Bull. Environ. Contam. Toxicol. (2006) 77:638–642

DOI: 10.1007/s00128-006-1110-z

Bulletin of Environmental Contamination and Toxicology

Effect of Drying on Organophosphorus Pesticide Residues in Peppermint (*Mentha piperita* L.)

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Received: 16 February 2006/Accepted: 20 October 2006[0]

Peppermint is among the economically important individual herbs in Turkey. This herb is widely used as a supplement for dietetic products and especially for "self medications" in the general population. Dried herb is usually used to brew tea.

The presence of high residues of pesticides in herbs can have detrimental effects on public health especially when the plants are freshly consumed. Therefore, it is important to know the residue levels in these plants, but there are a few studies on pesticide residues in herbs (Abou-Arab and Abou-Donia 2001; Ahmed et al. 2001; Zuin and Vilegas 2000).

Information on the effect of drying on residues of pesticide in herbs or other crops is also limited in the literature. Natural drying and hot air drying are still most widely used methods to produce dried herb flakes, because of their lower cost (Soysal and Öztekin 2001). Since the drying process concentrated the herb about 6 times, the amount of pesticide residues in crop might increase theoretically by a similar rate and may reaches dangerous levels if no losses occur due to dehydration (Cabras et al. 1997).

The purpose of this study is to investigate the effect of natural drying on pesticide residues in peppermint and to examine the relationship between physical-chemical properties of pesticides and the dissipation rate of residues during drying. Post-harvested pesticide-free peppermint was treated with malathion, fenitrothion, chlorpyrifos, dimethoate and pirimiphos-ethyl, which are organophosphorus insecticides. Residues were determined using gas chromatograph equipped with a Flame ionisation detector (FID).

MATERIALS AND METHODS

Pesticide standards, malathion (98,1%), fenitrothion (97,6%), dimethoate (99,9%), chlorpyrifos (99,8%) and pirimiphos-ethyl (98,7%) were purchased from Promochem Ltd. (Germany). The pesticide-free fresh peppermint was supplied from local market.

Immediately after harvest, pesticide-free fresh peppermint leaves were separated from stems (2.5 kg) and spread on a metal tray as a thin layer. To allow the

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penetration of the pesticides into the leaves, they were soaked in the pesticide solutions (solution I: dimethoate, pirimiphos-ethyl, malathion and solution II: fenitrothion and chlorpyrifos), where the concentration of each pesticide was 10 mg ml^{-1}, prepared in ethyl acetate (500 mL). After evaporating the excess solvent at room temperature in a fume cupboard for two hours, time-zero samples were taken for analysis. The rest of the samples were dried in a shady, well-ventilated room at the temperature of 20±2 °C for 10 days. The herb was analysed for residues and moisture content at two days intervals during drying. Moisture content was determined according to James (1995).

A 25 g of the herb was homogenized with ethyl acetate (100 mL) and anhydrous sodium sulphate (10 g) in a high-speed blender for 2 min. The homogenate was filtered and the residue was extracted twice with ethyl acetate (2x50 mL). The combined extracts were concentrated to ca. 20 mL in vacuo at 40 °C using a rotary evaporator. Clean up by gel permeation chromatography was performed as previously described (Uygun 1997).

Gas chromatography was performed using a HP5890 gas chromatograph equipped with an FID and capillary column (Alltech AT-1, 30 m x 0.32 mm ID, 0.25 μm film thickness) using nitrogen carrier gas at a flow rate of 2 mL min^{-1}. The oven temperature program was: initial temperature isothermal at 150 °C for 5 min, then from 150 °C to 250 °C at 10 °C min^{-1}, then hold 15 min at 250 °C. Injector and detector temperature was 250 °C. Quantification of the pesticides was performed by comparing the peak areas to that of a calibration curve of standards. Correlation coefficients were found to be higher than 0.98 in all cases, indicating a good linearity.

The recoveries of the pesticides were determined by analysing pesticide-free cut up leaves (25 g), to which were added 1 mg kg^{-1} of the pesticide standards prior to extraction. Then the samples were subjected to the above procedure. The average recoveries from two replicates were determined ranging from 85 to 109.5 % with a maximum standard deviation of 4.6 %.

To determine degradation kinetics, plots of concentration against time were made for each pesticide and the maximum square of correlation coefficients found was used to determine the equation of the best fitting curve. An exponential relation was found to apply for all pesticides under study, corresponding pseudo-first order kinetics equations. Confirmations of the pseudo-first order kinetics were further made graphically from the linearity of the plots of ln$C$ against time.

The rate constant k was calculated from the pseudo-first order kinetics equation;

$$C_t = C_o e^{-kt}$$

where C_t represents the concentration of pesticide at any time t, C_o represents the initial concentration (both concentrations expressed in mg kg^{-1}) and k is the rate constant in $days^{-1}$. The half-lives ($t_{1/2}$) were calculated from the equations.

Table 1. Residue levels* of the pesticides in peppermint leaves during drying (mg kg^{-1}).

Time (day)	fenitrothion	chlorpyrifos	dimethoate	malathion	pirimiphos-ethyl
0	15.94[a]	12.62[a]	4.36[a]	9.94[a]	12.42[a]
2	15.06[b]	8.02[b]	4.09[b]	9.12[b]	11.09[ab]
4	7.69[c]	3.70[c]	2.95[c]	6.05[c]	9.47[b]
6	2.95[d]	2.94[d]	0.414[d]	2.37[d]	5.42[c]
8	1.78[e]	1.05[e]	0.411[d]	0.930[e]	1.38[d]
10	1.37[f]	0.917[f]	0.405[d]	0.874[e]	1.25[d]

*Data are the means of four replicates and expressed on a dry basis.

Table 2. Physical-chemical properties of the pesticides under study ([a]Tomlin 1994; [b]Suntio et al. 1988).

Pesticides	Solubility (mg/L)[a] (at 20°C)	Octanol-water partition coefficient[a] (Log K_{ow})	Vapour pressure (Pa)[b] (at 20°C)
Chlorpyrifos	1.4	4.7	0.0025
Pirimiphos-et.	2.3	5	0.00068[a]
Fenitrothion	21	3.43	0.00040
Dimethoate	23300	0.7	0.021
Malathion	145	2.75	0.0010

Data were statistically evaluated by one-way analysis of variance (ANOVA) procedure (Table 1). When significant differences were found, the LSD (Least Significant Difference) test was used to determine the differences among means.

RESULTS AND DISCUSSION

In this study, for creating an acceptable model similar to the residues of pesticides applied on the plant in field, the pesticide-free leaves were soaked in the pesticide solution to allow penetration of the pesticides into the leaves.

The natural drying in the shade (20±2 °C) reduced the moisture content of the leaves from 85 % to 10.4 %. Higher drying rate was observed during the initial phase, which was the first four days of the drying. Approximately 85.7 % of the water was removed in this period. The drying rate showed a gradual decrease approaching a constant rate (10.4 %) before the end of the drying periods.

A multi-residue pesticide analysis was used for determination of the pesticides in the peppermint leaves during drying. The compounds were identified from their chromatogram and confirmed by comparison with authentic standards. ANOVA results (Table 1) showed that the pesticide residues decreased significantly during drying. Although the concentration factor due to the drying process in peppermint was about 8, the residues were found to be lower in the dried herb than in the time zero sample. The amount of pesticide residues in dried herb did not increase as it was expected theoretically. High amount of losses occurred due to dehydration.

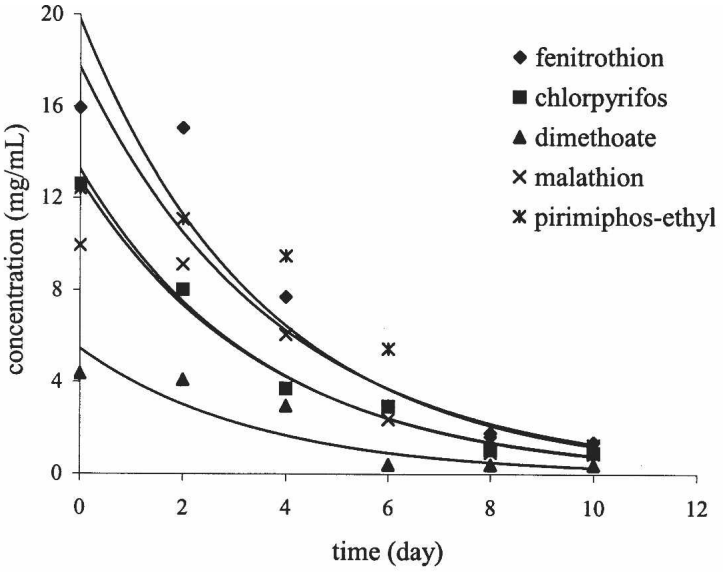

Figure 1. Dissipation of pesticides in peppermint during drying.

Most of the pesticides disappeared during the initial phase of drying, where the drying rate was high. The remaining pesticides in herb could depend to a very high degree on, the physical-chemical properties (Table 2) such as the water-solubility (Ws), the octanol-water partition coefficient (K_{ow}), vapour pressure (Vp).

The disappearance of residues followed the pseudo-first order kinetics as it is presented in Figure 1. Chlorpyrifos showed the fastest decay rate ($t_{1/2}$ = 2.55 days) among the pesticides studied. It has the second highest Vp after dimethoate. The high amount of dimethoate was removed during the evaporating the excess of the solvent from the leaves before drying, probably due to its high Ws. After four days of drying, dimethoate residues did not change as it is presented in Table 1. The present results agree with dimethoate remained constant on dried apricot observed by Cabras et al. (1997).

Fenitrothion decreased by the average decay rate ($t_{1/2}$ = 3.24 days). Malathion has similar dissipation rate ($t_{1/2}$ = 3.43 days) to fenitrothion probably depending on its similar K_{ow} and Vp values to that of fenitrothion. Pirimiphos-ethyl has the highest K_{ow} and the lowest Vp among the pesticides under the study. Therefore, its dissipation rate was the slowest ($t_{1/2}$ = 4.01 days) among others. This also indicated that a proportion of the lipophilic insecticide was retained in peppermint, which contained high level of essential oil.

The results observed in present study indicated that the dissipation rate of pesticides residues during drying was satisfactory, except pirimiphos-ethyl because high octanol-water partition coefficient and low vapour pressure.

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