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Research Article

CHARACTERIZATION OF HEAVY METAL AND PESTICIDE CONTAMINATION IN SOILS OF KASARGOD DISTRICT, KERALA

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ABSTRACT

Increased rate of agricultural activities during the last few decades have deteriorated the soil entity and ground water quality of Kasargod district, Kerala. As a consequence, the study on both the soil and water quality of the district has become paramount priority for contamination assessment programme. Thus the soil characteristics in Kasargod district was carried out by collecting 11 soil samples from high land mid land regions. Trace metals (Fe, Ni, Mn, Mg, Co, Zn, Cu, Pb, Cd) as well as Organ chlorine pesticides in soil were analysed concurrently. The observation resulted from the study signifies that, most of the area is contaminated by Pb, Ni and Co. A serious attention should be needed to find out the source and the remedial measures to reduce this trace metal concentration level. Besides, in the Cheemeni area, the concentration of endosulfan α (0.977 mg/kg) and endosulfan β (0.2332 mg/kg) showed anomalous values than the rest of the stations.

Key Words: *Kasargod District, Kerala, Organ Chlorine Pesticides, Heavy Metal Contamination*

INTRODUCTION

Soil may be defined as material of variable depth with substantial solid content at the Earth's surface which is undergoing change as a consequence of chemical, physical and biological processes. Soil is a complex medium which both responds to and influences, environmental processes and conditions. Consequently, they are subjected to a number of pollutants due to different anthropogenic activities (Industrial, agricultural, transport etc.) (Facchinelli *et al.*, 2001 and Jonathan *et al.*, 2004). The chemical composition of soil, particularly its metal content is environmentally important, because toxic metal concentration can reduce soil fertility, further increase the input to food chain, leading to accumulation of toxic metals in food stuffs, and finally endangered to human health. Because of its environmental significance, studies to determine risk caused by metal levels in soil on human health and forest ecosystem have attracted attention in recent years (Denti *et al.*, 1998; Sandaa *et al.*, 1999; Arantzazu *et al.*, 2000 and Krzyztof Losk *et al.*, 2004). In India, the main drinking water sources are surface water and ground water. Contamination of drinking water supply is alarmingly increasing and causes threat to the public health. The pesticide residues which remained in the soil due to their earlier application become a source of pesticide pollution to the water body through land runoff, leaching and ultimately contaminate the drinking water resources. The same scenario was observed in Kasargod district (Akhil and Sujatha, 2012). Trace metal characterization was also included in order to reveal the dynamics and distribution of metal contamination in the study region. Unveiling the sedimentology of ground water aquifers opens the gateway for the distribution of minerals and the type of sediment dwelling in the area. The seasonal allocation of these physico-chemical parameters is significant since it opens the key to unlock the complex activities prevailing in the selected prominent sites. Limited scientific work was carried out previously on soil and ground water quality in Kasargod district (Akhil *et al.*, 2013). The present investigation is an attempt to examine the soil facies of Kasargod district, especially the occurrence of Agricultural pesticide residues and their degradation products along with the distribution of trace metals in the soil of this tropical district.

MATERIALS AND METHODS

Study Area

The name Kasargod is said to be derived from the word 'Kusirakood' meaning Kanjirakuttam. The district is bounded on the east by Karnataka state, west by Lakshadweep Sea, north by Canara district of Karnataka and on the south by Kannur district with Latitude N12^0 05'-12^0 48' and Longitude E 74^{0}26'-75^{0}25'. The district is agrarian with cash crops of Areca nut, cashew and rubber dominating over food crops. Kasargod district is an area, which receives maximum rainfall in the state in a short duration during southwest monsoon and northeast monsoon periods. Though this area receives large quantity of rainfall, the same area suffers maximum due to drought. Geologically Kasargod area predominantly occupies by crystalline rocks and is widely lateritised. Physiographical the district can be divided into three distinct units, the coastal plains, the midlands and the eastern highland region. The coastal plain occur as a narrow belt of alluvial deposits parallel to the coast with varying width of maximum 10 km. East of the coastal belt is midland region with general slope towards the west. The highland areas are hill ranges of Western Ghats with rugged topography. Lateritic soil is the predominant soil type of the area, which occurs in the midland area. Alluvial soil is seen in the western coastal tract of the district which also encountered along the banks of the rivers. Forest loamy soils are found in the hill ranges of the area of which the southern part is very rich in organic matter and become very fertile.

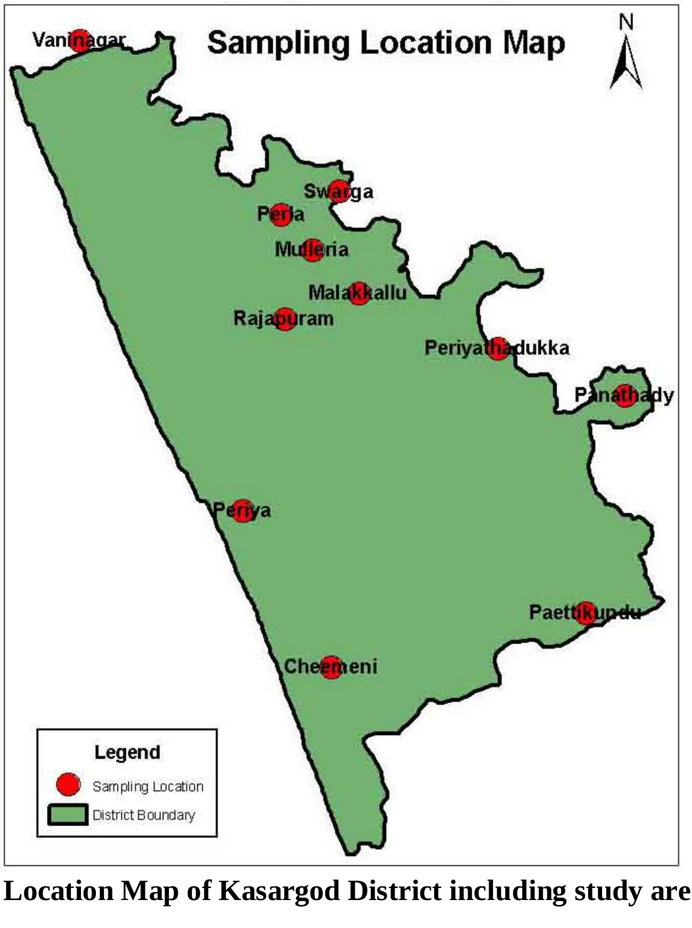

Figure 1: Location Map of Kasargod District including study area

In this study 11 soil samples were collected from highland, midland and also from industrially and agriculturally active areas during the post-monsoon season of 2011 (Figure 1). Soil samples were collected from the surroundings of the open wells with plastic spatula and were transferred to zip lock polythene bags/glass bottles and made airtight and handled conveniently to the laboratory. In the laboratory soil samples were preserved at -5 ^{0}C in deep freezer.

For estimation of trace metals, the dried soil sample were finely powdered and 1 gm accurately weighed and digested with a 1:5 mixture of $HClO_4$ - HNO_3 in a prewashed Teflon beaker. The soil samples were evaporated to dryness at moderate temperatures 65 - 70 ^{0}C. Finally, samples were filtered and diluted up to 25 ml with milli Q water. A blank containing the reagents are also prepared simultaneously for the analysis (APHA 1995). Trace metals in the soil samples were analyzed with AAS (Perkin Elmer AAS 3110).

About 5gm of the sample was accurately weighed and extracted twice with 50mL portions of 1:1 hexane-acetone mixture (HPLC grade, Glaxo, Mumbai, India) and the combined extract was subjected to a cleanup procedure involving elution through a Florisil column (60 cm x 22mm i.d) with 50mL 1:1 hexane-acetone mixture. The extract was concentrated to about 5-6mL by means of a rotary evaporator at 50-60 ^{0}C for further analysis. Separation and analysis of the OCP's were performed on a gas chromatograph (GC) (model 7890A, Agilent, Waldbronn, Germany) with a Ni-63 ECD and equipped with capillary column (HP-35, 30m x 0.320mm x 0.5 mm) using nitrogen as carrier gas (1.5mLmin$^-$1). Details of experimental methodology adopted have been described earlier. The GC was calibrated with a standard solution of a pesticide mixture (Supelco, USA) prepared in HPLC grade n-hexane. Solvent blanks were used to confirm the absence of any pesticide residues. Analytical reproducibility was checked by replicate measurements. Identification and quantification of OCP's were accomplished by using reference solutions supplied by EPA (USA) and Supelco (USA).

The following GC conditions are maintained: injection port temperature 250 ^{0}C, detector temperature 350 ^{0}C, oven temperature program: 110 ^{0} C (5 min) at 5 ^{0} C min^{-1} to 190 ^{0}C (2 min) at 15 ^{0}Cmin $^{-1}$ to 280 ^{0}C (10 min). The following organ chlorine pesticides were quantified.α-hexachlorobenzene (BHC),β-BHC,α-BHC, heptachlor, aldrin, heptachlor epoxide (B), 4,40-DDE, dieldrin, endrin, 2,40-DDD, 4,40-DDD, 2,40-DDT, 4,40-DDT, α-endosulfan and β-endosulfan. 1 mL of aliquot samples was injected onto the column.

RESULTS AND DISCUSSION

Trace metals like Co, Cu, Mg, Zn, Cd, Mn, Pb, Ni and Fe were analyzed in the soil samples and their corresponding values are given in the Table 1. Analytical data revealed that Fe is the major heavy metal present in these 11 soil samples.

Table 1: Distribution of Trace metals

Stn. No.	Cu (ppm)	Co (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Cd (ppm)	Fe (ppm)	Mg (ppm)	Zn (ppm)
1	25.77	21.55	15.14	067.77	64.09	5.14	095000	2236	052.77
2	20.91	33.70	21.15	000.53	59.14	3.51	060096	2528	050.00
3	26.83	22.64	10.77	088.56	49.52	3.32	062980	1211	026.49
4	14.25	20.05	06.51	069.15	21.69	3.02	058018	2207	050.38
5	15.35	30.72	13.22	034.62	62.98	5.53	092307	1985	054.47
6	27.01	28.58	15.98	083.38	37.26	3.92	075000	1573	125.83
7	31.23	16.84	11.32	060.05	25.94	4.48	068867	1183	083.68
8	35.61	47.36	41.61	104.76	48.59	6.04	108018	3075	219.62
9	26.84	25.80	06.56	065.19	39.15	5.57	062264	2113	093.30
10	25.82	22.16	04.66	078.79	59.62	4.52	071153	2100	050.72
11	40.04	23.01	06.55	080.45	33.00	3.70	061000	2205	138.05

Most often metals found as contaminants in vegetables (including As, Cd and Pb). These metals can pose as a significant health risk to humans, particularly in elevated concentrations which are above the very low body requirements (Gupta and Gupta, 1998).The contamination of agricultural soils is often a direct or indirect consequence of anthropogenic activities (McLaughlin *et al*., 1999). Generally sources of anthropogenic metal contamination in soils include - urban and industrial wastes; mining and smelting of non-ferrous metals and metallurgical industries (Singh, 2001). Commercial and residential vegetable growing areas are often located in urban areas, and are subjected to anthropogenic contamination. The study describes that the trace metals like Ni, Cd and Pb were in the elevated concentration above the permissible level. The maximum acceptable limit of Pb in soil was 50 ppm. But most of the stations were above this limit. Also showed similar results in the case of Ni and Co. In the case of nickel, acceptable limit was 30 ppm, but for Cd, it was 8 ppm. From the earlier literature, it was found that the major sources of these heavy metal pollution is automobile and also from other industries. But no such sources were observed in the study region. So serious attention should be given to the sources that caused the heavy metal pollution in the Kasargod district.

The use or misuse of pesticides may lead to serious groundwater contamination and consequently results in health hazards. Depending on the phenotype and density of the plant type, it is estimated that an average of 35-50% of the plant protection material is deposited on soil immediately after spraying. The behavior of pesticide in soil and ground water involves persistence, movement and metabolism. The formation of residues in soil mainly depends on water solubility and the binding capacity of both organic and inorganic constituents of soil. Understanding the fate of a pesticide in soil is fundamental to the accurate assessment of its environmental behavior and vital in ensuring the safe use of new and existing products. It is also necessary to develop and validate computer simulation models for use as predictive tools in future environmental fate assessments.

Table 2: Distribution of Organ chlorine pesticides

Stn. No.	*α*-BHC (mg/kg)	*β*-BHC (mg/kg)	Heptachlor (mg/kg)	Aldrin (mg/kg)	Heptachlor Epoxide (B) (mg/kg)	4,4'-DDE (mg/kg)	Dieldrin (mg/kg)	Endrin (mg/kg)	Endosulfan (α) (mg/kg)	Endosulfan (β) (mg/kg)
1	0.003	BDL	BDL	0.007	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	0.022	BDL	0.005	0.014	0.019	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	0.019	0.024	0.161	0.00053	BDL
4	BDL	0.025	BDL	BDL	0.014	0.018	BDL	BDL	BDL	BDL
5	BDL	BDL	0.034	BDL	0.068	BDL	BDL	BDL	0.977	0.2332
6	BDL	BDL	0.004	BDL	0.014	0.019	BDL	0.161	0.00789	BDL
7	BDL	BDL	0.005	BDL	BDL	0.02	BDL	BDL	0.00097	BDL
8	BDL	BDL	0.003	0.005	0.014	0.02	BDL	BDL	BDL	BDL
9	BDL	BDL	BDL	0.005	0.015	0.02	0.024	BDL	0.0212	BDL
10	BDL	BDL	BDL	BDL	BDL	0.019	0.026	BDL	BDL	BDL
11	BDL	BDL	0.002	BDL	BDL	0.019	BDL	BDL	BDL	BDL

The presence of banned endosulfan in soils of this district indicates its persistent and lipophilic nature. The cashew plantations owned by the Plantation Corporation of Kerala (PCK) at Kasargod District has been aerially sprayed with the organochlorine pesticide endosulfan between 1978 and 2001 regularly three times every year. The occurrence of relatively low proportions of β isomer of endosulfan is due to the vapors pressure and different time intervals in the existence of these isomeric compounds. From soils, the α isomer of endosulfan disappears more rapidly as it is more volatile than the β isomer (UNEP/FAO 2007) and it photo-isomerizes to β isomer (Walia and Dureja 1993). Therefore it could be revealed that the elevated concentration of α isomer may be due to the recent usage of such pesticides in these studied areas. Station no.5, Cheemeni showed a very high concentration of α isomer. People in district are complaining from peculiar and complex diseases hitherto unknown. Some of the isomers/metabolites detected might be the result of their prolonged persistence in the environment and the promotion by agriculture sector through expanding the market for pesticides and other agro chemical fertilizers. There is an urgent need for awareness among farmers so that illegal use could be controlled. Strict action against sellers of banned or spurious pesticides and adoption of integrated pest management practices could be a possible way to overcome/bring down the present residue levels in the future. Frequent monitoring studies are encouraged to advocate regular water quality assessment with special attention to these xenobiotic OCP's. Kasargod district has been regularly studied for pesticide pollution by the government authorities and the effects on the life of people were always attributed to the toxic effects of pesticides. This raises significant environmental concern and calls for urgent attention and appropriate response. Among the pesticides, endosulfan reigns the highest. Further, trace metal enrichment was also observed in the study which enhances the necessity for serious studies about trace metals, sources and their pathways.

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