Organochlorine and synthetic pyrethroid pesticides in agricultural soil and water from Chamaranagar district, Karnataka, India

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Eight Organochlorine (OC) and two synthetic pyrethroids (SP) were measured in soil, rice field, and sub canal and river water in samples collected from around Chamaranagar District, Karnataka State, India. The soil and water samples were extracted by Multi-residue Method and analyzed during Gas Chromatograph equipped with ECD (Electron Capture Detector). The average contamination with OC and SP in soil (0.00 to 46.60 µg/kg) which was higher than sub canal water (0.25 to 34.12 µg/l) and the average residue of both was more than the rice field water (0.15 to 4.65 µg/l). The Endosulfan residues were generally the highest in the soil samples in comparison with water and the average values were in the order of: soil (68.20 µg/kg) > sub canal water (32.26 µg/l) > rice field water (2.57 µg/l). The average residue of Cypermethrin in soil (8.60 µg/kg) was highest followed by field water (0.92 µg/l) and sub canal (0.247 µg/l) whereas contamination with Fenvalerate was: sub canal (20.57) > soil (19.20 µg/kg) > field water (0.47).

Key words: Organochlorines, synthetic pyrethroids, soil, water, GC/ECD.

INTRODUCTION

Contamination of water resources is a worldwide phenomenon. The improper use of plant protection chemicals has resulted in many environmental implications and one such is surface water contamination (Bhatnagar et al., 1992, Bhattachrya et al., 2003, Das et al., 2003). Today the pesticide residues are among the dominant contaminants of water as plenty of pesticides are used to combat the insect-pest complex of agriculture and other fields related to health programme (Kumari et al., 2007). As a consequence wide spread contamination of different water sources viz., stream river, ground, surface, marine and ground water has been reported all over the world. After application of pesticides in agricultural crops, a fraction used reaches the soil, even when applied to plant foliage (Fenoll et al., 2006).

Organochlorine pesticides have been reported to cause serious diseases in humans as well as they are detrimental to soil microflora and microfauna (Battu et al., 1989; Agnihorti et al., 1996; Ares et al., 1999; Titus et al., 2001; Das et al., 2003; Nawab et al., 2003). In many developing countries including India, two forms of HCH are used: technical HCH (a mixture of α-, β-, γ- and δ-HCH) and lindane (only γ-HCH) until the ban was imposed in 1997. However, restricted use of lindane still continues.

Pyrethroids are synthetic derivatives of pyrethrins, the natural insecticides that are produced by certain species of Chrysanthemum. Pyrethroids of greatest interest to water quality include cypermethrin and fenvalerate. Pyrethroids are extremely toxic to aquatic organisms, with lethal concentration (LC50) values less than 1.0 ppb. They are applied in urban areas primarily for structural pest control, in agricultural areas and in the home as pet sprays and shampoos. Some of the new pyrethroids such as cypermethrin, which is used in much lower amounts, could be up to 20 times more toxic than permethrin (Amweg et al., 2005).

The primary transport pathway for pyrethroids is receding waters from agricultural and urban applications through runoff. Pyrethroids are persistent compounds and feebly soluble in water (Laskowaski, 2002). Several recent monitoring studies in California have reported...
synthetic pyrethroid contamination of both surface waters and sediments (Hengel et al., 1997; Weston et al., 2004; Gan et al., 2005). The objective of this study is identification and determination of residues eight Organochlorine (OC) and two synthetic pyrethroids of Chamaraghar district of Karnataka state, India.

MATERIALS AND METHODS

Sample collection

An area of rice field was selected around Cauvery river basin across Chamaraghar District, Karnataka, India for sampling. Five soil samples from 0 to 25 cm depth were collected randomly in 2007. Samples were separately stored in labeled polyethylene bags and transported to the laboratory, air dried in shade, powdered by passing through 1 mm sieve and mixed homogenously. The water samples were collected in a clean plastic container from Cavery River, and a sub-canal of rice crop. Both the samples were stored in refrigerator at 4°C. Each sample of water and soil is representative of five points within the farmland.

Extraction (soil)

For analysis of pesticide residues in soil, 50g sample was weighed and ammonium chloride was added (NH₄Cl 0.2M) in a 500 Erlenmeyer flask followed by 50:50 acetone/petroleum ether and shaken for 20 minutes on a mechanical shaker for 12 hours and, filtered through Whatman No. 1 filter paper. Fifty ml of acetone was added to the extract, again shaken manually for 20 min, and filtered. To remove excess solvents, Rotary Evaporator, Temperature 45-50°C was used.

Clean-up

The crude extracts were cleaned up by florosil Column chromatography. Glass columns (40 cm × 1.1 cm i.d.) were packed from the bottom with glass wool plug, 8 cm of activated florosil and 4 cm anhydrous Na₂SO₄ to remove excess oil, fat and moisture contents respectively. The packed column was rewashed with 50 ml petroleum ether. The extracts were transferred to the column diluted with 160 ml petroleum ether mixed with diethyl ether. The combined extracted were reduced to dryness and the final volume was made to 5 ml with n-hexane.

Extraction (water)

The OC and SP were extracted by the water immiscible non-organic solvent, dichloromethane. To 500 ml of water sample 50 ml dichloromethane and 10 ml of saturated sodium chloride was added to break the emulsion in a separating funnel. This process was repeated thrice to ensure maximum recovery of the residues. The Combined organic phases were filtered through anhydrous sodium sulphate using glass column. Filtered extract was concentrated to near dryness on rotary vacuum evaporator.

Gas chromatograph

The GC analysis was performed on Shimadzu, Japan model GC 2010 equipped with ECD (Electron Capture Detector). A fused silica capillary column (BP5, 5%phenyl), 95% Dimethyl polysiloxane, 30m length and 0.25 µm ID, film thickness 0.25 µm) was used for the analysis of general purposes. Samples were injected in split mode at 240°C. Extract aliquots of 1 µl were directly injected in the GC system.

Calibrations and estimation

Injecting 1µl of the standard solution or the cleaned up extract into the GC and identified the peaks by their retention times and by recording the peak areas. A Gas Chromatograph (Shimadzu 2010, Japan) equipped with Ni⁶³ Electron Capture Detector was used for estimation of residues. A capillary column of 30 m×0.25 mm ID with film thickness 0.25µm was used. The injection and the column oven temperature were set at 260°C and also detector temperature was 300°C with a nitrogen flow rate of 3 ml/min.

Calculation

\[
\text{Residues value } \mu g/g = \frac{A_s \times V_{std} \times C_{std} \times D_t}{A_{std} \times V_s \times W_s}
\]

Where;
- \(A_s\) = peak area of sample injected (mv)
RESULTS

The pesticide chosen for this study included eight OC and two SP. The standard solutions were separately injected into GC followed by a sample injection to identify qualitatively the analytes of interest on the basis of their respective retention time. Results of analysis Dichlorodiphenyldichloroethylene and metabolites (p,p'- DDT, DDE, pp'-DDD), α- and β- Endosulfan, α-cypermethrin and Fenvalerate in soil and water are shown in Table 1. The ADI determined by Australian (2006) is 0.006, 0.05, 0.002, 0.003, 0.02 mg/kg body weight for endosulfan, cypermethrin, DDT, γ-HCH, fenvalerate respectively ant has been reported that the intake was 0.360, 3.00, 0.120, 0.180, 1.20 mg/day per person, respectively. Based on the residues calculated the intake for a 60 kg body weight consuming 3 liter of water daily presented in table 2. The result showed that endosulfan and DDT value is above and γ-HCH, α- cypermethrin, fenvalerate in comparison with Australian guideline value (2006) was below ADI.

Comparison of residues in soil, water and sub canal water

The average contamination of OC and SP in soil “0.00 to 46.6μg/kg” is higher than sub canal water “0.257 to 34.125μg/l” and average residue of both is more than rice field water “0.15 to 4.65μg/l”. The Endosulfan residues were generally the highest in the soil samples in comparison to water and the average value followed: soil > sub canal water and rice field water. The average of Σ-HCH in soil (19.8μg/l) is higher than in rice field water (7.55μg/l) and sub canal water (2.15μg/l). The average Σ-DDT in rice field water (5.075μg/l) is less in soil (52μg/kg) and sub canal water (41.25μg/l). The average residue of cypermethrin in soil (8.6μg/kg) is higher than field water (0.925μg/l) and sub canal (0.247μg/l) whereas contamination of fenvalerate is highest in sub canal (20.575μg/l).

DISCUSSION

Several investigators have recorded the presence of OC and SP compounds in soil and water (Lytikainen et al., 2003; Ownby et al., 2004; Prakash et al., 2004; Fendoll et al., 2005; Marina and Ronco 2005; Nyangabobo et al., 2005; Tao et al., 2005; Ahad et al., 2006; Zafar 2006; Kumari et al., 2007; Mekebri et al., 2008).

The persistence of organochlorine pesticides is reported to vary from 50 days to 30 years (Tomlin 2002, Lee 2003). The residue levels recorded in this study are supported by several earlier reported events. Prakash et al. (2004) observed the sum of all isomers of HCH in soils as “0.20 to 212.20μg/kg”. In Spain, OCP such as HCH and DDT were detected at levels ranging from moderate to severe pollution in stream sediments, in spite of ban a few decades ago (González et al., 2005). Tao et al. (2005) reported an average of (45.8±141 μg/kg) HCH in soil. The analysis of some soil samples in northern Portugal revealed the presence of persistent pesticides, parent compounds and degradation products such as Endosulfan, DDE, DDD and alachlor (Goncalves et al., 2006; Zhang et al., 2006).

DDT found in the environment might be because of the historical use as a general insecticide when large quantities of DDT were directly applied to agricultural soils specifically for vector control (Vieira et al., 2001; Torres et al., 2002). On the other hand, agricultural applications of DDT persistent in the environment, with a reported half-life of 2 to15 years (Howard et al., 1991). India, for many years, was a major consumer of BHC Li (1999), which is in fact a technical mixture of HCH isomers, and its concentrations in the Indian population are among the highest in the world (Allsopp et al., 1995 & 1998).

India banned the use of technical HCH in 1997 (Kalra et al., 1999). However, Local application now and then is preferred as it is a cost effective agent. Although limited use of γ-HCH still continues in India, industries engage in export of γ-HCH, generate α-, β-, γ- HCH as by product and discard waste in the open (Prakash et al., 2004). The HCH residues possibly reach soils as a result of run-offs from dumping sites to adjoining sites and contaminate the water resources besides agricultural products.

The widespread occurrence of γ-HCH further indicated that instead of restriction, excessive and indiscriminate use of technical HCH and Lindene (γ-HCH) still continues due to low cost and popularity of formulations among farmers. Also for National Malaria Eradication programme (NMEP) (Pesticide Residue Research, 2004). The presence of higher ΣHCH in soil and water could also be due to leaking of HCH isomers through rain as well as water during irrigation and hence decreased
accessibility to microbial degradation as opined by (Ares et al., 1999). Interestingly, ground water, drinking water and even soft drinks were found to contain very high levels of HCH residues in metropolitan cities like Delhi and Mumbai (Narain 2003).

Conclusion

Out of five samples (62%), four main fields, four sub canal and one river water 82.5%, 77.5% and 80% of the samples were contaminated with different Organochlorines and synthetic pyrethroids pesticide residues respectively. The presence of residues showed degradation of OC and SP are very slowly, persistent compounds, not very soluble in water and also farmer using frequently in the field. The higher of trace in the samples presented they could be hazards health in the ecosystems. The extraction and clean-up gave good result. Gas Chromatography equipped with Electron Capture is more efficient technique for the analysis of Organochlorines and Synthetic Pyrethroids.

REFERENCES


Table 1. Concentration of organochlorine and synthetic pyrethroid (µg/kg) in soil and water samples (µg/l) from Chamraganagar district of Karnataka

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ND= Not Detected, 1(Endosulfan), 2(Cypermethrin), 3(Fenvalerate), 4(Rice field), 5(Sub-canal) and 6(Cauvery)

Table 2. Daily intake for River Cauvery from Chamaranagar, Karnataka.

<table>
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<tr>
<th>Sample type</th>
<th>γ-HCH</th>
<th>endosulfan</th>
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Lee CM (2003). Environmental fate evaluation of DDT, Chlordane and Lindane, Dep of Envir Eng and Sci Clemson Univ, Clemson, SC


