

Variations of chemical element composition of bee and beekeeping products in different taxons of the biosphere



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ABSTRACT

Geographical variations in element composition of bee products are poorly investigated though a lot of attempts are made to utilize the data in ecological monitoring. So the comparison of chemical element composition of bee and beekeeping products in different taxons of the biosphere may become valuable to test the efficiency of such approach. For this purpose content of 25 elements in bee body, bee bread, propolis and honey from Ribnitsa district of Moldavia (unpolluted area, control), Henty province of Mongolia (selenium deficient area) and Voskresensk district of Moscow region (mineral fertilizers production) were determined by means of the ICP-MS. Among 3 investigated regions Mongolia was characterized by the lowest Se levels and the highest accumulation of Al, Ca, Cd, Cu, Co, K, Mn, Mg, Na, Ni, P, Zn and V in bee bodies. The highest levels of Pb, Cr, Fe, Si, Sr and B, Se, Li, Sn were typical for Voskresensk and Moldavia bees accordingly. The highest correlation coefficients were registered between element concentrations in bee body and bee bread ($r = +0.97-0.99$, $P < 0.0001$), less significant – in bee body and propolis ($r = +0.5-0.7$; $P < 0.001$) and no correlation was demonstrated between element composition of bee body and honey. Propolis was characterized by significantly higher capacity to accumulate Pb, Cr, Sn and Al than bee body. Compared to bee body honey accumulated the lowest level of Mn and the highest of Si in Se-deficient Mongolia but the opposite phenomenon was demonstrated in Moldavia with moderately increased Se content in the environment. The results suppose that the most promising object for ecological monitoring is bee body. Element composition of propolis seems to reflect prolonged accumulation of elements, especially Pb, Al, Sn and Cr, by plant resin rather than dynamic temporal elements loading. Accumulation levels of elements in bee bread may be used on a par with bee body mineral content only in cases with equal honey content in bee bread. Honey utilization in monitoring of geochemical elements loading should be used with caution due to peculiarities of pollen/nectar elements distribution.

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1. Introduction

Constantly increasing environmental pollution due to industrial development, intensification of traffic and mining industry, utilization of fertilizers and pesticides determines deterioration of habitat for all living beings including bees (Patricio-Roberto and Campos, 2014; Roman, 2010; Brodschneider and Crailsheim, 2010). Gathering nectar, pollen, tree-resin and drinking water bees become affected by intensive anthropogenic factors not only decreasing their number but also elevating the content of toxic

metals in bee body and beekeeping products (Roman, 2004; Uren et al., 1998; Hoffel, 1985). Thus, according to Hoffel data (Hoffel, 1985), Pb and Cd concentrations in bee body from industrial regions are 8–10 times higher than from unpolluted territories. High response of bees to environmental pollution and their ability to accumulate exclusively bioavailable forms of macro and trace elements (Roman, 2009) supposes the possibility of beekeeping products utilization in environmental monitoring (Rashed and Soltan, 2004; Kaigorodov and Kuleshova, 2014; Bogdanov et al., 2007; Zhelyazkova, 2012; Formicki et al., 2013).

Meanwhile, fragmentariness of investigations devoted to element composition in a system “bee body-propolis-bee bread-honey” is an obstacle for adequate evaluation of ecological risks. Determination of LD₅₀ for several elements in bees (Roman, 2010) are characterized by wide ranges of concentrations of metal

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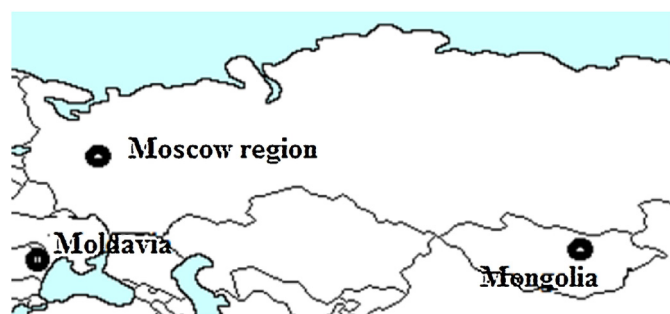


Fig. 1. Regions of investigation.

compounds: 12–20 $\mu\text{g Pb/bee}$; 6–30 $\mu\text{g Cd/bee}$; 50–250 $\mu\text{g Cu/bee}$, and are supposed to reflect the accumulation of various chemical forms of elements. On the other hand, it does not exclude the possibility that the results are connected with the ability of bees' adaptation to increased anthropogenic loading (Rashed and Soltan, 2004).

The aim of the present study was comparative evaluation of macro and trace elements accumulation by bee body, propolis, bee bread and honey in conditions of Moldavia (ecologically pure region), Mongolia (Se deficiency) and Voskresensk district of Moscow region (production of mineral fertilizers).

2. Material and methods

Polyfloral honey, propolis, bee bread and bee bodies from 4 apiaries of Ribnitsa region, Pridnestrovie (Moldavia, 40 hives at each apiary) (N47.797062°, E29.020375°; N47.858700°, E29.073552°; N47.905033°, E28.982758°; N47.947327°, E28.872069°), 3 apiaries of Binder district Henty province, Mongolia (48°36'50.7"N 110°36'02.4"E; 125 hives in a whole) and 2 apiaries of Voskresensk district, Moscow region, Russia (55°19'N, 38°42'E; 45 hives at each apiary) were used (Figs. 1 and 2). The first region is known to possess no environmental pollution due to lack of industrial plants and major highways, the second one is situated in Se deficient area (Erdenetsogt et al., 2014) and is supposed to be exposed by negative impact of Pt mining industry (Mongolia, 2006), the third region is under the press of contamination associated with the production of mineral fertilizers ("Voskresensk Mineral fertilizers" plant). Two apiaries in Voskresensk region, were situated (a) in the immediate vicinity of phosphogypsum storage polygon (Lopatino) and (b) remote by 8 km from the polygon in Novoselki settlement only 1.5 km from the plant producing cement ("Cemgigant") (Fig. 2). No abnormalities in bee growth and reproduction were registered neither in Moldavian, Mongolian or Russian apiaries investigated. Samples of spring bee bodies (3 from each apiary), containing not less than 150 bees were dried at 70 °C to constant weight before the analysis and homogenized. 3 samples of honey, propolis and bee bread were analyzed separately from each apiary investigated. Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, I, K, Li, Mg, Mn, Na, Ni, P, Pb, Si, Sn, Sr, V and Zn content in samples was determined using ICP-MS on quadruple mass-spectrometer Nexon 300D (Perkin Elmer, USA) in the Center of Biotic Medicine (Moscow). Rhodium ^{103}Rh (SCP Science, Champlain, NY) was used as an internal standard to eliminate instability during measurements. Quantitation was performed using external standards (Merck IV, multi-element standard solution) and all the standard curves were obtained at 5 different concentrations. For quality control purposes, internal controls and reference materials were tested together with the samples on a daily basis. Acidic digestion of samples were achieved according to standard method (Skalny et al., 2009)

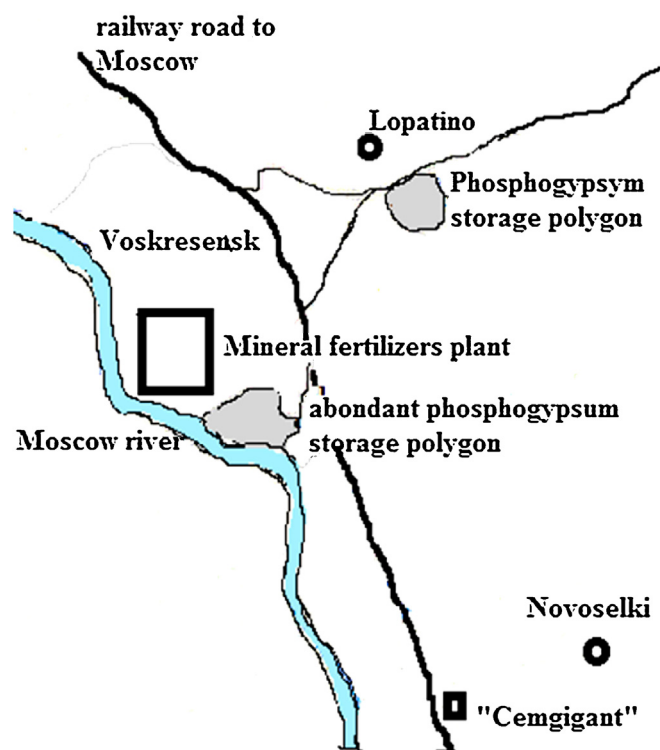


Fig. 2. Location of apiaries in Voskresensk suburbs.

using microwave oven technique (SpeedWave four, "Berghof", Germany).

Se was analyzed using fluorimetric method previously described for tissues and biological fluids (Alfthan, 1984). Homogenized samples were digested via heating with a mixture of nitric-chloral acids, subsequent reduction of Se+6 to Se+4 with a solution of 6N HCl, and formation of a complex between Se+4 and 2,3-diaminonaphthalene. Calculation of Se concentration was achieved by registration of piazoselenol fluorescence value in hexane at λ emission 519 nm and λ excitation 376 nm. Each determination was achieved in triplicate. Precision of the results were verified using in each determination a reference standard- lyophilized muscles (Agricultural Research Center of Finland) with Se concentration 364 $\mu\text{g/kg}$.

Statistical analysis was achieved using Student *t*-criterion.

3. Results and discussion

3.1. Bee body

Element composition of bee bodies from 3 investigated regions are shown in Table 1. Significant differences in macro and trace elements content are supposed to reflect possible geochemical peculiarities and anthropogenic loading levels not only for Mongolia, Moldavia and Moscow region but also for different apiaries within one region situated on different distances from phosphogypsum storage polygon (Voskresensk district of Moscow region).

According to received data, bees of Henty province (Mongolia) demonstrate the most intensive accumulation of Al, Ca, Cd, Cu, Co, K, Mn, Mg, Na, Ni, P, Zn and V and very low levels of Se. The highest levels of Pb, Cr, Fe, Pb, Se, Si and Sr are typical for bee bodies of Lopatino. Bees from Pridnestrovie are characterized by elevated levels of B, Se, Li, and Sn. These results are supposed to reflect both geochemical characteristics and anthropogenic loading of the

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