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RESEARCH ARTICLE

Determination of polychlorinated biphenyls in honeybee, pollen, and honey samples from urban and semi-urban areas in Turkey

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Abstract

In recent years, honeybees and bee products such as pollen and honey have been used as bioindicators for monitoring environmental pollution. Unfortunately, there are few studies about polychlorinated biphenyl (PCB) concentrations in honeybees and bee products from Turkey. Honeybee and pollen samples were taken between May and September 2017, and honey samples were taken between July and September 2017 at urban and semi-urban areas in Bursa (Turkey). PCB concentrations measured by gas chromatography-microelectron capture detector (GC-μECD) were found to be 135.46 ± 6.53, 81.47 ± 23.52, and 106.35 ± 21.60 ng g^{-1} dry weight (dw) for honeybee, pollen, and honey samples in the urban area, respectively; and 126.35 ± 26.54, 67.57 ± 27.34, and 118.88 ± 55.28 ng g^{-1} dw for honeybee, pollen, and honey samples in the semi-urban area, respectively. Pearson correlation was made between meteorological parameters and pollutant concentrations. According to the correlation results, a significant relationship was found between the pollen and honey results and the total cloudiness and temperature in the semi-urban area. The coefficient of divergence (COD) and Pearson correlation coefficient (PCC) methods were applied to determine the similarities and differences between the pollutant concentrations and sources of the two areas and the temporal variation. According to these two methods, PCB concentrations and emission sources in honeybee and pollen samples in urban and semi-urban areas were generally different in May and June, and similar in August and September.

Keywords Biomonitoring · PCB · Honeybee · Bee products · COD · Meteorological parameters

Introduction

Honey is a natural foodstuff consisting of sugars and other components such as enzymes, amino acids, organic acids, carotenoids, vitamins, minerals, and aromatic substances. The composition, color, aroma, and flavor of honey depend mainly on flowers, geographical areas, climatic conditions, and the type of honeybee; however, these also depend on weather conditions, processing, manipulation, packaging, and storage time (Da Silva et al. 2016). Every day 10,000–25,000 honeybees (*Apis mellifera* L.) come out of the hive approximately 10 times to collect nectar, water, and pollen from flowers in a 7-km^2 area (Rissato et al. 2007). A single honeybee exits from a hive and moves through 80–100 flowers per day (Nisbet et al. 2013), and during this process, various microorganisms, chemicals, and particles are kept in the body of honeybees (Rissato et al. 2007). Pollen is a common component of honey and propolis, and it is a good source of energy as well (Badolato et al. 2017). Pollen grains, in addition to their various geometric shapes, may have different colors ranging from dark brown-black to bright yellow depending on the presence of polyphenols and colored compounds (Human and Nicolson 2006; Amores-Arrocha et al. 2018). Pollen contains compounds such as amino acids, antioxidants, vitamins, and lipids which are especially important for human health (Ares et al. 2018). Pollutants can reach honeybees and bee products (pollen, honey, nectar) through the air, water, plants, and soil and are carried to hives by honeybees (Bogdanov 2006). Honeybees can be used to monitor the distribution and effects of various hazardous chemicals, including organic contaminants such as pesticides, polychlorinated biphenyls (PCBs), plasticizers, bisphenol A (BPA), and inorganic contaminants such as trace elements and heavy metals (Bromenshenk et al. 1991; Al-Waili et al.

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2012; Di Bella et al. 2015; David et al. 2016; Lo Turco et al. 2016). Due to these characteristics, the use of honeybees and bee products as bioindicators of environmental pollution has been increasing in recent years (de Oliveira et al. 2016).

PCBs are complex compounds formed by direct chlorination of biphenyls (Ziegler et al. 2017). Due to their high stability and lipophilic properties, these contaminants often cause accumulation in lipid-rich tissues (Abella et al. 2016). These compounds, which are extremely persistent due to their chemical properties, show bioaccumulation in food chains (Putschögl et al. 2015) and about 90% of total PCB intake in humans is through the consumption of food (Jankovic et al. 2015). The toxicity, carcinogenicity, and bioaccumulation properties of PCBs have caused the US Environmental Protection Agency (US-EPA) to classify them as important compounds in terms of human health (Shaban et al. 2016). In 2016, the International Agency for Research on Cancer (IARC) increased the classification of PCBs from "possible carcinogens for humans" (Group 2A) to the class of "carcinogens for humans" (Group 1A) (Zani et al. 2017).

In recent years, there have been numerous studies on persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbon (PAH) and organochlorine pesticide (OCP) in honeybees and bee products in the literature (Benuszak et al. 2017; Hakme et al. 2017; Kargar et al. 2017; Saitta et al. 2017; Chiesa et al. 2016; Lambert et al. 2012; Moret et al. 2010). However, there are very few studies in which PCB concentrations and meteorological parameters are analyzed in honeybees and bee products. The aims of this study are (i) to determine PCB concentrations in honeybees and bee products, (ii) to determine the effect of meteorological parameters on concentration changes, (iii) to compare PCB concentrations between urban and semi-urban areas, and (iv) to assess similarities or differences between pollutant concentrations and sources and temporal variation by using the coefficient of divergence (COD) and Pearson correlation coefficient (PCC) methods.

Materials and methods

Overview of the study areas and sampling program

Bursa is one of the most important industrial cities in Turkey, located between 40° 11′ 34″–40°3 7′ 96″ N and 28° 70′ 07″–29° 30′ 82″ E. The Ovaakca and Cumalikizik regions, which are the sampling areas, represent urban and semi-urban areas, respectively. The urban area is located in a region where traffic and industry are concentrated due to its proximity to the Bursa-Ankara ring road (1.5 km) and Demirtas Organized Industrial Area (3 km), which has 428 active enterprises. The semi-urban area is located 3 km from the settlement and approximately 5 km from the nearest highway (Fig. 1).

Honeybee and pollen samples were collected from two urban and semi-urban sampling areas between May and September 2017 (beekeeping period) by two volunteer beekeepers. Honey samples were collected between July and September in 2017 when the flow of honey was intense. All the samples were taken each 2 weeks. Samples of honeybee and pollen were taken homogeneously from all hives to represent all areas. In order to avoid any contamination during the carriage of the samples, they were wrapped in aluminum foil, placed in sealed pouches and taken to the laboratory in bags with ice molds. Samples contained in the sealed pouches were transported without contact with air and held at − 20 °C in the deep freeze until their analysis.

Sample preparation and analysis

Extraction

Approximately 2 g of the honeybee and 2 g of the pollen samples were crushed into two separate glass bottles. Fifty-milliliter petroleum ether:dichloromethane (PE:DCM) (1:1 v:v) solution was added to the crushed honeybee and pollen samples. Then, 1 mL of the surrogate standard (PCB#14, PCB#65, and PCB#166) was added to calculate the recovery efficiencies (Odabasi et al. 2015). The prepared samples were left in the shaker for 2 h. Next, the samples from the shaker were subjected to ultrasonic extraction (Elmasonic S 80 H Model, Germany) for 15 min. After taking the extract from the samples, 40 mL of a hexane:acetone (HEX:ACE) (1:1 v:v) solution was added and subjected to ultrasonic extraction for 30 min (Ozgunerge Falay et al. 2013).

One gram of honey sample was taken into the small glass beaker and 10 mL of pure water was added and mixed thoroughly (Lambert et al. 2012). The dissolved honey sample was poured into the separating funnel and 50 mL of methanol (MeOH), 50 mL of saturated salt solution, 50 mL of pure water, 40 mL of DCM solution, and 1 mL of the surrogate standard were added, respectively (Esen et al. 2010). The extraction was conducted with third times section of 40 mL DCM (40 mL of DCM was used in each step). Then, all samples were handled by liquid-liquid extraction (immediately) (Lambert et al. 2012). Finally, the solvents were passed through a column containing 25 g of sodium sulfate (Na_2SO_4) and filtered.

Cleanup

After the extraction, the sample volumes were reduced to 5 mL with the help of a rotary evaporator (Laborota 4001-Heidolph, Germany) at a speed of about 30 rpm. After adding 15 mL of HEX to the samples reduced to 5 mL, the volumes

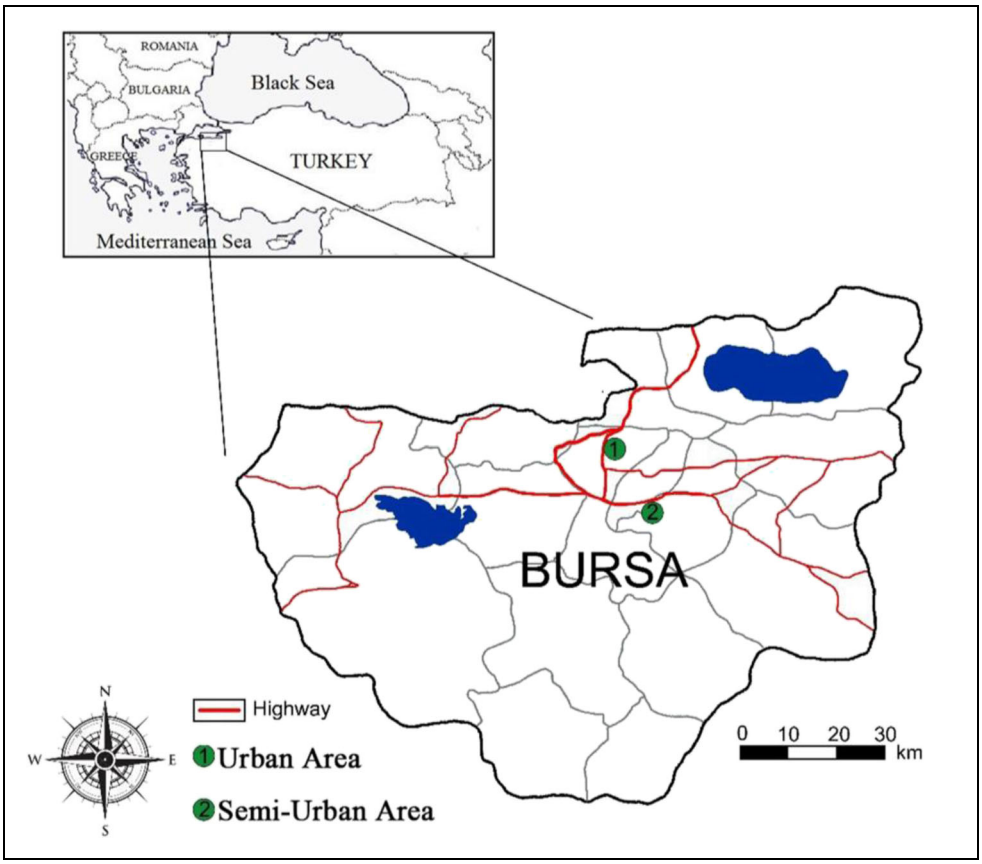

Fig. 1 Sampling area

were reduced to 2 mL (Tasdemir and Esen 2007). Then, the samples were passed through a gel permeation chromatography column (GPC) for final cleaning. At least 30 mL of HEX:DCM (1:1 v:v) was passed through the columns, before the GPC procedure was applied, to clean the columns. When 1 mL of solvent was left on the media in the column, the sample was dropped on the sample media using a pasteur pipette. As soon as the media absorbed the sample, it was passed through a 15-mL HEX:DCM (1:1 v:v) column and collected in a beaker. Then, 35 mL of solvent was added to the column and all the extracts were collected in the flask. The collected 35 mL solvent was reduced to 2 mL with a rotary evaporator.

Reduced volume samples were then passed through a cleaning column containing 3 g of silicic acid (3% pure water), 2 g of alumina (6% pure water), and 2 g of Na_2SO_4 (Tasdemir et al. 2005; Esen et al. 2008; Esen et al. 2010). The column was first purged with 20 mL of DCM followed by 20 mL of PE. Then, 25 mL of PE was added and the PCB samples were collected. The volume of the PCB samples was reduced to 2 mL by changing the solvent to HEX (Günindi and Tasdemir 2010). To protect the chromatographic peaks from any contamination, the 2 mL sample was cleaned with concentrated H_2SO_4 and the volume was reduced to 1 mL (Cindoruk et al. 2007).

Instrumental analysis

Field blanks with a ratio of at least 10% of the samples were collected in order to determine possible contamination during the transportation, storage, and preparation of the samples. Mass values of honeybee and bee product samples and blank samples were determined by HP 7890A-μECD (microelectron capture detector) instrument. The oven temperature program was 70 °C (2 min), with increases of 25 °C min^{-1} to 150 °C, followed by 3 °C min^{-1} up to 200 °C, then 8 °C min^{-1} up to 280 °C (8 min), then 10 °C min^{-1} up to 300 °C (2 min). The injector inlet temperature was 250 °C and the detector temperature was 320 °C. Helium gas was used as the carrier gas at a flow rate of 1.9 mL min^{-1} and high purity nitrogen gas was used as the make-up gas with helium gas. An HP-5 capillary column with dimensions of 30 m × 0.32 mm × 0.25 μm was used during the measurement. Forty-six PCB congeners discussed in this study include the following: PCB #6, 8/5, 19, 15/17, 16/32, 26, 31, 21, 22, 45, 44, 37/42, 100, 74, 61/70, 66/95, 91, 99,

119, 86, 85, 135/144, 118, 123, 131, 138/163, 128, 167, 174, 156/171/202, 172, 180, 200, 169, 207, and 206.

Meteorological parameters and software package

The meteorological parameters of the measurement stations were obtained from the National Oceanic and Atmospheric Administration (NOAA). The meteorological parameters consisted of the mean sea level pressure (hPA), 2-m temperature (°C), 2-m relative humidity (%), total cloudiness (%), wind direction (°), and wind speed (m s^{-1}). In this study, Pearson correlation analysis was done with the Statistical Package for the Social Sciences® (SPSS) version 23.0 and figures were created in the SigmaPlot® version 13.0. The meteorological parameters discussed during the sampling period are summarized in Table 1.

Quality assurance/quality control

The GC-μECD was calibrated before determining the mass values of the samples. Six levels of calibration standards (1.0, 2.5, 5.0, 10.0, 25.0, and 40.0 ng mL^{-1}) were used to calibrate the device. For all calibration levels, the r^2 value was > 0.99. In addition, a medium-level calibration standard (5.0 or 10.0 ng mL^{-1}) was read in every 25 samples and the calibration requirement of the GC-μECD was determined. In this study, sensitivity and intermediate precision were evaluated by relative standard deviation (RSD) values. RDS values obtained in this study ranged from 0.18 to 1.94% (1.20 ± 0.49). Samples with recovery efficiencies between 40 and 120% were taken into account in the calculations. For the determination of the analytical recovery efficiencies of the samples, a surrogate standard consisting of PCB#14 (3,5-dichlorobiphenyl), PCB#65 (2,3,4,5,6-tetrachlorobiphenyl), and PCB#166 (2,3,4,4′,5,6-hexachlorobiphenyl) at a concentration of 4 ng mL^{-1} was added to the extraction. The average recovery efficiencies (average ± S.D.) throughout the measurement period for PCB#14, PCB#65, and PCB#166 were 71.44 ± 30.17, 66.10 ± 8.99, and 68.94 ± 5.03 for honeybee samples; 72.24 ± 34.86, 75.17 ± 8.47, and 82.92 ± 12.78 for pollen samples; and 73.15 ± 21.12, 76.34 ± 20.22, and 83.53 ± 26.01 for honey samples, respectively.

The limit of detection (LOD) values were calculated for each measured congener as the average mass of blanks plus three times the standard deviation (average + 3.S.D.) (Esen and Kayikci 2018). LOD values obtained in this study were calculated ranged from < 0.001 to 2.534 ng. PCB congeners under the LODs were not included in the calculation (Günindi and Tasdemir 2010). Limit of quantitation (LOQ) values were calculated for each measured PCB as an average mass in blank plus ten times the standard deviation (average + 10.S.D) (Orecchio 2011). LOQ values were calculated ranged from < 0.001 to 7.387 ng. In order to minimize the effects of possible contamination on the concentration values, the mean of the blank was removed from the sample values and the blank correction was applied.

Result and discussion

Honeybee, pollen, and honey concentrations

Samples were taken from urban and semi-urban areas in Bursa to determine the total PCB concentration values in the honeybee, pollen, and honey. Honeybee and pollen samples were taken between May and September 2017 and honey samples were taken between July and September 2017, when the honey flow was high.

The total concentrations of 46 PCB congeners ($\sum_{46}$PCBs) were found to be between 130.25 and 143.22 ng g^{-1} dw (135.46 ± 6.53; average ± S.D.) for urban area honeybee and between 93.31 and 166.91 ng g^{-1} dw (126.35 ± 26.54) for semi-urban honeybee (Fig. 2). The PCB concentrations in honeybee samples from both sampling areas showed the highest concentration levels in July and the lowest concentration levels in May. PCB concentrations in honeybees from the semi-urban area did not show homogeneous distribution, while PCB concentrations in honeybees from the urban area generally showed a homogeneous distribution.

In the study conducted by Drummond et al. (2017), they determined the behavioral effects of traffic-related emissions on honeybees with Aroclor 1254 (PCB mixture). In that study, they reported that the honeybees exposed to Aroclor 1254 (100 ng mL^{-1}) attempted to fly about seven times more than the honeybees exposed to traffic emissions (Drummond et al. 2017). Since the urban sampling area represents an area where traffic is dense, it is thought that honeybees in this area tend to fly less than honeybees in the semi-urban area. Therefore, they will be in contact with fewer contaminants and homogeneous distribution throughout the months will be observed. The

Table 1 Summary of meteorological parameters from sampling areas

	SLP (hPa)	T (°C)	RH (%)	TC (%)	WD (°)	WS (m s^{-1})
Urban	1013.34	19.82	64.17	24.85	123.98	2.86
Semi-urban	1013.21	19.40	63.82	25.21	131.34	2.66

SLP sea level pressure, *T* average 2-m temperature, *RH* average 2-m relative humidity, *TC* total cloudiness, *WD* wind direction, *WS* wind speed

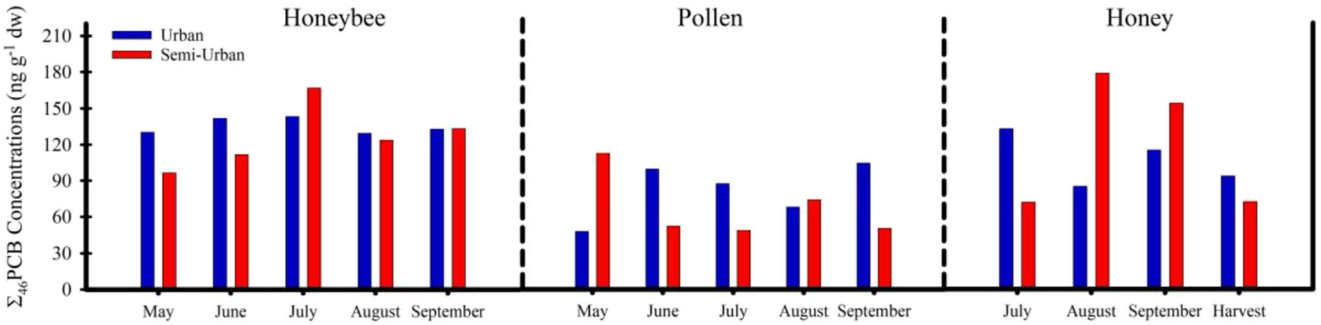

Fig. 2 Honeybee, pollen, and honey concentrations during the measurement period

highest PCB concentrations for both areas were in July. Honeybees are in direct contact with plants and ambient air, and then they tend to be affected by PCB concentrations in ambient air. This is also consistent with the fact of evaporation of PCBs and other POPs during hot seasons (Kim and Masunaga 2005; Hogarh et al. 2013).

The average $\sum_{46}$PCB concentration measured in the pollen from the urban area was between 47.81 and 104.67 ng g^{-1} dw (81.47 ± 23.52), and in the semi-urban area, between 48.59 and 112.86 ng g^{-1} dw (67.57 ± 27.34). There was no significant difference between the average PCB concentration measured in pollen from the urban and semi-urban areas. PCB residues are not taken up by plants grown in contaminated soils due to the low solubility of POPs in water such as PCBs. On the other hand, PCBs can be deposited on the surface of the leaves. However, depending on the meteorological events such as temperature, rain, and wind, POPs will leave the leaf layer. Therefore, low pollutant levels can be observed in pollen (Sanchez-Bayo and Goka 2016; Tavera Busso et al. 2018). Pollen concentrations decrease and honeybee concentrations increase in the summer months (Fig. 2). In this case, PCBs evaporate from the soil in hot months which increases the PCB concentrations in the ambient air and, consequently, the adsorption of them by bees during scavenging.

The average $\sum_{46}$PCB concentration measured in the honey from the urban area was between 84.76 and 132.56 ng g^{-1} dw (106.35 ± 21.60), and in the semi-urban area, between 71.57 and 178.36 ng g^{-1} dw (118.88 ± 55.28) (Fig. 2). In a study conducted by Erdogrul (2007), an average of a total of 7 PCB ($\sum_{7}$PCB) concentration in honey samples in Turkey was 1.48 ± 1.12 ng g^{-1}. Lower PCB concentrations obtained in the study conducted by Erdogrul (2007) were probably caused by filtering honey samples before the extraction. Similarly, Roszko et al. (2016) reported an average of total PCB ($\sum_{6}$PCB) concentration in honey samples were as 194.3 ± 79.1 pg g^{-1}. Furthermore, the differences between the concentration values are also originated by the fluctuations among the number of PCB congeners considered. Similar to the pollen samples, there was no significant difference in the average PCB concentrations in honey samples measured in both regions. In a study by Chiesa et al. (2016), they found a non-significant difference between the PCB concentrations obtained from the honey samples taken from three different regions, and the sample origin was not a relevant factor of the PCB contamination in honey (Chiesa et al. 2016). When the three sampling media were taken into consideration, the highest concentration levels for both regions were found in honeybees, then honey and pollen, respectively. High concentration levels in the honeybees are due to their hairy body that makes them easily keep the pollutants in their bodies (Lambert et al. 2012).

Correlation between meteorological parameters and pollutant concentrations

Meteorological parameters such as pressure, temperature, relative humidity, wind direction, and wind speed can affect the chemical reactions in the atmosphere and, consequently, change the pollutant concentrations (Bahrami Asl et al. 2018). The relationship between meteorological parameters and the PCB concentrations measured in the honeybee, pollen, and honey media was calculated by using the Pearson correlation method for the urban and semi-urban areas. The *R* values obtained as a result of the calculation are shown in Table 2.

In cases where there was a positive correlation between the sample media and temperature values, strong convection and unstable atmospheric conditions were effective (Lorga et al. 2015) and in case of negative correlation, other meteorological parameters such as relative humidity, pressure, or wind speeds were effective (Barbas et al. 2018). In cases where there was a positive or negative correlation between sample media and temperature, the pressure, relative humidity, and total cloudiness were inversely correlated to the temperature. In this case, meteorological parameters such as pressure, relative humidity, and total cloudiness were more effective in the distribution of PCB concentrations measured in pollen and honey samples in the semi-urban region.

Table 2 Results of the Pearson correlation coefficient between meteorological parameters and sample media

	Urban area			Semi-urban area		
	Honeybee	Pollen	Honey	Honeybee	Pollen	Honey
Sea level pressure (hPa)	− 0.59	− 0.03	− 0.31	− 0.67	0.23	0.56
Temperature (°C)	0.37	0.63	0.24	0.82*	− 0.83*	− 0.62
Relative humidity (%)	− 0.28	− 0.78	− 0.61	− 0.57	0.63	0.21
Total cloudiness (%)	− 0.44	− 0.67	− 0.79	− 0.88*	0.88*	0.80
Wind direction (°)	0.27	0.38	0.45	− 0.50	− 0.02	0.06
Wind speed (m s^{-1})	− 0.11	− 0.77	− 0.01	0.27	0.44	− 0.38

*The significance level at 95%

When the correlation between wind speeds and directions and sample media were analyzed, all the samples, with the exception of pollen samples in the urban area, showed generally low correlation levels ($-0.5 \le R \le 0.5$) (Table 2). Negative correlation with wind speed indicates that the turbulence in the atmosphere showed the expected dilution effect on pollutant concentrations (Harrad and Mao 2004), whereas a positive correlation means that flux events had a significant effect on pollutant concentrations (Huang et al. 2014). Where there was a positive correlation between wind speed and sample media, there was a negative correlation between sample media and wind direction. In this case, honeybee and pollen media in the semi-urban area were highly influenced by atmospheric flux events.

Divergence and correlation analysis

The coefficient of divergence (COD) is a statistical approach used to assess similarities or differences between pollutant concentrations and sources between two areas (Liu et al. 2017; Bano et al. 2018). Another statistical approach method used to determine the relationship between the two areas is the Pearson correlation coefficient (PCC) (Bano et al. 2018). PCC and COD were calculated as follows:

$$\mathrm{PCC}_{jk} = \frac{\sum_{i=1}^{p} \left(x_{ij} - x_j\right) x \left(x_{ik} - x_k\right)}{\sqrt{\sum_{i=1}^{p} \left(x_{ij} - x_j\right)^2 x \sum_{i=1}^{p} \left(x_{ik} - x_k\right)^2}} \quad (1)$$

$$\mathrm{COD}_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^{p} \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}}\right)^2} \quad (2)$$

where ij and ik refer to the average concentration of ith PCB congeners for the urban and semi-urban areas, respectively; $\bar{x}$ is the average concentration at sites; and p is the number of individual PCB congeners (Chuang et al. 2019; Bano et al. 2018; Liu et al. 2017; Yadav and Turner 2014).

PCC and COD values can be used together or separately to understand temporal and spatial changes in pollutant concentrations (Yadav and Turner 2014). COD values close to "0" indicate that the emission sources are similar, whereas COD values close to "1" indicate that there is a difference for the two areas (Li et al. 2019). In general, COD values less than 0.2 indicate that the emission sources between the two regions are

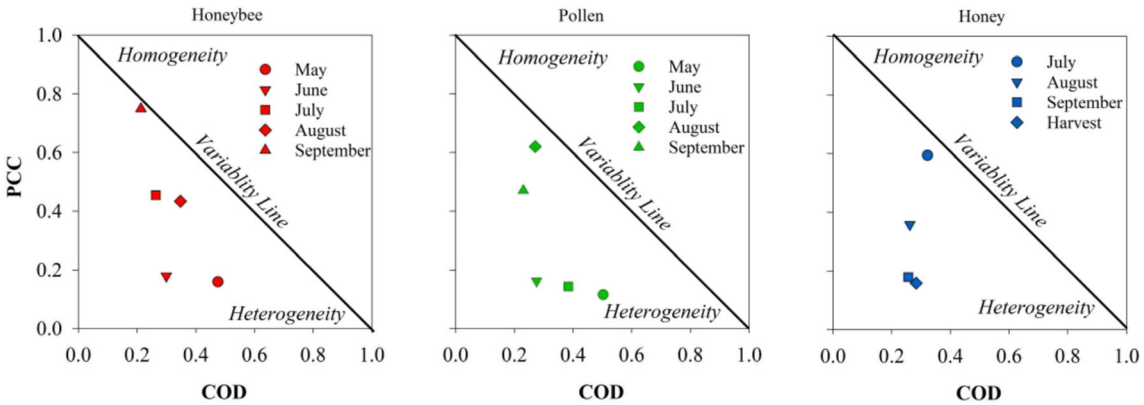

Fig. 3 Pearson correlation coefficient (PCC) plotted against the coefficients of the divergence (COD) for the honeybee, pollen, and honey

similar (Chuang et al. 2019; Li et al. 2019; Sun et al. 2019). In some studies, values of 0.269 are used as indicator values (Liu et al. 2017). However, high PCC (> 0.7) and low COD (< 0.2) values indicate that the two regions have similar temporal variation and pollutant sources (Liu et al. 2017). In this study, PCC and COD results obtained for honeybee and bee products in urban and semi-urban areas are shown in Fig. 3.

When the COD values calculated for honeybee samples were taken into consideration, it was seen that the lowest value was in September (0.213) and the highest value was in May (0.475). The lowest PCC results were in May (0.160) and the highest were in September (0.749). The high PCC and low COD values calculated in September show that the temporal changes of the two regions with the pollutant concentrations are homogeneous, and the calculated lower PCC values with the calculated high COD in May show that there were heterogeneity differences between the temporal changes of the two regions and the pollutant concentrations. Air temperature is known to have a significant effect on the flying activity of bees (Kasper et al. 2008; Switanek et al. 2017). It is thought that honeybees decrease their flying activity in low air temperatures and consequently, that they are less contaminated with pollutants (Kasper et al. 2008); for this reason, the COD value was low and PCC value was high in September.

The lowest COD values measured in pollen samples were observed in September (0.230) and the highest values in May (0.503), while the lowest PCC values were observed in May (0.116) and the highest values in August (0.620). In May, high PCC and low COD values were found in pollen samples as well as honeybee samples. Depending on this situation, it was concluded that both honeybee and pollen samples were affected more from local sources in May.

The lowest PCC values measured in honey samples were observed in September (0.159) (harvest honey) and the highest in July (0.594), while no significant change was observed in COD values. The COD and PCC values determined in honey media did not change significantly during the measurement period. However, since the determined COD values were > 0.2, it is thought that honey samples were affected by local sources.

Conclusion

PCB concentrations in the honeybee, pollen, and honey were investigated in urban and semi-urban areas in Bursa. The highest average total PCB concentrations during the measurement period were in honeybees. High concentration levels in honeybees are due to their hairy body and their capacity to easily keep the pollutants in their bodies. The urban area was in a zone where traffic was very dense, which reduced the flying activities of the bees. Consequently, the concentration of honeybees measured in the urban area was shown to be homogeneous throughout the measurement period, and the impact of traffic emissions in this region was high. The lowest average total PCB concentrations during the measurement period were in pollen from the two sampling areas. A similarity was observed between pollen concentrations in urban and semi-urban areas. This is due to the low water solubility of the PCBs, which prevents soil contaminated by PCB from transmitting these pollutants to plants, resulting consequently in the low concentrations of PCB in pollen. Similar to the pollen samples, there was no significant difference in the average PCB concentrations in honey samples measured in both areas. When the three sampling media were taken into consideration, the highest concentration levels for both regions were found in honeybees, then honey, and pollen, respectively.

The Pearson correlation method was applied to determine the relationship between meteorological parameters and pollutant concentrations. No correlation was found between the honeybee, pollen, and honey samples and the meteorological parameters measured in the urban area as a result of the correlation. On the contrary, a significant relationship was found ($p < 0.05$) between the temperature and total cloudiness and the samples of honeybee and pollen measured in the semi-urban area. According to this result, meteorological parameters did not have a significant effect on the pollutant concentrations measured in the urban area.

The COD and PCC statistical methods were used to determine the relationship between the PCB concentrations and sources measured in the urban and semi-urban areas. According to these two methods, we concluded that in urban and semi-urban areas, honeybee and pollen samples measured in May were more affected by local sources and that the pollutant concentrations and sources between the two areas were homogenous in September. Finally, we found that high COD values were determined in honey samples and that the samples in both areas were affected by local sources.

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References

Abella V, Pérez T, Scotece M, Conde J, Pirozzi C, Pino J, Lago F, González-Gay MÁ, Mera A, Gómez R, Gualillo O (2016) Pollutants make rheumatic diseases worse: facts on polychlorinated biphenyls (PCBs) exposure and rheumatic diseases. Life Sci 157: 140–144. https://doi.org/10.1016/j.lfs.2016.06.010

Al-Waili N, Salom K, Al-Ghamdi A, Ansari MJ (2012, 2012) Antibiotic, pesticide, and microbial contaminants of honey: human health hazards. Sci World J. https://doi.org/10.1100/2012/930849

Amores-Arrocha A, Roldán A, Jiménez-Cantizano A, Caro I, Palacios V (2018) Evaluation of the use of multiflora bee pollen on the volatile compounds and sensorial profile of Palomino fino and Riesling white young wines. Food Res Int 105:197–209. https://doi.org/10.1016/j.foodres.2017.11.013

Ares AM, Valverde S, Bernal JL, Nozal MJ, Bernal J (2018) Extraction and determination of bioactive compounds from bee pollen. J Pharm Biomed Anal 147:110–124. https://doi.org/10.1016/j.jpba.2017.08.009

Badolato M, Carullo G, Cione E, Aiello F, Caroleo MC (2017) From the hive: honey, a novel weapon against cancer. Eur J Med Chem 142: 290–299. https://doi.org/10.1016/j.ejmech.2017.07.064

Bahrami Asl F, Leili M, Vaziri Y, Salahshour Arian S, Cristaldi A, Oliveri Conti G, Ferrante M (2018) Health impacts quantification of ambient air pollutants using AirQ model approach in Hamadan, Iran. Environ Res 161:114–121. https://doi.org/10.1016/j.envres.2017.10.050

Bano S, Pervez S, Chow JC, Matawle JL, Watson JG, Sahu RK, Srivastava A, Tiwari S, Pervez YF, Deb MK (2018) Coarse particle (PM10–2.5) source profiles for emissions from domestic cooking and industrial process in Central India. Sci Total Environ 627:1137–1145. https://doi.org/10.1016/j.scitotenv.2018.01.289

Barbas B, de la Torre A, Sanz P, Navarro I, Artíñano B, Martínez MA (2018) Gas/particle partitioning and particle size distribution of PCDD/Fs and PCBs in urban ambient air. Sci Total Environ 624: 170–179. https://doi.org/10.1016/j.scitotenv.2017.12.114

Benuszak J, Laurent M, Chauzat MP (2017) The exposure of honey bees (Apis mellifera; Hymenoptera: Apidae) to pesticides: room for improvement in research. Sci Total Environ 587–588:423–438. https://doi.org/10.1016/j.scitotenv.2017.02.062

Bogdanov S (2006) Contaminants of bee product. Apidologie 37:1–18. https://doi.org/10.1051/apido

Bromenshenk et al (1991) Le rappor t à l'eau et à la terre dans la construction de territoires multisitués : le cas palestinien. Espac Geogr 22:359–369. https://doi.org/10.1051/apido

Chiesa LM, Labella GF, Giorgi A, Panseri S, Pavlovic R, Bonacci S, Arioli F (2016) The occurrence of pesticides and persistent organic pollutants in Italian organic honeys from different productive areas in relation to potential environmental pollution. Chemosphere 154: 482–490. https://doi.org/10.1016/j.chemosphere.2016.04.004

Chuang H-C, Sun J, Ni H, Tian J, Lui KH, Han Y, Cao J, Huang R-J, Shen Z, Ho K-F (2019) Characterization of the chemical components and bioreactivity of fine particulate matter produced during crop-residue burning in China. Environ Pollut 245:226–234. https://doi.org/10.1016/j.envpol.2018.10.119

Cindoruk SS, Esen F, Tasdemir Y (2007) Concentration and gas/particle partitioning of polychlorinated biphenyls (PCBs) at an industrial site at Bursa, Turkey. Atmos Res 85:338–350. https://doi.org/10.1016/j.atmosres.2007.02.004

Da Silva PM, Gauche C, Gonzaga LV, Costa ACO, Fett R (2016) Honey: chemical composition, stability and authenticity. Food Chem 196: 309–323. https://doi.org/10.1016/j.foodchem.2015.09.051

David A, Botías C, Abdul-Sada A, Nicholls E, Rotheray EL, Hill EM, Goulson D (2016) Widespread contamination of wildflower and bee-collected pollen with complex mixtures of neonicotinoids and fungicides commonly applied to crops. Environ Int 88:169–178. https://doi.org/10.1016/j.envint.2015.12.011

de Oliveira RC, Queiroz SC d N, da Luz CFP, Porto RS, Rath S (2016) Bee pollen as a bioindicator of environmental pesticide contamination. Chemosphere 163:525–534. https://doi.org/10.1016/j.chemosphere.2016.08.022

Di Bella G, Lo Turco V, Potortì AG, Bua GD, Fede MR, Dugo G (2015) Geographical discrimination of Italian honey by multi-element analysis with a chemometric approach. J Food Compos Anal 44:25–35. https://doi.org/10.1016/j.jfca.2015.05.003

Drummond J, Williamson SM, Fitchett AE, Wright GA, Judge SJ (2017) Spontaneous honeybee behaviour is altered by persistent organic pollutants. Ecotoxicology 26:141–150. https://doi.org/10.1007/s10646-016-1749-0

Erdogrul O (2007) Levels of selected pesticides in honey samples from Kahramanmaraş, Turkey. Food Control 18:866–871. https://doi.org/10.1016/j.foodcont.2006.05.001

Esen F, Kayikci G (2018) Polycyclic aromatic hydrocarbons in indoor and outdoor air in Turkey: estimations of sources and exposure, environ. Forensics 19(1):39–49. https://doi.org/10.1080/15275922.2017.1408162

Esen F, Tasdemir Y, Vardar N (2008) Atmospheric concentrations of PAHs, their possible sources and gas-to-particle partitioning at a residential site of Bursa, Turkey. Atmos Res 88:243–255. https://doi.org/10.1016/j.atmosres.2007.11.022

Esen F, Tasdemir Y, Cindoruk SS (2010) Dry deposition, concentration and gas/particle partitioning of atmospheric carbazole. Atmos Res 95:379–385. https://doi.org/10.1016/j.atmosres.2009.10.010

Günindi M, Tasdemir Y (2010) Atmospheric polychlorinated biphenyl (pcb) inputs to a coastal city near the marmara sea. Mar Pollut Bull 60:2242–2250. https://doi.org/10.1016/j.marpolbul.2010.08.012

Hakme E, Lozano A, Gómez-Ramos MM, Hernando MD, Fernández-Alba AR (2017) Non-target evaluation of contaminants in honey bees and pollen samples by gas chromatography time-of-flight mass spectrometry. Chemosphere 184:1310–1319. https://doi.org/10.1016/j.chemosphere.2017.06.089

Harrad S, Mao H (2004) Atmospheric PCBs and organochlorine pesticides in Birmingham, UK: concentrations, sources, temporal and seasonal trends. Atmos Environ 38:1437–1445. https://doi.org/10.1016/j.atmosenv.2003.12.002

Hogarh JN, Seike N, Kobara Y, Masunaga S (2013) Seasonal variation of atmospheric polychlorinated biphenyls and polychlorinated naphthalenes in Japan. Atmos Environ 80:275–280. https://doi.org/10.1016/j.atmosenv.2013.07.076

Huang RJ, Zhang Y, Bozzetti C, Ho KF, Cao JJ, Han Y, Daellenbach KR, Slowik JG, Platt SM, Canonaco F, Zotter P, Wolf R, Pieber SM, Bruns EA, Crippa M, Ciarelli G, Piazzalunga A, Schwikowski M, Abbaszade G, Schnelle-Kreis J, Zimmermann R, An Z, Szidat S, Baltensperger U, El Haddad I, Prévôt ASH (2014) High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514:218–222. https://doi.org/10.1038/nature13774

Human H, Nicolson SW (2006) Nutritional content of fresh, bee-collected and stored pollen of Aloe greatheadii var. davyana (Asphodelaceae). Phytochemistry 67:1486–1492. https://doi.org/10.1016/j.phytochem.2006.05.023

Jankovic S, Djinovic-Stojanovic J, Stefanovic S, Radicevic T, Curcic M, Nikolic D, Spiric D (2015) ScienceDirect non-dioxin like polychlorinated biphenyls in mackerel (Scomber scombrus) available on the Serbian market. Procedia Food Sci 5:113–116. https://doi.org/10.1016/j.profoo.2015.09.031

Kargar N, Matin G, Matin AA, Buyukisik HB (2017) Biomonitoring, status and source risk assessment of polycyclic aromatic hydrocarbons (PAHs) using honeybees, pine tree leaves, and propolis. Chemosphere 186:140–150. https://doi.org/10.1016/j.chemosphere.2017.07.127

Kasper ML, Reeson AF, MacKay DA, Austin AD (2008) Environmental factors influencing daily foraging activity of Vespula germanica (Hymenoptera, Vespidae) in Mediterranean Australia. Insect Soc 55:288–295. https://doi.org/10.1007/s00040-008-1004-7

Kim KS, Masunaga S (2005) Behavior and source characteristic of PCBS in urban ambient air of Yokohama, Japan. Environ Pollut 138:290–298. https://doi.org/10.1016/j.envpol.2005.03.011

Lambert O, Veyrand B, Durand S, Marchand P, Le Bizec B, Piroux M, Puyo S, Thorin C, Delbac F, Pouliquen H (2012) Polycyclic aromatic hydrocarbons: bees, honey and pollen as sentinels for

environmental chemical contaminants. Chemosphere 86:98–104. https://doi.org/10.1016/j.chemosphere.2011.09.025

Li H, Wang D, Cui L, Gao Y, Huo J, Wang X, Zhang Z, Tan Y, Huang Y, Cao J, Chow JC, Lee S c, Fu Q (2019) Characteristics of atmospheric PM2.5 composition during the implementation of stringent pollution control measures in shanghai for the 2016 G20 summit. Sci Total Environ 648:1121–1129. https://doi.org/10.1016/j.scitotenv.2018.08.219

Liu Y, Yan C, Ding X, Wang X, Fu Q, Zhao Q, Zhang Y, Duan Y, Qiu X, Zheng M (2017) Sources and spatial distribution of particulate polycyclic aromatic hydrocarbons in Shanghai, China. Sci Total Environ 584–585:307–317. https://doi.org/10.1016/j.scitotenv.2016.12.134

Lo Turco V, Di Bella G, Potortì AG, Tropea A, Casale EK, Fede MR, Dugo G (2016) Determination of plasticisers and BPA in Sicilian and Calabrian nectar honeys by selected ion monitoring GC/MS. Food Addit Contam - Part A Chem Anal Control Expo Risk Assess 33:1693–1699. https://doi.org/10.1080/19440049.2016.1239030

Lorga G, Balaceanu Raicu C, Stefan S (2015) Annual air pollution level of major primary pollutants in Greater Area of Bucharest. Atmos Pollut Res 6:824–834. https://doi.org/10.5094/APR.2015.091

Moret S, Purcaro G, Conte LS (2010) Polycyclic aromatic hydrocarbons (PAHs) levels in propolis and propolis-based dietary supplements from the Italian market. Food Chem 122:333–338. https://doi.org/10.1016/j.foodchem.2010.02.041

Nisbet C, Guler A, Yarim GF, Cenesiz S, Ardali Y (2013) Relationship between environmental and flora change with mineral content of honey bee products. Turkish J Biochem 38:494–498. https://doi.org/10.5505/tjb.2013.07269

Odabasi M, Ozgunerge Falay E, Tuna G, Altiok H, Kara M, Dumanoglu Y, Bayram A, Tolunay D, Elbir T (2015) Biomonitoring the spatial and historical variations of persistent organic pollutants (POPs) in an industrial region. Environ Sci Technol 49:2105–2114. https://doi.org/10.1021/es506316t

Orecchio S (2011) Polycyclic aromatic hydrocarbons (PAHs) in indoor emission from decorative candles. Atmos Environ 45:1888–1895. https://doi.org/10.1016/j.atmosenv.2010.12.024

Ozgunerge Falay E, Tuna G, Altiok H, Kara M, Dumanoglu Y, Bayram A, Tolunay D, Elbir T, Odabasi M (2013) Spatial variation of polycyclic aromatic hydrocarbons (PAHs) in air , soil and tree components in Iskenderun Industrial Region, Turkey. Int J Chem Environ Biol Sci 1:263–267

Putschögl FM, Gaum PM, Schettgen T, Kraus T, Gube M, Lang J (2015) Effects of occupational exposure to polychlorinated biphenyls on urinary metabolites of neurotransmitters: a cross-sectional and longitudinal perspective. Int J Hyg Environ Health 218:452–460. https://doi.org/10.1016/j.ijheh.2015.03.009

Rissato SR, Galhiane MS, de Almeida MV, Gerenutti M, Apon BM (2007) Multiresidue determination of pesticides in honey samples by gas chromatography-mass spectrometry and application in environmental contamination. Food Chem 101:1719–1726. https://doi.org/10.1016/j.foodchem.2005.10.034

Roszko MŁ, Kamińska M, Szymczyk K, J drzejczak R (2016) Levels of selected persistent organic pollutants (PCB, PBDE) and pesticides in honey bee pollen sampled in Poland. PLoS One 11:1–22. https://doi.org/10.1371/journal.pone.0167487

Saitta M, Di Bella G, Fede MR, Lo Turco V, Potortì AG, Rando R, Russo MT, Dugo G (2017) Gas chromatography-tandem mass spectrometry multi-residual analysis of contaminants in Italian honey samples. Food Addit Contam - Part A Chem Anal Control Expo Risk Assess 34:800–808. https://doi.org/10.1080/19440049.2017.1292054

Sanchez-Bayo F, Goka K (2016) Impacts of pesticides on honey bees. Beekeeping and Bee Conservation-Advances in Research, Chapter 4. https://doi.org/10.5772/62487

Shaban YA, El Sayed MA, El Maradny AA, Al Farawati RK, Al Zobidi MI, Khan SUM (2016, 2016) Laboratory and pilot-plant scale photocatalytic degradation of polychlorinated biphenyls in seawater using CM-n-TiO2 nanoparticles. Int J Photoenergy. https://doi.org/10.1155/2016/8471960

Sun J, Shen Z, Zhang L, Lei Y, Gong X, Zhang Q, Zhang T, Xu H, Cui S, Wang Q, Cao J, Tao J, Zhang N, Zhang R (2019) Chemical source profiles of urban fugitive dust PM2.5samples from 21 cities across China. Sci Total Environ 649:1045–1053. https://doi.org/10.1016/j.scitotenv.2018.08.374

Switanek M, Crailsheim K, Truhetz H, Brodschneider R (2017) Modelling seasonal effects of temperature and precipitation on honey bee winter mortality in a temperate climate. Sci Total Environ 579:1581–1587. https://doi.org/10.1016/j.scitotenv.2016.11.178

Tasdemir Y, Esen F (2007) Urban air PAHs: concentrations, temporal changes and gas/particle partitioning at a traffic site in Turkey. Atmos Res 84:1–12. https://doi.org/10.1016/j.atmosres.2006.04.003

Tasdemir Y, Odabasi M, Holsen TM (2005) Measurement of the vapor phase deposition of polychlorinated bipheyls (PCBs) using a water surface sampler. Atmos Environ 39:885–897. https://doi.org/10.1016/j.atmosenv.2004.10.032

Tavera Busso I, Tames F, Silva JA, Ramos S, Homem V, Ratola N, Carreras H (2018) Biomonitoring levels and trends of PAHs and synthetic musks associated with land use in urban environments. Sci Total Environ 618:93–100. https://doi.org/10.1016/j.scitotenv.2017.10.295

Yadav V, Turner J (2014) Gauging intraurban variability of ambient particulate matter arsenic and other air toxic metals from a network of monitoring sites. Atmos Environ 89:318–328. https://doi.org/10.1016/j.atmosenv.2014.02.030

Zani C, Ceretti E, Covolo L, Donato F (2017) Do polychlorinated biphenyls cause cancer? A systematic review and meta-analysis of epidemiological studies on risk of cutaneous melanoma and non-Hodgkin lymphoma. Chemosphere 183:97–106. https://doi.org/10.1016/j.chemosphere.2017.05.053

Ziegler S, Schettgen T, Beier F, Wilop S, Quinete N, Esser A, Masouleh BK, Ferreira MSV, Vankann L, Uciechowski P, Rink L, Kraus T, Brümmendorf TH, Ziegler P (2017) Accelerated telomere shortening in peripheral blood lymphocytes after occupational polychlorinated biphenyls exposure. Arch Toxicol 91:289–300. https://doi.org/10.1007/s00204-016-1725-8