

Relationships Between Soil Solution Composition and Soil Water Content of Hungarian Salt-Affected Soils

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Soil solution fractions retained in the soil with water potentials not reaching $-1,500$ kPa were centrifuged from three salt-affected soils. Hyperbolic relationships were set up in a wide range of soil water contents (from -250 kPa water potential to 1:10 soil:water ratio) between water content and electrical conductivity as well as concentrations of the dominant ions present in the liquid phase. It was shown that the parameters of the equations reflected the salt content and composition of the soils, as well as the change of the solubilities of the salts and ion exchange processes with soil water content. Ion pair concentrations and "free" ion activities were computed by taking into account the electrostatic interactions of ions in the solution. The Na^+ /divalent cation ratio (SAR) was expressed from cation concentrations and activities. It was shown that, depending on salt content and composition as well as on water content of the soil, (1) the ratio of ion activities to concentrations was variable (in some cases, at field capacity, in concentrated solutions, divalent ion activities were even 6 times lower than concentrations); (2) SAR was always higher (at field capacity, for example, nearly 2 times) if it was calculated from activities, and increased more with decreasing soil water content than SAR obtained from measured cation concentrations.

Keywords ion activities, sodium adsorption ratio, soil liquid phase, solution extraction, water potential

Soil solution is the mobile liquid phase in the soil at field water contents. No exact methods are available at present for the determination of its actual chemical composition in the natural undisturbed state, without the destruction of the complicated system of the soil (Rhoades, 1982). The isolation of the "true" soil solution has not yet been solved (Sposito, 1986). There exist a number of methods for the separation of the liquid phase from the wet soil in order to approximate the actual chemical composition of the "true" soil solution. In situ extraction techniques apply vacuum-suction or free-drainage soil solution samplers in the field (Barbee & Brown, 1986; Rhoades & Oster, 1986; Litaor, 1988; Zabowski & Ugolini, 1990). Several laboratory methods have been developed for obtaining the liquid phase from undisturbed bulk soils or from air-dried, ground, and

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rewetted soil samples. The most important methods are high-speed centrifugation with and without the use of an immiscible liquid, displacement in column by various organic solvents, hydraulic pressing, and pressure filtration (Komarova, 1968; Gillman, 1976; Mubarak & Olsen, 1976; Adams *et al.*, 1980; Sato *et al.*, 1981; Sonneveld *et al.*, 1990). There are only few publications that discuss the energy status of the separated soil solution (Gillman, 1976; Csillag & R edly, 1989; Zabowski & Ugolini, 1990; Jones & Edwards, 1993).

The chemical composition of the soil solution is greatly influenced by the water content of the soil. Some studies make an attempt at the quantitative prediction of the effect of the change in soil water content on the concentration and composition of the liquid phase (Reitemeier, 1946; Ulrich & Khanna, 1972; Gillman & Bell, 1978; Baron & Tokarev, 1979; Arbelo *et al.*, 1989; Csillag & R edly, 1989; Sonneveld *et al.*, 1990). The liquid phase of the soil, especially at high salt concentration, can be considered as a multicomponent electrolyte solution in which, due to the interactions of the dissolved components, different species ('free' hydrated ions, ion pairs, complexes, and molecules) are present. The physicochemical properties of such solutions are determined by the activity and ratio of these 'species' (described by, among others, the Debye-H uckel and Bjerrum theories; cited in Erdey-Gr uz, 1974).

The change in the concentration, ionic composition, and pH of the soil solution may lead to the dissolution of certain minerals or, inversely, may result in the formation of poorly soluble compounds. A shift in the cation exchange equilibria between the solid and liquid phases of the soil may also take place. A change in the ratios of the different species present in the liquid phase may influence the above processes (Rao *et al.*, 1968; Tanji, 1969; Lindsay, 1979; Darab *et al.*, 1980; Bresler *et al.*, 1982; Sposito, 1986; Csillag & Kapoor, 1987; Heck & Mermut, 1992; Arslan & Dutt, 1993).

The objectives of this work are (1) to present a method that is suitable for the separation of soil solution fractions with physically defined energy state and (2) to describe quantitatively the dependence of the solution concentration and composition (implying the electrostatic interactions of ions) from soil water content.

Materials and Methods

Chemical Analysis

The air-dried samples of the salt accumulation horizon of three salt-affected soils (Table 1) characteristic on the Hungarian Plain (Szabolcs, 1965) were moistened to different water potentials in the range of -0.1 to -250 kPa. The soil solutions were separated with centrifugation by modifying Gillman's (1976) method. Special double-bottomed centrifuge tubes (Figure 1) were applied, which were developed in our institute from the 500 mL tubes of the Beckman J2-21 type centrifuge (Beckman, 1980). Before every centrifuge application, a standard pretreatment procedure was applied: the perforated teflon consoles were soaked in $1M$ HNO_3 solution overnight, then washed daily with fresh distilled water. As a result of the pretreatment, the adsorption of the elements by the teflon from salt solutions, which was significant formerly in some cases, became negligible (Table 2).

The centrifugal speed was calculated by applying an equation used by Cassel and Nielsen (1986), to correspond to $-1,500$ kPa water potential, to a value representing the conventional wilting point of plants, i.e., the conventional upper limit of the potential exerted by plant roots. The relationship between the centrifugation speed (n) and the average water potential (h) was expressed as follows:

Table 1.
Main characteristics of the studied soils

Site	Location		Soil type (FAO classification)	Plant species	Annual precipitation (mm)	Annual temperature (°C)
	N Latitude	E Longitude				
Apaj	47°15'	19°10'	meadow solonetz (Calcic Solonetz)	<i>Festuca pseudovina</i> <i>Achillea</i> sp. <i>Centaurea</i> sp.	565	10
Bócsa	46°35'	19°30'	soda solonchak (Sodic Solonchak)	<i>Artemisia santonicum</i> <i>Festuca pseudovina</i>	583	10.5
Szarvas	46°50'	20°33'	solonchakized meadow solonetz (Haplic Solonetz)	<i>Artemisia santonicum</i> <i>Festuca pseudovina</i> <i>Lolium perenne</i>	495	10

Site	b. Physical and chemical properties									
	Depth (cm)	Horizon	SP	<0.02 mm (%)	Total CaCO ₃ (%)	Total soluble salts (%)	pH _{H₂O}	Organic matter (%)	CEC (cmol _c kg ⁻¹)	ESP
Apaj	13-31	B ₁	64	36	34	0.1	9.8	2.9	13	35
Bócsa	0-5	A	34	11	4.5	0.5	9.8	1.0	6.5	*
Szarvas	45-75	B ₃	75	72	0.2	0.6	7.8	1.0	39	20

SP, saturation percentage; <0.02 mm, clay + silt fraction; pH_{H₂O}, measured in 1:2.5 soil:water suspension; CEC, cation exchange capacity; ESP, exchangeable sodium percentage. Dominant soluble salts for Apaj are Na₂CO₃, NaHCO₃; for Bócsa are Na₂CO₃, NaHCO₃, NaCl; and for Szarvas are Na₂SO₄, MgSO₄, CaSO₄.

*Not interpretable because of the soil properties.

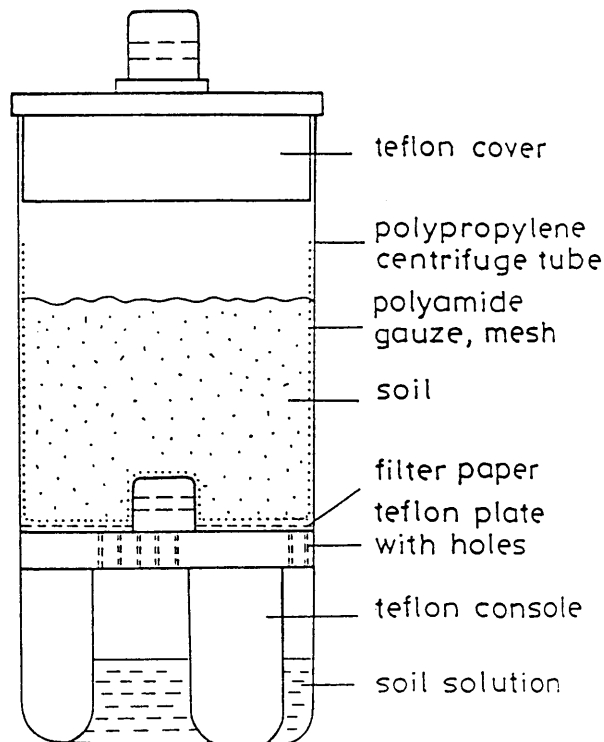


Figure 1. Centrifuge tube for the separation of the soil solution.

$$h = (-\omega^2/6g)(2r_2 + r_1)(r_2 - r_1)$$

where $\omega = 2\pi n/60$, the angular velocity (min^{-1}), n is the centrifugation speed (rpm), g is the acceleration due to gravity (m s^{-2}), and for r_1 and r_2 (m) see Figure 2. The centrifugation speed in the Beckman J2-21 centrifuge when the potential (h) is set to $-1,500$ kPa is 5,000–5,400 rpm (depending on the quantity of the soil, i.e., on the value of r_1).

Besides the separation of the soil solution, saturation extracts and aqueous soil extracts (with soil:water ratios of 1:1, 1:2, 1:5, 1:10) were also prepared from the three soils with standard procedures (Rhoades, 1982). The saturation paste and the 1:1, 1:2 soil suspensions were centrifuged with a speed corresponding to -500 kPa, while the suspensions of 1:2, 1:5, and 1:10 were filtered by paper. pH and Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_3^{2-} , HCO_3^- , SO_4^{2-} , and Cl^- concentrations in the solutions were measured with standard analytical methods (Rhoades, 1982).

Calculation

For the prediction of the electrostatic interactions of the ions in the soil solution in the field water content range and also at higher water contents, the measured ion concentrations and pH of the solutions were used as the input data of a computational model developed earlier, based on the Bjerrum ion association theory and the Debye-Hückel theory (Csillag & Darab, 1985). Taking into account the ion pair formation of HCO_3^- , CO_3^{2-} , and SO_4^{2-} with the monovalent and divalent cations and calculating the ion activity coefficients from the ionic strength values of the solutions, the activities of "free" hydrated ions were

Table 2.
Study of the adsorption of different components from single salt test solutions in pretreated centrifuge tubes (ion concentrations of salt solutions before and after 3-Hour incubation of the teflon)

	3-Hour incubation	
	Before	After
	Cations (me L ⁻¹)	
Ca ²⁺	4.4	4.4
	4.4	4.4
	9.5	9.2
Mg ²⁺	0.7	0.7
	0.7	0.7
	3.4	3.4
Na ⁺	4.9	4.3
	19.4	17.3
	19.4	18.2
	97.3	89.5
K ⁺	0.3	0.8
	4.0	2.8
	4.0	2.8
	Anions (me L ⁻¹)	
HCO ₃ ⁻	3.3	2.9
	3.3	2.9
	3.7	4.8
Alk.	3.7	3.3
	3.7	3.3
	6.6	6.2
SO ₄ ²⁻	6.6	6.0
	7.7	9.1
	20.7	20.2
	20.7	22.6
Cl ⁻	104.0	104.0
	4.0	3.9
	4.0	4.0
	12.0	12.4

Values shown are concentrations (me L⁻¹) of the model solutions. Alk. (alkalinity) = CO₃²⁻ + HCO₃⁻.

computed. It was shown previously on the example of a solonetz and a chernozem soil that the computed Na⁺, Cl⁻, Ca²⁺, and Ca²⁺ + Mg²⁺ activities agreed well with those measured in the soil solutions by ion selective electrodes (Csillag & Rédy, 1989).

Results and Discussion

Separation of Soil Solution

The soil solution fractions separated with -1,500 kPa are considered to represent the liquid phase available for the plant at natural soil water contents because they are retained in the

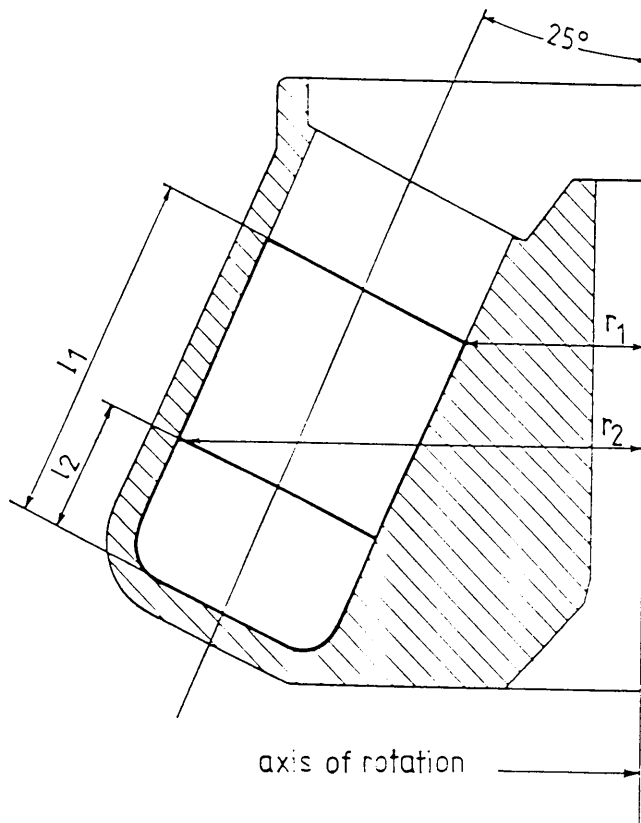


Figure 2. Parameters for the calculation of the centrifugal speed (modified scheme of the instruction manual of Beckman, 1980): l_1 is height of the perforated teflon console and the soil sample (Figure 1), l_2 is height of the perforated teflon console (0.045 m), r_1 is the shortest sample distance from the rotation axis, and r_2 is the longest sample distance from the rotation axis (0.142 m).

soil with suctions not reaching the suction corresponding to the wilting point. From water-saturated soil, for example, solutions at soil water potentials between $-1,500$ and -0.1 kPa are centrifugated, while from the sample having field capacity, solutions at $-1,500$ to -20 kPa can be obtained. By analyzing these solution fractions, the quantity and chemical composition of the soil solution utilizable (in the sense of energy conditions) for the plant is "modeled."

Other methods applied widely for the separation of the soil solution do not represent soil moisture available to plants. In the case of suction methods, for example, the maximum suction that can be exerted is -100 kPa, whereas plants can exert much higher values. Displacement methods also do not give information about the quantity and energy status of the solution remaining in the soil after the extraction. It is also probable that the extreme high pressures applied to the moist soil samples in a hydraulic pressure apparatus during the extraction of the soil solution, disturb the prevailing equilibrium between the soil phases.

Soil Solution Concentration–Water Content Relationships

As the separation of the soil solution fractions is difficult and time consuming, and usually requires a large amount of soil, the possibility of predicting their concentration and

composition from aqueous soil extracts would be desirable. Therefore, in the case of the three salt-affected soils having different chemical and physical properties (Table 1), the effect of the change of soil water content on the chemical composition of the liquid phase was studied. The measured concentrations (c) of the dominant ions in the solutions and the electrical conductivity values (EC) were plotted against soil water content (θ), i.e., against the corresponding water potential values. With decreasing θ (i.e., with increasing suction), the solutions extracted are more and more strongly retained, and their concentration increases. This tendency is shown in Figure 3 on the example of EC of the solutions. In the case of all three soils, the increase of EC is more pronounced in more strongly retained solution fractions, in the narrow range of field water contents (from -250 to -0.1 kPa water potential). Above saturation (-0.1 kPa) the EC is smaller, partly because of the higher water content of the saturation paste and soil suspensions, partly because of the dissimilar separation technique applied. [Centrifugation with a speed corresponding to -500 kPa or paper filtering provide less concentrated solutions than centrifugation with $-1,500$ kPa (compare Table 4 of Csillag & Rédy, 1989)]. Total soluble salt content (measured in the saturation paste) is somewhat lower in Bócsa soil than in Szarvas soil (Table 1), but at lower water contents (below saturation) the soil solution becomes more concentrated in the former soil. At higher dilutions, in the aqueous extracts, the EC values are highest in the Szarvas soil (Figure 3).

In the wide water content range (from -250 kPa water potential to 1:10 soil:water ratio) the relationships between c or EC and θ values were roughly approximated by hyperbolic equations (Table 3). This function was chosen, as in the case of pure, simple

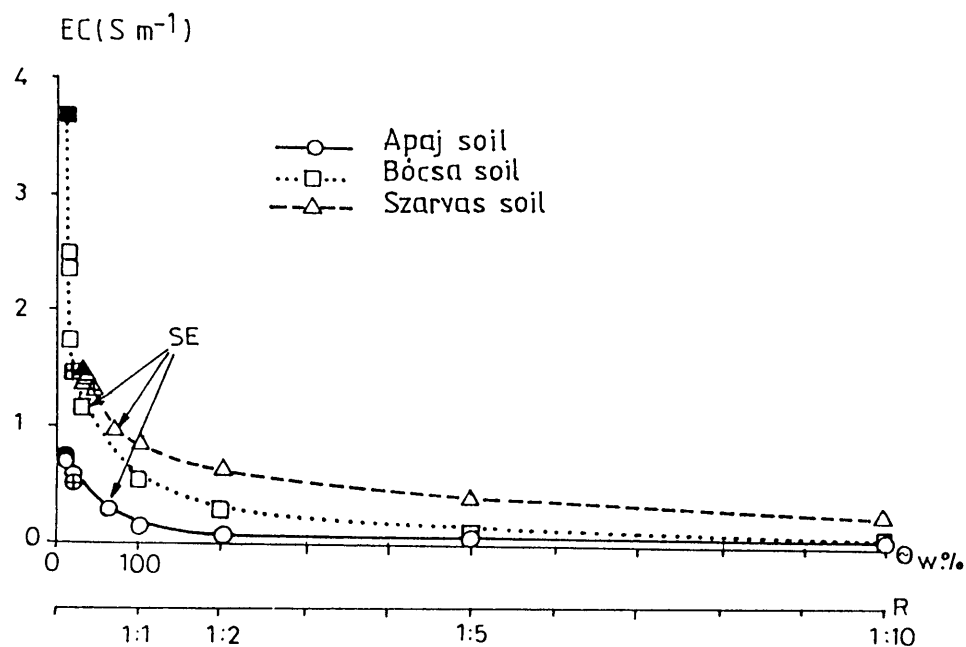


Figure 3. The dependence of the electrical conductivity of soil solutions, saturation extracts (SE), and aqueous extracts of salt-affected soils on soil water content (θ_w , expressed in weight percent) or on soil:water ratio (R). Symbols indicate that the soil solution is separated from the soil of -250 kPa (solid symbols) and -0.1 kPa (crossed symbols) initial water potential. (In the swelling soils, saturation percentage is higher than the water content at -0.1 kPa).

Table 3.

Parameters of hyperbolic relationships 1 and 2 obtained from the data of centrifuged soil solutions (-250 to -0.1 kPa), as well as of saturation extracts and of aqueous soil extracts (soil:water ratios of 1:1, 1:2, 1:5, 1:10)

Para- meter	EC (S m ⁻¹)		Ca ²⁺		Mg ²⁺		Na ⁺		Alk.		SO ₄ ²⁻		Cl ⁻	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Apaj soil														
<i>a</i>	0.1	0.07	—	—	—	—	19.8	14.9	7.5	6.3	11.8	12.9	2.9	2.6
<i>b</i>	4.5	7.7	—	—	—	—	403	728	66.2	149	223	146	98.2	123
<i>d</i>	0	-23.8	—	—	—	—	0	-2.4 × 10 ³	0	-623	0	579	0	-189
<i>r</i> ²	0.926	0.974	—	—	—	—	0.888	0.954	0.642	0.737	0.911	0.923	0.965	0.972
Bócsa soil														
<i>a</i>	0.3	0.1	—	—	—	—	27.9	13.0	17.5	9.2	13.9	12.0	4.3	-1.9
<i>b</i>	17.6	30.5	—	—	—	—	2.2 × 10 ³	3.4 × 10 ³	656	1.3 × 10 ³	246	393	819	1.3 × 10 ³
<i>d</i>	0	-91.9	—	—	—	—	0	-8.5 × 10 ³	0	-4.7 × 10 ³	0	-1.0 × 10 ³	0	-3.5 × 10 ³
<i>r</i> ²	0.817	0.848	—	—	—	—	0.853	0.870	0.469	0.503	0.583	0.598	0.760	0.781
Szarvas soil														
<i>a</i>	0.6	0.5	16.2	13.0	20.2	12.4	53.5	30.5	1.7	1.5	72.8	62.4	7.3	2.0
<i>b</i>	7.7	18.3	145	374	384	944	719	2.2 × 10 ³	4.6	19.3	1.2 × 10 ³	1.8 × 10 ³	257	552
<i>d</i>	0	-77.3	0	-1.8 × 10 ³	0	-4.4 × 10 ³	0	-1.2 × 10 ⁴	0	-115	0	-5.0 × 10 ³	0	-2.1 × 10 ³
<i>r</i> ²	0.750	0.914	0.780	0.962	0.806	0.967	0.667	0.957	0.338	0.659	0.876	0.911	0.780	0.897

Dash indicates that, because of the low concentrations (Table 4), there was no purpose for setting up the $c = f(\theta)$ relationship. Hyperbolic relationships are 1, $c_1 = a + b [1/(\theta_w - \theta_w)]$; and 2, $c_2 = a + b [1/(\theta_w - \theta_w)] + d [1/(\theta_w - \theta_w)]^2$, where c_1 is ion concentration (me L⁻¹), θ_w is soil water content (wt %), and θ_w' is soil water content at -1,500 kPa potential. r^2 is coefficient of determination of the regression equation.

solutions of very soluble salts (such as NaCl) the change of the solution concentration with dilution is described by the reciprocal “dilution law,” i.e., by a hyperbolic relationship. In the case of the wet soil, the slope (b) of the linearized $c = a + b [1/(\theta_w - \theta_w^*)]$ equations characterizes the change of ion concentrations in the solution with changing soil water content, while the intercept (a) would give the concentrations at infinitive dilution. The asymptote of the vertical part of the hyperbola, θ_w^* , is soil water content at $-1,500$ kPa potential, i.e., the wilting point. More strongly retained solution is conventionally not available for the plant and cannot be separated by centrifugation with $-1,500$ kPa.

The parameters a and b of the hyperbola reflect on salt content and salt composition of the soils, as well as on the change of the solubilities of salts and the ion exchange equilibria with soil water content. The slope is decreased by soil chemical reactions taking place with increasing water content (i.e., desorption of exchangeable sodium and dissolution of poorly soluble salts). The small b values, for example, in the case of Apaj soil, show its lower salt content (Table 1). The steep slopes of EC, Na^+ , alkalinity, and Cl^- curves of Bócsa soil are the consequences of the fact that at lower soil water contents very soluble Na salts are accumulated in the liquid phase. On the other hand, with increasing dilution the desorption of exchangeable sodium is insignificant; it does not decrease the b value because, in this sandy soil, its amount is relatively low. In the case of Szarvas soil, Na, Mg, and Ca sulfates are present in significant amounts. The presence of the less soluble salts (such as gypsum), which continuously dissolve with increasing soil water content, relatively decreases the slope of the curves. The desorption of exchangeable cations with the dilution is also considerable in this soil.

The above-mentioned chemical processes are also responsible for the fact that parameter a differs from the theoretically expected zero value. The probable process that increases the value of a is, in the case of Apaj soil, the desorption of exchangeable sodium, while for Szarvas soil the process is, in addition to desorption, the dissolution of poorly soluble salts at high water:soil ratios.

It is presumable that the hyperbolic relationships can serve as rough estimations for the prediction of the concentration and composition of the soil solution from the data of routine analyses of aqueous soil extracts. For this purpose the application of a quadratic member in the regression seems to be more advantageous because it considerably improved the goodness of the data fit (Table 3).

Electrostatic Interactions

As the equilibria between the phases of salt-affected soils may be influenced by the electrostatic interactions of the ions present in the liquid phase, the concentration of ion pairs and the activity of “free” hydrated ions were computed (Csillag & Darab, 1985). “Free” ion activity values are smaller than concentrations, as they characterize the nonideal behavior of the “real” solutions and give the amount of “active” ions that are really effective in soil physicochemical processes.

It was previously demonstrated, with the example of the profile of a meadow solonetz soil having high Na_2SO_4 , CaSO_4 , MgSO_4 content, that the difference between measured ion concentration (c_T) and “free” ion activity (a_F) depends on the charge and concentration of ions present in the solution (Figure 4). The $c_T - a_F$ difference is higher in the case of divalent than monovalent ions because the former have better ability to form ion pairs and their activity coefficients are also lower. The difference increases with increasing solution concentration because of the strengthening of the electrostatic interactions.

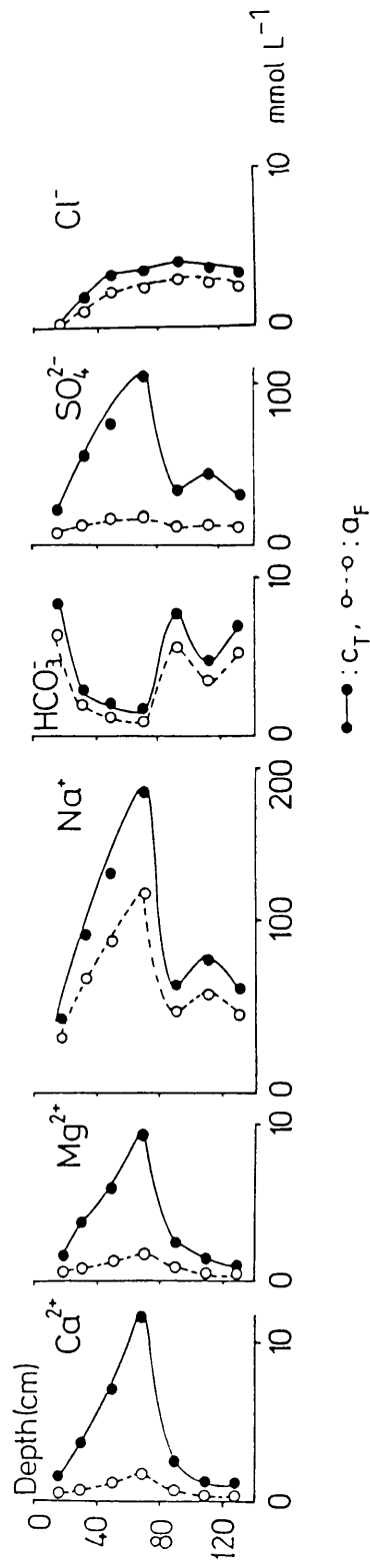


Figure 4. Measured total ion concentrations (c_T) and the activities of "free" ions (a_F) in the saturation extracts of a meadow solonetz soil (from Csillag & Darab, 1985).

Table 4. Ion concentration and activity values in the liquid phase of salt-affected soils at different water contents

Soil	θ_w or soil: water ratio	Ca ²⁺		Mg ²⁺		Na ⁺		CO ₃ ²⁻ + HCO ₃ ⁻		SO ₄ ²⁻		Cl ⁻	
		c _T	a _F	c _T	a _F	c _T	a _F	c _T	a _F	c _T	a _F	c _T	a _F
Apaj	18.5 (FC)*	0.4	0.1	0.5	0.1	62.6	48.3	12.4	8.9	16.0	5.6	12.3	9.6
	22.2 (MC)*	0.4	0.1	0.4	0.1	55.6	43.3	12.7	9.1	14.1	5.2	10.5	8.2
	64.0 (SP)**	0.1	0.05	0.4	0.1	29.1	24.0	10.1	7.8	5.6	2.6	6.5	5.4
Bócsa	1:5	0.2	0.1	2.2	0.7	18.7	15.4	5.5	4.5	9.9	4.3	2.4	2.0
	13.7 (FC)*	0.4	0.05	0.5	0.06	318	212	91.6	52.1	24.6	4.4	97.0	64.1
	34.3 (SP)**	0.3	0.04	0.1	0.02	130	93.6	48.3	29.4	9.5	2.6	50.0	36.3
Szarvas	1:5	0.6	0.2	2.4	0.8	18.8	15.6	9.5	7.6	7.5	3.3	3.0	2.5
	28.7 (FC)*	16.1	2.6	31.1	5.1	130	88.3	2.2	1.4	92.0	14.7	31.5	21.3
	36.2 (MC)*	15.7	2.5	29.8	4.8	120	81.1	2.5	1.6	90.8	14.9	31.0	21.1
75.0 (SP)**	11.3	2.1	18.1	3.5	68.5	49.0	2.0	1.4	57.5	11.9	13.0	9.4	
	1:5	7.4	1.8	5.8	1.4	34.0	26.1	1.6	1.2	28.8	8.4	3.0	2.3

c_T, measured "total" ion concentration (mmol L⁻¹); a_F, calculated "free" ion activity (mmol L⁻¹); θ_w , soil water content (expressed in weight percentage); FC and MC, field capacity and maximum water capacity, respectively; SP, saturation percentage; 1:5, the aqueous soil extract is separated by simple paper filtering from the 1:5 soil:water suspension.

*The solution is separated by a centrifugation speed corresponding to -1,500 kPa.

**The solution is separated by a centrifugation speed corresponding to -500 kPa.

Therefore, the highest $c_T - a_F$ difference was found in the saturation extracts of the B horizon.

The effect of the change of soil water content on the electrostatic interactions of ions, on the difference between c_T and a_F values is shown in Table 4 at some characteristic soil water contents (field capacity, maximum water capacity, saturation percentage, and 1:5 soil:water ratio). In the case of all three soils, concentrations and activities, as well as the $c_T - a_F$ difference, generally increase with decreasing soil water content. In the case of Na^+ and Cl^- it can be seen that $c_T - a_F$ increases with the salt content of the soil (Apaj < Szarvas < Bócsa).

In the case of Ca^{2+} and Mg^{2+} in Szarvas soil, the activity values are much lower than the concentrations because higher charges cause stronger electrostatic interactions. The $c_T - a_F$ difference is especially large at SO_4^{2-} because of its charge and high concentration; since it has a high ability for association with Ca^{2+} , Mg^{2+} , and Na^+ and a low activity coefficient, only about 1/6 of it remains "active" in the field water content range.

Similarly for the $c = f(\theta)$ functions, the relationships between the calculated activity of "free" ions and soil water content were approximated by hyperbolic equations in the wide range of water content studied. The a and b parameters of the linearized equations are given in Table 5. Their interpretation is similar to the case of the $c = f(\theta)$ functions, but their absolute values are lower, especially at divalent ions. In many cases the slope characterizing the change of activities with changing soil water content is less than half of the corresponding b value of the $c = f(\theta)$ equation. In Szarvas soil, for example, the b value of the Na^+ activity curve is only slightly lower while that of the SO_4^{2-} activity curve is lower by more than an order of magnitude in comparison with the concentration curve (Table 3).

The $a = f(\theta)$ relationships make possible the prediction of ion activities in the soil solution by calculating ion activities in aqueous soil extracts from measured concentration values.

Dependence of SAR

SAR, the ratio of the concentrations of Na^+ and divalent cations in the solution, an important diagnostic parameter in the chemistry of salt-affected soils and irrigation waters, increases with decreasing soil water content (solid curves on Figure 5). As the amounts of dissolved salts are shifted in favor of more soluble Na salts in concentrated solutions, in the case of all three soils, the increase of SAR is higher in the field water content range (d in Figure 5). SAR is highest in the case of Bócsa soil because of the dominance of Na salts and lowest in Szarvas soil, where the salts of divalent cations are present in considerable amounts.

Partly as a consequence of the different ability to form ion pairs and partly due to the differing activity coefficients, the real ratio of monovalent and divalent ions in the solution is higher than expected from cation concentrations. This ratio also increases much more with decreasing soil water content than expected from the different solubilities of their salts. Therefore, SAR is also influenced by the electrostatic interactions of the ions: higher values are obtained if it is calculated from "free" cation activities (dashed curves on Figure 5) than expected from the measured cation concentrations. Their difference also increases with decreasing water content. (In the case of the three soils, at field capacity for example, SAR calculated from activities was about 2 times higher than that calculated from concentrations.) It means that the true Na^+ /divalent cation ratio is higher in soil

Table 5.

Parameters of the hyperbolic relationships 1 and 2 obtained from the data of centrifuged soil solutions (-250 to -0.1 kPa), as well as of saturation extracts and of aqueous soil extracts (soil:water ratios of 1:1, 1:2, 1:5, 1:10)

Para- meters	Ca ²⁺		Mg ²⁺		Na ⁺		Alk.		SO ₄ ²⁻		Cl ⁻	
	1	2	1	2	1	2	1	2	1	2	1	2
Apaj soil												
<i>a</i>	—	—	—	—	16.6	12.7	5.9	5.1	5.9	6.2	2.6	2.2
<i>b</i>	—	—	—	—	294	554	32.7	88.0	57.4	39.7	73.0	96.3
<i>d</i>	—	—	—	—	0	-2.0 × 10 ³	0	-414	0	132.3	0	-175
<i>r</i> ²	—	—	—	—	0.876	0.954	0.526	0.668	0.850	0.859	0.959	0.969
Bócsa soil												
<i>a</i>	—	—	—	—	24.0	13.3	13.4	8.7	6.1	6.0	4.1	-0.5
<i>b</i>	—	—	—	—	1.4 × 10 ³	2.3 × 10 ³	247	623	14.7	23.2	529	903
<i>d</i>	—	—	—	—	0	-6.1 × 10 ³	0	-2.7 × 10 ³	0	-60.2	0	-2.7 × 10 ³
<i>r</i> ²	—	—	—	—	0.877	0.909	0.398	0.463	0.252	0.258	0.790	0.821
Szarvas soil												
<i>a</i>	3.5	3.2	4.0	3.1	32.6	24.0	1.2	1.12	18.7	16.8	3.7	0.9
<i>b</i>	16.7	37.3	63.0	147	605	1.4 × 10 ³	2.4	9.8	114	285	191	456
<i>d</i>	0	-188	0	-764	0	-7.4 × 10 ³	0	-67.8	0	-1.6 × 10 ³	0	-2.4 × 10 ³
<i>r</i> ²	0.809	0.905	0.834	0.949	0.856	0.975	0.257	0.450	0.773	0.909	0.857	0.986

See Table 3 footnote. Hyperbolic relationships are 1, $a_F = a + b [1/(\theta_w - \theta'_w)]$; and 2, $a_F = a + b [1/(\theta_w - \theta'_w)] + d [1/(\theta_w - \theta'_w)]^2$, where a_F is activity of "free" ions (me L⁻¹).

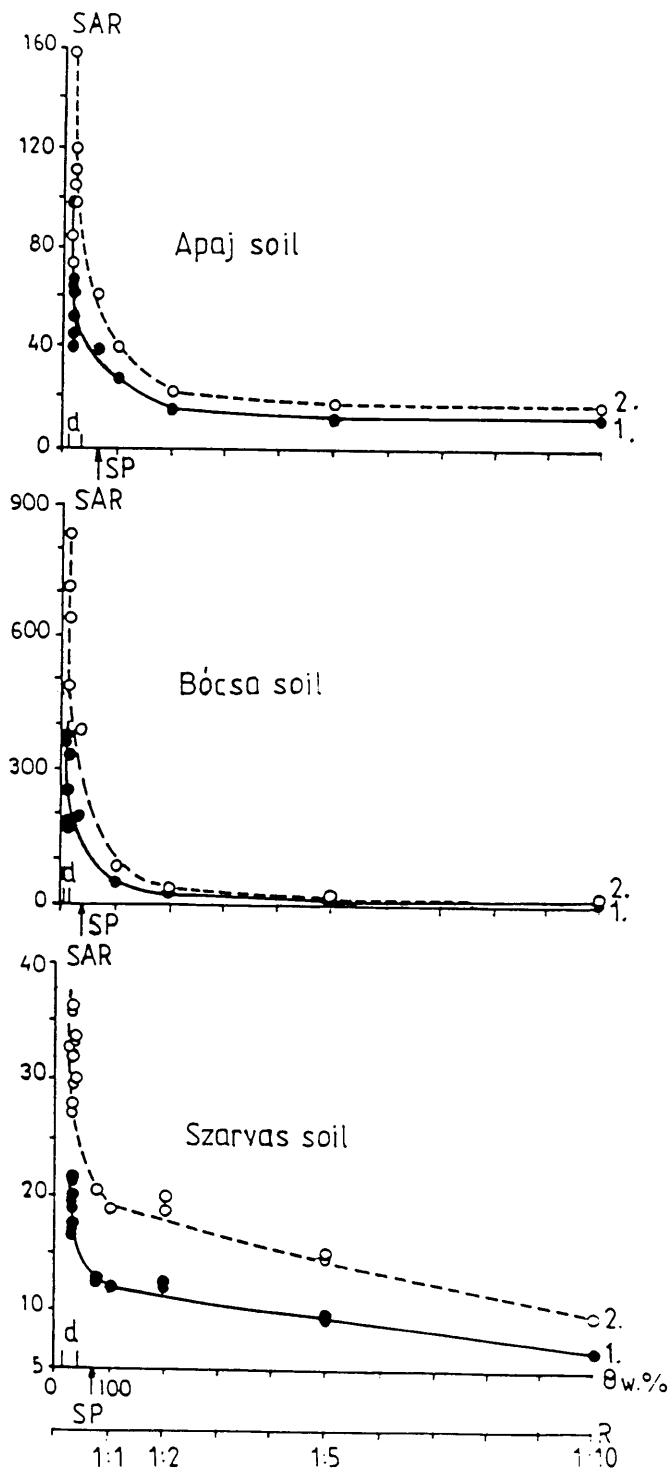


Figure 5. The dependence of sodium adsorption ratio (SAR), calculated from measured cation concentrations (curve 1) and from "free" cation activities (curve 2) on soil water content or soil:water ratio. $SAR = Na^+ / (Ca^{2+} + Mg^{2+})^{0.5}$, $(mmol L^{-1})^{0.5}$; for θ_w and R, see Figure 3; SP, saturation percentage; d, water potentials between -250 and -0.1 kPa.

solutions at field water content and when the electrostatic interactions of the ions are considered than is expected from the analyses of the more diluted aqueous soil extracts.

Conclusions

The influence of the change in soil water content on the concentration and composition of the soil solution is important in the characterization of the liquid phase at field water content available to plants, and for the interpretation of data regarding soluble salts measured in aqueous soil extracts of different soil:water ratios.

The above results should be taken into consideration during the evaluation of solubility and ion exchange processes in salt-affected soils. The increase of the absolute and relative Na^+ concentrations in the liquid phase with decreasing soil water content, and the additional effects of the electrostatic interactions of ions, result in a shift of the cation exchange processes in favor of sodium under the above conditions. It shows higher possibility of swelling, dispersion of clay particles, and formation of natric B horizon (characteristic to solonetz soils) than that based on the interpretation of concentration data.

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