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# Solid-phase microextraction /gas-chromatographic /mass-spectrometric analysis of p-dichlorobenzene and naphthalene in honey

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6 **spectrometric analysis of *p*-dichlorobenzene and naphthalene in honey**  
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## Abstract

Protection of honey combs from wax moth *Galleria mellonella* involves the use of physical, biological or chemical control methods. Chemical control may result in residues in the extracted honey. The presence of residues of *p*-dichlorobenzene and naphthalene in honey were investigated by means of solid-phase microextraction (SPME) coupled to GC/MS. The method was linear between 5 µg/kg and 200 µg/kg of honey for *p*-dichlorobenzene and 1 µg/kg and 200 µg/kg of honey for naphthalene. Limits of detection were 1 µg/kg and 0.1 µg/kg respectively. The relative standard deviations were 2.6 % and 7.9 % for *p*-dichlorobenzene and naphthalene respectively. Application of the method to 90 unifloral Greek honeys revealed that in 25.6% of the samples the concentration of either one of the pesticides exceeded the Maximum Residue Level (MRL). Maximum concentrations were 163.03 µg/kg of honey for *p*-dichlorobenzene and 193.74 µg/kg of honey for naphthalene. Naphthalene was found in traceable amounts in 78.9% of the samples, but only 5.6% of them contained concentrations above the MRL. This indicates the use of pre-contaminated honey comb foundations or built combs. Nevertheless, because naphthalene is naturally present in some plant species growing in Greece, the contribution of nectar from such a floral source should not be overlooked.

**Keywords:** honey, *p*-dichlorobenzene, naphthalene, solid-phase microextraction, gas chromatography-mass spectrometry

## Introduction

Apiculture faces a great deal of pests, including mites, insects and a number of important diseases. Two insects problems that are fed on the comb wax are the greater wax moth, *Galleria mellonella* L., and the lesser wax moth *Achroia grisella* Fabricius. Infestation of brood combs, extracting combs, comb honey and other wax materials that have been stored at temperatures above 15 °C especially by the greater wax moth *G. mellonella*, results in considerable economic lose. Beekeepers can protect their honey combs by storing them and applying physical, biological or chemical control methods (Cantwell and Smith 1970; Burges 1978).

Chemical control is effective and easy to use and usually is applied as fumigants such as *p*-dichlorobenzene and naphthalene. Wax moth action is prevented when the unused combs are stocked in the hive boxes and the fumigant is placed on top of the stock because the fumes are heavier than air (Morse and Hooper 1985). There is a risk of harmful residues in the extracted honey, regardless of the type of fumigant used (Burges 1978). In Greece, *p*-dichlorobenzene and naphthalene had been used for almost 60 years (Nikolaidis 1947; Dermatopoulos 1954), until the situation changed when European Regulation (EC) No 396/2005 set a limit of 10 µg/kg honey for those substances where no Maximum Residue Level (MRL) for honey had been established, including the two aforementioned insecticides.

Due to the lipophilic character of these two compounds, they are readily adsorbed by the wax and thereafter end up in honey stored by the bees. Their high volatility makes headspace techniques suitable for isolation and quantification of these analytes (Bogdanov et al., 2004; Takanaki et al., 2005). In addition, many publications have shown that solid-phase microextraction is an effective procedure to isolate a variety of

1  
2  
3 pesticide residues from honey (Jiménez et al. 1998; Fernández et al. 2001; Campillo et al.  
4  
5  
6 2006; Rial-Otero et al. 2007).

7  
8 This paper presents the development of an isolation and quantification method for  
9  
10 *p*-dichlorobenzene and naphthalene residues in honey by means of solid-phase  
11  
12 microextraction coupled to GC/MS. The results of the application of this method to 90  
13  
14 unifloral Greek honey samples are presented.  
15  
16

## 21 22 **Experimental**

### 23 *Reagents*

24  
25 The reagents used for this work were of analytical grade (>99%). *p*-dichlorobenzene  
26  
27 was purchased from Riedel de Haën and naphthalene from Fluka Chemika.  
28  
29 Benzophenone used as an internal standard was also purchased from Fluka Chemika.  
30  
31 Stock solutions of these analytes were prepared in methanol of analytical grade.  
32  
33  
34

### 35 *Honey samples*

36  
37 A total of 90 honey samples from various botanical sources were employed. These  
38  
39 samples were collected during the years 1999-2003.  
40  
41  
42

### 43 *Extraction*

44  
45 Extraction was performed by means of a Solid-Phase Microextraction (SPME) device  
46  
47 (Supelco, Bellefonte, USA), using a DVB/carboxen/PDMS fibre to isolate headspace  
48  
49 volatiles. The samples (solution of 3g of honey for every mL of water) were placed in  
50  
51 15 ml screw-top vials with PTFE/silicone septa. Benzophenone was used as internal  
52  
53 standard and a portion of 20 µL (10 µg/mL in methanol) was added prior to extraction.  
54  
55 The vials were maintained in a water bath at during equilibration and extraction and  
56  
57 were partially submerged so that the liquid phase of the sample was in the water (Miller  
58  
59  
60

1  
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3 and Stuart 1999). Optimal conditions for the extraction were as follows: 30 min  
4 equilibration time, 60 min sampling time, 6 mL sample volume, and 60 °C water bath  
5 temperature.  
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8  
9

#### 10 *Gas chromatography-Mass Spectrometry*

11  
12 The analysis of the extracts was performed using a Hewlett Packard 5890 II GC,  
13 equipped with a Hewlett Packard 5972 MS detector. The column used was an HP-5MS  
14 (Crosslinked 5% PH ME Siloxane) capillary column (30 m X 0.25 mm i.d., 0.25 µm  
15 film thickness) and the gas carrier was Helium, at 1 mL/min rate. The injector and MS-  
16 transfer line temperatures were maintained at 220 °C and 290 °C respectively. Oven  
17 temperature was held at 40 °C for 3 min, raised to 160 °C at 3 °C/min and then to 200 °C  
18 at 10 °C/min. Electron impact mass spectra recorded at 40-500 mass range. An electron  
19 ionization system was used with ionization energy of 70 eV.  
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#### 31 *Quantification*

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33 The calibration curves were established by adding known concentrations of the analytes  
34 to a residue-free honey. Twelve concentrations were employed, ranging from 1 to 10  
35 000 µg/kg of honey. For each concentration and analyte, two repetitions were made. For  
36 quantitative determination of *p*-dichlorobenzene and naphthalene in honey samples,  
37 three replicates were obtained.  
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## 48 **Results and discussion**

### 49 *Method parameters*

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53 *Limits of detection and quantification.* The limit of detection (LOD) was considered as  
54 the amount of the analyte required to give a signal-to-noise ration of 3 and was found to  
55 be 1 µg/kg for *p*-dichlorobenzene and 0.1 µg/kg for naphthalene. The limit of  
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1  
2  
3 quantification (LOQ) requires a signal-to-noise ration more than 10 and it was found to  
4  
5 be 5 µg/kg for *p*-dichlorobenzene and 1 µg/kg for naphthalene.  
6  
7

8 *Linearity.* Preliminary tests showed that the method was linear for concentrations up to  
9  
10 200 µg/kg for both pesticides, and, thus, calibration curves were prepared for  
11  
12 concentrations up to this value. Specifically, the following concentrations were used; 1,  
13  
14 5, 10, 20, 50, 100, and 200 µg/kg of honey. Calibration curves (see Figures 1 and 2)  
15  
16 were prepared using the ratio of the peak area of the analyte against the peak area of the  
17  
18 internal standard ( $R_{D/B}$  and  $R_{N/B}$  for *p*-dichlorobenzene and naphthalene respectively).  
19  
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21

22 The regression equations are:

23  
24 for *p*-dichlorobenzene:  $R_{D/B} = (0.097 \pm 0.004) D - (0.793 \pm 0.331)$ , and

25  
26 for naphthalene:  $R_{N/B} = (0.121 \pm 0.005) N - (0.710 \pm 0.471)$ .  
27  
28

29 The correlation coefficients ( $R^2$ ) were 0.9948 and 0.9902 respectively.  
30  
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32

33  
34 [Insert Figure 1 about here]

35  
36 [Insert Figure 2 about here]  
37  
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41 *Repeatability.* The repeatability of the procedure was estimated on a residue-free sample  
42  
43 spiked with 10 µg/kg of honey for both analytes, which is the MRL value according to  
44  
45 the European Regulation (EC) No 396/2005. Figure 3 shows a TIC chromatogram of  
46  
47 this sample. The relative standard deviation (RSD) values were 2.6% and 7.9% for *p*-  
48  
49 dichlorobenzene and naphthalene respectively (n=5).  
50  
51  
52

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54  
55 [Insert Figure 3 about here]  
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59  
60 *Method application*



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3 The method was applied to 90 samples of different botanical origin and the results are  
4 shown in Table I. Honeys were placed in two groups, according to the season of harvest.  
5  
6 Group A includes summer (thyme, cotton) or early autumn (pine) harvests, while Group  
7  
8 Group B comprises honeys harvested either in spring (citrus, fir chestnut, eucalyptus) or late  
9  
10 autumn (heather). The maximum concentrations were 163  $\mu\text{g}/\text{kg}$  of honey for *p*-  
11  
12 dichlorobenzene and 194  $\mu\text{g}/\text{kg}$  of honey for naphthalene. Both samples possessing  
13  
14 these concentrations belong to Group A, as do most of the samples in which high  
15  
16 concentrations of the pesticides were estimated. In Figure 4, the chromatogram of a real  
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18 honey sample (sample No 19) containing both *p*-dichlorobenzene and naphthalene at  
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20 concentrations above the MRL values is shown.  
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29 [Insert Table I about here]  
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31  
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34 [Insert Figure 4 about here]  
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39 Table II summarizes the results of Table II, regardless of the botanical origin. The  
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41 percentage of samples *p*-dichlorobenzene was detected was 46.7%, while for  
42  
43 naphthalene it raised up to 78.9%. In 18.9% of the samples for *p*-dichlorobenzene and  
44  
45 5.6% for naphthalene, the concentration exceeded the MRL value of 10  $\mu\text{g}/\text{kg}$  of honey.  
46  
47 Finally, 84.4% of the samples contained either one of the analytes, and 25.6% of them  
48  
49 were improper for human consumption. It must be emphasized that the samples used  
50  
51 were harvested prior to 2002, well before the limit of 10  $\mu\text{g}/\text{kg}$  honey was established.  
52  
53 The analysis of samples collected after the European regulation 396/2005 EC shows a  
54  
55 dramatic decrease in numbers of contaminated samples (Tananaki et al., 2006) due to  
56  
57 the use of alternative ways for protecting honeybee wax combs.  
58  
59  
60

[Insert Table II about here]

An important aspect of the results in Table II is the relatively few samples containing naphthalene at high concentrations, with respect to the number of samples in which this analyte was detected. Only 7% exceeded the MRL value, which suggests the use of wax foundation pre-contaminated with naphthalene. This is the case for *p*-dichlorobenzene and it has been concluded that lipophilic substances accumulate in the wax and residues can be found in recycled wax used for the foundation (Bogdanov *et al.*, 2004). In a likewise manner, detectable amounts can end up in honey by the use of built combs that had been treated with naphthalene in the past. For *p*-dichlorobenzene, the respective percentage was 40%.

Table III shows the results with respect to the botanical origin of the samples. The problem is crucial for group A, as 77.5% of the samples were found to contain *p*-dichlorobenzene and 90% naphthalene, while those exceeding the MRL value were 30% and 10% respectively. During this period, the environmental conditions are favorable for the wax moth, and the use of pesticides seems indispensable for the beekeepers.

[Insert Table III about here]

In contrast, group B includes 22% of samples contaminated with *p*-dichlorobenzene, 10% of which above the MRL. Naphthalene was detected in 70% of the samples, but only one (2%) was above the MRL. In particular, in 30 out of 33 citrus honeys naphthalene was detected, but in only one the concentration exceeded the MRL. In fact, 29 out of 30 samples had concentrations below the LOQ (see Table I). Citrus

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3 honey is harvested in early to mid spring, a period with relatively low temperatures that  
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5 are not suitable for the development of the wax moths, thus the application of pesticides  
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7 is not essential. The occurrence of naphthalene in almost 91% of citrus honeys  
8  
9 reinforces the hypothesis for pre-contaminated wax foundations or built combs.  
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13 Less likely, but still important to be mentioned, is the possibility that low  
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15 proportions of naphthalene are of natural origin. Analysis of the essential oil of  
16  
17 *Valeriana tuberosa* L., a common plant in southern Greece, revealed the presence of  
18  
19 naphthalene at the stems, leaves and inflorescence (Fokialakis et al., 2002).  
20  
21 Naphthalene has also been traced in the essential oil of *Ononis viscosa* subsp. *breviflora*  
22  
23 (Erdemgil et al., 2002).  
24  
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## 29 **Conclusions**

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31 The pesticides *p*-dichlorobenzene and naphthalene have been used as an effective tool to  
32  
33 control the wax moths in stored honey combs. These substances are adsorbed in the  
34  
35 comb and end up in honey, due to their lipophilic character. According to the European  
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37 Regulation (EC) No 396/2005, the limit for these two substances is set at 10 µg/kg  
38  
39 honey. Solid-phase microextraction proved efficient for isolating and quantifying these  
40  
41 two analytes. LOD values were 1 µg/kg and 0.1 µg/kg and LOQ values 5 µg/kg and 1  
42  
43 µg/kg for *p*-dichlorobenzene and naphthalene respectively. The RSD values were 2.59%  
44  
45 and 7.92%.  
46  
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50  
51 The method was applied in 90 samples of unifloral honeys from different  
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53 botanical origin and 46.7% of them contained *p*-dichlorobenzene in traceable amounts,  
54  
55 78.9% naphthalene and 84.4% either of the two pesticides. In total, 25.6% of the  
56  
57 samples were improper for human consumption, as either one of the pesticides exceeded  
58  
59 the MRL value. Even though naphthalene was traced in 78.9% of the samples, only in  
60

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3 7% of them overreached the MRL, indicating the use of pre-contaminated honey comb  
4 foundations or built combs, however there is a possibility that nectar from a floral  
5 source naturally containing naphthalene could contribute to honey production.  
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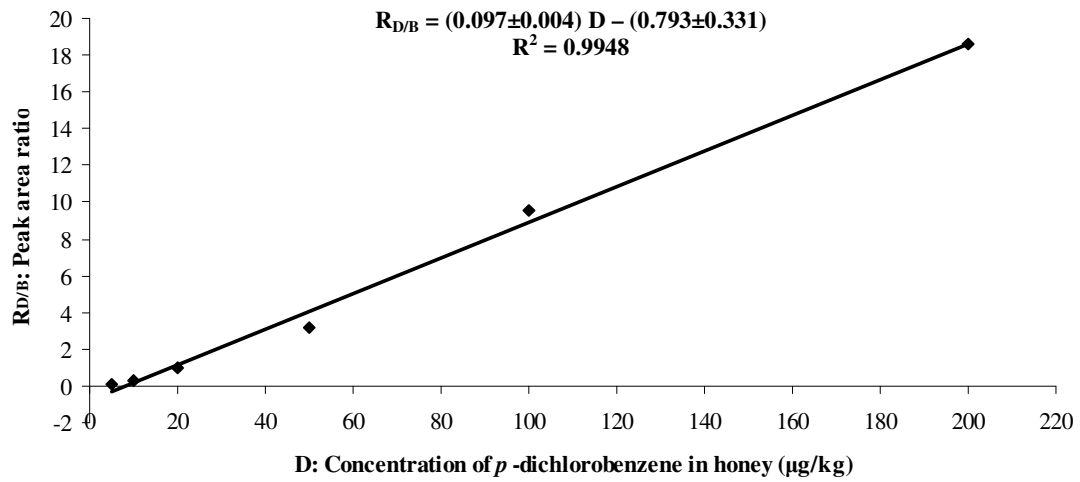


Figure 1. Calibration curve of *p*-dichlorobenzene.

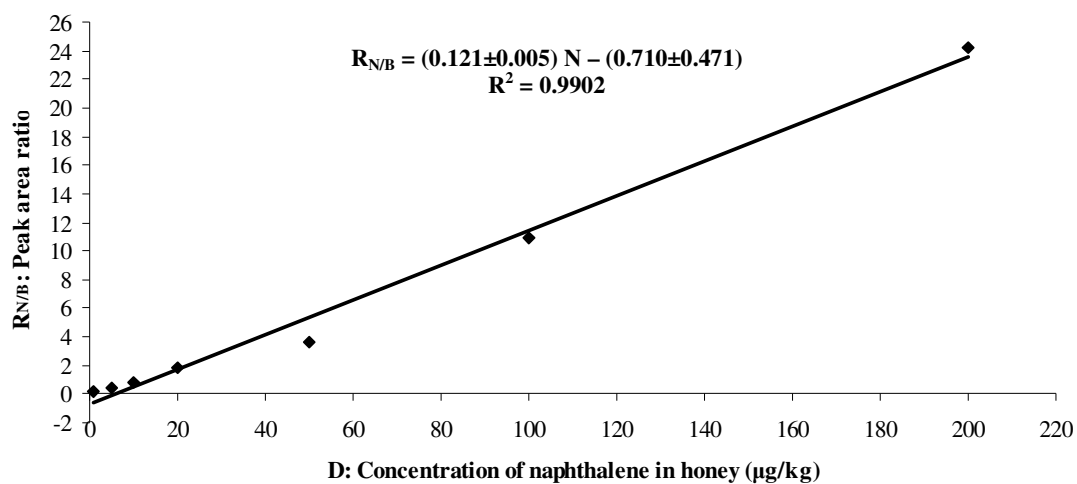


Figure 2. Calibration curve of naphthalene.



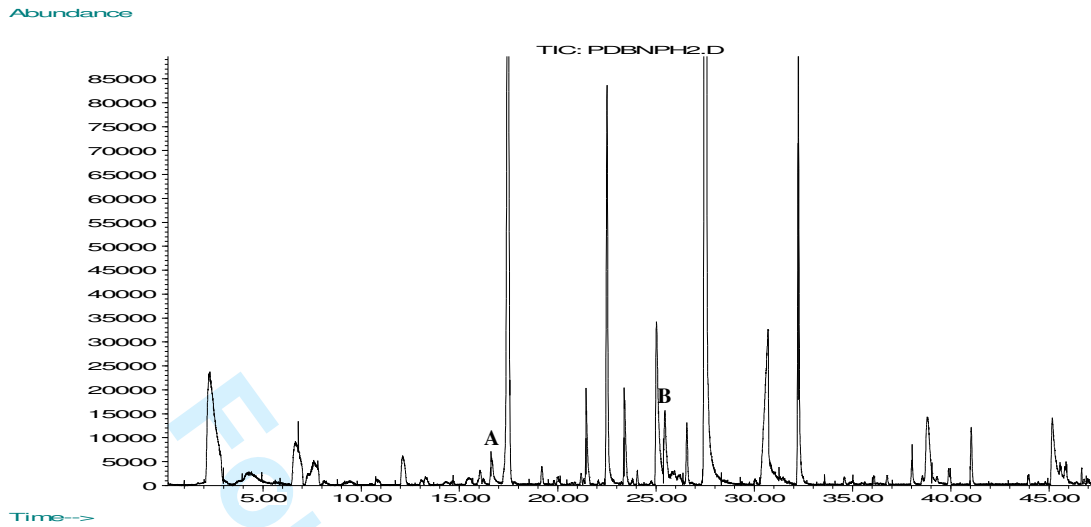


Figure 3. TIC chromatogram of a residue-free sample spiked with 10  $\mu\text{g}/\text{kg}$  of honey for both *p*-dichlorobenzene (A) and naphthalene (B).

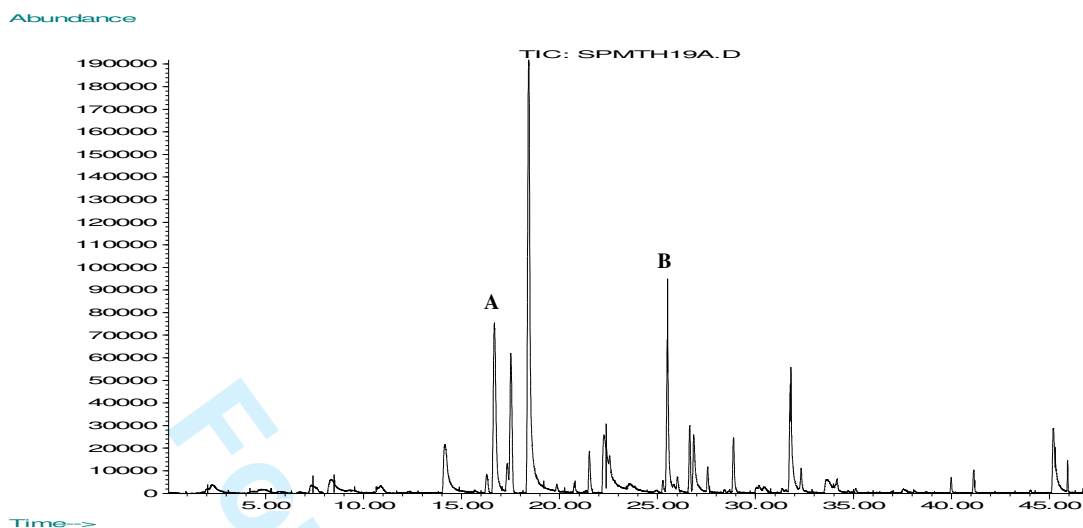


Figure 4. Total ion chromatogram of a real honey sample (thyme honey No 19) containing both *p*-dichlorobenzene (A) and naphthalene (B) at concentrations above the MRL.

Table I. Concentration of *p*-dichlorobenzene and naphthalene in analyzed Greek honeys.

Group A						Group B					
No	Honey Type	<i>p</i> -dichlorobenzene		naphthalene		No	Honey Type	<i>p</i> -dichlorobenzene		naphthalene	
		µg/kg	SD (%)	µg/kg	SD (%)			µg/kg	SD (%)	µg/kg	SD (%)
1	thyme	ND		<LOQ		41	citrus	ND		ND	
2	thyme	12.01	3.10	<LOQ		42	citrus	ND		ND	
3	thyme	ND		<LOQ		43	citrus	ND		ND	
4	thyme	ND		<LOQ		44	citrus	ND		<LOQ	
5	thyme	ND		<LOQ		45	citrus	14.65	2.71	<LOQ	
6	thyme	ND		<LOQ		46	citrus	10.86	4.74	<LOQ	
7	thyme	25.59	6.57	<LOQ		47	citrus	ND		<LOQ	
8	thyme	11.37	6.97	<LOQ		48	citrus	ND		<LOQ	
9	thyme	<LOQ		7.00	3.44	49	citrus	9.87	2.80	<LOQ	
10	thyme	ND		193.74	0.66	50	citrus	12.41	2.40	<LOQ	
11	thyme	12.18	12.39	<LOQ		51	citrus	ND		<LOQ	
12	thyme	<LOQ		21.08	0.58	52	citrus	ND		<LOQ	
13	thyme	<LOQ		7.14	2.24	53	citrus	ND		<LOQ	
14	thyme	9.69	1.63	9.16	1.48	54	citrus	ND		<LOQ	
15	thyme	<LOQ		<LOQ		55	citrus	ND		<LOQ	
16	thyme	9.38	6.12	<LOQ		56	citrus	ND		<LOQ	
17	thyme	<LOQ		<LOQ		57	citrus	ND		<LOQ	
18	thyme	<LOQ		<LOQ		58	citrus	ND		<LOQ	
19	thyme	31.19	3.34	18.19	1.36	59	citrus	ND		<LOQ	
20	thyme	<LOQ		82.58	1.14	60	citrus	38.26	1.06	22.03	1.52
21	thyme	10.84	5.87	7.06	2.68	61	citrus	ND		<LOQ	
22	thyme	9.61	4.08	9.27	3.29	62	citrus	ND		<LOQ	
23	thyme	<LOQ		<LOQ		63	citrus	ND		<LOQ	
24	thyme	ND		<LOQ		64	citrus	9.72	4.11	<LOQ	
25	thyme	23.63	2.17	<LOQ		65	citrus	ND		<LOQ	
26	thyme	15.98	3.61	8.02	2.07	66	citrus	ND		<LOQ	
27	thyme	13.25	3.14	9.64	1.67	67	citrus	ND		<LOQ	
28	thyme	<LOQ		ND		68	citrus	ND		<LOQ	
29	cotton	8.94	6.88	8.46	1.54	69	citrus	ND		<LOQ	

30	cotton	ND		<LOQ		70	citrus	<LOQ		<LOQ	
31	cotton	<LOQ		<LOQ		71	citrus	ND		<LOQ	
32	cotton	<LOQ		<LOQ		72	citrus	ND		<LOQ	
33	cotton	164.03	1.51	<LOQ		73	citrus	ND		<LOQ	
34	cotton	10.64	5.80	<LOQ		74	fir	11.60	2.76	ND	
35	cotton	19.07	7.88	9.51	2.37	75	fir	ND		<LOQ	
36	pine	ND		<LOQ		76	fir	ND		ND	
37	pine	<LOQ		ND		77	fir	ND		ND	
38	pine	11.44	6.74	ND		78	fir	ND		ND	
39	pine	<LOQ		<LOQ		79	fir	ND		ND	
40	pine	9.78	3.60	ND		80	fir	ND		ND	
						81	heather	ND		ND	
						82	heather	ND		ND	
						83	heather	ND		<LOQ	
						84	heather	<LOQ		8.41	3.98
						85	chestnut	ND		ND	
						86	chestnut	12.87	1.48	<LOQ	
						87	chestnut	ND		ND	
						88	eucalyptus	ND		ND	
						89	eucalyptus	<LOQ		<LOQ	
						90	eucalyptus	ND		ND	
ND: not detected. LOQ: limit of quantification.											

Table II. Summarized results for *p*-dichlorobenzene and naphthalene in the 90 samples analysed.

Residues	Detection number (percentage)	Number of samples with concentration > 10 µg/kg honey (percentage of samples)
<i>p</i> -dichlorobenzene	42 (46.7%)	17 (18.9%)
naphthalene	71 (78.9%)	5 (5.6%)
<i>p</i> -dichlorobenzene or naphthalene	76 (84.4%)	23 (25.6%)

Table III. Detection results of *p*-dichlorobenzene and naphthalene in honey samples from various botanical origins.

Botanical origin (number of samples)	<i>p</i> -dichlorobenzene		naphthalene	
	Detection number (percentage)	Number of samples with concentration > 10 µg/kg honey (percentage of samples)	Detection number (percentage)	Number of samples with concentration > 10 µg/kg honey (percentage of samples)
<b>Group A</b>				
thyme (28)	21 (75.0%)	9 (32.1%)	27 (96.4%)	4 (14.3%)
cotton (7)	6 (85.7%)	2 (28.6%)	7 (100.0%)	0 (0.0%)
pine (5)	4 (80.0%)	1 (20.0%)	2 (40.0%)	0 (0.0%)
<b>Sum (40)</b>	<b>31 (77.5%)</b>	<b>12 (30%)</b>	<b>36 (90.0%)</b>	<b>4 (10%)</b>
<b>Group B</b>				
citrus (33)	7 (21.2%)	3 (9.1%)	30 (90.9%)	1 (0.3%)
fir (7)	1 (14.3%)	1 (14.3%)	1 (14.3%)	0 (0.0%)
heather (4)	1 (25.0%)	0 (0.0%)	2 (50.0%)	0 (0.0%)
chestnut (3)	1 (33.3%)	1 (33.3%)	1 (33.3%)	0 (0.0%)
eucalyptus (3)	1 (33.3%)	0 (0.0%)	1 (33.3%)	0 (0.0%)
<b>Sum (50)</b>	<b>11 (22.0%)</b>	<b>5 (10.0%)</b>	<b>35 (70.0%)</b>	<b>1 (2.0%)</b>