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SALT MINERALOGY IN A SELECTED "SALORTHID" OF TEXAS HIGH PLAINS AS A FUNCTION OF SEASONAL TEMPERATURE VARIATIONS

H. MOJALLALI[1]

Department of Soil Science, College of Agriculture, University of Tabriz, Tabriz, Iran.

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ABSTRACT

Studies on the mineralogy of salts in a selceted Salorthid profile of the Texas High Plains were undertaken to determine the changes in the amount and kind of salt minerals as a function of seasonal temperature variations. A variety of minerals has been reported in studies where the crystalline state of the salt minerals was determined. Bloedite along with the minerals mirabilite, thenardite, epsomite and halite were identified. In this study, scanning electron microscopy and X-ray energy dispersive analysis were used to determine the influence of seasonal temperature variations in the mineralogy of salts. Halite was the dominant salt in both seasons, followed by mirabilite, thenardite, and bloedite. Mirabilite was present in preliminary sampling of salt crusts in November. Thenardite was present in February and June samples, and bloedite was present in June samples of salt crusts.

1. Assistant Professor.

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بررسی کانی شناسی نمکها در پروفیل یک خاک سال‌اورتید *(Salorthid)* به عنوان تابعی از نوسانات فصلی دما در دشتهای مرتفع تکزاس

حسام مجللی
گروه خاکشناسی، دانشکده کشاورزی، دانشگاه تبریز، تبریز، ایران.

چکیــده

بررسی‌های کانی شناختی نمکهای محلول در قشر نمک پروفیل یک خاک سال‌اورتید *(Salorthid)* واقع در دشتهای مرتفع شمال غرب تکزاس به منظور تعیین تغییرات در مقدار و نوع نمکهای محلول به عنوان تابعی از نوسان‌های فصلی دما بعمل آمد. کانی بلوئدیت همراه با کانیهای میرابیلیت، تناردیت، اپسومیت و هالیت شناسایی شدند. در این بررسی‌ها از تحلیل‌های پراش پرتو ایکس، اسکن الکترن میکروسکوپ و پراکنش انرژی پرتو ایکس برای تعیین تأثیر نوسانات فصلی دما در کانی‌شناختی نمکها استفاده شد. هالیت نمک غالب در هر دو فصل نمونه‌برداری (زمستان و تابستان) بود و به دنبال آن به ترتیب میرابیلیت، تناردیت و بلوئدیت قرار گرفتند. همچنین میرابیلیت در نمونه‌برداری مقدماتی از قشر نمک در ماه نوامبر (اواسط پاییز) و تناردیت فقط در نمونه‌های ماه‌های فوریه (اواسط زمستان) و ژوئن (اوایل تابستان) شناسایی شدند.

INTRODUCTION

Temperature affects the reaction rates as well as the solubility and stability of specific minerals in saline soils. Driessen and Schoorl (7) reported that much attention had been given to salt effects on physical and chemical properties of soils in arid and semiarid regions, but the mineralogical composition and the morphology of the efflorescent salts had rarely been studied. The occurrence of mirabilite ($Na_2SO_4.10H_2O$) during winter months and its subsequent transformation to thenardite (Na_2SO_4) during summer months were reported by these authors for the Great Konya Basin of Turkey. Bloedite [$Na_2Mg(SO_4)_2.4H_2O$], along with mineral associations of mirabilite/thenaridite/epsomite/halite were also identified by these authors.

The intricate mixture of soil particles and sulfates forming the surface layer of puffed salthrids corresponds to a $Na_2SO_4.H_2O$ system with or without NaCl (7). Two important sulfate-containing minerals may then be expected, i.e. mirabilite and thenardite. A metastable heptahydrite is possible in theory but, in fact, does not occur in nature (4).

The accumulation of sulfates in the surface soil may partly be explained by the temperature-dependent solubility of sodium sulfate (5). Average surface soil temperatures in the Great Konya Basin range from over 30°C in June and August to below the freezing point in January (18). This corresponds to a decrease in solubility of sodium sulfate from 92 to 11g $100ml^{-1}$. This combination with uneven rainfall distribution explain why the sodium sulfate, accumulated in the surface soil during summer, is not completely leached during the cold winter season. The different phases of sodium sulfate also depend on temperature. The mirabilite/thenardite transition temperature decreases substantially in the presence of halite but never exceeds 32.4°C. This means that mirabilite present in the cold season is transformed into thenardite in summer. Both phases were observed in the puffed layer.

Thenardite occurs solely in the upper part of the puffed zone which is exposed to the air and solar radiation. Mirabilite is exclusively found at the depth of several centimeters. These needle-shaped mirabilite crystals push the soil aggregates apart thus causing the fluffy character of the surface soil (12). As expected, precipitation plays an important role in the distribution of salts within soil profiles. In aridic moisture regimes, saline soils are characterized by the concentration of salts in surface horizons with a regular decrease in salt content with depth (2). In less arid situations, salts tend to be more disseminated through the profile (6).

X-ray diffraction (XRD) is the most widely used method for determination of mineralogy of the relatively soluble salts. A high degree of care must be exercised in the identification of these minerals, since changes in H_2O vapor pressure can transform some minerals from one species to another (8, 19). Optical and scanning electron microscopy (SEM) techniques can be used in some cases (1, 9, 10, 11, 13). Actual identification of salt minerals in soil by SEM techniques is often difficult because there may be no identifiable crystal form (9), or because drastic changes may occur under high vaccuum in the electron beam.

The objectives of this study were to 1) determine the mineralogy of salts present in the upper part of soil horizon, and 2) quantify the changes in the amount and kind of salt minerals as a function of seasonal temperature variations. The findings may be used in planning reclamation schemes for saline soils.

MATERIALS AND METHODS

The study site was selected after field reconnaissance and consultation with Soil Conservation personnel in the area. The soil selected was mapped as an Arch fine sandy loam [classified as fine loamy, mixed, thermic Ustochreptic, i.e. Calciorthid with advent of soil taxonomy (16) in Lynn Co., Texas. When the soil survey of Lynn Co. was made in the 1950's (15), the area was apparently in cultivation and had not become salinized. The time of abandonmentt is unknown. A new series of fine loamy, mixed, thermic Aquollic Salorthid will be established for this soils as part of the updating of the soil survey in the Major Land Resopurce Area (MLRA) 77. The site was in an abandoned field about 5 km from a saline playa which has been present throughout historic time. It was about 100 km south of the city of Lubbock, Texas. At the time of the winter sampling, the water table was at 80-cm depth. Present vegetation is mostly salt cedar (*Tamarix* spp.) and annual forbs. Horizon symbols used in the profile description were those presently used by the Soil Survey Staff (17). Bulk samples of each horizon were collected for laboratory analysis. Undisturbed surface crust samples were collected in Kubiena containers at the same time.

Particle-size distribution analysis for soils in each horizon was performed on air dried, 50-g samples using a modified hydrometer method (3). Because of flocculation, the standard method was modified. The supernatant solution was decanted after flocculation, more dispersant added, and sample remixed. This was done to rid the sample of soluble salts (and gypsum) so that it could be dispersed. The process was repeated until complete dispersion was achieved.

Analysis of extracts from saturated pastes, equilibrated for 24 hr (14) was made to measure electrical conductivity (ECe) and soluble ions. Sodium was determined by flame photometry while Ca and Mg were analyzed by atomic absorption (AAS).

X-ray powder patterns of surface efflorescence were obtained using a Phillip Norelco diffractometer, model 1130/80. The measurements were made from 2° to 70° 2θ; peak positions were determined and d-spacings were calculated and compared to standard samples (20).

Scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) were used in which fragments of salt crusts in Kubiena boxes were carefully separated from the main body of samples and then mounted on copper sample holders with adhesive tape and coated with carbon. The entire surfaces were then coated with gold, a few nanometers thick, using a sprayer. The prepared samples were placed in the scanning electron microscope Jem-100CX analytical, and images for salt crystals were observed and selected photographs made.

RESULTS AND DISCUSSION

Morphological properties of the soil studied are given in Table 1. The soil is formed in a semiarid climate (average annual precipitation is 470 mm and average annual temperature is 15.3°C), and recent rise of groundwater table within 80 cm of soil surface (at the time of February sampling) has caused accumulation of soluble salts in the profile. Small masses of very fine gypsum crystals were tentatively identified in the three upper horizons (the identification was later confirmed in micromorphological observations). The thickness of A horizon is surprising when compared to most soils, which have thin A horizons in the area. The soil may have been somewhat more moist because it is in a slight topographic depression. The increase in dry color values with depth reflect an increase in gypsum and/or $CaCO_3$ or both. Soil texture becomes more clayey with depth.

Amounts of soluble salts increase with proximity to the surface (Table 2). Fine pores accompanied by negative pressure from the soil surface serve as conduits for soluble salts to move toward the soil surface where electrical conductivities (ECe's) have risen to very high values of 170 and 200 dS/m. ECe values in the profile decreases with depth in the profile. Accordingly, soluble Na, the most concentrated cation in soil solution, has also increased at the soil surface. This increase is somewhat less in the summer. There is no noticeable difference in pH values within the soil profile between February and June samplings because most soluble salts in soil solution are either neutral or have low alkalinity.

Powder XRD analysis of salt crusts sampled at two different times of the year is given in Table 3. Halite has one apparent morphology (Fig. 1a), but its amount in the salt crusts has increased from February to June (Table 3). In a preliminary sampling of salt crust done in November in the same general area, small amounts of mirabilite were observed. They were not detected in February and June samples. Only small quantities of thenardite were present in both February and June samples. There is no ready explanation why thenardite exists in February sample when the soil is moist and temperatures are moderately low. Explanation for June sample may be dehydration of mirabilite to thenardite at higher temperatures. Bloedite was present in low amounts in the salt crusts sampled in June.

Table 1. Morphological properties of the studied soil.

Horizon	Depth (cm)	Color		Field texture†	Structure*	Consistency¶	
		Dry	Moist			Dry	Moist
Ap	0–15	10YR 5/3	10YR 4/2	SCL	1Sbk	H	Fr
Apy	15–26	10YR 5/3	10YR 3/3	SCL	1Sbk	Vh	Fr
Ay	26–43	10YR 4/3	10YR 3/2	CL	1Sbk	Vh	Fr
BAy	43–58	10YR 6/2	10YR 4/2	CL	1Sbk	Vh	Fr
BKy	58–72	10YR 7/2	10YR 6/2	C	M	Vh	Fi

† SCL = Sandy clay loam; CL = clay loam; C = clay.

* 1 Sbk: weak subangular blocky; M: massive.

¶ Fr: friable; Fi: firm; H: hard; Vh: very hard.

Table 2. Physical and chemical properties of the studied soil and groundwater.

Horizon	Depth (cm)	Sand %	Silt %	Clay %	February Sampling*					June Sampling*				
					pH	ECe ds/m	Na^+	Ca^{2+} meq/l	Mg^{2+}	pH	ECe ds/m	Na^+	Ca^{2+} meq/l	Mg^{2+}
Salt Crust	-	-	-	-	8.47	170	5000	28	417	8.57	200	5100	23	833
Ap	0-15	60	15	25	8,43	55	2000	28	250	8.40	49	2000	27	500
Apy	15-26	57	16	27	8.08	49	2000	28	250					
Ay	26-43	49	18	33	8.05	44	1800	28	250					
BAy	43-58	45	17	38	8.33	44	1800	24	250					
BKy	58-72	26	19	55	8.25	41	1800	24	167					
Groudwater 80					7.52	44.2	1900	26	84					

* Na^+, Ca^{2+} and Mg^{2+} are the concentrations of soluble cations in saturation extract.

Table 3. Powder X-ray diffraction analysis of salt crusts sampled at two different times of the year.

Halite				Thenardite				Bloedite			
Reference Values[a]		Measured Values		Reference Values[a]		Measured Values		Reference Values[a]		Measured Values	
		February	June			February	June			February	June
d(nm)	I/I_o	d(nm)	d(nm)	d(nm)	I/I_o	d(nm)	d(nm)	d(nm)	I/I_o	d(nm)	d(nm)
0.282	100	0.283xx[b]	0.282xxx	0.273	100	0.279x	0.277x	0.325	100	-	0.325x
0.199	55	0.199x	0.199x	0.466	73	0.467x	-	0.456	95	-	0.454x
0.165	15	0.163x	0.163x	0.318	51	0.319x	0.319x	0.329	95	-	0.328x

a. X-ray powder data file (20).
b. Number of x's denote the relative intensities of the peaks.

Scanning electron microscope (SEM) images for halite crystal and the corresponding X-ray spectra (EDAX) showing Na and Cl lines as the main elements are given in Fig. 1a and 1b. These crystals tend to be cuboidal and range upward to 50 µm in size. SEM images for mirabilite crystals and corresponding EDAX obtained from salt crystals to explain Na, S and O lines as the main elements in the composition of mirabilite are given in Fig. 2a and 2b. These crystals tend to be cuboidal and range upward to 50 µm is size. SEM images for for mirabilite crystals and corresponding EDAX obtained from salt crystals to explain NA, S and O lines as the main elements in the composition of mirabilite are given in Fig. 2a and 2b. These crystals are diamond-shaped and range up to 50 µm in size. In soil solutions, soluble Mg concentrations increased in June while soluble calcium concentrations were relatively constant. Detection of bloedite crystals in June samples is probably related to higher Mg concentrations.

CONCLUSIONS

Groundwater salinity has been the prime reason for recent soil salinization in Texas High Plains. In addition to kind and amount of salts present in soil, salt mineralogy can be a prime factor when reclamation is carried out and salts are washed out of the soil. Studies on salt mineralogy were conducted by using XRD, SEM and EDAX. Halite has one apparent morphology but its amount in the salt crusts had increased from winter to summer. Thenardite was found in both winter and summer samples. Mirabilite was found in a preliminary sampling of the mid-fall soil crusts. Bloedite was present in the summer sampling of the crusts.

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