Delta J. Sci. 12 (2) 1988 482-491

DETERMINATION OF PARATHION AND CHLOROTHALONIL AND ITS RELATED RESIDUES IN HONEY

BY

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Received : 30-6-1988

ABSTRACT

Chlorothalonil (tetrachloroisophthalonitrile a fungicide and parathion (O,O-diethyl-O-p-nitrophenyl phosphorothioate) used against some Lepidopterous insects (Ferris and Litchtenstein, 1980, Gorden and Litchtenstein, 1980) were applied to a cranberry bog. Since chlorothalonil appears not to repel bees as other fungicides do (Marucci, 1985), there was a possibility that significant amounts would appear in the honey. After the 1985 and 1986 growing season, honey taken from hives at the National Cranberry Research Center was analyzed to determine residues of parathion, chlorothalonil, its metabolite, 4-Hydroxy- 2,5,6-trichloro- isophthalonitrile (SDS-3701), Hexachlorobenzene, (HCB) and Pentachlorobenzonitrile, (PCBN). Chlorothalonil and its metablite did appear in the honey over the course of the two year study on this cranberry bog. The residue levels in the second year were 4 to 25

Keywords: honey, parathion, chlorothalonil

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times higher for chlorothalonil and 2 to 23 times higher for the metabolite than in the first year. There should be further increases in the residue levels in the honey if chlorothalonil is used on the other nineteen bogs. In contrast, parathion, which was applied to all twenty bogs at 1/2 to 1/8 the rate, was not found in the honey at lowest level of detection.

INTRODUCTION

Chlorothalonil is used as a fungicide on some economic plants to control certain pathogenic fungi (Ballee et al. , 1976). Parathion is widely used against some Lepidopterous insects infesting cranberry bogs. In 1985 chlorothalonil was applied on June 25 at 2.6 lbs./acre and again on July 2 at 8.34 lbs./ acre for a worst case fungus outbreak. Parathion was applied May 10 and July 12 at 1 lb./acre. Honey samples were taken from individual hives on Aug. 13, 1985 and kept in a freezer at- 20° C until analysis in 1986. In 1986 chlorothalonil was applied at 10 lb./acre in June and July while parathion was kept at 1 lb./acre. On Jan. 16, 1987 honey samles were taken from the same hives for analysis. The residues of parathion were determined using gas chromatography (F . P. D.-G. C.) provided with a flame photometric detector. The other residues in the study were determined using the G. C. provided with an electron capture detector (E . C. -G . C).

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MATERIALS AND METHODS

A. Materials

The same materials and standards for the determination of chlorothalonil and metabolites in cranberries (El-Nabarawy and Carey, 1988) were used with only changes in honey sample preparation being required. In addition, parathion, O,O-diethyl-O-p-nitrophenyl phosphorothioate, 97% pure was used for recovery studies and a standard solution was prepared at 0.1 ug/ml in hexane for this study. For the determination of chlorothalonil and its metabolites the method of El-Nabarawy and Carey, 1988 was used. For the determination of parathion a Tracor gas chromatograph was used (F.P.D.-G.C.) with a Flame Photometric Detector using a phosphorous filter and a 183 cm.x 2 mm. i.d. column containing a mixture of 1.5% SP 2250 and 1.9% SP 2401 liquid phases on 100-120 mesh Supelcoport with 30 ml,/min. N_2 as carrier gas, 80 ml./min. each of H_2 and Air. Temperatures in degrees C. were inlet 220, oven 178 and detector 200.

B. Extraction of Honey Samples

Honey samples were originally subjected to the method used for cranberry analysis. However, emulsions formed which resulted in unseparated phases and poor recoveries. The revised sample preparation avoided these problems. Honey samples (2g) were dissolved in 2 ml of water in a small

beaker. The solution was quantitatively transferred into 250 ml separatory funnel using 70 ml of petroleum ether. The funnel was shaken for 2 min. and vented. At this point the procedure of El-Nabarawy and Carey, 1988 was then followed for extraction, clean-up and methylation of the honey samples with parathion in extract A.

C. Quantitation

Three drops of keeper solution was added to each flask. The solvent was evaporated to approx. 1 ml. using the rotary evaporator. The remaining solvent was allowed to evaporate in a fume hood. The residues were dissolved in 2 ml of hexane for quantitation of chlorothalonil, HCB, PCBN and the methylated metabolite (SDS-3701) by E.C.- G.C. Parathion residues were determined using F.P.D.- G.C.

RECOVERY STUDIES

Honey samples were fortified by the addition of standard solutions of Chlorothalonil, SDS-3701, HCB and PCBN at levels from 0.1 to 1.0 ppm. These fortified samples were processed through all the steps of the analytical method to validate the assay procedure. Recovery studies were performed separately for parathion also at the same levels. Results of the recoveries of the compounds under investigation are shown in table (1).

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RESULTS AND DISCUSSION

All glassware used in this study was baked at 140 C. overnight and stored for use. This simple safeguard eliminated many of the interferences which previously appeared in the chromatograms. All organic solvents used in the study were checked for interferences before use

TABLE (1)

Residue Recoveries from Honey*

PPM	Parathion	SDS-2787	HCB	PCBN	SDS-3701
1.0	100.0	92.5	82.5	87.5	94.5
0.5	95.0	99.2	72.5	81.6	97.5
0.1	95.0	96.0	92.0	100.0	96.6
Std. Dev.0.5		0.87	0.56	1.21	0.82

* % Recovery, mean of two determinations

by evaporating 50 ml. of each solvent to 1 ml. and chromatographed by E.C.-G.C. There was a problem of emulsion formation when the cranberry extraction method was used. This problem could be completely avoided by the modifications described in the extraction section. In addition, it was not necessary to adjust the pH for the extraction of chlorothalonil, PCB and PCBN. Direct extraction of the metabolite is not possible because many interferences are found in the area of interest before and after the methylation step. Therefore, it is necessary to first extract the

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samples for the four compounds and then p[illegible]e second extraction for the metabolite. Blank samples of honey were run through the method and showed no parathion, chlorothalonil or its related residues. [illegible]Table (2) shows

TABLE (2)

Residues * [illegible] Chlorothalonil and its [illegible] Honey

Hive No.	Parathion	SDS-2787	HCB	PCBN	SDS-3701
		8-13-85 Samples			
1	0	0	0	0.007	0.014
2	0	0.007	0.003		0.019
3	0	0		0.023	0.033
4	0	0	0	0	0
5	0	0	0	0	0
6	0	0	0	0	0
		1-16-87 Samples			
1	0	0.091	0	0	0.07
2	0	0.184	0	0	0.32
3	0	0.026	0		0.28
4	0	0.054	0	0	0.21
5	0	0.14	0	0	0.072
6	0	0.05	0	0	0.19

* Conc. PPM

** The date was written according to the American System.

that only hive No. 2 from 1985 has a chlorothalonil residue while the related and the metabolite were found in a few other samples. However, all 1987 samples contained chlorothalonil and SDS-3701 residues at more significant levels. HCB and PCBN at a minimum detectable level of 0.005 ppm. were not found. Samples of 1985 and 1987 showed no residues of parathion with a minimum detectable level of 0.005 ppm. E. Laurence Atkins (The Hive and the Honev Bee, 1984) indicated that honey is not easily contaminated by pesticides because of the hive social structure. However, studies by A.I. Illarionov, 1977 indicate that sugar feeding stations 1.5 km. from a hive and containing insecticides resulted in those insecticides being brought into the hive with nectar and honey in quantities sufficient to kill young bees. Other studies (Pourtallier and Taliercio, 1967; Ogata and Bevenue, 1973; Sundaram, 1974; Grandi, 1975 and Bentler and Frese, 1981) indicate that honey collected worldwide is contaminated with low levels of pesticides including the organochlorine, organophosphorous and carbamate compounds, generally below the 1 p.p.b. level and within limits of international honey standards (Tsverlkova et al. 1981)

ACKNOWLEDGEMENT

The authors thank Prof. P. E. Marucci, Dir., National Cranberry Res. Center for his help with the experimental plots and his encouragement and also Frank Wojcik, who maintains the hives and sampled the hive honey.

This project was supported by state and Hatch funds, New Jersey Agricultural Experiment Station, Publication No. D-07117-1-88.

REFERENCES

Ballee, D.L., Duane, W.C., Stallord, D.E. and Wolfe, A.L. (1976) Analytical Methods for Pesticides and Plant Growth Regulators (8) 263-274.

Bentler, W. and Frese, E. (1981) Archiv. fur Lebensmittel-hygiene 32 (4) 130-135

El-Nabarawy I.M. and Carey, W.F., (1988) J.A.O.A.C. 71 (2) pp. 358-360

Ferris, I.G., Litchtenstein, E. P. (1980) J.Agric Food Chem. 28 (5), 1011-1019

Gorder, G. W.; Litchtenstein, E.P. (1980) J. Can. Microbiol. 26 (4) 475-481

Grandi, A. (1975) Revista di Scienza e Techologia degli Alimenti e di Nutrizione Umana 5 (2): 103-105

Illarionov, A.I. (1977) Pchelovodstvo (11), 31

Marucci, P.E. Director of the Cranberry Research Center, Chatsworth, NJ 08019

Ogata. J.N. and Bevenue, A. (1973) Bul. Env. Contam. and Toxicol. 9 (3) 143-147

Pourtallier, J. and Taliercio, Y (1967) Bull. Epic. Inf. Docum. Scient. Tech. 10(1) 51-62

Delta J. Sci. 12 (2) 1988
I.M. El-Nabarawy and W.F. Carey

Sundaram, K.M.S. (1974) Information Report, Chemical Control Researh Institute, Environment Canda Forest Service, No. CC-x-63, pp 25

The Hive and the Honey Bee. Seventh Printing 1984, Journal Printing Co., Carthage Illinois pp. 663-696

Tsverlkova, T.; Peneva, V. and Grigoorova, D. (1981) Veteri varnomedetsinski Nauki 18 (1), 93-98.

تقدير متبقيات الباراثيون ،الكلوروثالونيل ونواتج تمثيله في عسل النحل

د٠ ابراهيم متولى النبراوى د٠ وليام ف٠ كيرى
المركز القومى للبحوث بالدقى ـ القاهرة ـ مصر٠
نيو جيرسى ـ قسم علوم البيئة ـ جامعة رتجرسى ـ امريكا

بعد معاملة محصول الكرانبيريزبمبيدى الكلوروثالونيل والباراثيون فى ولاية نيوجيرسى بالولايات المتحدة الامريكية خلال موسمى الزراعة ١٩٨٥ ، ١٩٨٦ تم أخذ عينات عسل نحل من مناحل مختلفة بالمركز القومىللكرانبيريز لتقدير متبقيات الباراثيون ، الكلوروثالونيل وناتج تمثيله الميثيلى ، الهكساكلوروبنزين والبنتاكلوروبنزونيتريل وحيث أن مبيد الكلوروثالونيل ليس له تأ ثير طارد لنحل العسل كبقية المبيدات الفطرية الاخرى فانه من المحتمل وجود كميات معنويه من هذا المبيد فى العسل وقد وجد كل من الكلوروثالونيل وناتج تمثيله الميثيلى فى عسل النحل المأخوذ بعد انتهاء موسمى الزراعة تحت الدراسة وكانت كمية الكلوروثالونيل فى عام ٨٦ أعلى بمقدار من ٤ـ٢٥ مرة عن عام ٨٥ بينما كانت كمية ناتج تمثيله الميثيلى فى عام ٨٦ أعلى بمقدار من ٢ـ٢٣ مرة عن عام ٨٥ ومن المحتمل زيادة وجود هذا المبيد وناتج تمثيله اذا ما استخدم هذا المبيد فى مساحات أكبر من ذلك٠ وقد لوحظ عدم وجود مبيد الباراثيون الذى استخدم فى مساحات كبيرة من هذا المحصول وذلك بأقل حد للتقدير٠