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Bio-monitoring of cadmium, lead, arsenic and mercury in industrial districts of Izmir, Turkey by using honey bees, propolis and pine tree leaves

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ABSTRACT

In this study honey bees, propolis and leaves of pine trees were sampled from five different points of industrial district in Izmir-Turkey during spring 2014. These samples were used as biological indicators for heavy metal pollution of the environment. Heavy metals including cadmium, lead, arsenic and mercury were determined in samples. Results showed the high levels of heavy metal contamination, especially in propolis samples. Mercury not detected in the all analyzed samples.

1. Introduction

Nowadays, increasing levels of chemical pollutants in the environment were seen due to urbanization, industrialization and agricultural activities. Various environmental matrices like water, air and soil are subjected to organic and inorganic pollutants (Serbula et al., 2013). Due to increased public awareness about environmental and health issues, inspect contamination, especially by bio-monitoring has been considered (Girotti et al., 2013).

Among chemical pollutants, heavy metals are seriously toxic and exposure of living organisms (human, animals and plants) affects their health negatively. Environmental pollution causes heavy metals existence in the food chain. Due to physiological functions of heavy metals through the food chains, they are classified as the main group of inorganic pollutants (Serbula et al., 2013; Rodriguez et al., 2012; Sun et al., 2010; Conti and Botrè, 2001; Michalak, 2006). They have long-term presence and accumulate in the environment due to their rapid and sustained release, capacity for mobilization and dispersion, non-biodegradable and long half-life (Rodriguez et al., 2012; Sun et al., 2010).

According to the high cost of sampling equipment, attention for bio-monitoring has been increasing, especially for air pollution monitoring (Girotti et al., 2013; Sun et al., 2010). Foraging honey bee for gathering nectar, plant resins and water, visit more than thousand flowers in the border of 7 km^2 around her hive every active days (Girotti et al., 2013; Amorena et al., 2009; Finger et al., 2014). Owing to their great mobility and direct contact with apiaries environment, honey bees take samples through inhalation, digestion and their hair covered bodies from the environment and carry them to the hive (Girotti et al., 2013; Amorena et al., 2009; Finger et al., 2014; Stanciu and Mititelu, 2004). Due to these features, honey bee has been proposed as a contaminant multi sample collector; also mortality rate of honey bees made them potential biosensors of insecticides and genetically modified organism (GMO), (Amorena et al., 2009; Han et al., 2010).

Propolis is one of the important hive products. In the case of availability of plant resin in the bud of some plants, honey bee, gather them and mix with salivary secretions and wax and make propolis (Finger et al., 2014; Stanciu and Mititelu, 2004). Propolis is applicable in medicine because of its anti-bacterial, anti-viral and anti-fungal effects (Finger et al., 2014; Stanciu and Mititelu, 2004). Components of propolis depend on various factors such as geographical area and plant resources that plant gum has been gathered and the bee species. Propolis mainly contains phenolic

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compounds, steroids, terpenes and amino acids (Michalak, 2006; Finger et al., 2014; Stanciu and Mititelu, 2004), also due to sticky nature of gum, propolis potentially could be show atmospheric heavy metal contamination and might be used as an indicator of pollution of heavy metals (Finger et al., 2014; Stanciu and Mititelu, 2004).

Higher plants are so current for monitoring programs in urban and industrial areas (Serbula et al., 2013). Because of utilization of water resources, soil and air by plants, they are considerable as good indicators for environment conditions. Accumulation of heavy metals in plants depends on plant species and its tissues and type of metal (Conti and Botrè, 2001). Some heavy metals like Co, Fe, Mn, Ni, Zn and Cu are essential elements for normal growth of plants and have important roles in metabolisms at trace concentration but higher concentrations are toxic and lead to defects in plant growth, decrease in biomass and plant death. Some heavy metals like Pb, Cd, Cr, Hg and etc., have potentially high toxicity for plants. Different plant species are used for atmospheric biomonitoring (Rodriguez et al., 2012) but the pine trees due to widespread geographical expanding and being evergreen are more considerable in this issue (Serbula et al., 2013; Girotti et al., 2013); thick epicuticular wax layer and needle-shaped leaves made pines most frequent indicator for monitoring of airborne pollution (Serbula et al., 2013; Conti and Botrè, 2001). Pines can absorb heavy metals in active or passive way by stomata or via deposition on the foliage surfaces from the atmosphere (Serbula et al., 2013; Rodriguez et al., 2012; Conti and Botrè, 2001). The concentration of pollutants in the surface of their leaves is the reflection of these pollutants in surrounding air (Serbula et al., 2013).

2. Materials and methods

2.1. Sampling site description and biological matrices

This study was performed on border larger than 10 km^2, at "Bozkoy" village, Aliaga—Izmir—Turkey. The village is situated near the industrial district, is involved petrochemical industry, iron and steel factories, ship breaking factories, refineries, gas turbines, natural gas combined cycle power plants and etc. Aliaga's unique natural resources (especially pine forests) since 1961 with first step toward being heavy industrial area, started to get lose and get weaker. So this study try to show the environmental condition in the area and besides proving bio-monitoring program with honey bees, also inform officials about green space in decline.

Honey bee hives located in each five different sites in "Bozkoy" village pine forests and the nearest green landscapes to "Aliaga Industrial Zone" (Izmir—Turkey). Hives were rented from selected apiaries in the area. During the sampling period smoke, pesticides, fungicides and other chemicals were not assisted in hives control process. The location of five sampling sites and the prevailing wind direction is represented in map (Fig. 1). Station 1 was located near to high-way, station 2 was located next to main road of Bozkoy village and stations 3, 4 and 5 are nearer to industrial region's borders respectively.

Samples were collected during April–May, 2014. The aim of choosing this period of time was accurate study of heavy metals contamination during the monitoring period. Target biological indicators were collected one time at the end of period of study. All samples were collected without using metallic equipment and were saved in safe plastic or glass containers. Foraging bees were collected from hive entrances, were gathered in the closed glass jars and were stored in dark and cold conditions. After transporting the samples to the lab, pollens and other unwanted materials were removed from dead bees, and then the samples were lyophilized at −48 °C and 0.027 mBar pressure for 24 h. Dried samples were kept in deep freezer until analysis. Propolis samples were collected from plastic traps that were replaced on the top of the hives during sampling period. The probable herbal resource of resin as main substance of propolis in this area is pine trees, so pine needles which were grown during the sampling period were collected randomly and dried by freeze drier and stored in deep freezer until analysis.

2.2. Reagents and chemicals

Nitric acid, magnesium nitrate, palladium chloride, ammonium pyrrolidine di-thiocarbamate and carbon tetrachloride were purchased from Merck (Darmstadt, Germany). Argon with 99.999% purity and acetylene were provided by Air products (UK) and Sabalan Oxygen Co. (Iran), respectively.

2.3. Instruments and apparatus

Plastic trapes which used for propolis sampling were obtained from Sepe natural company (Turkey).A perkin-elmer atomic absorption spectrophotometer model AAnalyst 600 (USA) equipped with graphite furnace and electrodless discharge lamps (EDL) was used for mercury and arsenic analysis. A perkin-elmer flame atomic absorption spectrophotometer model 3300 AA equipped with hollow cathode lamps (HCL) was used for cadmium and lead analysis.

2.4. Sample preparation

2.4.1. Wet digestion of the samples

2 grams of lyophilized samples of honey bees, plants and propolis were carefully weighed and were homogenized in a glass mortar. Homogenized samples were transferred to the test tube. Then 5 ml concentrated nitric acid was added and heated at 50 °C for 2 h and then 110 °C for 18 h. In the next step 5 ml hydrogen peroxide was added to the digested sample and was heated for 6 h. Finally the solution was cooled and passed through Whatman filter papers. The solution was made to the final volume of 25 ml.

2.4.2. Liquid–liquid extraction of lead from digested samples

Digested samples were used for arsenic and mercury analysis using electrothermal atomic absorption spectrophotometry and cadmium determination using flame atomic absorption spectrophotometer. But lead samples need further steps of sample preparation for pre-concentration. Due to low concentrations of lead, usage of extraction methods for pre-concentration of the samples is necessary.

For this purpose, 10 ml of digested sample was poured into a test tube and 2 mg of ammonium pyrrolidine dithiocarbamate as ligand was added. Mixture of 1 ml carbon tetrachloride and 3 ml methanol was used as the extraction solvent. After centrifugation, organic phase was separated and was used for lead measurement (Sun et al., 2010; Conti and Botrè, 2001).

2.4.3. Electrothermal atomic absorption spectrophotometry

Atomic absorption spectrophotometry is one of the most powerful techniques in heavy metal analysis with two different modes, flame and electrothermal atomic absorption spectrophotometry. Electrothermal atomizers provide us some important advantages. Low limits of detection in the $\mu g\,L^{-1}$ range and very low sample volumes (20 μl) in comparison with flame atomizers with minimum 5 ml sample volume. These advantages made the electrothermal methods suitable for analysis of biological samples, due to low concentrations of the analytes and limited sample quantity. So, electrothermal atomic absorption spectrophotometry was selected for determination of arsenic and mercury. Arsenic and mercury