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SURFACE CHARGE PROPERTIES AND OTHER SOIL CHARACTERISTICS IN SHAMIL-ASHKARA CATCHMENT, IRAN

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By

ABOLHASSAN MOGHIMI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Doctor of Philosophy

May 2012

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DEDICATION

This thesis is dedicated to my wife and my son, Mobin. Their patience, encouragement, and support have allowed me to achieve my goals.

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

SURFACE CHARGE PROPERTIES AND OTHER SOIL CHARACTERISTICS IN SHAMIL-ASHKARA CATCHMENT, IRAN

By

ABOLHASSAN MOGHIMI

May 2012

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Iran is one of the countries with most parts affected by arid condition (> 90%) with accumulation of calcareous materials in some soils as well as salt in some others. There is no reported study showing the relation between soil characteristics and aggregate stability in southeast Iran and study on surface charge properties and relationship between soil characteristics and surface charge in arid regions. The stability of soil aggregates in this area is deteriorating due to intensive agriculture practices, land use change, low organic matter content, high content of sodium and groundwater saline water. This study outlines principal characteristics of soils that occur in the arid region of southeastern Iran and deems significant, as the data obtained will provide empirical information concerning the effect of minerals and soil properties on the aggregate stability and surface charge characteristics of soils in this catchment. The objectives of this study were (I) to identify the major physico-chemical and mineralogical properties of the soil of southeastern Iran and (II) to appraise their effects on the clay dispersion and surface charge characteristics of these arid soils. To attain these objectives, eight

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soils representing areas of the alluvial plain and the colluvial fan sediments along the slope area in Shamil-Ashkara catchment, Iran, were investigated. The soils were internationally classified using the criteria of Soil Taxonomy (Soil Survey Staff, 2010) and the FAO (2007) world reference base for soil resources. They are in the recent stage of development. They were identified as 1 calcic haplosalids, 3 aridic ustorthents and 4 aridic ustifluvents. The soils are calcareous and alkaline. The soils physico-chemical properties do not show any clear trend with depth. The results assent with the nature of alluvial and colluvial deposition that varies from time to time. All soils have pH values above 7 and the electrical conductivity (EC) vary from slightly saline to saline. The organic carbon content was low in all soils, which is common for soils of these regions where the vegetation is strongly influenced by the climatic conditions. The soils tend to be massive when the silt content is high, otherwise the structure would be single grain when the sand content is high, resulting in their weak and structurally unstable properties.

The major minerals present in the parent material samples are Chlorite, illite, smectite, kaolinite, palygorskite, feldspars, quartz, calcite and interstratified illite-smectite. In the soil, the common minerals are quartz, feldspars, smectite, palygorskite, chlorite, illite, kaolinite and sepiolite. Arid soils are structurally unstable and disperse easily in water. Soil pH affects stability aggregates the most as indicated by high significant correlation between pH and water-dispersible clay (WDC) (r = 0.78**). There is the highest positive significant correlation between soil EC and WDC (r = 0.95**). Multiple linear regression analysis also indicated that EC has the highest influence on WDC. Among the minerals present,

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palygorskite significantly influences the WDC (r = 0.70**) the most, while chlorite has the least significant effect. The results indicated that the significant positive factors affecting WDC are in the order of electrical conductivity (EC) > pH > permanent negative charge (σ_p) > K^+ >CEC > Na^+ >palygorskite > SAR > Mg^{2+} >clay content. Soil surface charge characteristics also affect soil minerals and properties. The point of zero charge (pH_0) is one of the most important parameters used to describe variable-charge surfaces. The results indicated that PZC values are low (2.8 – 3.37) in all samples and lower at the surface than in subsurface horizons. There is a positive significant correlation between pH_0 values, organic carbon percentage and crystalline Fe (Fe_d). The points of zero net charge (PZNC) values are low (< 2) in the pedons studied, which refers to large amounts of negative charge in these soils. The permanent charge (σ_p) of the soils studied is also large and negative, which agrees with the amount of clay and the mineralogy of these soils. There is a positive significant correlation between σ_p and WDC, clay content, palygorskite, CEC, OC, Fe_d, Mg, Na, pH, SAR. The highest positive correlation was recorded between σ_p and WDC (r = 0.78**).

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

CIRI-CIRI CAS PERMUKAAN DAN SIFAT-SIFAT LAIN TANAH DI PERMATANG SHAMIL-ASHKARA, IRAN

Oleh

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Iran merupakan salah satu negara yang kebanyakan bahagiannya terdiri daripada keadaan arid (>90%) dengan lambakan bahan-bahan berkapur dan bergaram dalam sebahagian siri tanah tertentu. Tiada kajian direkodkan berkaitan hubungan antara sifat-sifat tanah dan kestabilan agregat di Selatan-Timur Iran. Kajian berkaitan ciri cas permukaan serta hubungan antara sifat tanah dan cas permukaan di kawasan arid juga tidak direkodkan. Kestabilan agregat tanah di kawasan ini semakin merosot ekoran aktiviti pertanian secara tidak terkawal, perubahan penggunaan tanah, kandungan bahan organik yang rendah, kandungan garam yang tinggi dan air tanah yang tinggi kandungan garamnya. Kajian ini memberi perhatian terhadap ciri-ciri utama tanah yang terdapat di bahagian arid di Selatan-Timur Iran, di mana data-data yang diperolehi akan digunakan sebagai garis panduan untuk menentukan kesan mineral-mineral dan sifat tanah ke atas kestabilan agregat dan sifat cas permukaan tanah di kawasan ini. Objektif kajian ini adalah untuk (I) mengenalpasti ciri-ciri fisiko-kimia dan mineralogi tanah di

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Selatan-Timur Iran dan (II) untuk menilai kesannya terhadap kestabilan agregat, serakan lempung dan cas permukaan di kawasan arid. Bagi mencapai objektif-objektif tersebut, lapan tanah berbeza yang mewakili dataran alluvial dan mendapan kollovial sepanjang kawasan bercerun di Shamil-ashkara, Iran telah dikaji. Berdasarkan criteria-kriteria daripada Taksonomi Tanah (Soil Survey Staff, 2010) dan rujukan sumber tanah FAO (2007), tanah-tanah ini telah dikelaskan mengikut sistem pengkelasan antarabangsa. Kesemua tanah tersebut dikenalpasti sebagai tanah muda dan dibezakan berdasarkan rejim kelembapan masing-masing. Tanah-tanah tersebut dikenalpasti sebagai Calcic haplosalids, aridic ustorthents dan aridic ustifluvents. Kesemua tanah ini adalah berkapur dan bersifat alkali. Kedalaman tanah tidak memberikan perbezaan yang jelas ke atas sifat-sifat fisiko-kimia tanah. Data yang diperolehi berkait rapat dengan sifat mendapan alluvial dan kollovial yang berubah dari masa ke masa. Kesemua jenis tanah mempunyai nilai pH lebih daripada 7 dan kekonduktian elektrik (KE) berbeza-beza, bermula dengan sedikit masin kepada masin. Kandungan karbon organik adalah rendah bagi semua tanah, di mana merupakan kebiasaan bagi tanah di kawasan ini dan tumbuhannya dipengaruhi oleh cuaca. Tanah cenderung untuk bersifat masif apabila kandungan kelodaknya tinggi. Sebaliknya, kandungan pasir yang tinggi menghasilkan struktur bijian tunggal, mengakibatkan struktur menjadi lemah dan tidak stabil.

Mineral-mineral utama yang terdapat dalam batuan induk adalah klorit, illit, smektit, kaolinit, palygorskit, feldspar, kuarza, kalsit dan gabungan illit-smektit. Mineral-mineral yand ditemui dalam sampel-sampel tanah ini adalah mineral umum seperti kuartz, feldspar, smektit, palygorskit, klorit, illit, kaolinit dan sepiolit. Tanah arid mempunyai struktur yang tidak stabil dan mudah berserak di

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dalam air. Nilai pH tanah paling banyak mempengaruhi kestabilan seperti ditunjukkan oleh korelasi bererti antara pH dan air-serakan lempung (WDC) (r = 0.78**). Di antara mineral-mineral yang ditemui, palygorskit paling banyak mempengaruhi WDC (r = 0.70**) secara bererti, manakala klorit memberi pengaruh yang paling kurang. Keputusan menunjukkan faktor positif secara bererti mempengaruhi WDC secara urutan EC > pH > cas tetap ($σ_p$) > K^+ > KPK > Na^+ > palygorskit > SAR > Mg^{2+} > kandungan lempung. Sifat-sifat cas permukaan tanah juga mempengaruhi sifat–sifat dan mineral dalam tanah. Titik cas bersih sifar (pH_0) merupakan salah satu petunjuk paling penting yang digunakan untuk menggambarkan cas berubah permukaan. Keputusan menunjukkan nilai-nilai TCBS adalah rendah (2.8 – 3.37) dalam kesemua sampel dan nilai yang lebih kecil didapati di permukaan berbanding di horizon sub-permukaan. Terdapat korelasi positif bererti di antara nilai-nilai pH_0, peratusan karbon organik dan Fe kristalin (Fe_d). Nilai-nilai Titik Cas Bersih Sifar (TCBS) adalah kecil (< 2) dalam pedon kajian, menunjukkan kedapatan cas negatif yang banyak dalam tanah-tanah ini. Cas tetap ($σ_p$) tanah-tanah ini juga banyak dan bercas negatif, membuktikan kedapatan lempung yang tinggi dan sifat mineralogi tanah ini. Terdapat kaitan positif bererti antara $σ_p$ dan WDC, kandungan lempung, palygorskit, KPK, OC, Fe_d, Mg, Na, pH dan SAR. Korelasi positif tertinggi dicatatkan antara $σ_p$ dan WDC (r = 0.78**).

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I certify that a Thesis Examination Committee has met on (10 May 2012) to conduct the final examination of Abolhassan Moghimi on his thesis entitled "Surface Charge Properties and Other Soil Characteristics in Shamil-Ashkara Catchment, Iran" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

ABOLHASSAN MOGHIMI

Date: 10 May 2012

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LIST OF ABBREVIATIONS

WDC	Water-dispersible clay
OC	Organic carbon
SOC	Soil organic carbon
EC	Electrical conductivity
CEC	Cation exchange capacity
CCE	Calcium carbonate equivalent
ρ_b	Bulk density
ρ_p	Particle density
σ_p	Permanent negative charge
σ_{max}	Maximum permanent negative charge
FAO	Food and Agriculture Organization of the United Nations
FC	Field capacity
IUSS	International Union of Soil Sciences
PWP	Permanent wilting point
PZC	Point of zero charge
PZNC	Point of zero net charge
CCE	Calcium carbonate equivalent
PZC	Point zero charge
P/ET^o	Precipitation/Potential evapotranspiration
OM	Organic matter
POM	Particulate organic matter
SOM	Soil organic matter
SIM	Soil inorganic matter
TOC	Total organic carbon

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TOM	Total organic matter
WRB	World Reference Base for Soil Resources

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CHAPTER 1

1 INTRODUCTION

1.1 Background

Arid and semi-arid zones account for more than one-third of the earth's land area and are inhabited by about 16% of the world's population (Clüsener-Godt, 2002). Common soil orders for arid and semiarid zones are Aridisols, Entisols, Vertisols, and to lesser extent Mollisols, Inceptisols, and Alfisols (OALS, 2005). Many of the soils in arid and semiarid climates are calcareous with free calcium carbonate developed from calcareous parent materials, where weathering has not been intensive enough to remove all the carbonates. Parent materials and topography are important factors controlling the development of soils in the arid region. Iran is one of the countries where more than 90% of their areas fall under arid condition with accumulation of calcareous materials in some soils as well as other salts in some other areas.

Soils of arid and semi-arid regions possess chemical properties that would cause certain nutritional problem, like: 1) nitrogen volatilization losses of surface applied ammonium or ammonium-forming fertilizers due to alkaline soil reaction and high Ca^{2+} activity; 2) phosphorous retention/fixation (precipitation of available fertilizer-P into less available forms) due to alkaline soil pH and high Ca^{2+} activity; 3) reduction in plant uptake of potassium due to poor aeration resulting from excessive soil moisture content; 4) micronutrient deficiencies due

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to reduced solubility of Fe, Mn, Zn and Cu under alkaline soil reaction; and 5) restricted root development due to poor structure and hardpan.

Sustainable use of soil resources particularly the calcareous soils requires extensive knowledge about their characteristics, genesis and classification. Soil genesis and classification studies have made contributions to research design and data acquisition in other fields of soil science, including biogeochemical redistribution of nutrients in ecological systems, ecology of microbes and mycorrhizae, and the availability and distribution of plant essential nutrients such as phosphorous and nitrogen in different types of soils (Buol, 2003).

Aggregation of soil particles to develop soil structure is affected by clay particles, shrinking, and swelling of clay masses. Clay particles carry a negative charge on their surface that can cause them to repel each other, but attract and adsorb cations present in the soil. Stacks of clay particles can form when their negative surface charge is neutralized by tightly adsorbed polyvalent cations, such as Ca^{2+} and Al^{3+}. Further, Ca^{2+}, Fe^{2+} and Al^{3+} flocculate (clump together) stacks of clay particles, and with humus (negatively-charged, highly decomposed, stable organic matter), bind to form, stable soil aggregates.

Previous studies showed that in the arid and semi-arid area dominant clay minerals are palygorskite, smectite, chlorite, kaolinite and vermiculite. It has long been recognized that the minerals in the clay (< 2µm) fraction of soils is

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commonly dominated by clay minerals, which, play a crucial role in determining their major soil chemical and physical properties such as cation exchange capacity and surface area and inevitably, questions concerning the origin and formation of these minerals have assumed some prominence in soil science research (Dixon and Weed, 1989). Minerals can be classified according to their chemical composition and crystal structure, or according to whether they are primary (inherited from the parent material without chemical alteration) or secondary (formed by chemical weathering of other, pre-existing minerals). Knowing the structure and properties of soil minerals is essential for understanding the mineral transformation (including weathering) and transport processes that are important in soil genesis (Schaetzl and Anderson, 2005). Minerals have a major influence on the physical, chemical and biological behavior of the soil. The mineral assemblage also provides information on the potential fertility level and the transformations occurring during pedogenesis (Kimpe, 1993).

Minerals make up about 50% of the volume of most soils (Dixon and Weed, 1989). They provide physical support for plants, and create the water- and air-filled pores that make plant growth possible. Mineral weathering release plant nutrients that are retained by other minerals through adsorption, cation exchange and precipitation. Minerals are indicators of the amount of weathering that have taken place, and presence or absence of particular minerals gives clues as to how soils are formed. The physical and chemical characteristics of soil minerals are important considerations in planning, constructing and maintaining buildings, roads and airports.

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Soil sustainability and crop production affect stability of soil aggregates, which is an important factor in the formation of soil properties. For sustainable use of soil and preserving soil productivity, minimizing soil degradation and sustainable agriculture high soil aggregate stability is a necessity (Amezketa, 1999). Soil aggregation is extremely important because it influences nutrient cycling, soil stability, gas exchange between the soil and atmosphere, soil water movement, plant root and microbial development (Valmis et al., 2005). In the arid regions, the stability of soil aggregates is an important issue to address because of the problems that arise from intensive agriculture practices, land use change, low content organic matter, and high content of sodium in the soil. Aggregation is formed by flocculation, cementation and the rearrangement of particles (Duiker, 2003). In general, high content of base minerals tend to increase the stability of soils, due to the chemical bonding of the aggregates.

The nature and relative presence of clay minerals determine to great extent soil properties in addition, characteristics, fertility status, and management practices. For example, phosphorous, potassium and ammonium retention show a direct relationship with the type of clay minerals present in soil (Bajwa, 1980). The stability of aggregates in soils is affected by the chemical properties and the kinds of clay minerals present (Morgan, 2005). In soils dominated by 2:1 clays, mainly polyvalent metal-organic matter complexes that form bridges between the negatively-charged clay platelets (Six et al., 2000) affect the aggregate stability. However, the stability in 1:1 clay-dominated soils is attributed mainly to the binding capacity of the minerals themselves (Oades and Watera, 1991). Aggregate stability effects increase with increasing clay content due to high

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aggregate stability of clay soils. A similar trend was found for illitic soils, whereas, for kaolinitic soils, the trend was less pronounced probably due to presence of a large amount of oxides (Six et al., 2000).

Clay minerals are very reactive because of their large surface area and because they commonly "carry" a charge. The existence of the charge is in the basis for the exchange capacity and the swelling that makes an understanding of these properties essential to agronomists and soil engineers. The structural layers (tetrahedral and octahedral sheets) of clay minerals usually have a charge. There are two types of charge: structural (or permanent) and variable charge (or pH-dependent). The charge that originates at clay surfaces is usually due to chemical reactions that occur at the surface of minerals, but it can also be caused by adsorption of surfactant ions (Stumm and Morgan, 1981). This charge is pH dependent and originates, not within the interior of the layers as with the permanent charge, but on the basal surfaces of the tetrahedral sheets (in 2:1 clays), on the basal surfaces of both tetrahedral and octahedral sheets (in 1:1 clays), and along the edges of the sheets of both 1:1 and 2:1 clays.

Similar to smectite, the fibrous clay minerals are formed in a wide spectrum of environments, including arid soils, lacustrin, marine sediments, and near sites of hydrothermal activity (Dixon and Weed, 1989).

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Palygorskite is fibrous silicate clay mineral formed in a wide spectrum of environments. A large body of information is available on the occurrences of palygorskite in soils of arid and semi-arid regions. Due to the state of various types of H_2O associated with this mineral, as well as the characteristics of its adsorption sites palygorskite plays an appreciable role in agrochemistry of soils in which they occur. Carbonates exist along with palygorskite in most soils of arid and semi-arid regions. Electron microscopic studies have shown a close association between this group of minerals in which larger crystals are usually covered by the relatively small and minute palygorskite fibers. The particle-to-particle association shows that this fibrous clay mineral provide a large reactive surface area in the soil system, even in the presence of carbonates, which may significantly influence the sorption behavior of the soil in which they occur. Previous studies have shown that palygorskitic soils have a higher P sorption capacity than those dominated with other silicate clays (Sayin et al., 1990). Due to its large external surface area where the P sorption sites occur, it seems that the P sorption capacity of this mineral exceeds that of other silicate clay minerals.

Due to the chemical and physical characteristics, palygorskite seem to play a significant role in sorption and solubility of P in the calcareous environments where they occur. This maybe through particle-to-particle interactions of clay with calcite present in the system on by release of Mg and Si, which inhibit the formation of insoluble Ca-phosphates. By the same mechanism, but to a lower degree, other silicate clay minerals such as montmorillonite may affect the P sorption reactions in a carbonate system.

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One of the important agricultural regions in Hormozgan Province in Southeastern Iran was selected for this study. The climate is arid with an average annual precipitation and evaporation of about 162 mm and 4243 mm, respectively. The moisture regimes are aridic and ustic with a hyperthermic temperature regime.

1.1 Objectives

The general objective of this study was to characterize and classify the soil and to establish the correlation between aggregate stability indices and surface charge properties in the studied area. The specific objectives were:

I) to determine the physical, chemical, and mineralogical characteristics of soils in Shamil-Ashkara Catchment, Iran;

II) to study the surface charge characteristics of the soils and the effects of soil properties and mineralogy on the surface charge chemistry;

III) to determine the effects of soil properties and mineralogy on the soil aggregate stability; and

IV) to classify the soils according to the international classification system.

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