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VALIDITY OF GAPON'S CONSTANT IN PREDICTING SOIL SODICITY

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ABSTRACT

Validity of Gapon's equation to predict ESP of salt affected soils was examined from the available data. Experimental evidences indicate that Gapon's constant is not constant for all soils and varies with salinity, ESP, anionic composition, soil type, cation exchange capacity weather ability, organic matter and lime content of thr soils. Better prediction of exchangeable sodium achieved with Gapon's equation by using the kg value obtained for presentage can be representative soils involving similar saline-sodie conditions. Merits and demerits of Gapon's equation have been discussed.

Various attempts have been made from time to time to find out a suitable equation which could satisfactorily explain the cation exchange equilibria so as to predict the exchangeable cation status from the analysis of the soil and the equilibrium constant of the exchange material.

Various approaches and cation exchange equations suggested can be broadly classified into five categories, viz. empirical, kinetic, mass action type, diffuse double layer and thermo-dynamic. These have been critically reviewed from time to time for their theoretical developments, assumptions and applicability for varying types of soils and clay minerals (Bolt, 1967, 1979; Babcock and Schulz, 1963; Pal and Ponnia, 1978; Bruggenwert and Kamphorst, 1979; Levy, 1984).

GAPON'S EQUATION

By virtue of its simplicity and ease of estimation of necessary constituents, Gapon's equation as modified by US Salinity Laboratory Staff (USSLS, 1954) is widely used for salt-affected soils. It has been found quite satisfactory to predict soil sodicity (ESP) for a wide range of saline and sodic conditions by using a different value for the Gapon's constant (USSLS, 1954; Paliwal and Maliwal, 1971b; Jensen and Babcock, 1973; Gheyi and Van Bladel, 1975; Elseewi et al., 1977; Pal et al., 1984; Frenkel and Alperovitch, 1983, 1984 and others). The present discussion is confined to some factors affecting Gapon's constant (Kg) to predict exchangeable sodium status, particularly, in saline-sodic conditions.

Originally, Gapon (1933) proposed the equation on kinetic considerations using Gedroitz's (1922) data and concluded: "The ratio of the cation concentrations in solution is proportional to the ratio of the concentrations of the cations absorbed on soil". But it is independent of the kind of surface or the nature of the soil. The constant K will have the same value for a given cation (only Ca^{++}) replaced by a given cation (only $NH4^+$) For Ca saturated soil and Na in solution, the equation can be written as:

$$\frac{Na_{ex}}{Ca_{ex}} \cdot \frac{(Ca^{++})^{\frac{1}{2}}}{Na^+} = Kg$$

Since in salt-affected soils, magnesium, a divalent cation, is invariably present in sufficient amounts USSLS (1954) assumed it to behave like Ca in cation exchange reactions, coupled it with Ca, and modified the Gapon's equation to :

$$\frac{Na_{ex}}{(Ca+Mg)_{ex}} \cdot \frac{(Ca^{++} + Mg^{++})^{\frac{1}{2}}}{Na^+} = Kg$$

and termed $Na^+ / (Ca^{++} + Mg^{++})^{\frac{1}{2}}$ as sodium adsorption ratio (SAR) $mmol/l)^{\frac{1}{2}}$ and $Na_{ex} / Ca + Mg)_{ex}$ as exchangeable sodium ratio (ESR). The concentration of cations in the equilibrium soil solution is in mmol / l and the exchangeable cations in meq/100 g soil. Hence, Gapon's equation for Na, Ca, Mg system of an exchange material can be expressed as :

$$ESR/SAR = Kg\,(mmol/l)^{-\frac{1}{2}}$$

Extensive studies involving Na-Ca or Na, Ca, Mg with varying saline-sodic soils under laboratory or field conditions, have revealed that Gapon's constant is not a constant and is variable. It is influenced by types of soil and clay minerals, CEC, salinity, nature of cations and anions; ESP, lime and organic matter content and weathering characteristics of the soil materials.

FACTORS AFFECTING GAPON'S CONSTANT (KG.)

Nature of Exchange Material

In general, Kg value is quite low for montmorillonite, high for kaolinite and intermediate for illite. In soils, it generally decreases with the increase of clay content and CEC (Levy and Mor, 1965; Paliwal and Maliwal, 1970, 1971a,b; Agarwal 1973; Paliwal and Gandhi, 1976; Gheyi and Van Bladel, 1975, 1976, Chi et al, 1977; Frenkel and Alperovitch, 1984).

Kg value appears to be constant (Dixit, 1984) except at the lowest and the highest end of isotherm as shown earlier (Sheta et al., 1981). It varied from 0.0077 to 0.0259 with a mean value of 0.0163 $(mmol/l)^{-\frac{1}{2}}$ for all soils. But, in general, Gapon's equation explains Na-Ca exchange equilibria satisfactorily with a constant near to that of USSLS (1954), except for one soil, the overall difference being < 6% till about 35 SAR. Similarly the Kg value for West Bengal varied soils from 0.013 to 0.037 $(mmol/l)^{-\frac{1}{2}}$) for SAR from 5 to 48 the ESR-SAR were correlated (r=0.912) (Banerjee, 1959). Kg value for six typical soils of Israel varied from 0.0072 to 0.0169 $(mmol/l)^{-\frac{1}{2}}$ (Shainberg and Oster, 1978). The ESR-SAR relationships (Harron et al., 1983) for solenetzic soil association of east-central Alberta was highly significant, but was different for each profile layer. Kg value indicated that Na adsorption (relative to calcium) was about 3 times more strong in the B horizon than in the A horizon, mainly due to the variation in ESP, organic matter and clay content. In the soils of Sao Palto, Gapon's equation could be used to predict ESP; B_2 horizon had higher Kg and ESP values than Ap horizon (Kinjo and Marcos, 1982). So was also shown by Poonia and Talibudeen (1977). In general, Kg value decreases with increase in clay content, CEC and organic matter.

Salinity

Nature of chemical composition and total salt concentration of the soil solution influence the Kg value. Keeping the same SAR and even the same proportion of anions (mostly Cl and SO_4) in the equilibrium solution, an increase in salinity slightly decreases the Kg value; the magnitude of decrease depends upon the nature of exchange material (Rao et al., 1968; Doering and Wills, 1980; Frenkel and Alperovitch, 1984; Jurinak et al., 1984 and Poonia et al., 1984). But Bower (1959) observed no significant variation in Kg value for china clay in the salinity range of 50 to 200 meq/l.

With increasing SAR(upto 140) and salinity (39 to 1057 me/l) on strip mine spoil soil from North Dakota, Kg value decreased from 0.0163 to 0.085 $(mmol/l)^{-\frac{1}{2}}$ (Doering and Wills, 1980; Doering et al., 1982). Similarly Jurinak et al. (1984) with SAR upto 80 $(mmol/l)^{-\frac{1}{2}}$ noted decrease in Kg value with increase of salinity from 10 to 500 me/l in 3 soils with varying magnitude. But on correcting for anion repulsion, Kg was unaffected at low concentration (20 me/l), while at higher concentration (500 me/l), the Kg value for uncorrected soil was less than that for corrected one. At still higher salt concentration from 0.05 to 5 N and SAR (10 and 20), Alperovtch and Shainbreg (1973) concluded that Gapon's equation was not valid for high electrolyte concentration in the solution.

Gapon's constant decreases with the increase of total salt concentration, though ESP also slightly increases with salinity. In the salinity (25–100 me/l) Kg $(mol/l)^{\frac{1}{2}}$ value decreased from 0.48 to 0.24 for a forest soil and from 0.66 to 0.50 for a cultivated soil (Poonia et al., 1984).

Ca:Mg ratio

USSLS (1954) regarded Ca^{++} and Mg^{++} together as a single divalent cation. But evidences are there that Ca and Mg do not show the same chemical affinity to all types of exchange materials (Singh and Ramamoorthy, 1965). Apart from vermiculite (Wild and Keay, 1964), hydroxy aluminium-coated montmorillonite clay, allophane, organic soil and soils containing amorphous material showed preference for calcium over magnesium (Peterson et al., 1965; Rhoades. 1967; Dulcater et al., 1968; Hunsaker and Pratt, 1971; Rahman and Rowell, 1979; Van Bladel and Gheyi, 1980). But most soils show only slight preference for Ca over Mg mainly due to hydrated ionic radius of magnesium. Consequently sodium adsorption is more in Na–Mg than in Na–Ca system of soils and clay minerals. On the other hand, on a montmorillonite soil, having Mg saturation, upto 30 per cent there was no preference for Ca or Mg (Levy et al., 1972).

Table 1. Effect of Ca : Mg Ratio on ESR - SAR relationship

Ca : Mg Ratio	ESR + SAR (r)	Regression Equation (ESR = Kg SAR + a)
4:1	0.920	ESR = 0.00899 SAR + 0.1381
2:1	0.894	ESR = 0.01134 SAR + 0.0642
1:1	0.892	ESR = 0.01122 SAR + 0.1199
1:2	0.877	ESR = 1156 SAR + 0.0948
1:4	0.919	ESR = 0.01262 SAR + 0.8855

*Based on means of three soils of Rajasthan (Paliwal and Gandi, 1976)

On irrigating soils at the same salinity and SAR, the exchangeable Na was more with higher Mg/Ca ratio and the effect was more visible (Table 1) on coarse (low CEC <10 me 100 g) than on ffne textured (High CEC' ≈ 35 me/100 g soils (Paliwal and Maliwal, 1970, 1971a, b, Paliwal and Gandhi, 1976; Mehta et al., 1938; Alperovitch et al., (1981). The Kg value increases with Mg/Ca ratio. However, four soils of Haryana) did not show spectacular preferences for Ca^{++} or Mg^{++} with varying canditions of SAR (15-19) and Ca/Mg ratio (1:3 and 3-1; Conc.–100 me/l) (Poonia and Pal, 1979). Such inconsistency in selectivity coefficient may be due to the presence of cementing agents as hydroxy - Al and hydroxy–Fe and their interactions with soil clay (Levy et al., 1972; Keren, 1979).

Anionic composition

Not only the cations, even the nature of associated anions, particularly bicarbonate, carbonate and sulphate in the electrolyte solution, in fluence sodium absorption.

In Na^{-}Ca-Mg systems, some anions like CO_3^{--}, HCO_3^{-} and SO_4^{--} make ion pair with Ca and Mg and reduce the activity of these divalent cations (Rao et al., 1968; Sposito and Mattigod, 1977). Consequently, sodium adsorption is more in sulphate rich than in chloride dominant systems. In theree different soils with Na-Ca and Na-Mg in chloride and sulphate dominant systems, Mehta et al.(1985) observed that at a given SAR, ESP was more in sulphate than in chloride dominant system as reflected in their respective Kg values. However, on considering ion pairs viz. $MgSO_4^{\circ}$, $CaSO^{\circ}_4$, $NaSO^{-}_4$, the differences were narrowed down.

A lower degree of accuracy in more saline/sodic conditions may be due to precipitation and complex formation Sposito and Mattigod (1977), though accepted the applicability of practical SARp to predict ESP by Gapon's constant, emphasised that anions (SO_4^{-}, CO_3^{-}, HCO_3^{-}) present in soil solution/irrigation water have a tendency to form more stable complexes with Ca^{++} and Mg^{++} than with Na^{+}. Consequently, the activity of Ca^{++} and Mg^{++} will be less than Na^{+} leading to more effective SAR than the estimated one, causing more variations in the predicted ESP values as also pointed out by Rao et al., (1968).

However, SAR on concentration or activity basis, correlated well upto about 20 SAR with the regression equation: $SARa = 0.08 + 1.115\ SAR$ for 105 samples where SAR is on the basis of activity cations. Later work of Oster and Sposito(1980) showed the ESR-SAR relationships for SAR not above 40, there was no difference between SAR corrected for activities and complex formation from SAR simply on concentration basis. Thus, SAR upto 35-40 can safely be used to predict ESP using a suitable Kg value for the concerned exchange material.

Exchangeable Sodium Percentage

ESR-SAR relationship is also influenced by ESP level of the soil. With varying levels of salinity (39-1057 me/l) and SAR (< 140), Doering et al. (1982) concluded that exchangeable sodium status could be better judged by Gapon's equation on Kg value if SAR is upto 20 irrespective of salinity level. Using 26 soils, Poonia and Talibudeen(1977) showed that Kg can describe Na-Ca exchange equilibria upto 50 ESP as was obtained for illite (Bolt, 1955) and soiis (Bower, 1959; Pratt and Grover, 1964; Gheyi and Van Bladel, 1975).

In three illite dominating soils, using 50 me/1 with varying Na equivalent fraction, Kg value increased [0. 577–0. 741, 0. 725-1. 075 and 0. 979-1. 734 $(mmol/l)^{-\frac{1}{2}}$] with ESP indicating a higher specificity of Na at higher ESP (Baruah et al., 1983). This suggests that as Kg is variable with ESP and soil type, a mean Kg value be taken for different ESP ranges of different soils.

Organic Matter

In soils rich in organic matter and calcium carbonate, sodium adsorption is less as Na has less chemical affinity than Ca or Mg (Pratt and Grover, 1964) indicating lower Kg value. A multiple regression equation was obtained (Table 2) between Kg, OM and $CaCO_3$ content (Gheyi and Van Bladel, 1976). Poonia and Talibuddeen (1977) also showed that Kg was always smaller for surface than the corresponding sub-soils, and was inversely related surface charge density and organic matter content, Poonia et al. (1980) also showed further that Kg value decreased with incease (0. 10 - 1. 90% OC) of organic matter both for Na - Ca and Na – Mg systems for the whole range of exchange isotherm of 7 soils of Haryana, and between Ca and Mg. Kg value was smaller for Ca–Na than Mg-Na system indicating greater preference for Ca than for Mg. The effect of organic matter on Kg value was more at low ESP. Between Ca and Mg, organic matter shows greater preference to Ca than Mg as organic matter makes more stable organo-metallic complexes with Ca than Mg (Schnitzer and Skinner, 1967) Lower Kg for suface than sub-surface soils has also been shown for 5 Algerian soils (Dixit, 1984), mainly because surface soils had more organic matter content than the lower layer.

Table 2. Effect of organic matter (OM), $CaCO_3$ and clay content on Gapon's constant (Kg) for some soils

		Regression Equation			R_2
Kg X 10^3 (mcl/1) $-\frac{1}{2}$	=	9.75	– 0.86 (OM)	– 0.05 (Ca CO_3)	0.60
		(0.89)*	(0.26)	(0.02)	
	=	4.89	– 0.66 (OM)	+0.06 (clay)	0.68
		(1.41)	(0.24)	(0.02)	
	=	6.5	– 0.77 (OM)	– 0.04 ($CaCO_3$)	
		(1.21)	(0.20)	(0.017)	0.81
				+0.06 (clay)	
				(0.02)	

*Gheyi and Van Bladel (1976). Figures in parentheses are standard errors of the Regression Equation. Contribution of clay, organic matter and $CaCO_3$ in Kg value is 49, 36 and 15%, respectively

PREDICTABILITY OF ESP UNDER FIELD CONDITIONS

Despite variations in soil type, salinity, SAR, pH etc. USSLS (1954) found a satisfactory ESR-SAR relation for 57 field soils of western USA, and suggested the following equation to predict ESP

$$ESP = \frac{100\ (-0.0\ 126 + 0.0147\ SAR)}{1 + \ (-0.0\ 126 + 0.0\ 147\ SAR)}$$

Later Bower (1959) modified it to :

$$ESP = \frac{100\,(0.0057 + 0.0\,173\ SAR)}{1 + (0.0057 + 0.073\ SAR)}$$

India, on the basis of cation exchange equilibria on five typical soils of Rajasthan, with varying levels of salinity and SAR, Paliwal and Maliwal (1971) proposed the following equation

$$ESP + \frac{100\,(0.23 + 0.0042\ SAR)}{1 + (0.23 + 0.0042\ SAR)}$$

which fitted better than USSLS (1954) and Bower (1959) for field soils.

Frenkel and Alperovitch (1984) examined the ESR-SAR relationship for 623 field soils from the arid and semi-arid regions of Israel and concluded that Kg value depended on soil salinity and water saturation percentage (SP) of the soils (indirectly, on clay content, etc). The Kg decreased with increase of salinity (Table 3) and for a given salinity it decreased with increase of SP. Further, there was no ESR-SAR relationship for soils of low (20-40) SP or low (0.2 – 2 dSm^{-1}) sailnity.

Table 3 : Kg as affected by Satuation percentage (SP)*

ECe (dSm^{-1})	SP	No. of samples	Mean Kg $(mmol/l)^{-\frac{1}{2}}$
0.2–2.0	20 – 30	28	0.1510
	30 – 40	29	0.0645
	40 – 50	53	0.0399
	50 – 60	42	0.0245
	60 – 80	179	0.0207
	> 80	126	0.0154
2 - 20	30 – 40	9	0.0269
	40 – 50	15	0.0269
	50 – 60	41	0.0168
	60 - 80	39	0.0168
	> 80	62	0.0146

*Frenkel and Alperovitch (1984)

A lack of correlation between ESR-SAR, at low concentration may be due to wethering of soil minerals and lime, leading to release of calcium and reduction in SAR; and as salt concentration increases, the effect of release of Ca and Mg becomes less important. Thus rate of weathering of soil constituents of different soils at varying salinity conditions influence both the total soluble and exchangeable cations.

Further, because of low CEC of coarse soils, variations in Kg value are likely to be more in soils of low (< 10 me/100 g) than high (= 30 me/100 g soil) CEC. Morever, under widely heterogenous field conditions in relation to salinity, ESP, texture, clay type, organic matter etc.; a lack of true equilibrium also influences ESR : SAR relationship to a great extent.

A comparison of Gapon's equation with other cation exchange equations developed on various concepts, under equilibrium conditions in the laboratory shows Gapon's equation to fit better than those of Krishnamoorthy and Overstreet (1950), Vanselow, Donnan and Kerr for Na-Ca and/or Mg systems. It is mainly due to its formation; and on reducing them to the same form on taking the square root of the selectivity coefficient, all equations are nearly at par in predicting ESP (Paliwal and Maliwal, 1971a). Sposito (1977) also criticised Gapon's equation for expressing exchangeable cations in me / 100 g and soluble cation concentration in mmol/ 1 and proposed a corrected equation on molar basis of the cations in the exchange phase as :

$$Kg = \frac{SAR_T}{2\,E_{Na}} \left(1 - E^2_{Na} \right)^{\frac{1}{2}}$$

where SAR_T is SAR on the basis of activity of cation and E_{Na} is equivalent fraction of Na in exchange phase.

It may, therefore, be concluded that Gapon's eonstant is not constant even for a very wide range of saline-sodic conditions. Generally Kg value decreases with the increase of salinity organic matter and CEC. It is influenced by SAR level, nature of anions, degree of complex formation and weathering of soil constitents. To achieve better predictability of ESP of field soils, it is essential to find out the Kg value, describing the experimental methodology for each representative soil group showing minimum variation in salinity, ESP, cation anion composition, organic matter etc. and be applied for similar soil conditions. Despite these limitations, Gapon's equation can satisfactorily be used upto moderate levels of salinity and sodicity for quick appraisal of soil sodicity in land reclamation or saline water irrigated areas.

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