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Heavy Metals in Honey from Contaminated Sites: a Case from Lithuania

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Abstract

Honey as a biomarker can be used to determine environmental exposure to selected contaminants, including heavy metals. Twelve sites were selected for experimental studies close to major pollution sources such as industrial sites, landfills, railroads, and highways. Honey samples were burned to ash and heavy metals in the ash were measured using aqua regia digestion in a microwave digestion system. Concentrations of heavy metals (Cd, Cr, Cu, Pb, and Ni) were measured using a Buck Scientific Model 210 VGP Atomic Absorption Spectrophotometer with a graphite furnace nebulizer and acetylene air flame. Average amounts of these heavy metals were detected in the honey samples analysed. It was 0.0030 mg/kg for Cd, 0.0179 mg/kg for Pb, 0.0317 mg/kg for Cr, 0.0999 mg/kg for Cu and 0.0332 mg/kg for Ni. The results obtained were compared with studies of honey samples conducted in other countries. It is difficult to compare heavy metal levels in honey from different countries due to factors such as honey type, soil composition, rainfall, temperature, harvested plants and vegetation length. And flowering and the level of anthropogenic pollution varies by region. With the exception of the Pb content in honey samples, the heavy metal contents tested in honey were low and did not pose a risk to human health. Relationships between heavy metal levels were evaluated to determine exposure to pollutants. (Traffic and industry), statistical analysis was performed [1]. Means, medians, standard deviations, confidence intervals and Spearman coefficients were performed. Correlation analysis showed strong negative correlation coefficients between heavy metals.

Keywords: Natural organic; Mononitrides; FPLMTO

Introduction

In recent years, a healthy environment has become a major goal of European countries. Anthropogenic pollution is responsible for a large part of the disease burden in Europe, as noted in the EEA report. Industrial and agricultural activities, transportation, and other anthropogenic activities release large amounts of heavy metals into the soil, air, and water. As a result, the concentration of heavy metals in the environment rises significantly, compromising ecosystem balance and human health [2]. Heavy metals in the atmosphere pose serious threats to health and the environment, including food safety, human health and ecosystems. These heavy metal particles are deposited in water and on the ground and can readily bioaccumulation in the food chain. Heavy metals are potentially harmful compounds that enter food from the environment, enter the human body through food, and are rapidly absorbed into the biological cycle. Food safety has become an important quality feature of food.

Honey is a nutritious natural organic product with antiseptic and stimulant properties. Its value depends on species, location, environment, collection time and climatic conditions. Honey's valuable properties as a natural organic product depend on its variety and origin. Quantitative and qualitative ratios of chemical elements are characteristic of each flower of plants in each region of the country, so honey is a good indicator of pollution levels, so the total amount of minerals varies from country to country. France, Greece, Italy, Lithuania, Poland, Romania, Slovakia and other continents (Australia, Bangladesh, China, Iran, Turkey). The amount of minerals in honey varies greatly from region to region. This is because the qualitative and quantitative relationships of chemical constituents differ from region to region. We need as much data as possible on the transport and accumulation of heavy metals in the environment and their effects on ecosystems and people. The amount of heavy metals in plants varies with location, type, soil contamination, distance to transport routes, and industrial sites that release heavy metals. In air, heavy metals are deposited on the soil surface and migrate to deeper layers. The highest concentrations are found in the topsoil layer. It is surprising that heavy metals still find their way into the upper parts of plants, despite their protective function in the roots. The amount of heavy metals entering stems and leaves increases with increasing heavy metal concentrations in the soil. In soils contaminated with heavy metals, relatively high concentrations of these metals are found in aboveground plant parts. The European Union is the second largest honey producer in the world after China. Each year, about 600,000 beekeepers and their 20 million beehives produce about 218,000 tons of honey. Honey consumption varies greatly from country to country. Annual honey consumption is increasing and is estimated at 0.3–0.4 kg/person in Italy and France, 1.0–1.8 kg/person in Germany and Austria, and 0.07 kg/person in Brazil. The results of the study are evaluated by comparing them to acceptable levels for key foods whose presence may pose a toxicity risk. Maximum levels of chemical elements (MRLs) are set according to the World Health Organization (WHO), the Joint Food Code Commission (FAO), and the Food Law of the Republic of Lithuania and the recommendations of the country's actual situation. In many countries, health authorities have issued recommended dietary guidelines for restrictive populations that include required daily nutrient restrictions in addition to basic nutritional content. Concerns about food quality require constant monitoring, analysis of the latest research methods, and evaluation of heavy metals [3].

Lithuania is currently subject to Commission Regulation (EC)

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No 1881/2006, which sets limits for hazardous substances in certain commodities (OJ 2006 L 364, p. 5). Set limits for Pb, Cd, Hg, and Sn in foods of pant and animal origin. According to Council Directive 2001/110/EC on honey, "Honey is produced from the nectar of plants, the excrement of living plant parts or the excrement of plant-sucking insects on living plant parts. It is a natural sweet substance obtained by the bees of the bees, which are collected, transformed, deposited, drained, stored, and matured in the hive in combination with certain substances of the bees themselves." , which defines honey as of plant and animal origin, limits can only be set as ranges [4].

Materials and Method

Sampling points

Twelve sites were selected for experimental studies and specific 'small urticarial' (nuclei) were used for the study. Honey samples were collected from bee hives in the Chepkeria reserve (Linegeriai village) and Druskininkai in Mizalai village. Since bees can collect honey up to 4 km away from the hive, heavy metal contamination of honey samples reflects environmental contamination at that distance from the hive [5]. A description of the sampling site, GPS coordinates, and distance from the contamination source is included.

Reagents and Instruments

All chemicals and reagents used in the experiments were of high purity (Sigma Aldrich, Darmstadt, Germany). Aqueous solutions were prepared by mixing standards with high-purity deionized water. Metal standards from VWR Chemicals (Lutterworth, UK) were used to calibrate the Graphite Furnace Atomic Absorption Spectrometer (GFAAS) and Flame Atomic Absorption Spectrometer (FAAS). All experimental flasks were emptied with 5 MHNO3 for 24 hours and thoroughly washed 3–4 times with deionized water. A high accuracy Radwag AS 60/220.R2 analytical balance was used to weigh the honey Sample preparation for metal analysis.

Honey samples were enriched by combustion because heavy metal concentrations can be very low and difficult to measure. The ash samples were then decomposed in a microwave oven. Each honey sample (100 g) was dried in an oven at 100 ± 5 °C to constant mass. After that, the temperature was gradually raised from 100° C/1 hour to 500±20.0° C. over 2 hours in a muffle furnace. The resulting ash was allowed to cool to ambient temperature. The moisture in the ash slowly evaporates as it cools to room temperature. Total recoverable heavy metals in the ash were determined using the aqua regia splitting technique (3:1, v/v, HCl to HNO3). A honey ash sample (approximately 1.0 g) was digested in a Teflon container for approximately 50 minutes using a Milestone Ethos Touch Control microwave digestion system Milestone SRL, Sorisole, Italy. This solution was quantitatively filtered through a 0.45 µm PTFE membrane filter.

The amount of heavy metals in honey ash was calculated considering the measured concentration of the analyte in solution, the volume of the sample, the dilution factor and the amount of honey ash used in the test. The amount of heavy metals in a honey sample was determined by multiplying the amount of analyte in the ash by the weight of ash (in grams) obtained by burning 100 g of honey in a muffle furnace, 100 (initial weight of honey before burning).

Concentrations of all metals in the standard solutions used were equal to 1000 mg/L at 2% HNO3. Aqueous working standard solutions containing Cu, Pb, Cd, Cr, and Ni were prepared by serially diluting certified reference metal standard solutions for atomic absorption spectrometry with deionized water. Appropriate standard solutions were used to generate calibration curves for each chemical element by diluting a 1000 mg/L stock solution of each chemical element supplied by VWR Chemicals (UK). A free honey sample was taken from each hive. All experiments were performed his triplicate and the mean of triplicate values are presented. Two blank samples (without metal ions) were used for each measurement [6].

Statistical analysis of the data was performed using Excel and Statistica. Spearman's rank correlation coefficient and cluster analysis were used to examine the relationship between heavy metal contents in honey samples. Means, medians, standard deviations, confidence intervals, and Spearman's rank coefficients were calculated at the significance level of 0.05.

Heavy metal levels analysed in almost all honey samples were within limits, indicating their purity. It is difficult to compare specific levels of heavy metals in honey samples with other scientists' results. This is due to differences in honey varieties, soil conditions, rainfall levels, temperature, plant types from which the honey was harvested, and contamination levels. Continuous exposure to even small amounts of lead and cadmium can cause serious health problems, including: B. Impaired intellectual development and irregularities in blood function by limiting the formation of haemoglobin and shortening the life span of red blood cells. Cluster analysis (CA) was used to compare contaminant-normalized mass concentration data with population sample locations. Distances between measurement points were calculated using Euclidean distance [7-17]. To determine the distance between groups, the hierarchical group method of Ward's analysis of variance (linkage) methodology was used the dendrograms resulting from applying CA to heavy metal concentrations at various sampling sites.

Discussion and Conclusion

By combining the calculated electron mechanics and lattice mechanics contributions, we were able to construct the Gibbs free energy (or the Helmholtz free energy at zero pressure). This free energy is a basic quantity of thermodynamics, but it is usually not measured directly. Therefore, instead of explicitly verifying the ab initio free energy in the experiment, we compared the results with other theories and models developed for graphite. our first-principles free energy, along with the quasi-harmonic theory (QH), CALPHAD and the EOS model . The quasi-harmonic free energy was calculated from the GIBBS2 package using the energy determined by the FPLMTO calculation of graphite. The same approximation was performed to keep the axial c/a ratio constant at the experimental value for all FPLMTO calculations and QH modelling. QH modelling of graphite has been studied, but no free energy data were found in the literature. Surprisingly, the CALPHAD and EOS models are in excellent agreement. This is expected given that both are thermodynamically consistent representations of the experimental data. Furthermore, the figure shows good agreement between the anharmonic theory of the underlying principle and the two empirical models. We therefore conclude that the anharmonic approximation is sufficient even at very high graphite temperatures. QH processing, on the other hand, is meaningful up to about 1000 K, but becomes increasingly inaccurate after that. This is certainly not unexpected. Similar behaviour was observed in thermodynamic studies of actinide monocarbohydrates and mononitrides. We then focused on the specific heat at constant pressure. Similar to the free energy, we obtained Cp as the sum of the electronic and lattice contributions. In co l is still included in the total specific heat, but the contribution is not clearly visible.

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