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Minor and trace elements in different honey types produced in Siena County (Italy)

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Abstract

The concentrations of 23 chemical elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sr, Th, Tl, U, Zn) were determined in 51 honey samples of different botanical origin produced in Siena County (Italy). K, Ca, Na and Mg were the most abundant elements, with mean contents of 1195, 257, 96.6 and 56.7 mg/kg, respectively. The Fe, Zn and Sr contents generally ranged from 1 to 5 mg/kg. Except for Ba, Cu, Mn and Ni, the trace element contents were below 100 μg/kg. The analytical data indicated a good level of quality of the honeys, especially with regard to the concentrations of toxic trace elements, such as As, Cd, Pb and Sb, and suggested a significant influence of the botanical origin on the element composition. Some local geological and geochemical features also seemed to affect the chemistry of the honey.

Keywords: Honey; Honeydew; Element composition; Minor and trace elements; Botanical origin; Siena County; Italy

1. Introduction

Honey is a product of the elaboration of flower nectar or honeydew by bees. Nectar is a sugary liquid that originates from the lymph of plants, while honeydew is an extrafloral secretion produced from plant lymph by parasitic insects (mostly *Metcalfa pruinosa* Say).

The general features and elemental composition of honey depend on its botanical and geographical origin. Recognition procedures help to protect honey consumers from mislabelling concerning the floral and geographical provenance. The traditional method for determining the geographical and/or botanical origin of honey is the identification and study of pollen types present in the sample (melissopalynology). Several authors have proposed alternative procedures based on chemometrical analysis of the elemental composition of honey. The application of path recognition techniques allows honey classification simply by measuring a few parameters (Fernández-Torres et al., 2004; Latorre et al., 1999). The elemental composition of honey has also been used to detect adulteration, such as dilution with water, extension with sugars and syrups, mixing of honey of different botanical/geographical origins and bee feeding with artificial syrups (Rashed & Soltan, 2004).

An important aspect of honey quality is the presence of contaminants due to environmental contamination or pharmacological (antiparasitical or acaricidal) treatment. Honey may contain potentially toxic species, such as heavy elements (As, Cd, Pb). This kind of contamination may be caused by external sources or by incorrect procedures during the honey processing and conservation phases. In fact, due to the acidic nature of honey, the release of elements (such as Cr, Pb, Zn) from metallic tools or containers is likely to occur.

Studies have suggested that honey could be used to monitor geogenic or anthropogenic trace element anomalies in the area around the hives (Golob, Doberšek, Kump, & Nečemer, 2005; Latorre et al., 1999; Paramás et al., 2000; Sanz, Perez, Herrera, Sanz, & Juan, 1995). As bee products are the final step of a bioaccumulation process, the chemical study of honey may provide useful information

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about the environmental quality of the area in which the bees feed, estimated to be about 7 km^2. Indeed, honey has proved to be an effective environmental marker of environmental pollution by heavy elements (Crane, 1975; Jones, 1987; Leita, Muhlbachova, Cesco, Barbatini, & Mondini, 1996; Przybyłowski & Wilczyńska, 2001; Üren, Serifoglu, & Sarikahya, 1998). High heavy element contents have been found in honey coming from areas with heavy industrial activities or busy highways (D'Ambrosio & Marchesini, 1982; Gajek, Gdanski, & Gajewska, 1987). Leita et al. (1996) confirmed the utility of honey as an environmental marker; they found a high correlation between cadmium concentrations in honey and *Trifolium pratensae* L. samples from the same area.

In the present chemical study of honey produced in Siena County (Tuscany, Italy), we determined the element composition of honey samples of different botanical and geographical origins. Herein we report the concentrations of 23 chemical elements determined in 51 honey samples. The aims of the study were: (i) to chemically characterize the honey samples; (ii) to define the honey quality with regard to several toxic trace elements, such as lead, arsenic, antimony and cadmium; (iii) to highlight possible relationships between the element composition of honey and its botanical and/or geographical origin; (iv) to identify possible pollution sources in the area surrounding the hives or problems linked to the processing phases.

1.1. The study area

All the honey samples were produced in Siena County, which extends for about 3800 km^2 in southern Tuscany (Italy). Siena County is a relatively clean area, since there are few industrial centres (mostly located in the NW sector) and the vehicular traffic is rather low in comparison with European standards. Moreover, the urban centres are small and the main town, Siena, is an historical city with 55,000 inhabitants.

The economic activities of the territory are mainly agricultural. Cultivated fields and woods cover about 35% of the county. Vineyards are also well represented and are found mainly in the northern sector of the study area (i.e., Chianti zone).

The geology is quite complex, with geological formations of different origin, composition and age. Marine and lacustrine sandy to clayey sediments crop out extensively throughout the territory, filling a wide NW–SE graben-type tectonic trench (Pliocene basin of Siena). Clayey, arenaceous and calcareous-marly flysches mainly form the borders of the Siena basin, whereas siliceous rocks characterize the geology of the western sector of the study area (Monticiano-Roccastrada ridge).

The surface geochemical features of the region are well known and several studies of the geochemistry of stream sediments and soils were recently carried out in the area (Di Lella, Protano, Riccobono, & Sabatini, 2003; Protano, Riccobono, & Sabatini, 1998).

2. Materials and methods

The analytical work was carried out on 51 samples of natural honey of different botanical origins produced in 2004 (May–August) in several zones of Siena County by hobby and professional beekeepers (Fig. 1). According to information from the producers, the samples were mainly nectar multifloral honeys (41 samples), but they also included sulla (*Hedysarum coronarium* L., three samples) and clover (*T. pratensae* L., three samples) honeys. Four honeydew honeys were also investigated.

All honey samples (about 500 g in weight) were collected in clean glass vessels and transferred to the laboratories of the Department of Environmental Sciences of the University of Siena. The honey samples were homogenized by heating at +40 °C and sonication. About 1 g of each sample was mineralized by acid digestion in a microwave oven (Ethos 900 by Milestone), with the addition of 4 ml of HNO_3 and 1 ml of H_2O_2. Ultrapure trace-grade reagents and ultrapure water were used in these procedures.

Depending on the element concentration, chemical analyses were carried out by inductively coupled plasma optical emission spectroscopy (ICP–OES), using a Perkin–Elmer Optima 2000 spectrophotometer, and by inductively coupled plasma mass spectrometry (ICP-MS), using a Perkin–Elmer Sciex Elan 6100 spectrometer. The following 23 chemical elements were determined: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sr, Th, Tl, U, Zn.

The analytical quality was checked using the certified reference material 8413 Corn (*Zea mais*) Kernel distributed by the U.S. Department of Commerce, National Bureau of Standards. The analytical accuracy and precision were within 5% for all the elements.

Univariate statistical analysis and analysis of variance (ANOVA) were carried out using R version 2.4.0. Principal component analysis (PCA) was used to investigate the multivariate structure of the dataset and to highlight possible trends among the data.

Principal component analysis reduces the number of dimensions of a dataset by a linear combination of the initial variables and maximizes the information content of a group of data. Decomposition of the correlation matrix into eigenvalues and eigenvectors leads to the linear combination with the above mentioned dataset simplifications. The eigenvectors represent the linear combination coefficients and the corresponding eigenvalues represent the variance described by each linear combination. As the eigenvalues are in non-decreasing order, the first linear components account for the largest amount of variance. Once derived, the principal components (PCs) can be used for further analyses to visualize the data grouping, to verify the presence of outlier values and to determine the variables that discriminate among groups.

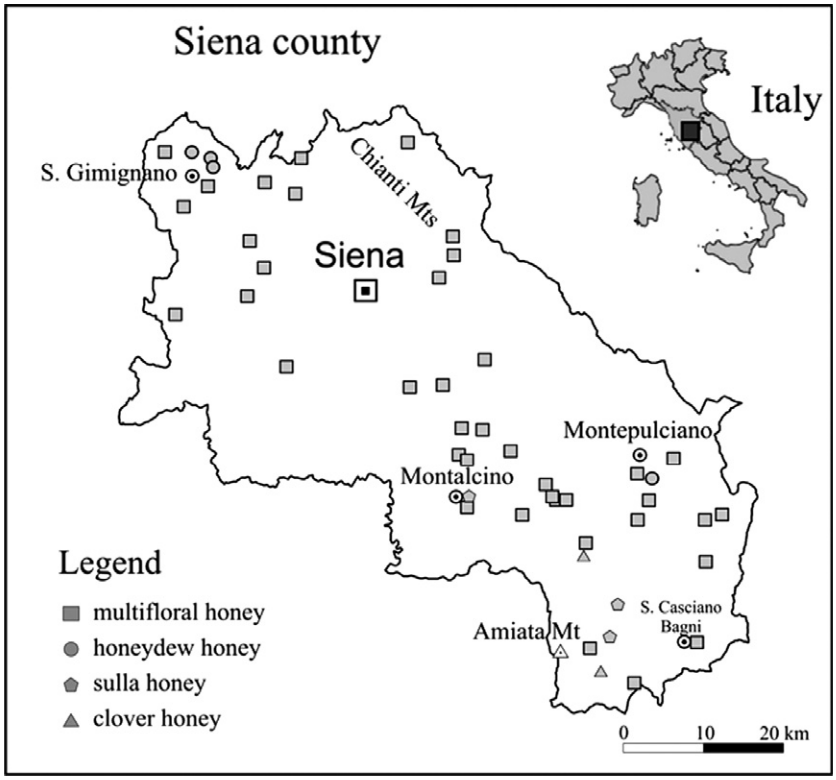

Fig. 1. Provenance of the honey samples in Siena County (Italy).

3. Results and discussion

3.1. General features

The results of the univariate analysis of the element concentrations in the honey samples (mean, median, standard deviation, minimum and maximum values) are shown in Table 1. It must be pointed out that the honey samples were not statistically homogeneous because of a dominance of multifloral honeys, reflecting the main production in Siena County.

There was a certain variability of the element composition in the honey samples. K, Ca, Na, Mg, Fe, Zn and Sr were the most abundant elements, with average contents exceeding 1 mg/kg. The potassium concentrations were highest (mean 1147 mg/kg), followed by calcium (257 mg/kg), sodium (96.6 mg/kg) and magnesium (56.7 mg/kg). The Fe, Zn and Sr contents were generally in the range 1–5 mg/kg.

The concentrations of Ba, Cu, Mn and Ni were usually between 100 and 1000 μg/kg, whereas the other trace elements had contents lower than 100 μg/kg. The As, Cd, Co, Sb and U concentrations were in the range 1–10 μg/kg, whereas the Th contents were usually below 1 μg/kg.

The Al, Cr, Se and Tl contents were below the respective levels of quantification (LOQ) in several multifloral and sulla samples, while they were always quantifiable in the honeydew and clover honeys. For instance, the Al concentration was below the LOQ (2.5 mg/kg) in 73% of the multifloral samples, but the average contents were 7.4 and 5.5 mg/kg in the honeydew and clover honeys, respectively. Only Hg was negligible in all the honey samples, with contents constantly lower than the quantification level for the adopted analytical procedure (2 μg/kg).

The range of variation of each element was usually wide. Among the minor elements, only calcium was homogeneously distributed. The minimum and maximum values were of the same order of magnitude (137–409 mg/kg) and the median (264 mg/kg) practically coincided with the mean (257 mg/kg). In contrast, the concentrations of the chemical species in each botanical honey type were quite symmetrical; the mean and median values agreed quite well, except in a few cases (Table 1).

On the whole, the concentrations of the elements in the Siena honeys were consistent with the composition of honeys produced in clean uncontaminated geographical areas.

3.2. Minor elements[1]

In agreement with previous studies (Conti, 2000; Fernández-Torres et al., 2004; Latorre et al., 1999; Yilmaz & Yavuz, 1999), potassium was the most abundant chemical

[1] In geochemistry, the distinction among major, minor and trace elements in rocks is made on a quantitative basis. Chemical elements in quantities exceeding 1% are named major elements, those between 1% and 0.1% minor elements and those below 0.1% trace elements. Here, we arbitrarily consider minor elements to be those having a concentration in honey of more than 1 mg/kg and trace elements those below this value.

Table 1
Statistics of the minor and trace element contents in different types of honey produced in Siena County

	N	Statistics	mg/kg								μg/kg									
			Na	Mg	K	Ca	Fe	Mn	Zn	Sr	Ba	Cu	Co	Ni	As	Cd	Sb	Pb	Th	U
All samples	51	Mean	96.6	56.7	1195	257	3.07	1.54	1.82	1.43	906	906	11.0	308	6.96	3.91	3.76	76.0	0.70	9.66
		Median	91.4	42.2	659	264	1.98	0.36	1.71	1.46	827	389	6.67	201	6.56	2.58	2.84	55.3	0.42	9.63
		Stand dev	30.3	36.2	1087	56	2.57	3.29	0.74	0.23	404	1272	11.5	398	2.71	3.33	2.49	52.7	0.62	1.68
		Min	56.6	22.2	147	137	0.97	0.13	0.72	0.85	218	172	1.56	77	2.78	1.00	1.20	28.2	0.13	4.53
		Max	232	159	4136	409	13.7	16.9	3.66	2.01	2634	5900	56.6	2760	20.2	15.3	13.3	304	2.94	14.8
Honey dew	4	Mean	148	139	3440	356	10.1	1.70	1.87	1.76	1061	4400	44.5	531	12.3	2.68	7.54	93.9	1.79	11.3
		Median	128	135	3340	348	9.79	1.65	1.89	1.72	1054	4966	41.2	475	10.6	2.55	7.15	86.7	1.59	10.4
		Stand dev	59.0	7.9	439	38	3.24	0.41	0.79	0.18	190	1812	8.10	137	5.42	0.58	1.16	38.0	0.85	2.44
		Min	101	134	3056	322	7.07	1.35	1.07	1.59	842	1770	39.1	440	7.97	2.17	6.63	55.7	1.04	9.58
		Max	232	150	4023	409	13.7	2.15	2.63	2.01	1294	5900	56.6	734	20.2	3.47	9.24	147	2.94	14.8
Multifloral	41	Mean	94.9	52.3	1093	254	2.49	1.68	1.85	1.42	915	647	8.64	273	6.59	4.25	3.40	76.4	0.64	9.65
		Median	92.0	42.7	672	264	1.88	0.37	1.71	1.47	812	395	6.69	188	6.47	2.73	2.78	55.2	0.39	9.51
		Stand dev	22.2	28.3	896	46	1.36	3.61	0.74	0.19	424	624	5.72	413	1.86	3.58	2.19	55.9	0.53	1.43
		Min	60.2	22.2	178	159	0.97	0.13	0.72	0.90	408	201	2.89	77	2.78	1.00	1.20	28.2	0.13	6.51
		Max	147	158.8	4136	373	6.26	16.9	3.66	1.81	2634	2795	30.2	2760	11.1	15.3	13.3	304	2.28	12.5
Sulla	3	Mean	74.1	28.3	207	172	1.77	0.19	1.01	1.14	529	240	3.40	378	6.15	1.92	2.26	64.6	0.27	7.88
		Median	77.5	26.6	228	159	1.68	0.20	1.03	1.13	560	254	3.59	97	6.64	2.15	2.22	44.1	0.25	8.61
		Stand dev	16.0	6.8	52	44	0.23	0.02	0.04	0.30	296	62	1.76	501	1.17	0.71	0.22	41.2	0.13	3.05
		Min	56.6	22.6	147	137	1.60	0.17	0.97	0.85	218	172	1.56	81	4.81	1.13	2.07	37.7	0.16	4.53
		Max	88.1	35.9	246	221	2.04	0.21	1.04	1.45	808	293	5.06	957	6.99	2.49	2.50	112	0.41	10.5
Clover	3	Mean	63.6	26.2	274	262	2.83	0.28	2.31	1.27	980	216	4.80	487	5.22	2.34	4.78	50.0	0.49	9.26
		Median	63.2	25.8	273	261	2.63	0.27	2.24	1.28	966	203	4.60	480	5.31	2.33	2.62	50.6	0.50	9.12
		Stand dev	1.8	2.5	6	14	1.04	0.03	0.38	1.37	60	31	0.61	174	0.58	0.09	4.31	2.9	0.04	0.36
		Min	62.1	23.9	269	248	1.91	0.25	1.97	1.13	928	194	4.32	316	4.60	2.26	1.97	46.8	0.45	8.99
		Max	65.6	28.8	281	276	3.96	0.31	2.72	1.41	1046	252	5.48	664	5.75	2.44	9.74	52.5	0.53	9.67

element in the honeydew and multifloral honeys produced in Siena County. The K concentrations spanned the wide range of 147–4136 mg/kg (Table 1) and about 25% of the values exceeded 2000 mg/kg. The highest contents were measured in honeydew samples (mean 3440 mg/kg). Significantly lower concentrations were found in the clover (274 mg/kg) and sulla honeys (207 mg/kg). The multifloral honeys had a mean potassium content of 1093 mg/kg.

The potassium content in the Siena honey was significantly higher than that measured in honey from other central Italian regions, south-eastern Anatolia (Turkey) and Ireland, whereas it was comparable with the content in Spanish honey (Table 2). However, comparisons with the literature data may present some difficulties. Many studies refer to different botanical types of honey and this feature may substantially affect the chemical composition. Furthermore, different methods of sample solubilization (i.e., microwave-digestion, wet-digestion, dry-ashing) and different analytical techniques may also affect the results.

Table 2
Comparison of the element contents of honeys produced in different geographical areas

	Present study[a] ($n = 50$)	Italy[b] (Latium region) ($n = 84$)	Spain[c] ($n = 40$)	Spain[d] (Galizia) ($n = 22$)	Spain[e] ($n = ?$)	Turkey[f] (Anatolia) ($n = 30$)	Ireland[g] ($n = 50$)
K (mg/kg)	1195	472	1124	1345	1778	296	566
Ca (mg/kg)	257	47.7	169	**	113	51	111
Na (mg/kg)	96.6	96	76	115	279	118	98
Mg (mg/kg)	56.7	37	39	77	136	33	31
Fe (mg/kg)	3.07	4.5	**	3.7	9.19	6.6	8
Zn (mg/kg)	1.82	3.1	3.9	2.0	5.65	2.7	5
Mn (mg/kg)	1.54	3.0	3.4	5.2		1.0	4
Sr (mg/kg)	1.43	**	0.6	**	0.41	**	

[a] Present study.
[b] Conti (2000).
[c] Fernández-Torres et al. (2004).
[d] Latorre et al. (1999).
[e] Terrab et al. (2005).
[f] Yilmaz and Yavuz (1999).
[g] Downey et al. (2005).

The mean calcium and sodium contents in the Siena honey were 257 mg/kg and 96.6 mg/kg, respectively (Table 1), and the ranges were narrow (Ca = 137–409 mg/kg; Na = 57–232 mg/kg).

The highest calcium concentrations were found in the honeydew honey (mean 356 mg/kg) and in multifloral honey samples from zones where carbonate rocks dominate the geology of the area. The calcium content was usually lower in multifloral honey and similar to that in clover honey (262 mg/kg). The lowest concentrations of calcium were measured in the sulla honey (172 mg/kg; Table 1).

Fig. 2 shows the trend of potassium and calcium contents with respect to the total element content in the different honey types. In honeydew honey, potassium was clearly more abundant than was calcium (84% vs 9%) while, in nectar honey, the difference between the two elements decreased from multifloral to clover honey. In fact, the clover honey had practically the same percentages of potassium and calcium (43% and 41%, respectively).

Sodium contents were particularly high in honeydew honey (mean 148 mg/kg) and in a multifloral honey sample produced in a sector of Siena County where clays with sulphate-rich marine evaporite lenses crop out. The mean sodium contents decreased from multifloral (95 mg/kg) to sulla (74 mg/kg) to clover (64 mg/kg) honey (Table 1).

The sodium contents in the Siena honeys corresponded with the usual levels in honey, while the calcium concentrations were significantly higher than those reported in the literature (Table 2). The latter finding could be related to the extensive carbonate rock outcrops in Siena County.

Magnesium was the fourth most abundant element in the Siena honey, with contents ranging from 22.2 to 159 mg/kg (mean 56.7 mg/kg). The highest concentrations were found in honeydew honey (mean 138 mg/kg) and the lowest contents in the sulla (28.3 mg/kg) and clover (26.2 mg/kg) honeys (Table 1).

The Siena honeys had similar mean values of zinc (1.82 mg/kg), manganese (1.54 mg/kg) and strontium (1.43 mg/kg). Zinc and strontium exhibited no peculiar pattern of distribution in the different honey types, although the lowest concentrations were constantly related to sulla honey. Manganese was more abundant in honeydew honey than in the nectar honeys. Nevertheless, the highest manganese contents (from 12.2 to 16.9 mg/kg) were measured in three multifloral honey samples produced in zones dominated by a carbonate-evaporite formation (Calcare cavernoso).

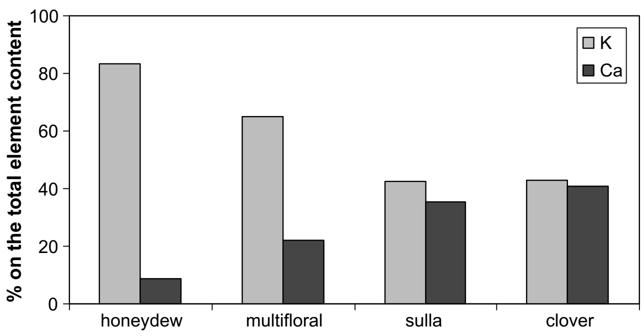

Fig. 2. Percentage of potassium and calcium with respect to the total element content in different botanical types of honey produced in Siena County.

3.3. Trace elements

On the whole, the contents of trace elements in the Siena honey were quite low and comparable with the usual contents in honey from uncontaminated areas (Delbono, Ghidini, & Campanini, 1999; Latorre et al., 1999; Tuzen, Silici, Mendil, & Soylak, 2007). This underlines the good quality of Siena honey, especially with regard to the contents of toxic trace elements, such as As, Cd, Pb, Sb.

The differences in trace element concentrations among the different types of honey were less marked than those for the minor elements, except for cobalt, copper and thorium. The concentrations of the last three chemical species were much higher in honeydew honey than in the nectar honeys (Table 1). ANOVA confirmed this finding and an *F* Test completely excluded the hypothesis that the cobalt, copper and thorium contents were not dependent on the botanical origin of the honey samples.

The copper levels in the Siena honey (mean 906 μg/kg) were similar to those recorded in other studies, while the cadmium concentrations (3.9 μg/kg) were usually lower (Conti & Botrè, 2001; Delbono et al., 1999; Latorre et al., 1999; Tuzen & Duran, 2002; Tuzen et al., 2007). For instance, honey produced in the Pomeranian region had an average cadmium content of 15 μg/kg (Przybyłowski & Wilczyńska, 2001), about one order of magnitude higher than the contents in our honey samples.

Owing to the toxicological importance of lead, many studies of Italian honey have focussed on this element (Abete & Voghera, 1999; Delbono et al., 1999; Galeno, Rocca, Ferrari, Mulinelli, & Acrossa, 1992; Oddi & Bertani, 1987; Pinzauti, Biondi, & Panizzi, 1989; Sangiorgi & Ferretti, 1996). The World Health Organization has designated a P.T.W.I. (Provisional Tolerable Weekly Intake) of lead of 3 mg for adults and 0.3 mg for babies, children and old people.

Lead concentrations in the Siena honey ranged from 28.2 to 304 μg/kg, with a mean of 76 μg/kg. These values are in agreement with levels found in other clean zones of Italy (Table 3). Significantly higher Pb contents, up to 2370 μg/kg, were found in contaminated Italian areas (D'Ambrosio & Marchesini, 1982). As a useful reference, it should be mentioned that, since 1977, honeys with lead concentrations above 215 μg/kg cannot be sold in Germany (Otto & Jekat, 1977). Among the Siena honeys, only one sample of multifloral honey, collected in the thermal area of S. Casciano Bagni, showed a lead concentration higher than this threshold (304 μg/kg).

Table 3
Comparison of the mean lead contents of honeys produced in different Italian regions

	Geographical origin	Year of production	Pb (μg/kg)
present study	Siena County (Tuscany)	2004	76
Oddi and Bertani (1987)	Veneto	1987	230
Pinzauti et al. (1989)	Tuscany	1989	172
Galeno et al. (1992)	Liguria	1992	75
Sangiorgi and Ferretti (1996)	Emilia-Romagna and Lombardy	1993	37
Abete and Voghera (1999)	Turin County (Piedmont)	1996–1997	65
Delbono et al. (1999)	Emilia-Romagna	1996–1998	150

The As, Cr, Sb, Se, Th, Tl and U contents in the Siena honey were comparable with the few analytical data available in the literature (Conti & Botrè, 2001; Tuzen et al., 2007).

Chromium was in the range <2.0–54 μg/kg, with 10 nectar honey samples below the quantifiable level of the element.

The mean contents of arsenic and antimony were 6.96 and 3.76 μg/kg, respectively. Arsenic was slightly more abundant (10.2–20.2 μg/kg) in the honeydew honey and in a multifloral honey sample produced in a zone close to a highway and a railway. Antimony showed a similar distribution pattern, although the peak concentration (13.3 μg/kg) was recorded in a multifloral honey sample produced in the basin of Siena.

Selenium was found in the range <2.0–17.3 μg/kg, with contents below the quantifiable level in 12 of the 51 samples. The highest concentrations were above 15 μg/kg and occurred mainly in multifloral honey samples produced in the NW sector of the study area.

The thallium contents ranged between <0.2 and 5.12 μg/kg. The highest values (above 2 μg/kg) were in honeydew and multifloral honey samples from the SE sector of the study area (Montepulciano zone), which has a series of outcrops of carbonatic terrains, as well as in a multifloral honey sample from the volcanic area of Mt. Amiata, in the southern part of the study area.

Interestingly, the mean concentration of uranium in the Siena honey (9.7 μg/kg) was much higher than that of thorium (0.7 μg/kg). Hence, the ratio of these elements in the honey samples was completely different from the usual Th/U ratio in rocks and soils (about 4/1). This is likely due to the different mobility and bioavailability of the two chemical species. Uranium is more mobile than is thorium in the surface environment, including the biosphere. The geochemical behaviour of uranium and thorium (like that of many other elements) is affected by the oxidation state. Under surface conditions, uranium easily oxidizes to the hexavalent state, forming very mobile species, such as the uranyl ion (UO_2^{2+}). Instead, thorium exists only in the tetravalent state and thus is practically immobile. Therefore, thorium's low solubility and bioavailability to plants explains the inverse Th/U ratio found in the honey samples.

3.4. Botanical origin and chemical composition of the Siena honey

The botanical origin of the Siena honeys had a significant influence on their chemical composition. The honeydew samples had the highest total element content (mean 4111 mg/kg), while the clover and sulla honeys had the lowest values (641 mg/kg and 487 mg/kg, respectively). These figures agree with the typical mineral contents of honeydew honey (>1%) and nectar honey (0.1–0.2%; Hernández, Fraga, Jiménez, Jiménez, & Arias, 2005). The influence of the botanical origin on the elemental composition of the Siena honey was evident for both essential elements such as K, Ca, Na, Mg, Fe, Mn, Cu, Co, and for toxic species, such as As, Pb, Th, Tl, U.

The differences among the honey types were highlighted by the PCA analysis. The first two components were chosen to examine the dataset and they explained 53% of the total variance. All the elements were used in the PCA procedure, except Al, Cr, Hg, Se and Tl, since their concentrations were below the quantifiable level in most samples. Fig. 3a shows the loadings of the variables (the element concentrations) in the plane defined by the two principal components (PC1 and PC2). PC1 has a negative correlation with most elements, while PC2 has a negative correlation with the Ba, Cd and Pb concentrations and a moderate positive correlation with Zn. Fig. 3b represents the score plot of the honey samples. There is a clear separation of the honeydew and nectar samples. The honeydew samples

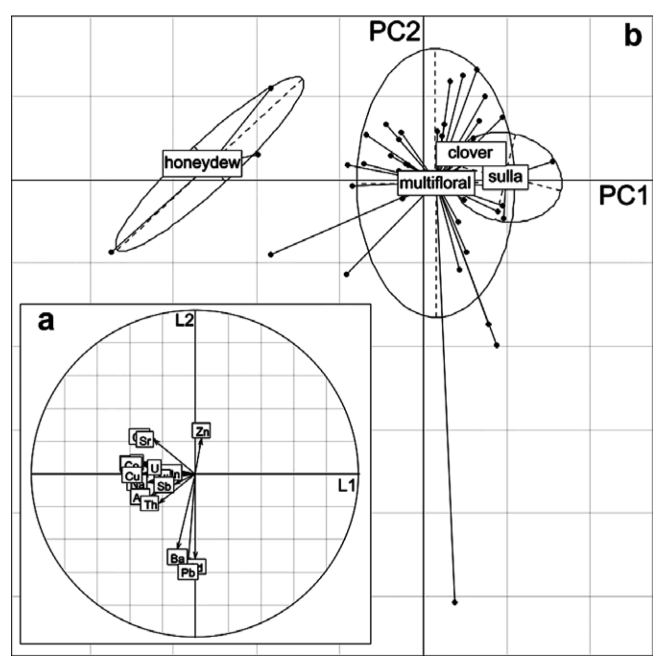

Fig. 3. (a) Factorial map for the element concentrations of the honey samples of Siena County; (b) factorial map for the honey samples of Siena County.

are situated on the left side of the plot, as they mostly have negative values of PC1. This means that these samples had the highest concentrations of most of the elements. As expected, there is a crowded group of nectar honey samples on the right side of the plot, since these samples had lower element contents. The position of a single sample in the bottom part of the plot is interesting. This multifloral honey, collected near a thermal area (San Casciano Bagni), is in the part of the plot where Ba, Cd and Pb prevail, and it represents an outlier with respect to the contents of all these elements.

The analytical data also revealed a correlation between the honey colour and the chemical composition. The highest element contents were found in the darkest honey samples and the lowest concentrations in the palest ones.

4. Conclusions

The present chemical study furnished a detailed picture of the element composition of honey produced in Siena County (Italy), through the analysis of 23 elements in 51 honey samples of different origins. The main results of the study are:

1. The analytical data exhibited a certain variability of the element composition of honey samples. Nevertheless, K, Ca, Na and Mg were the most abundant elements (in that order), with concentrations constantly above 10 mg/kg. Except for Ba, Cu, Mn and Ni, the trace element contents were below 100 μg/kg.
2. Honey from Siena County contains very low quantities of potentially dangerous chemical species, such as As, Cd, Sb and Pb, and its chemical features match the composition of honey produced in clean uncontaminated geographical areas.
3. The results confirm the highly significant influence of the botanical origin of honeys on their chemical composition. The PCA analysis highlighted the relationship between the element distribution and the honey type.
4. Some geological and geochemical features appeared to affect the honey chemistry, especially with regard to Ca, Na and Mn.
5. The honey sample from the thermal area of San Casciano Bagni clearly represents an outlier in the dataset. In fact, the chemistry of this multifloral honey, with high contents of Pb, Ba and Cd, is probably affected by the diffuse hydrothermal activity in this area.
6. The Th/U ratio observed in the honey likely reflects the quite different geochemical mobility of these elements in the surface environment, which in turn affects their phytoavailability.

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