

Sulphate and chloride salt efflorescences and their relationships with groundwaters and soils in Hungary

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Introduction

Salt accumulation in soils is a worldwide problem in agriculture and an enhanced attention invariably is devoted to its study. The investigations of salt efflorescences on soil surfaces may contribute to the above-mentioned research.

Earlier the studies on salt efflorescences were based on the ion composition of their water extracts. Later mineralogical investigations opened new opportunities: the direct determination of solid phases, i.e. salt minerals.

The present paper aims to contribute to the knowledge on surface efflorescences of salt affected soils in Hungary with their mineralogical investigation. A generally accepted approach for solving a problem is to start with a simple system, and proceed with a more complex one. Thus salt efflorescences dominated by sodium sulphate minerals were selected for the investigation (and only one profile with dominant sodium chloride efflorescences was found, which was also examined). Moreover, sodium sulphate minerals were the most common salt minerals in efflorescences during our project. Studies on more complex systems, e.g. sodium carbonate – sulphate – chloride surface efflorescences will be published later.

Material and methods

The study of salt efflorescences was based on 24 samples collected between 1999 and 2005 from 16 sites out of 39 sites visited.

Coordinates of the sites were recorded using GPS (from 2000) on the visited spots, land use and plant associations, as well as characteristic plant species were reported. Electrical conductivity (EC) of the samples from the surface soil (approx. 0–40 cm) was determined with an SCT 12 field bulk electrical conductivity meter.

At six sites open pits were excavated, described, and samples were taken from each horizon (according to the Hungarian Soil Survey Manual: SZABOLCS, 1966).

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The soil types according to the Hungarian soil classification, their code numbers, their correlation with the World Reference Base for Soil Resources (WRB) (IUSS Working Group, 2006) and the location of sites are given in Table 1. The location of all investigated sixteen sampling sites are shown in Fig. 1.

Powder and undisturbed samples taken from the efflorescences were stored in tightly closed glass jars.

Table 1

Codes of soil types according to the Hungarian soil classification and approximate correlation with the World Reference Base for Soil Resources (WRB) system (IUSS Working Group, 2006), location of sites where classification was based on profile description and evaluation of laboratory data

Codes	Soil types according to the Hungarian soil classification	Approximate correlation with WRB	Location of sites
20	solonchak	Solonchak or Hyposalic Gleysol*	Alap, Dinnyés, Sarród
22	meadow solonetz	Solonetz	Egerlövő, Szabadkígyós, Zám

Remarks: *The soils with gleyic colour pattern typically do not meet the 50 cm requirement, but have deeper occurrence of this feature. For location of sites: see Fig. 1



Fig. 1

Location of the investigated sixteen sampling sites.

Legend: • profiles; + surface sampling. For code numbers see Table 1

Soil analyses (pH-value, CaCO₃ and salt contents, analysis of water and saturation paste extracts), as well as the analyses of groundwaters were carried out according to international standard methods (RICHARDS, 1954; BUZÁS, 1988).

X-ray diffractograms were registered using Philips PW 1710, 1050/3710 or 1820 diffractometers, with CuK_α radiation, 40 kV excitation potential, 30 mA tube current, graphite monocromator.

Scanning electron microscope (SEM) investigations and microanalyses were carried out on an AMRAY 1830i SEM Energy Dispersive X-ray Spectroscopy (EDAX or EDS) or 9900 EDS: 20 kV excitation potential, 10 A sample current.

In the evaporation experiments 10–15 ml of groundwaters were evaporated in a Sanyo Versatile 350 HT environmental test chamber.

Results and discussion

The results are discussed from different aspects, such as occurrence of salt minerals in surface efflorescences, the influences of groundwater (water table) and soil.

Minerals and mineral associations of dominant sodium sulphate or sodium chloride efflorescences

The amounts of salt minerals in surface efflorescences of the investigated salt affected soils are shown in Table 2. From these data the frequency of occurrence of salt minerals and that of salt mineral associations can be calculated (total number of samples = 100%): bloedite: 4%, gypsum: 54%, mirabilite: 8%, thenardite: 75%.

Mineral associations are as follows: bloedite – gypsum – thenardite: 4%, gypsum – halite – thenardite: 4%, gypsum – thenardite: 29%. Monomineralic occurrences: gypsum: 13%, mirabilite: 8%, thenardite: 33%. In addition to this: 4% gypsum – halite, and 4% halite – natron – thenardite mineral associations were determined (only traces of halite or natron were found in them).

The above-mentioned data represent a unique case: common sulphate salt minerals form rare mineral associations as compared to worldwide data (compiled by SZENDREI & TÓTH, 2006).

Sodium chloride dominant mineral association, namely gypsum – halite mineral association occurred only in one locality (Zám, 2005).

Relationships of the dominant sodium sulphate or sodium chloride efflorescences to groundwaters

Salt accumulations in soils are due to saline groundwater with shallow water level in Hungary.

The *first aspect* is how the groundwater compositions are reflected in the mineralogy of the precipitated evaporites of groundwaters in the experiment. Aliquots of groundwater samples (from Alap, Dinnyés, Egerlövő, Szabadkigyós, Zám) were evaporated in an environmental test chamber under two conditions (30 °C, 55%

Table 2
Salt minerals in predominantly sulphate and chloride efflorescences of the studied salt affected soil surfaces in Hungary (1999–2005), %

Locality	Sampling date	Bloedite	Gypsum	Halite	Mirabilite	Thenardite
Alap	23 Aug 2000					5
	24 Aug 2000		tr			6
	23 July 2004					18
	25 July 2005		tr			2
Dinnyés*	24 Aug 2000			+		15
	14 July 2003					22
Egerlövő	9 Aug 2000		tr	+		21
	26 July 2005		tr			
Fertőújlak	28 Aug 2000		tr			7
Hajdúdorog	10 April 2002				+	
Hajdúnánás	8 Aug 2003					2
Hajdúvid	10 April 2002				+	
Polgár	15 Sept 1999					<1
Sarród	28 Aug 2000	1	tr			3
Szabadkígyós	7 Sept 1999		1			9
	7 Sept 1999		tr			10
	20 July 2005		1			3
Szikszo	14 June 2005		+			
Tépe	15 Sept 1999					tr
Tarnaszentmiklós	7 Aug 2000					5
Tiszakécske	7 Aug 2003					3
Tiszanána	7 Aug 2000		1			4
Zám (Hortobágy)	16 April 2000		+	50		
	26 July 2005		2			

Remarks: tr :traces, *: + natron; +: traces observed by Scanning Electron Image (SEI)

relative humidity (RH) and 35 °C, 45% RH). Groundwaters were grouped according to 15% ion concentrations.

Data in Tables 3 and 4 clearly indicate that ions above a given concentration in groundwaters are reflected in the mineral associations of the precipitated evaporites. Calcite monohydrate precipitated (aliquot evaporated at 30 °C, 55% RH) from the groundwater with Ca-CO₃+HCO₃ ions > 15% (Egerlövő). Northupite crystallized from the groundwater with Na-Mg-CO₃+HCO₃-Cl ions > 15% (Dinnyés). Burkeite was determined in the evaporates of groundwaters with Na-CO₃+HCO₃-SO₄-ions > 15% (Dinnyés, Egerlövő). From the groundwater with Mg-Cl ions > 15% (Zám) bischofite (30 °C, 55% RH), or bloedite (35 °C, 45% RH) crystallized.

Table 3
Minerals in the evaporates of groundwaters in the experiment, %

Place of origin of groundwater sample, year of sampling	Temperature, relative humidity	Bischofite	Bloedite	Burkeite	Gypsum	Halite	Jarosite	Monohydrocalcite	Northupite	Thenardite
Alap, 2005	30 °C, 55%					57			2	41
Dinnyés, 2005	30 °C, 55%			1		65	<1		3	30
	35 °C, 45%*			4		73				23
Egerlövő, 2005	30 °C, 55%					47		12		41
	35 °C, 45%		–	35		65				
Szabadkígyós, 2005	30 °C, 55%					58				42
	35 °C, 45%					58				42
Zám, 2005	30 °C, 55%	3			1	96				
	35 °C, 45%		1			99				

Remark: * = traces of nahcolite

Table 4
Ions with concentrations greater than 15% in the studied groundwaters

Ions > 15 wt%	CO ₃ ²⁻ +HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻
Na ⁺	Alap (2004), Dinnyés (2003, 2005), Egerlövő (2000, 2005), Sarród (2000), Szabadkígyós (1999)	Alap (2000, 2004, 2005), Dinnyés (2003, 2005), Egerlövő (2000, 2005), Sarród (2000), Szabadkígyós (2005)	Alap (2000, 2004, 2005), Dinnyés (2003, 2005), Sarród (2000), Szabadkígyós (1999, 2005), Zám (2005)
Mg ²⁺	Dinnyés (2005), Egerlövő (2000, 2005), Sarród (2000)	Dinnyés (2005), Egerlövő (2000, 2005), Sarród (2000)	Dinnyés (2005), Sarród (2000), Zám (2005)
Ca ²⁺	Egerlövő (2000, 2005)	Egerlövő (2000, 2005)	

The *second aspect* is how the ions in groundwaters are reflected in the mineral associations of surface efflorescences of salt affected soils. As shown by Tables 2 and 4 calcium ions are mineral forming components in gypsum (Egerlövő 2000, 2005), magnesium ions are indicated by the presence of bloedite (Sarród 2000). Minerals of CO₃ or HCO₃ ions were hardly present, which can be explained by the fact that the increase in sodium sulphate and sodium chloride concentration in groundwaters (and in soil solutions) reduces the solubility of sodium carbonates (KOVDA, 1965). As a consequence, these minerals crystallize at the beginning of the process. It is feasible that these minerals had already been formed in the depth

of profiles. Chloride minerals were not detected in the sample from Zám (2000), the evaporation process has not reached the final stage (when halite crystallizes).

The *third aspect* is whether there are any relationships between dominant sulphate surface efflorescences and the depth of the groundwater level. The distribution of groundwater depths under dominant sodium sulphate and sodium carbonate efflorescences is given in Table 5.

Table 5
Frequency of occurrences (%) of groundwater level depths under dominant sodium sulphate and chloride versus sodium carbonate efflorescences

Depth of groundwater level cm	Frequency of occurrence of		Depth of groundwater level cm	Frequency of occurrence of	
	Na-CO ₃ -HCO ₃	Na-SO ₄ -NaCl		Na-CO ₃ -HCO ₃	Na-SO ₄ -NaCl
	efflorescences, %			efflorescences, %	
20–40	2	0	180–200	2	30
40–60	10	0	200–220	2	10
60–80	30	10	220–240	0	0
80–100	24	10	240–260	2	0
100–120	14	0	260–280	2	0
120–140	2	20	280–300	0	0
140–160	2	20	>300	2	0
160–180	6	0			

As shown in Table 5, there is a maximum of carbonate efflorescences (groundwater level depth: 40–120 cm), and a range of sulphate efflorescences (groundwater level depth: 60–220 cm with a maximum at 120–220 cm). The average of groundwater level depths was the lowest in the case of sodium carbonate efflorescences, and the highest for sodium chloride efflorescence (250 cm), and it was between the above-mentioned values (175 cm) for sodium sulphate efflorescences. These differences can be explained by the fact that the least soluble sodium salt (i.e. sodium carbonate) reaches the surface from a shallow depth, while easily soluble salts (like sodium chloride) reach the surface from a greater depth in soil solution. In case of sodium sulphate – with solubility between the values of sodium carbonate and sodium chloride – the groundwater level is intermediate. This suggestion is valid only if the solubility sequence is mentioned, namely natron → thenardite → halite below ~ 28 °C (LAST, 2002). The solubility of halite hardly changes with increasing temperature, but there are considerable changes in the solubility of natron (no data available for trona) and thenardite, thus the increasing sequence of solubility is: halite → thenardite → termonatrite. The above-mentioned temperature is not feasible in deeper layers in Hungary.

The *fourth aspect* is the influence of groundwater changes in time.

In the 19th century (when several data became available on salt efflorescences) huge areas of the lowland were wetland. In the second half of the 19th century and in the first decades of the 20th century great water regulation works were conducted in the Great Hungarian Plain, which led to a decrease in the extent of surface waters and thus that of wetlands. Changes also occurred in the groundwater level depth, e.g. the data from the period of 1931–1980 indicated some increase (RÓNAI, 1961), while a considerable decline was observed e.g. in the mid-Danube–Tisza Interfluve region (MAJOR, 1986; MAJOR & NEPEL, 1988; BAKACSI, 2001; KUTI et al., 2002). VÁRALLYAY (1967) carried out a detailed study on the salt accumulation processes in the soils of the Danube Valley. KUTI et al. (1998) reported a general groundwater level decline of 0.5–3.0 m in the Great Hungarian Plain during the two decades following 1975. Due to the water regulation works and their consequences, the hydromorphic influence diminished and a process of steppe formation was generated in the soil cover (SZABOLCS, 1961).

As it was proven earlier, if sodium carbonate, sulphate or chloride is the major component in the efflorescences, a close relationship can be established with the depth of the groundwater.

According to literature data published before 1998 the major components of surface efflorescences were sodium carbonates and sodium carbonates-chloride, while sodium sulphate was the dominant salt in the samples collected between 1998 and 2005.

In areas of salt affected soils with sodium carbonate efflorescences, with the decline in the groundwater level, the sodium carbonate accumulated below the surface, in the depth of the profile. This may explain why the frequency of sodium carbonate surface efflorescences decreased, and sodium sulphate surface efflorescence became more frequent.

Relationships between dominant sodium sulphate (and chloride) efflorescences and soil types. Effect of the soil matrix

Soil types were determined by profile description and evaluation of laboratory data. Considering all soil profiles with surface salt efflorescences (n=14 profiles): 50% was found on solonchak, 6% on solonchak-solonetz and 44% on meadow solonetz soils. The frequency of occurrence of sodium sulphate or sodium chloride efflorescences (n=6) was a little higher (50%) on meadow solonetz. As it was mentioned earlier, the groundwater level depths under soils with sulphate efflorescences were between 60 and 220 cm, which is partly in accordance with the depth of the groundwater level (150–350 cm) characteristic for meadow solonetz soils in the Hungarian classification system (SZABOLCS, 1966).

The salt mineral associations of surface efflorescences differed from those of the experimentally precipitated evaporites of groundwaters.

It is possible to differentiate between evaporation processes taking place in a pond on the soil surface and those taking place on the surface from ascending solutions in soil pores. When the solution is evaporated in a pond minerals of the whole solubility sequence can be found, whereas in the latter case some minerals may

form in the depth of the soil profile (TIMPSON et al., 1986; SKARIE et al., 1987). Thus the rest of the solution will crystallize on the surface, the solubility sequence of the minerals is not complete, the products of the initial stage of the process are missing on the surface. We were unable to find a complete paragenesis corresponding to the solubility sequence in the investigated surface efflorescences, thus the formation of efflorescence from ascending soil solution is proven. Accordingly, it is reasonable to consider the effect of the soil matrix on the evaporation of salt minerals.

Tables 2 and 3 show that the dominant salt mineral (i.e. thenardite) is common in both series. Tiller (cit. RODRIGUEZ-NAVARRO et al., 2000) reported that heterogeneous crystal seed formation is preferred for thenardite, thus the soil matrix is a more favourable environment than solutions. In their experiments, VIZCAYNO et al. (1995) studied the matrix effect on crystallization and their experiences supported that the soil matrix is favourable for sodium sulphate formation. The soil matrix effect can be taken into account on minerals occurring only in surface efflorescences. The mineral that occurs almost only in surface efflorescences is gypsum. In groundwater the crystallization of calcium carbonate minerals can be expected when $\text{Ca} < \text{HCO}_3 + \text{CO}_3$. Thus these minerals crystallize and the concentration of calcium (and magnesium) diminish in soil solutions. Gypsum in the surface efflorescences forms only when the redissolution of calcium ions occurs in the profile (the soils investigated were generally calcareous from the surface or from the near surface). When $\text{Ca} > \text{HCO}_3 + \text{CO}_3$ is in the solutions calcium ions are in excess and calcium sulphate precipitates. In spite of lower solubility, calcium and sulphate ions can reach the surface due to the shorter distance and crystallize. In the saturation extracts the amounts of calcium ions increased from the subsoils to surface in the profiles investigated.

Halite occurred in almost all experimentally precipitated evaporites of groundwaters (Table 3), while it was very rare in the surface efflorescences (Table 2). It may be suggested that on soil surface this process is not complete in all cases (the final products of the process with high solubility – like halite – are missing).

Summary

The aim of the present study is a better understanding of the distribution and formation of salt efflorescences by mineralogical examination. Dominant sodium sulphate and sodium chloride surface efflorescences were selected for investigation. 24 samples were collected between 1999 and 2005 from 16 sites. The soil types were solonchak and meadow solonetz.

Basic soil and groundwater analyses were performed according to the standard methods. Minerals were determined by X-ray diffractometry and SEM combined with microanalysis. The evaporation experiments were carried out in a Sanyo Versatile 350 HT environmental test chamber.

It was concluded that common sulphate salts form rare and unique mineral associations on salt affected soils in Hungary.

Comparing the groundwater compositions and the mineral associations of surface efflorescences or that of precipitated evaporites of groundwaters, the conclusion can be drawn that groundwater composition is reflected much better by the mineral association of experimentally precipitated evaporates of the groundwater than by the mineral associations of surface efflorescences. These differences suggest that the soil matrix may have an effect on the crystallization of minerals (e.g. gypsum, thenardite) in the efflorescences. The differences also suggest that in the surface efflorescences the precipitation process does not come to the end in all cases (minerals with high solubility are missing).

Concerning the data on groundwater level depths in case of different (sodium carbonate versus sodium sulphate and sodium chloride) efflorescences, there is a tendency of declining groundwater table in the sequence of these soils. This difference can be explained by the difference (increase) in the solubility of various salt minerals.

It was recognized that the change in the major component of surface efflorescences in time (i.e. the sodium carbonate and sodium carbonate chloride versus sodium sulphate efflorescences before and after 1998) can be explained by the decline of the groundwater level and by the decreasing hydromorphic influence in the lowland area during the 19th and 20th century.

Finally it can be stated that the presented research – which mainly focused on mineralogical aspects – has contributed to the earlier knowledge on surface salt efflorescences, which was based only on their chemical composition.

Keywords: evaporation, groundwater, salt affected soils, salt efflorescence, salt minerals

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