results of the soil physical parameters (bulk density, pore size distribution, saturated hydraulic conductivity, aggregate stability) do not confirm the visible differences in the slaking behaviour (Fig. 1) of the sodium and the calcium nitrate plots in spring, 1976. The Ca^{2+}_{exch} contents in Table 1 give a first hint that there must have been a change in

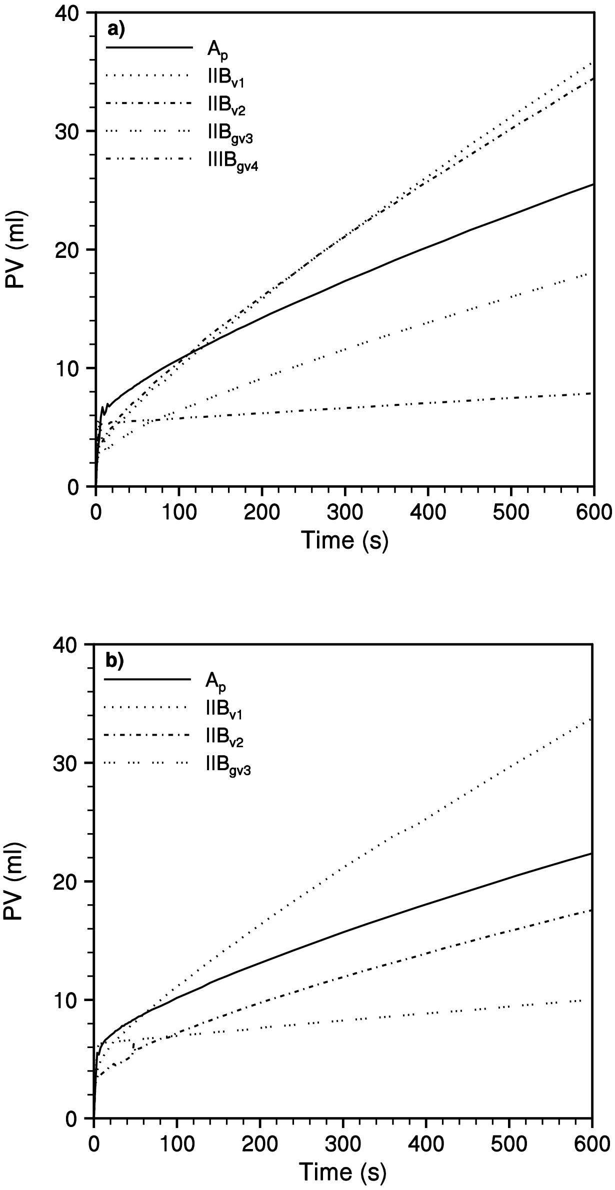

Fig. 4. Mean cumulative water volumes percolated (PV) within 10 min through aggregate (1-2 mm) samples of the calcium nitrate plot (a), the sodium nitrate plot (b).

the composition of the applied fertilizers. There are only very small differences in 1999, although they were expected to be at least as high as for Na^{+}_{exch} on a relative basis. An interview with the trial manager (from the Institute of Plant Nutrition) brought to light an altered cropping history after 1976. Table 2 depicts the cumulative amounts of Na and Ca which were supplied via both nitrate fertilizers during three selected time periods (1976-1980, 1981-1983, 1984-1997). In 1981 calcium nitrate was replaced by calcium ammonium nitrate (74% NH_4NO_3 + 22% $CaCO_3$) and in 1984 sodium nitrate was substituted by calcium nitrate + cattle salt (or

T a b l e 2. Amounts of sodium and calcium (kg ha^{-1}) applied to the original sodium nitrate and calcium nitrate plots during the field trial on nitrogen fertilizer types

Years	Plots with		
	sodium nitrate		calcium nitrate
	Na	Ca	Ca
1976-1980	681	0	663
1981-1983[a]	642	0	120
1984-1997[b]	238	3320	702
1976-1997	1561	3320	1485

[a] since 1981 calcium ammonium nitrate, [b] since 1984 replacement of sodium nitrate by calcium nitrate + cattle-salt (cattle lick) (NaCl with impurities).

cattle lick). Table 2 indicates that since the reorganization of the supply of nitrate fertilizers in 1984, the sodium nitrate plots received more than twice the amount of Ca compared to the calcium nitrate plots. At the same time, the supply of Na to the sodium nitrate plots was reduced to about 10% with respect to the foregoing years. In view of these changes in management, significant differences in soil structural properties cannot be expected. This is the main reason why the formerly clearly visible differences in surface slaking (1976) could not be confirmed by soil physical analyses in 1999.

Between 1976 and 1984, the year of replacement of the sodium nitrate fertilizer, the mean annual supply of Na amounted to 165 kg ha^{-1}. The mean annual supply of Ca from 1976 to 1980 was 133 kg ha^{-1}. Assuming that these values were constant since the start of the experiment in 1932, the plots have received a total of 7 278 kg Na ha^{-1} and 5 832 kg Ca ha^{-1} until spring, 1976, when the pictures of Fig. 1 were taken. At that time, a surplus of 1 446 kg Na ha^{-1} existed. According to the data in Table 2, the sodium nitrate plots received a total of 8 839 kg Na ha^{-1} and – since 1984 – also 3 320 kg Ca ha^{-1}, whereas the calcium nitrate plots received 7 317 kg Ca ha^{-1} in total. As mentioned above, it is important that since 1984 the sodium nitrate plots received an additional total amount of 3 320 kg Ca ha^{-1} while the calcium nitrate plots received almost one fifth that of the sodium nitrate plots – or only 702 kg Ca ha^{-1} – during the same period. Thus, the Ca/Na ratio of the sodium nitrate plot increased from zero to about 14. The adverse effects of Na^+ on soil physical properties, especially on soil slaking as evidenced by the small differences in percolation volumes, was subsequently offset by the high supply of Ca^{2+} during the last 15 years of the trial. This time has obviously been sufficient to remediate the soil structural properties, especially aggregate stability and soil dispersion. These findings are supported by Keren *et al.* (1983), Plessis and Shainberg (1985), Ben-Hur (1991) and Valzano *et al.* (2001a; 2001b) who found that the amendment of phosphogypsum or gypsum ($CaSO_4$) counteracts the unfavourable effect of high contents of exchangeable sodium. This means that deteriorated structural properties - at least those of topsoil layers – which have been caused by a surplus of monovalent cations like Na^+, may be remediated by a longer lasting amendment of Ca^{2+} containing fertilizers, at least to a certain degree.

CONCLUSIONS

1. In 1976, the effect of sodium nitrate on aggregate slaking in the field was optically clearly visible in the field.

2. During the 23 years until sampling could finally be carried out, the change of fertilizer type from sodium nitrate to calcium nitrate + cattle salt balanced this effect.

3. Subsequently, almost no differences in soil physical parameters between the original sodium and calcium nitrate plots could be detected.

4. The change of the fertilizer type has remediated the soil structure of the sodium nitrate plots, at least with respect to slaking.

REFERENCES

Anonymous, 1994. Bodenkundliche Kartieranleitung. 4th Ed. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Becher H.H. and Kainz M., 1983. Auswirkungen einer langjährigen Stallmistdüngung auf das Bodengefüge im Lößgebiet bei Straubing. Z. Acker- u. Pfl.-bau, 152, 152-158.

Ben-Hur M., 1991. The effects of dispersants, stabilizer and slope length on runoff and water-harvesting farming. Austral. J. Soil Res., 29, 553-563.

Boekel P., 1976. Possibilities for improvement of structure of fine-textured soil. Med. Fac. Landbouww. Rijksuniv., Gent, 41, 79-83.

Brümmer G., Grundtwaldt H.-S., and Schroeder D., 1971. Beiträge zur Genese und Klassifizierung der Marschen. II. Zur Schwefelmetabolik in Schlicken und Salzmarschen. Z.f. Pflanzenern. u. Bodenkd., 128, 208-220.

Gusli S., Cass A., MacLeod D.A., and Blackwell P.S., 1994a. Structural collapse and strength of some Australian soils in relation to hardsetting: I. Structural collapse on wetting and draining. Eur. J. Soil Sci., 45, 15-21.

Gusli S., Cass A., MacLeod D.A., and Blackwell P.S., 1994b. Structural collapse and strength of some Australian soils in relation to hardsetting: II. Tensile strength of collapsed aggregates. Eur. J. Soil Sci., 45, 23-29.

Hartge K.H., 1965. Die Bestimmung von Porenvolumen und Porengrößenverteilung. Z. Kulturtech. u. Flurber., 6, 193-206.

Hartge K.H., 1966. Ein Haubenpermeameter zum schnellen Durchmessen zahlreicher Stechzylinderproben. Z. Kulturtech. u. Flurber., 7, 155–163.

Keren R., Shainberg I., Frenkel H., and Kalo Y., 1983. The effect of exchangeable sodium and gypsum on surface runoff from loess soil. J. Soil Sci. Soc. Am., 47, 1001-1004.

Keren R., Singer M.J., 1988. Effect of low electrolyte concentration on hydraulic conductivity of sodium/calcium-montmorillonite-sand system. J. Soil Sci. Soc. Am., 52, 368-373.

Kuntze H., 1965. Die Marschen – Schwere Böden in der Landwirtschaftlichen Evolution. Parey Verlag, Hamburg.

Le BissonnaisY., Singer M.J., and Bradford J.M., 1993. Assessment of soil erodibility: The relationship between soil properties, erosion processes and susceptibility to erosion. In: Temperate Plains Environment and Hills. Farm Land Erosion (Ed. Wicherek S.). Elsevier, Amsterdam, 87-96.

Levy G.J., Shainberg I., Alperovitch N., and Merwe A.J. van der, 1991. Effect of Na-hexametaphosphate on the hydraulic conductivity of kaolinite-sand mixture. Clays and Clay Min., 39, 131-136.

Levy G.J. and Watt H.V.H. van der, 1990. Effect of exchangeable potassium on the hydraulic conductivity and infiltration rate of some South African soils. Soil Sci., 149, 69-77.

Little I.P., Ringrose-Voase A.J., and Ward W.T., 1992. Surface structure in grey clays of northwestern New South Wales in relation to micromorphology, cation suite and particle-size attributes. Austral. J. Soil Res. 30, 1-16.

Martin W., 1988. Die Erodierbarkeit von Böden unter simulierten und natürlichen Regen und ihre Abhängigkeit von Bodeneigenschaften. PhD. thesis, Technical University, Munich, Freising-Weihenstephan.

Müller W., 1959. Besonderheiten der Marschböden durch den Einfluß des Meeres während ihrer Entstehung. Z.f. Pflanzenern. u. Bodenkd., 84, 289-296.

Müller W., 1964. Unterschiede in den chemischen und physikalischen Eigenschaften von fluviatilen, brackischen und marinen Sedimenten. Developments in Sedimentology, 1, 239-299.

Plessis H.M. du and Shainberg I., 1985. Effect of exchangeable sodium and phosphogypsum on the hydraulic properties of several South African soils. S. Afr. J. Plant Soil, 2, 179-186.

Regea M., Yano T., and Shainberg I., 1997. The response of low and high swelling smectites to sodic conditions. Soil Sci., 162, 299-307.

Schlichting E., Blume H.-P., and Stahr K., 1995. Bodenkundliches Praktikum, 2nd Ed. Blackwell-Wissenschafts-Verlag, Berlin.

Schroeder D. and Brümmer G., 1969. Beiträge zur Genese und Klassifizierung der Marschen. I.Problematik der Marschen-Genese und – Klassifizierung und Untersuchungen zum Ca/Mg-Verhältnis. Z.f. Pflanzenern. u. Bodenkd., 122, 228-249.

Shainberg I., 1985. The effect of exchangeable sodium and electrolyte concentration on crust formation. Adv. Soil Sci., 1, 101-122.

Shainberg I., Keren R., Alperovitch N., and Goldstein D., 1987. Effect of exchangeable potassium on the hydraulic conductivity of smectite-sand mixtures. Clays and Clay Min., 35, 305-310.

Shainberg I. and Levy G.J., 1992. Physico-chemical effects of salts upon infiltration and water movement in soils. In: Interacting Processes in Soil Science. (Eds Wagenet R.J., Baveye P., Stewart B.A.). Lewis Publ., Boca Raton, 37-93.

So H.B. and Aylmore L.A.G., 1993. How do sodic soils behave? The effects of sodicity on soil physical behaviour. Austral. J. Soil Res., 31, 761-777.

Uppenkamp N., 1986. Mechanische Maßnahmen zur Sicherung des Feldaufganges von Zuckerrüben bei verkrusteter Bodenoberfläche. Forsch.-Ber. Agrartechnik Max-Eyth-Ges., 127, Bonn.

Valzano F.R., Greene R.S.B., Murphy B.W., Rengasamy P., and Jarwal S.D., 2001a. Effects of gypsum and stubble retention on the chemical and physical properties of a sodic grey Vertisol in western Victoria. Austral. J. Soil Res., 39, 1333-1347.

Valzano F.P., Murphy B.W., and Greene R.S.B., 2001b. The long-term effects of lime ($CaCO_3$), gypsum ($CaSO_4$ H_2O) and tillage on the physical and chemical properties of a sodic red-brown earth. Austral. J. Soil Res., 39, 1307-1331.