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## On Certain Aspects of Quality of Irrigation Water on the Cationic Equilibrium in Typical Soils of Tamil Nadu

by

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Under permanent irrigation agriculture, the quality of irrigation determines the equilibrium cationic composition of soil colloids. Much understanding has been made on the attainment of equilibrium conditions through the study of ion exchange properties of soil colloidal surface. The colloidal surfaces with counter ions behave like condensers, and electro-kinetic theory of double-layer on the surface was first developed by Helmholtz (1881). To explain the exponential decrease on ionic concentration from surfaces towards the bulk of the liquids was further developed by Guoy (1910) and later by Chapman independently on the diffused double layer theory. Pauli and Valko (1929) used empirical hyperbolic equations to describe the ion exchange phenomenon. Gans (1913) and Kerr (1928) used Law of Mass action principles to study ion-exchange phenomenon. The kinetically derived formulae of Gapon (1937) and Jenny (1936) also follows the Law of Mass action.

The application of Donnan equilibrium was further extended to diffuse layer and the Donnan and Guoy theories led to the same conclusions on ionic equilibrium and represented two different ways of approaching the problem. The electro-kinetic and electro-chemical potentials of the charged surfaces, arising from diffuse layer acting as Donnan membrane in creating the differential distribution of ions near the surface and the bulks of liquid phase, explain the physical and chemical properties of soil colloids and also determine the equilibrium conditions. Helmy (1964) has further described an exchange equation based on positive adsorption. Heald, Frere and Dewit (1965) studied the problem of ion exchange equilibrium with Guoy and Stern model. These equations are based on a model of equilibrium between ion-pairs at the surface and a diffuse Guoy layer.

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Most of the fundamental works were done with pure clays considering one or two ions. But under practical irrigation agriculture where number of ions have to be considered, it is very difficult to describe the equilibrium. But, Guoy Stern and Donnan models can be thermodynamically based and much advance has been made with the derivation of ratio laws by Schofield based on these models.

Wilcox (1948) was first to try to establish a relation between SAR of irrigation water and equilibrium composition of soil colloids. Similar work on some soils of Israel was taken up by Levy *et al.* (1965).

As activities of ion on either side of the diffuse layer has to attain equilibrium, an attempt is made to study the equilibrium between cationic composition of soil colloids and soil solution using Guoy-Stern electrical model with the diffused layer acting as Donnan membrane creating potential differences on either side of the diffused double layer in a simplified fashion.

**Materials and Methods:** A typical red, black, alluvial and latosol of Tamil Nadu were taken for the purpose of the study. The composition of exchangeable ions were determined by the conventional methods. The water with a total salt content of 2000 ppm prepared from different salts of potassium, sodium, calcium and magnesium was used for the study. Five grams of soil was allowed to come in equilibrium with 50 ml of water. The solution phase was separated by centrifuging and analysed for potassium and sodium by Flame Photometer and calcium and magnesium by Versenate method. The solid phase was washed with 60% alcohol and exchangeable ions determined by the conventional methods. The soils were treated with saline water again and after that the composition of exchangeable bases of the solution were determined to confirm the attainment of equilibrium composition of soil colloids.

The concentration in solution phase is expressed in millimoles/litre. At solid phase the concentration expressed as mole fraction expressed as percentage so that concentration terms are avoided (Ranganathan, 1968). The relation between activity ratio of the element in liquid phase and the distribution of ions at exchange site (expressed as mole fraction) was studied using the simplified model used in the studies of cationic equilibrium with reference to alkalisation of soils (Ranganathan, 1968).

**Results and Discussion:** The activity ratio at the liquid phase and the distribution of ions on the solid phase are given in Tables 1 and 2. It may be seen that even at the time of first leaching, the system has tended to reach the equilibrium as shown by the constancy of the ratio of activity ratio of element in the liquid phase to the mole fraction of that element at solid phase. Of

course, there are small variations which have very little significance for practical purposes, though theoretically they may be of value in studying the bonding energies as affected by other ions.

TABLE 1. *The activity ratio of Na and K on the liquid phase and mole fraction (as %) at the solid phase*

**SODIUM :**

Soil group		Liquid phase SAR	Solid phase $X_{Na} \%$	$\frac{SAR}{X_{Na} \%} = \text{Constant 'K'}$	Average 'K'
Alluvial	1	47.83	49	0.97	0.94
	2	48.91	53	0.92	
Laterite	1	55.18	62	0.89	1.05
	2	97.83	81	1.21	
Red	1	36.39	52	0.70	1.10
	2	102.20	68	1.50	
Black	1	42.72	35	1.20	1.10
	2	42.72	48	1.00	

**POTASSIUM :**

Soil group		Liquid phase KAR	Solid phase $X_K \%$	$\frac{KAR}{X_K \%} = \text{Constant 'K'}$	Average 'K'
Alluvial	1	13.08	38	0.34	0.34
	2	20.19	60	0.34	
Laterite	1	26.00	38	0.68	0.57
	2	23.69	50	0.47	
Red	1	23.00	37	0.62	0.73
	2	44.86	53	0.85	
Black	1	11.37	25	0.45	0.52
	2	21.15	35	0.60	

TABLE 2. *The activity ratio of Ca and Mg on the liquid phase and mole fraction (as %) at the solid phase*

**CALCIUM :**

Soil group		Liquid phase CaAR	Solid phase $X_{Ca} \%$	$\frac{CaAR}{X_{Ca} \%} = \text{Constant 'K'}$	Average 'K'
Alluvial	1	2.14	81	0.03	0.035
	2	3.16	84	0.04	
Laterite	1	1.51	63	0.03	0.05
	2	3.36	47	0.07	
Red	1	1.02	130	0.008	0.0075
	2	1.28	187	0.007	
Black	1	0.91	82	0.01	0.01
	2	0.97	88	0.01	

## MAGNESIUM:

Soil group		Liquid phase MgAR	Solid phase $X_{Mg\%}$	$\frac{MgAR}{X_{Mg\%}} = \text{Constant 'K'}$	Average 'K'
Alluvial	1	3.59	78	0.05	0.06
	2	5.48	80	0.07	
Laterite	1	7.61	89	0.09	0.08
	2	6.97	96	0.07	
Red	1	4.39	180	0.02	0.03
	2	6.92	192	0.04	
Black	1	2.66	92	0.03	0.04
	2	4.27	90	0.05	

CaAR = Calcium Adsorption Ratio

MgAR = Magnesium Adsorption Ratio

The constant K for the particular element (ratio of the activity ratio in liquid phase in the mole fraction of the element at solid phase) depends on the soil groups and perhaps is determined by the nature of clay minerals. From this study, it also appears that the four soil groups of Tamil Nadu taken up are fundamentally different, each having a different clay mineral and even if they contain the same clay minerals, their proportions in different soil groups are quite different.

The constant K for different elements are different from the same soil group. This is quite understandable as different ions have different bonding energies and the strength of adsorption on charged surface depends on ionic size and valency.

From the constant K, it is possible to calculate the ultimate mole fraction of a particular element when the soils are treated with a particular water of known composition. This is important in cases of alkalinisation and de-alkalinisation of soils and also in case of K to calculate the amount of K, that can be fixed at exchange sites. This information is quite essential for fixing the dose of potash that has to be applied and the need for split application. In tea, already based on some theoretical deductions the fertilizer dose that can be applied at a time is fixed based on CEC, soil pH and the nature of clay mineral (Ranganathan, 1969). The constant K with respect to calcium and magnesium are also helpful for studying liming and gypsum application in reclaiming acidic and alkali soils respectively. The use of activity terms for concentration may improve the constancy but in this study, ordinary concentration terms are used to enhance its practical utility.

**Conclusion:** The simplified model developed by Ranganathan to study cationic equilibrium was used. The cationic equilibrium with respect to

different elements is studied in the representative soils of four soil groups of Tamil Nadu. The present investigation indicates that the constant K introduced to overcome the differences in the expression of concentration in the liquid phase and solid phase by Ranganathan can be used as a criterion of equilibrium and this will serve for studying the ionic composition of soil as affected by the composition of irrigation waters. The constant K depends on the nature of ion and also soil groups. The practical utility of this study is also indicated.

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