



Monitoring and Surveillance of Synthetic Pyrethroids and Organophosphate in Different Brands of Soft Drinks

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ABSTRACT

The present endeavour entitled "Monitoring and Surveillance of Synthetic Pyrethroids and Organophosphate in Different Brands of Soft Drinks" was carried out for the fulfilment of aforesaid with nine different brands of samples viz. Pepsi, Mountain Dew, Thums up, Mirinda, Fanta, Sprite, Limka, Coca-Cola and Slice were collected. The total 28 samples including all nine different brands were processed, extracted and clean up by using multi-residues technique, finally the insecticidal residues of synthetic pyrethroids and organophosphate were determined through Gas Liquid Chromatography (GLC). The result obtained are- Residues of synthetic pyrethroids:- Residues of deltamethrin, fenvalerate, cypermethrin and permethrin were recorded in 25%, 7%, 18%, and 3% of the total cold drink samples of different brand. Residues of organophosphate, insecticide:- residues of dimethoate, Quinolphos, malathion, ethion and monocrotophos were recorded in 25%, 14%, 11%, 11% and 7% of the total samples of cold drink of different brands.

Keywords: Gas liquid Chromatography, Organophosphate, Pyrethroids, Soft drink

INTRODUCTION

India is the third largest consumer of pesticide in the world and highest among the South Asian countries. Over the years pesticides consumption of India has increased several hundred folds from 154 MT in 1953-54 to 80,000 MT in 1994-95. However, thereafter the consumption of pesticide steadily declined to the present level of 54,135 MT (based on 1999-2000 demand). The decline was primarily because of ban on use of organochlorine pesticides such as HCH, DDT, Aldrin etc. The government of India has banned the use of DDT in Agriculture from January 1994 and that of HCH from April 1997. Up to 1995-96 the major group of chemicals used in agriculture were insecticides (80%) followed by fungicides (10%), herbicides (7%) and others (3%). The consumption of insecticides in 1999-2000 was 60%, fungicides 21%, herbicides 14% and others 5%. It is observed that the percentage consumption of insecticides declined with simultaneous increase in the percentage consumption of herbicides and fungicide. An area wise consumption of pesticides show that, the state of Tamilnadu, Andhrapradesh, Maharastra, Punjab, Gujrat, West Bengal, Haryana and M.P accounts for 82% of total pesticides consumption. At present Tamilnadu is highest in

pesticides consumption accounting to 2500 Mt (16% of total consumption) followed by Andhrapradesh, Uttar Pradesh and Maharashtra.

MATERIALS AND METHODS

The present study entitled "Monitoring and Surveillance of Synthetic Pyrethroids and Organophosphate in Different Brands of Soft Drinks" was carried out by adopting the following materials and methods.

1. Materials

a. Equipment:

- (i) Single pan electric balance,
- (ii) Refrigerator for storage of technical grade pesticides and sample extracts,
- (iii) Rotatory vacuum evaporator with temperature controlled water bath,
- (iv) GLC (Gas liquid Chromatography) GC 17A Ver.3 model,
- (v) Micro Syringe (10 μ L capacity),

b. Glass Wares: Separatory funnel (1000 ml), Beaker (100 ml), Measuring cylinder (500 ml cap), Glass rod, Absorbent column (2.5 cm ID and 15 cm long), Iodine flask, Graduated test tube (10 ml), Stopped cylinder (100 ml), Micro pipette (1 ml).

c. Chemical and miscellaneous: Distilled n-Hexane, Methylene Chloride, Sodium Chloride, Activated Anhydrous Sodium Sulphate, Distilled acetone, HPLC grade n-hexane, HPLC grade acetone

2. Experimental procedure:

a. Sampling: 500 ml cold drink bottle of different brands of from sites of Kanpur City and its adjoining area were collected and stored in refrigerator for analytical work.

b. Extraction and clean up of cold drink: The extraction of cold drink sample was done by the following methods-

(i) 500 ml of cold drink sample was taken in one liter separatory funnel and to this 10 gram of sodium chloride was added. The funnel was soaked to dissolve sodium chloride completely,

(ii) The residues were extracted thrice with methylene chloride (50:25:25 ml), each time shaking vigorously for 1 minute releasing the pressure intermittently.

(iii) Dry lower organic layer by passing through about 1.5¹¹ anhydrous sodium sulfate supported on washed clean wool in 4¹¹ funnel,

(iv) Combined the organic layers and concentrated to 0.5 ml using vacuum rotatory evaporator at 40⁰C. Concentration step was repeated thrice in the presence of distilled hexane to remove all traces of methylene chloride

(v) The residues were dissolved in 10 ml graduated test tube and finally make up the volume with HPLC grade n-hexane.

c. Estimation: The multi residues of pesticides were estimated in accordance with the following analytical process and the specific parameter of GLC for particular insecticide. **Instrument:** (GLC Shimadzu 17 A ver.3 model, Detector =ECD (electron capture detector) equipped with N⁶³). **Column:** (Capillary column D B-1. Film thickness, 0.25 μ m. Inner diameter: 0.25 ID, Column length: 30 m). **Temperature: For synthetic pyrethroid:** Oven = 220⁰C, Column = 260⁰C, Detector = 300⁰C, **For organophosphate:** Oven = 200⁰C, Column = 250⁰C, Detector = 280⁰C. **Carrier gas:** Nitrogen @40ml /minute, Hydrogen @30 ml/minute, O Air @30 ml/ minute, Attention 1 for 0⁰C & sp and O for, OP, Column mode- 2ml/minute, Injection mode-Split, Split ratio-20.

d. Recovery studies: A representative sample of 50ml cold drink of each brand was fortified at 1-ppb. Level either different standards of Organochlorine, Synthetic pyrethroid and organophosphate. The fortified sample were processed as per the methodology and residues of organochlorine synthetic pyrethroid and organophosphate were estimated by GLC technique (Gas Liquid chromatography)

3. **Calculation:** Residues level in sample was calculated as follows.

$$\text{Residues level in mg kg}^{-1} = \frac{A_s}{A_{std}} \times \frac{M}{M_1} \times \frac{V}{V_1}$$

Where

AS=Peak area of unknown sample

Astd= Peak area of the standard

M=μL of standard injected-1μl

M₁=μL of sample extract injected-2μl

V= Volume of the sample extract in ml.

V₁= Volume of the sample in litre.

RESULTS AND DISCUSSION

Synthetic pyrethroids:-Table-1 reveals that all the brands of cold drink also found contaminated with different pyrethroids. The results are described separately under the following heads pertaining to each insecticides.

1. **Deltamethrin residues:-** Table-1 shows that deltamethrin residues are found in Mountain Dew, Mirinda, Sprite and Slice brand of cold drink, but their concentration of contamination is too low i.e. ND(non detectable) to 0.009, 0.008, 0.009 and 0.009 μg/L respectively. Mountain Dew cold drink sample only three out of six samples analysed, found to be contaminated with deltamethrin. In mirinda cold drink samples showed 50% contamination in range of 0.007 to 0.008 μg/L. In Sprite and slice cold drink samples also found to be contaminated with 50% of total samples analysed. Pepsi, Thums-up, Fanta, Limca and Coca-cola brands not found contaminated with deltamethrin.

2. **Cypermethrin residues:-** Results show (table-1) that only Mirinda, Sprite and Slice brands of cold drink found to be contaminated with cypermethrin. While their level of concentration are very low i.e in range of 0.009, 0.009 and 0.008 μg/L respectively. The Pepsi, Mountain-Dew, Thums-up, Fanta, Limca and Coca-cola drink samples are not found contamination with cypermethrin.

3. **Permethrin residues:-** Summary table-1 reveals that out of nine brands only one brands of cold drink samples found to be contaminated with permethrin. Two Fanta cold drink samples analysed and one samples contaminated with permethrin in low concentration i.e 0.008μg/L. Pepsi, Mountain Dew, Thums-up, Mirinda, Sprite, Limca, Coca-Cola and Slice brands of cold drink not found contaminated with Permethrin.

4. **Fenvalerate Residues:-** Summary table -1 reveals that only two brand of cold drink i.e Sprite and Slice drink was contaminated with Fenvalerate insecticide. Their level of concentration was also found to be low (0.009 μg/L), others brands of cold drink showed not detection of fenvalerate pyrethroid. The report published by CSE (Centre for Science and Environment) on the presence of pesticides in packaged water and soft drinks created not only awareness but also over reaction by public considering the seriousness of the matter, the government constituted a joint parliamentary committee. Committee recorded that the findings of CSE are correct on the presence of pesticides in carbonated water in respect of three samples each of 12 brand products of Pepsi and Coca Cola. CSE analysed 36 samples of different brands products of Pepsi and Coca-Cola and tested for 32 most used pesticides of India (16 OC_s, 12 OP_s and 4 SP_s). CSE detected lindane and Chlorpyrifos in all 36 samples, malathion in 35 and DDT and its metabolites in 29. Synthetic Pyrethroids were not found in any of the 36 samples. Some of the samples were also independently analysed at CFTRI Mysore and CFL (Central Food Laboratory) Kolkata and the results were confirmed by the use of GC-MS [1].

Organophosphorous insecticides:- Twenty eight cold drink samples were collected of different brand and they were found contaminated with organophosphorous insecticides. The results are described separately under the following heads.

1. **Dimethoate residue:-** Summary table -2 shows that dimethoate are found in Mountain Dew, Mirinda, Fanta and Sprite brand of cold drink. In Mountain Dew cold drink out of four samples, only two samples were contaminated with dimethoate in concentration of 0.006 and 0.012μg/l respectively. Mirinda cold drink three samples were contaminated within range of 0.006, 0.007 and 0.008 μg/L respectively. One samples of mirinda could not detected dimethoate. Fanta drink also found contaminated with dimethoate in range of 0.009 μg/L. Sprite cold drink was found contaminated in range of 0.008 μg/L. One samples each of both Fanta and Sprite cold drink was found not

contaminated with dimethoate. Pepsi, Thums-up, Limca, Coca-Cola and Slice cold drink were found free from dimethoate concentration.

2. Quinolphos residue:- Summary table -2 shows out of nine brands of cold drink only three brands were found contaminated with quinolphos. Results shows Pepsi brand was contaminated with quinolphos in range of 0.004 and 0.006 $\mu\text{g/L}$ respectively. Mountain Dew cold drink showed in only one sample contaminated with quinalphos while other two samples showed not any detection of quinolphos. In sprite drink one sample was contaminated in range of 0.012 $\mu\text{g/L}$. There are reports regarding the presence of HCH and DDT in drinking water samples collected from Faridabad, Bhivani, Thajjor, Rohtak, Hissar and Kiathal. Few of the samples have also been reported to contain residues of quinalphos, chlorpyriphos and DDVP. Only one samples showed the residues above MRL (3ppb) in respect of γ -HCH, while 13 out of 30 exceeded WHO permissible limit of DDT i.e ppb [2].

3. Malathion residues:- Summary table-2 showed that only two cold drink brand out of nine brands was contaminated with melatherion. Pepsi and Mountain-Dew cold drink, total 10 samples analysed and only three samples were found to be contaminated with Malathion in range of 0.013, 0.021 and 0.016 $\mu\text{g/L}$. Agnihotri et al. [1993] reported that pesticide application in agriculture affects the quality of river and ground water [3]. Samples of ground water, drain water, soil, sub-soil and river water were contaminated with residues of DDT, HCH, Aldrin, Heptachlor, Malathion, Methylparathion, Quinolphos and Monocrotophos.

4. Ethion residue:- Results showed that total 28 samples of cold drink were analysed for ethion insecticides and only three samples were found contaminated in range of 0.011, 0.008 and 0.006 $\mu\text{g/L}$ respectively. MountainDew cold drink contained ethion residues in only two samples out of six. One samples of Fanta drink contained ethion in concentration of 0.006 $\mu\text{g/L}$.

5. Monocrotophos residues:- Summary tables-2 results showed that only two samples of Mountain-Dew cold drink found to be contaminated with ethion in very low concentration of 0.003 and 0.001 $\mu\text{g/L}$. Other brands of cold drink could not be detected monocrotophos insecticides. Pathak et al. [1992] and Prabhaker [2003] reported that out of the 322 samples of ground and surface water, 105 samples were contaminated with DDT residues, 149 samples with the HCH, 88 samples with endosulfan and 93 samples with other commonly used organochlorine and organophosphorus pesticides [4, 5].

Table:1 Conc. of synthetic pyrethroids in cold drinks ($\mu\text{g/L}$)

Name of Brands	Delta methrin	Cypermethrin	Permethrin	Fenvalerate
Pepsi	ND	ND	ND	ND
Mountain Dew	ND-0.009	ND	ND	ND
Thumps UP	ND	ND	ND	ND
Mirinda	ND-0.008	ND-0.009	ND	ND
Fanta	ND	ND	ND-0.008	ND
Sprite	ND-0.009	ND-0.009	ND	ND-0.009
Limca	ND	ND	ND	ND
Coca Cola	ND	ND	ND	ND
Slice	ND-0.009	ND-0.008	ND	ND-0.009

Table: 2 Conc. of organo -phosphate insecticides in cold drinks ($\mu\text{g/L}$)

Name of Brands	Dimethoate	Quinolphos	Malathion	Ethion	Monocrotophos
Pepsi	ND	ND-0.008	ND-0.013	ND	ND
Mountain Dew	ND-0.012	ND-0.007	ND-0.021	ND-0.011	ND-0.003
Thumps UP	ND	ND	ND	ND	ND
Mirinda	ND-0.008	ND	ND	ND	ND
Fanta	ND-0.009	ND	ND	ND-0.006	ND
Sprite	ND-0.008	ND-0.012	ND	ND	ND
Limca	ND	ND	ND	ND	ND
Coca Cola	ND	ND	ND	ND	ND
Slice	ND	ND	ND	ND	ND

CONCLUSION

From the forgoing study it is concluded that cold drink of different brands was found to be contaminated with above mentioned pesticides. HCH was found to be dominant contaminant followed by DDT, Dicofol, Endosulfan and chlorpyrifos. Synthetic Pyrethroids and organo phosphates were also found in some cold drink samples.

REFERENCES

- [1]. Anonymous, Joint parliamentary committee report. *Pesticides Research J.*, **2004** **16(2)**:81-96.
- [2] Anonymous. Annual reported [1997-98] AICRP on pesticides residues. CCS Haryana Agricultural University, Hissar, **1999**, pp: **35**
- [3] Agnihotri, N.P. Gajbhiye, V.T. and Mahapatra, S.P., Contribution of agricultural application of pesticides on quality of river and ground water. National conference on eco friendly approaches in the management of pests, disease and industrial effluents. Dec.**1993**, **PP: 85**.
- [4] Pathak, S.P., Kumar, S., Ramteke, P.W., Murthy, R.C. Singh K.P., Bhattacharjee, J.W and Ray, P.K. Riverine pollution in some northern and eastern states of India. *Environ Mohit. Assessment*, **1992**, **22**: 227-236.
- [5] Prabhakar, V.P. DDT, HCH and Endosulfan in water sample. *Pesticides research J.*, **2003**, **15(1)**: 110.