DR. AMALIA SIMONETTI (Orcid ID : 0000-0003-4144-5340)

Minerals content in Basilicata region (southern Italy) honeys from areas with different anthropic impact

Running head: Minerals in Basilicata region honeys

Perna Annamaria, Grassi Giulia, Gambacorta Emilio, Simonetti Amalia[*]

School of Agricultural, Forestry, Food and Environmental Sciences, University of Basilicata, Potenza, Viale dell'Ateneo Lucano 10-85100, Italy

[*]Corresponding author: amalia.simonetti@unibas.it

Tel.:+390971 205301; Fax.+390971 205099.

Summary

The aim of this study was to examine the minerals content (toxic elements, macro-elements, and trace elements) of Basilicata region (southern Italy) honeys and compare the mineral profile of honeys classified as rural, industrial, and urban according to anthropic characteristics of geographical origin. Overall, Ca, Na, Mg, Fe, Al, Zn, and Mn were the most abundant elements detected in honeys, with average contents exceeding 1 ppm; whereas, heavy metals content was lower than the maximum limit established for honey. Statistical analysis revealed significant differences ($P<0.05$) among honeys as function of anthropic characteristics of geographical origin, with the exception for Se, Co, and Ag content. Industrial honeys were characterized by the highest Zn, Cr, Sn, Cd and Pb content, urban honeys showed the highest As, Fe, Ni, Mn, Na, Mg and Ca content, whereas rural honeys showed the highest Cu, Al, and Ba content ($P<0.05$). The findings of this study highlighted that honeys mineral profile is closely related to different content of elements in environment, which is affected by anthropogenic activities.

Introduction

Honey is a natural product of honey bees, closely linked to the territory, characterized by high concentration of sugars, water, minerals, proteins, vitamins, organic acids, flavonoids, phenolic acids and enzymes. It is strongly influenced by both natural and anthropogenic factors which vary based on its botanical and geographical origins (Perna *et al.,* 2012).

In fact, it is considered as the result of a bioaccumulation process of many metals and it plays an important role as environmental bio-indicator (Tuzen *et al.,* 2007; Rashed *et al.,* 2009; Perna *et al.,* 2014). Although honey contains 0.02-1.03% of minerals, these play a fundamental role in determining its quality. In fact, some macro (Ca, K, Mg, Na) and microminerals (Co, Cr, Cu, Fe, Mn, Ni, Se, Zn) have important functions in several biochemical processes as constituents of many bioactive compounds (Tuzen *et al.,* 2007; Perna *et al.,* 2014), whereas others (As, Cd, Hg, Pb) are considered toxic for human metabolism (Yarsan *et al.,* 2007; Altundag *et al.,* 2015).

Minerals presence and content in honey reflects the area surrounding the apiary; the foraging activity of the bees extends for about 10 km^2 and when the bees collect nectar or pollen these elements are transferred, contributing to the levels in the honey. This is why apiaries located in proximity to polluted areas can help in monitoring heavy metals from various sources. Basilicata honey production is heavily based on the availability of rural and native bush vegetation; in fact, Basilicata region is characterized by areas with different climatic characteristics and a high diversity of botanical species collected by bees. Moreover, current trend is the production of urban honey as an artisanal product; in urban environments there is an abundant presence of resources for bees, however, the close proximity to human activities influences the presence of particular trace elements and contaminants in honey. To date, several studies (Aldgini *et al.,* 2019; Hungerford *et al.,* 2020) detected in honey and its products different mineral profiles according to the anthropic characteristics of the geographical origin (urban, rural and industrial), highlighting the role of honey as indicator of anthropic impact and for quality control. Thus, the aim of this study was to examine and compare the mineral profile of honeys from Basilicata region (southern Italy) areas characterized by different anthropic impact.

Materials and Methods

Samples

During 2019, sixty honey samples were collected directly from beekeepers in different Basilicata region areas characterized by different anthropic impact (rural, industrial, and urban). In particular, 20 rural honeys were collected in agricultural and forestry areas, 20 urban honeys were collected in metropolitan areas, and 20 industrial honeys were collected in areas with manufacturing industries, such as metallurgical and chemical industries (Figure 1). Honeys samples were obtained from apiary located at a maximum distance of 5 km from the area of interest. All samples were subjected to melissopalynological analyses and classified as multifloral honeys. Two hundred and fifty grams of each honey sample were placed into clean glass bottles and stored at room temperature in the dark until analysed.

Metals analysis

Trace elements (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn, Sr, V and Zn) in honeys were analyzed in triplicate by inductively coupled plasma - mass spectrometry (ICP-QMS; Elan DRC II, Perkin-Elmer SCIEX, CT, USA) as reported by Perna *et al.* (2014), and the results were expressed as μg metal per kg honey. Minerals (Ca, Mg, and Na) were analyzed in triplicate by inductively coupled plasma – optical emission spectrometry (ICP-OES; model iCAP 6000, Thermo-Scientific, Cambridge, UK) as reported by Perna *et al.* (2012), and the results were expressed as mg metal per kg honey.

Statistical analysis

Statistical analysis was performed using the general linear model (GLM) procedure of statistical analysis system (SAS Institute, 1996) using a monofactorial model. Differences among metal content in different geographical areas were analysed using Student's t test and differences between means at the 95 % ($P < 0.05$) confidence level were considered statistically significant. A Pearson's correlation test was conducted to determine the linear correlation between the variables.

Results and discussion

Trace elements, macro-elements, and heavy metals in southern Italy honeys

In Table 1 are reported the results (mean, median, standard deviation, minimum and maximum values) of mineral content detected in 60 studied honey samples. Mineral profile included toxic elements (Al, As, Ba, Be, Cd, Pb), macro-elements (Ca, Mg, Na), and trace elements (Ag, Co, Cr, Cu, Fe, Mo, Mn, Ni, Se, Sn, Sr, V, and Zn). The findings highlighted a certain variability in elements composition of honey samples; this is due to different botanical and geographical origin, as reported by several authors (Rashed *et al.,* 2004; Fernández-Torres *et al.,* 2005; Pisani *et al.,* 2008). Ca, Na, Mg, Fe, Al, Zn, and Mn were the most abundant elements, with average contents exceeding 1 mg/kg. In particular, among macro-elements, Na content was the highest (49.15 mg/kg), followed by Ca (44.09 mg/kg), and Mg (19.30 mg/kg). Na content detected in studied honeys was in line with what found in Croatian honeys (44.04 ppm; Bilandžić *et al.*, 2017), whereas it resulted lower than that detected in Italian (96 mg/kg; Conti, 2000; Pisani *et al.,* 2008), and Malaysian honeys (358.64 mg/kg; Chua *et al.,* 2012). Na plays a key role in maintaining optimal blood pressure, kidney, nerve and muscle functions (Hall, 2003; Sobotka *et al.,* 2008). Ca content detected in studied honeys was lower than that detected in Croatian (109.24 ppm; Bilandžić *et al.*, 2017), Italian (257 mg/kg; Pisani *et al.,* 2008), Spanish (169 mg/kg; Fernández-Torres *et al.,* 2005), and Irish honeys (111 mg/kg; Downey *et al.,* 2005). The variations in the Ca content were certainly due to the different pedo-climatic characteristics of the geographical origin of honeys (Bogdanov *et al.,* 2007; Perna *et al.,* 2014). Ca is an essential mineral with important functions in the cardiac, nervous, and musculoskeletal system, it is also essential for bone and tooth formation, mineral homeostasis, as well as acting as a cofactor for many enzymes (Theobald, 2005; Huskisson *et al.,* 2007; Morgan 2008). Mg content in studied honeys ranged from 9.00 to 38.89 mg/kg (Table 1). Mg is an essential element for all living organisms: acts as a cofactor for up to 300 enzymes, most of which are involved in antioxidant reactions; it is involved in the structure of proteins, lipids and carbohydrates; Mg deficiency in humans can cause muscle spasms and cardiovascular diseases such as hypertension (Durlach *et al.*, 1998; Huskisson *et al.,* 2007). Mn values ranged from 113.06 to 9021.14 µg/kg, with a average value of 1603.06 µg/kg (Table 1). Mn, naturally present in many types of rock and soil, is an element with low toxicity and high biological function (Yazbeck, 2011). The Mn average value detected in this study was in line with what detected by Pisani *et al.* (2008) in honeys from Siena County (Italy), but it was much lower than that found in honeys from other Italian areas (about 3 mg/kg; Conti, 2000; Bontempo *et al.,* 2017), and in Australian (3.80 mg/kg; Hungerford *et al.*, 2020), Spanish (3.40 mg/kg; Fernández-Torres *et al.,* 2005), and Bengal honeys (2.27 mg/kg; Sarker *et al.,* 2015). On the contrary, Mn

content in studied honeys was higher than that found in Turkish (45.60 µg/kg; Altun *et al.,* 2017), Argentine (700 µg/kg; Conti *et al.,* 2014), and Irish honeys (40 µg/kg; Downey *et al.,* 2005). Al, third on the list of most abundant elements in the earth's crust, has a negative toxicological impact on the central nervous, skeletal and hematopoietic systems, in addition, its ions can hinder various metabolic processes due to competitive reactions with ions, as Ca, Mg, and Fe, F (Yokel *et al.,* 2008). In this study, Al content ranged from 630.26 to 3844.39 µg/kg, with a average value of 1395,73 µg/kg (Table 1); it was in line with that found by Czipa *et al*. (2015) in Croatian honeys (1.03 mg/kg), but was lower than that reported by Di Bella *et al.* (2015) in Italian honeys (5.67 mg/kg). Bees during foraging activity are exposed to Al from several sources; in addition, a further exposure to Al can be due to secondary sources, such as metal containers used for storage during harvesting and handling processes, in fact, Al contamination is usually accompanied by Cr contamination from the same source (Pisani *et al.,* 2008). Fe is an essential element for the production of red blood cells, in fact a deficiency causes anemia; moreover, it mediates electron transfer in the catalysis of enzymatic reactions which is toxic because it catalyze the conversion of hydrogen peroxide into free radicals (Andrews, 1999). Fe content in studied honeys ranged from 477.38 to 3954.53 µg/kg (Table 1). The Fe average content found in this study was lower than that detected in Italian honeys and, in particular, in Siena Country (Toscana Region) honeys (3.07 mg/kg; Pisani *et al.,* 2008) and Lazio Region honeys (4.50 mg/kg; Conti, 2000), and in French honeys (11.03 mg/kg; Devillers *et al.,* 2002); whereas, it was higher than that found in Romanian honeys (22.70 µg/kg; Oroian *et al.*, 2016). After Fe, Zn is the most abundant transition metal in organisms (NRC, 2000). It is the unique metal which arises in all enzyme tribes and is considered an antioxidant because is found in nearly 100 specific enzymes (Broadley *et al.,* 2007). Zn content varied between 503.67 and 1971.91 µg/kg, and its average content (1081.13 µg/kg) was markedly lower than that found in an our previous study on honeys from the same geographical area (Perna *et al.,* 2012), whereas was slightly lower than that detected in central Italy honeys, and in particular in Siena Country (1.82 mg/kg, Pisani *et al.,* 2008) and Lazio Region honeys (3.1 mg/kg; Conti, 2000). Zn is an essential element for humans, but high levels in the diet can cause anemia and decreased of Cu and Fe absorption (Roohani *et al.,* 2013). Overall, the trace elements content detected in studied honeys was very low and the value was comparable to content found in honeys from uncontaminated areas (Tuzen *et al.,* 2007). Cu is one trace heavy element essential for life; its Recommended Dietary Allowance (RDA) for adult is 1.0 mg/day, whereas the Provisional Maximum Tolerable Daily Intake (PMTDI) is 0.5 mg/ kg of body weight, an excess of Cu can

cause disease of Wilson (WHO, 1982). The Cu average content detected in studied honeys (236.65 µg/kg) was higher compared to found in Turkish honeys (68.50 µg/kg; Altun *et al.,* 2017), whereas it was lower than that detected in Argentine honeys (Conti *et al.,* 2014). Co value ranged between 0.82 and 14.99 µg/kg; it is an integral part of vitamin B12 and is therefore essential for the functioning of the cell (Yamada, 2013). In this study, Ni content (32.89 µg/kg) was markedly lower than that found in Turkish honeys (Yücel & Sultanoglu, 2013). At low concentrations Ni is necessary for plants, however at high concentrations it is toxic (Seenivasan *et al.,* 2008). Se is an important micronutrient, in particular for immune system and thyroid function, it also plays an essential role in antioxidant metabolism (Triggiani *et al.*, 2009). Se average content detected in our honey samples (3.21 µg/kg) was much lower than that found in Argentine honeys (10 µg/kg; Conti *et al.,* 2014). Cr content detected in our honeys varied from 7.00 to 28.66 µg/kg, with an average value (17.57 µg/kg) markedly lower than that found in an our previous study in honeys from the same geographical area (0.71 mg/kg; Perna *et al.*, 2014), by Conti & Botrè (2001) in Italian honeys, and by Lanjwani & Channa (2019) in Pakistan honeys. Chromium plays a fundamental role in the metabolic processes of sugars and fats (Chowdhury *et al.,* 2003). In the literature there are few data on the Mo, Ag, Ba, Be, Sn, and V concentration in honey; however, the contents detected in this study were lower than that found in Australian (Hungerford *et al.,* 2020) and in Greece honeys (Karabagias *et al.,* 2017a,b). Pb, Cd, and As are highly toxic elements and their presence in honey indicates environmental pollution (Bogdanov *et al.,* 2007). As content found in the studied honeys ranged between 0.40 and 2.05 µg/kg, and the average value (0.96 µg/kg) was markedly lower than that detected in multifloral Italian honeys (6.95 mg/kg; Pisani *et al.,* 2008), monofloral Hungary honeys (5.22–22.8 mg/kg; Czipa *et al.,* 2015), and monofloral New Zealand honeys (0.04 mg/kg; Vanhanen *et al.,* 2011). Pb concentration in the studied honeys ranged from 3.40 to 24.08 ppb, showing an average value (11.07 ppb) much lower than the maximum limit (0.1 µg/kg) established by the EC Reg. 2015/1005. Moreover, the Pb average content was lower than that found in Mediterranean honeys (Tuzen *et al.,* 2007; Silici *et al.,* 2008; Yucel & Sultanoglu, 2013). Cd content found in this study in honeys varied between 0.40 and 9.36 µg/kg (Table 1), with an average content (3.31 µg/kg) lower than that found in honeys collected in different Italian areas (Conti *et al.*, 2018 ; Perna *et al.,* 2012; Quinto *et al.,* 2016), and clearly lower than that reported for honeys collected in six continents (Solayman *et al.,* 2016). Furthermore, Pb and Cd content detected in this study were markedly lower than those found in an our previous study in the same area (Basilicata region, 0.25 mg/kg; Perna *et al.,* 2014); this could be explained by the

use of automotive engine catalysts over the past 10 years. Pearson's correlation analysis was applied to examine the relationship between metal concentrations in honey samples (Table 2). Overall, in agreement with what reported by many authors in literature (Bogdanov *et al.,* 2007; Quinto *et al.,* 2016; Sarker *et al.,* 2015) statistically significant correlations were observed between metals, indicating that the levels of the elements are closely interlinked with one another. In particular, some significant positive correlations were detected between elements with affinity in the periodic table, such as Ba and Sr ($r = 0.911$; $P < 0.001$), Mg and Ca ($r = 0.871$; $P < 0.001$), this could be due to a similar absorption mechanism soil - plants − honey. A strong positive correlation was observed between the Mn and Cu contents ($r = 0.868$; $P < 0.001$), this could be due to same influential anthropic factors (Esmaeili et al., 2014). The other significant positive correlations found between metals with same anthropic origin were: Cd and Pb ($r = 1.000$; $P < 0.001$), Cd and Zn ($r = 0.986$; $P < 0.001$), Pb and Zn ($r = 0.986$; $P < 0.001$). Thus, the results of Pearson's correlations can only be explained by the mutual affinity of metals and / or anthropic factors.

Comparison of mineral profile in honeys from urban, industrial and rural area

Table 3 summarizes the results of the trace elements, macro-elements, and heavy metals in Basilicata region honey samples classified as rural, industrial, and urban according to anthropic characteristics of geographical origin. The presence and level of chemical elements in the bees' forage area affected the chemical composition of the hive products. Statistical analysis revealed significant differences among honeys from different areas, with the exception for Se, Co and Ag content ($P > 0.05$). Significant differences between urban and rural honeys was found for all studied elements, with the exception for As, Cr, Be, and Sr content; no significant difference was also detected between urban and industrial honeys for Al, V, Cu, Zn, Be, and Sn content; in addition, no significant difference was found between rural and industrial honeys for Na, Mg, Ca, Sn, Cu, Mn, and Ni content. In this study, industrial honeys showed higher Cr, Zn, Cd and Pb levels compared to honeys from other studied areas. Several studies (Bratu & Georgescu, 2005; Perna *et al.,* 2012; 2014) reported higher concentrations of toxic trace elements or heavy metal in honeys from industrial areas. Furthermore, as we expected, Pd and Cd content was lower in rural honeys (Table 3). Thus, we can say that the differences in toxic elements content among honeys from studied areas are due to environmental or geographical factors, to which the anthropogenic source must be added. In fact, traffic-related pollution and chemical-intensive agriculture can

contribute to the increasing levels of these elements in honey (Street *et al.,* 2009; Silici *et al.,* 2013). The Cr presence detected in all honey samples may be due to both the contact of stainless steel surfaces during harvesting, processing and/or preparation, in fact honey due to its acidity is corrosive (Ajibola *et al.,* 2012), and to other contamination sources as stationary point sources, coal, and oil combustion. In this study, Zn level was higher in industrial and urban honeys (1369.15 and 1137.41 µg/kg, respectively) than in rural honeys (866.55 µg/kg; $P < 0.05$), whereas Al, Cu, V, Ba and Sr content was higher in rural honeys compared to honeys from other studied areas ($P < 0.05$). The highest Na, Mg, Ca, Ni, Fe, and Mn content was found in urban honeys ($P < 0.05$). Certainly the beekeeping practices, honey processing, and environment contribute to the diversified mineral content in honey (Anklam, 1998; Pohl, 2009). However, in addition to these factors, the different mineral profile of the studied honeys was clearly explained by the different content of elements in the soil of studied areas, which is due to anthropogenic activities, such as agricultural practices, proximity to industries, waste dumps, and urban centers.

Conclusions

The present study furnished a detailed picture of mineral profile of honeys collected in areas of Basilicata region (southern Italy) characterized by different anthropic impact. All chemical elements detected in this study can be both from natural sources (soil, plants) and anthropogenic sources. Overall, in studied honeys, Ca, Na, Mg, Fe, Al, Zn, and Mn were the most abundant elements, with average contents exceeding 1 ppm, whereas the toxic elements content was really low and the variations reflect the anthropic characteristics of considered areas. Moreover, several differences of mineral profile was detected among honeys collected in area with different anthropic impact, with the exception for Se, Co and Ag content. In particular, industrial honeys were characterized by the highest Zn, Cr, Sn, Cd and Pb content, urban honeys showed the highest As, Fe, Ni, Mn, Na,Mg and Ca content, whereas rural honeys showed the highest Cu, Al, and Ba content. The findings of this study highlighted that the mineral profile of honeys is closely related to the degree of trace element contamination of the environment. These results are useful for both evaluate the nutritional quality of honey and greater consumers' confidence in purchasing and consuming this product.

Conflict of interest

The authors declare no conflicts of interest.

Ethical Guidelines

Ethics approval was not required for this research

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Table 1. Trace elements, macro-elements, and heavy metals in Basilicata region (southern Italy) honeys

	Mean	SD[1]	Min.[2]	Max.[3]	Median	LOD[4]	LOQ[5]
	μg/kg						
Al	1395.73	828.85	630.26	3844.39	1100.68	85.75	288.62
Cr	17.57	5.53	7.00	28.66	17.00	1.46	5.13
Fe	1359.48	543.46	477.38	2954.53	1452.62	88.02	288.81
V	2.19	1.19	0.79	5.24	1.96	0.09	0.28
Ni	32.89	16.02	14.95	106.02	28.94	1.80	5.85
As	0.96	0.53	0.40	2.05	0.82	0.09	0.27
Se	3.21	0.65	3.00	6.64	3.00	0.52	1.76
Co	3.77	2.55	0.82	14.99	3.36	0.16	0.62
Zn	1081.13	350.51	503.67	1971.91	1043.39	15.25	57.14
Mn	1603.06	2202.16	113.06	9021.14	296.62	9.82	30.21
Cu	236.65	113.05	26.42	668.47	224.51	5.76	17.23
Be	0.12	0.04	0.10	0.24	0.10	0.03	0.10
Mo	4.71	1.33	2.63	9.05	4.58	0.08	0.27
Ag	0.36	0.11	0.23	0.84	0.33	0.04	0.14
Sr	114.63	43.87	33.20	198.32	112.11	2.20	6.65
Sn	28.76	17.43	1.50	72.18	26.10	0.62	1.85
Ba	187.82	122.04	10.77	544.41	170.90	1.08	2.99
Cd	3.31	2.33	0.40	9.36	2.66	0.05	0.16
Pb	11.07	5.49	3.40	24.08	9.44	0.53	1.59
	mg/kg						
Na	49.15	18.39	25.58	119.78	45.06	2.20	6.36
Mg	19.30	6.43	9.00	38.89	19.16	1.12	3.81
Ca	44.09	16.08	23.46	93.31	40.51	2.52	7.09

[1] SD: standard deviation; [2]Min.: minimum; [3]Max.: maximum; [4]LOD: limit of detection; [5]LOQ: limit of quantification

Table 2. Pearson correlation coefficients between metals in the investigated honeys.

	Al	Cr	Fe	V	Ni	As	Se	Co	Zn	Mn	Cu	Be	Mo	Ag	Sr	Sn	Ba	Cd	Pb	Na	Mg
Al	1.000																				
Cr	-0.373^{**}	1.000																			
Fe	0.334^{**}	-0.999^{***}	1.000																		
V	0.997^{***}	-0.442^{***}	0.404^{**}	1.000																	
Ni	-0.177^{ns}	-0.847^{***}	0.869^{***}	-0.102^{ns}	1.000																
As	0.291^{*}	-0.996^{***}	0.999^{***}	0.362^{**}	0.890^{***}	1.000															
Se	-0.526^{***}	-0.593^{***}	0.626^{***}	-0.461^{***}	0.930^{***}	0.661^{***}	1.000														
Co	0.955^{***}	-0.632^{***}	0.599^{***}	0.975^{***}	0.123^{ns}	0.561^{***}	-0.250^{ns}	1.000													
Zn	-0.940^{***}	0.667^{***}	-0.635^{***}	-0.963^{***}	-0.169^{ns}	-0.599^{***}	0.205^{ns}	-0.999^{***}	1.000												
Mn	-0.404^{**}	-0.698^{***}	0.727^{***}	-0.334^{**}	0.972^{***}	0.758^{***}	0.990^{***}	-0.114^{ns}	0.069^{ns}	1.000											
Cu	0.805^{***}	0.251^{ns}	-0.291^{*}	0.758^{***}	-0.727^{***}	-0.334^{**}	-0.928^{***}	0.592^{***}	-0.554^{***}	0.868^{***}	1.000										
Be	0.980^{***}	-0.552^{***}	0.516^{***}	0.992^{***}	0.024^{ns}	0.477^{***}	-0.345^{**}	0.995^{***}	-0.989^{***}	-0.212^{ns}	0.669^{***}	1.000									
Mo	0.918^{***}	-0.710^{***}	0.680^{***}	0.945^{***}	0.228^{ns}	0.646^{***}	-0.146^{ns}	0.994^{***}	-0.998^{***}	-0.008^{ns}	0.503^{***}	0.979^{***}	1.000								
Ag	0.924^{***}	-0.699^{***}	0.669^{***}	0.950^{***}	0.213^{ns}	0.634^{***}	-0.161^{ns}	0.996^{***}	-0.999^{***}	-0.024^{ns}	0.516^{***}	0.982^{***}	1.000^{***}	1.000							
Sr	0.663^{***}	-0.942^{***}	0.927^{***}	0.717^{***}	0.620^{***}	0.909^{***}	0.288^{*}	0.855^{***}	-0.878^{***}	0.417^{***}	0.089^{ns}	0.800^{***}	0.906^{***}	0.899^{***}	1.000						
Sn	-0.997^{***}	0.295^{*}	-0.255^{*}	-0.988^{***}	0.257^{*}	-0.211^{ns}	0.595^{***}	-0.927^{***}	0.909^{***}	0.478^{***}	-0.851^{***}	-0.960^{***}	-0.882^{***}	-0.889^{***}	-0.599^{***}	1.000					
Ba	0.912^{***}	-0.720^{***}	0.690^{***}	0.941^{***}	0.241^{ns}	0.657^{***}	-0.132^{ns}	0.993^{***}	-0.997^{***}	0.006^{ns}	0.491^{***}	0.976^{***}	1.000^{***}	1.000^{***}	0.911^{***}	-0.876^{***}	1.000				
Cd	-0.871^{***}	0.781^{***}	-0.754^{***}	-0.905^{***}	-0.330^{**}	-0.723^{***}	0.040^{ns}	-0.978^{***}	0.986^{***}	-0.098^{ns}	-0.409^{**}	-0.952^{***}	-0.994^{***}	-0.993^{***}	-0.945^{***}	0.827^{***}	-0.996^{***}	1.000			
Pb	-0.871^{***}	0.781^{***}	-0.754^{***}	-0.905^{***}	-0.330^{**}	-0.723^{***}	0.040^{ns}	-0.977^{***}	0.986^{***}	-0.098^{ns}	-0.409^{**}	-0.952^{***}	-0.994^{***}	-0.993^{***}	-0.945^{***}	0.827^{***}	-0.996^{***}	1.000^{***}	1.000		
Na	-0.607^{***}	-0.511^{***}	0.547^{***}	-0.545^{***}	0.890^{***}	0.584^{***}	0.995^{***}	-0.343^{**}	0.300^{*}	0.972^{***}	-0.960^{***}	-0.435^{***}	-0.242^{ns}	-0.257^{*}	0.193^{ns}	0.670^{***}	-0.228^{ns}	0.138^{ns}	0.137^{ns}	1.000	
Mg	-0.047^{ns}	-0.909^{***}	0.926^{***}	0.028^{ns}	0.991^{***}	0.942^{***}	0.874^{***}	0.251^{ns}	-0.296^{*}	0.933^{***}	-0.631^{***}	0.154^{ns}	0.353^{*}	0.338^{*}	0.717^{***}	0.129^{ns}	0.366^{***}	-0.450^{***}	-0.450^{***}	0.823^{***}	1.000
Ca	-0.532^{***}	-0.587^{***}	0.620^{***}	-0.467^{***}	0.927^{***}	0.655^{***}	1.000^{***}	-0.257^{*}	0.213^{ns}	0.989^{***}	-0.931^{***}	-0.352^{**}	-0.153^{ns}	-0.168^{ns}	0.281^{*}	0.600^{***}	-0.140^{ns}	0.048^{ns}	0.047^{ns}	0.996^{***}	0.871^{***}

$***P < 0.001$; $**P < 0.01$; $*P < 0.05$; ns not significant.

Table 3. Trace elements, macro-elements, and heavy metals in Basilicata region (southern Italy) honeys classified according to the antropic characteristics of the origin area (rural, industrial, and urban).

	Urban		Industrial		Rural	
	Mean	SD[1]	Mean	SD	Mean	SD
	μg/kg					
N° of samples	20		20		20	
Al	1166.55[a]	488.83	1038.35[a]	449.55	1943.19[b]	1072.41
Cr	14.64[a]	5.03	21.58[b]	3.67	16.57[a]	5.46
Fe	1718.97[c]	187.79	894.21[a]	436.45	1458.22[b]	565.92
V	1.93[a]	0.77	1.66[a]	1.03	2.91[b]	1.34
Ni	41.14[b]	8.72	24.58[a]	5.56	28.28[a]	11.36
As	1.28[b]	0.40	0.58[a]	0.26	1.03[b]	0.61
Se	3.39[a]	1.03	3.15[a]	0.51	3.10[a]	0.94
Co	3.75[a]	1.04	3.59[a]	1.18	3.97[a]	1.38
Zn	1137.41[b]	257.87	1369.15[b]	329.91	866.55[a]	282.60
Mn	4321.97[b]	1940.76	347.41[a]	80.21	237.35[a]	93.53
Cu	198.26[a]	77.03	234.92[a,b]	139.76	274.09[b]	108.25
Be	0.11[a,b]	0.02	0.10[a]	0.01	0.13[b]	0.05
Mo	4.71[b]	1.37	3.76[a]	0.87	5.61[c]	1.03
Ag	0.36[a]	0.08	0.33[a]	0.06	0.39[a]	0.16
Sr	125.01[b]	48.61	89.96[a]	33.90	127.96[b]	40.06
Sn	32.01[b]	9.42	32.58[a,b]	15.54	22.17[a]	8.04
Ba	189.03[b]	65.84	72.09[a]	9.02	294.72[c]	98.55
Cd	3.03[b]	0.81	5.78[c]	2.23	1.24[a]	0.5
Pb	10.52[b]	3.50	16.41[c]	4.88	6.69[a]	2.69
	mg/kg					
Na	62.64[b]	23.27	45.80[a]	12.58	39.70[a]	8.74
Mg	23.91[b]	6.60	15.59[a]	5.83	18.45[a]	4.04
Ca	54.58[b]	19.85	40.60[a]	8.96	37.54[a]	12.95

[1] SD: standard deviation

[a,b,c] Means within a row with different superscripts differ ($P < 0.05$).

Figure 1. Map of honey samples collection sites in Basilicata region (southern Italy)