

Isotope Tracer Method in Ion Exchange Studies on Alkali Soils

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Where low productivity of soils is caused by a considerable amount of sodium carbonate prerequisites of soil amelioration and utilization are a leaching of soluble salts and a decrease in the amount of exchangeable Na by the use of chemical amendments. Taking into account the above mentioned processes it is necessary to determine, for the characterization of alkali soils as well as for the selection of proper methods of amelioration, the following in the soil:

1. The quantity of soluble salts.
2. The quantity of the sodium carbonate and sodium bicarbonate.
3. The absolute and relative quantities of exchangeable Na.

Most methods commonly known and used for the determination of exchangeable cations in soils are based on colloid-chemical principles. The measured values of exchangeable cations depend on the following variables: the kind of cations used for the exchange of the soil's exchangeable cations, the pH value of the solution, the ratio of solid to liquid phases. But, if the same method is used consistently, in most cases comparative data of acceptable accuracy may be obtained.

The determination of exchangeable cations by colloid-chemical methods, however, imposes difficulties when the soil contains considerable calcium carbonate and/or it contains calcium sulphate and a considerable amount of soluble sodium salts. In the last 20 years isotope analysis of equilibrium systems has been established for the determination exchangeable cations and cation exchange capacity [1, 2, 3, 5, 12, 14, 15].

This method differs in principle from the previously mentioned methods and has the advantage that the quantities of exchangeable cations are determined on the basis of the distribution of their own isotopes in aqueous equilibrium suspensions. It has more sensitivity, because of the lower limit of error of activity measurement. Very probably the presence of calcium carbonate and the increased quantity of soluble salts have less effect on the reliability of the determination by this, than by any other method. However, with this isotope method we also need to know the proper conditions for making measurement. Examinations were carried out to compare the isotope method with the ammonium acetate method, widely used in international practice, and with the modified MEHLICH's method.

The mechanical composition of the soil samples, the electrical conductivity of saturated soil paste, the chemical composition and pH value of the saturation extracts and 1 : 5 aqueous extracts of soils, the cation exchange capacity and the quantity of exchangeable Ca^{2+} and Na^+ ions (by ammonium acetate, MEHLICH's and isotope dilution methods) were determined.

From the sodium adsorption ratio of saturation extracts the ESP values of the soils were calculated and compared with values determined by the ammonium acetate and isotope methods [11].

The applicability of the isotope method in the case of amelioration was examined by comparing the data of original and ameliorated alkali soils from Armenia. In these soils the degree of alkalization and salinization, the amount of soluble salts and calcium carbonate, as well as the mechanical composition varied widely (Table 1).

The quantity of exchangeable Na^+ and Ca^{2+} determined by different methods (Table 1) was nearly identical in the case of profile 1 which contained no calcium carbonate and only a very small amount of soluble salts.

In the cases of profiles 2, 3 and 5 the soluble salt content of the soils was high as compared with that of profile 1 and it varied within the profiles in the various soil horizons. The amounts of exchangeable sodium determined by the BaCl_2 method were considerable. In certain cases, for instance in the "B" horizon of profile 3, the measured amount of exchangeable sodium surpassed the value of the adsorption capacity. This method does not require the subtraction of soluble salts, therefore the Na^+ ions and the exchangeable Na^+ ions are measured together in the BaCl_2 extract.

The amount of exchangeable sodium ions determined by the ammonium acetate method was usually considerably lower in the soil samples containing a higher quantity of soluble salts and it was close to the quantity determined by the isotope method. In the case of the ammonium-acetate method the amount of sodium measured in the saturation extract was subtracted from the quantity of sodium extracted by the NH_4 -acetate solution.

The mechanical composition of profiles 6 and 7 was very coarse and the soluble salt content was high. In these two profiles the quantity of exchangeable sodium determined by the ammonium-acetate method was high, in some cases it surpassed the value of the cation adsorption capacity and it was always higher than the amount of sodium determined by the "isotope" method.

The amount of exchangeable calcium was always highest when obtained by the ammonium-acetate method with calcareous soils.

In the ammonium-acetate method the pH value of the exchange solution was 7. At this pH value part of the soil's calcium carbonate content dissolves during ammonium acetate extraction of the soil.

The amount of exchangeable calcium determined with the MEHLICH method was always lower than that determined with the ammonium-acetate method.

In certain cases, in spite of this, the measured values of the MEHLICH method were still high. For instance, in the "B" horizon of profile 3 the cation adsorption capacity was 23 me/100 g and the value of the exchangeable calcium was 19.5 me/100 g. This suggests that the soil was 80 per cent saturated with calcium-ions. This is apparently erroneous, for if we consider the relatively high amount of soluble salts and the high pH value of the soil,

Table 1
Some analytical data and the exchangeable Na⁺ and Ca²⁺ content and CEC values of alkali soils determined by different methods

Profile N° and depth cm	pH	Total salt content %	CaCO ₃ %	Phys. sand Phys. clay	Exchangeable Na ⁺ me/100 g			Exchangeable Ca ²⁺ me/100 g			CEC me/100 g	
					Mehlich	NH ₄ -acetate	isotope	Mehlich	NH ₄ -acetate	isotope	Mehlich	NH ₄ -acetate
1.												
0— 6	5.7	—	—	0.4	0.3	0.4	0.4	10.7	11.1	11.8	26.0	33.7
6— 15	5.6	—	—	0.4	0.4	0.3	0.3	10.7	11.2	8.8	29.4	37.0
20— 30	6.6	—	—	0.2	1.3	1.3	0.8	13.4	12.4	8.3	34.6	41.6
2.												
0— 3	6.3	0.1	—	0.2	7.8	4.4	3.3	4.0	4.1	2.7	25.0	19.8
3— 13	7.8	0.5	—	0.8	19.8	14.7	17.2	3.5	3.0	2.6	33.0	25.2
13— 18	8.3	0.9	—	0.8	25.8	19.2	24.2	2.8	2.6	4.5	35.4	32.1
3.												
0— 1	7.5	0.0	6.3	2.2	1.6	1.1	1.3	19.0	31.8	5.2	20.0	19.7
1— 11	8.6	0.2	9.7	1.6	8.0	6.3	4.4	14.9	30.0	6.5	23.5	19.9
11— 26	9.4	1.4	26.5	1.7	26.3	13.4	14.0	19.5	18.5	16.5	23.0	21.7
5.												
0— 12	9.1	1.2	9.7	3.0	17.9	10.0	13.8	10.5	21.0	5.8	15.2	14.2
12— 30	9.0	0.6	19.9	2.1	8.2	10.6	15.8	15.5	26.5	5.3	21.5	15.4
30— 40	9.2	0.4	29.6	2.4	5.7	9.6	9.1	14.0	26.2	3.6	18.2	12.7
6.												
0— 2	8.9	0.2	14.0	5.8	—	7.2	2.1	—	31.4	3.3	—	10.7
5— 15	9.6	0.4	23.5	2.1	—	25.1	4.6	—	30.6	14.8	—	21.1
35— 45	9.7	1.1	27.1	2.9	—	20.6	6.9	—	29.9	7.6	—	12.0
7.												
1— 15	9.7	1.4	10.8	5.5	—	31.5	4.8	—	36.2	3.2	—	9.8
15— 25	9.8	2.0	16.7	4.5	—	36.5	4.0	—	37.8	1.5	—	12.1
25— 34	9.7	2.0	22.1	3.9	—	16.8	4.2	—	35.3	1.1	—	12.2
8.												
0— 12	8.8	0.2	21.3	2.7	—	9.0	2.6	—	15.8	10.0	—	20.8
12— 25	9.5	0.4	28.3	3.4	—	19.0	6.6	—	31.7	9.4	—	17.7
30— 40	9.5	0.6	21.6	4.1	—	22.3	7.8	—	33.8	8.3	—	19.1
50— 60	9.5	0.3	28.4	4.5	—	44.1	4.5	—	32.1	10.7	—	22.3
9.												
10— 20	—	0.3	4.0	—	—	1.3	0.9	—	17.0	20.0	—	31.1
40— 60	—	0.3	14.0	—	—	7.1	3.0	—	25.1	29.6	—	36.0
60— 80	—	0.6	17.3	—	—	5.3	4.5	—	25.1	35.8	—	35.3
80— 100	—	—	23.0	—	—	2.5	3.9	—	26.5	24.0	—	33.5
10.												
0— 10	9.1	0.2	15.8	1.8	—	12.1	1.9	—	32.1	5.9	—	29.6
11— 22	9.3	0.2	17.3	1.4	—	9.9	1.0	—	54.3	7.5	—	20.3
30— 40	9.4	0.2	18.3	1.6	—	7.6	1.0	—	36.2	5.5	—	16.3

sodium saturation must be considerable. Also, the amount of exchangeable calcium determined by the tracer method was much lower than the values obtained by the MEHLICH method.

According to comparative evaluations, data obtained for both calcium and sodium by isotope analysis of equilibrium systems best reflect the properties of calcareous soils and of soils containing large amounts of soluble salt.

Table 2

Exchangeable Na^+ and Ca^{2+} content, CEC and ESP values of saline-alkali soil determined with the NH_4 -acetate and isotope methods

Profil N°	Depth of sample cm	Exchangeable Na^+ me/100 g		Exchangeable Ca^{2+} me/100 g		CEC me/100 g		ESP by isotope method
		NH_4 -acetate	isotope	NH_4 -acetate	isotope	NH_4 -acetate	isotope	
8.	0—12	9.94	2.55	15.83	10.0	20.76	20.6	12.35
	15—25	19.03	6.58	13.71	9.4	17.72	15.4	42.70
	30—40	22.28	9.79	33.81	8.3	19.13	16.6	58.70
	50—60	44.13	4.50	32.11	10.7	22.28	16.2	27.80

In order to study the isotope method, the amounts of exchangeable calcium and sodium were determined by the isotope tracer method and the ammonium acetate method using highly calcareous salt affected soil of light mechanical composition. The cation adsorption capacity was determined by the ammonium acetate method and, after saturating the soil with Ca^{2+} ions, by the isotope method also (Table 2). The values obtained for the adsorption capacity were nearly identical for both methods. The amounts of the exchangeable Na^+ were quite different and those of exchangeable Ca^{2+} differed even more between the methods. The total amount of exchangeable Na^+ and Ca^{2+} determined with the ammonium acetate method always surpassed the adsorption capacity of the soil. The values measured with the isotope method were lower. The value of the Na saturation percentage calculated from data obtained with the isotope method satisfactorily reflected the changes in soil alkalinity.

Table 3

The quantity of alkali soils' sodium ions dilutable with ^{24}Na isotope and the amount of their exchangeable Na^+ ions determined by the isotope and NH_4 -acetate methods

Profile N° and depth, cm	Na^+ dilutable with ^{24}Na isotope	Exchangeable Na^+ me/100 g			CEC me/100 g NH_4 -acetate
		isotope	corrected	NH_4 -acetate	
3.					
0—1	3.7	1.3	2.0	1.1	19.7
1—11	10.3	4.4	7.5	6.3	19.9
11—26	34.5	14.0	14.7	13.4	21.7
9.					
10—20	3.5	0.9	0.7	1.4	31.1
40—60	9.1	3.0	5.9	7.1	36.0
60—80	10.9	4.5	5.0	5.3	35.3
80—100	10.9	3.9	3.3	2.5	33.5
10.					
0—11	14.1	1.9	11.2	12.1	29.6
11—22	9.8	1.0	8.5	9.9	20.3
30—40	9.3	1.0	8.1	7.6	16.3

Table 1

 Values of ESP calculated and measured by the NH_4 -acetate and isotope methods

Profile N° and depth, cm	Exchangeable Na^+ me/100 g		CEC me/100 g	ESP		
	NH_4 -acetate	isotope		measured		calculated
				NH_4 -acetate	isotope	
2.						
0— 3	4.3	3.3	19.8	21.8	16.7	7.5
5— 13	14.7	17.2	25.2	54.2	68.5	13.7
13— 18	19.2	24.2	32.6	61.1	74.5	34.6
3.						
0— 1	1.1	2.0	19.7	5.7	7.4	2.4
1— 11	6.3	7.5	19.9	31.8	37.8	31.1
11— 26	13.4	14.7	21.7	61.7	67.6	73.5
5.						
0— 12	10.0	13.8	14.2	70.2	96.5	61.2
12— 30	10.6	15.8	15.4	69.2	100.0	49.4
30— 40	9.5	9.1	12.7	75.5	72.1	22.2
7.						
1— 15	31.5	4.8	9.8	100.0	49.2	81.2
15— 25	36.5	4.0	12.1	100.0	39.2	69.8
25— 34	16.8	4.2	12.2	100.0	34.0	66.7
9.						
10— 20	1.4	0.7	31.1	4.3	2.4	11.6
40— 60	7.1	5.9	36.0	19.7	13.6	20.3
60— 80	5.3	5.0	35.3	15.3	14.0	37.3
80—100	2.5	3.3	33.5	7.5	9.9	40.0
10.						
0— 11	12.1	11.2	29.6	41.0	38.0	20.3
11— 22	9.9	8.5	20.3	48.7	42.0	17.4
30— 40	7.6	8.1	16.3	46.5	49.8	25.3

The determination of exchangeable Na by the isotope method was carried out with a suspension of a relatively high ratio of water to soil. The original equilibrium between exchangeable cations and cations of the soil solution was thus upset and a new equilibrium corresponding to the changed concentrations of the soil solution was established. In certain cases the hydrolysis of exchangeable sodium must be taken into account. This is indicated by data obtained in connection with profiles 3, 9 and 10. To determine the influence of exchangeable Na^+ ion hydrolysis on the exactness of the isotope method, we corrected the measured data taking into account the quantity of Na^+ determined in saturation extracts (Table 3). Hydrolysis had little influence on the accuracy of the measurement if the soils were rich in soluble salts or had a low degree of Na^+ -ion saturation. When soils contained a moderate quantity of soluble Na-salts and they were 10–50 per cent saturated with Na^+ -ions the corrected data were close to the data determined by the ammonium-acetate method. In these cases we have accounted for the hydrolysis of exchangeable Na^+ -ions as a possible source of error and such corrected values should be used.

The ESP values of the soils were calculated and compared with the

Table 5

The quantity of sodium ions dilutable with ^{24}Na isotope and the amount of exchangeable sodium in alkali soils before and after the amelioration

Profile N°	Depth cm	Total salt content %	CaCO_3 %	Na^+ me/100 g		CEC me/100 g	ESP	The require- ments of chemi- cal amendments me/100 g
				dilat. with ^{24}Na	exchan- geable			
I. before the amelioration	0—20	1.80	16.8	48.6	21.9	17.6	>100	22.0
	20—40	1.30	14.2	52.3	26.0	33.1	78.6	28.0
	40—60		12.5	43.1	23.9	29.9	80.0	26.8
I. after the melioration	0—20	0.06	13.8	1.53	1.2	29.9	4.02	
	20—40	0.05	12.1	1.78	1.4	27.5	5.10	
	40—60		15.0	2.36	1.7	31.5	5.40	
II. before the amelioration	0—25	1.60	20.30	41.40	13.2	22.2	58.50	
II. after the amelioration	0—25	0.90	9.20	13.65	6.5	22.3	29.1	

values determined by the ammonium acetate method as well as the values determined by the isotope method (Table 4).

The measured and the calculated values were, in certain cases, relatively close. In other cases, however, considerable differences were found. The calculated values in most of the cases reflected the changes in soil alkalinity in the various horizons. The calculated and measured data cannot, however, be compared in a reliable way and the calculated values are suitable only for a general characterisation of salt affected soils.

To select the proper method of soil amelioration and to control the change in the ameliorated soil's properties it is necessary to determine the amount of soluble sodium salts and the quantity of exchangeable Na^+ -ions.

The measured values of isotopically dilutable sodium ions in sodic soil from Armenia before and after amelioration reflect well the changes that occurred in the total quantities of soluble and exchangeable sodium (Table 5). The amount of Na^+ measured in saturation extracts and the quantities of exchangeable Na^+ determined by the isotope method show the decrease that resulted from amelioration.

It seems that the isotope tracer method is only slightly influenced by the soluble salt reserve and the CaCO_3 content of the soil. Although this method is conventional, it supplies comparable data on the amount of both exchangeable Ca^{2+} and Na^+ ions even for highly calcareous soils rich in salts. It is suitable, not only for the general characterization of alkali soils containing large amounts of soluble salts and CaCO_3 , but also to follow the changes in soil properties resulting from amelioration.

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