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Monitoring the water quality of lakes for Organochlorine Pesticides in and around Dharwad city, Karnataka, India

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Abstract
Organochlorine pesticide (OCP) residues were determined in water from four lakes of Dharwad district. The aim was to assess the levels of pesticide contamination as the lakes are important sources of domestic water in the area. The residue level of pesticide were quantified in 4 samples during the year 2017, water samples from Hirekere, keleger, Navaloor and Nuggikene lake region of Northern Karnataka. Samples were extracted from pesticide preparation prior to analysis with gas chromatography. A total of 17 organochlorine pesticides were examined. The experimental results revealed that Heptachlor, Heptachlor epoxide, in Hirekere lake and only Heptachlor epoxide detected in Navaloor lake whereas in Keleger lake and in Nuggikere lake pesticide residue not detected.

Keywords: lakes, Dharwad, GCMS, pesticide residues

1. Introduction
Pesticide are substances or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (US EPA, 2007). The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators and others. Among these, organochlorine insecticides, used successfully in controlling a number of diseases, such as malaria and typhus, were banned or restricted after the 1960s in most of the technologically advanced countries. Ideally a pesticide must be lethal to the targeted pests, but not to non-target species, including human beings (Gomez, Gamon *et al*., 1998) [2].

Surface water contamination with pesticides residues, associated with decreased water quality and increased exposure of human and wildlife has been detected in lakes, rivers and streams in various locations, especially in areas with intense and prolonged pesticides applications (Zhou *et al*., 2006; Gao *et al*., 2008; Poolpak, 2008) [10, 4, 5]. Pesticides can reach surface waters through various pathways, including agricultural run-offs, spray drifts during applications, atmospheric fallout, direct spills and accidental discharge. Irrigation, which are frequently taken from surface water sources in agricultural areas, may also transfer contaminants from land to the water body (Zhang *et al*., 2002) [6]. The types and concentrations of pesticides found in surface waters can be affected by a number of factors including properties of the chemical, application history, season of the year and physico-chemical characteristics of the water and the underlying sediments (Carabias e al., 2003) [7].

Materials and Methods
Four lakes selected for sampling they are 1. Hirekere lake,2. Kelegere lake, 3. Navaloor, 4. Nuggikere lake, keeping in view, the important industrial waste discharge zones and nature of domestic activities and agricultural run-off. For the analysis of pesticide residues, water samples were collected in one liter amber colored bottles transferred to a separating funnel. Sodium sulphate (10g) was added to the separating funnel and shaken well. The water sodium sulphate mixture was extracted with dichloromethane (3x100 ml). After each separation, the upper organic layer was collected in a separate beaker and the lower aqueous layer was again extracted with 100 ml of dichloromethane. The combined dichloromethane layers were reduced in volume on a rotary evaporator to about 5ml. The crude extracts were cleaned up by florisil column chromatography. Glass columns were packed from the bottom with a glass wool plug, 8 cm of deactivated florisil and 4 cm anhydrous Na2SO4 to remove excess oil and fat and moisture content respectively. The packed column was pre-washed with 50 ml of petroleum ether. The extract was transferred to the column and eluted with 200 ml petroleum ether, mixed with diethyl ether (85:15). The combined extracts were evaporated almost to dryness and the final volume reached to 5 ml with GC grade solvent as described in (APHA,1995) standard methods and the water extracts were subjected to GC analysis. The extracts were transformed to the column eluted with 160 ml petroleum ether mixed with diethyl ether. The combined extracts were evaporated almost to dryness and the final volume of 5 ml was obtained with GC grade solvents. The identification and quantification of compounds were carried out using a Gas Chromatography (Chemito GC 1000), with Electron Capture Detector. GC column employed were capillary column, DB-1701 and DB-5. Pure analytical grade pesticide standards were used for GC analysis is reference standards. The temperature programs of GC were: injector 230^{o}C, column 220^{o}C and detector 260^{o}C. Ultra pure nitrogen gas was used as carrier gas. Winchrome 1000 chromatography data processor was used to record the chromatograms and peak areas were used to calculate the pesticide residues in the

samples. These compounds were identified as individually resolved peaks based on retention times, in comparison with the corresponding peak height of the standards.

Results and Discussion

Table 1: Pesticide residue concentrations of water samples of Lakes

Name of the Pesticides	Unit	IN-08 Hirekere Lake	IN-09 Keleger Lake	IN-10 Navaloor Lake	IN-11 Nuggikere Lake
Alpha-HCH	PPb	Absent	Absent	Absent	Absent
Gamma-HCH	PPb	Absent	Absent	Absent	Absent
Heptachlor	PPb	5.75	Absent	Absent	Absent
Aldrin	PPb	Absent	Absent	Absent	Absent
Beta-HCH	PPb	Absent	Absent	Absent	Absent
Delta-HCH	PPb	Absent	Absent	Absent	Absent
Heptachlor epoxide	PPb	100	Absent	112	Absent
Endosulphan-1	PPb	Absent	Absent	Absent	Absent
4,4-DDE	PPb	Absent	Absent	Absent	Absent
Dieldrin	PPb	Absent	Absent	Absent	Absent
Endrin	PPb	Absent	Absent	Absent	Absent
Endosulphan-11	PPb	Absent	Absent	Absent	Absent
4,4-DDD	PPb	Absent	Absent	Absent	Absent
4,4-DDT	PPb	Absent	Absent	Absent	Absent
Endrin Aldelyde	PPb	Absent	Absent	Absent	Absent
Endosulfan Sulfate	PPb	Absent	Absent	Absent	Absent
Methoxychlor	PPb	Absent	Absent	Absent	Absent

The total of 17 organochlorine pesticides were examined out of 4 samples of lakes, two were found to be contaminated with Heptachloro and Heptachloro epoxide. Detection of pesticide residues in the water samples of lakes summarized (Table 1) and residue levels of organochlorines were represented in (Figs. 1,2,3,4). It shows that, organochlorine residues in the water samples are Heptachloro (5.75 ppb) and Heptachloro epoxide (100 ppb) in the Hirekere lake and only Heptachloro epoxide (112 ppb) detected in Navaloor lake. Pesticide residues not detected in the water samples of Keleger lake and Nuggikere lake.

Heptachlor is applied as a soil treatment, as a seed treatment (maize, small grains and sorghum) or directly to foliage. It is used to control ants, cutworms, maggots, termites, thrips, weevils, wireworms and many other insect pets in both cultivated and uncultivated soils. Heptachlor also controls household insects and pests of humans and domestic animals(Worthing,1991) [13]. In many countries, heptachlor is banned or applied only by subsurface injection. Heptachlor epoxide is not commercially available but is an oxidation product of heptachlor (IARC, 1979) [12].

Heptachlor s moderately persistent in soil, where it is mainly transformed into its epoxide. It may undergo significant photolysis, oxidation and volatilization (Mabey *et al*.,1981: Callahan *et al*.,1979: Mill *et al*.,1982) [14, 15, 16]. It binds to soil particles and migrates slowly(Tzapko *et al*.,1967) [17]. The soil half-life of heptachlor under certain conditions may be as long as 2 years (Vrocinsky *et al*., 1980) [18]. Heptachlor epoxide is very resistant to further chemical or biological changes in soil. It binds to soil particles and migrates slowly. Its half-life in various soils has been reported to be as long as several years (US EPA, 1988).

Clinical case-studies of acute exposure (via the oral, dermal or inhalation route) to chlordane-containing heptachlor document a pattern of central nervous system effects similar to that found in animals (e.g., irritability, salivation, labored respiration, muscle tremors, convulsions)(Dadey and Kammar, 1953) [20]. Heptachlor does not appear to be carcinogenic in humans)(Wang *et al*.,).

Conclusion

Based on the experimental results it can be concluded that, the important harmful effect of these pesticides occurs in aquatic systems. They can accumulate in water and then show their toxic effects. This effect causes the decrease of usable waters and has a bad effect on aquatic organisms directly. Because of these effects, water source should be monitored continuously (Sait Bulut *et al*., 2010) [1]. In view of our observations suggest that further investigation on surface water for persistent organochlorine pesticides are needed to elucidate future pollution trends and to assess especially human and children health risk.

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