

THE MAJOR HONEYS AS INDICATORS OF METALS IN THE EGYPTIAN ENVIRONMENT

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ABSTRACT

Eighteen honey samples were collected and classified according to their plant origin and distance from the main roads where the apiaries situated. Seven minerals (Potassium, Sodium, Calcium, Zinc, Iron, Lead, and Cadmium) were determined by atomic absorption spectrometry (A.A.S.). Potassium content is the predominant mineral in citrus, clover and cotton honeys with a mean values of 694.01, 1161.86 and 421.29 mg./kg. respectively. Sodium is the second dominant mineral in the tested honeys where presented in quantities of 141.92, 133.19 and 145.47mg./kg. respectively. Other elements (Ca, Zn and Fe) were in small amounts in the three types of honey. Pb content was higher in the shortest (5.00 mg./kg.), than longest (1.25 mg./kg.) distances of main roads. On the other hand, the level of cadmium element was approximately similar in honey collected from the different previous distances.

Results of this study indicated that the level of lead in the Egyptian honeys is to be considered an excellent indicator of environmental pollution in Egypt.

INTRODUCTION

Many botanical origins to be considered as a natural sources to collect floral honey by honeybee workers in Egypt, among them three main honey sources mostly cultivated in a large areas *i.e.*, citrus, (*Citrus* spp.), clover, (*Trifolium alexandrinum* L.) and cotton, (*Gossypium barbadens* L.) where the major Egyptian honeys produced from them, (El-Sherbiny et al., 1980; Nour, 1988 and Nafea, 2004). It is known that honey is one of most foodstuffs produced by nature and certainly the only sweetening agent that can be used by human without processing, (Rodriguez-otero *et al.*, 1994). It contains mainly monosaccharide and water, while the proteins, flavonoids, flavor and aroma, phenolic compounds, free amino acids, organic acids, vitamins constitute and all the essential minerals to health and are presented in a minor components within honeys (Gonzalez-Miret, *et al.*, 2005). Minerals contained in honey are varied in their quantity and quality according to geographical origin and plant sources of it as reported by many researchers, (Vorlova&Celechovska; 2002, Terrab *et al.*; 2004 a&b, Rashed& Soltan, 2004; Nozal Nalda, 2005 and Nafea &Tharwat, 2006). On the other hand, the area of honeybee forging activity surrounding the bee yard generally extends over a surface of approximately seven km²., (Crane, 1975). Therefore, honeybee workers are continuously exposed to the environmental

contaminants present in the foraging area for a long period of the year. So, the honeybees and their products have been considered an ideal bioindicator of chemical pollution, (Tong *et al.*, 1975; Franco *et al.*, 1997 and Raes *et al.*, 1992). In general, heavy metals such as lead, cadmium and chromium are characterized by latent and non-immediate toxicity and therefore involved direct parameters of bioaccumulation in the tissues of insects and their products, (Conti, 2000). The level of heavy metals in honey is strongly varied from region to another, (Jones, 1987; Balestra *et al.*, 1992; Al-khalifa & Al-Arity, 1999 and Atrouse *et al.*, 2004) and obviously increased when the honeybee colonies were situated near an industrial areas, (Tong, *et al.* 1975), near a busy highway, (Cesco, *et al.*, 1994 and Leita, *et al.*, 1996) or in the mining lands, (Kronic, *et al.*, 1989 and Iskander, 1996). Therefore, Munoz & Palmero, (2006) reported that heavy metals in honey are of interest not only for quality control, but can be considered as an indicator of environmental pollution.

The aim of this study is to determine the mineral contents in the major Egyptian honeys collected from different Governorates and the representative level of heavy metals as a reliable index of environmental contamination using Atomic Absorption Spectrometry.

MATERIALS AND METHODS

The present work was conducted at Beekeeping Research section, Plant Protection Research Institute, Agriculture Research centre, Ministry of Agriculture, Dokki, Giza.

The Egyptian honey samples collected from different sources and Governorates (Giza, Fayoum, Beni suif, El-Menya, Assiut, Suhaj, Qina, Luxor, Siwa Oasis, New valley, Matruh, Alexandria, Kfer-El-Shiekh, El-Gharbia, El-Sharkia, El-Dakahlya, El Qalyubia, Suez and Sina.

All samples were classified according to the plant origin (Citrus, Clover and Cotton). On the other hand, honey samples were divided according to the distance between the apiaries and the main roads, in order to investigate the effect of the ecological pollution on the honey contents with heavy metals.

Determination of micro elements in honey:

Analysis was made on a known weight (0.5g), which digested with concentrated sulfuric acid in the presence of digestion catalysts (a mixture of copper sulfate and anhydrous sodium sulfate (1:10), wet ashing were follows as (A.O.A.C., 2000).

Minerals of calcium (Ca), Iron (Fe), Zinc (Zn), Lead (Pb), Cadmium (Cd), Potassium (K) and Sodium (Na) in the digested solution were measured by Atomic Absorption Spectrometry (A.A.S.) according to A.O.A.C (2000).

RESULTS AND DISCUSSION

1. Mineral contents in citrus ,clover and cotton honeys :

Five mineral content, Iron (Fe), Zinc (Zn), Calcium (Ca), Sodium (Na) and Potassium (K) were identified and quantified in the Egyptian citrus,

clover and cotton honeys and represented as range and mean±se in Table (1). Potassium content is the predominant mineral in the three types of honeys. However, its contains in clover honey was significantly exceeded the others and ranged from 753.88-1773.84 with a mean value of 1161.86±212.28 mg./kg.. Citrus honey came next in this manner where the range of K was 532.15-1019.96 with a mean of 694.01±87.27 mg./kg.. Cotton honey has the last position in K content and does not significant with its value in citrus honey. The range of K in cotton was 131.93-565.41 with a mean of 421.29±83.18 mg./kg. (Fig.1). This is in agreement with many authors such as White, 1978; La Torre *et al.*, 2000 and Gonzalez-Miret, 2005.

Table (1): Minerals content in the three major Egyptian honeys (mg./kg.)

Honey type	Fe	Zn	Ca	Na	K
Citrus(5)*					
Range	0.0-37.18	2.136-6.781	21.86-31.586	53.22-178.77	532.15-1019.96
Mean	17.53±6.45 a	4.70±0.99 a	25.55±1.93 b	141.92±22.50 a	694.01±87.27 b
Clover(5)*					
Range	1.716-9.636	3.997-11.66	11.83-53.94	90.07-163.76	753.88-1773.84
Mean	5.06±1.56 b	6.20±1.43 a	31.98±6.86 b	133.19±14.21 a	1161.86±212.28 a
Cotton(5)*					
Range	5.583-9.328	2.676-5.610	62.89-93.64	120.09-163.76	131.93-565.41
Mean	7.61±0.71 ab	4.14±0.62 a	77.47±5.19 a	145.47±9.58 a	421.29±83.18 b
L.S.D.	12.03	3.28	15.68	50.31	434.19

se: standard error *: number of samples

Data followed by different litters have significant difference and data followed by the same litters have no significant difference vertically.

Sodium is the second dominant mineral in the tested honeys where presented in similar quantities. Its value were ranged from 120.09-163.76 (mean of 145.47±9.58 mg./kg.) in cotton honeys, 90.07-163.76 (mean of 133.19±14.21 mg./kg.) in clover honeys and it was from 53.22-178.77 with a mean value 141.92±22.50 in citrus honeys Fig.(1) . This is agreement with Fernández-Torres *et al.*, 2005 and Terrab *et al.* 2004a&b. The content of calcium in cotton honeys was significantly higher than those in both citrus and clover honeys. Calcium content ranged from 62.89-93.64 (77.47±5.19 mg./kg.) in cotton honey; 21.86-31.586 (25.55±1.93 mg./kg.) in citrus honey and it was from 11.83-53.94 (31.98±6.86 mg./kg.) in clover honey (Fig. 1). This findings were agreed with Terrab *et al.* 2004a&b

Zinc came with non significant between the three types of honeys; citrus, clover and cotton. In clover it was ranged from 3.997-11.66 with a mean value of 6.20±1.43 mg./kg..In citrus honey the range was 2.136-6.781 with a mean value of 4.70±0.99 mg./kg. and finally it ranged from 2.676-5.610 with a mean value of 4.14±0.62 mg./kg. in cotton honey.

On the other hand, iron showed significant values between citrus and clover honeys were it ranged in citrus honey from 0.0-37.18 with a mean value of 17.53±6.45 mg./kg., It ranged from 1.716-9.636 with a mean value of 5.06±1.56 mg./kg.. In cotton, the Fe content was in intermediate value

where its range was 5.583-9.328 with a mean value of 7.61 ± 0.71 mg./kg. (Fig.1). The above mentioned results are in agreement with the results obtained by many investigators such as Slinas *et al.*, 1994; Poiana *et al.*, 1996; Conti, 2000; Przybylowski and Wilczynska, 2001; Terrab *et al.*, 2003; Fernández-Torres *et al.*, 2005 and Munoz and Palmero, 2006).

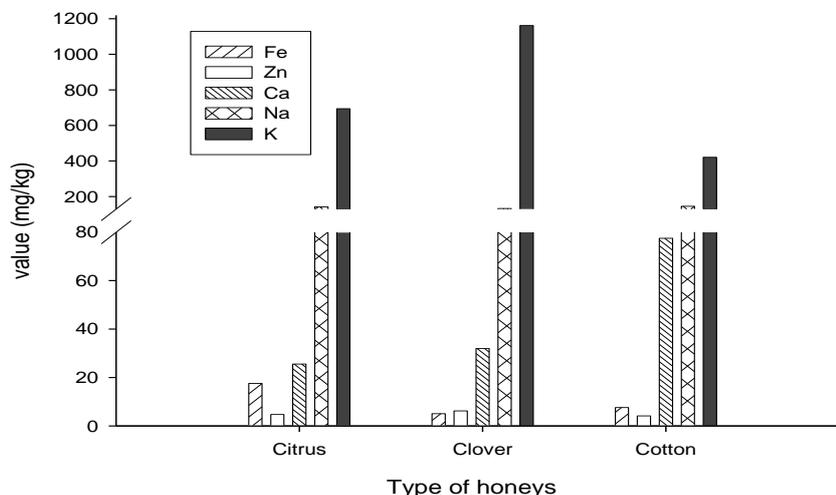


Fig.1: Minerals content in the three major Egyptian honeys. (mg./kg.)

2. Heavy metals in honey samples according to the distance between the apiaries and the main roads:

Values of lead and cadmium elements as range and mean with the corresponding standard error (se) are shown in table (2) and illustrated in Fig. (2). It is appeared that collected honey samples from apiaries located at more than 5km. from the main roads have low mean content of lead (1.25 mg./kg.) and cadmium (0.83 mg./kg.). the corresponding Figures for samples of honeys that obtained from apiaries located at a distance ranged from 1-5 km. of the main roads were 2.08 ± 1.36 mg./kg. and 0.92 ± 0.27 mg./kg. for the previous metals, respectively Fig.2. However samples gathered from apiaries adjacent to main roads, (from 0-1 km.), had values of 5.0 ± 1.71 mg./kg. and 0.83 ± 0.11 mg./kg. for the two heavy metals, respectively. Statistical analysis showed that there's significant difference in Pb content between the shortest and longest distances, were the mean values of lead were 5.00 ± 1.71 mg./kg. and 1.25 ± 1.25 mg./kg., respectively. The middle distance caused an intermediate accumulation of lead as appeared in Table (2) and Fig.(2). On the other hand, the level of cadmium element was approximately similar in honey collected from the different distances. Its values were 0.83 ± 0.11 ; 0.92 ± 0.27 and 0.83 ± 0.31 for the near, medium and far distances, respectively.

Table (2): Heavy metals in honey samples collected from

Distance from towns and main roads (in m.)	Pb		Cd	
	Range	Mean \pm se	Range	Mean \pm se
<1000	0.0-7.5	5.00 \pm 1.71 a	0.5-1.0	0.83 \pm 0.11 a
1000-5000	0.0-7.5	2.08 \pm 1.36 ab	0.0-2.0	0.92 \pm 0.27 a
>5000	0.0-7.5	1.25 \pm 1.25 b	0.0-2.0	0.83 \pm 0.31 a
L.S.D _{0.05}		3.60		0.77

apiaries located in different distance from main road:

Data followed by different litters have significant difference and data followed by the same litters have no significant difference vertically.

It's obvious from the obtained results that the level of lead in all the Egyptian honey samples was above the allowable limits. So, the accumulation of this risk metal, Pb, in honeys reflexed the level of environmental pollution in the region of study. These findings were agreed with those recorded by Shalaby, (2001). He gathered honey from colonies located at El-Gabal El-Asfer, (adjacent to Cairo city) and found lead in concentration of 6.857 \pm 0.423 in citrus honey and 1.385 \pm 0.067 in clover honey. Leita, *et al.*, (1996) found that honey contained large amounts of heavy metals (Pb and Cd) when collected from honeybee colonies placed about 50m. from a road carrying an average of 104 vehicles/day.

Therefore, it could be concluded that the level of lead in the Egyptian honeys is to be considered an excellent indicator of environmental pollution in Egypt.

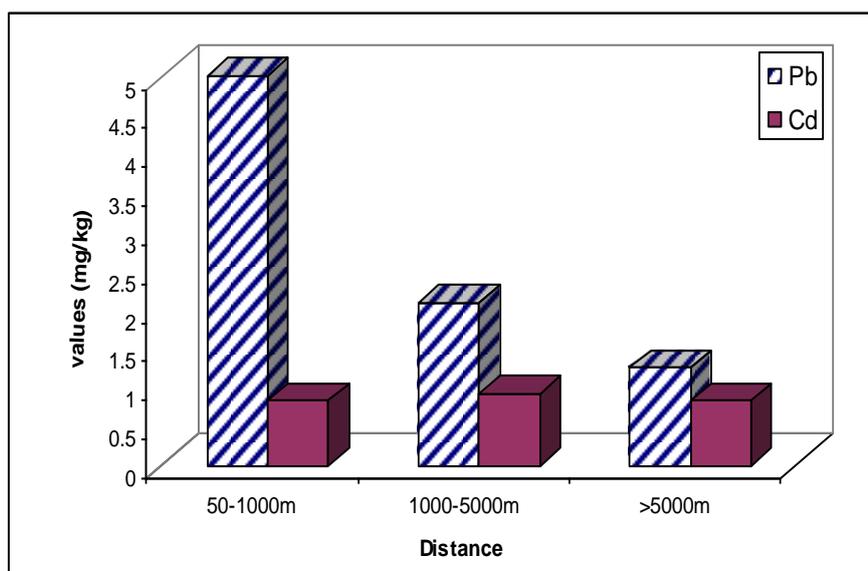


Fig. 2: Heavy metals in honey samples collected from apiaries located in different distance from main road.

REFERENCES

- Al-Khalifa, A.S. and Al-Arify, I.A. (1999). Physicochemical characteristics and pollen spectrum of some Saudi honeys. *Fd. Chem.*, Vol. 67, Iss. 1, October, P. 21-25
- A.O.A.C. (2000). *Method of analysis*. Association of Official Agriculture Chemists 16th ed, Washington D. C. USA.
- Atrouse-OM; Oran-SA and Al-Abbadi-SY (2004). Chemical analysis and identification of pollen grains from different Jordanian honey samples. *Int. J. Fd. Sci. Tech.* 39: 4, 413-417; 20 ref.
- Balestra, V.; Celli, G. and Porrini, C. (1992). Bees, honey, larvae and pollen in biomonitoring of atmospheric pollution *Aerobiologia*. 8: 1, 122-126; 5 ref.
- Cesco, S.; Barbattini, R. and Agabiti, MF. (1994). Honey bees and bee products as possible indicators of cadmium and lead environmental pollution: an experience of biological monitoring in Portogruaro city (Venice, Italy). *Apicoltura*. No. 9, 103-118.
- Conti, M.E. (2000). Lazio region (central Italy) honeys: a survey of mineral content and typical quality parameters. *Fd. Control*, Vol. 11, Iss. 6, December, P. 459-463.
- Crane, E. (1975). *Honey: A comprehensive survey*, William Heinemann in Co-operation with International Bee Research Association, Rondon, UK.
- El-Sherbiny-GA; Rizk-SS; El-Ashwah-FA and Heikal-HA. (1980). Chemical composition of citrus honey produced in A.R.E. *Horticultural Res. Inst.*, Min. Agric., Egypt.
- Fernández-Torres, R.; Pérez-Bernal, J.L.; Bello-López, M.A.; Callejón-Mochón, M.; Jiménez-Sánchez, J.C. and Guiraúm-Pérez, A. (2005). Mineral content and botanical origin of Spanish honeys. *Talanta*, Vol. 65, Iss. 3, 15 February, P. 686-691.
- Franco, M. A.; chessa, M.; Sferlazzo, G.; Giaccio, M.; Di Giacomo, F. and Prota, R. (1997). "Bee pollen as an indicator of environmental pollution by heavy metals" *Riv. Merceal.*, 36, 67-78.
- Gonzalez-Miret, M. L.; Terrab, A.; Hernanz, D.; Ferandez-Recamales, M. A. and Heredia, F. J. (2005). Multivariate correlation between color and mineral composition of honeys and by their botanical origin. *J. Agric. Food Chem.*, 53:2574-2580.
- Iskander, F.Y. (1996). Assessment of trace elements in honey produced on uranium mining reclaimed land. *Sci. of The Total Environment*, Vol. 192, Iss. 1, 29 November, P. 119-122.
- Jones, KC. (1987). Honey as an indicator of heavy metal contamination water, Air, and Soil Pollution. 33: 179-189.
- Krunic, MD.; Terzic, LR. and Kulincevic, JM. (1989). Honey resistance to air contamination with arsenic from a copper processing plant. *Apidologie*. 20: 3, 251-255.
- La Torre, M. J.; Peita, R.; Garcia, S. and Herrero, C. (2000). Authentication of Galician (N. W. Spain) honeys by multivariate techniques based on metal content data. *Analyst*, 125:307-312.

- Leita, L.; Muhbachova, G.; Cesso, S.; Barbattini, R. and Mondini, C. (1996). "Investigation on the use of honeybees and honeybee products to assess heavy metals contamination". *Environ. Monit. Assess.*, 43:1-9.
- Nafea, E.A. (2004). The biological effect of honeybee products as environmentally safe substance against some pathological microorganisms. PH.D. thesis, Department Agric. Sci. Ins. Envir. Studies, Ain Shams Uni. Egypt.
- Nafea, E.A. and Tharwat, E.A. (2006). Minerals and enzymes composition of honeys of different botanical origin in Saudi Arabia. *J. Agric. Sci. Mansoura Univ.*, 30 (12): 8217 - 8221, 2005.
- Munoz, E. and Palmero, S. (2006). Determination of heavy metals in honey by potentiometric stripping analysis and using a continuous flow methodology. *Fd. Chem.* 94, 478-483.
- Nour, M.E.E. (1988). Some factor effecting quality of Egyptian honeys, P.hD. thesis, fac. Agric., Cairo Univ., Cairo, Egypt.
- Nozal Nalda, MJ.; Bernal Yague, JL.; Diego Calva, JC. and Martin Gomez, MT.(2005). Classifying honeys from the Soria Province of pain via multivariate analysis. *Anal. Bioanal. Chem.* May;382(2):311-9.
- Poiana, A.; Fudo, S.; Manzin, A.; Postrino, S. and Mincione, B. (1996). Ricerche sui mieli cobbmercializzati in Italia, La componente minerale *Ind. Aliment.*, 35: 522-530.
- Przybulowski, P. and Wileznaska, A. (2001). A. Honey as environmental marker. *Food Chem.*, 74:289-291.
- Raes, H.; Cormelis, R. and Rzeznik, U. (1992). "Distribution accumulation and depuration of administered lead in adult honeybees". *Sci. Total Environ.*, 113:269-279.
- Rashed, M.N. and Soltan, M.E. (2004). Major and trace elements in different types of Egyptian mono-floral and non-floral bee honeys. *J. Fd. Composition and Analysis*, Vol. 17, Iss. 6, December, P. 725-735
- Rodriguez-Otero, J. L.; Pasrio, P.; Simal, J. and Cepeda, A. (1994). "Mineral content of honeys produced in Galicia (North-west Spain). *Food Chem.*, 49:169-171.
- Shalaby, M.M. (2001). Effect of some environmental pollutants on honeybee and its products, with special reference to methods of pollution minimization. PhD. Thesis, Dep. Agri. Sci. Ins. Env. Stu. & Res. Ain Shams University
- Slinas, F.; Montero, V.; Osorio, E. and Lazana, M.(1994). Determinacion de elementas minerales en mieles de diverses origenes florales por analisis de inyeccion en flujo acoplada a la espectroscopia atomica. *Rev. Esp. Cienc. Tecn. Aliment.* 34:441-449.
- Terrab, A.; Gonzalez, A. G.; Dierz, M. J. and Heredia, F. J. (2003). Mineral content and electrical conductivity of the honeys produced in north-west Morocco and their contribution to the characterization of unifloral honeys. *J. Sci. Food Agric.*, 83: 637-643.
- Terrab, A.; Hernanz, D. and Heredia, KJ. (2004a). Inductively coupled plasma spectrometric determination of mineral in thyme honeys and their contribution to geographical discrimination. *J. Agric. Fd. Chem.* Jun 2;52(11):3441-5.

- Terrab, A.; Recamales, A.F.; Hernanz, D. and Heredia F.J. (2004b). Characterisation of Spanish thyme honeys by their physicochemical characteristics and mineral contents. *Fd. Chem.*, Vol. 88, Iss. 4, December, P. 537-542.
- Tong, S. S. C.; Morse, R. A.; Bache, C. A. and Lisk, D. J. (1975). "Elemental analysis of honey as an indicator of pollution". *Arch. Environ. Health*, 30:329-332.
- Vorlova, L. and Celechovska, O. (2002). Activity of enzymes and trace element content in bee honey. *Acta Vetennana'Bmo*. 71: 3, 375-378; 10 ref.
- White, J. W. (1978). Honey. *Adv. Food Res.*, 24:287-375.

الأعسال الرئيسية كمؤشر للعناصر في البيئة المصرية
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ثمانية عشرة عينة من الأعسال تم تجميعها وتصنيفها تبعا للمصدر النباتي وكذلك تبعا للمسافة بين المناحل والطرق الرئيسية القريبة منها وقد تم تقدير العناصر (البوتاسيوم، الصوديوم، الكالسيوم، الزنك والحديد) في تلك الأعسال باستخدام جهاز قياس الإمتصاص الذري. البوتاسيوم كان العنصر الرئيسي بمتوسطات، ٦٩٤،٠١، ٨٦، ١١٦١ و ٤٢١، ٢٩ مجم./كجم. في أعسال الموالح، البرسيم والقطن يليه الصوديوم في الأعسال المختبرية حيث كانت متوسطات ١٤١، ٩٢، ١٣٣، ١٩ و ١٤٥، ٤٧ مجم./كجم. في كل من الموالح، البرسيم والقطن على التوالي. بينما ظهرت بقية العناصر (الكالسيوم، الزنك والحديد) بنسب صغيرة في تلك الأعسال المختبرية. الرصاص أظهر إرتفاع في قيمة في حالة المناحل القريبة من الطرق الرئيسية عن البعيده عن تلك الطرق، كما أظهرت المسافة المتوسطة للقرب من الطرق الرئيسية قيمة بينية بين السابقتين وكانت قيمة الرصاص ٥، ٠٠، ١، ٢٥ و ٢، ٠٨ مجم./كجم. أما مستويات عنصر الكاديوم فكانت متقاربة للثلاث مسافات موضع الدراسة وبمتوسطات ٠، ٨٣، ٠، ٨٣ و ٠، ٩٣ مجم./كجم. على التوالي. من السابق يمكن القول أن مستويات الرصاص في الاعسال المصرية يمكن ان تكون مؤشر جيد للتعرف على مقدار للتلوث البيئي في مصر.