



**Identification and Determination of Mineral Contents in Gazelle licked soils in northern Darfur by Atomic Absorption Spectroscopy**

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**ABSTRACT**

This study aimed to identify the distinctive features of the natural soils licked by Gazelle in Alkuma area (Northern Darfur), and to characterize and determine the type of minerals as the major attractant for Gazelle to visit these sites frequently. Samples were collected from six soil- lick fields, and were analyzed for chemical and physical properties, such as pH values, moisture content, total-water soluble solids and electrical conductivity. The minerals were extracted using the sequential extraction technique and their concentrations were determined using atomic absorption spectroscopy and flame photometry. The soil samples solutions showed high electrical conductivity values (mean 689.441ms), basic pH values (mean 7.449), different moisture content values (mean 1.973%) and almost similar total water-soluble solids values (408.82mg/L). mineral content determination showed high concentrations of iron Fe, potassium K, calcium Ca, sodium Na and magnesium Mg. Cobalt was absent in all samples except No.(8 and 9). Lead was not detected in any sample. Chromium, manganese nickel and copper showed considerable concentrations. Cadmium showed the lowest mean concentration.

The quantified minerals were extracted in different steps, e.g., sodium, magnesium, Nickel, Manganese, zinc and cadmium showed significant concentrations in all fractions. Potassium and calcium were almost extracted in the first fraction and small amounts in the second fraction. Chromium, iron and cobalt ions were almost extracted in the last fraction.

Results of sequential extraction showed that the mobility of elements in the order: K>Ca>Na>Mg>Fe> Mn>Zn≈ Ni>Cu≈ Cr>Cd>Co.

The orders of elements mobility for the second fractions were found to be: Fe> Ca >K >Mg >Na >Mn >Zn >Ni > Cu > Cd ≈ Cr.

The mobility of elements in third fraction was: Fe≈ Na> K> Mg> Ca> Ni> Mn> Cr> Zn> Cu> Cd>Co.

The order of mobility of the elements in the fourth fraction was: Fe>K>Mg>Mn>Cu>Cr>Zn>Ni >Mg>Co>Cd. Pb is absent in all samples.

**المستخلص**

هدفت هذه الدراسة لقياس الخواص الكيميائية للتربة الطبيعية التي تلغها الغزلان بمنطقة الكومة- شمال دارفور، ولتحديد العناصر الرئيسية التي تجذب هذه الغزلان للتردد على هذه المواقع. جمعت العينات من ست حقول مختلفة، وتم تحليل خواصها الفيزيائية والكيميائية، والتي تضمنت قيم الأس الهيدروجيني، محتوى الرطوبة، المحتوى الكلي للمواد الصلبة الذائبة في الماء و التوصيل الكهربائي لمحاليل التربة.

استخلصت العناصر باستخدام تقنية الإستخلاص المتدرج بطريقة ال (BCR sequential extraction) وتم قياس المحتوى المعدني باستخدام تقنيتي الإمتصاص الذري ومطيافية اللهب.

محاليل العينات اظهرت قيم توصيل كهربى عالية (المتوسط 689.441 ملليسيمنز)، قيم أس هيدروجيني قاعدية (المتوسط 7.449)، اختلاف في قيم محتوى الرطوبة (متوسط 1.973%)، وتشابه في قيم المواد الصلبة الذائبة في الماء (متوسط 408.82 ملجم/ لتر).

تقدير المحتوى المعدني أظهر وجود تراكيز عالية: للحديد، البوتاسيوم، الكالسيوم، الصوديوم والمغنيزيوم، على الترتيب. لم يظهر وجود لعنصر الكوبالت في كل العينات عدا العينات رقم 8 و 9. لم يظهر وجود لعنصر الرصاص في كل العينات. أظهرت عناصر الكروم، المنجنيز، النيكل و النحاس تراكيز مقدرة. الكاديوم اظهر أقل متوسط تركيز. تراكيز الأيونات المعدنية المستخلصة اختلفت من خطوة إلى أخرى. فمثلا: الصوديوم، المغنيزيوم، النيكل، المنجنيز، الزنك والكاديوم اظهرت تراكيز معتبرة في الخطوات المختلفة. البوتاسيوم والكالسيوم استخلصا بصورة كبيرة في الخطوة الأولى ويتركز أقل في الخطوة الثانية. أيونات الكروم، الحديد والكوبالت استخلصت في الخطوة الأخيرة بصورة أساسية.

نتائج الإستخلاص المتتابع في الخطوة الاولي اوضحت وجود العناصر بالترتيب التالي:

$K > Ca > Na > Mg > Fe > Mn > Zn \approx Ni > Cu \approx Cr > Cd > Co$

وفي الخطوة الثانية من الإستخلاص على النحو:

$Fe > Ca > K > Mg > Na > Mn > Zn > Ni > Cu > Cd \approx Cr > Co$

واظهرت العناصر التي استخلصت في الخطوة الثالثة تراكيز وفق الترتيب التالي:

$Fe \approx Na > K > Mg > Ca > Ni > Mn > Cr > Zn > Cu > Cd > Co$

أما في الخطوة الرابعة فكان الترتيب على النحو:

$Fe > K > Mg > Na > Mn > Cu > Cr > Zn > Ni > Mg > Co > Cd$

**KEYWORDS:** *Geophagy, mineral licks, exchangeable fractions, wildlife animals, BCR.*

## INTRODUCTION

Geophagy is defined as the practice or habit of eating earthy substances, for example, clay or chalk among people of all races<sup>(1)</sup>. It is considered a nearly universal cross-cultural phenomenon with various manifestations in the Mediterranean world of Roman and later times in medieval western Europe, in present-day Iran, India, china, and extensively, in the tropical peasant world of Indonesia, Oceania, and Africa<sup>(2, 3)</sup>. Ingestion of soils and clays by humans and animals has been linked to nutritional, taste, cultural, medical, social, spiritual, religious, ritual and physiological aspects. It has been practiced for thousands of years in many parts of the world<sup>(4)</sup>. In United States, parts of Africa, and India, pregnant women eat clay to eliminate nausea, apparently because clay coats the gastrointestinal tract and absorbs toxins. Clay may also provide iron and calcium for the development of fetus<sup>(4)</sup>. Since 1850, geophagia has been at the centre of research and

debate amongst scientists who question the usefulness, versus, the harmfulness of the practice of eating earthy substances. Research findings indicate that clays such as bentonite, and aluminum phyllosilicate, acts as a digestive aid, whereas, kaolin acts as both a digestive aid and a base for some medicines; and attapulgite is an active ingredient in many anti-diarrheal medicines<sup>(5)</sup>. Wildlife animals and Ruminants attain the majority of their nutritional needs through the plant material they ingest; however, some nutrients that are required in relatively large quantity by animals are not required or required in low amount by plants<sup>(6)</sup>. Sodium is the best example of such elements<sup>(7)</sup>. Sodium is needed during lactation, because of Na lost through lactation, and also when forages are high in potassium in early growing season or following fertilization<sup>(8)</sup>. Although sodium in natural licks is considered to be the primary attractant, some argue that

elements such as Ca and Mg are equally important in attracting animals<sup>(9)</sup>. Furthermore little is known about the attractive importance of trace elements, e.g., (Co, Cu) in natural mineral licks<sup>(10)</sup>. Geophagy is less common in birds, especially at natural licks, but has been reported in a range of bird species from different families and in different parts of the world<sup>(11-15)</sup>. Observation of Gazelle consuming soil from natural mineral licks has been reported throughout northern Darfur (Alkuma area). Some studies have identified sodium as the mineral element of high abundant in ungulate-licked soils<sup>(9)</sup>. Soils are the reservoir for many harmful constituents, elemental and biological, including heavy and trace metals<sup>(16)</sup>. Total metal content of soils is useful for many geochemical applications but often the speciation (bioavailability) of these metals is more of an interest agriculturally in terms of what is biologically extractable<sup>(17)</sup>. Various species of metals are more biologically available than others<sup>(18)</sup>. If bioavailability and the mobility of metals are related, then, the higher concentration of mobile toxic metals (Cu, Pb, Cd, and Al) in the soil column which increases the potential for plant uptake, and animal/human consumption<sup>(19,20,21)</sup>. Elements in soils are present in various physicochemical forms, which in turn influence their availability. Sequential chemical extraction techniques have been widely used to examine these physicochemical forms, and thus to better understand the processes that influence element availability<sup>(22)</sup>.

#### **Sequential Extraction Procedure**

Since their introduction in the late 1970s, sequential extraction procedures have experienced a rapid increase in use, where many studies were performed about modification and development of sequential

extraction technique<sup>(31, 33, 34, and 35)</sup>.

Sequential extraction was applied for a large number of potentially toxic elements in a wide range of sample types<sup>(23)</sup>. General applications of Sequential extraction schemes can be summarized as follows:

- i. Characterization of pollution sources.
- ii. Evaluation of metal mobility and bioavailability. Identification of binding sites of metals for assessing metal accumulation, pollution and transport mechanisms<sup>(24, 25)</sup>.
- iii. Identification of binding sites of metals for assessing metal accumulation, pollution and transport mechanisms<sup>(24, 25)</sup>.
- iv. Identification and quantification of the different, defined species, forms or phases in which an element occurs<sup>(26)</sup>.

All sequential extraction procedures (SEPs) facilitate fractionation. A. Tessier et al (1979) named these fractions exchangeable, carbonate bound, Iron (Fe) and manganese (Mn) oxide bound, organic matter bound, and residual<sup>(26)</sup>. These are also known as exchangeable, weakly absorbed, hydrous-oxide bound, organic bound, and lattice material components, respectively<sup>(27)</sup>. The exchangeable fraction corresponds to the form of metals that is most available for plant uptake and can be removed by changing the ionic composition of water allowing metals sorbed to the exposed surfaces of sediment to be removed easily. A salt solution is commonly used to remove the exchangeable fraction. The carbonate-bound fraction is susceptible to changes in pH; it is sensitive to pH changes and can become mobilisable when pH is lowered, an acid solution is used second. Metals bound to Fe and Mn oxides are particularly susceptible to reducing conditions so a solution capable of dissolving insoluble sulfide salts is used third. To remove metals

bound in the organic phase, the organic material must be oxidized. The residual fraction consists of metals incorporated into the crystal structures of minerals. This fraction is the hardest to remove and requires the use of strong acids to break down silicate structures<sup>(24, 25, and 26)</sup>. Most SEPs follow similar fractional degradation with little variation. Ure et al, (1993) extracted the exchangeable and carbonate-bound fractions in a single step versus the two steps used in the Tessier procedure. The SEP used by the Geological Survey of Canada (GSC) divides the Fe and Mn oxide fractions into the amorphous oxyhydroxides and crystalline oxides, thereby increasing sequential fractionation from five to six steps<sup>(28)</sup>. Other SEPs with greater fractions include the procedure developed by Zeien and Brümmer<sup>(29)</sup> which included EDTA extractable, moderately reducible, and strongly reducible fractions for a total of seven; and that by Miller et al (1986) which consisted of nine fractions designed to test waste amended and agriculturally polluted sediments.

A sequential extraction procedure, a three-step protocol (Community Bureau of Reference) proposed by the Standards, Measurements and Testing programme of the European Union, was applied to soil samples for the determination of metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn). This procedure provides measurements of extractable metals from media such as acetic acid ( $0.11 \text{ mol L}^{-1}$ ), hydroxyl ammonium chloride ( $0.1 \text{ mol L}^{-1}$ ) and hydrogen peroxide ( $8.8 \text{ mol L}^{-1}$ ) plus ammonium acetate ( $1 \text{ mol L}^{-1}$ ), which are exchangeable, reducible and oxidisable metals, respectively<sup>30</sup>. This procedure is largely similar to that produced by Tessier et al. (A. Tessier et al 1979) with the chief difference in the first fraction of the procedure.

Instead of evaluating the exchangeable and carbonate bound separately, the Community Bureau of Reference (BCR) procedure combines both in the first fraction<sup>(31)</sup>. There are many SEPs that can be utilized in the process of understanding the behavior of metals in various soils. A researcher trying to determine which procedure is most appropriate for their samples must take into consideration many factors including soil type, contamination level, and result comparison methods, as well as the potential problems or limitations associated with a specific SEP<sup>(32)</sup>. An understanding of the behavior of metal contaminants at various biologically available fractions is still necessary especially when human consumption is becoming more of a global concern with the current growth rate of populations, especially in urban settings. More work needs to be done on improving the specificity of reagents and with combining SEP data with analytical data such as that obtained via X- ray diffraction. Reliance on the SEP alone is not feasible and needs to be complemented with either X- ray diffraction analysis or some other kind of analytical technique to positively identify the solid components involved. This will provide enough data to make a better calculated determination on the amounts of metals in a soil as well as their potential speciation<sup>(32)</sup>.

#### **STUDY AREA**

This study was conducted within Alkuma Locality, (Northern Darfur State). The lick sites under study are scattered within the locality with approximate distance ranging from 20 to 50Km from each other and from Alkuma town between longitudes 26.0'0-29.0'0 and latitude 13.30'0-14.30'0, Figure (1). Samples were collected from separate soil lick sites, within, a certain fields. Lick sites were determined by observation of Gazelle

visiting from time to time, and they are known by Gazelle hunters in the area,

as well as the physical appearance of the soil.

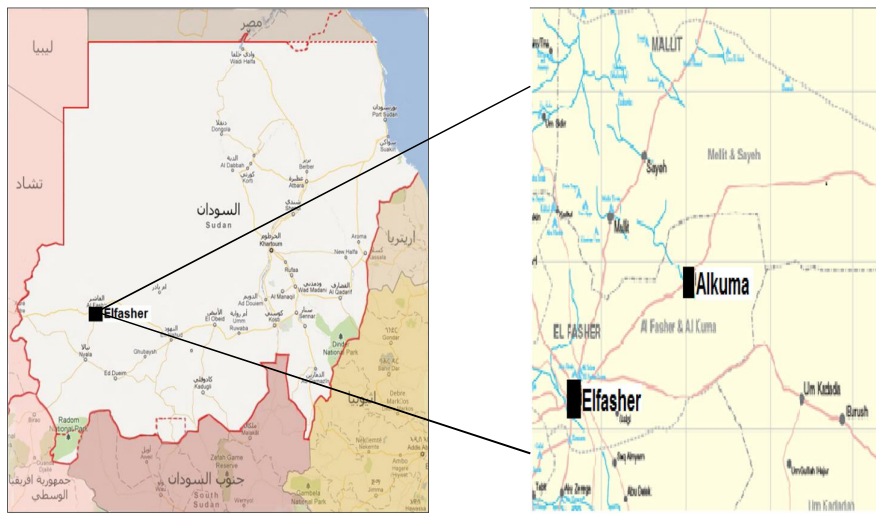


Figure (1): The study area

## MATERIAL AND METHODS

Samples were collected from the top 10cm depth in each sites during winter-summer transition time, kept in clean, dry, plastic containers then analyzed for physical and chemical properties.

Sequential extraction technique was applied using Community Bureau of Reference sequential extraction procedure. Minerals extracted depend upon chemical form:

- 1- Exchangeable and acid soluble minerals.
- 2- Minerals bound to Iron and Manganese Oxides.
- 3- Minerals bound to organic matter and sulfides
- 4- Minerals in the last residue.

### Chemicals

All chemicals used were of analytical grade.

- Glacial Acetic acid, Riedel-De Haenag, Hannover
- Ammonium acetate, CDH, India.
- Hydrogen peroxide, Abu sameh, Khartoum.
- Hydrochloric acid, Loba chemie, India.
- Hydroxyl ammonium chloride, Loba Chemie, India.
- Nitric acid, Techno pharmachem, India.

### Instruments

- pH/ ion meter Pinnacle -555 - JENWAY.
- Conductivity meter 4320 JENWAY.
- Atomic absorption spectroscopy-Spectra AA220Z - Varian.
- Flame photometer PFP7- JENWAY.

## RESULTS AND DISCUSSION

The results of pH measurements, moisture content and electrical conductivity of soil lick samples are presented in Table (1).

*Table (1): Physical and chemical properties (average values) of the collected material from lick sites.*

Sample No	pH suspension	Electrical conductivity/ms	Total soluble solids mg/L	Moisture content%
1	6.971	761	456	4.97
2	7.238	915	550	3.29
3	7.489	248	148.8	0.88
4	7.583	476	286	1.77
5	7.685	437	262	1.20
6	7.462	264	158.6	4.03
7	7.610	1261	758	1.19
8	7.683	1199	673	0.21
9	7.320	644	387	0.22
Average value	7.449	689.44	408.82	1.973

All samples are neutral to slightly alkaline and had a mean pH value of 7.449.

Results strengthen the hypothesis that, soil licks have anti-acid effects; so the pH results obtained in this study were almost in the same range as those obtained in previous studies for soil licks that are usually visited by wildlife animals; so the samples result showed considerable variations in their moisture content. Moisture content ranged from 0.21% to 4.97%. Samples (1 and 2) had the highest moisture content. Samples (3), (8), and (9) had moisture less than 1%. The variation of the moisture content might be attributed to local environmental conditions or variation in chemical composition of soil lick sites.

Electrical conductivity of samples filtrate ranged from 248 ms to 1261 ms. Samples (7) and (8) showed the highest electrical conductivity value of 1261ms and 1199ms; and total soluble solids of 758 and 673 mg/L, respectively. Samples (3 and 6) showed lowest electrical conductivity values and lowest total soluble solids. Colleen. T. Downs (2006), showed electrical conductivity values ranged from 1290 ms to 2668 ms in soil licks used by African Olive Pigeon. Change it could be observed from the macro- and micro-minerals findings presented in Table (2) that most of the samples showed lowest percentage for cadmium (Cd) and highest percentage for iron (Fe).

Table (2): Macro and micro minerals concentrations in ppm using Atomic Absorption Spectrometry

Sample No.	Na	Fe	K	Ca	Mg	Cu	Zn	Mn	Ni	Co	Cd	Cr	Pb
1	65.4	334.786	24.8	110.237	28.15	0.543	0.618	5.881	0.624	N. d	0.006	1.075	N. d
2	129.04	98.241	77.8	107.671	21.831	1.058	0.918	1.072	0.929	N. d	0.009	0.321	N. d
3	34.6	156.624	30	36.289	20.11	0.877	0.62	4.898	0.208	N. d	0.003	0.555	N. d
4	46.8	188.468	30.6	72.628	21.65	1.759	0.486	4.791	0.641	N. d	0.001	0.462	N. d
5	39.8	348.581	50	73.132	20.49	1.639	0.55	5.253	0.975	N. d	0.001	0.910	N. d
6	37.4	199.208	26.6	46.105	20.95	1.372	0.238	9.297	0.223	N. d	0.001	0.617	N. d
7	19	293.028	489	10.093	22.86	3.087	1.658	4.913	0.805	N. d	0.004	0.845	N. d
8	20	260.165	308.4	16.23	26.71	0.37	0.946	4.876	0.628	0.08	N. d	1.182	N. d
9	53	526.403	147.8	28.313	34.07	0.788	1.358	8.127	1.352	0.13	0.004	1.11	N. d
Average value	49.449	267.278	131.67	55.633	24.091	1.277	0.8213	5.380	0.7094	0.023	0.0032	0.7863	0.00

Soil lick samples showed the presence of elements in major concentration in the following order:

Fe ( $267.278 \times 10^{-3}$ ) > K ( $131.67 \times 10^{-3}$ ) > Ca ( $55.633 \times 10^{-3}$ ) > Na ( $49.449 \times 10^{-3}$ ) > Mg ( $24.088 \times 10^{-3}$ )

Elements of minor levels concentrations in the samples showed, highest concentration of manganese and their presence is in the order:

Mn ( $545.64 \times 10^{-5}$ ) > Zn ( $82.133 \times 10^{-5}$ ) > Cu ( $127.7 \times 10^{-5}$ ) > Cr ( $78.63 \times 10^{-5}$ ) >

Ni ( $70.94 \times 10^{-5}$ ) > Co ( $2.33 \times 10^{-5}$ ) > Cd ( $0.322 \times 10^{-5}$ ) > Pb (0.00)

The observed distribution of heavy metals in samples indicates the mobility and bioavailability of the ions of these metals.

Results of sequential extraction which is described in Figs (2, 3, 4 and 5), the mobility of elements in first fractions was: K > Ca > Na > Mg > Fe > Mn > Zn ≈ Ni > Cu ≈ Cr > Cd > Co; Figure (2).

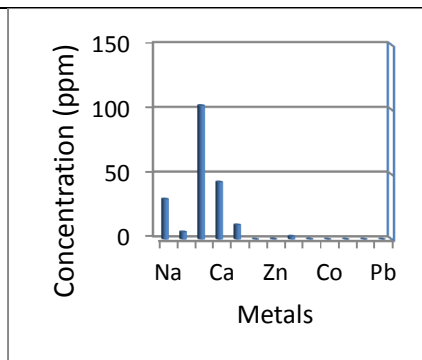


Figure (2): Mineral Concentrations in exchangeable Fractions

The orders of mobility of the elements for the second fractions were:  $Fe > Ca > K > Mg > Na > Mn > Zn > Ni > Cu > Cd \approx Cr$ ; Figure (3).

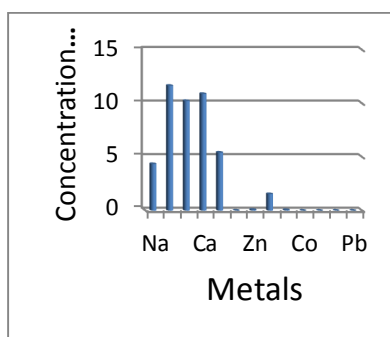


Figure (3): Mineral Concentrations in Reducible Fractions

The mobility of elements in third fraction was:  $Fe \approx Na > K > Mg > Ca > Ni > Mn > Cr > Zn > Cu > Cd > Co$ ; Figure (4).

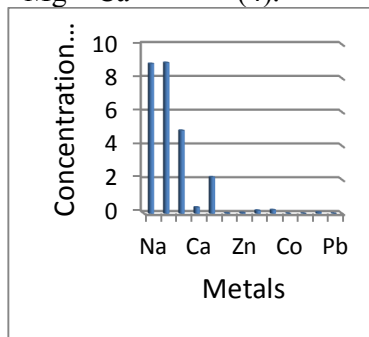


Figure (4): Mineral Concentrations in Oxidisable Fractions

The order of mobility of the elements in the fourth fraction was:  $Fe > K > Mg > Mn > Cu > Cr > Zn > Ni > Mg > Co > Cd$ ; Figure (5) Pb is absent in all samples.

Iron appeared to be the highest mineral in all samples except sample (No. 2), that, showed low concentration. The major portion of iron was associated with the residual fraction; Figure (5).



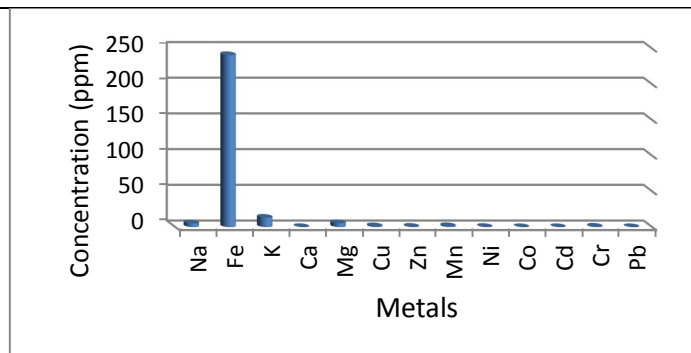


Figure (5): Mineral Concentrations in residual Fractions

High iron concentrations in residual fraction may suggest the presence of iron as chemical combined forms insoluble in aqueous media, and free iron ions can be obtained, only, under drastic conditions. Iron concentrations obtained in this study enhances the hypotheses, Gazelles, May, consume soil licks for Iron as a main stimulus or attractant, beside the other elements. All samples showed high concentrations of sodium, Sample (2) showed the highest sodium concentration. Samples (7 and 8) showed low sodium concentration. A major portion of Sodium in this study was associated as exchangeable, (water-acid soluble form). This means high sodium availability in lick soils, Figure (2). Sodium concentrations obtained by this study support the hypothesis assuming that, Gazelles consume soil licks for their sodium content. Potassium (K) concentration is relatively high in samples 7, 8 and 9; (highly visited soils). Sample no (1) showed the lowest potassium content. Potassium was extracted in the exchangeable step (water and acid soluble fraction). So potassium is highly available in this soil fraction. Calcium content did not, significantly, vary in all samples except for samples 7 and 8, where it showed low levels, major ratio of total calcium concentration was extracted in exchangeable step (water and acid soluble). The high concentration of

calcium in acid soluble could support the suggestion that, soil licks may be used as anti-acids for some species of ruminants. Magnesium is one of the nutritional elements. It showed high concentration in all samples, except sample (9) Mg content did not show significant variations in the eight lick sites samples. A major portion of magnesium (46.058%) was found in exchangeable fraction (water and acid soluble fraction). This ratio suggests, high availability of magnesium which may be present as acid soluble. Accordingly magnesium may one of main elements that attract Gazelles to lick sites to consume soils or clays. About 42.8%, of total nickel, was found in residual fraction, so, nickel had low availability in first three fractions. Copper has shown an average low concentration in all samples but it has shown the highest concentration in sample (7) and the lowest concentration by sample (8). Major amount of copper was extracted in fraction four (residual fraction). Cadmium showed low average concentration in all samples and not detected in sample No (8). The major cadmium extract was observed in first fraction (exchangeable and acid soluble). Cobalt and chromium elements showed lower concentration in all soil lick samples Chromium showed low concentration in all samples but has shown relatively high concentration in samples (1, 8 and 9).

Cobalt showed low concentrations in samples 8 and 9, and zero values in the other samples. Major Manganese concentration was extracted in fraction 01. Significant amounts were also extracted in fraction 02 and the residual fraction. The lowest concentration was extracted in the third fraction (organically bound). This indicates that manganese occurs in easily mobile forms in lick soils. Zinc

showed low mean percentage in lick samples. Zinc is considered almost immobile, because of elevated percentage of these elements in the residual fraction. The poisonous trace element lead was absent (not detected) in all samples of this study. Minerals were classified to three types based on based on their average concentration (Tables 3, 4, 5).

*Table (3): Major minerals average concentration in ppm*

Mineral	Na	Fe	K	Ca	Mg
Average value	49.449	267.278	131.67	55.633	24.091

*Table (4): Minor minerals average concentration in ppm*

Mineral	Cu	Zn	Mn
Average value	1.277	0.8213	5.380

*Table (5): Trace minerals average concentration in ppm*

Mineral	Ni	Co	Cd	Cr	Pb
Average value	0.7094	0.023	0.0032	0.7863	0.00

## CONCLUSIONS

- Analysis of the collected samples shows pH values greater than seven, samples are generally basic, different moisture content values, different Electrical conductivity values. Water soluble solids concentrations are high.
- The results obtained in this study by application of BCR sequential extraction procedure showed appreciable agreement with some previous studies carried in other countries. Sometimes the results obtained were almost typical with other studies.
- Such similarity may strongly enhance the postulates which consider physiological and nutritional needs stand behind the consumption of Geophagic soils by wildlife animals, in general, and Gazelles as special soil lick visitors.

- The total available amounts of the elements as means in Elkuma soil lick sites indicate original rocks of the soils in the area. Soils can be classified as rich or deficient in certain ions.
- The total absence of lead and low cadmium content is an advantage for the area soils, i.e. there is no environmental risk related to lead and cadmium.
- The present study could be considered an additional new information to the behavior of wild animals that could, benitially, be used.

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