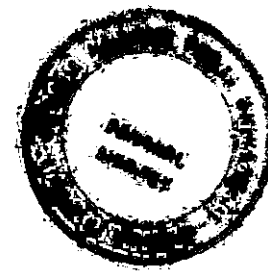
HEAVY METAL CONTAMINATION OF LATERITES BY ACCUMULATION OF SOLID WASTES

By

DIVYA VIJAYAN, V.
(2010-21-112)



THESIS

Submitted in partial fulfillment of the
Requirement for the degree of

Doctor of philosophy in Agriculture

Faculty of Agriculture
Kerala Agricultural University

Department of Soil Science and Agricultural Chemistry
COLLEGE OF HORTICULTURE
KERALA AGRICULTURAL UNIVERSITY
THRISSUR 680 656
KERALA, INDIA

2015

DECLARATION

I, hereby declare that this thesis entitled "Heavy metal contamination of laterites by accumulation of solid wastes" is a bona-fide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, fellowship or other similar title, of any other university or society.

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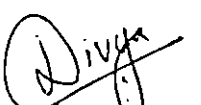

Divya Vijayan, V.

(2010-21-112)

CERTIFICATE

Certified that this thesis, entitled **"Heavy metal contamination of laterites by accumulation of solid wastes"** is a record of research work done independently by **Ms. DIVYA VIJAYAN V.** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.

Dr. P.K. Sushama

Chairperson, Advisory Committee

Vellanikkara

CERTIFICATE

We, the undersigned members of the Advisory Committee of **Ms. Divya Vijayan, V. (2010-21-112)**, a candidate for the degree of **Doctor of Philosophy in Agriculture** with major in **Soil Science and Agricultural Chemistry,** agree that the thesis entitled **"Heavy metal contamination of laterites by accumulation of solid wastes"** may be submitted by **Ms. Divya Vijayan, V.** in partial fulfilment of the requirements for the degree.

Dr. P.K. Sushama
(Chairperson, Advisory Committee)
Professor and Head
Department of Soil Science and
Agricultural Chemistry
College of Horticulture
Vellanikkara

Dr. P.Sureshkumar
(Member, Advisory Committee)
Professor and Head
Radiotracer Laboratory
College of Horticulture
Vellanikkara

Dr. R. Gopinathan
(Member, Advisory Committee)
Professor
Department of Agronomy
College of Horticulture
Vellanikkara

Dr.D.Girija
(Member, Advisory Committee)
Professor and Head
Department of Agrl. Microbiology
College of Horticulture
Vellanikkara

Sri. S. Krishnan
(Member, Advisory Committee)
Professor and Head
Department of Agricultural Statistics
College of Horticulture
Vellanikkara

Dr. S.S. Prakash
(External Examiner)
Professor
Department of Soil Science and Agrl. Chemistry
College of Agriculture, V.C.Farm, Mandya

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Introduction

1. INTRODUCTION

Nearly all human activities generate waste, and the way in which it is handled, stored, collected and disposed can pose risks to environment and public health. Solid wastes other than hazardous and radioactive materials are often referred to as municipal solid waste. The composition of solid waste is influenced by many factors such as culture affluence and location.

Estimated municipal solid waste generated in India is around 55 million tones/year and municipal solid waste dumping yards are increasing in India day by day. In this scenario of waste management and handling, Kerala is no way different from other states, with an annual estimate of waste production of 9983.80 tones day^{-1}. The composition of wastes varies from biodegradable (68%) and the rest, including cloth, timber, plastic, rubber, glass, syringe and brick. Improper management of solid waste is one of the main causes of environmental pollution in most of the cities. In Kerala the significant per capita waste generation varied from 0.034 kg to 0.707 kg day^{-1}. On an average 50 per cent of this waste is generated from households and about 35% from various institutions (Varma, 2008). The construction sector and street sweepings together contributes 15 per cent. However the waste is dominantly of compostable material to the tune of 72-84 per cent and is characterized by high moisture content, low calorific value and high nutrient concentration.

Municipal waste dumping sites are designated places set aside for waste disposal. As there are a variety of wastes at the dumping site, it will pollute the natural resource of the area, due to the production of toxic chemicals and pollutants like heavy metal (Loaniyan *et al.,* 2011). Most of the cities lack solid waste management regulations and facilities for disposal of harmful waste like infectious, toxic heavy metals or radioactive substances.

A heavy metal is defined as metals that have a high atomic number, atomic weight (>20) and a specific gravity greater than 5 Mg m^{-3}. Heavy metals include some metalloids, transition metals, basic metals, lanthanides and actinides. Heavy

metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials. Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts. Most of the heavy metals are extremely toxic because of their solubility in water. Even low concentrations of heavy metals have damaging effects to man and animals because there is no good mechanism for their elimination from the body (Ideriah *et al.*, 2010). Heavy metal once it enters the food chain through the plant causes serious health hazards in human being and animal. So understanding the characteristics of heavy metals in soil and its relation with other factors have become very important today.

Soil can act both as source and sink for many of the inorganic contaminants which are harmful to the environment. Soils become contaminated by the accumulation of heavy metals/ toxic metals and metalloids. There are two main sources of heavy metals in the soil (i) natural heavy metal concentration derived from parent rocks; (ii) anthropogenic contamination, including agrochemicals, organic amendments, animal manure, mineral fertilizer, sewage sludge and industrial wastes.

Heavy metals uptake by plants from the soil and successive accumulation in human and biomagnifications through the food chain causes both human health and environmental concern. Various heavy metal reduction techniques are being reported elsewhere. Composting is the process in which organic matter is transformed into compost by aerobic microorganisms which comprises three major phases such as mesophilic, thermophilic and cooling phase. In anaerobic composting, all three phases are absent. However, the slurry will be free from toxic pollutants, due to the less movement of metals along with the leachate. Phytoremediation is the mechanism by which plants are able to remove, transfer, stabilize and degrade contaminant from soil, sediment and water.

With this broad understanding the present study was conducted with the following objectives:

1. To investigate the extent of distribution of heavy metals (Ni, Cd, Cr, Pb, Hg and Co) in waste dumping sites of laterite as influenced by soil and climatic conditions using geostatistical technique
2. To correlate the activity of major soil enzymes with the contents of heavy metal.
3. To explore the potential of phytoremediation as well as aerobic and anaerobic methods of composting for the removal of heavy metals in solid wastes and
4. To evaluate the performance of amaranthus under different decontaminated methods adopted.

Review of literature

2. REVIEW OF LITERATURE

Any metal (or metalloid) species may be considered a "contaminant" if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. Metals/metalloids include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U) (Mcintyre, 2003 and Singh *et al.*, 2011). Thus heavy metals as a contaminant upset the ecosystem, living organisms like plants, animals and the natural resources in its environment which in turn alters the soil flora and fauna.

2.1 Heavy metals in the periodic table

The position of heavy metals in the periodic table is represented in Fig. 2.1. In the periodic table the heavy metals & metalloids mainly belongs to the groups between 3 to 16 and the periods greater than 4. This includes the transition metals, metalloids, lanthanides and actinides.

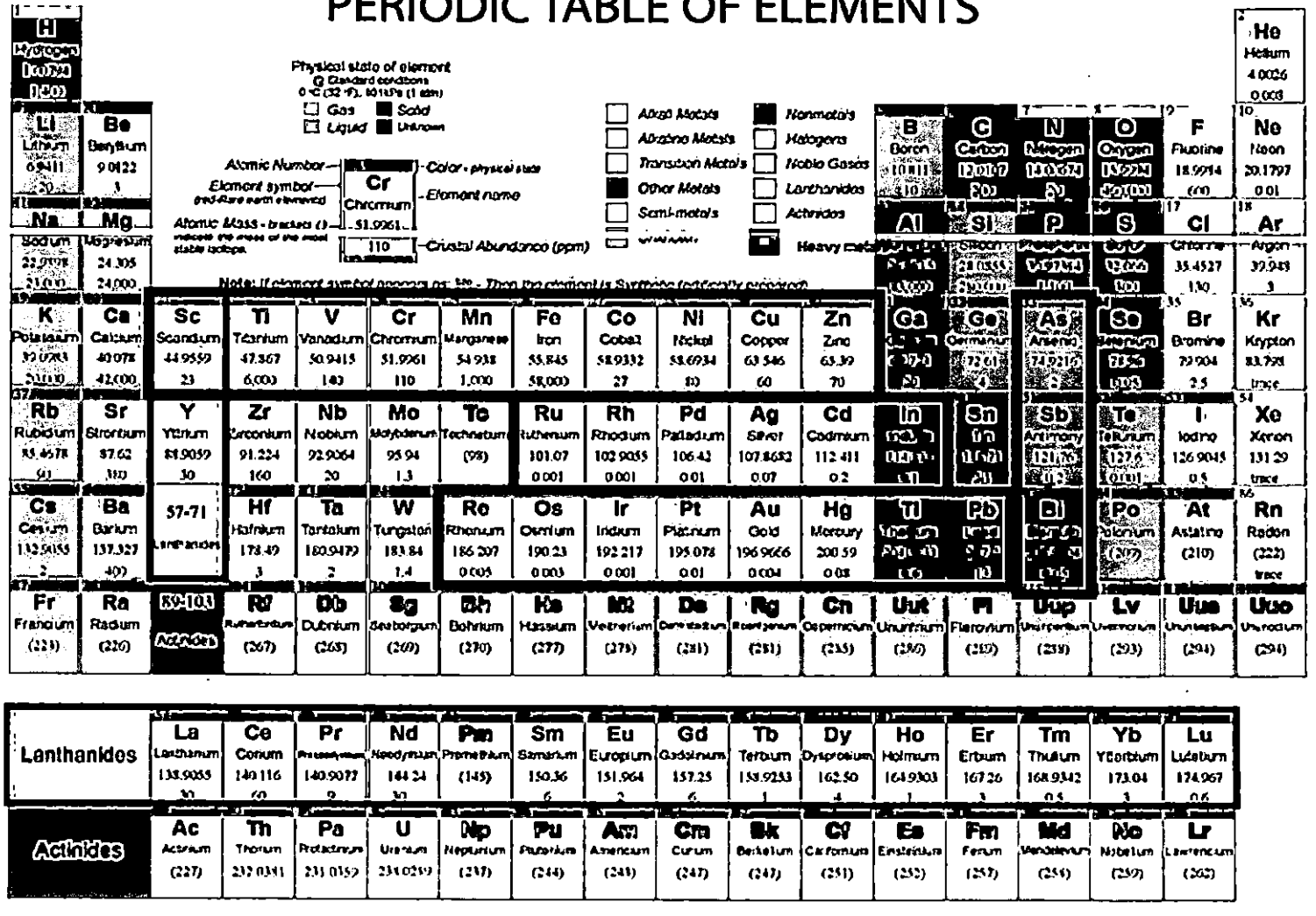

Figure 2.1 Periodic table of elements highlighting heavy metals

A thorough search for the origin of the heavy metals was undertaken and the year as well as the scientists behind the discoveries of heavy metals is being documented in Table.2.1.

Table 2.1. Heavy metals, year of discovery and scientists discovered

Heavy metal	Year of Discovery	Scientist discovered
Cobalt	1735	Georg Brandt
Cadmium	1817	Friedrich Stromeyer Sir Humphry Davy
Magnesium	1755	Joseph Black
Calcium	1808	Sir Humphry Davy
Chromium	1797	Louis Nicolas Vauquelin
Manganese	1774	Johan Gottlieb Gahn
Iron	2500 BC	Not available
Nickel	1751	Axel Fredrik Cronstedt
Arsenic	c.1250	St. Albertus Magnus
Molybdenum	1781	Peter Jacob Hjelm
Lead	1000 BC	Not available
Mercury	1500 BC	Not available

(Andraos, 2005)

2. 2 General characteristics of major heavy metals (Das, 2007)

2.2.1 Cobalt

Cobalt (atomic weight 58.93 and density of 8.80 Mg m^{-3}) group 9 element has been found to be retained in soils mainly as specifically adsorbed exchangeable Co^{2+} form or as clay organic matter complexes (clay-Co organic matter). The Co chemistry is found to be similar to other heavy metals like Fe, Mn and Zn and has a strong affinity to form chelates in soils. Factors affecting Co availability in soil are pH, organic matter, $CaCO_3$, clay mineral and effect of Iron. Cobalt concentration in the dry matter of plants grown in soils normally lies between 0.02 to 0.5 mg kg^{-1}. Co content of less than 0.25 mg kg^{-1} is deficient and more than 0.35mg kg^{-1} is sufficient.

2.2.2 Cadmium

Cadmium (atomic weight 112.40, sp. gravity 8.65 Mg m^{-3}) the group II B transition element is relatively rare in the earth crust. In natural soils, the amount of Cd varies with the type of parent materials. It is high and low in soils derived from basaltic and granitic rocks respectively. In normal soil Cd vary from 0 to 0.7 mg kg^{-1} (Azad *et al*, 1986). Increase in pH decreased the availability of Cd, while the increase in redox potential, plant uptake of Cd was found to be increased, organic matter decrease availability of Cd due to adsorption, increase of $CaCO_3$ decreased the availability of Cd, clay mineral and hydrous oxide of Fe, Mn and Al decreased the availability of Cd in soil. Increase in submergence decrease the availability of Cd. Cadmium mimics Zn in its behavior, but in excess Cd is toxic to both plant and animal.

2.2.3 Lead

Lead (atomic weight 207.21, sp.gravity 11.34 Mg m^{-3}) a group IV A element, is metallic and it is highly toxic to human being. Lead is not readily lost from soil. In some soil it forms various complexes with Pb bearing minerals. Lead is easily absorbed by roots but weakly transported by shoots. The extractable Pb was negatively correlated with pH, but positively with EC, organic carbon and clay content. Pb contamination by inorganic form in soils is restricted to the surface soil

layers. Lead interferes with plant metabolism and enzyme system leading to reduced plant growth.

2.2.4 Nickel

Nickel (atomic weight 58.71, sp gravity 8.9 Mg m^{-3}) is a group VIII element. Most soils contained only very small amount Ni, usually less than 100 mg/kg, and well below the level at which Ni toxicity occurs. Soils derived from ultra basic igneous rocks particularly serpentine. Nickel in its soluble form is taken up by plant roots and micro organism.

2.2.5 Arsenic

Arsenic (atomic weight 33, sp.gravity 5.73 Mg m^{-3}) a group IV A element, is metallic and it is highly toxic to human being. It makes up to 1.5 ppm of earths crust and soil contains 1-10 ppm. Arsenic compounds resemble in some respects those of phosphorus which occupies the same group of the periodic table. It causes toxicity to multicellular life due to its presence in quantities far larger than needed. Arsenic contamination of groundwater is a problem that affects millions of people across the world.

2.2.6 Mercury

Mercury (atomic weight 200.59, specific gravity 13.546 Mg m^{-3} at 20°C) occurs uncombined in nature to a limited extent. It rarely occurs free in nature and is found mainly in cinnabar ore (HgS) Mercury is easily absorbed by roots but weakly transported by shoots.

2.3 Distribution of heavy metals in living conditions

The concentration of heavy metals is highly varied in lithosphere, soil and plant and it changes with the pedogenetic and anthropogenic activities. Living organisms also requires varying level of heavy metals for the life processes and its concentration if exceeded the limit will cause adverse effect on organisms. The details are furnished in Table 2.2.

Table 2.2. Distribution of heavy metal in lithosphere, soil and plant

Heavy metal	Lithosphere	Soil	Plant
	mg kg^{-1}		
Cd	0.2	0.01-0.7	2-8
Co	40	1-40	0.05-0.5
Cr	200	5-3000	0.2-1
Cu	70	2-100	4-15
Fe	50000	7000-550,000	140
Hg	0.5	0.01-0.3	0.015
Mn	1000	1000-4000	15-100
Mo	2.3	0.2-5	1-10
Ni	100	10-1000	1
Pb	16	2-200	0.1-10
Sn	40	2-200	0.3
Zn	80	10-300	8-100

(Allaway, 1968)

Different elements have different role in the metabolism of the living organisms and their toxicity level also varies with organisms. A brief outline of the toxicity level of plant, mammals and biological functions as influenced by heavy metals is given in the table 2.3.

Table 2.3. Role of heavy metals in biological functions and their toxicity

Element	Biological Function	Phtyo-toxicity (ug/g) Conc. In leaf tissue	Soil mg/kg
Al	Activates succinic de-hydrogenase	Moderate (50-200)	10,000 - 300,000
As	None in animals phosopholipid in algae and fungi	Moderate to high (5-20)	3.6 - 8.8
Cd	None known	Moderate to high (5-30)	0.06 - 1.1
Cr	Sugar metabolism in mammals	Moderate to high (5-30)	20- 85
Cu	Essential to all organisms-redox enzymes-oxygen transport pigments	Moderate to high (20-100)	14 - 29
Fe	Essential to all organisms-cofactor in many enzymes, proteins	Low (>1000)	50 -1000
Hg	None Known	High (1-3)	0.04 - 0.28
Mn	Essential to all organisms-splits water in photosynthesis	Low to moderate (300-500)	260- 840
Mo	Essential to almost all organisms-cofactor in Nitrogen fixation	Modearte (10-50)	0.35 - 5.8
Ni	Essential to all plants	Moderate to high (10-100)	13 -30
Pb	None Known	Moderate (10-100)	17 - 26
Se	Essential to mammals and plants	Modeate to high (5-30)	0.019 -1.05
Zn	Essential to all organisms	Low to moderate (100-400)	34 -84

(Hagedorn, 1996)

One of the main sources of heavy metals is the industrial remains which may accumulate in the soil to the toxic extent and cause contamination to the surrounding environment. The industrial source of heavy metal content in soil is given below in table 2.4.

Table 2.4. Source of heavy metals

Heavy metals	Type of Industry
Chromium	Mining, industrial coolants, chromium salts manufacturing, leather tanning
Lead	Lead acid batteries, paints, E-waste, Smelting operations, coal- based thermal power plants, ceramics, bangle industry
Mercury	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste, electrical appliances
Arsenic	Geogenic/natural processes, smelting operations, thermal power plants, fuel
Copper	Mining, electroplating, smelting operations
Vanadium	Spent catalyst, sulphuric acid plant
Nickel	Smelting operations, thermal power plants, battery industry
Cadmium	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations and fuel combustion
Molybdenum	Spent catalyst
Zinc	Smelting, electroplating

(Gautam, 2011)

The content of trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) in surface soils in the area surrounding the largest coal-fired power plant in Serbia was determined to assess the contribution of emissions to pollution. Analysis of mutual associations between the trace elements and their correlation with soil particle size fractions indicated anthropogenic origin at most sampling sites and enrichment factor analysis confirmed these findings. Common patterns in trace element concentrations

of the analysed soils were identified by hierarchical cluster analysis. Explanatory spatial analysis, used for characterization and mapping of spatial variability patterns, revealed the highest concentrations of trace elements in areas in predominant wind directions (Dragovića *et al.*, 2013). Geo-environmental evaluation of heavy metals in/and around hazardous waste disposal sites located in the north-western part of Hyderabad was carried out by Partha *et al.*, (2011), to define the degree of contamination of soil environment. Study on different heavy metals revealed that the average concentrations of As, Cr and Pb were found to exceed the threshold and natural background values, whereas the upmost concentrations of Cu, Ni and Zn exceeded the prescribed threshold limit.

2.5 Heavy metals contamination of in laterite soils

Heavy metal and its fractions in soils of Koratty region Kerala was analysed by Prasanth *et al.*, 2013. The fractions showed that Fe was the most mobile element, while Cd and Cu were least mobile. The order of mobility in the exchangeable fractions was Fe>Mn>Pb>Ni>Zn>Cu=Cd. The degree of contamination, enrichment factor and index of geoaccumulation revealed that cadmium, nickel and lead were pollutants in that region. The adsorption of heavy metal to lateritic soil using batch sorption isotherm showed that the adsorption capacity of the soil for Pb, Cd, and As increased with increase in the sorbate concentration. The adsorption capacities obtained in the study were indicative of the affinity of these contaminants to the soil (Udoeye *et al.*, 2010). A study was conducted on assessing the competitive sorption characteristics of Pb, Zn, Ni, and Mn in batch equilibrium experiments using the natural laterite soil from the northern Thailand showed that, Pb had the greatest sorption capacity as estimated by the maximum sorption parameter (Qmax) of the Langmuir equation (Putthividhya, 2008).

2.6 Climatic condition on heavy metal accumulation

The physico-chemical properties of contaminated soils of three municipal waste dumpsites in Allahabad showed that the pH of the dumpsite soils is in neutral or alkaline pH, water holding capacity was high and organic matter was higher at dumpsites as compared to their adjoining areas. Total metal concentrations of Cr, Cu, Fe, Ni, Pb and Zn were in elevated levels at dumpsites. Cr and Cd were not detectable from all adjoining areas while Pb, Zn, Fe, Ni and Cu were present in least amounts. Correlation studies showed that concentrations of Zn were highly correlated with the concentrations of Cu, Ni and concentrations of Cr was also significantly correlated with Ni and Pb (Tripathi and Misra, 2012). Assessment of heavy metal toxicity in soils of the nearby municipal solid waste dumping site at Mathuradaspura in Jaipur was studied. The soil samples were collected in all the four seasons, analysed and it was evident from the result that iron content was maximum in the soil of study area and heavy metal such as lead and cadmium were not traceable. The other heavy metals such as zinc was found in higher quantity in the summer and winter seasons. Chromium was higher in summer and monsoon season while the values are low for winter and autumn. Nickel was present in low concentration in all the seasons of the year. Copper was present in least quantities mainly in summer, monsoon and autumn season. Cadmium was absent in three seasons while found in traces in summers. Same result was obtained for lead. Over all the sequence of available heavy metal concentrations in these soils was found to be Fe > Zn >Cr > Ni > Cu > Pb > Cd. Influence of rainfall and temperature on DTPA (diethylene triamine pentaacetic acid) extractable nickel (DNi) and fractional (DNi / total Ni = F-DNi) concentrations of soils derived from ultramafic serpentine rock under temperate semiarid continental and Mediterranean climates were studied by Univer *et al.* (2013). The result showed that annual precipitation and mean air temperature had remarkable influence on the DNi and F-DNi amounts and the effect was more pronounced under Mediterranean conditions than semiarid temperate continental climate regions

2.7 Influence of physico chemical properties of soil on the release of heavy metals

The physico-chemical properties of contaminated soils of three municipal waste dumpsites in Allahabad showed that the pH of the dumpsite soils was in neutral or alkaline in reaction (Tripathi and Misra, 2012). Enhanced value of Pb, Mn and Fe seen to be associated with high values of organic matter, pH and conductivity in soil (Deka & Sarma, 2012). Roseta and Kelechi, (2012) carried out survey in Owerri municipal, the regional capital of Imo State, to characterize the heavy metal content and physicochemical properties of waste dump sites for more than 15 years. Soil samples were collected from two different locations (Otamiri hilltop dumpsite and Otamiri Gully dumpsites). Heavy metal contents were generally higher at deeper depths (40-60 cm) and the hill top waste dump site had higher values compared to the gulley dump site only at shallow depth (0-40 cm). Statistically, there was a significant ($p<0.05$) difference in heavy metal content, exchangeable cations and soil pH as well as and bulk density between two sites. Generally the solid wastes increased the values for soil pH, CEC, heavy metals, aggregate stability, organic matter and total nitrogen when compared to adjacent uncontaminated soil. Generally Pb and Cd availabilities decrease as soil pH range increase in the range of pH typical for soils. This reduction of metal availability was an effect of their greater adsorption and precipitation in neutral environments.

Assessment of heavy metal content in soil samples from various localities of Bijapur taluka, Karnataka had been undertaken. The soil characterization was carried out for parameters like pH, electrical conductivity, nitrogen, phosphorous, potassium and heavy metals like copper, iron, manganese, zinc etc. The higher values were indicative of anthropogenic inputs, either due to excess application of fertilizers or to industrial or mining activities (Pujjar *et al.*, 2012).

A study on quality of soil with reference to Zn, Pb, Fe, Mn and organic carbon in the soils of Eastern Guwahati Industrial zone, Assam revealed that the top soils in the area were heavily polluted with heavy metals. Statistical analysis of the data was presented to find out the correlation among measured variables. Resulting coefficient

of correlation between heavy metals and other soil properties such as organic matter, pH etc. established a nonlinear relationship between the parameters (Deka and Sarma, 2012).

A study conducted by Oyedele *et al.* (2008) reported significant relationship between soil heavy metal content and plant uptake, which varied significantly amongst the dump sites and also amongst the species of the heavy metals. The study showed that changes in physico-chemical characteristics at dump sites could be attributed to interactions of different soil properties rather a single factor.

2.8 Heavy metal influence on soil enzyme

The effect of Cu^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, Mo^{6+} and Al^{3+} at 25 and 75 µmole concentrations on acid phosphatase, alkaline phosphatase, aryl sulfatase and urease activities in the tea soils of south India was studied. The acid and alkaline phosphatase activities were inhibited effectively by Cu in the soils of Anamallas and Munnar and by manganese in the case of Nilgiris. Zinc inhibited aryl sulfatase activity to a very large extent in the soils of Munnar and Vandiperiyar and molybdenum in the case of Nilgiris. Inhibition of aryl sulfatase activity was as high as 79% due to addition of copper. Urease activity was the highest in Nilgiris followed by Vandiperiyar and its inhibition was up to 81% due to copper contamination. Zinc was an effective inhibitor in Anamallais and Munnar, whereas Al and Mn played significant roles in the soils of Nilgiris and Vandiperiyar, respectively (Venkatesan and Sethurpandian, 2006). The soil enzymes like urease, lipase, oxidase, alkaline and acid phosphatases were examined in soil from a refined-oil contaminated community in Isiukwuato, Abia state, three years after oil spill (Akbugwo *et al.*, 2009). Results showed a significant ($P< 0.05$) decrease in the activities of these enzymes in the contaminated soil relative to the control. Soil temperature, organic carbon, organic matter, exchangeable acidity, saturation base and effective cation exchangeable capacity were significantly higher ($p<0.05$) in the polluted soil. Soil N, P, Ca and Mg were also elevated in contaminated soil.

Frankenberger and Tabatabai (1991) conducted an experiment and reported the heavy metals like Ag, Cd, Hg, Pb inhibited the L-asparginase activity in the soil. Alkaline Phosphatase and urease enzyme activities are significantly reduced in the presence of Cr, Mn and Pb (Erdogan, 2008). Bing *et al.* (2009) in a study conducted to evaluate the influence of heavy metals on enzymatic activity in contaminated soil reported that the high concentration of Cr, significantly inhibited dehydrogenase activity and slightly inhibited alkaline phosphatase activity. An investigation carried out by Nwaugo *et al.* (2008) on soil bacterial flora and enzymatic activities in lead and zinc contaminated soil of Ishiagu, Nigeria concluded that soil enzymatic activities correlated negatively with heavy metal concentration. Among the different enzymes studied urease, dehydrogenase activity, hydrogen peroxidase and polyphenol oxidase were adversely affected but alkaline phosphatase did not show any significant effect. Soil enzymes appeared as sensitive indicators for assessing soil biochemical quality in trace metal contaminated soils.

2.9 Heavy metal toxicity in plants

At low metal concentrations, the plant cell could resort to a number of avoidance mechanisms such as metal exclusion, translocation and complexation in the cytoplasm (Vangronsveld and Clijisters, 1994). At high concentration when primary barriers were broken down, avoidance was insufficient, free metal concentration increased and both redox and non redox species could stimulate the production of reactive oxygen species (ROS) imposing oxidative stress (Aust *et al.*, 1998). Although oxygen itself was not harmful molecule, it could potentially be reduced to form toxic ROS. In the plant system, ROS were always formed by the inevitable leakage of electrons in to molecular O_2 from the electron transport activity of the chloroplast, mitochondria and plasma membranes. Actually, metals such as Cr, Hg, Ni and Pb exhibited the ability to increase the normal production of ROS, resulting in lipid peroxidation (Quartacci *et al.*, 2001).

2.10 Phytoremediation for removal of contaminant

Phytoremediation is innovative, economical and environmentally compatible method for heavy metal remediation. It was widely applied to large areas and is useful for solving a wide variety of contaminants (Padmavathiamma and Li, 2007). Phytoremediation study conducted by Angelova *et al.* (2004) found that vetiver was the most suitable candidate for detoxification of the Cu contaminated soils thus avoiding the entry of heavy metals in food chain. Investigating the efficiency of vetiver for phytoremediation technique by Roongtanakiat (2009) concluded that in low to moderately contaminated soil, vetiver can be used efficiently, as the harvested vetiver (after phytoremediation) can be used safely for bioenergy production, compost or even as material for handicrafts, but for extremely polluted sites, it was found to be more suitable to use in conjunction with other remediation methods.

2.11 Role of composting on removal of heavy metal

Singh and Kalamhad, (2012) concluded from their study that composting can reduce the heavy metal content. They concluded that during composting process, the metals content can be reduced by addition of some chemicals, microbial inoculants and earthworm. In comparison to other chemicals, natural zeolite was a good amendment because it had ability to exchange Na and K with toxic metals. The inoculation of microorganisms could be very useful to improve the composting process by enhancing enzymatic activity and quality level of the compost was acceptable, with very low heavy metal content. During the vermicomposting earthworm could accumulate the high concentration of heavy metals in the non-toxic forms and capable of reducing possible toxic effects of unessential heavy metals by utilizing them for physiological metabolism.

Saha *et al.,* 2010 analyzed the metal content in soil samples along the main highways in the central part of Hail city. Composts prepared from source separated biogenos wastes contained, on average, higher organic matter (by 57%), total N (by 77%) and total P (by 78%), but lower concentrations of heavy metals Zn (by 63%),

Cu (by 78%), Cd (by 64%), Pb (by 84%), Ni (by 50%), and Cr (by 63%) as compared to those prepared from mixed wastes. Zennaro *et al.* (2005) reported that municipal solid waste with accumulation of heavy metal when subjected to the composting resulted in large removal of heavy metal which was more critical without a substantial yield loss. In a pot culture experiment conducted to study the effect of accumulated contaminant elements in cultivated crops and their biomagnifications, Rao and Reddy (2009) concluded the heavy metal present in different crops poses no toxic pollution problem in the food chain, as well the heavy metal concentrations in the plant samples are within the limit. Composting of contaminated soils can convert hazardous wastes into innocuous end products (Semple *et al.*, 2001).

2.12. Decontaminated soil and performance of crops

The spatial and temporal variability of soil properties before and after the application of organic and inorganic amendments in a trace-element-polluted soil using statistics and geostatistical methods was addressed by Burgos *et al.* (2006). In both years, mean values of total concentrations of As, Cd, Cu, Pb and Zn were higher than the background values in the area. In general, amendment application increased soil pH and total organic carbon content and decreased heavy metal solubility; however it did not have a clear effect on total and available trace-element contents. Experimental semi variograms were developed to determine the spatial dependence of soil properties and were adjusted to spherical and linear models with nugget effect. Then, the spatial distribution of the different variables was estimated by kriging to design contour maps. These contour maps helped to identify the pollution patterns and delineate the range of contamination. A spatial similarity pattern among total As and Pb (the lesser mobile elements) and total S content was found in both samplings revealing a correspondence between the contamination and spots of residual sludge. Levels of metal pollution were influenced by soil pH. Despite those clean-up efforts the soil presented significant levels of pollution related to the presence of remaining sludge in the soil.

2.13. Use of geostatistical techniques for heavy metal study in soil

The spatial distribution of some soil chemical properties and trace element contents of a plot affected by the mine spill were investigated using statistical and geostatistical methods to assess the extent of soil contamination. The spatial distribution of the different variables was estimated by kriging to design contour maps. These maps allowed the identification of specific zones with high metal concentrations and low pH values corresponded to spots of residual sludge. Moreover, kriged maps showed distinct spatial distribution and hence different behaviour for the elements considered (Burgos, 2010).

Materials and methods

3. MATERIALS AND METHODS

The study entitled "Heavy metal contamination of laterites by accumulation of solid waste" was conducted at the department of Soil Science and Agricultural Chemistry, College of Horticulture during the period 2010-2014 in order to meet the objectives as detailed in Chapter 1. The work has been undertaken in a systematic manner as described in the flow chart given below (Fig 3.1).

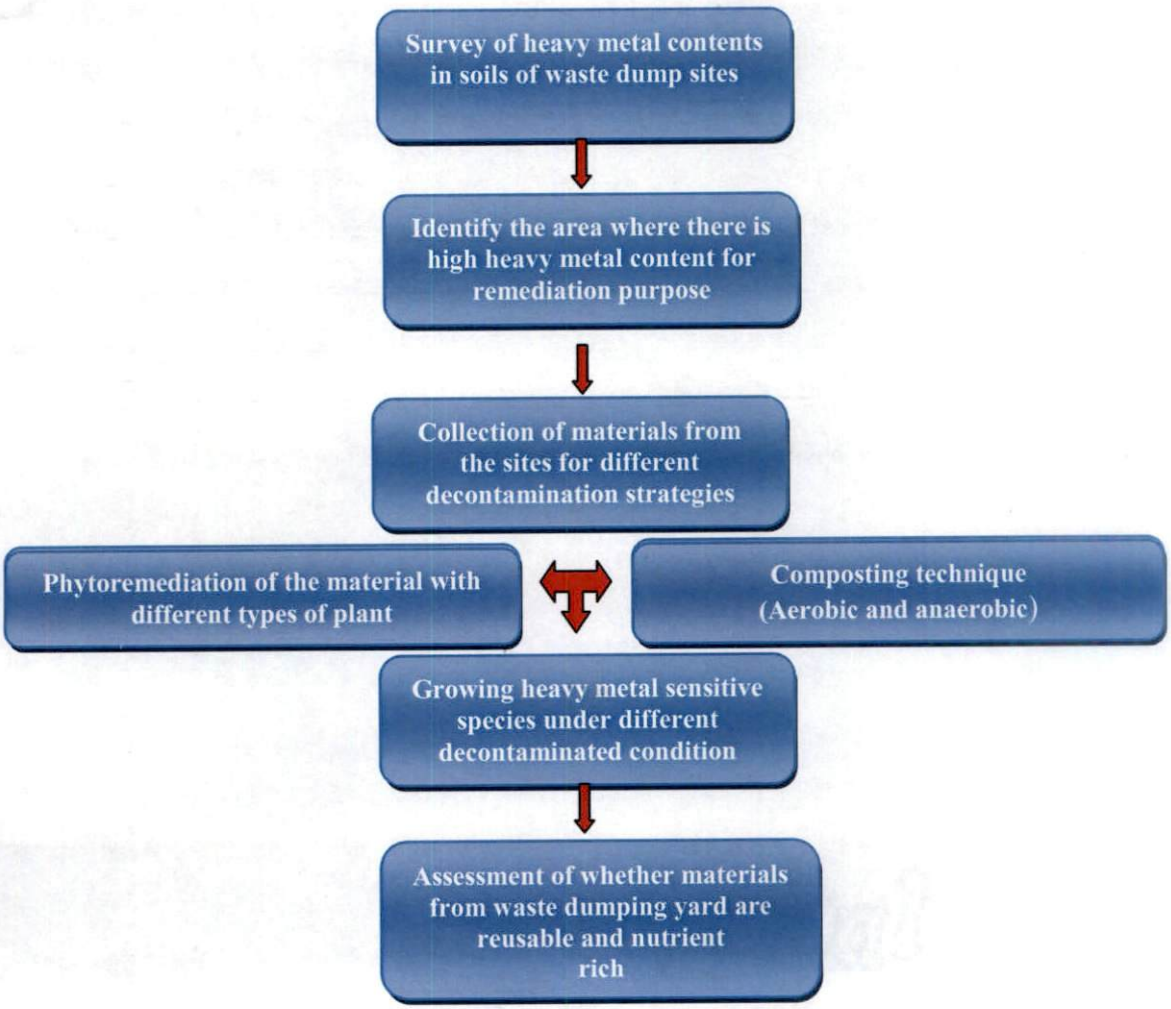

Figure.3.1. Flow chart describing the works undertaken for the study

Four separate but continuous experiments were undertaken as detailed in sections 3.1, 3.2, 3.3 and 3.4.

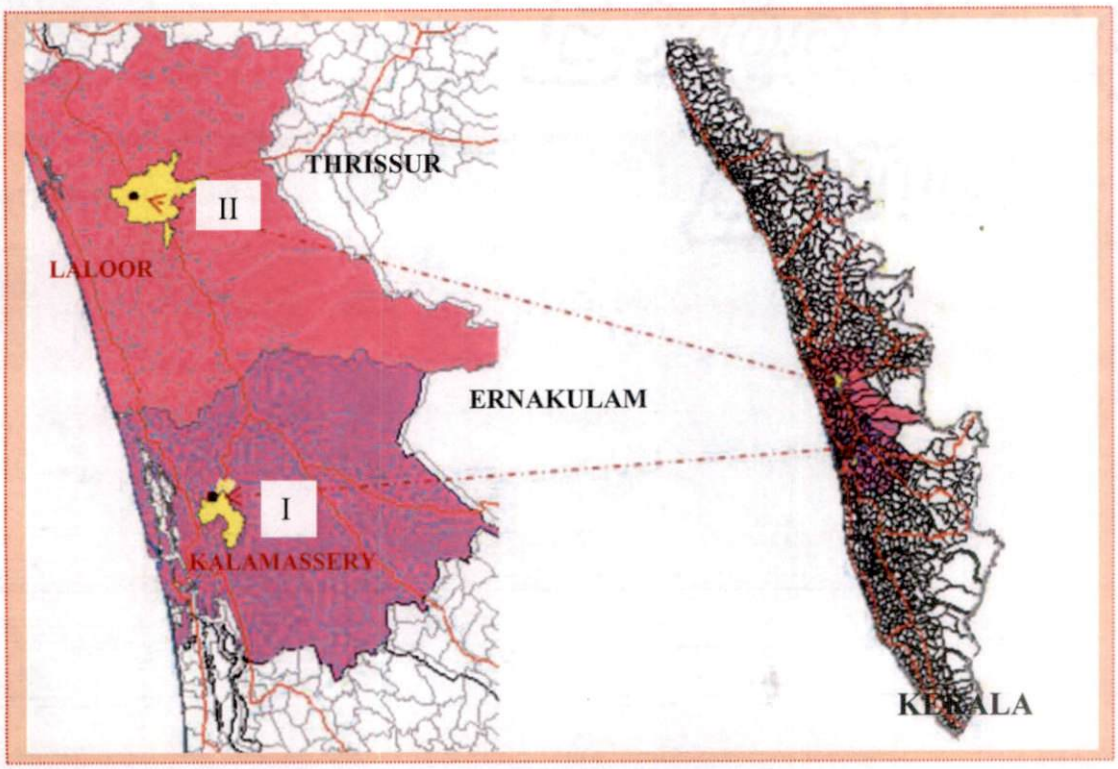

Fig.3.2. Map of Kerala showing the study area at Kalamassery (I) and Laloor (II)

3.1 Effect of climatic and soil factors on heavy metal accumulation using geostatistical techniques

3.1.1 Study area

Locations were identified at two major waste dumping sites in central Kerala, (I) Kalamassery in Eranakulam (II) Laloor in Thrissur district. (Fig.3.2)

Kalamassery in Ernakulam district is a concentrated region of industrialization with several factories such as Apollo, HMT and FACT. The whole area (1.18 ha) is a suburb of Kochi city located at 10° 3′ 7.09″ N latitude and 76° 18′ 56.78″ longitude.

Laloor in Thrissur district located at 10° 30′ 48.88″ N latitude and 76° 11′ 43.32″ E longitude is a residential area at a distance 5 km from the city. The entire area (3.37 ha) was considered as the centralized waste dumping site of erst while Kochi rajyam & Thrissur Corporation. The waste dumping at Laloor started more than quarter century ago.

3.1.2 Climate

Climate of the study area was generally tropical with heavy rains during June to September. Southwest monsoon and Northeast monsoon are the main rainy seasons. The average annual rainfall at the sampling sites during the survey period (2011-12) was around 3000 mm. In general, Kerala has hot and humid climate during April-May and cold climate in December-January. The average minimum temperature in Kerala 22^0C and average maximum 34^0C and the average annual rainfall in the state were recorded to be 2923.4 mm (Appendix I).

3.1.3. Soil sampling and data collected for study

The location of sampling was identified with the help of GPS (Table 3.1). Sampling was done from July 2011 to November 2012 at an interval of every three months (Appendix II). Soils were sampled along different directions within a radial distance of 1m from the centre of dumpsite to 10 to 20 cm depth. Soil samples were mixed to form composite surface soil samples in triplicates in each direction and at the centre of dumpsite at quarterly intervals. Samples were also collected from non dumping areas. A total of four samples for each site were pooled and analysed. The illustrations are presented in plate 3.1, 3.2. Bulky inorganic objects like cloth, plastic, rubber, metal, plastic, medical syringes, bulbs had been sorted out manually, and the details are given in Appendix IIIa and IIIb. The samples were air dried and ground to pass through a 2 mm sieve and the soil samples were kept in polythene bag for further analysis.

3.1.4 Soil Analysis

The collected samples were analysed for the various physico-chemical properties including the heavy metal contents and enzymatic activities. Total heavy metal content of soil samples was estimated by digesting soil samples with diacid mixture extractant (nitric acid and perchloric acid in the ratio 2:1). Methodology adopted for the determination of physical, chemical and biological properties of soil was described in Table 3.3.

3.1.5 GIS Analysis

GIS map of the two locations were generated using ArcGis 10.1 software. The Location of Kalamassery and Laloor was identified in high resolution google map using the GPS points taken during the ground survey. The images were digitized and geo referenced and converted to GIS layers. The result of heavy metal analysis was added as attribute to the GIS layers created for the different sites of location Kalamassery and Laloor using the GIS points taken during survey with GPS. The different maps were generated.

The indices that were worked out for the map were as follows and the ranges are given in Appendix V.

Index of geoaccumulation (I geo) proposed by Müller (1969) has also been widely used to evaluate the degree of metal contamination in terrestrial, aquatic as well as marine environments in comparison to background contents.

$Igeo = \log_2 Cn/1.5\ Bn$

Cn = concentration of the examined element in the examined environment

Bn = geochemical background of a given element in reference environment

Modified contamination degree (mC_d)

A modified and generalized form of Hakanson (1980) equation for the calculation of the overall degree of contamination was defined as the sum of all contamination factors (CF) for a given set of pollutants divided by the number of analyzed pollutants just as bellow (Abrahim and Parker, 2008)

$$mC_{d=}{}^{i=n}\,\Sigma_{i=1}\,CF^{i}/n$$

where n= number of analyzed elements, i= i^{th} element

CF^i = sum of all contamination factors (CF) for a given set of pollutants.

CF =Mx/Mb where Mx and Mb respectively refer to the mean concentration of a pollutant in the contaminated soil samples and the baseline concentration in reference environment like rock in this study.

Table 3.1. Details of the samples collected from the municipal waste dumping site at Kalamassery and Laloor

Serial No	Details of samples	Notation	Latitude	Longitude
1	Kalamassery dumping site 1	KLM 1	N 10^0 3' 53.823"	E 76^0 19'39.330"
2	Kalamassery dumping site 2	KLM 2	N 10^0 3' 54.698"	E 76^0 19'42.614"
3	Kalamassery dumping site 3	KLM 3	N 10^0 3' 51.597"	E 76^0 19'43.426"
4	Kalamassery non dumping site 4	KLM 4	N 10^0 3' 56.649"	E 76^0 19'40.411"
5	Laloor dumping site 1	LAR 1	N 10^0 30'53.823"	E 76^0 11'5.859"
6	Laloor dumping site 2	LAR 2	N 10^0 30'55.177"	E 76^0 11'9.188"
7	Laloor dumping site 3	LAR 3	N 10^0 30'53.86"	E 76^0 11'15.671"
8	Laloor non dumping site 4	LAR 4	N 10^0 30'52.505"	E 76^0 11'13.385"

Plate 3.1. Waste dumping yard at Kalamassery

Plate 3.2. Waste dumping yard at Laloor

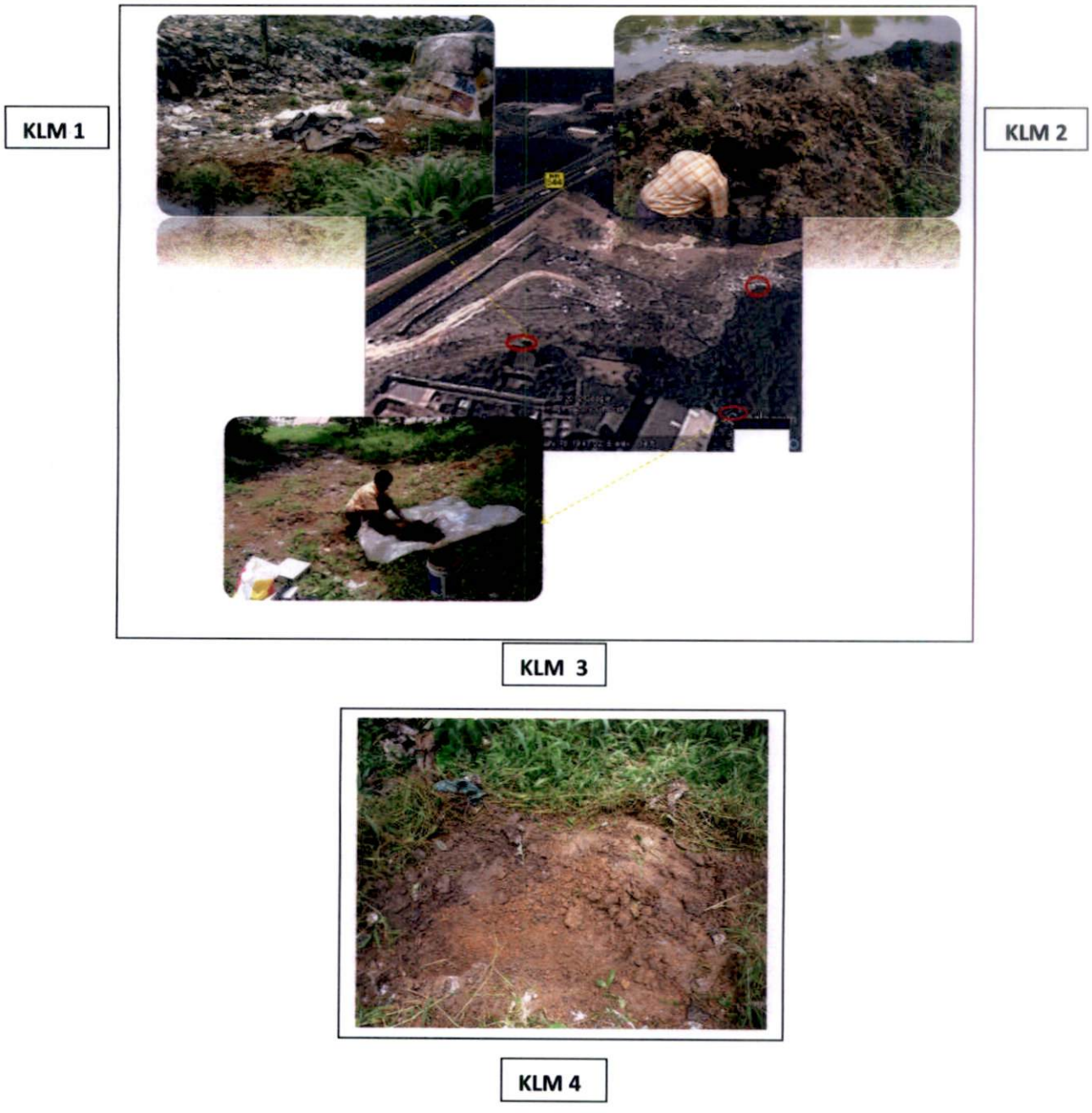

Plate 3.3. Sites of sample collection at Kalamassery

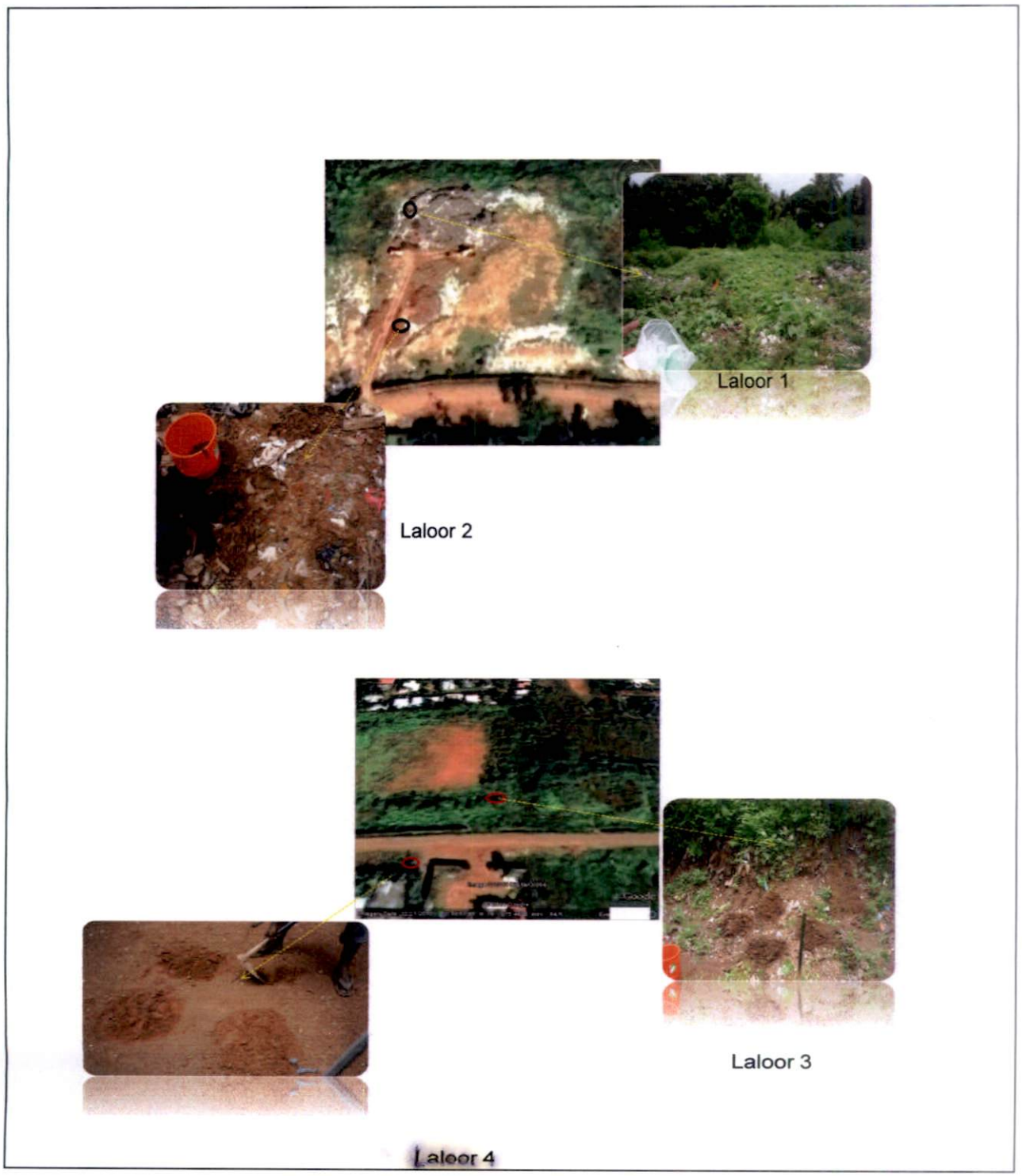

Plate 3.4. Sites of sample collection at Laloor

Table 3.2. Methods used to determine physico -chemical and biological properties of soil

Sl. No.	Property	Method		Reference
		Extraction	Estimation	
1	pH	1: 2.5 soil water suspension	Potentiometry	Jackson, 1958
2	Electrical conductivity	Supernatant liquid used for pH determination	Conductometry	Jackson, 1958
3	Organic matter	Wet digestion method		Walkley and Black, 1934
4	Total nitrogen		CHNS analyzer	Model: Elementar's vario EL cube
5	Total phosphorus	Di acid digestion (HNO_3:$HClO_4$)	ICP AES	Hesse,1994
6	Total potassium	Di acid digestion (HNO_3:$HClO_4$)	ICP AES	Hesse,1994
7	Total calcium	Di acid digestion (HNO_3:$HClO_4$)	ICP AES	Hesse,1994
8	Total magnesium	Di acid digestion (HNO_3:$HClO_4$)	ICP AES	Hesse,1994
9	Micronutrients	Di acid digestion (HNO_3:$HClO_4$)	ICP AES	Hesse, 1994
10	Heavy metals	Di acid digestion (HNO_3:$HClO_4$)	ICP AES	Hesse, 1994

Sl. No.	Property	Method		Reference
		Extraction	Estimation	
1	Urease	THAM buffer +toluene+urea	NH_4.N estimation by steam distillation with 0.2g MgO	Tabatabai and Bremner, *et al.*, 1972
2	Dehydrogenase	Triphenyl Tetrazolium Chloride	Triphenyl formazan developed with pink colour and intensity measured at 485 nm	Schinner, *et al.*, 1996
3	Phosphatase	p-nitrophenyl phosphate (PNP)	yellow colour intensity measured at at 440nm	Tabatabai and Bremner, 1969

3.2 Effect of phytoremediation on the decontamination of waste material collected from Laloor

Laloor was identified as the major dumping site and so waste material collected from laloor used for phytoremediation studies. Details given in appendix II b

3.2.1 Experiment details

Design: Completely Randomised Design

Replications: 5

Treatments: 3 types of crop

The following crops were selected for the study

- Vetiver grass (*Chrysopogon zizanioides*)
- Marigold (*Tagetes erectas*)
- Sunflower (*Helianthus annuus*)

3.2.1.2 Details of crops grown for phytoremediation studies

Vetiver (*Chrysopogon zizanioides*) is a perennial grass of the Poaceae family, native to India, was well known for its phytostabilisation and hyper accumulation property. Vetiver was grown for one year. Vetiver has a massive, deep root system

and stuff erect stiff shoot and can tolerate any adverse situations. Marigold (*Tagetes erecta)* is a herbaceous plants or Compositae grown for three months. It can grow well in all types of soil.

Sunflower (*Helianthus annuus)* is an annual plant in the family Asteraceae, with a large flower head, with duration of (90-110 days).

Marigold (*Tagetes erectas)* is an annual plant of the Asteraceae family, with duration of (100-130 days).

3.2.2. Planting of the crop

Fifteen concrete pots each with a capacity of 100 kg were used for the study. Soil along with waste material from Laloor and inert sand material in the ratio 2:1 was used for filling the pot. One seedling each of vetiver was planted. And two seedling each of sunflower and marigold were planted in the pot. (Plate.3.3)

3.2.3. Harvest and Plant analysis

Vetiver crop was harvested after one year and harvested roots and shoots were separated, cleaned and oven dried. Marigold and sunflower was harvested after flowering season and shoots, leaves, flower and root separately harvested, cleaned, dried and ground for plant analysis of heavy metal. The soil after phytoremediation was also analysed for heavy metals.

Vetiver

Sunflower

Marigold

Plate 3.5. Crops used for phytoremediation studies

3.2.4. Phytoremediation indices

Based on the heavy metal accumulation in different parts of the plants, the following indices were worked out for comparison of their potential in phytoremediation.

Translocation Factor (TF) =the metal concentration in shoots/the metal concentration in roots.

Bio concentration factor (BCF) = the heavy metal concentration in the plant/ initial concentration of metal in soil. (Subhashini *et al.,* 2013) (calculated based on whole plant total heavy metal uptake)

Removal ratio

$RCr = (B_s \times C_s + B_r \times C_r)/C_T \times$ Weight of initial material taken

Where, B (g) is biomass. C (mg g^{-1}) is the concentration of heavy metal, the subscript of B or C represents shoot (s), root (r) and treated soil (T).

3.3 Effect of aerobic and anaerobic methods of composting on the composition of heavy metals in the waste material

The material collected from Laloor was subjected to aerobic and anaerobic methods of composting with the use of equal quantities of cow dung and waste material for a period of two months.

3.3.1 Experiment details

Design: Completely Randomised Design

Replications: 5

Treatments: 3

Details of treatments were as follows:

1. Waste material (control) – A heap of 100 kg waste material was kept as control under aerobic conditions.
2. Aerobic composting – 100 kg waste material was taken and mixed with cowdung in the ratio 1:1. Moisture level was uniformly maintained at 60 to 70 per cent by moistening with water at specific intervals of study.
3. Anaerobic composting (Biogas method) -Biogas unit of 0.5 m^3 capacity was used for anaerobic composting. For the study 100 kg waste material and 100 kg cowdung was used. Each day 20 kg material (cowdung: waste material in the ratio 1:1) was fed to the biogas unit and a total of 20 liters of biogas slurry was collected. Five biogas units of 0.5 m^3size were used with a intake capacity of 18-20 kg day^{-1}.

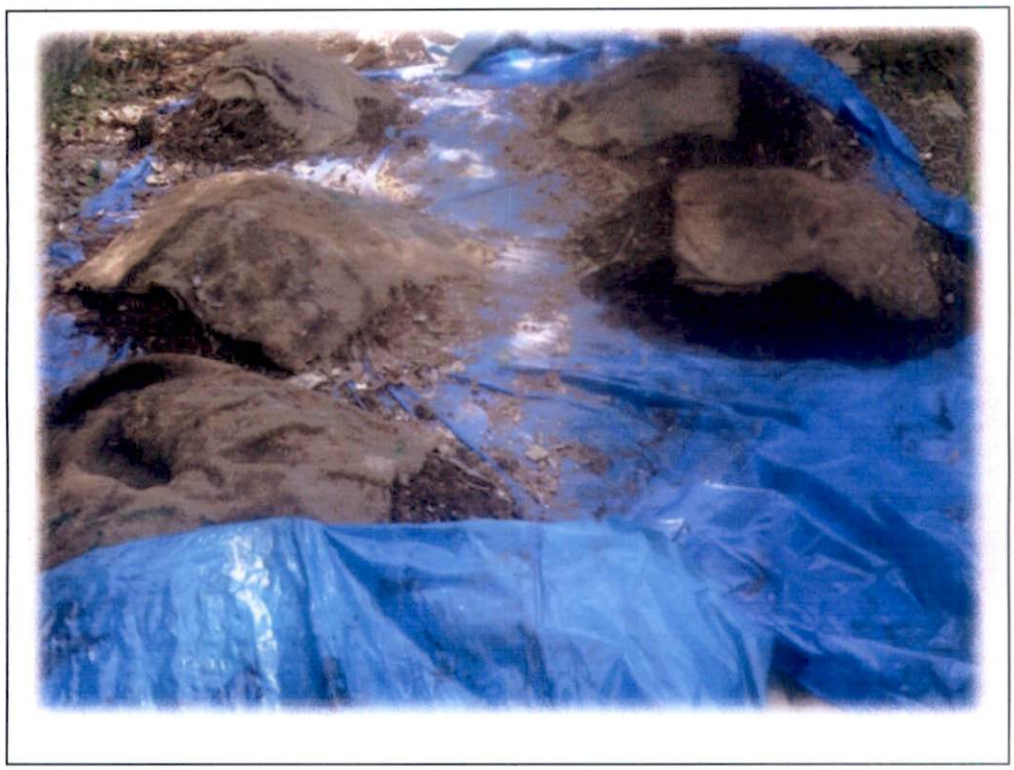

Plate 3.6. Treatment with aerobic composting

Plate 3.7. Treatment with anaerobic composting

3.4 Comparative performance of amaranthus grown in soil under different methods adopted for reducing heavy metal contamination

A pot culture study of amaranthus was conducted with the test variety Arun with a total duration of two months. An irrigated crop was raised and the pot was filled with the treatment material and sand, in the ratio 1:1 (8 Kg each per pot).

3.4.1 Experiment details

Design: Completely Randomised Design

Replications: 3

Treatments: 7

Table 3.3. Details of the treatments used for the pot culture study using amaranthus

Treatment notation	Details
T_1	Absolute control- soil from Vellanikkara
T_2	T_1+recommended dose of FYM (50 t ha^{-1})
T_3	T_1+recommended dose of FYM+N.P.K. (50:50:50 kg ha^{-1})
T_4	Material after phytoremediation
T_5	Biodegraded waste material- (control of compost experiment)
T_6	Aerobic compost
T_7	Bio-gas slurry (anaerobic compost)-Equal dose of slurry was given

Plate 3.8. Amaranthus pot culture study

3.4.2 Planting of amaranthus

The Seeds of Arun variety of amaranthus was sown in nursery and three seedlings each were transplanted at two leaf stage pot of 20 kg capacity. The treatments T_1 to T_7 were maintained at field capacity, whereas for T_7 the slurry was applied at the rate of 200 ml per pot at an interval of two days. So as to keep the treatments at the same moisture level of other treatments.

3.4.3 Harvest and plant analysis

Observations like plant height and number of leaves were taken at each interval. At harvest, plants were uprooted plant parts separated, cleaned and oven dried for heavy metal analysis.

Table 3.4. Methods used for plant analysis

Sl. No.	Property	Method		Reference
		Extraction	Estimation	
1	Total carbon	CHNS analyzer	CHNS analyzer	Model: Elementar's vario EL cube
2	Total nitrogen	CHNS analyzer	CHNS analyzer	Model: Elementar's vario EL cube
3	Total phosphorus	Di acid digestion	ICP AES	Piper,1966
4	Total potassium	Di acid digestion	ICP AES	Piper,1966
5	Total calcium	Di acid digestion	ICP AES	Piper,1966
6	Total magnesium	Di acid digestion	ICP AES	Piper,1966
7	Micronutrients	Di acid digestion	ICP AES	Piper,1966
8	Heavy metals	Di acid digestion	ICP AES	Piper, 1966

3.5. Computation of the data and statistical analysis

Statistical softwares used for the study were SPSS, MSTAT C and WASP 2.0 (ICAR, GOA).

Two Factor ANOVA experiments for first experiment

Correlation studies for first experiment

Analysis of variance (ANOVA) technique was used with Duncan's Multiple Range Test (DMRT) was applied to see the significance of difference among treatment means for second, third and fourth experiment.

Results

4. RESULTS

The results of the investigation on "Heavy metal contamination of laterites by accumulation of solid waste" are presented experiment wise below

4.1. Experiment 1: Effect of soil and climatic factors on heavy metal accumulation

The soil samples drawn at quarterly intervals from each of the four sites at the two locations (Kalamassery and Laloor) were analysed for the different physico-chemical properties and the results are presented in this section.

4.1.1. Soil moisture (%)

The soil moisture contents at the dumping as well as non dumping sites of two locations, Kalamassery and Laloor recorded at quarterly intervals. The data are being presented in Table 4.1.1.

Table. 4.1.1. Soil moisture (%) for sampling sites of two locations at different quarterly intervals

Sampling Site / Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site/ location
KLM 1	5.10 (2.37)	0.50 (1.00)	8.50 (3.00)	1.00 (1.22)	**3.80 (1.93)**
KLM 2	15.50 (4.0)	3.40 (1.97)	1.50 (1.41)	1.50 (1.41)	**5.50 (2.20)**
KLM 3	3.80 (2.07)	2.20 (1.64)	4.2 (2.17)	0.5 (1.0)	**2.70 (1.72)**
KLM 4 Non dumping	2.20 (1.64)	0.10 (0.77)	1.80 (1.52)	0.50 (1.0)	**1.20 (1.23)**
Mean (KLM)	**6.65 (2.52)**	**1.55 (1.35)**	**4.0 (2.02)**	**0.88 (1.16)**	**3.27 (1.76)**
LAR 1	11.20 (3.42)	0.20 (0.84)	2.80 (1.82)	0.50 (1.0)	**3.70 (1.77)**

Table 4.1.1. Continued

LAR 2	11.40 (3.45)	0.10 (0.77)	7.00 (2.74)	0.10 (0.77)	**4.70 (1.93)**
LAR 3	8.80 (3.05)	0.20 (0.84)	2.1 (1.61)	0.4 (0.95)	**2.9 (1.61)**
LAR 4 Non dumping	4.40 (2.21)	0.10 (0.77)	2.10 (1.61)	0.10 (0.77)	**1.70 (1.34)**
Mean (LAR)	**9.00 (3.05)**	**0.2 (0.81)**	**3.5 (1.95)**	**0.28 (0.87)**	**3.21 (1.66)**
Mean for comparing quarter	**7.80 (2.77)**	**0.90 (1.07)**	**2.30 (1.98)**	**0.60 (1.02)**	
CD1	**CD for comparing each site -NS**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-0.58**		**CD 4**	**CD for comparing Location -NS**	

Values expressed in parenthesis indicate square root transformation

In general, the lowest moisture content was recorded at the dumping site of Laloor (0.10%) during quarter II and quarter IV, and the highest (15.5%) at the dumping site of Kalamassery 2, during the first quarter. The soil moisture content in case of non-dumping site was (1.20%) and (1.70%) and a maximum value was reported at the dumping sites with (5.50%) and (4.70%) at Kalamassery and Laloor respectively. With reference to comparison of soil moisture content at the different locations within quarter, the mean content varied from 0.88% to a maximum of 6.65% at Kalamassery and 0.20% to 9.0% for Laloor, which was found to be non significant. While comparing the mean soil moisture content quarter wise, the maximum soil moisture per cent was observed during quarter I (7.80%), followed by quarter III (2.30%), quarter II (0.90%) and quarter IV (0.60%), the mean value during quarter I found to be significantly different from other quarters. Regarding the mean content of soil moisture, irrespective of all the quarters, it was 3.27% at Kalamassery and 3.21% at Laloor and was on par with each other.

4.1.2. Soil temperature (^{0}C)

The variation in the temperature (^{0}C) at two locatons i.e, Kalamassery and Laloor including dumping and non dumping sites, were recorded at quarterly intervals and the data is presented in the Table 4.1.2.

Table 4.1.2. Soil temperature (^{0}C) for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site / location
KLM 1	33.40	35.00	34.00	30.00	33.10
KLM 2	32.10	34.00	34.00	32.00	33.03
KLM 3	32.00	34.00	33.00	29.00	32.00
KLM 4 Non dumping	29.00	34.00	32.00	28.00	30.75
Mean (KLM)	**31.63**	**34.25**	**33.25**	**29.75**	**32.22**
LAR 1	34.50	37.00	36.00	29.50	34.25
LAR 2	36.50	37.00	36.00	29.00	34.63
LAR 3	35.00	32.00	36.00	31.00	33.50
LAR 4 Non dumping	33.00	32.00	36.00	30.00	32.75
Mean (LAR)	**34.75**	**34.50**	**36.00**	**29.88**	**33.78**
Mean for comparing quarter	**33.19**	**34.38**	**34.63**	**29.81**	

CD1	**CD for comparing site -NS**	**CD 2**	**CD for comparing locations within quarters -1.97**
CD3	**CD for comparing quarter- 1.39**	**CD 4**	**CD for comparing location - 0.98**

While comparing the temperature, the minimum of 28^{0}C was recorded at the non dumping sites during quarter IV at Kalamassery to a maximum of 37^{0}C at dumping site during quarter II in Laloor. The mean temperature for the different sites were on par with each other, though the non dumping sites of each location recorded slightly lower temperature of 30.75^{0}C and 32.75^{0}C and the maximum temperature of

33.10^{0}C and 34.63^{0}C, was recorded at the dumping sites of Kalamassery and Laloor respectively. With reference to the mean soil temperature quarter wise within locations, the soil temperature varied from the least value of 29.75^{0}C to a maximum of 34.25^{0}C at Kalamassery and 29.88^{0}C to 36^{0}C in Laloor, which was significantly different. On perusal of the data during quarter, it was found to be the lowest during quarter IV (29.82^{0}C) and the highest during quarter III (34.63^{0}C) which was also found to be significantly different from other quarters, though there was no significant difference between mean soil temperature during quarter II and III. There was a significant variation in temperature of the two locations which was comparatively higher at Laloor (33.78^{0}C) than Kalamassery (32.22^{0}C).

4.1.3. Soil reaction (pH)

The variation in pH at the dumping as well as non dumping site two location i.e, Kalamassery and Laloor was being recorded at quarterly intervals and the data has been presented in table 4.1.3

Table 4.1.3. Soil pH for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	6.2	6.5	6.6	6.9	**6.6**
KLM 2	6.4	5.8	6.9	5.8	**6.2**
KLM 3	6.1	5.0	5.2	5.8	**5.5**
KLM 4 Non dumping	5.1	4.6	4.9	6.1	**5.2**
Mean (KLM)	**6.0**	**5.5**	**5.9**	**6.2**	**5.9**
LAR 1	6.8	6.6	6.0	6.6	**6.5**
LAR 2	6.1	6.1	6.3	6.8	**6.3**
LAR 3	6.4	6.2	6.4	6.4	**6.4**

Table 4.1.3 continued.

LAR 4 Non dumping	6.5	6.2	6.1	5.8	6.2
Mean (LAR)	**6.5**	**6.3**	**6.2**	**6.4**	**6.4**
Mean for comparing quarter	**6.2**	**5.9**	**6.1**	**6.3**	

CD1	**CD for comparing site - NS**	**CD 2**	**CD for comparing locations within quarters -NS**
CD3	**CD for comparing quarter-NS**	**CD 4**	**CD for comparing Location – 0.343**

Generally, the pH values ranged from minimum of 4.6 at non dumping site to a maximum of 6.9 at dumping site of Kalamassery. The result of the mean pH value at the different sites of the two locations showed that the non-dumping sites recorded the lowest pH value of 5.2 at Kalamassery and 6.2 at Laloor, whereas the highest values of 6.6 and 6.5 were found at the dumping sites of Kalamassery 1 and Laloor1 respectively. With reference to the mean pH values at different sites, the soil pH varied from minimum of 5.5 to a maximum of 6.2 at Kalamassery and 6.0 to 6.5 at Laloor which was found to be non significant. While comparing the quarter wise mean within locations, there was no significant difference. The highest soil pH value of 6.3 was recorded during quarter IV and the lowest of 5.9 was recorded during quarter II. On consideration of the mean value of pH at two locations, there was a significant difference and it was comparatively higher at Laloor (6.4) compared to Kalamassery (5.9).

4.1.4. Electrical conductivity (EC dS m^{-1})

The variation in electrical conductivity at the dumping as well as non dumping site of two location i.e, Kalamassery and Laloor was being recorded at quarterly intervals and the data has been presented in table 4.1.4.

Table 4.1.4. Soil electrical conductivity for the sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	0.02	0.04	0.09	0.06	**0.05**
KLM 2	0.20	0.03	0.04	0.04	**0.08**
KLM 3	0.04	0.01	0.02	0.04	**0.03**
KLM 4 Non dumping	0.03	0.01	0.01	0.02	**0.02**
Mean (KLM)	**0.07**	**0.02**	**0.04**	**0.04**	**0.04**
LAR 1	0.04	0.03	0.03	0.09	**0.04**
LAR 2	0.04	0.03	0.01	0.06	**0.03**
LAR 3	0.02	0.04	0.04	0.02	**0.03**
LAR 4 Non dumping	0.03	0.02	0.03	0.02	**0.02**
Mean (LAR)	**0.03**	**0.03**	**0.02**	**0.05**	**0.03**
Mean for comparing quarter	**0.051**	**0.026**	**0.029**	**0.043**	

CD1	**CD for comparing site - NS**	**CD 2**	**CD for comparing locations within quarters -NS**
CD3	**CD for comparing quarter-NS**	**CD 4**	**CD for comparing Location – 0.343**

Generally, the electrical conductivity values ranged from minimum of 0.02 dS m^{-1} at non dumping site to a maximum of 0.08 dS m^{-1} at dumping site of Kalamassery. The result of the mean electrical conductivity value at the different sites of the two locations showed that the non-dumping sites recorded the lowest value of 0.02 at Kalamassery and Laloor, whereas the highest values of 0.08 and 0.04 dS m^{-1} were found at the dumping sites of Kalamassery 2 and Laloor1 respectively. With reference to the mean EC values at different sites, it varied from minimum of 0.02 to a maximum of 0.08 dS m^{-1} at Kalamassery and 0.02 to 0.04 dS m^{-1} at Laloor which was found to be non significant. While comparing the quarter wise mean within

locations, there was no significant difference. The highest soil pH value of 0.051 dS m^{-1} was recorded during quarter I and the lowest of 0.026 dS m^{-1} was recorded during quarter II. On consideration of the mean value of EC at two locations, there was no significant difference and it was comparatively higher at Kalamassery (0.04 dS m^{-1}) compared to Laloor (0.03 dS m^{-1}).

4.1.5. Soil organic matter (%)

The relative content of organic matter and its variations in dumping and non dumping sites of two locations at different quarterly intervals are furnished in Table 4.1.5.

Table 4.1.5. Soil organic matter (%) for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM1	2.59 (1.76)	2.42 (1.71)	3.79 (2.07)	1.43 (1.39)	**2.55 (1.73)**
KLM 2	3.83 (2.08)	4.31 (2.19)	4.45 (2.22)	2.33 (1.68)	**3.73 (2.05)**
KLM 3	5.51 (2.45)	2.99 (1.87)	3.75 (2.06)	2.40 (1.70)	**3.66 (2.02)**
KLM 4 Non dumping	1.66 (1.47)	1.31 (1.35)	1.34 (1.36)	2.38 (1.70)	1.67 (1.47)
Mean	**3.40 (1.94)**	**2.76 (1.78)**	**3.33 (1.93)**	**2.13 (1.62)**	**2.91 (1.82)**
LAR1	1.99 (1.58)	2.36 (1.69)	6.16 (2.94)	5.36 (2.42)	4.47 (2.22)
LAR2	1.72 (1.49)	4.19 (2.16)	4.75 (2.29)	1.92 (1.56)	3.14 (1.91)
LAR 3	4.28 (2.19)	4.16 (2.16)	2.36 (1.69)	2.65 (1.78)	3.36 (1.96)
LAR 4	1.22	2.08	2.58	1.12	1.75

Table 4.1.5. Continued.

Non dumping	(1.31)	(1.61)	(1.69)	(1.27)	(1.5)
Mean	**2.30 (1.64)**	**3.20 (1.9)**	**3.96 (2.17)**	**2.76 (1.76)**	**3.18 (1.87)**
Mean for comparing quarter	**2.85 (1.63)**	**2.98 (1.84)**	**3.89 (1.90)**	**2.45 (1.57)**	

CD1	**CD for comparing site -1.78**	**CD 2**	**CD for comparing locations within quarters-NS**
CD3	**CD for comparing quarter-NS**	**CD 4**	**CD for comparing Location -NS**

Values expressed in parenthesis indicate square root transformation

In general, the soil organic matter content ranged from 1.12 per cent at non dumping sites at Laloor 4, to 6.16 per cent for the dumping site at Laloor 1. The mean of organic matter content at the different sites of Kalamassery and Laloor was found to be significantly different. The organic matter content was reported to be low for the non-dumping sites with a value of 1.67 and1.75 % to a high value of 3.73 % and 4.47 % for dumping sites at Kalamassery and Laloor respectively; these values were on par with each other. With reference to the mean of soil organic matter for locations within quarter it varied from a minimum value of 2.13 % to maximum of 3.40 % at Kalamassery and 2.30 % to 4.46 % at Laloor, which was also found to be non-significant. For both the locations, the maximum soil organic matter content (%) was observed during quarter III (3.89%), followed by quarter II (2.97%), which were closely followed by quarter I (2.84%) and quarter IV (2.45%), which was found to be not significant. Regarding the mean of soil organic matter at two locations, it was found to be comparatively higher in Laloor (3.18%) than Kalamassery (2.91%), but not significantly different.

4.1.6. Total nitrogen content of soil (%)

The total (N) content (%) were determined at two locations ie., Kalamassery and Laloor including dumping and non dumping sites was recorded at quarterly intervals and the data is presented in the Table 4.1.6.

Table 4.1.6. Total nitrogen (%) for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	0.06 (0.56)	0.08 (0.58)	0.18 (0.68)	0.01 (0.51)	**0.08 (0.58)**
KLM 2	0.26 (0.76)	0.11 (0.61)	0.14 (0.64)	0.15 (0.65)	**0.17 (0.67)**
KLM 3	0.14 (0.64)	0.11 (0.61)	0.11 (0.61)	0.09 (0.59)	**0.11 (0.61)**
KLM 4 Non dumping	0.01 (0.51)	0.01 (0.51)	0.01 (0.51)	0.08 (0.58)	**0.03 (0.53)**
Mean	**0.12 (0.62)**	**0.08 (0.58)**	**0.11 (0.61)**	**0.08 (0.58)**	0.10 (0.60)
LAR1	0.02 (0.52)	0.03 (0.53)	0.77 (1.27)	0.34 (0.84)	**0.29 (0.79)**
LAR 2	0.05 (0.55)	0.22 (0.72)	0.27 (0.77)	0.15 (0.65)	**0.17 (0.67)**
LAR 3	0.14 (0.64)	0.17 (0.67)	0.28 (0.78)	0.22 (0.72)	**0.20 (0.70)**
LAR 4 Non dumping	0.04 (0.54)	0.06 (0.56)	0.04 (0.54)	0.02 (0.52)	**0.04 (0.54)**
Mean	**0.06 (0.56)**	**0.12 (0.62)**	**0.34 (0.84)**	**0.18 (0.68)**	0.18 (0.68)
Mean for comparing quarter	**0.09 (0.63)**	**0.10 (0.57)**	**0.22 (0.73)**	**0.13 (0.62)**	
CD1	**CD for comparing site- NS**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-NS**		**CD 4**	**CD for comparing Location -NS**	

Values expressed in parenthesis indicate square root transformation

On perusal of the data on total N content the highest value of 0.77 % was recorded at Laloor 1 and the lowest value of 0.01 % was recorded at Kalamassery 3. However, the value of the mean total nitrogen for the different sites ranged from 0.03

% for the non dumping site at Kalamassery 4 to a highest value of 0.17 % at dumping site of Kalamassery 2 and 0.04 % at the non dumping site to 0.29 % at the dumping site of Laloor 4 and Laloor 1 respectively. With reference to the total N (%) quarter wise within location, it varied from a minimum of 0.08 per cent (quarter IV)) to a maximum of 0.12 per cent (quarter I) at Kalamassery and 0.06 to 0.34 per cent at Laloor which was also found to be not significant. In general, considering the mean of total soil N during quarters, the highest total nitrogen content of 0.22 % was recorded during quarter III and the lowest value of (0.09 %) was recorded during quarter I and there was no significant difference between them. Taking the mean of two location the total N was found to be comparatively higher at Laloor (0.18%) than Kalamassery (0.10%), but not significantly different.

4.1.7. Total phosphorous content of soil (%)

The variation in total phosphorous at the dumping site as well as non dumping site of two locations i.e., Kalamassery and Laloor is being recorded at quarterly intervals and the data has been presented in Table 4.1.7.

Table 4.1.7. Total phosphorous (%) for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	0.10 (0.77)	0.10 (0.77)	0.12 (0.79)	0.07 (0.75)	**0.10 (0.77)**
KLM 2	0.06 (0.75)	0.07 (0.76)	0.07 (0.76)	0.06 (0.75)	**0.07 (0.76)**
KLM 3	0.07 (0.75)	0.08 (0.76)	0.08 (0.76)	0.06 (0.75)	0.07 (0.76)
KLM 4 Non dumping	0.09 (0.77)	0.04 (0.73)	0.04 (0.73)	0.08 (0.76)	**0.06 (0.75)**
Mean	**0.08 (0.76)**	**0.07 (0.76)**	**0.08 (0.76)**	**0.07 (0.75)**	**0.07 (0.76)**

Table 4.1.7. Continued.

LAR1	0.06 (0.75)	0.09 (0.77)	0.15 (0.81)	0.15 (0.81)	**0.11 (0.78)**
LAR 2	0.05 (0.74)	0.07 (0.75)	0.13 (0.80)	0.10 (0.78)	**0.09 (0.77)**
LAR 3	0.12 (0.79)	0.10 (0.77)	0.10 (0.77)	0.14 (0.80)	**0.12 (0.78)**
LAR 4 Non dumping	0.05 (0.74)	0.07 (0.76)	0.06 (0.75)	0.07 (0.76)	**0.06 (0.75)**
Mean	**0.07 (0.76)**	**0.08 (0.76)**	**0.11 (0.78)**	**0.12 (0.78)**	**0.10 (0.77)**
Mean for comparing quarter	**0.08 (0.76)**	**0.08 (0.76)**	**0.10 (0.77)**	**0.12 (0.78)**	
CD1	**CD for comparing site-NS**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-NS**		**CD 4**	**CD for comparing Location -0.013**	

Values expressed in parenthesis indicate square root transformation

Generally the total P per cent ranged from a minimum of (0.04%) at Kalamassery 3 to (0.15 %) at Laloor1 at quarter III and quarter IV. The data on the mean total P site wise for the two locations showed that the non dumping sites recorded the lower P content with (0.07 %) at Kalamssery and (0.06 %) at Laloor and the dumping sites recorded the higher value of (0.10%) and (0.12 %) at Kalamassery and Laloor respectively. Perusal of data on the mean total P content at the locations within quarters showed that it ranged from 0.07% to 0.08% at Kalmassery and 0.07% to 0.12% at Laloor, which was on par with each other. On comparison of the mean total P quarter wise, it was observed that the highest P content ranged from 0.08% during quarter I and to 0.12% quarter II during quarter IV and there was no significant difference between them. With reference to the mean at two locations, there was a significant difference in total P content which is found to be higher at Laloor (0.10%) than Kalmassery (0.07%).

4.1.8. Total potassium content of soil (%)

The relative content of total K and its variation in dumping and non dumping sites of two locations at different quarterly intervals are furnished in Table 4.1.8.

Table 4.1.8. Total potassium (%) for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	0.28 (0.88)	0.23 (0.86)	0.26 (0.87)	0.30 (0.89)	**0.27 (0.88)**
KLM 2	0.19 (0.83)	0.14 (0.80)	0.31 (0.90)	0.24 (0.86)	**0.22 (0.85)**
KLM 3	0.15 (0.81)	0.10 (0.77)	0.16 (0.81)	0.19 (0.83)	**0.15 (0.81)**
KLM 4 Non dumping	0.12 (0.79)	0.12 (0.79)	0.16 (0.81)	0.13 (0.80)	**0.13 (0.80)**
Mean	**0.20 (0.83)**	**0.16 (0.80)**	**0.24 (0.85)**	**0.22 (0.85)**	**0.21 (0.83)**
LAR 1	0.15 (0.81)	0.14 (0.80)	0.41 (0.95)	0.34 (0.92)	**0.26 (0.87)**
LAR 2	0.12 (0.79)	0.12 (0.79)	0.40 (0.95)	0.27 (0.88)	**0.23 (0.85)**
LAR 3	0.12 (0.79)	0.17 (0.82)	0.23 (0.87)	0.26 (0.85)	**0.19 (0.83)**
LAR 4 Non dumping	0.10 (0.78)	0.12 (0.79)	0.13 (0.80)	0.15 (0.81)	**0.13 (0.79)**
Mean	**0.12 (0.79)**	**0.14 (0.80)**	**0.29 (0.89)**	**0.26 (0.87)**	**0.20 (0.84)**
Mean for comparing quarter	**0.15 (0.81)**	**0.14 (0.80)**	**0.26 (0.87)**	**0.24 (0.85)**	
CD1	**CD for comparing site-NS**		**CD 2**	**CD for comparing locations within quarters-0.030**	
CD3	**CD for comparing quarter-0.043**		**CD 4**	**CD for comparing Location -NS**	

Values expressed in parenthesis indicate square root transformation

In the case of total K content (%) the values varied within a range of minimum 0.10 percent at Kalamassery 3 to a maximum of 0.41 per cent at Laloor 1. The mean total K for the different sites at Kalamassery and Laloor was found to be non significant which was reported as (0.13%) at the non dumping sites of Kalamassery and Laloor, and the highest value was reported at the dumping site of Kalamassery (0.27 %) and Laloor (0.26%). With reference to the mean total K content (%) for the locations within quarter, it varied from the lowest value of 0.16 per cent (quarter II) to the highest value of 0.24 per cent (quarter III) at Kalamassery and the lowest value of 0.12 per cent (quarter I) to the highest value of 0.26 per cent (quarter III) at Laloor, which was also found to the significantly different. Whereas quarter I and quarter II was found to be on par with each other. While comparing the mean of total K quarter wise, the maximum total K content was observed during the quarter III (0.26 %) followed by quarter IV (0.24%) then quarter I (0.15%) and quarter II (0.14%) which was found to be significantly different between the quarters. Comparing the mean of total K at two locations, it was found that the total K content of soil at Kalamassery recorded (0.21%) and Laloor (0.20%), which was on par with each other.

4.1.9. Total calcium content of the soil (%)

The variation in total Ca content was recorded at the dumping and non dumping sites of the two locations i.e., Kalamassery and Laloor for different quarterly intervals and the data has been provided in the Table 4.1.9.

Table 4.1.9. Total calcium (%) for sampling sites of two locations at different quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	0.23 (0.86)	0.43 (0.96)	0.84 (1.16)	2.12 (1.62)	**0.90 (1.15)**
KLM 2	0.33 (0.91)	0.45 (0.97)	0.76 (1.12)	0.25 (0.86)	**0.45 (0.97)**
KLM3	0.44 (0.97)	0.12 (0.79)	0.14 (0.80)	0.52 (1.01)	**0.30 (0.89)**
KLM 4 Non dumping	0.15 (0.81)	0.23 (0.85)	0.44 (0.97)	0.18 (0.82)	**0.25 (0.86)**
Mean	**0.29 (0.89)**	**0.31 (0.90)**	**0.55 (1.02)**	**0.76 (1.12)**	**0.48 (0.99)**
LAR 1	0.70 (1.09)	0.72 (1.10)	1.76 (1.50)	1.48 (1.41)	**1.16 (1.28)**
LAR 2	0.20 (0.84)	0.23 (0.85)	0.71 (1.10)	1.21 (1.31)	**0.59 (1.03)**
LAR 3	0.59 (1.04)	0.53 (1.02)	0.47 (0.98)	0.54 (1.02)	**0.53 (1.02)**
LAR 4 Non dumping	0.15 (0.81)	0.24 (0.86)	0.19 (0.83)	0.17 (0.82)	**0.19 (0.83)**
Mean	**0.41 (0.95)**	**0.43 (0.96)**	**0.78 (1.13)**	**0.85 (1.16)**	**0.62 (1.06)**
Mean for comparing quarter	**0.35 (0.92)**	**0.37 (0.93)**	**0.67 (1.08)**	**0.81 (1.14)**	
CD1	**CD for comparing site-NS**		**CD 2**	**CD for comparing locations within quarters-0.030**	
CD3	**CD for comparing quarter-0.043**		**CD 4**	**CD for comparing Location -NS**	

Values expressed in parenthesis indicate square root transformation

In general, the total Ca content ranged from a minimum of 0.12% at Kalamassery 3 to a maximum of 1.76% at Laloor 1. The mean of total Ca at the different sites at Kalamassery and Laloor was found to be non significant which ranged from the lowest value of0.25% and (0.19%) at the non dumping sites to the highest value of (0.90%) and (1.16%) at dumping sites of Kalamassery and Laloor respectively. The mean for the total Ca percentage of the two locations within quarter varied from a minimum of 0.29 % to a maximum of 0.76 % at Kalamassery and 0.41 % to 0.85 % for Laloor which was also found to be significant. Comparing the mean for different quarters, the maximum total Ca content was observed during quarter IV 0.81% which was closely followed by quarter III 0.67%, quarter II 0.37% and quarter I 0.35% and the variations were found to be significant. The mean of two locations was found to be the highest in Laloor 0.62% when compared to that of Kalamassery 0.48% and the values were found to be on par with each other.

4.1.10. Total magnesium content of soil (%)

The total Mg contents at the dumping as well as non dumping sites of two locations, Kalamassery and Laloor were recorded at quarterly intervals. The data being presented in Table 4.1.10.

Table 4.1.10. Total magnesium (%) for sampling sites of two locations at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	0.30 (0.89)	0.24 (0.86)	0.16 (0.81)	0.34 (0.91)	**0.26 (0.87)**
KLM 2	0.27 (0.88)	0.13 (0.79)	0.20 (0.83)	0.18 (0.82)	**0.19 (0.83)**
KLM3	0.17 (0.82)	0.17 (0.82)	0.15 (0.80)	0.17 (0.82)	**0.16 (0.81)**
KLM 4 Non dumping	0.12 (0.79)	0.09 (0.77)	0.08 (0.76)	0.16 (0.81)	**0.12 (0.78)**
Mean	**0.21 (0.84)**	**0.16 (0.81)**	**0.15 (0.80)**	**0.21 (0.84)**	**0.18 (0.82)**
LAR 1	0.16 (0.81)	0.18 (0.83)	0.27 (0.88)	0.22 (0.85)	**0.21 (0.84)**

Table 4.1.10 Continued

LAR 2	0.13 (0.79)	0.18 (0.83)	0.20 (0.84)	0.19 (0.83)	**0.18 (0.82)**
LAR 3	0.16 (0.81)	0.15 (0.81)	0.15 (0.81)	0.18 (0.82)	**0.16** (0.81)
LAR 4 Non dumping	0.12 (0.79)	0.14 (0.80)	0.12 (0.79)	0.14 (0.80)	**0.13** (0.81)
Mean	**0.14 (0.80)**	**0.16 (0.81)**	**0.19 (0.83)**	**0.18 (0.82)**	**0.17 (0.79)**
Mean for comparing quarter	**0.18 (0.82)**	**0.16 (0.81)**	**0.17 (0.82)**	**0.20 (0.83)**	
CD1	**CD for comparing site-.038**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-0.035**		**CD 4**	**CD for comparing Location -NS**	

Values expressed in parenthesis indicate square root transformation

The total Mg content of soil ranged from a minimum of 0.08% to a maximum of 0.34% at Kalamassery 4 and Kalamassery 1, respectively. There was a significant variation observed between the mean total Mg content of different sites of the two locations. However, the non dumping sites recorded the lowest Mg content of 0.12% and 0.13 % at Kalamassery 4 quarter (I) and Laloor 4 quarter (IV) and the highest value of 0.26 % and 0.21% were recorded at the dumping site of Kalamassery 1 and Laloor 1, respectively. With reference to the mean of the total Mg % for the locations within quarter, the variations was within a range of 0.15 % to 0.21% at Kalamassery and 0.14 % to 0.19 % at Laloor which were found to be significantly different. While comparing the mean during the quarters, the highest total Mg content was 0.20% during quarter IV and the minimum was (0.16%) during quarter II, which was found to be non significant. On perusal of data of the location mean there was no significant variation in total Mg%, though Kalamassery registered higher mean value of 0.18% which was on par with Laloor (0.17%).

4.1.11. Total zinc content of soil (mg kg^{-1})

During the experimental period, the variation in Zn content (mg kg^{-1}) at the dumping as well as non dumping sites of two locations i.e., Kalamassery and Laloor was being recorded at quarterly intervals and the data has been presented in Table 4.1.11.

4.1.11. Total zinc content of soil (mg kg^{-1}) for sampling sites of two locations at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	247.10 (15.74)	284.20 (16.87)	226.70 (15.07)	222.50 (14.93)	**245.13 (15.67)**
KLM 2	100.00 (10.02)	98.00 (9.92)	106.35 (10.34)	123.00 (11.11)	**106.84 (10.36)**
KLM 3	230.00 (15.18)	226.30 (15.06)	215.35 (14.69)	271.65 (16.50)	**235.83 (15.37)**
KLM 4 Non dumping	86.50 (9.33)	86.30 (9.32)	89.40 (9.48)	100.00 (10.02)	**90.55 (9.54)**
Mean	**165.90 (12.90)**	**173.70 (13.20**	**159.45 (12.65)**	**179.29 (13.41)**	**169.58 (13.04)**
LAR 1	124.00 (11.16)	153.45 (12.41)	178.00 (13.36)	184.85 (13.61)	**160.08 (12.67)**
LAR 2	120.50 (11.00)	125.50 (11.22)	239.05 (15.48)	281.45 (16.79)	**191.63 (13.86)**
LAR 3	410.00 (20.26)	407.30 (20.19)	484.20 (22.02)	489.50 (22.14)	**447.75 (21.17)**
LAR 4 Non dumping	78.00 (8.86)	97.00 (9.87)	127.10 (11.30)	101.80 (10.11)	**100.98 (10.07)**
Mean	**183.13 (3.55)**	**195.81 (14.01)**	**257.09 (16.05)**	**264.40 (16.28)**	**225.11 (15.02)**
Mean for comparing quarter	**221.84 (14.91)**	**208.27 (14.45)**	**184.76 (13.56)**	**174.51 (13.23)**	
CD1	**CD for comparing site– 1.67**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter- NS**		**CD 4**	**CD for comparing Location -NS**	

Values expressed in parenthesis indicate square root transformation

The total Zn content generally varied from 78 to 489 mg kg^{-1} at Laloor 4 and Laloor 3 respectively, when both the locations are considered together. There was significant variation observed for the mean of total Zn content at the different sites of the two locations, where the non dumping sites of Kalamassery and Laloor recorded the minimum Zn content of 90.55 mg kg^{-1} and 100.98 respectively and a maximum of 245.13 mg kg^{-1} and 447.75 mg kg^{-1} at Kalamassery 1 and Laloor 3 respectively. The mean total Zn content at the two locations within quarters was found to be on par with each other which ranged from 159.45 to 179.29 mg kg^{-1} at Kalamassery and 183.13 to 264.40 mg kg^{-1} at Laloor. Comparing the mean total Zn content for the four quarters, it followed the order of the highest total Zn content of 221.84 $mgkg^{-1}$ (quarter IV), followed by 208.27 $mgkg^{-1}$ (quarter III), followed by 184.76 $mgkg^{-1}$ (quarter II) and the lowest value of 174.5 $mgkg^{-1}$ during quarter I. With reference to the mean total Zn for the locations they are found to be on par, though the value was comparatively higher at Laloor (225.1 mg kg^{-1}) than Kalamassery (169.58 mg kg^{-1}).

4.1.12. Total copper content of the soil (mg kg^{-1})

The total Cu content (mg kg^{-1}) was determined for the two locations i.e., Kalamassery and Laloor for both the dumping and non dumping sites at quarterly intervals and the data furnished in the Table 4.1.12.

Table 4.1.12. Total copper (mg kg^{-1}) for sampling sites of two locations at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	112.5 (10.63)	73.4 (8.64)	103.2 (10.18)	57.45 (7.61)	86.64 (9.26)
KLM 2	36.4 (6.07)	37.5 (6.16)	44.9 (6.74)	41.1 (6.45)	39.96 (6.36)
KLM 3	37.8 (6.19)	52.9 (7.31)	47.1 (6.90)	37.6 (6.17)	43.83 (6.64)
KLM 4 Non dumping	34.1 (5.88)	27.9 (5.32)	26.6 (5.21)	39.3 (6.30)	31.95 (5.68)
Mean	**55.2 (7.46)**	**47.9 (6.96)**	**55.4 (7.48)**	**43.8 (6.66)**	**50.59 (7.15)**
LAR1	86.6 (9.33)	52.3 (7.27)	161.1 (12.71)	77.3 (8.82)	94.33 (9.53)
LAR 2	28.5 (5.39)	54.15 (7.39)	63.65 (8.01)	41.95 (6.52)	47.06 (6.83)
LAR 3	148.5 (12.21)	118.95 (10.93)	153.65 (12.42)	185.45 (13.64)	151.64 (12.30)
LAR 4 Non dumping	36 (6.04)	26.1 (5.16)	26.8 (5.22)	33.25 (5.81)	30.54 (5.56)
Mean	**74.90 (8.68)**	**62.88 (7.96)**	**101.30 (10.09)**	**84.49 (9.22)**	**80.89 (9.02)**
Mean for comparing quarter	**65.05 (8.10)**	**55.39 (7.48)**	**78.37 (8.88)**	**64.16 (8.04)**	
CD1	**CD for comparing site-1.64**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter- NS**		**CD 4**	**CD for comparing Location -1.55**	

Values expressed in parenthesis indicate square root transformation

In general the total Cu content (mg kg^{-1}) varied from a minimum of 26.1 to a maximum value of 185.45 mg kg^{-1}at Laloor 4 and Laloor 3 respectively, while

considering both locations. The mean of total Cu content at the different sites of Kalamassery and Laloor were found to be significantly different, with the lowest for the non dumping sites 31.95 mg $kg^{-1}$and 30.54 mg $kg^{-1}$and the highest of 86.64 mg $kg^{-1}$and 151.64 mg lit^{-1} at dumping sites of Kalamassery 1 and Laloor 3 respectively. Comparing the mean total Cu (mg kg^{-1}) for the locations within quarters it varied from 43.8 mg $kg^{-1}$to of 55.4 mg kg^{-1}at Kalamassery and 62.88 to 101.30 mg kg^{-1}at Laloor. When comparing the mean total Cu for each quarters for both location the maximum Cu content was observed during quarter III (78.37 mg kg^{-1}) which was closely followed by quarter I (65.05 mg kg^{-1}), quarter IV (64.16 mg kg^{-1}) and quarter II (55.39 mg kg^{-1}) the variations found to be non significant. On perusal of the data on the mean of two locations, it was found that there was significantly higher Cu content at Laloor (80.89 mg kg^{-1}) than Kalamassery (50.59 mg kg^{-1}) location.

4.1.13. Total iron content of the soil (%)

The variations, in total Fe content of the soil at the dumping as well as non-dumping site of two locations i.e., Kalamassery and Laloor was recorded at quarterly intervals and the data has been presented in Table 4.1.12.

Table 4.1.13. Total iron (%) for sampling sites of two locations at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	3.28 (1.94)	4.39 (2.21)	3.82 (2.08)	3.95 (2.11)	**3.86 (2.09)**
KLM 2	2.45 (1.72)	4.29 (2.19)	4.62 (2.26)	4.12 (2.15)	**3.87 (2.08)**
KLM3	2.67 (1.78)	3.74 (2.06)	4.24 (2.18)	5.30 (2.41)	**3.99 (2.11)**
KLM 4	2.27	3.74	4.63	4.11	**3.69**

Table 4.1.13 Continued

	(1.66)	(2.06)	(2.26)	(2.15)	**(2.03)**
Mean	**2.67**	**4.04**	**4.33**	**4.37**	**3.85**
	(1.78)	**(2.13)**	**(2.20)**	**(2.20)**	**(2.08)**
LAR1	2.22	4.32	3.39	3.74	**3.42**
	(1.65)	(2.2)	(1.97)	(2.06)	**(1.97)**
LAR 2	1.61	8.96	3.59	3.48	**4.41**
	(1.45)	(3.08)	(2.02)	(2)	**(2.14)**
LAR 3	3.36	3.14	3.07	4.17	**3.43**
	(1.96)	(1.91)	(1.89)	(2.16)	**(1.98)**
LAR 4	1.88	3.53	2.89	3.10	**2.85**
	(1.54)	(2.01)	(1.84)	(1.90)	**(1.82)**
Mean	**2.27**	**4.99**	**3.24**	**3.62**	**3.53**
	(1.65)	**(2.30)**	**(1.93)**	**(2.03)**	**(1.98)**
Mean for comparing quarter	**2.47**	**4.11**	**3.90**	**4.03**	
	(1.71)	**(2.21)**	**(2.06)**	**(2.12)**	
CD1	**CD for comparing site-NS**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-0.24**		**CD 4**	**CD for comparing Location – NS**	

Values expressed in parenthesis indicate square root transformation

In general, the total Fe content (%) varied from a minimum of 1.62 per cent to a maximum value of 8.96 per cent at Laloor 2. While considering both locations, there was no significant variation in the total Fe content at the different sites of two locations, however the non dumping site of Kalamassery and Laloor recorded the lowest value of 3.69 % and 2.85 % respectively. The highest total Fe content was recorded at the dump site of Kalamassery 3 and Laloor 2, which was 3.99 % and 4.41% respectively. The mean of the soil Fe content (%) for the locations within quarters varied from a minimum of 2.67 per cent to maximum of 4.37 per cent at Kalamassery and 2.27 to 4.49 per cent at Laloor. While comparing the mean total Fe during the four quarters the highest Fe content was recorded during quarter II (4.11 %) and the lowest during quarter I (2.47%) which was significantly different. On consideration of the location mean, there was no significant difference for total iron

of two locations which was comparatively higher at Laloor 4.41 % than Kalamassery 3.99%.

4.1.14. Total aluminium content of soil (%)

The relative content of total Al and its variations in dumping and non-dumping sites of two locations at different quarterly intervals are furnished in table 4.1.14.

Table 4.1.14. Total aluminium (%) for sampling sites of two locations at quarterly intervals

Sampling Site /Period	**Quarter I**	**Quarter II**	**Quarter III**	**Quarter IV**	**Mean Site /location**
KLM 1	5.96 (2.54)	5.98 (2.55)	4.54 (2.25)	4.21 (2.17)	**5.17 (2.38)**
KLM 2	4.36 (2.20)	5.61 (2.47)	4.99 (2.34)	3.88 (2.09)	**4.71 (2.28)**
KLM 3	4.29 (2.19)	4.34 (2.20)	3.97 (2.11)	4.35 (2.20)	**4.24 (2.18)**
KLM 4 Non dumping	2.33 (1.68)	3.02 (1.88)	4.29 (2.19)	2.55 (1.75)	**3.05 (1.87)**
Mean	**4.23 (2.17)**	**4.74 (2.29)**	**4.45 (2.22)**	**3.75 (2.06)**	**4.29 (2.19)**
LAR 1	2.64 (1.77)	3.62 (2.03)	2.67 (1.78)	2.17 (1.63)	2.78 (1.80)
LAR 2	2.30 (1.67)	2.45 (1.72)	2.83 (1.82)	1.68 (1.48)	2.31 (1.67)
LAR 3	0.32 (0.90)	3.07 (1.89)	3.00 (1.87)	3.39 (1.97)	2.44 (1.66)
LAR 4 Non dumping	1.54 (1.43)	1.85 (1.53)	1.62 (1.46)	1.82 (1.52)	1.71 (1.49)
Mean	**1.70 (1.48)**	**2.75 (1.80)**	**2.53 (1.74)**	**2.26 (1.66)**	**2.31 (1.68)**
Mean for	**2.97**	**3.74**	**3.49**	**3.01**	

Table 4.1.14 Continued

comparing quarter	(1.86)	(2.06)	(2)	(1.87)	
CD1	CD for comparing site-0.63		CD 2	CD for comparing locations within quarters-NS	
CD3	CD for comparing quarter- NS		CD 4	CD for comparing Location -1.01	

Values expressed in parenthesis indicate square root transformation

In general, the total Al (%) content varied within a wide range of (0.32 % to 5.98%). There was significant difference between the total Al contents of the different sites of the two locations (site mean). The site mean values ranged from 3.05 to 5.17 percent at the non dumping to dumping site of Laloor and 1.71 to 2.78 percent at the non dumping to dumping site of Kalamassery. On perusal of the data on the mean soil Al content for the locations within quarter, it varied from a minimum of 3.75 per cent to 4.74 per cent at Kalamassery and 1.70 per cent to 2.75 per cent at Laloor which was also found to be non significant. When comparing the mean total Al content for the quarters it was noticed that the maximum soil Al (%) content was observed during quarter II (3.74%) which was closely followed by quarter III (3.49%) quarter IV (3.01%) and quarter I (2.97%) ;which were found to be non significant. But there was a significant difference observed in case of mean of two locations which was found to be comparatively higher at Kalamassery (4.29%) than Laloor (2.31 %).

4.1.15. Total lead content of the soil (mg kg^{-1})

The total Pb content of soil (mg kg^{-1}) was determined at the dumping and non dumping site of two locations i.e., Kalamassery and Laloor at quarterly intervals and the data are presented in the table 4.1.15.

Table 4.1.15. Total lead (mg kg^{-1}) for sampling sites of two locations at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM1	15.23 (3.97)	14.99 (3.94)	15.11 (3.95)	13.95 (3.80)	**14.82 (3.91)**
KLM2	16.64 (4.14)	18.49 (4.36)	16.26 (4.09)	18.16 (4.32)	**17.39 (4.23)**
KLM 3	22.35 (4.78)	23.25 (4.87)	18.75 (4.39)	17.95 (4.30)	**20.58 (4.58)**
KLM 4 Non dumping	9.23 (3.12)	9.33 (3.14)	9.88 (3.22)	9.76 (3.20)	**9.55 (3.17)**
Mean	**15.86 (4.04)**	**16.52 (4.13)**	**15.00 (3.94)**	**14.96 (3.93)**	**15.58 (4.01)**
LAR1	145.4 (12.08)	147.4 (12.16)	146.57 (12.13)	143.57 (12)	**145.74 (12.09)**
LAR 2	136.13 (11.69)	148.96 (12.23)	143.61 (12)	71.06 (8.46)	**124.94 (11.09)**
LAR 3	32 (5.7)	36 (6.04)	45 (6.75)	34 (5.87)	**36.75 (6.09)**
LAR 4 Non dumping	24.47 (5)	25.44 (5.09)	25.19 (5.07)	20.66 (4.60)	**23.94 (4.94)**
Mean	**84.50 (9.22)**	**89.45 (9.48)**	**90.09 (9.52)**	**67.32 (8.24)**	**82.84 (9.13)**
Mean for comparing quarter	**50.18 (7.12)**	**52.99 (7.31)**	**52.55 (7.28)**	**41.14 (6.45)**	
CD1	**CD for comparing site-0.929**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-NS**		**CD 4**	**CD for comparing Location -1.56**	

Values expressed in parenthesis indicate square root transformation

The total lead content (mg kg^{-1}) of soil ranged from a minimum of 9.23 mg kg^{-1} Kalamassery 3 to a maximum of 148.96 mg kg^{-1} Laloor 2. A significant difference was observed between the means of total Pb content at the different sites, where the non-dumping sites of both locations recorded low values of 9.55 mg $kg^{-1}$and 23.94 mg kg^{-1}at Kalamassery and Laloor and a maximum of 20.58 mg $kg^{-1}$and 145.74 mg kg^{-1}at the dumping site of Kalamassery 3 and Laloor 1, respectively. The mean total lead content (mg kg^{-1}) at different locations within quarter varied from the lowest value of 14.96 mg kg^{-1} (quarter IV) to a maximum of 16.52 mg kg^{-1} (quarter II) at Kalamassery and 66.32 mg kg^{-1} (quarter IV) to 90.09 mg kg^{-1} (quarter III) at Laloor which was also found to be non significant. Considering the mean Pb content during the quarters, the lowest Pb content of 41.14 mg $kg^{-1}$was recorded during quarter IV, followed by 50.18 mg kg^{-1}quarter I, 52.55 mg kg^{-1}(quarter III) and 52.99 mg kg^{-1} (quarter II). With reference to the mean of two locations, it was found to be comparatively higher for Laloor (22.84 mg kg^{-1}) compared to Kalamassery (15.58 mg kg^{-1}) and these variations were found to be significantly different.

4.1.16. Total cobalt content of soil (mg kg^{-1})

The relative content of cobalt Co (mg kg^{-1}) and its variations in dumping and non dumping sites of two locations at different quarterly intervals are furnished in Table 4.1.16.

Table 4.1.16. Total cobalt content (mg kg^{-1}) of soil for two sampling sites at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM1	8.10 (2.93)	7.60 (2.85)	4.50 (2.24)	7.55 (2.84)	**6.94 (2.71)**
KLM2	8.20 (2.95)	6.70 (2.68)	6.95 (2.73)	5.70 (2.49)	**6.89 (2.71)**
KLM 3	4.60 (2.26)	6.75 (2.69)	3.45 (1.99)	6.25 (2.60)	**5.26 (2.38)**
KLM 4 Non dumping	4.20 (2.17)	5.60 (2.47)	5.65 (2.48)	5.10 (2.37)	**5.14 (2.37)**
Mean	**6.28 (2.58)**	**6.66 (2.67)**	**5.14 (2.36)**	**6.15 (2.57)**	**6.06 (2.55)**
LAR 1	6.50 (2.65)	9.60 (3.18)	7.30 (2.79)	6.70 (2.68)	**7.53 (2.82)**
LAR 2	4.70 (2.28)	17.20 (4.21)	7.05 (2.75)	6.15 (2.58)	**8.78 (2.95)**
LAR 3	8.70 (3.03)	8.05 (2.92)	8.80 (3.05)	10.20 (3.27)	**8.94 (3.07)**
LAR 4 Non dumping	5.00 (2.35)	5.55 (2.46)	7.00 (2.74)	6.10 (2.57)	**5.91 (2.53)**
Mean	**6.23 (2.58)**	**10.10 (3.10)**	**7.54 (2.83)**	**7.29 (2.78)**	**7.79 (2.84)**
Mean for comparing quarter	**6.25 (2.58)**	**8.38 (2.93)**	**6.34 (2.60)**	**6.72 (2.67)**	
CD1	**CD for comparing site– 0.27**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-NS**		**CD 4**	**CD for comparing Location -1.56**	

Values expressed in parenthesis indicate square root transformation

In general, the total Co content (mg kg^{-1}) of soil ranged from 4.20 mg kg^{-1} to 17.20 mg kg^{-1}. The non dumping site at Laloor 4 recorded the lowest mean of total Co content (5.91 mg kg^{-1}) and maximum (8.94 mg kg^{-1}) was found at the dumping site Laloor 3. The non dumping site at Kalamassery 4 recorded the lowest Co content of (5.14 mg kg^{-1}) to a highest of 6.94 mg kg^{-1}at the dump site (Kalamassery1) which was found to be non significant. with reference to the mean Co content for locations within quarters, the soil Co content varied from a minimum content of 5.14 mg $kg^{-1}$to a maximum of 6.66 mg kg^{-1}at Kalamassery and 6.23 mg $kg^{-1}$to 10.10 mg kg^{-1}in case of Laloor which was also found to be non significant. Regarding the quarterly variation the maximum soil Co content was observed during quarters II (8.38 mg kg^{-1}), followed by Quarter IV (6.72 mg kg^{-1}), then (6.34 mg kg^{-1}) quarters III, which was closely followed by (6.25 mg kg^{-1}) quarter I, which was found to be not significant between the quarters. But there was a significant difference between the mean of two locations, where the highest value of 7.79 mg $kg^{-1}$was recorded at Laloor and comparatively the lowest at Kalamassery 6.06 mg kg^{-1}.

4.1.17. Total nickel content of the soil (mg kg^{-1})

The variation in total Ni content (mg kg^{-1}) of the soil at the dumping as well as non-dumping site of two locations i.e., Kalamassery and Laloor was recorded at quarterly intervals and the data has been presented in Table 4.1.17.

Table 4.1.17. Total nickel content (mg kg^{-1}) of soil for two sampling sites

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM1	61.80 (7.89)	55.90 (7.51)	39.50 (6.32)	44.15 (6.68)	**50.34 (7.10)**
KLM 2	49.40 (7.06)	52.65 (7.29)	48.10 (6.97)	40.05 (6.37)	**47.55 (6.92)**
KLM 3	39.80 (6.35)	39.25 (6.30)	33.95 (5.87)	47.25 (6.91)	**40.06 (6.36)**
KLM 4 Non dumping	31.50 (5.66)	37.80 (6.19)	39.85 (6.35)	29.85 (5.51)	**34.75 (5.93)**
Mean	**45.63 (6.79)**	**46.40 (6.85)**	**40.35 (6.39)**	**40.33 (6.39)**	**43.18 (6.61)**
LAR 1	32.2 (5.72)	40.95 (6.44)	34.65 (5.93)	27.65 (5.31)	**33.86 (5.85)**
LAR2	25.4 (5.09)	64.45 (8.06)	28.4 (5.38)	23.2 (4.87)	**35.36 (5.85)**
LAR 3	45.4 (6.77)	46.95 (6.89)	43.35 (6.62)	50.5 (7.14)	**46.55 (6.86)**
LAR 4 Non dumping	22.6 (4.81)	25.25 (5.07)	31.5 (5.66)	26.25 (5.17)	**26.40 (5.18)**
Mean	**31.4 (5.65)**	**44.4 (6.70)**	**34.475 (5.9)**	**31.9 (5.69)**	**35.54 (6.00)**
Mean for each quarter	**38.51 (6.21)**	**45.40 (6.77)**	**37.41 (6.16)**	**36.11 (6.05)**	
CD1	**CD for comparing site– 0.94**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-NS**		**CD 4**	**CD for comparing Location – 0.604**	

Values expressed in parenthesis indicate square root transformation

Generally, the total Ni content (mg kg^{-1}) ranged from 22.6 (mg kg^{-1}) (Laloor 4) to 64.45 mg kg^{-1} (Laloor 2). There was significant difference for the mean of total

Ni at the different sites at the two locations, the non dumping site at Kalamassery 4 recorded the lowest Nickel content from a minimum of 34.75mg $kg^{-1}$to a maximum of 50.34 mg kg^{-1}at the Kalamassery 1 dumping site. Similarly for Laloor, Ni content was minimum of 34.75 mg kg^{-1} (non dump) to a maximum of 46.55 mg kg^{-1}at Laloor 3 (dumping site). The mean of the total Ni content ranged from a least value of 40.33 mg kg^{-1} (quarter IV) to 31.40 mg kg^{-1} (quarter II) at Kalamassery and 31.40 mg kg^{-1} (quarter I) to 44.4 mg kg^{-1} (quarter II) at Laloor, which were not significantly different. Regarding the period of sampling there was no significant difference among the Ni content during different quarters and the maximum content was at quarter II (45.40 mg kg^{-1}) followed by quarter I (38.51 mg kg^{-1}) quarter III (37.41 mg kg^{-1}) and the least during quarters IV (36.11mg kg^{-1}). Regarding the mean of Ni at the two locations irrespective of four quarters, there was a significant difference, which were found to be comparatively higher at Kalamassery (43.18 mg kg^{-1}) than Laloor (35.54 mg kg^{-1}).

4.1.18. Total mercury content of the soil (mg kg^{-1})

The relative content of total mercury (mg kg^{-1}) and its variations at the dumping and non dumping sites of two locations for quarterly intervals are furnished in Table 4.1.18.

Table 4.1.18. Total mercury content (mg kg^{-1}) of soil for two sampling sites at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM1	0.60	0.60	0.51	0.56	**0.57**
KLM 2	0.41	0.59	0.50	0.59	**0.53**
KLM 3	0.57	0.62	0.73	0.60	**0.63**
KLM 4 Non dumping	0.64	0.49	0.50	0.49	**0.52**

Table 4.1.18 Continued

Mean	**0.56**	**0.58**	**0.56**	**0.56**	**0.56**
LAR 1	0.48	0.38	0.49	0.40	**0.44**
LAR 2	0.53	0.43	0.49	0.46	**0.48**
LAR 3	0.55	0.50	0.64	0.45	**0.54**
LAR 4 Non dumping	0.18	0.17	0.14	00.14	**0.15**
Mean	**0.45**	**0.39**	**0.45**	**0.38**	**0.42**
Mean for comparing quarter	**0.60**	**0.60**	**0.51**	**0.56**	
CD1	**CD for comparing site– 0.019**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-NS**		**CD 4**	**CD for comparing Location – 0.076**	

Values expressed in parenthesis indicate square root transformation

The total mercury content in general varied from a range of minimum 0.20 (mg kg^{-1}) at Laloor 4 to a maximum of 0.73 mg kg^{-1} at Kalamassery 3 irrespective of locations and quarters. The site mean for the total Hg content at Kalamassery and Laloor was found to be significantly different. The mean of total Hg at the different sites showed that the content was lowest for the non dumping sites and it was 0.52 mg $kg^{-1}$and 0.15 mg kg^{-1} of Kalamassery and Laloor respectively and maximum of 0.63 mg kg^{-1} and 0.54 mg lit^{-1} for the dumping sites at Kalamassery 3 and Laloor 3 respectively. The mean of the soil Hg content varied from a least of 0.56 mg kg^{-1} to maximum of 0.58 mg kg^{-1} at Kalamassery and 0.38 mg kg^{-1} to 0.45 mg kg^{-1} at Laloor, which was found to be non significant. Comparing the mean of each quarter for both locations the maximum soil Hg content 0.51 mg kg^{-1} quarter III, closely followed by (0.50 mg kg^{-1}) quarter II, followed by (0.48 mg kg^{-1}) quarter II and (0.47 mg kg^{-1}) quarter IV where then was no significant difference between them during different season. While taking mean the Hg content was reported to be higher at Kalamassery with a mean value of 0.57 mg kg^{-1} which was significantly different from laloor with Hg content of 0.42 mg kg^{-1}.

4.1.19. Total chromium content of the soil (mg kg^{-1})

The variation in total chromium (Cr) content (mg kg^{-1}) at the dumping as well as non-dumping site of two locations i.e., Kalamassery and Laloor was being recorded at quarterly intervals and the data has been presented in table 4.1.19.

Table 4.1.19. Total chromium content (mg kg^{-1}) of soil for two sampling sites at quarterly intervals

Location	Quarter I	Quarter II	Quarter III	Quarter IV	Site mean
KLM 1	156.00 (12.51)	86.20 (9.31)	102.90 (10.17)	72.25 (8.53)	**104.34** **(10.24)**
KLM 2	132.90 (11.55)	124.00 (11.16)	99.40 (9.99)	86.80 (9.34)	110.78 (10.55)
KLM 3	157.00 (12.55)	135.10 (11.64)	132.00 (11.51)	108.45 (10.44)	133.14 (11.56)
KLM 4 Non dumping	100.00 (10.02)	87.00 (9.35)	68.00 (8.28)	79.00 (8.92)	83.50 (9.17)
Mean	**136.48** **(11.70)**	**108.08** **(10.42)**	**100.58** **(10.05)**	**86.63** **(9.33)**	**107.94** **(10.41)**
LAR 1	134.90 (11.64)	126.15 (11.25)	120.00 (10.98)	112.00 (10.61)	**123.26** **(11.12)**
LAR 2	108.50 (10.44)	126.10 (11.25)	106.00 (10.32)	100.00 (10.02)	**110.15** **(10.52)**
LAR 3	134.00 (11.60)	133.00 (11.55)	123.00 (11.11)	120.00 (10.98)	**127.50** **(11.31)**
LAR 4 Non dumping	109.00 (10.46)	100.00 (10.02)	98.00 (9.92)	100.00 (10.02)	**101.75** **(10.11)**
Mean	**121.60** **(11.05)**	**121.31** **(11.04)**	**111.75** **(10.59)**	**108.00** **(10.42)**	**115.67** **(10.78)**
Mean for each quarter	**129.04**	**114.69**	**106.16**	**97.31**	
CD1	**CD for comparing site– 0.91**		**CD 2**	**CD for comparing locations within quarters-0.612**	
CD3	**CD for comparing quarter- 0.866**		**CD 4**	**CD for comparing Location – 0.433**	

Value expressed in parenthesis indicate Square root transformation

Generally the total Cr content (mg kg^{-1}) values ranged from a minimum of 68.0 mg kg^{-1}(Kalmassery 4) to maximum of 157 mg kg^{-1} (Kalmassery 1). A significant variation was observed between the mean total Cr at the different sites of two locations, where the non-dumping sites recorded minimum Cr content of 83.50 mg kg^{-1} and 101.75 mg kg^{-1} and the dump sites recorded the highest value of 133.14 mg kg^{-1} and 127.50 mg kg^{-1} for both Kalamassery 3 and Laloor 3 respectively. With reference to the mean of total Cr, for locations within quarters, the soil Cr content varied from a least content of 86.63 mg kg^{-1} to a maximum of 1136.48 mg kg^{-1} at Kalamassery and 108 mg kg^{-1} to 121.60 mg kg^{-1} at Laloor which was not founded to be significantly different. While comparing the mean of total Cr for four quarters the highest soil Cr content was recorded as (mg kg^{-1}) range of 129.04 (quarter I) was recorded and closely followed by 114.69 mg kg^{-1} (quarter II), 106.16 mg kg^{-1} (quarter III) and 97.37 mg kg^{-1} (quarter IV) and there was significant difference among them. On consideration of the location mean of four quarters, there was no significant variation in soil Cr content of two locations which is comparatively higher at Kalamassery (107.94 mg kg^{-1}) than Laloor (115.67mg kg^{-1}).

4.1.20. Total cadmium content of the soil (mg kg^{-1})

The total cadmium content (mg kg^{-1}) was determined at two locations i.e., Kalamassery and Laloor including dumping and non dumping sites was recorded at quarterly intervals and the data are presented in the table 4.1.20.

Table 4.1.20. Total cadmium content (mg kg^{-1}) of soil for two sampling sites at quarterly intervals

Sampling Site /Period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site /location
KLM 1	1.79 (1.51)	1.71 (1.49)	0.63 (1.06)	0.70 (1.10)	**1.21 (1.29)**
KLM 2	0.17 (0.82)	0.10 (0.77)	0.15 (0.81)	0.00 (0.71)	**0.11 (0.78)**
KLM 3	1.31 (1.35)	0.70 (1.1)	0.49 (0.99)	0.30 (0.89)	**0.70 (1.08)**
KLM 4	0.04 (0.73)	0.03 (0.73)	0.01 (0.71)	0.04 (0.73)	**0.03 (0.73)**
Mean	**0.83 (1.10)**	**0.64 (1.02)**	**0.32 (0.89)**	**0.26 (0.86)**	**0.51 (0.97)**
LAR 1	0.10 (0.77)	0.06 (0.75)	0.44 (0.97)	0.56 (1.03)	**0.29 (0.88)**
LAR 2	0.04 (0.73)	0.07 (0.75)	0.09 (0.77)	0.47 (0.98)	**0.17 (0.81)**
LAR 3	0.27 (0.88)	0.33 (0.91)	0.54 (1.02)	0.78 (1.13)	**0.48 (0.98)**
LAR 4	0.01 (0.71)	0.07 (0.75)	0.19 (0.83)	0.09 (0.77)	**0.09 (0.77)**
Mean	**0.11 (0.78)**	**0.13 (0.79)**	**0.32 (0.9)**	**0.48 (0.98)**	**0.26 (0.86)**
CD for comparing quarter	**0.47 (0.94)**	**0.38 (0.91)**	**0.32 (0.89)**	**0.37 (0.92)**	
CD1	**CD for comparing site– .213**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter- .280**		**CD 4**	**CD for comparing Location – NS**	

Values expressed in parenthesis indicate square root transformation

In general, the total cadmium content (mg kg^{-1}), varied from minimum of 0.01 mg kg^{-1} Kalamassery 4 to a maximum of 1.79 mg kg^{-1} Kalamassery 1 in both the locations. The mean of total Cd for different sites of Kalamassery and Laloor was found to be significantly different, the Cd content was found to be low in non dumping sites with a value of 0.03 mg kg^{-1} and 0.09 mg kg^{-1} to a high value of 1.21 mg kg^{-1} and 0.48 mg kg^{-1} dumping sites of Kalamassery 1 and Laloor 3. With reference to the mean of soil Cd for the different locations within quarter it varied from a least of 0.26 mg kg^{-1} to 0.83 mg kg^{-1} in Kalamassery and 0.11 mg kg^{-1} to 0.48 mg kg^{-1} at Laloor. When comparing the mean of each quarters for both locations the maximum soil Cd content was observed during quarter I (0.47 mg kg^{-1}) which was followed by quarter II (0.38 mg kg^{-1}), closely followed by quarter IV (0.37 mg kg^{-1}) and quarter III (0.32 mg kg^{-1}), where a significant difference was found between the quarters. Regarding the mean of two locations it was found comparatively higher in Kalamassery (0.5mg kg^{-1}) than Laloor (0.26mg kg^{-1}), but not significantly different.

4.1.21 Soil Enzymes

4.1.21.1 Soil Phosphatase activity (µmol PNP g^{-1} h^{-1})

The soil phosphatse activity (µmol PNP g^{-1} h^{-1}) was determined at quarterly interval at two locations i.e., Kalamassery and Laloor for the dumping and non dumping sites was recorded and the data was presented in the Table 4.1.21

Table 4.1.21 Soil phosphatase activity (µmol PNP g^{-1} h^{-1}) for sampling sites of two locations at different quarterly intervals

Sampling Site/period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site/location
KLM 1	35.37 (5.99)	53.80 (7.37)	29.65 (5.49)	25.02 (5.05)	**35.96 (5.98)**
KLM 2	14.76 (3.91)	12.61 (3.62)	8.65 (3.03)	16.82 (4.16)	**13.21 (3.68)**
KLM 3	20.15 (4.54)	19.08 (4.43)	19.14 (4.43)	17.46 (4.24)	**18.96 (4.19)**
KLM 4 Non dumping	44.42 (6.70)	15.29 (3.97)	11.90 (3.52)	10.37 (3.30)	**20.50 (4.37)**
Mean (KLM)	**28.68 (5.40)**	**25.19 (5.07)**	**17.33 (4.22)**	**17.42 (4.23)**	**22.16 (4.76)**
LAR 1	32.96 (5.78)	31.06 (5.62)	10.43 (3.31)	26.77 (5.22)	**25.30 (4.98)**
LAR 2	46.27 (6.84)	57.81 (7.64)	25.22 (5.07)	28.24 (5.36)	**39.39 (6.23)**
LAR 3	24.28 (4.98)	30.03 (5.53)	8.73 (3.04)	13.66 (3.76)	**19.18 (4.33)**
LAR 4	14.90 (3.92)	39.66 (6.34)	10.06 (3.25)	6.3 (2.61)	**17.73 (4.03)**
Mean (LAR)	**29.60 (5.49)**	**39.64 (6.34)**	**13.61 (3.76)**	**18.74 (4.39)**	**25.40 (5.09)**
Mean for comparing quarter	**29.14 (5.44)**	**32.42 (5.74)**	**15.47 (4.00)**	**18.08 (4.31)**	
CD1	**CD for comparing site– 1.25**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter- 1.15**		**CD 4**	**CD for comparing Location – NS**	

Values expressed in parenthesis indicate square root transformation

In general, the phosphatase activity ranged from as low as 6.31 µ mol PNP g^{-1} h^{-1}(Laloor 4) to a maximum of 57.81 µmol PNP g-1 h^{-1}(Laloor 2).

There was a significant difference for the mean phosphatase activity at different sites and it ranged from 13.21 to 35.96 µmol PNP g^{-1} h^{-1} at Kalamassery and 17.73 to 39.39 µmol PNP g^{-1} h^{-1} at Laloor. The mean of phosphatase for the different quarters within locations varied from at least of 17.33 µmol PNP g^{-1} h^{-1}(quarter III) to a maximum of 28.68 µmol PNP g^{-1} h^{-1}(quarter I) at Kalamassery and 13.61(quarter II) to 39.64(quarter III) µmol PNP g^{-1} h^{-1} at Laloor which was found to be significantly different. Considering the mean at four quarters, there was a significant difference among them, where the maximum value was observed during quarter II (32.42 µmol PNP g^{-1} h-^{1}), followed by quarter I (29.14 µmol PNP g^{-1} h^{-1}), quarter IV (18.08 µmol PNP g^{-1} h^{-1}) and quarter III (15.47 µmol PNP g^{-1} h^{-1}). There was no significant difference between the location means of Laloor (25.40 µmol PNP g^{-1} h^{-1}) than Kalamassery (22.16 µmol PNP g^{-1} h^{-1}).

4.1.21.2 Soil Urease activity (µmol N-$NH_3g^{-1}h^{-1}$)

The variation in urease activity (µmol N-NH_3g^{-1} h^{-1}) at the dumping as well as non dumping site of two locations i.e., Kalamassery and Laloor was being recorded at quarterly intervals and the data has been presented in the table 4.1.22.

Table 4.1.22. Soil Urease activity (µmol N-$NH_3g^{-1}h^{-1}$) for sampling sites of two locations at different quarterly intervals

Sampling Site/period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site/location
KLM 1	5.60 (2.47)	14.00 (3.81)	8.4 (2.98)	9.1 (3.1)	**9.28 (3.09)**
KLM 2	2.10 (1.61)	7.00 (2.74)	1.05 (1.05)	7.00 (2.74)	**4.29 (2.08)**
KLM 3	9.45 (3.15)	31.50 (5.66)	25.55 (5.10)	7.70 (2.86)	**18.55 (4.19)**
KLM 4	4.90 (2.32)	17.50 (4.24)	11.55 (3.47)	10.50 (3.32)	**11.11 (3.34)**

Table 4.1.22. Continued

Mean	**5.51** (2.45)	**17.50** (4.24)	**11.68** (3.49)	**8.57** (3.01)	**10.81** (3.36)
LAR 1	13.65 (3.76)	17.50 (4.24)	11.55 (3.47)	13.3 (3.71)	**14.00** (3.8)
LAR 2	7.00 (2.74)	24.50 (5)	18.55 (4.36)	7 (2.74)	**14.26** (3.71)
LAR 3	8.75 (3.05)	10.50 (3.32)	4.55 (2.25)	4.9 (2.32)	**7.18** (2.73)
LAR 4	6.65 (2.67)	17.50 (4.24)	11.55 (3.47)	3.5 (2)	**9.80** (3.10)
Mean	**9.01** (3.08)	**17.50** (4.24)	**11.55** (3.47)	**7.18** (2.77)	**11.31** (3.44)
CD for comparing quarter	**7.26** (2.79)	**17.50** (4.24)	**11.62** (3.48)	**7.88** (2.89)	
CD1	**CD for comparing site– .922**		**CD 2**	**CD for comparing locations within quarters-NS**	
CD3	**CD for comparing quarter-0,922**		**CD 4**	**CD for comparing Location – NS**	

Values expressed in parenthesis indicate square root transformation

The soil enzyme urease activity generally ranged from a minimum of 2.10 µmol $N\text{-}NH_3g^{-1}h^{-1}$ (Kalamassery 2) to a maximum of 31.50 µmol$N\text{-}NH_3g^{-1}h^{-1}$ (Kalamassery 3). A significant difference was observed between the mean of urease activity for the different sites of both locations, however the non dumping sites recorded a value of 11.11 and 9.80 and the dumping site recorded 18.55 and 14.26 µmol $N\text{-}NH_3g^{-1}h^{-1}$ for both Kalamassery and Laloor respectively. With reference to the seasonal mean of individual locations, the soil urease activity ranged from a minimum activity of 5.51 to maximum activity of (17.50 µmol $N\text{-}NH_3g^{-1}h\text{-}^{1}$) at Kalamassery and 7.18 to 17.50 µmol $N\text{-}NH_3g^{-1}h\text{-}^{1}$ at Laloor. While comparing the mean of urease for the different locations within quarters, it was found that the highest urease activity of 17.50µmol $N\text{-}NH_3g^{-1}h\text{-}^{1}$ was recorded during quarter II and the lowest of 7.26µmol $N\text{-}NH_3g^{-1}h\text{-}^{1}$ was recorded during quarter I. On consideration of location means there was no significant variation in soil urease activity of two

locations, but comparatively higher value was recorded at Laloor (11.31µmol N-NH_3g^{-1} h^{-1}) than Kalamassery (10.81µmol N-NH_3g^{-1} h^{-1}).

4.1.21.3 Soil dehydrogenase activity (µmol TPF g^{-1} h^{-1})

The relative activity of dehydrogenase and its variations on dumping and non-dumping sites of two locations at quarterly intervals are furnished in Table 41.23.

Table 4.1.23 Soil dehydrogenase activity (µmol TPF g^{-1} h^{-1}) for sampling sites of two locations at different quarterly intervals

Sampling Site/period	Quarter I	Quarter II	Quarter III	Quarter IV	Mean Site/location
KLM 1	940.76 (30.7)	901.66 (30)	1211.86 (34.8)	856.00 (29.3)	**977.57 (31.2)**
KLM 2	116.67 (10.8)	91.2 (9.6)	120.06 (11)	104.00 (10.2)	**107.99 (10.4)**
KLM 3	698.00 (26.4)	586.00 (24.2)	823.00 (28.7)	986.00 (31.4)	**773.25 (27.7)**
KLM 4	900.00 (30)	876.00 (29.6)	953.00 (30.9)	824.00 (28.7)	**888.25 (29.8)**
Mean	**663.86 (25.78)**	**613.72 (24.78)**	**776.98 (27.88)**	**692.50 (26.32)**	**686.77 (26.22)**
LAR 1	1256.00 (35.4)	1700.00 (41.2)	168.08 (13)	214.00 (14.6)	**834.52 (26.1)**
LAR 2	876.78 (29.6)	845.97 (29.1)	800.85 (28.3)	798.20 (28.3)	**830.45 (28.8)**
LAR 3	450.00 (21.2)	402.84 (20.1)	475.99 (21.8)	398.00 (20)	**431.71 (20.8)**
LAR 4	247.18 (15.7)	210.00 (14.5)	79.10 (8.9)	101.30 (10.1)	**159.40 (12.3)**
Mean	**707.49 (26.61)**	**789.70 (28.11)**	**381.01 (19.53)**	**377.88 (19.45)**	**564.02 (23.76)**
Mean for comparing quarter	**685.68 (26.19)**	**701.71 (26.50)**	**579.00 (24.07)**	**535.19 (23.14)**	

Table 4.1.23. Continued

CD1	CD for comparing site– 8.01	CD 2	CD for comparing locations within quarters-NS
CD3	CD for comparing quarter-NS	CD 4	CD for comparing Location – NS

In general, the dehydrogenase activity, ranged from a minimum content of 79.10 µmolTPF g^{-1} h^{-1}at Laloor 4 to a maximum value of 1700 µmol TPF g^{-1} h^{-1} at Laloor 1. There was significant difference in the site mean and the dehydrogenase activity was 888.25 and 159.40 µmol TPF g^{-1} h^{-1} at the non-dumping site, where as it was 977.57 and 834.52 µmol TPF g^{-1} h^{-1} at the dumping sites of Kalamassery and Laloor respectively. With reference to the mean of the dehydrogenase activity for locations within quarters, it varied from a minimum of 613.72 to a maximum activity of 776.98 µmolTPF g^{-1} h^{-1} at Kalamassery and 381.01 to 789.70 µmol TPF g^{-1} h^{-1} at laloor, which was also found to be non- significant. While comparing the mean of each quarter for both locations the maximum dehydrogenase activity in soil was observed during the quarter II (701.75 µmol TPF g^{-1} h^{-1}) followed by quarter I (685.67 µmol TPF g^{-1} h^{-1}) quarter III (578.99 µmol TPF g^{-1} h^{-1}) and quarter IV, and there was no significant difference among the quarters. Regarding the mean of the locations, it was found that Kalamasery recorded higher value (686.77 µmol TPF g^{-1} h^{-1}) compared to laloor (564.02 µmol TPF g^{-1} h^{-1}) and it was on par with each other.

4.2 Effect of Phytoremediation on the decontamination of waste material collected from Laloor

The decontamination of the material through phytoremediation was carried out using three crops (vetiver, sunflower and marigold). The heavy metal content of the material before and after phytoremediation is presented below:

4.2.1. Heavy metal content of material used for phytoremediation

The analysis detail of the material taken from Laloor for phytoremediation is given in the table 4.2.1 below

Table 4.2.1. Heavy metal content of the initial material used for phytoremediation

Heavy metal range (mg kg^{-1})					
Material used for phytoremediation	Pb	Co	Ni	Cr	Hg
	198.6	11	57	105	0.5

4.2.2. Heavy metal content of material after phytoremediation with different crops

After growing different crops (treatments), the content of heavy metal in the soil was determined and the results of the analysis is as presented in the table 4.2.2.

Table 4.2.2. Heavy metal content of the soil after phytoremediation with different crops

Soil after treatment with	Pb	Co	Ni	Cr	Hg
	(mg kg^{-1})				
Vetiver	93.88	8.78	32.62	49.6	0.34
Sunflower	178.08	9.8	48.58	70.0	0.52
Marigold	175.00	10.18	49.28	71.4	0.49
CD	28.57	1.37	5.27	17.14	0.12

The Pb content in soil after phytoremediation with three different crops ranged from 93.88 mg kg^{-1} in soils phytoremediated with vetiver to 175 mg kg^{-1} in soils treated with marigold and the Pb content was 178.08 mg kg^{-1} for soils treated with sunflower. There was significant difference in the phytoremediated soil for Pb for vetiver, but the treatment with sunflower and marigold was on par with each other.

Cobalt content of the soil before treatment was 10.5 mg kg^{-1} and there was no significant difference in Co content in marigold (10.18 mg kg^{-1}) and sunflower (9.8 mg kg^{-1}). The soil phytoremediated with vetiver showed Co content of (8.78 mg kg^{-1}), there was no significant difference in Co content of the different treatments. After phytoremediation the soils showed reduction in Ni content which varied from 49.28 mg kg^{-1} in marigold treated soil to 32.62 mg kg^{-1} in soil treated with vetiver, which was significantly different. The treatments with marigold and sunflower showed no significant difference between them.

The initial content of chromium in the soils was 103 mg kg^{-1} and after phytoremediation it ranged from 49.6mg kg^{-1} in soils grown with vetiver, 70.0 mg kg^{-1} for soils grown with sunflower and 71.4 mg kg^{-1} in soils grown with marigold. There was significant difference in soils treated with vetiver and other two treatments were on par with each other.

The soil grown with marigold had 0.49 mg kg^{-1} and that grown with sunflower had a content of 0.52 mg kg^{-1} which was not significantly different with each other. The soils treated with vetiver had a mercury content of 0.34, which was significantly different from other treatment.

4.2.3. Heavy metal content of the different plants/ parts used for phytoremediation.

The details of the result of plant analysis for heavy metals of different plant parts are given in the following table 4.2.3.

Table 4.2.3. Heavy metal contents in the different plants/ parts used for phytoremediation

Plants/plant parts used for phytoremediation	Pb	Co	Ni	Cr	Hg
	Heavy metal content (mg kg^{-1})				
Roots	23.62	0.98	13.96	34.62	Traces
Sun flower	(4.49)	(1.18)	(3.62)	(5.79)	(0.71)
	14.9	0.825	12.83	37.68	0.023
Marigold	(3.89)	(1.15)	(3.53)	(6.73)	(1.19)
	13.6	1.675	21.2	50.38	0.12
Vetiver	(3.73)	(1.46)	(4.59)	(7.41)	(1.89)
CD	**2.32**	**0.39**	**1.77**	**0.6**	**0.6**
Shoots	5.6	0.2	5.85	19.7	Traces
Sun flower	(2.43)	(0.84)	(2.52)	(4.45)	(0.71)
	3.3	traces	3.05	28.82	0.029
Marigold	(1.92)	(0.71)	(1.79)	(5.19)	(0.79)
	6.95	0.6	12.03	54.95	0.06
Vetiver	(2.72)	(1.04)	(3.36)	(7.42)	(1.42)
CD	**0.18**	**0.003**	**0.73**	**1.39**	**0.013**
Leaf					
Sunflower	13.66	0.44	7.5	22.84	traces
Marigold	9.25	0.258	4.43	23.18	0.027
CD	**NS**	**1.32**		**NS**	
Flower					
Sunflower	2.84	0.42	5.68	18.86	trace
Marigold	4.7	0.5	17.97	40.05	0.015
CD	**NS**	**NS**	**3.9**	**4.4**	

Values expressed in parenthesis indicate square root transformation

The different parts of the plants used for phytoremediation separately subjected for chemical analysis. For sunflower and marigold the four parts like roots, shoot, leaves and flowers were separated and for vetiver only two parts shoot and root were separated and analyzed. The analytical results of heavy metal showed that

among the different crops, the sunflower root showed the highest accumulation of Pb 23.62 mg kg^{-1}, followed by marigold 14.9 mg kg^{-1} and vetiver 13.6 mg kg^{-1} root, which was not significantly different. Vetiver roots are poor accumulator of Pb. Among shoots vetiver was the highest accumulator of Pb 6.95 mg kg^{-1} than sunflower 5.6 mg kg^{-1} and marigold 3.3mg kg^{-1}.All the treatments showed significant difference in accumulation of Pb in the shoot. Sunflower leaf had the highest accumulation of Pb 13.66 mg kg^{-1} than marigold 9.25 mg kg^{-1}, but marigold flower 4.7mg kg^{-1} had highest Pb content than sunflower 2.64 mg kg^{-1}. There was no significant difference in the heavy metal accumulation of the leaf and flower parts of the two plants.

Chromium accumulation was higher in vetiver roots 50.38 mg kg^{-1} followed by marigold root 37.68 mg kg^{-1} and sunflower root 34.62 mg kg^{-1}, and there was significant difference in accumulation of Cr in the root part of different plants. Among the different shoots, vetiver shoots had the highest accumulation of chromium 54.95 mg kg^{-1} followed by sunflower shoot 19.7 mg kg^{-1} and marigold shoot 28.7 mg kg^{-1}. The chromium content of vetiver shoot was significantly different from each other. Marigold and sunflower shoot was on par with each other. Marigold leaf had higher Cr content 23.18 mg kg^{-1} than sunflower leaf 22.84 mg kg^{-1}, however the values were which on par with each other. Marigold flower accumulated the highest content of Cr 40.05mg kg^{-1} than sunflower flower 18.86 mg kg^{-1}.

The highest Nickel content was reported in the vetiver roots 21.2 mg kg^{-1} which was not significantly different from sunflower 13.96 mg kg^{-1} and marigold roots 12.83 mg kg^{-1}. Among the different plant shoots the highest content was in vetiver 12.03 mg kg^{-1} followed by sunflower (5.85 mg kg^{-1}) and marigold (3.05 mg kg^{-1}), which was significantly different from each other. Sunflower leaf had higher Ni content of 7.5 mg kg^{-1} than marigold leaf 4.43 mg kg^{-1}, but marigold flower accumulated 17.97 mg kg^{-1} Ni than sunflower flower 5.68 mg kg^{-1}, these were found to be significantly different.

Among the three different roots analysed for the Co content, the maximum accumulation was reported in vetiver root 1.68 mg kg^{-1} followed by other crops

sunflower 0.98 mg kg^{-1} and marigold 0.83 mg kg^{-1} the values were on par with each other. The result of Cobalt content in the shoot showed that the highest Co content in vetiver shoot 0.6mg kg^{-1} followed by sunflower 0.2mg kg^{-1} and only trace accumulation of Co seen in marigold shoot. There was significant difference in accumulation of Co in the shoot parts of the different plants. The sunflower leaves accumulated maximum amount of Co than marigold leaf and it was significantly different. There was no significant difference in accumulation of Co content in the flowers of sunflower 0.42 mg kg^{-1} and marigold 0.50mg kg^{-1}.

There was only trace accumulation of Hg in sunflower plant. Among roots only vetiver root accumulated Hg. Among shoots vetiver accumulated 0.06 mg kg^{-1} and marigold accumulated less amount of 0.029 mg kg^{-1} of Hg, which was found to be significantly different. Marigold leaf and flower accumulated Hg content at an extent of 0.027 and 0.015 mg kg^{-1} respectively.

4.2.4. Factors for comparing phytoremediation efficiency of the different crops

This translocation factor is a ratio indication of the ability of the plant to translocate metals from the roots to the aerial parts (stem, leaf and flower) of the plants and it was calculated based on the heavy metal content in the different plant parts. Bio concentration factor (BCF) was used to determine the quantity of heavy metals absorbed by the plant from the soil. The removal ratio of heavy metals with respect to different plants was also calculated. This factor was calculated based on total plant uptake /pot basis. The results of the translocation factor and bio concentration factor for the crops (treatments) and removal ratio for the different heavy metals were presented in the table 4.2.4

Table 4.2.4. Translocation factor, bio-concentration factor and the removal ratio for the various crops used for phytoremediation

Heavy metals	Translocation Factor	Bio concentration factor	Removal ratio
	Sun flower		
Pb	0.9	0.02	0.04
Co	1.1	0.02	0.03
Ni	1.4	0.06	0.11
Cr	1.8	0.10	0.23
Hg	-	-	-
	Marigold		
Pb	1.2	0.05	0.08
Co	0.9	0.04	0.07
Ni	2.0	0.24	0.41
Cr	2.5	0.47	1.02
Hg	1.2	0.08	0.11
	Vetiver		
Pb	0.5	0.35	1.10
Co	0.4	0.73	1.30
Ni	0.6	2.10	5.44
Cr	1.1	3.21	10.01
Hg	0.5	2.94	0.65

The table clearly shows that the sunflower has a translocation factor in the order 1.8>1.4>1.1>0.9 for different heavy metals Cr>Ni>Co>Pb, respectively. It is a hyper accumulator for all heavy metals except Pb, which was translocated less to upper part. The translocation factor for marigold was in the order 2.5>2>1.2=1.2>0.9 for different heavy metals Cr>Ni>Pb=Hg>Co, respectively. It was found that the plant translocated all elements except Co to upper part. The translocation factor for vetiver followed the order 1.1>0.6>0.5=0.5>0.4 for different elements

Cr>Ni>Pb=Hg>Co, respectively, which was the same order as marigold. Vetiver was found to be a phytostabilizer for almost all elements except Cr. The bio concentration factor for sunflower ranged in the order 0.1>0.06>0.02=0.02 for different heavy metals Cr>Ni>Pb=Co, respectively. The bio concentration factor for marigold ranged in the order 0.47>0.24>0.08>0.05>0.04 for different heavy metals Cr>Ni>Hg>Pb>Co, respectively. The bio concentration factor for vetiver ranged in the order 3.21 >2.94>2.10>0.73>0.35 for different heavy metals Cr>Hg>Ni>Co>Pb respectively. The removal ratio for sunflower ranged in the order 0.23>0.11>0.04>0.03 for different heavy metals Cr>Ni>Pb>Co respectively. The removal ratio for marigold ranged in the order 1.02>0.41>0.08>0.07>0.11 for different heavy metals Cr>Ni>Pb>Co>Hg, respectively. The removal ratio for vetiver ranged in the order 10.01 >5.44>1.30>1.10>0.65 for different heavy metals Cr>Ni> Co> Pb>Hg respectively.

4.3 Effect of aerobic and anaerobic methods of composting on the composition of heavy metals in the waste material

The material taken from laloor has been subjected to two different types of composting aerobic and anaerobic (slurry) and were compared to non treated material. The experimental result is presented in this section.

4.3.1 Primary and secondary nutrient contents of the composted material as compared to control

Composted materials (both aerobic and anaerobic) and control was analysed for C, N, P, K, Ca, Mg and S contents and presented in table 4.3.1

Table 4.3.1. Effect of different methods of composting on the physico chemical properties of the material

Treatments	Primary and secondary nutrients								
	pH	EC	C	N	P	K	Ca	Mg	S
		dS m^{-1}	(%)						
Control	6.7	0.05	3.76 (2.06)	0.28 (0.88)	0.12 (0.78)	0.18 (0.82)	0.53 (1.02)	0.17 (0.82)	Traces (0.73)
Aerobic	6.8	0.044	4.26 (2.17)	0.35 (0.92)	0.12 (0.77)	0.18 (0.82)	0.42 (0.96)	0.16 (0.81)	Traces (0.74)
Anaerobic	7.1	0.009	2.00 (1.8)	0.18 (0.82)	0.13 (0.78)	0.13 (0.79)	.20 (0.84)	0.12 (0.79)	0.40 (0.95)
CD	NS	NS	0.387	0.09	0.108	0.135	0.268	0.159	0.408

Values expressed in parenthesis indicate square root transformation

The pH values were higher in slurry (7.1) followed by aerobic compost (6.8) and control had least pH. The electrical conductivity found to be not significantly different among the different treatments with the highest value in control and the least value 0.009 for slurry treatment. The maximum total carbon (%) was in aerobic compost (4.26 %), followed by control (3.76%) and the least for slurry (2.0%) and there was significant difference for the treatments aerobic compost and control with slurry.

The result of the analysis show that there was no significant difference in total nitrogen among the treatments and it was the highest in aerobic compost (0.35 %) followed by control (0.28 %) and least in slurry (0.18 %). Total P content of all the treatments were on par with each other, control (0.12 %), aerobic (0.12%) and anaerobic slurry (0.13%). Total potassium content was same with no significant difference among the treatments, control had (0.18 %), followed by aerobic 0.18 % and slurry 0.13%. Among the treatments there were significant variation in total Ca

with control (0.53 %), followed by aerobic compost (0.42 %) and slurry (0.20 %). The Mg content was higher in control (0.17 %), followed by aerobic treatment and (0.16 %) and the least for anaerobic treatment and (0.12 %) and there was no significant difference in total Mg contents of the different treatments. The sulfur content was very less and there was no significant difference among the treatments.

4.3.2 Effect of different treatments on the micronutrient contents of the material

The micronutrient contents (Fe, Zn, Mn & Cu) of the different treatments control and composting (aerobic and slurry) are given in the table 4.3.2.

Table 4.3.2 Micronutrient contents of the three treatments after composting

Treatments	Fe	Zn	Mn	Cu
	(%)	(mg kg^{-1})		
Control	3.27 (1.94)	432.12 (20.79)	352.70 (18.78)	166.22 (12.91)
Aerobic	2.28 (1.67)	287.36 (16.46)	277.58 (16.22)	122.36 (10.74)
Anaerobic	3.13 (1.91)	10.24 (2.77)	48.42 (6.78)	5.00 (2.32)
CD	0.29	3.92	3.71	2.43

Values expressed in parenthesis indicate square root transformation

All the micronutrients Zn, Cu, Mn and Fe were higher in control and the least in slurry. Zinc content varied from 10.24 mg kg^{-1} in slurry to 432.12 mg kg^{-1} in control and aerobic compost had 287.36 mg kg^{-1}, in all the treatments, significantly different from each other. Mn content ranged 48.4 mg kg^{-1} in slurry to 352.7 mg kg^{-1} in control and aerobic compost had intermediate content of 277.58 mg kg^{-1}. The Mn content in slurry is significantly different from other treatments, but there was no significant difference noted in Mn content of control and aerobic compost. Cu content was the least in 5 mg kg^{-1} in slurry to 166.22 mg kg^{-1} in control and Cu content was intermediate for aerobic compost 122.36 mg kg^{-1}. There was significant difference in Cu content among the different treatments. Iron content was higher in control (3.27

%), followed by aerobic compost (2.28 %) and the least in anaerobic compost (3.13 %), and there was significant difference in Fe content of all the treatments.

4.3.3 Heavy metal contents of the three treatments after composting

The composted material was analysed for heavy metals and the results are given in the table 4.3.3.

Table 4.3.3 Heavy metal contents of the three treatments after composting

Heavy metal content of compost					
Treatment	Pb	Co	Ni	Cr	Hg
	(mg kg^{-1})				
Control	148.6 (11.8)	10.2 (3.27)	48.68 (7.01)	142.12 (11.94)	0.39 (0.94)
Aerobic	99.18 (9.81)	6.9 (2.67)	33.64 (5.69)	99.52 (9.77)	0.29 (0.88)
Anerobic	2.16 (1.67)	0.24 (0.86)	1.2 (1.23)	28.06 (5.34)	0.03 (0.72)
CD	1.67	0.50	1.15	1.88	2.7

Values expressed in parenthesis indicate Sqrt(x+0.5) transformation.

There were significant variations in the contents of heavy metals in the different treatments of the experiment. On perusal of data the heavy metals Pb, Co, Ni, Cr and Hg are found to be highest in control. The lead content of the control was 148.6 mg kg^{-1} followed by aerobic 99.18 mg kg^{-1} and slurry 2.16 mg kg^{-1}, the three treatments were found to be significantly different. Co content was the highest in control 10.2 mg kg^{-1}, followed by aerobic 6.9 mg kg^{-1} and the lowest Co content was in slurry (0.24 mg kg^{-1}). There was significant difference in Co content of the various treatments. The highest Nickel content was 48.68 mg kg^{-1}in control, followed by aerobic compost (33.64 mg kg^{-1}) and least was 1.22 mg kg-^{1} in slurry. Chromium content was high in control with 142 mg kg^{-1}, followed by aerobic compost 99.52 mg kg^{-1} and the least in slurry 28.06 mg kg^{-1} and there was significant difference between the different treatments. Mercury content was higher in control (0.39 mg kg^{-1})

followed by aerobic compost (0.29 mg kg^{-1}) which was not significantly different from each other. The least Hg content of 0.03 mg kg^{-1} was reported in slurry and this treatment was significantly different from others.

4.4 Comparative performance of amaranthus grown in soil under different methods adopted for reducing heavy metal contamination

A pot culture study was conducted with the test variety Arun for a total duration of two months with different treatments as mentioned in chapter 3. The yield and the result of plant and soil analysis are presented in this section.

4.4.1. Yield of the amaranthus crop

The amaranthus crop was harvested and the yield of the different treatments was recorded and is given in the table 4.4.1 below:

Table 4.4.1. Yield of amaranthus crop

Treatments	Yield (g pot^{-1})
Abs. control (T_1)	26.50
FYM (T_2)	56.33
POP (T_3)	48.50
Phytoremediation (T_4)	24.00
Waste (control) (T_5)	104.83
Aerobic compost (T_6)	325.67
Slurry (T_7)	81.17
CD	39.85

The amaranthus crop after harvest showed that the highest yield was recorded for crop under aerobic compost (325.67g), followed by waste (104.83 g), followed by slurry (81.17 g), then crops grown under FYM (56.33g), then followed by crops under POP recommendation (48.50g), which was followed by absolute control (26.50g) and the lowest was under phytoremediated material (24.00g). There was

significant difference for the yield under aerobic compost, waste and slurry and all other treatments were on par with each other.

4.4.2 Primary nutrient uptake of the amaranthus crop

The amaranthus plant harvested subjected to analysis and the total N, P and K uptake was calculated and presented in the table 4.4.2.

Table 4.4.2 Primary nutrient uptake of the amaranthus crop

Treatments	N	P	K
	g pot^{-1}		
Abs. control (T_1)	0.52	0.03	0.75
FYM (T_2)	0.86	0.12	1.44
POP (T_3)	1.06	0.15	1.70
Phytoremediation (T_4)	0.61	0.07	1.22
Waste (control) (T_5)	1.73	0.25	3.59
Aerobic compost (T_6)	4.53	1.05	11.02
Slurry (T_7)	1.39	0.19	3.07
CD	0.79	0.18	1.77

The result showed that the highest nitrogen uptake was for amaranthus grown under treatment with aerobic compost 4.53 g pot^{-1}, followed by treatment under waste 1.73 g pot^{-1}, then slurry 1.39 g pot^{-1}this was followed by treatment under POP recommendation 1.06 g pot^{-1}, followed by FYM 0.86 g pot^{-1}, then treatment under phytoremediation 0.61 g pot^{-1} and the least N uptake was for the amaranthus grown under absolute control 0.52 g pot^{-1}. There was significant difference in the N uptake for the treatment under aerobic compost, waste and slurry. The treatments with FYM and soil with phytoremediated material was on par with each other in the N uptake. The treatment under absolute control was significantly different from all other treatment. The P uptake was found to be higher in amaranthus plant grown under

treatment with aerobic compost 1.05 g pot^{-1}, followed by waste 0.25 g pot^{-1} and both were significantly different from other treatments, this was followed by amaranthus under slurry 0.19 g pot^{-1}, POP recommendation 0.15 g pot^{-1}, FYM 0.12 g pot^{-1}, under phytoremediated material 0.07 g pot^{-1} and all these were on par with each other. The least P uptake was for amaranthus under absolute control 0.03 g pot^{-1}. The potassium uptake was found to be maximum for the crops grown under treatment with aerobic compost 11.02 g pot^{-1}, followed by waste 3.59 g pot^{-1} and then slurry 3.07 g pot^{-1},which was significantly different from all the other treatments, followed by POP recommendation 1.70 g pot^{-1} and FYM 1.44 g pot^{-1}, both were on par with each other, followed by phytoremediated soil 1.22 g pot^{-1} and absolute control 0.75 g pot^{-1}, which was on par with each other.

4.4.3. Micronutrient contents of amaranthus shoots

The micronutrient contents of amaranthus shoot was analysed and presented in the table 4.4.3

Table 4.4.3. Micronutrient contents of the amaranthus shoots

Treatments	Zn	Cu	Mn	Fe
	(mg kg^{-1})			
Abs.control (T_1)	68.50 (7.95)	-	86.07 (8.89)	822.93 (28.64)
FYM (T_2)	55.10 (7.39)	-	80.13 (8.92)	718.37 (26.57)
POP (T_3)	87.70 (9.17)	-	87.77 (9.18)	591.03 (24.12)
Phytoremediation (T_4)	52.07 (7)	-	84.9 (9.05)	895.13 (29.90)
Waste (control) (T_5)	30.50 (5.52)	11.73	32.3 (5.72)	843.66 (29.05)
Aerobic compost (T_6)	60.30	13.13	62	764.43

Table 4.4.3. Continued.

	(7.79)		(7.9)	(27.61)
Slurry (T_7)	31.05 (5.60)	9.75	63.7 (7.87)	484.65 (21.92)
CD	1.42	-	4.09	7.69

Values expressed in parenthesis () indicate square root transformation

The total Zn content was reported to be maximum in the shoot of amaranthus grown under soil treated with POP recommendation (87.70 mg kg^{-1}), followed by abs. control (68.50 mg kg^{-1}), followed by soil treated with aerobic compost (60.30 mg kg^{-1}) and then soil with FYM (55.10 mg kg^{-1}), followed by soil treated with phytoremediated material (52.07 mg kg^{-1}), slurry (31.05 mg kg^{-1}) and the least for soil under waste (30.50 mg kg^{-1}). There was significant difference in the soil treated with POP recommended soil and absolute control and also between absolute control and aerobic compost from the other treatments. All other treatments were on par with each other. The total Cu content was traced only in the shoots of three treatments, that grown with aerobic compost (13.13 mg kg^{-1}), followed by waste (11.73 mg kg^{-1}) and slurry (9.75 mg kg^{-1}). There was significant difference for all the three treatments. The total Mn content was also higher in the amaranthus shoot grown under soil with POP recommendation (87.77 mg kg^{-1}), followed by soil under abs. control (86.07 mg kg^{-1}), followed by shoots grown under soil with phytoremediated material (84.9 mg kg^{-1}) and then soil treated with FYM (80.13 mg kg^{-1}), followed by soil treated with slurry (63.7 mg kg^{-1}) and aerobic compost (62 mg kg^{-1}) and the least for the shoot grown with waste (32.3 mg kg^{-1}). There was no significant difference for the shoots grown under any of the treatments. The total Fe content was found to be maximum in the shoots grown in soil treated with phytoremediated material (895.13 mg kg^{-1}), followed by waste (843.66 mg kg^{-1}) and then abs.control (822.93 mg kg^{-1}), followed by aerobic compost (764.43 mg kg^{-1}), followed by amaranthus shoot grown under FYM (718.37 mg kg^{-1}), all these treatments were significantly different from the rest. The treatment with FYM followed by POP recommended soil (591.03 mg kg^{-1}) and

the least for the shoots grown with slurry 484.65 mg kg^{-1} and they were on par with each other.

4.4.4. Heavy metal contents of amaranthus shoots

The amaranthus shoot was analysed for the heavy metal content and data are presented in the table 4.4.4

Table 4.4.4. Heavy metal contents of amaranthus shoots

Treatments	Pb	Co	Ni	Cr	Hg
	(mg kg^{-1})				
Abs. control (T_1)	0.53 (1.01)	0.57 (1.03)	2.87 (1.82)	44.43 (6.69)	Traces
FYM (T_2)	0.43 (0.927)	0.53 (1.02)	2.83 (1.82)	54.53 (7.42)	Trace
POP (T_3)	0.80 (1.12)	0.53 (1.02)	2.33 (1.66)	52.83 (7.3)	Trace
Phytoremediation (T_4)	3.45 (2.0)	0.83 (1.15)	2.6 (1.75)	52.6 (7.28)	0.053 (1.11)
Waste (control) (T_5)	5.3 (2.41)	0.57 (1.03)	2.63 (1.77)	52.03 (7.24)	0.060 (1.13)
Aerobic compost (T_6)	4.4 (2.18)	0.50 (1)	2.33 (1.68)	44.43 (6.7)	0.050 (1.09)
Slurry (T_7)	0.60 (1.05)	0.40 (0.95)	1.6 (1.44)	49.55 (7.08)	0.015 (0.85)
CD	.083	.003	.048	.074	0.012

Values expressed in parenthesis indicate square root transformation

The total Pb content was found to be maximum in the shoot grown under soil treated with waste (5.3 mg kg^{-1}), followed by aerobic compost (4.4 mg kg^{-1}) and phytoremediated soil (3.45 mg kg^{-1}), then followed by shoots grown under POP recommendation (0.8 mg kg^{-1}), followed by slurry (0.6 mg kg^{-1}), then abs. control

(0.53 mg kg^{-1}) and the least Pb content was recorded for shoots grown under soil treated with FYM (0.43 mg kg^{-1}). There was significant difference in the total Pb content of the treatments under soil with waste, aerobic compost and phytoremediated material, from other treatments. The total Co content of amaranthus shoot was almost similar with phytoremediated material showing higher content of 0.8 mg kg^{-1}, followed by waste 0.57 mg kg^{-1} and all other treatments in the same range and the least total Co content was recorded in the amaranthus shoot grown with slurry (0.4 mg kg^{-1}). The total Co content of all the treatments was on par with each other. The total Ni content was found to be highest in the shoots grown with abs.control (2.87 mg kg^{-1}), followed by the shoots grown with FYM (2.83 mg kg^{-1}), then waste (2.63 mg kg^{-1}) and phytoremediated material, followed by shoots grown with and POP recommendation and aerobic compost (2.33 mg kg^{-1}) and the least Ni content in shoots grown under slurry (1.6 mg kg^{-1}). There was no significant difference in the total Ni content in the shoots of amaranthus grown under different treatment. The total Cr content was found to be maximum in the shoots treated with FYM (54.53 mg kg^{-1}), followed by the shoots grown in soil treated with and POP and phytoremediated material (52.83 mg kg^{-1}) and 52.6 mg kg^{-1}, respectively, followed by waste material. The shoot grown under slurry had a total Cr content of 49.55 mg $kg^{-1}$and the least Cr content was found to be in abs.control on par with aerobic compost (44.43 mg kg^{-1}). There was no significant difference in the Cr content of shoots grown under all the different treatment.

4.4.5. Micronutrient contents of amaranthus roots

The micronutrient content of the roots were analysed and presented in the table 4.4.5.

Table 4.4.5. Micronutrient contents of amaranthus roots

Treatments	Zn	Mn	Cu	Fe
	(mg kg^{-1})			
Abs.control (T_1)	4.23	29.57 (4.99)	- (0.71)	332.63 (17.39)
FYM (T_2)	4.17	36.1 (6.04)	- (0.71)	403.13 (20.03)
POP (T_3)	4.5	51.2 (7.17)	- (0.71)	603.3 (24.44)
Phytoremediation (T_4)	6.9	53.8 (7.26)	- (0.71)	702.27 (26.43)
Waste (control) (T_5)	4.1	23.77 (4.92)	- (0.71)	462.4 (21.38)
Aerobic compost (T_6)	7.30	63.23 (7.91)	18.9 (4.37)	703.5 (22.73)
Slurry (T_7)	3.5	46.7 (6.87)	11.95 (3.53)	484.65 (21.94)
CD	2.89	2.43	0.46	13.1

Values expressed in parenthesis indicate square root transformation

On perusal of the data it was noted that the amaranthus root grown under aerobic compost reported (7.3 $mgkg^{-1}$) maximum Zn content, followed by the phytoremediation soil (6.9 mg kg^{-1}) root grown with POP recommendation (4.5 mg kg^{-1}). Almost all other treatments had a value on par with each other (4.1 to 4.2 mg kg^{-1}), and the lowest Zn content was noted in roots grown under slurry (3.5 mg kg^{-1}). The treatments with phytoremediation material and aerobic compost were showing significant difference, rest all are on par with each other. The total Mn content was also higher in the roots grown with soil under aerobic compost (63.23 mg kg^{-1}),

followed by the roots grown in soil treated with phytoremediated material (53.8 mg kg^{-1}), then the roots grown in soil under POP recommendation (51.2 mg kg^{-1}), then roots grown in soils under slurry (46.7 mg kg^{-1}), then for roots under FYM (36.1 mg kg^{-1}), followed by abs control (29.57 mg kg^{-1}) and the least in the root treated with waste material (23.77 mg kg^{-1}). The amaranthus root grown under treatment with aerobic compost only showed significant difference from other treatments. The total Cu content was found in the amaranthus root for only two treatments, one under aerobic compost (18.9 mg kg^{-1}) and the other for slurry and there was significant difference for Cu content for the two treatments. The total Fe content was found to be maximum in the roots grown under aerobic compost (703.5 mg kg^{-1}), followed by soil under phytoremediated material (702.27 mg kg^{-1}), then soil treated with FYM (603.3 mg kg^{-1}), which was followed by soil treated with slurry (484.65 mg kg^{-1}), followed by soil treated with waste material (462.4 mg kg^{-1}) and soil treated with FYM (403.13 mg kg^{-1}) and the least with soil under abs. control (332.63 mg kg^{-1}). There was no significant difference in any of the treatments for the total Fe content in the amaranthus root.

4.4.6 Heavy metal contents of amaranthus roots

The heavy metal content analysed for amaranthus shoot is analysed and presented in the table 4.4.6.

Table 4.4.6 Heavy metal contents of amaranthus roots

Treatments	Pb	Co	Ni	Cr	Hg
	(mg kg^{-1})				
Abs. control (T_1)	1.1 (1.26)	0.27 (0.87)	1.23 (1.31)	32.967 (5.74)	Traces (0.76)
FYM (T_2)	1.53 (1.42)	0.45 (0.89)	2.33 (1.68)	50.57 (7.14)	Traces (0.76)
POP (T_3)	1.23 (1.31)	0.73 (1.10)	2.47 (1.72)	51.4 (7.21)	Traces (0.76)
Phytoremediation (T_4)	5.03 (2.33)	0.43 (0.96)	1.9 (1.54)	51.53 (7.20)	0.015 (0.87)

Table 4.4.6. Continued.

Waste (control) (T_5)	5.8 (2.51)	0.67 (1.08)	2.6 (1.76)	51.5 (7.21)	0.051 (1.09)
Aerobic compost (T_6)	6.07 (2.55)	0.7 (1.09)	3.87 (2.08)	53.9 (5.15)	0.061 (1.29)
Slurry (T_7)	0.75 (1.16)	0.65 (1.07)	1.95 (1.56)	51 (7.17)	0.015 (0.86)
CD	0.32	0.19	0.3	2.75	0.23

The result of the heavy metal analysis of amaranthus root grown under different treatment showed that the total Pb content was reported to be maximum for roots grown in soil with aerobic compost (6.07 mg kg^{-1}), followed by roots grown in soil treated with waste (5.8 mg kg^{-1}) and then in roots grown under phytoremediated soil (5.03 mg kg^{-1}), then for roots under soil with FYM (1.53 mg kg^{-1}) and soil under abs.control and the least Pb content was found in treatment with slurry (0.75 mg kg^{-1}). The amaranthus grown under the treatment with aerobic compost, waste and material with phytoremediation showed significant difference from the rest of the treatments. The total Co content of the soil was reported to be maximum in soil treated with POP (0.73 mg kg^{-1}) and the root grown in soil treated with aerobic compost (0.7 mg kg^{-1}) and then followed by soil treated with soil treated with phytoremediation material (0.67 mg kg^{-1}), followed by slurry (0.65 mg kg^{-1}), then roots grown in soil treated with (0.45 mg kg^{-1}), followed by the roots grown under waste (0.43 mg kg^{-1}), and the least under soil treated under abs. control (0.27 mg kg^{-1}). There was significant difference in the total Co content in the amaranthus root grown under the aerobic compost, POP recommended treatment and phytoremediated material. The total nickel content was maximum reported in the amaranthus root treated in soil with aerobic compost (3.87 mg kg^{-1}), followed by the roots of plant grown under waste (2.9 mg kg^{-1}), followed by the roots in the soil with POP recommendation (2.47mg kg^{-1}), FYM (2.33 mg kg^{-1}), slurry and phytoremediated material (1.92 mg kg^{-1}) and the least for abs. control (1.23 mg kg^{-1}). There was significant difference in the total Ni content of the amaranthus roots grown under

aerobic compost, waste, POP and soil treated with FYM. The total Cr content was reported to be maximum for the amaranthus root grown under the treatment of aerobic compost (53.9 mg kg^{-1}), followed by waste, phytoremediated material, slurry and POP recommendation showing almost the same extent (51.4 to 51.5 mg kg^{-1}). The treatment with FYM showed a total Cr content of (50.57 mg kg^{-1}) and the least total Cr content was found to be in abs. control (32.96 mg kg^{-1}). The total Cr content of all the different treatments were on par with each other and didn't show any significant difference. The total Hg content was higher in the root grown under aerobic compost, followed by waste and then slurry and in roots grown in soil with slurry and phytoremediated material (0.015 %). All other treatments total Hg were in traces.

4.4.7. Primary nutrient contents of the soil after experimentation

After harvest of the crop the soil was analysed for the major nutrients and the result is represented in the table 4.4.7. below

Table 4.4.7. Primary nutrient contents of the soil after experimentation

Treatments	N	P	K
	(%)		
Abs.control (T_1)	0.028 (0.73)	0.04 (0.73)	0.11 (0.78)
FYM (T_2)	0.028 (0.73)	0.03 (0.73)	0.13 (0.79)
POP (T_3)	0.043 (0.74)	0.03 (0.73)	0.07 (0.75)
Phytoremediation (T_4)	0.085 (0.77)	0.02 (0.72)	0.07 (0.76)
Waste (control) (T_5)	0.135 (0.79)	0.056 (0.74)	0.15 (0.80)
Aerobic compost (T_6)	0.129 (0.79)	0.08 (0.76)	0.20 (0.84)
Slurry (T_7)	0.033	0.09	0.14

Table 4.4.7. Continued

	(0.73)	(0.77)	(0.80)
CD	0.056	NS	.257

Values expressed in parenthesis indicate square root transformation

The total nitrogen content was also less in the soil after harvest of amaranthus crop and it ranged from .028 per cent in the soil which was absolute control to (0.135 %) in soil with waste and (0.129%) in soil with compost which was on par with each other. There was significant difference among only three treatments the phytoremediated material (0.085 %), waste (0.135%) and aerobic compost (0.79 %). The total phosphorus content was very less in all the treatment, with maximum found in the treatment with absolute control slurry (0.09 %), followed by aerobic compost (0.08%), followed by waste (0.08 %) and the least found traces in all other treatments and there was no significant difference between the treatments. The total Potassium content was maximum in aerobic compost (0.20 %), followed by waste (0.15 %) and slurry (0.14 %) , then soils treated with FYM (0.13 %)then absolute control (0.11 %) and the least in POP recommended soil and phytoremediated soil (0.07).

The treatments with aerobic compost and waste material are significantly different from other treatments.

4.4.8. Micronutrient contents of the soil after harvest of amaranthus crop

After harvest of the crop the soil was analysed for micronutrients and its result is presented in the table 4.4.8.

Table 4.4.8 Micronutrient contents of the soil after harvest of amaranthus crop

Treatments	Zn	Mn	Cu	Fe
	mg kg^{-1}			
Abs.control (T_1)	0.05 (0.73)	220.63 (14.08)	25.13 (4.83)	13289.00 (109.82)
FYM (T_2)	18.97 (3.65)	171.33 (12.87)	33.37 (5.56)	14326.67 (116.51)
POP (T_3)	1.77 (1.28)	271.00 (16.46)	26.80 (5.17)	21630.00 (146.87)
Phytoremediation (T_4)	51.60 (7.13)	89.35 (9.22)	33.60 (5.63)	6482.50 (78.79)
Waste (control) (T_5)	154.27 (12.31)	175.20 (12.84)	65.20 (7.87)	12895.00 (112.06)
Aerobic compost (T_6)	198.47 (13.96)	230.13 (15.04)	83.93 (9.09)	19023.33 (136.8)
Slurry (T_7)	56.90 (7.51)	247.27 (15.73)	29.60 (5.47)	20576.67 (143.44)
CD	5.92	5.91	3.06	45.42

Values expressed in parenthesis indicate square root transformation

The result of micronutrient analysis of the soil after growing amaranthus with seven different treatments showed that Zn content was highest in treatment with compost (198.47 mg kg^{-1}) and the least with the absolute control soil (0.05 mg kg^{-1}).There was significant difference in Zn content only for three treatments the material after phytoremediation, waste and treatment with compost. The highest Mn content was in the POP treatment (271 mg kg^{-1}) followed by slurry (247.27 mg kg^{-1}), compost (230.13 mg kg^{-1}), absolute control (220.63 mg kg^{-1}) FYM (171.33 mg kg^{-1}) and the least with soil treatment with phytoremediated material (89.35 mg kg^{-1}). There was significant difference in the treatment with POP and slurry in the total Mn content. The total Cu content was highest in the soil treated with compost (83.93 mg kg^{-1}),

followed by soil treated with waste (65.20 mg kg^{-1}), then treatment with phytoremediated material (33.60 mg kg^{-1}) followed by treatment with FYM (33.37 mg kg^{-1}) and slurry (29.60 mg kg^{-1}), followed by treatment with POP (26.80 mg kg^{-1}) and the least in absolute control (25.13 mg kg^{-1}). The total Cu content showed significant difference for treatment with compost and waste material. The total Fe content of the soil also varied greatly for different treatments. The highest Fe content was for the treatment with POP (21630 mg kg^{-1}), followed by treatment with slurry (20576.67 mg kg^{-1}), followed by compost (19023.33 mg kg^{-1}) then treatment with FYM (14326.67 mg kg^{-1}), then treatment with waste and absolute control and the least Iron content was for the soils treated with material after phytoremediation (6482.57 mg kg^{-1}).

4.4.9 Heavy metal contents of the soil after harvest of amaranthus crop

The soil under seven treatments after harvest of amaranthus crop was subjected to heavy metal analysis and the result is given in the table 4.4.9 .

Table 4.4.9. Heavy metal contents of the soil after harvest of amaranthus crop

Treatments	Pb	Co	Ni	Cr	Hg
	(mg kg^{-1})				
Abs. control (T_1)	Traces (0.71)	5.53 (2.36)	11.30 (3.27)	100.50 (10.15)	Traces
FYM (T_2)	Traces (0.71)	5.50 (2.40)	10.37 (3.22)	102.00 (10.12)	Traces
POP (T_3)	Traces (0.71)	8.30 (2.97)	16.00 (4.06)	103 (10.17)	Traces
Phytoremediation-(T_4)	23.20 (4.78)	2.70 (1.76)	9.40 (3.1)	78.25 (8.87)	Traces
Waste (control) (T_5)	53.73 (7.25)	5.50 (2.39)	19.97 (4.42)	110.00 (10.51)	0.13

Table 4.4.9. Continued.

Aerobic compost (T_6)	69.10 (8.26)	7.37 (2.77)	25.00 (5.0)	94 (9.72)	0.13
Slurry (T_7)	Traces (0.71)	8.77 (3.04)	21.30 (4.66)	98 (9.92)	0.06
CD	1.61	0.92	1.52	2.01	NS

Values expressed in parenthesis indicate square root transformation

There was significant variation in the contents of heavy metals in the different treatments of the experiment. The Lead content was highest in treatment with compost (69.10 mg kg^{-1}), followed by control (53.73 mg kg^{-1}) and the soil treated with phytoremediated material (23.20 mg kg^{-1}). There was significant difference in the total Pb content of the soils treated with control (waste) and aerobic compost. Total Co content was highest in the soils treated with slurry (8.77 mg kg^{-1}) followed by soil treated with POP recommendation (8.30 mg kg^{-1}), followed by compost (7.37 mg kg^{-1}), followed by absolute control (5.50 mg kg^{-1}), followed by soils treated with waste and FYM (5.50 mg kg^{-1}) and the least total Co content was found in the soil treated with phytoremediated material. The highest Nickel content was in aerobic compost (25 mg kg^{-1}) followed by slurry (21.30 mg kg^{-1}) then waste (19.97 mg kg^{-1}) and then soil treated with POP recommendation (16 mg kg^{-1}), followed by abs. control (11.30 mg kg^{-1}) , soil treated with FYM (10.37 mg kg^{-1}) and the least is with the soil treated with phytoremediated material (9.40 mg kg^{-1}). There was significant difference in the treatment with aerobic compost and treatment with slurry; others were on par with each other. The Cr content of the soil after the harvest of amaranthus crop was higher for all the treatments. The lowest Cr content was for soil treated with phytoremediated material (78.25 mg kg^{-1}) and the highest for the soil under waste (110 mg kg^{-1}) and for all other treatments the values were on par with each other.

Discussion

5. DISCUSSION

The results of the various experiments conducted on "Heavy metal contamination of laterites by accumulation of solid wastes" were studied and presented in chapter 4, the details pertaining to the various findings are discussed below:

5.1 Effect of soil and climatic factors on heavy metal accumulation using geostatistical techniques

5.1.1. Map preparation using GIS technology

As detailed in 3.1.5 section of materials and methods, and the results are presented in section 4.1.15, 4.1.16, 4.1.17, 4.1.18, 4.1.19 and 4.1.20 the various indices were worked out. The details of indices are presented in appendices (Va, Vb and Vc).

The Location of Kalamassery and Laloor was identified in high resolution google map using the points taken during the ground survey with GPS. The images were digitized and georeferenced to make it to GIS layers. The result of the heavy metal analysis was added to the attribute field of GIS layers created for the different sites of location Kalamassery and Laloor (Elangovan, 2006). The different maps are generated and discussed as follows:

Kalamassery

5.1.1.1. Map showing the percentage distribution of heavy metal contents at the different sampling sites

Map showing the percentage distribution of heavy metal contents of the four sites (including the non dumping site) at the location Kalamassery is depicted in (Fig.5.1). The percentage distribution of heavy metals at the Kalamassery showed that at all the sites the heavy metals followed the same order of distribution as Cr> Ni> Pb> Co> Hg. Distribution of Cr ranged from 59 per cent at first site to 67 per cent at third site. Ni content ranged from 20 % in third site to 28 % in first site. Lead

content varied from (7-10%), Cobalt ranged from (3%-4%) and Hg (0.3%- 0.4 %) and Cd (traces - 0.7%).

5.1.1.2. Map showing the geoaccumulation index (I geo) at different sampling sites

The geoaccumulation index calculated for the individual heavy metals at the different sites showed that Hg was a pollutant for all the four sites of Kalamassery. Cadmium was pollutant at the first and third site. Mercury was pollutant for all the sites, though its concentration was very low. The map showing the geoaccumulation index of the different heavy metals at each site with geo accumulation greater than one (which is the polluted site) were depicted and Hg in red colour and Cd in blue colour (Fig.5.2) The table and range for I geo index value are given in appendices Vb and Vc respectively.

5.1.1.3. Map showing the modified contamination degree (mC_d) at different sampling sites

Map showing the mC_d of different sites are presented in Fig.5.3. The mC_d values showed that all the four sites were contaminated at Kalamassery. All the four sites were under moderate contamination degree for the heavy metals under study.

Laloor

5.1.1.4. Map showing the percentage distribution of heavy metal contents at different sampling sites

Map showing the percentage distribution of heavy metal contents of the four sites (including the non dumping site) at the location Laloor is depicted in Fig 5.4. The percentage distribution of heavy metals at Laloor showed that at the first and second sites the heavy metals followed the same order of distribution as Pb>Cr> Ni> Co> Hg>Cd. At the third and fourth sites the distribution was Cr> Ni> Pb> Co> Hg. The percentage distribution of Cr ranged from 59 per cent at first site to 67 per cent at third site. Ni content ranged from 20 % in third site to 28 % in first site. Pb content varied from (7-10%), Co ranged from (3%-4%) and Hg (0.3%- 0.4 %) and Cd (traces -0.7%).

5.1.1.5. Map showing the geoaccumulation index (I geo) at different sampling sites

The geoaccumulation index calculated for the individual heavy metals at the different sites showed that Pb, Cd and Hg were pollutants at Laloor. The geo accumulation index of Pb and Hg was greater than one for all the dumping sites of Laloor (Fig.5.5). The geo accumulation index of Cd was greater than one for the third dumping site of Laloor (Appendix Vb and Vc).

5.1.1.6. Map showing the modified contamination degree (mC_d) at different sampling sites

Modified contamination degree values for Laloor site revealed that first, second and third site were contaminated and were under moderate degree of contamination. The fourth site is under no to very low degree of contamination (Abrahim and Parker, 2008) (Fig.5.6) (Appendix Vb and Vc).

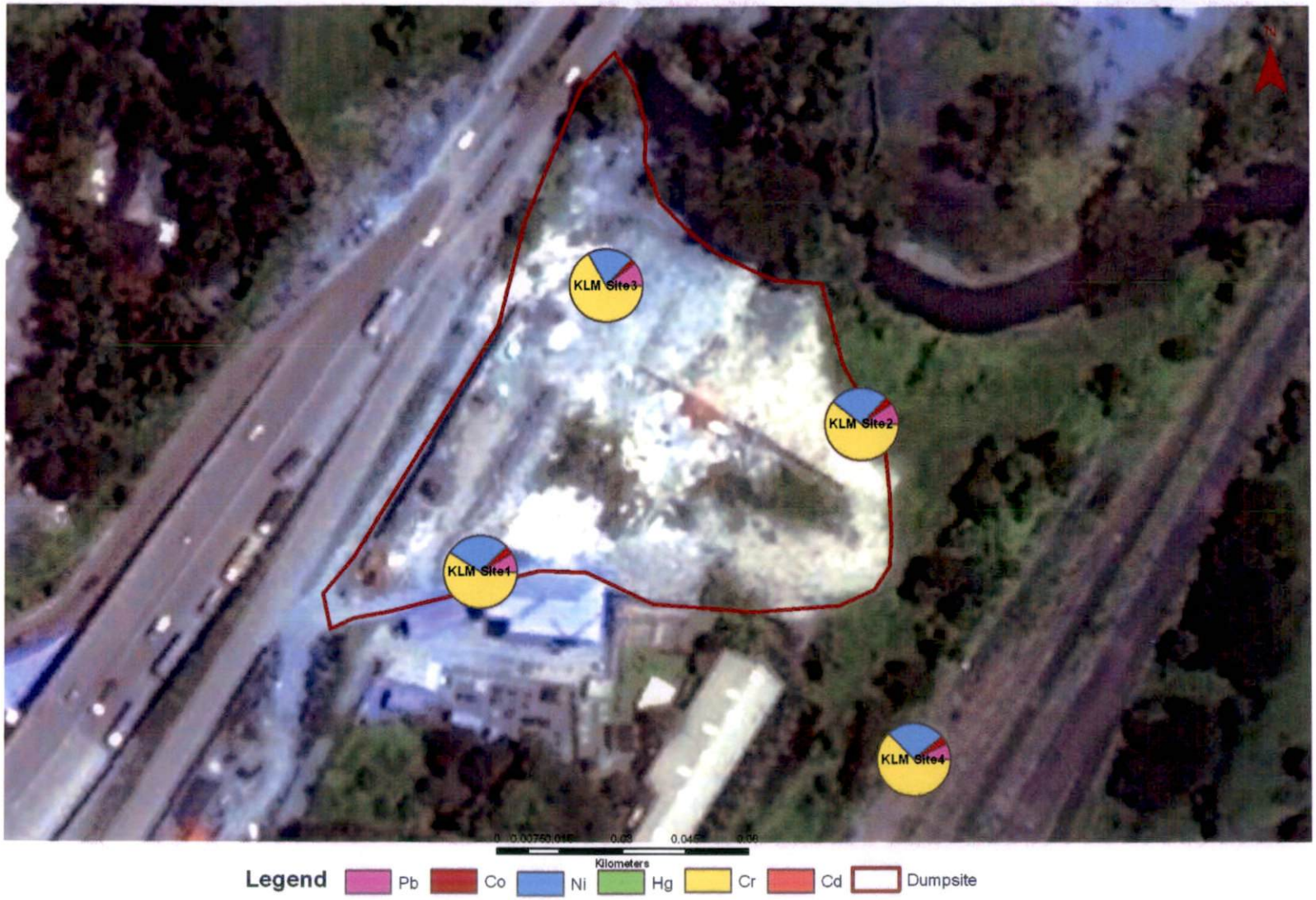

Fig.5.1. Percentage distribution of heavy metals at the different sampling sites of Kalamassery

Fig. 5.2. Geo accumulation index at different sites of Kalamassery

Fig.5.3. Modified contamination degree at different sites of Kalamassery

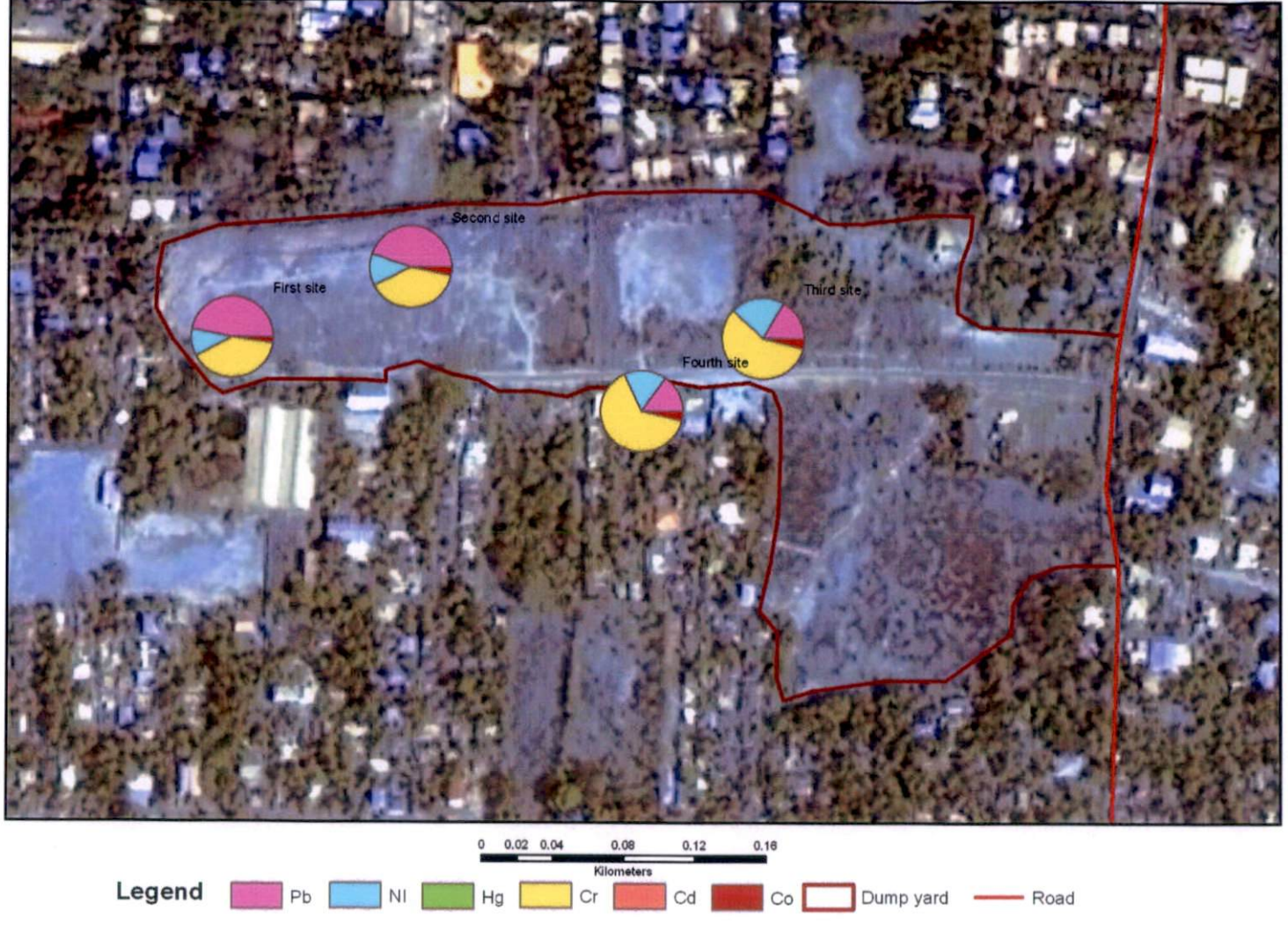

Fig.5.4. Percentage distribution of heavy metals at the different sampling sites of Laloor

Fig. 5.5. Geo accumulation index at different sites of Laloor

Fig.5.6. Modified contamination degree at different sites of Laloor

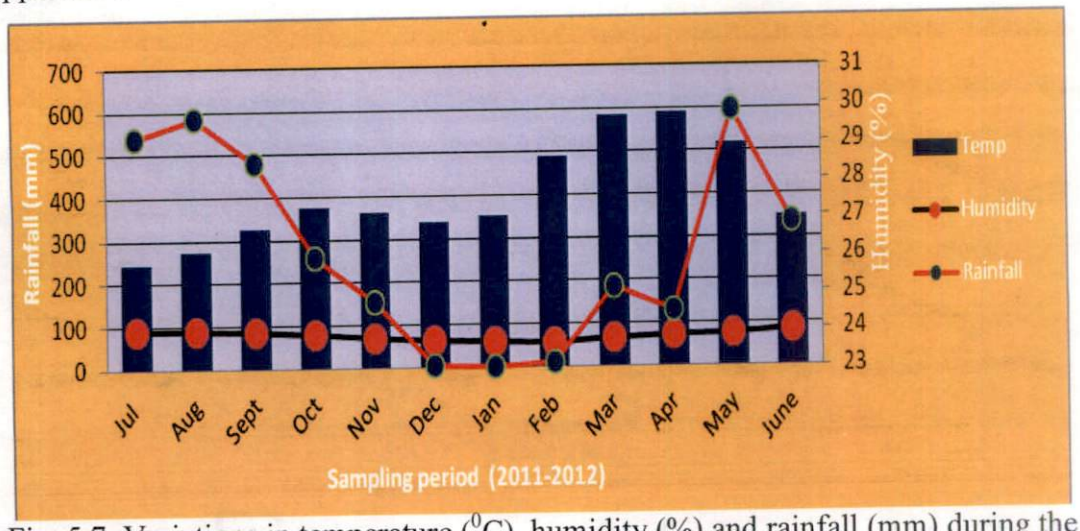

Fig. 5.7. Variations in temperature (^{0}C), humidity (%) and rainfall (mm) during the period of study at Kalamassery

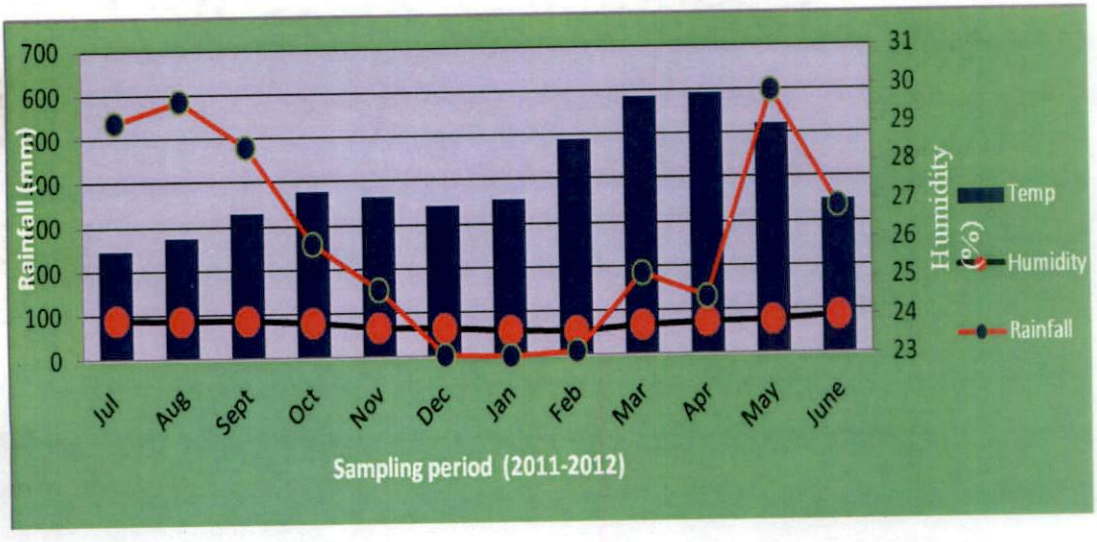

Fig.5.8. Variations in temperature (^{0}C), humidity (%) and rainfall (mm) during the period of study at Laloor

Fig.5.7 and 5.8 illustrates the variations in climatic factors during the different quarters of soil sampling at Kalamassery and Laloor respectively.

On perusal of the data it was found that the average temperature varied from 26^0C (quarter I) to 28.45^0C (quarter IV). Relative humidity ranged from 62.43quarter (III) to 85.5 (Q I) and rainfall with 43.8 mm (quarter III) to 556.8 mm (quarter I). It was clear that the maximum rainfall was received during the months of July, August and Sept 2011 at both sites of study. Rainfall was found to be positively correlated with humidity (0.942**) (Appendix IV). The temperature variations for Laloor ranged from 26.2 ^{0}C (quarter I) to 28.57^0C (quarter IV). Relative humidity was found to be too low as (59.67%) at Q III to the highest value of (86.7 %) at quarter I. Summer showers received at Laloor during quarter III was very meager as 0.1mm to the highest value at quarter I as 584.6 mm. At both the sites, the highest quantity of rainfall was received during the month of Aug 2011 as 605.5 mm at Kalamassery and 584.6mm at Laloor and this was during the first quarter of sampling period which extended from July 2011 to Sept 2011.

There was not much influence of climate on the total heavy metal contents, but in general it was observed that the heavy metal contents were lower during Q IV (rainy season and higher during Q III (summer). There was a negative correlation between Fe with rainfall and humidity (**-0.362***) and (**-0.478****), this may be due to the leaching of the water soluble Fe with rainfall (Das, 2007). The Cr showed negative correlation with temperature (**-0.477****).

Soil moisture (%) and soil temperature (^{0}C)

There was a positive correlation between rainfall and soil moisture (0.429*) and negative correlation between humidity and soil temperature **(-0.418*)** (Appendix IV b). The data clearly gives the indication that the effect of rainfall may be much pronounced on soil moisture in contrast to soil temperature. With reference to different quarters, the soil moisture showed significant variations (Fig.5.9). The highest soil moisture (15.5 %) was recorded during quarter I and the lowest (0.10 %) at quarter IV. Regarding the soil temperature (Fig.5.10) the maximum soil

temperature was recorded during quarter III which coincided almost with the atmospheric temperature and the lowest temperature (29.81) at quarter IV. The soil temperature recorded slightly lower values during monsoon season.

Soil reaction (pH)

Fig 5.10 showed the changes in pH as influenced by different periods of sampling. There was no significant difference in pH for the different quarters. The least value of 5.9 was recorded during quarter II and a value as high as 6.3 was noticed at quarter IV.

Soil organic matter and total nitrogen content of the soil (%)

Soil organic matter showed positive correlation with total N, P and K indicating the role of mineralization and release of major nutrients. Correlation between organic matter and nitrogen was 0.723**, between organic matter and total P was 0.564** and organic matter and K was 0.423*. The total nitrogen content showed negative correlation with humidity **(-0.358*)** and positive correlation with organic matter and total contents of P (0.667**), K (0.645**), Ca and Mg (Appendix IVb). Seasonal variations affected both the soil organic matter and nitrogen in the same way with the maximum contents at quarter III, followed by Quarter II, Quarter IV and Quarter I. In both cases the variations were not significant.

Total phosphorous and potassium content of the soil (%)

Climatic variables did not influence the soil P content, but temperature was found to be positively correlated with soil K content (0.461**) (Appendix IVb).

There was no significant variation among the total P contents recorded at four different quarters of sampling, with maximum at quarter IV and minimum at at quarter I. However there were significant variations noticed for the total K content among the different quarters with the maximum during quarter III, followed by quarter IV, quarter I and quarter II. Being a cation, potassium was severely affected by rainfall variations (Rao and Brar, 2009).

Total calcium and magnesium content of the soil (%)

In contrast to the total Mg content of the soil, there was significant variation for the total Ca content of the soil recorded at four different periods of sampling. The maximum content was registered at quarter IV followed by III and II quarters and minimum at quarter I which almost coincided with high rainfall period.

Total iron and aluminium content of the soil (%)

There existed a negative relationship between Fe and rainfall **(-0.478**)** and Fe and soil moisture **(-0.461**)** (Appendix IVc), such relationship was not noticed in the case of total Al content of the soil. Both Fe and Al followed the same seasonal variations with respect to different periods of sampling. The contents were found to be the maximum at quarter II, followed by quarter III, quarter IV and the quarter I. Though the influence of seasons was found to be significant for Fe, it was not significant for Al.

Total zinc and copper content of the soil (mg kg^{-1})

With the advancement of the period of sampling the total Zn content of the soil decreased. Whereas the total Cu was found to be maximum with quarter III and decreased with monsoon periods. In case of micronutrients the effect of period of sampling was found to be non significant.

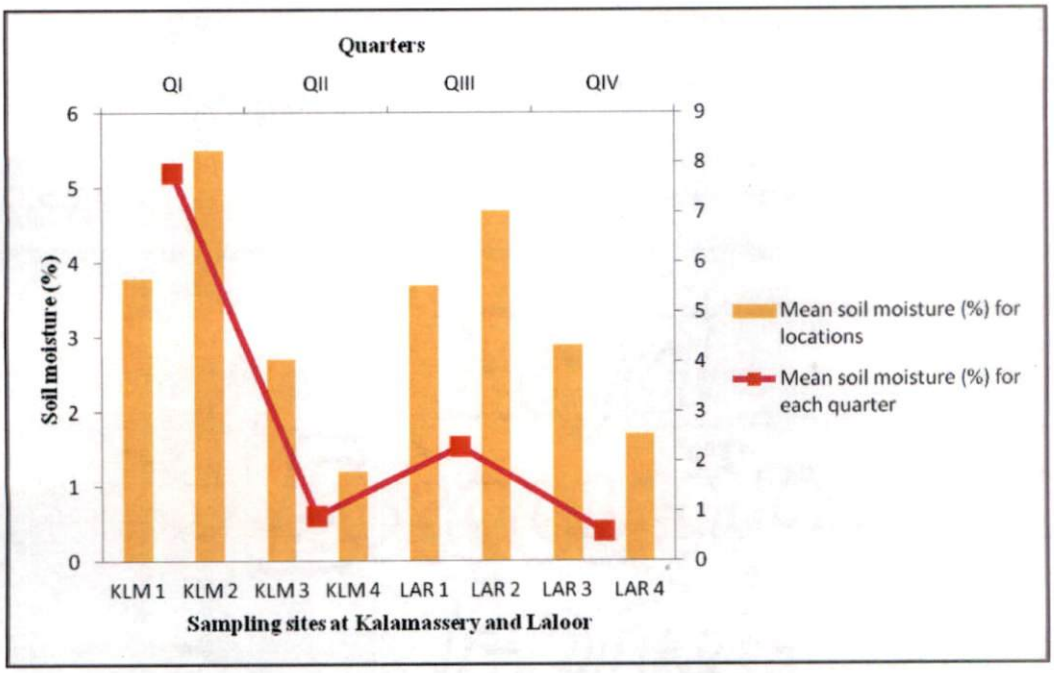

Fig.5.9. Quarter wise variation of Soil moisture at different sites of Kalamassery and Laloor

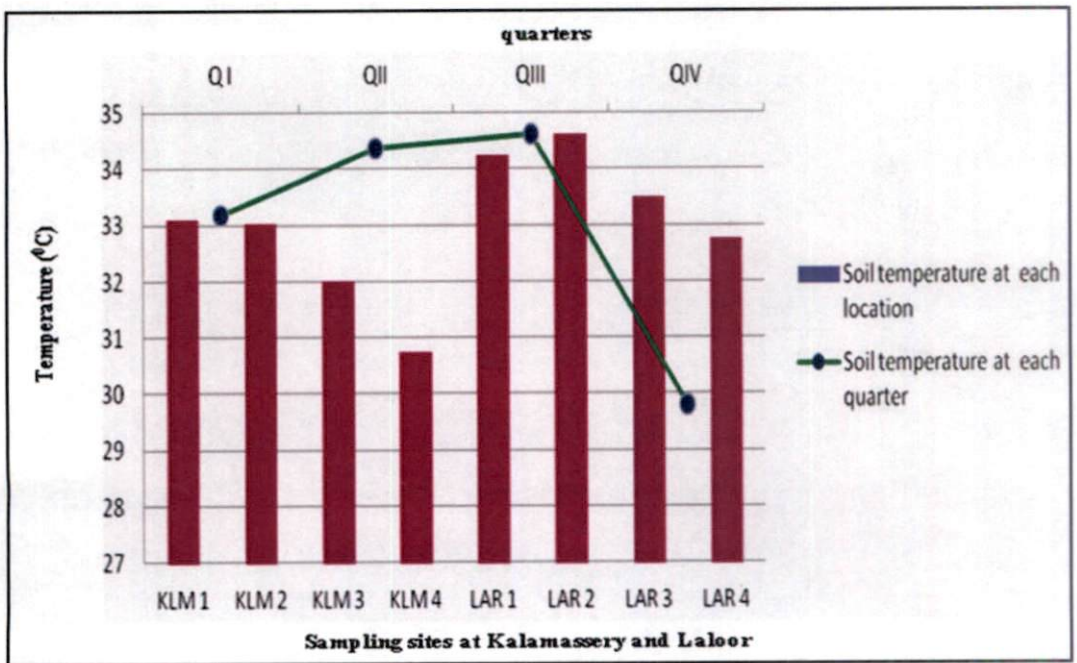

Fig.5.10. Quarter wise variation of soil temperature at different sites of Kalamassery and Laloor

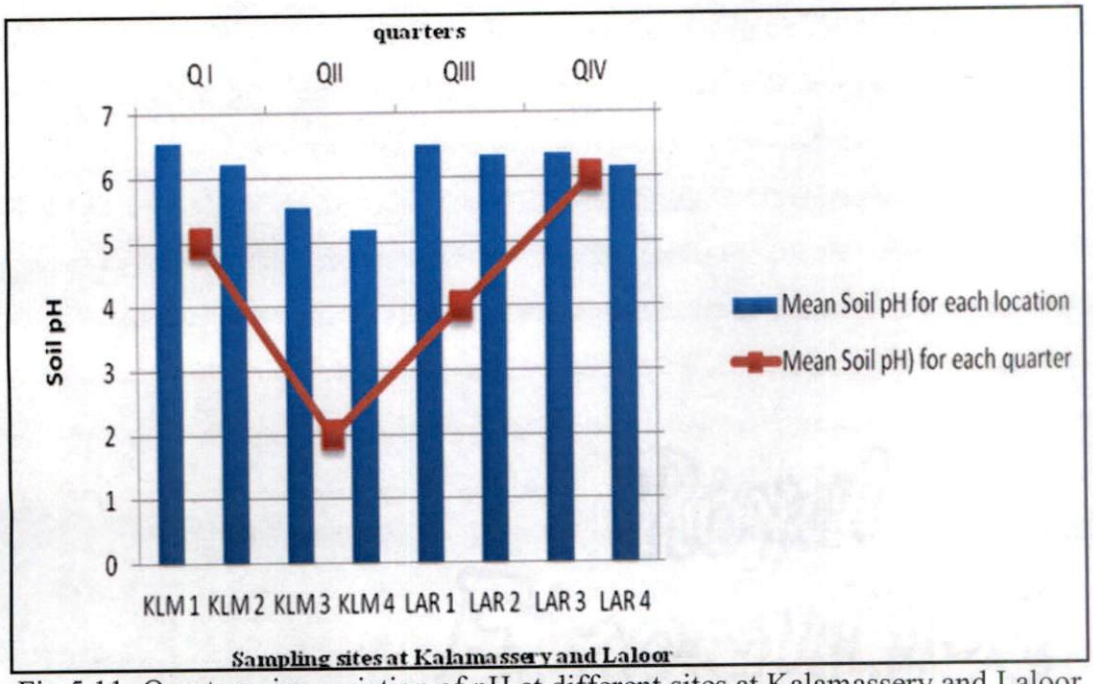

Fig.5.11. Quarter wise variation of pH at different sites at Kalamassery and Laloor

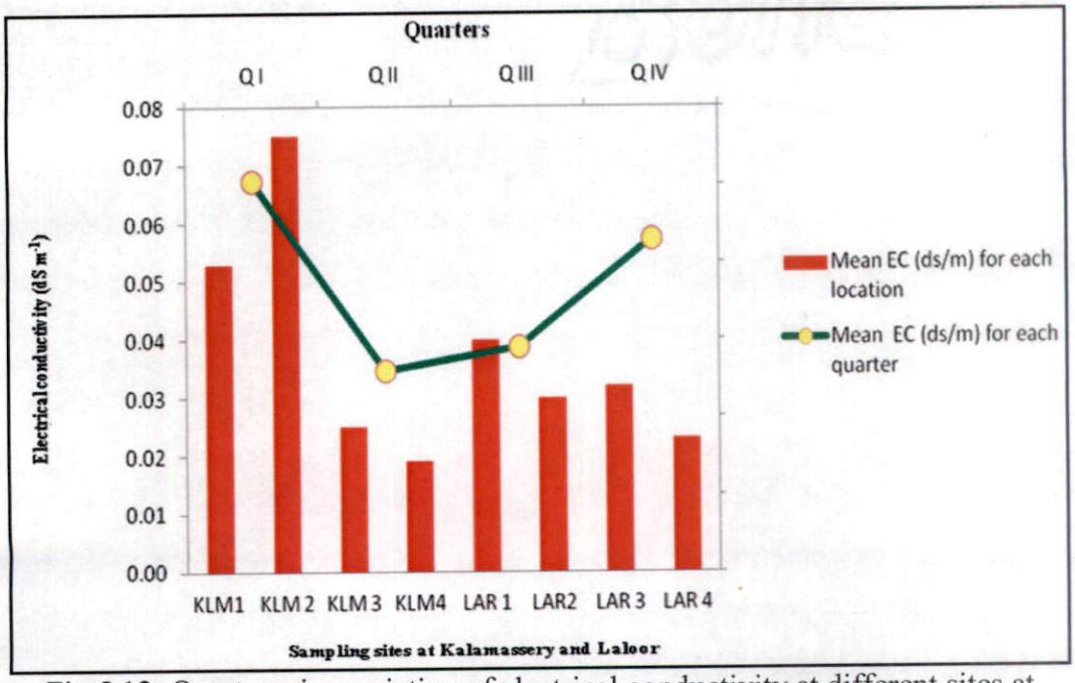

Fig.5.12. Quarter wise variation of electrical conductivity at different sites at Kalamassery and Laloor

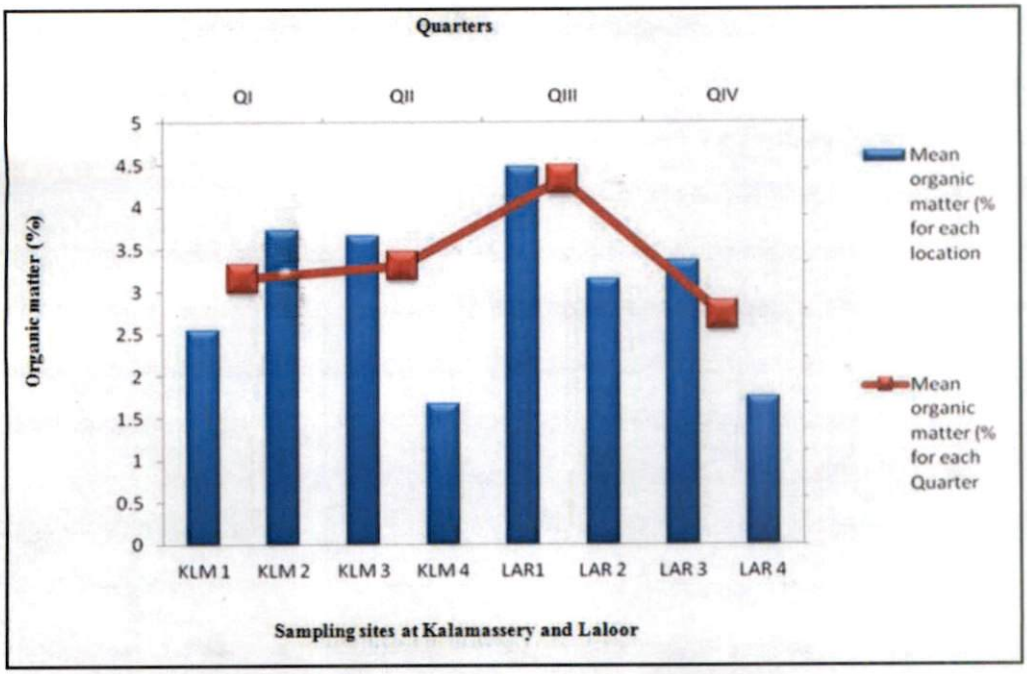

Fig.5.13. Quarter wise variation of organic matter at different sites at Kalamassery and Laloor

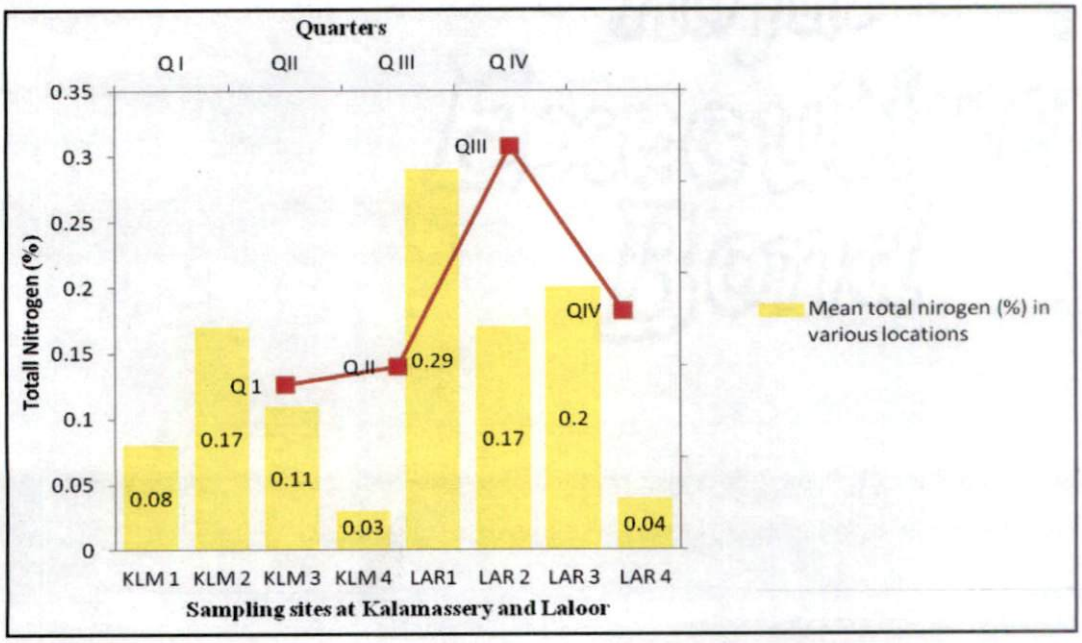

Fig. 5.14. Quarter wise variation of total nitrogen at different sites at Kalamassery and Laloor

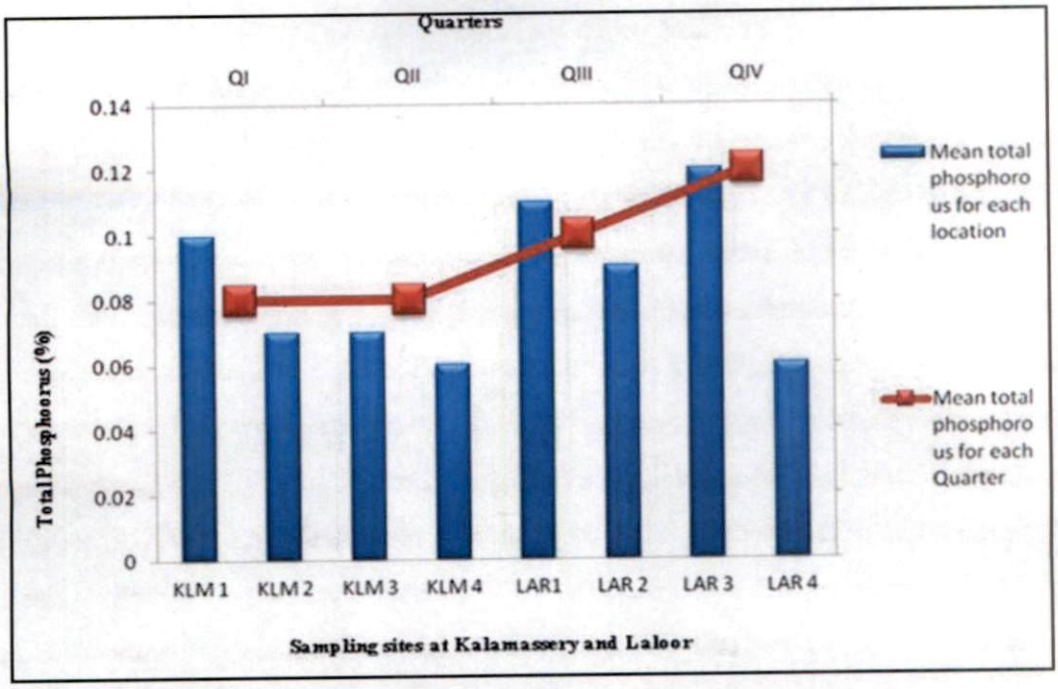

Fig.5.15. Quarter wise variation of total phosphorus at different sites of Kalamassery and Laloor

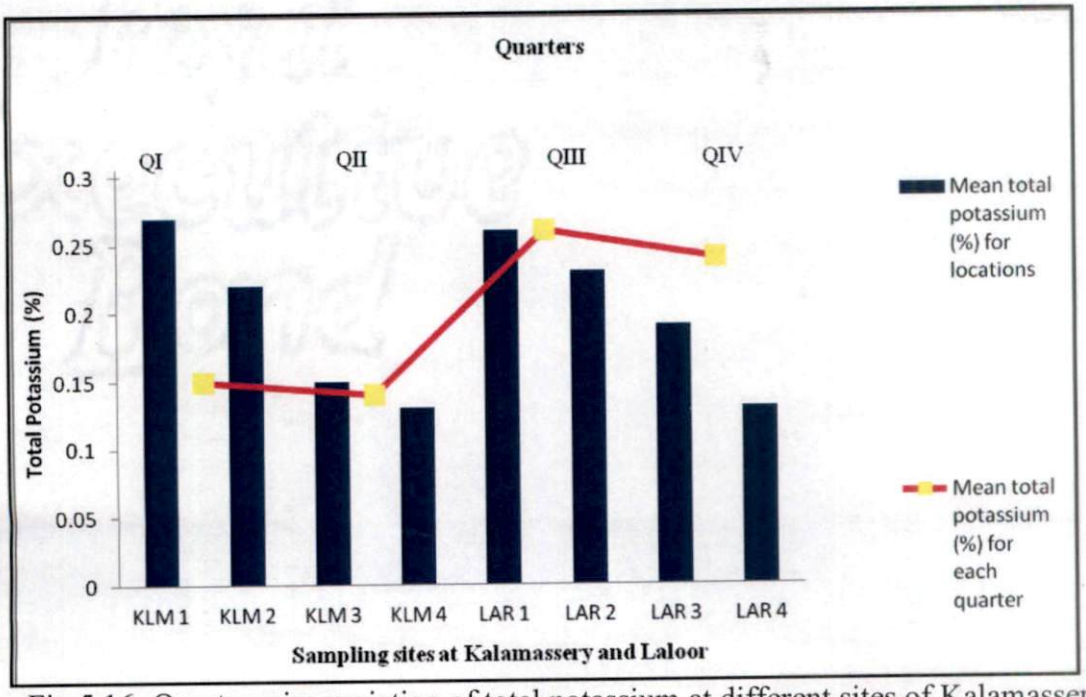

Fig.5.16. Quarter wise variation of total potassium at different sites of Kalamassery and Laloor

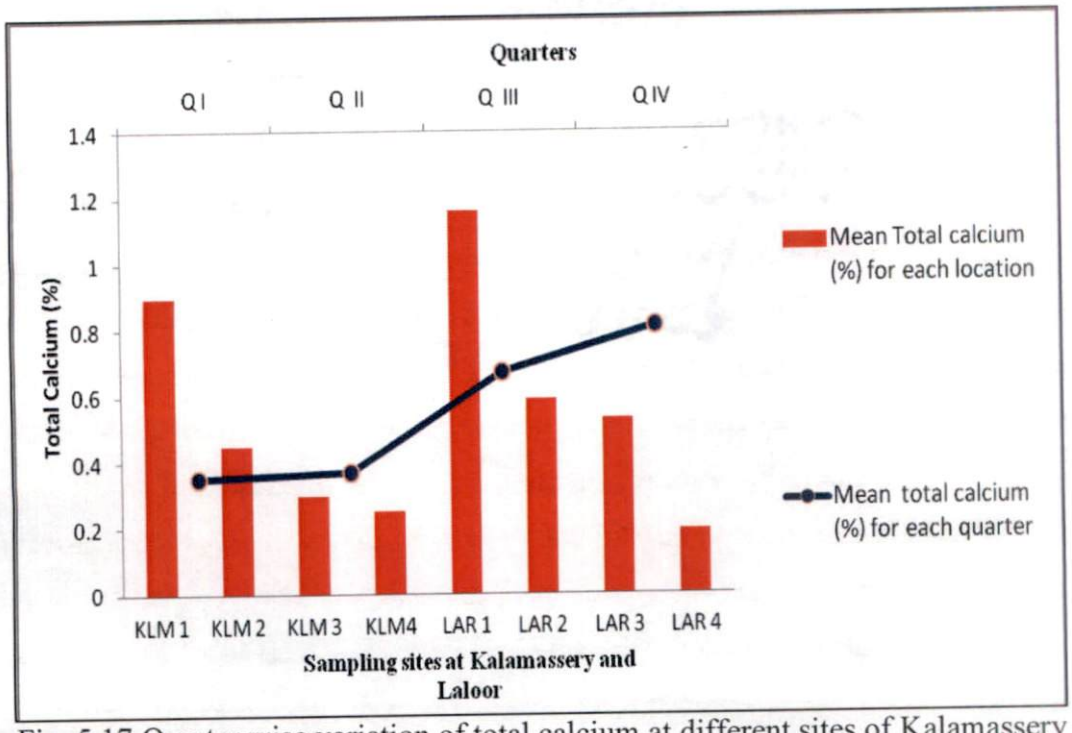

Fig. 5.17.Quarter wise variation of total calcium at different sites of Kalamassery and Laloor

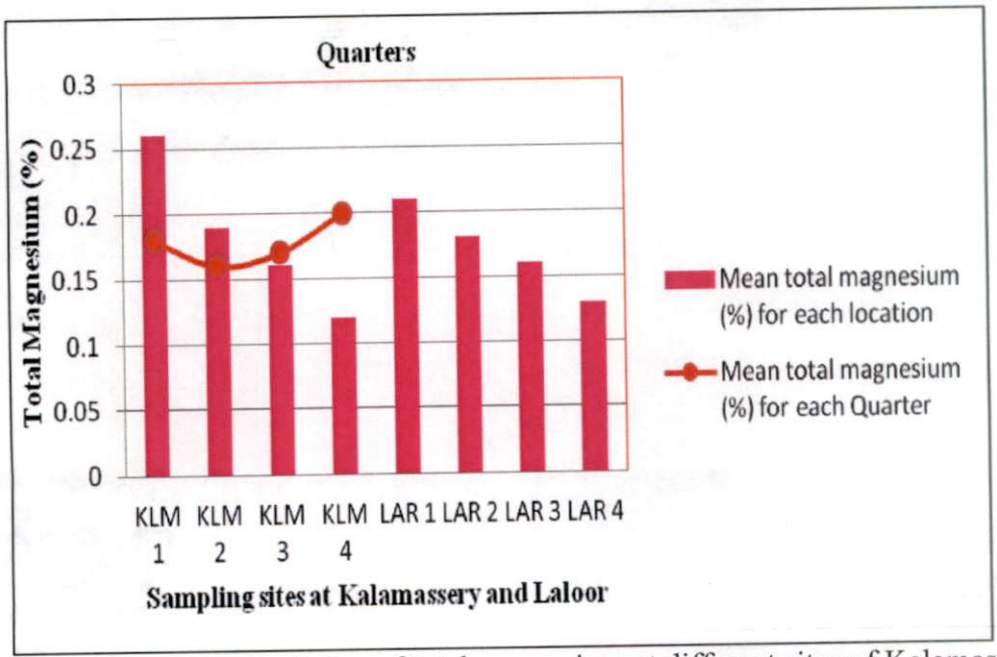

Fig.5.18. Quarter wise variation of total magnesium at different sites of Kalamassery and Laloor

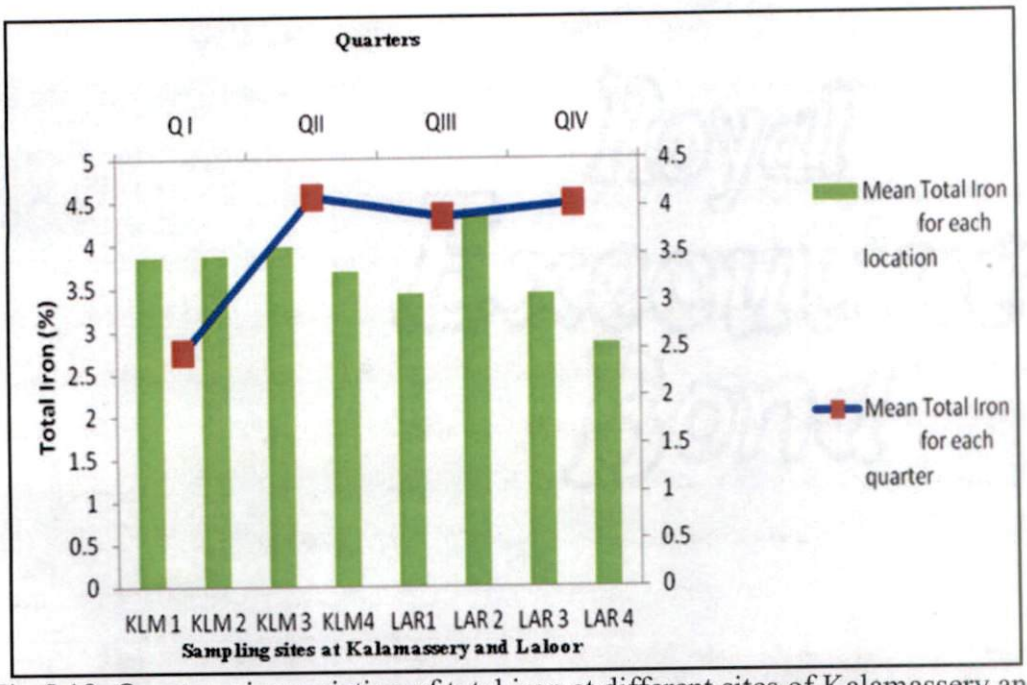

Fig.5.19. Quarter wise variation of total iron at different sites of Kalamassery and Laloor

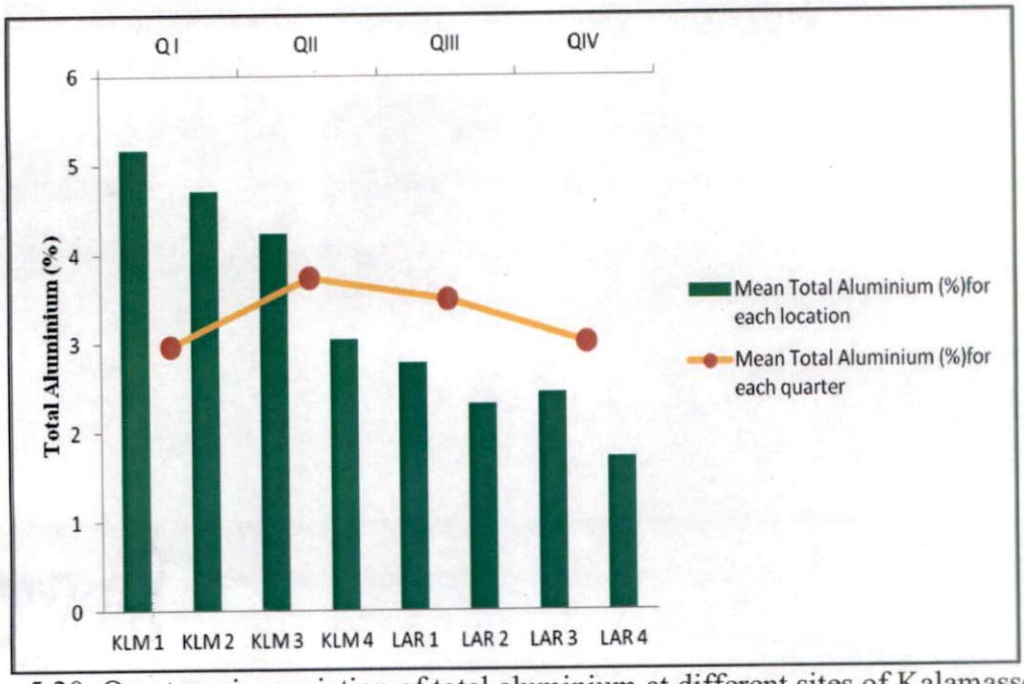

Fig. 5.20. Quarter wise variation of total aluminium at different sites of Kalamassery and Laloor

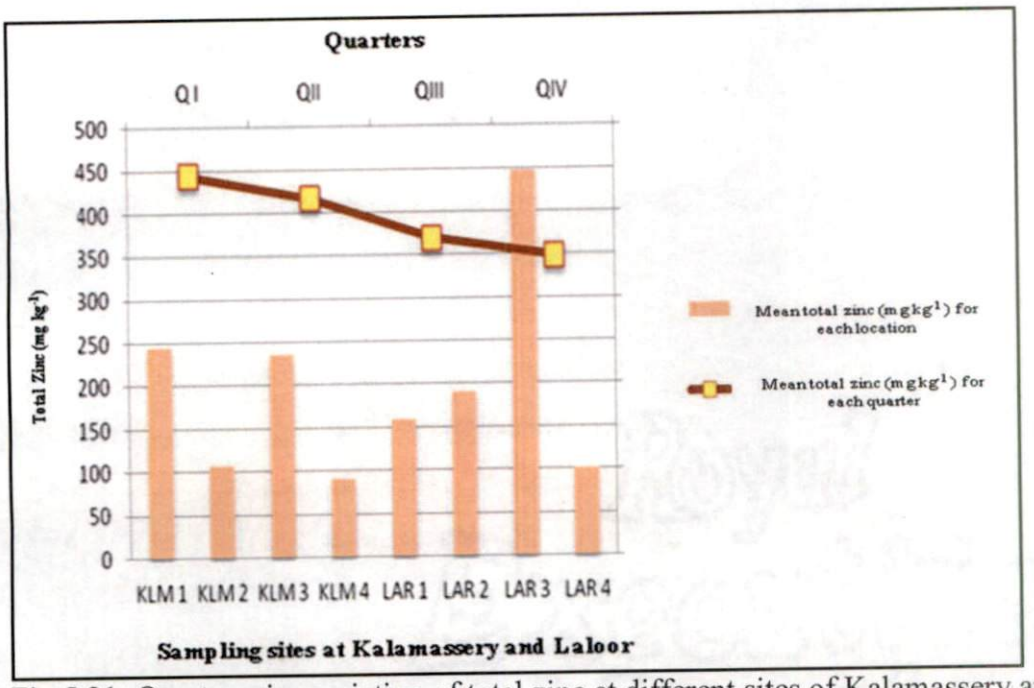

Fig.5.21. Quarter wise variation of total zinc at different sites of Kalamassery and Laloor

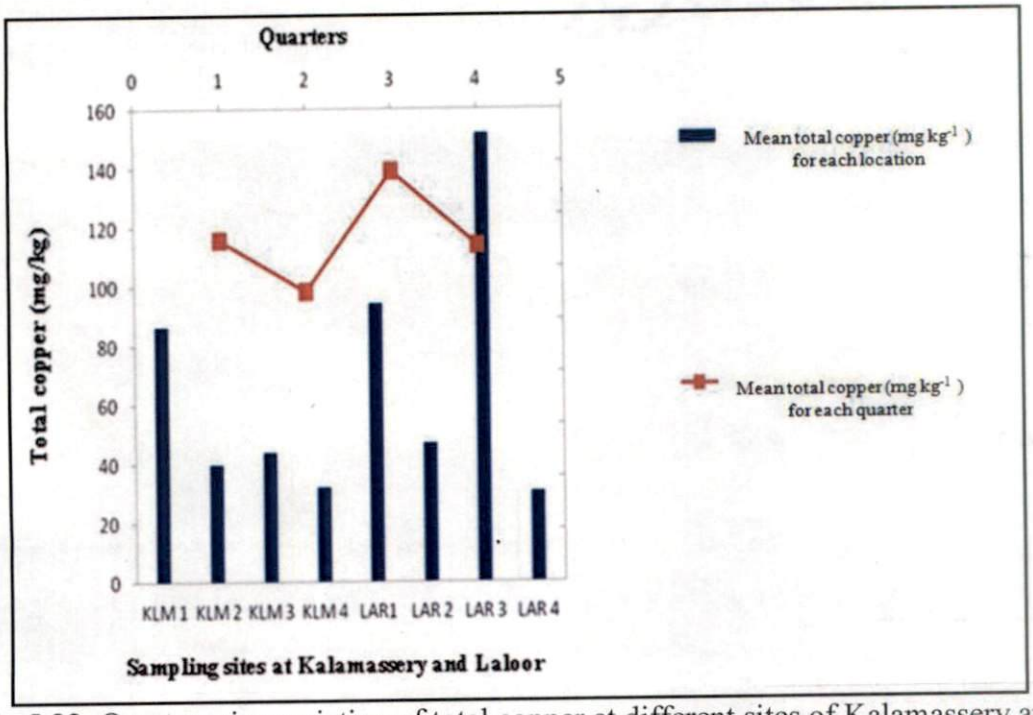

Fig.5.22. Quarter wise variation of total copper at different sites of Kalamassery and Laloor

Total lead and cobalt content of soil (mg kg^{-1})

Both Pb as well as Co was found to be positively correlated with soil temperature (0.388*). The variations were also found to be in the same manner as the highest at quarter II with the variation in soil temperature and the lowest at quarter IV. The effects of the different periods of sampling were found to be non significant in both cases.

Total nickel and chromium content of the soil (mg kg^{-1})

Though there was no influence for the climatic factors on total Ni content of the soil, the temperature variations negatively influenced the chromium (-0.477**) contents. Nickel followed the same trend as that of Co, whereas Cr followed the same trend of Cd with respect to the different periods of sampling. Maximum Ni content was noticed at quarter II and in the case of Cr, the highest was at quarter I closely followed by quarter II.

Total mercury and cadmium content of the soil (mg kg^{-1})

There was no significant variation in Hg during the four quarters in contrast to Cd, which showed significant difference at different quarters. It was found to be higher in quarter I, followed by quarter II, quarter IV and quarter III. However, the Hg content was found to be the least at quarter III (0.5 mg kg-^{1}).

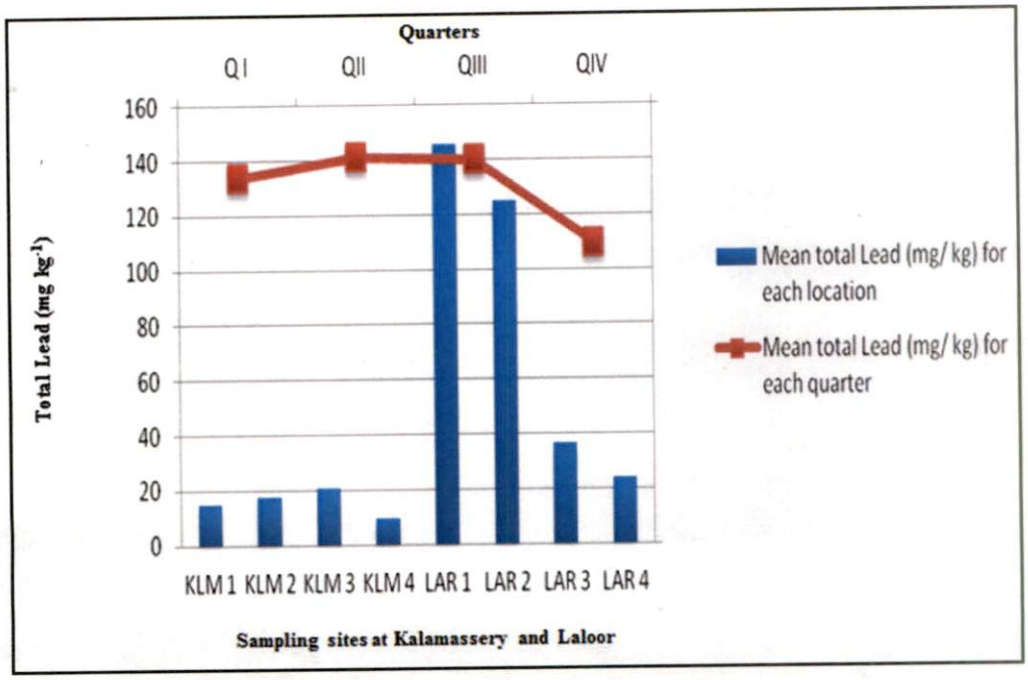

Fig. 5.23. Quarter wise variation of total lead at the different sites of Kalamassery and Laloor

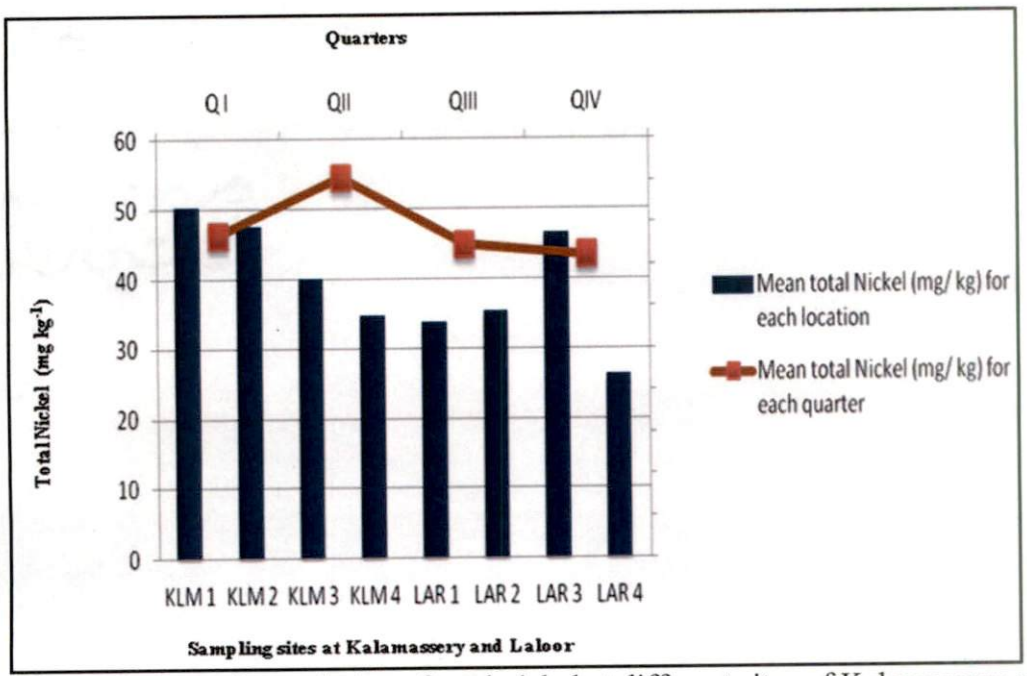

Fig. 5.24. Quarter wise variation of total nickel at different sites of Kalamassery and Laloor

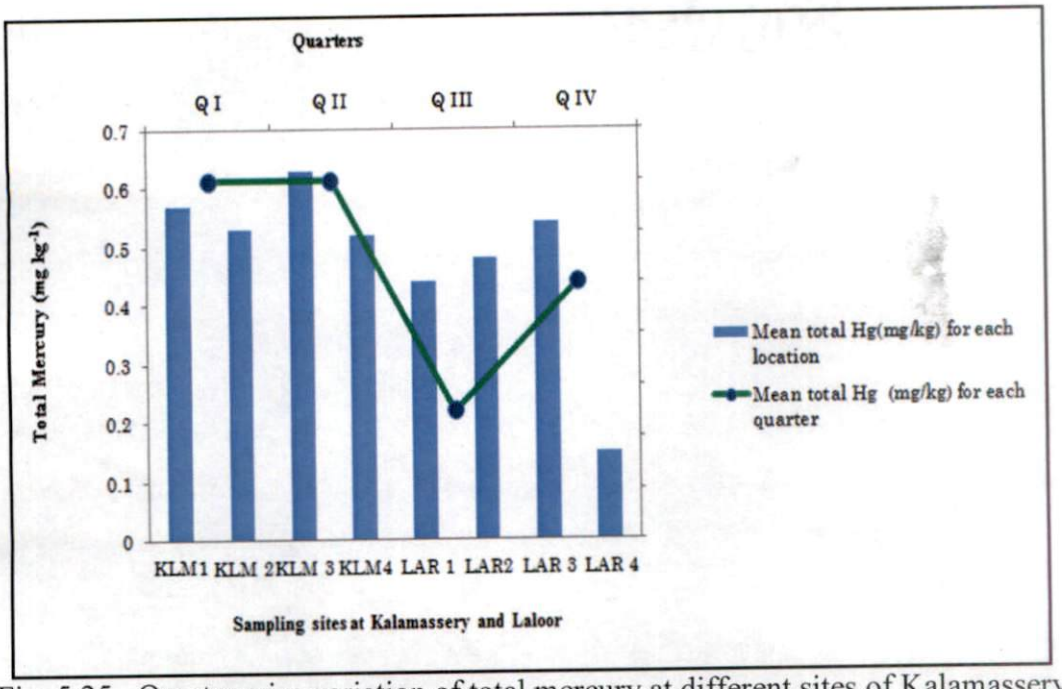

Fig. 5.25. Quarter wise variation of total mercury at different sites of Kalamassery and Laloor

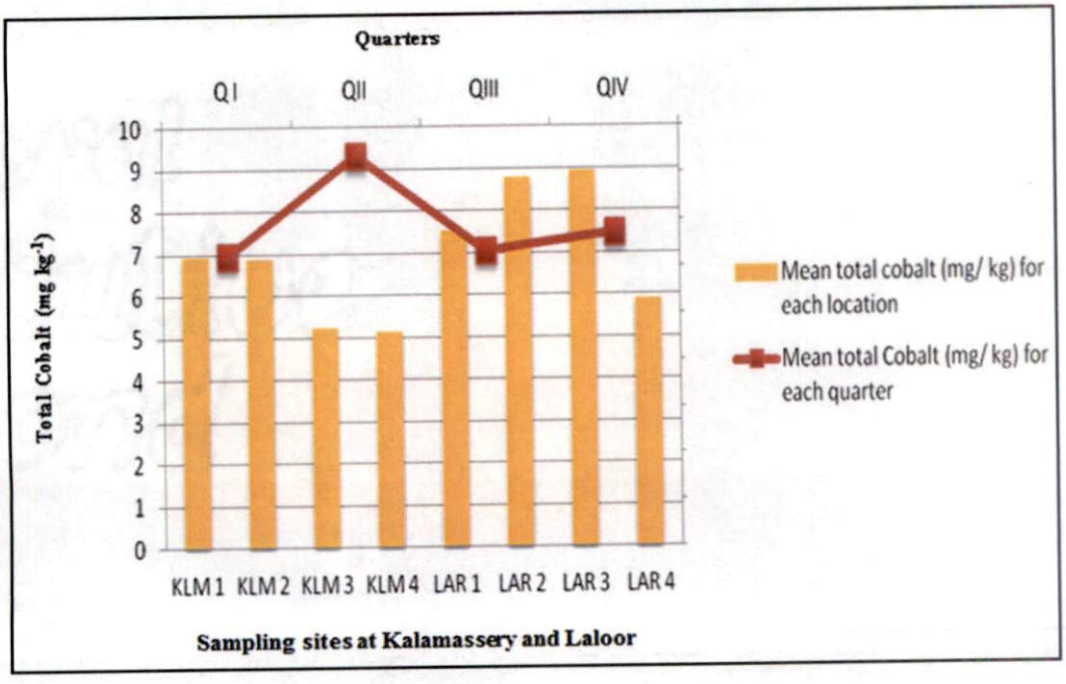

Fig. 5 26. Quarter wise variation of total cobalt at different sites of Kalamassery and Laloor

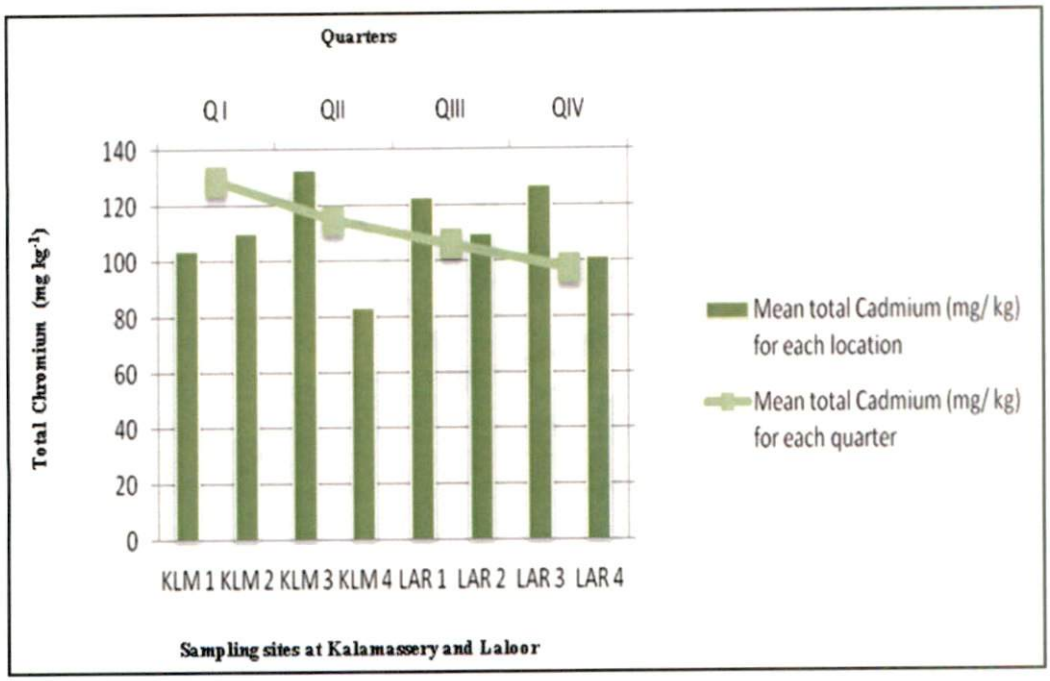

Fig. 5.27. Quarter wise variation of total chromium at different sites of Kalamassery and Laloor

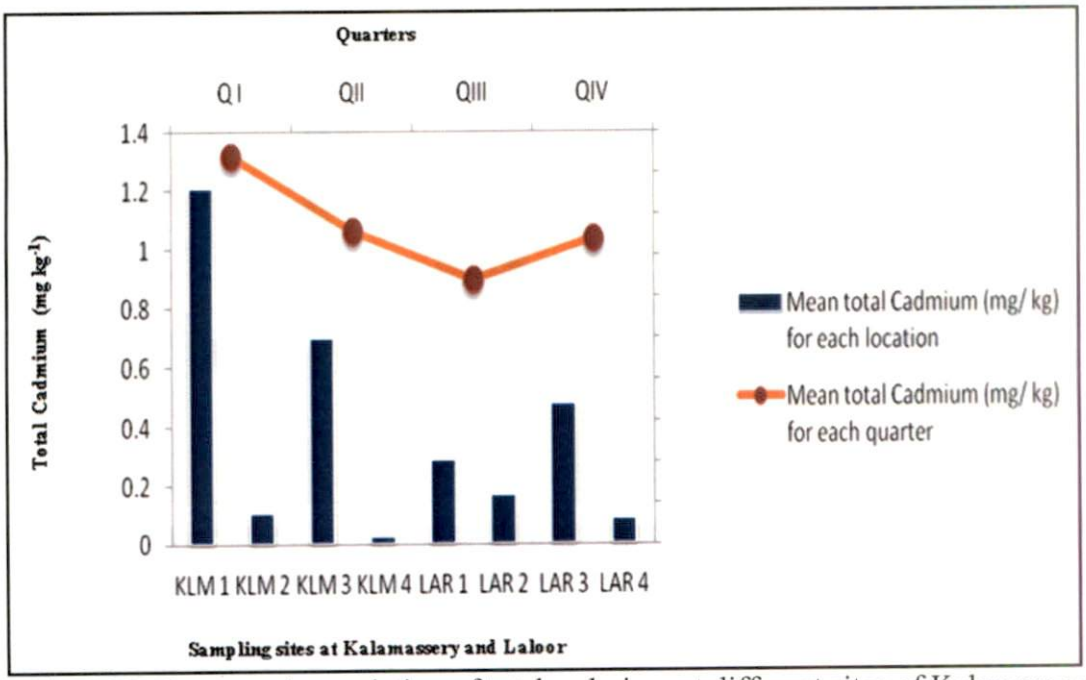

Fig 5.28. Quarter wise variation of total cadmium at different sites of Kalamassery and Laloor

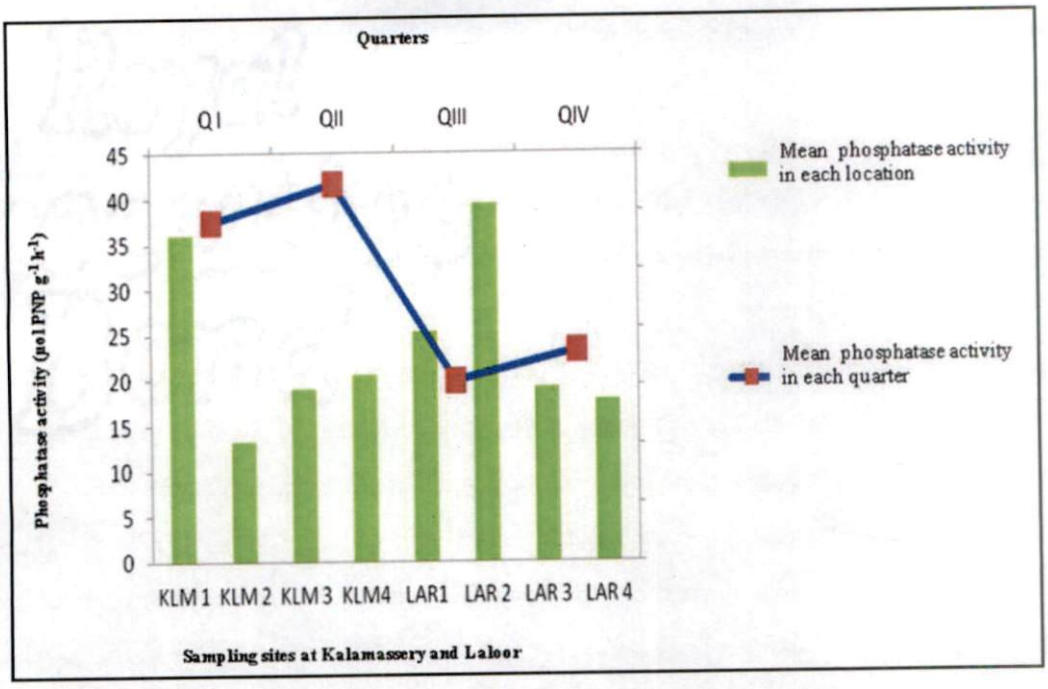

Fig.5.29. Quarter wise variation of phosphatase activity at the different sampling sites of Kalamassery and Laloor

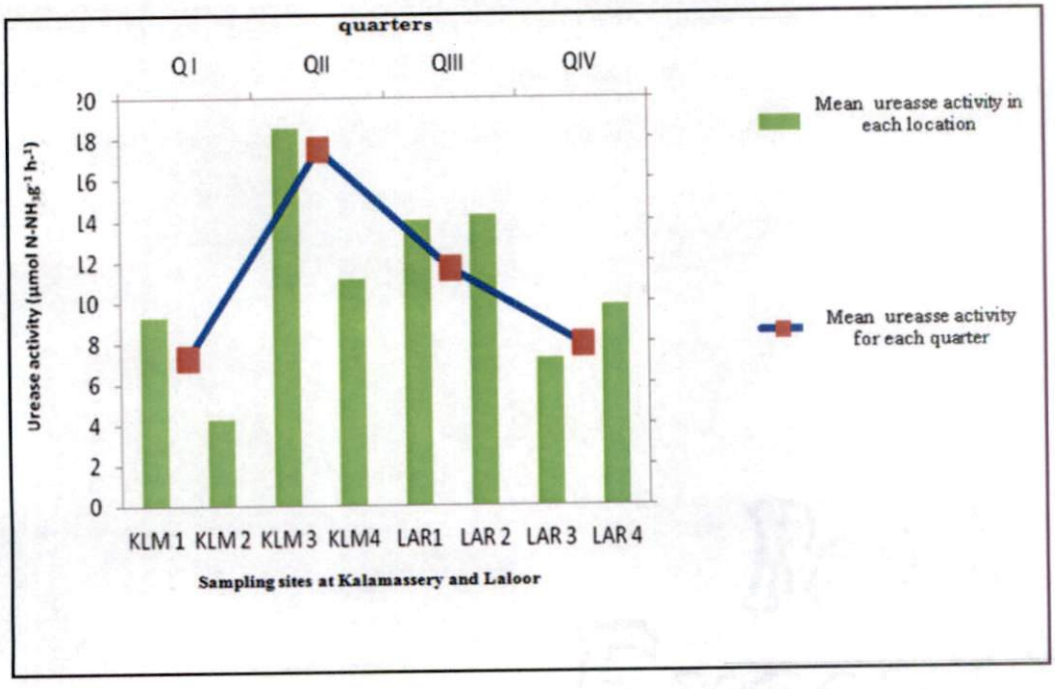

Fig.5.30. Quarter wise variation of urease activity at the different sampling sites of Kalamassery and Laloor

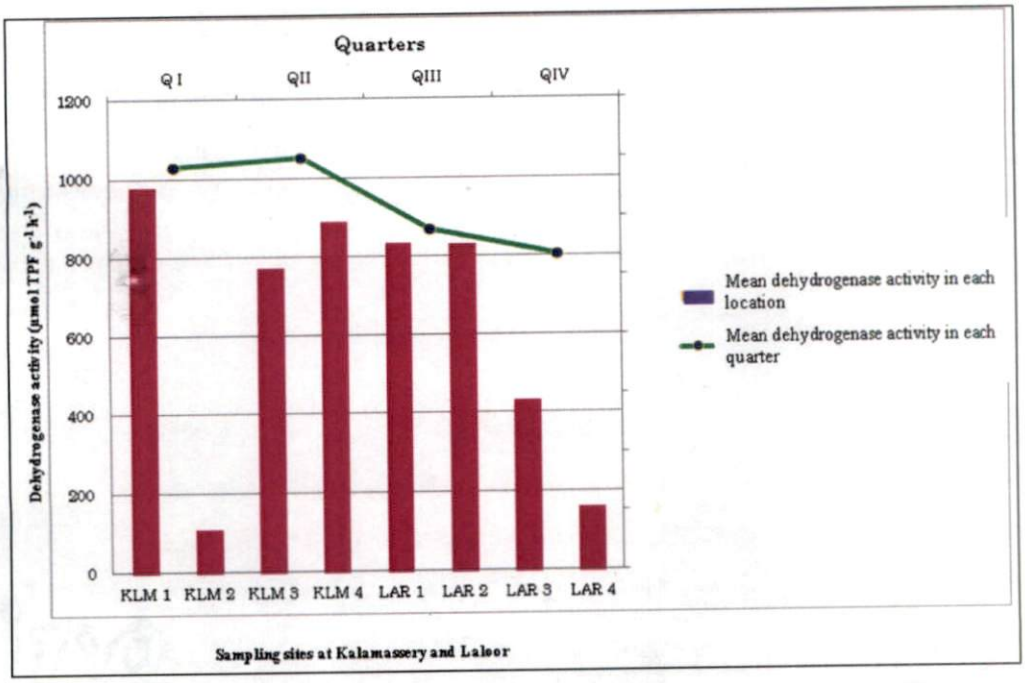

Fig. 5.31. Quarter wise variation of dehyddrogenase activity at the different sampling sites of Kalamassery and Laloor

5.1.3 Effect of climate/sampling intervals on enzymatic activity

Unlike dehydrogenase activity of the soil, phosphatase activity of the soil was found to be negatively correlated with temperature and urease was negatively correlated with humidity and rainfall. There was significant variation in the phosphatase and urease activity of the soil. However the dehydrogenase activity was not affected by the seasonal variations. On perusal of the Fig. 5.29, Fig.5.30 and Fig.5.31, the activity of almost all enzymes was found to be the highest during quarter II and the least at the quarter IV. At the quarter II, the environmental conditions in the soil including soil moisture, pH and organic matter content were found to be in the optimal level in contrast to the conditions at quarter IV. The activity of soil enzymes is also affected by different abiotic factors such as temperature, moisture, soil pH, and oxygen content. Pavel *et al.* (2004) reported that temperature and moisture influenced enzyme activities indirectly through microbial growth and substrate availability. All the enzymes showed higher contents during

quarter II as compared to other periods of sampling. It was also evident that the contents of heavy metals like Cu, Zn, Cd and Cr were found to be in the least during the period, whereas the contents of Fe, Al, Ni, Pb and Co were found to be at the highest during that period. At the IVth quarter at which all the enzymatic activities were at the minimum level, the Fe content was found to be at the highest level. As the organic matter contents at the dumping sites were higher than non dumping sites, the enzyme activities were also found to be higher at the dumping sites (Sylvia *et al.*, 2005) but there was no correlation found between enzyme and organic matter content. There was also a positive correlation noticed between the two enzymes phosphatase and dehydrogenase.

5.1.4. Physico-chemical properties of the soil/site specifications on heavy metal accumulation

The physico-chemical properties of the soil depend on both natural and anthropogenic factors. Natural pedogenic processes were related to parent material, geomorphology of the area, presence of vegetation, the climatic conditions and other interactions in the environment. The effects of these processes were strictly time dependent and exposed in a quite complex structure of soils. The physico-chemical properties of the soil were influenced by the waste disposition and consequent releaqse of elements in the soil. For instance the dumpsites contain mixture of both organic and inorganic waste materials such as food wastes, papers, card board, metals, tins, glass, ceramics, battery wastes, textile bags, plastics, sewage night soils other miscellaneous materials (Appendix II).

Soil moisture and soil temperature

As the total quantity of rainfall received at Kalamassery was comparatively higher, the soil retained more soil moisture throughout the period of sampling. The soils of the dumping sites at both the locations recorded more soil moisture percentage compared to non dumping site due to the presence of biodegradable materials at the dumping sites (Appendix II). This significant variation was not

accounted for the soil temperature of the dumping and non dumping sites, with more atmospheric temperature recorded at Laloor, significant higher soil temperature was noticed for the same location as compared to Kalamassery. The soil temperature had positive correlation with some heavy metals. There was a positive correlation between Pb and soil temperature (0.499*) and Co and soil temperature (0.388*).

Soil pH

The pH was found to be significantly positively correlated with bases like K, Ca and Mg. All these contents were found to be higher (Appendix II), the soil pH was found to be 6.3 at Laloor as compared to Kalamassery 5.9. A significant difference was also noticed for the same. At both locations, the pH at the dumping sites was found to be at the higher range, due to the higher biochemical activities at the dumping sites. Impact of muncipal solid waste disposal on soil properties revealed that the values for the physico-chemical parameters increased for the solid waste treated soil in comparison to control. A study on the impact of municipal solid waste dumping on soil quality revealed that the physico-chemical properties of the soil increased for solid waste treated soil than control soil (Goswami and Sarma, 2008).

Soil organic matter and nitrogen content of the soil

The total nitrogen content of the soil was positively correlated with organic matter. Both were found to be more at Laloor compared to Kalamassery. However the dumping sites of both locations recorded more organic matter due to biodegradable material at the dumping site (Goswami and Sarma, 2008). But these effects were not found to be significant for Laloor.

Total phosphorous and potassium content of the soil

Both total P and K were found to be positively correlated with each other and also with pH, organic matter, total N, Ca and Mg contents of the soil. There was significant difference in the total P at both locations and the highest at Laloor. But the total K content was found to be on par with each other. There was no significant difference for the total P and K contents of the soil between the dumping and non dumping sites.

Total calcium and magnesium content of the soil

Total Ca content showed positive correlation with pH, N, P, K and Mg; and for Mg there existed a positive correlation between pH, N, P, Ca and Al. Since the total Mg content varied with pH and total Ca, Laloor recorded more Ca content as compared to Kalamassery and for Mg contents, both the locations were on par. There was no significant variation between total Ca contents at dumping and non dumping site, but the Mg content showed the significant variation.

Total iron and aluminium content of the soil

Total Fe content showed negative correlation with soil moisture and total Al content was positively correlated with Mg content of the soil. Though the total Fe content was found to be on par with Kalamassery and Laloor, the Al content was comparatively higher at Kalamassery. No significant difference in the total Fe content with respect to dumping and non dumping sites in contrast to Al content which was found to be significantly the highest at dumping sites than at the non dumping sites.

Total zinc, copper and manganese content of the soil

There was positive correlation between Zn and Cu contents of the soil. (Appendix IV). The contents of Zn at Laloor were on par with that of Kalamassery. But location wise significant difference was noticed for total Cu (80.89 mg kg^{-1}) which was higher for Laloor compared to Kalamassery (50.59 mg kg^{-1}). Both Zn and Cu showed significant variation on dumping with wastes as the dumping sites at the both locations recorded high contents of the metals (Goswami and Sarma, 2008).

Total lead and cobalt content of the soil

There was no influence of the major physico-chemical properties on total Pb content of the soil, but Co is found to be positively correlated with Fe content of the soil. Laloor had significantly higher contents of both Pb and Co than Kalamassery. There was influence of waste material on the total Pb content as it was more at the dumping site in contrast to total contents of Co which showed no significant variation at dumping and non dumping sites of both locations.

Total nickel and chromium contents of the soil

Total Ni content of the soil showed positive correlation with Mg, Fe and Al content. But the different physico-chemical properties do not influence the Cr content of the soil. The contents of the Ni just like Cr found significant difference with regards to different locations. The contents of both the heavy metals significantly varied between dumping and non dumping sites. This may be due to the contamination of different metals on dumping of the waste materials (Appendix II).

Total cadmium and mercury content of the soil

Total Cd content and Hg contents were found to be more at Kalamassery than Laloor. There was no significant variation in Cd content at both locations. But Hg contents at Kalamassery were found to be significantly higher than at Laloor. At both locations, the dumping sites invariably concentrated with more heavy metals like Cd and Hg.

5.1.5. Effect of physico-chemical properties/ site specifications on soil enzyme activity

In general, the different physico-chemical properties do not significantly influence the various soil enzyme activities. However Fe content positively influenced the soil urease activity and the total content of Pb in the soil with phosphatase activity of the soil. The fraction of metal, in its bioavailable form, is crucial to understand the metal ecological toxicity. The bioavailability of heavy metals is related to their chemical forms in soil (Wang *et al.*, 2007). Here the availability of Fe and Pb will be within a limit in which it favours the soil enzymes urease and phosphatase activities, respectively. Location wise significant difference was noticed for any of the soil enzyme activities. However site wise variations were found to be significant. All the enzyme activities were found to be comparatively higher at Laloor than Kalamassery. The variation was found to be significant on dumping with waste material. The metal present at the dumpsite may inhibit the

enzyme activities of the soil. In contrast to Laloor, the main source of pollution at Kalamassery is from the heavy traffic by vehicles and consequent emission of polluted materials in the atmosphere. Finally these particles will be accumulated in the soil. Laloor mainly constitutes domestic wastes, with higher content of biodegradable material than Kalamassery. Correlation between organic matter, pH and various heavy metals were already reported. The anthropogenic or natural sources of Al in the soil are to be further investigated. Again regular accumulation of organic matter may increase the accumulation of heavy metals in the study area.

5.2 Effect of phytoremediation on the decontamination of waste materials collected from Laloor

As discussed in section 3.1.2, the waste material along with soil was collected from Laloor for phytoremediation studies. The results are presented in the section 4 and the values are as follows:

In general, the heavy metal contents of the initial material was 198.6 mg kg-^{1} for Pb, 11 mg kg^{-1} for Co, 57 mg kg^{-1} for Ni, 105 mg kg^{-1} for Cr and 0.5 mg kg^{-1} for Hg.

Except Co all other heavy metals were above the threshold limit in Laloor. Hence phytoremediation was carried out with material from Laloor. The crops such as vetiver (12 months), sunflower (3 months) and marigold (3 months) were grown (KAU, 2011).

5.2.1 Heavy metal content of material after phytoremediation with different crops

Lead

The results showed that the Pb content was least in the pot grown with vetiver. Hence the removal was maximum in the material grown with vetiver, followed by sunflower and it was least removed by marigold. The removal ratio followed the order vetiver (1.1) > marigold (0.08)> sunflower (0.04). Considering the

Chromium

The removal of Cr was found to be maximum in the material grown with vetiver, followed by sunflower and marigold. The removal ratio followed the order vetiver (10.01) > marigold> (1.02) sunflower (0.23). As the range for Cr is higher in vetiver, it was found to be a good phytoextractor of Cr.

Nickel

The removal of Ni was found to be maximum in the material grown with vetiver followed by sunflower and marigold. The removal ratio followed the order vetiver (5.4) > marigold> (0.41) sunflower (0.11). Vetiver is a good phtoextractor of Ni.

Cobalt

The removal of Co was maximum in the material grown with vetiver, followed by sunflower and marigold. The removal ratio followed the order vetiver (1.3) > marigold (0.7) > sunflower (0.03).

Mercury

The removal of Hg was mainly by vetiver and marigold crops. The removal ratio followed the order vetiver (0.65) and marigold (0.11).

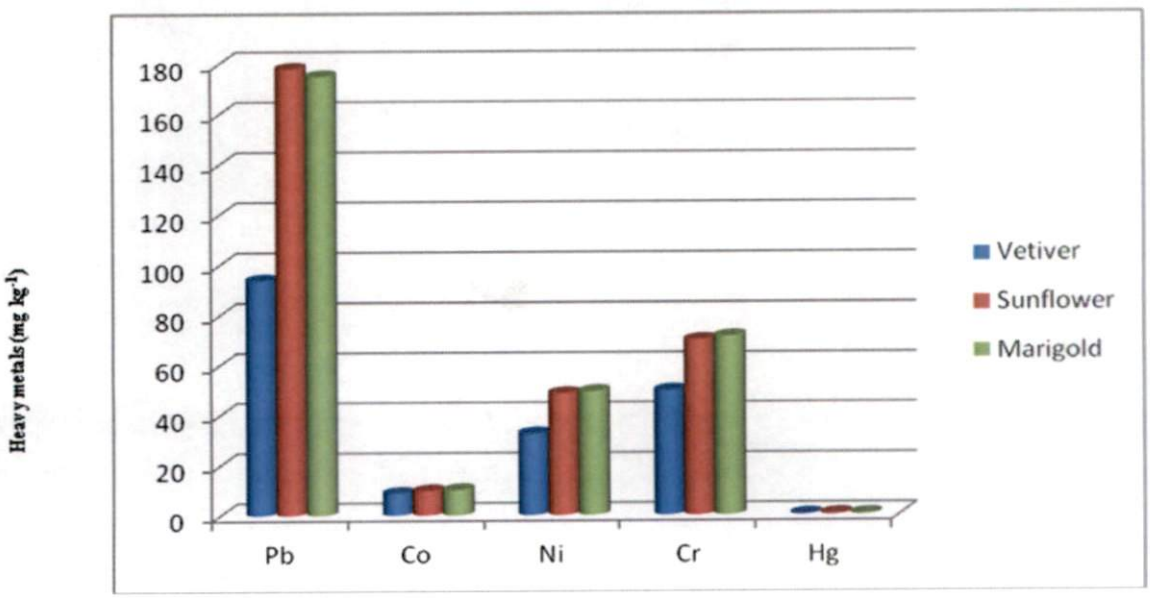

Fig. 5.32. Heavy metal content in the material after phytoremediation with different crops

5.2.2 Heavy metal content of the different plant/parts used for phytoremediation

The results are presented in section 4.2.3 and discussed as follows

Lead

The Pb content in the root parts showed that the highest accumulation was in sunflower followed by marigold and vetiver. Among the different shoots the vetiver was the best accumulator of Pb followed by sunflower and marigold. Among leaves sunflower accumulated more Pb than marigold, but for flowers marigold flowers accumulated more Pb than sunflower. In general, when the different plant parts are compared, it was revealed that there was maximum accumulation of Pb in sunflower roots, significantly different from other plant parts. It has been reported that Pb can adhere to root cell wall, especially in pyrophosphate form (Marschner, 1995). It is inevitable that the Pb accumulation in roots may be a factor which enhances tolerance against Pb toxicity. The translocation factor of Pb was maximum for marigold (1.2) followed by sunflower (0.9) and vetiver (0.5). Translocation factor was found to be lower for vetiver compaired to other crops.

Chromium

In general, the vetiver root accumulated more Cr followed by marigold and sunflower. Shoots also followed the same trend vetiver> marigold> sunflower. On comparison of heavy metal contents in the leaf and flower it was noticed that for both leaf and flower of marigold was better accumulator. The translocation factor of Cr followed the order marigold> (2.5) >sunflower (1.8)> vetiver (1.1). For Cr all the three crops are hyperaccumulators. On perusal of the data it was found that Cr has got some affinity towards marigold plant and the flower accumulated more Cr than other parts.

Nickel

The Ni content was found to be higher in vetiver roots followed by sunflower and marigold. The same trend followed for shoots also. There was no significant

variation in the content of Ni in vetiver roots whereas the content in shoots was significantly different. Sunflower and marigold treatments were on par with each other. Comparing the accumulation of Ni in the leaf and flower parts, sunflower leaf accumulated more Ni than marigold, but not significantly different. Marigold flowers accumulated more Ni compared with sunflower which was significantly different. The translocation factor was the highest for marigold (2.1), followed by sunflower (1.4) and vetiver (0.6).

The results showed that the vetiver is a phytostabiliser for Ni and others are hyperaccumulator and among them marigold accumulated more Ni in the upper part than sunflower.

Cobalt

The Co content was found to be more in vetiver root, followed by sunflower and marigold. There was no significant difference between vetiver and other crops. The same trend noticed for shoot part with less accumulation of Co. The Co content of the soil was also below the threshold level and hence the Co content was less in the plant parts. Co accumulated more in roots with a translocation factor of 0.6 for vetiver and sunflower (0.9) and for marigold (0.4).

Mercury

Mercury mainly accumulated in vetiver and to a lesser extent in marigold shoot and upper parts (leaf and flower). The translocation factor for vetiver was (0.65) and for marigold (1.2).

For the different heavy metals under study the same crop behaved in different way. It can be concluded that vetiver had good phytoremediation potential with a bioconcentration factor more than 2 for metals like Ni, Cr and Hg. Most of the metals are stabilized in the root, so it is a good phytostabilizer for almost all heavy metals except for Cr. Marigold translocated most of the heavy metals from soil except Co, as the contents of Co were also negligible in soil. Sunflower behaved as phytostabiliser for Pb and translocated other heavy metals like Ni, Co and Cr to the aerial part.

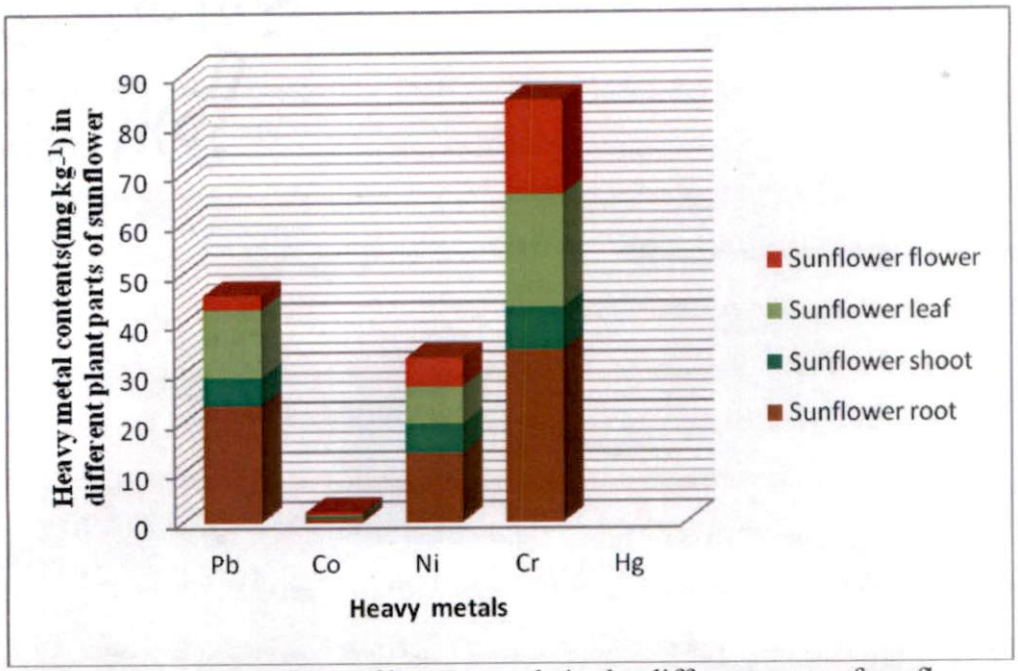

Figure 5.33. Comparison of heavy metals in the different parts of sunflower

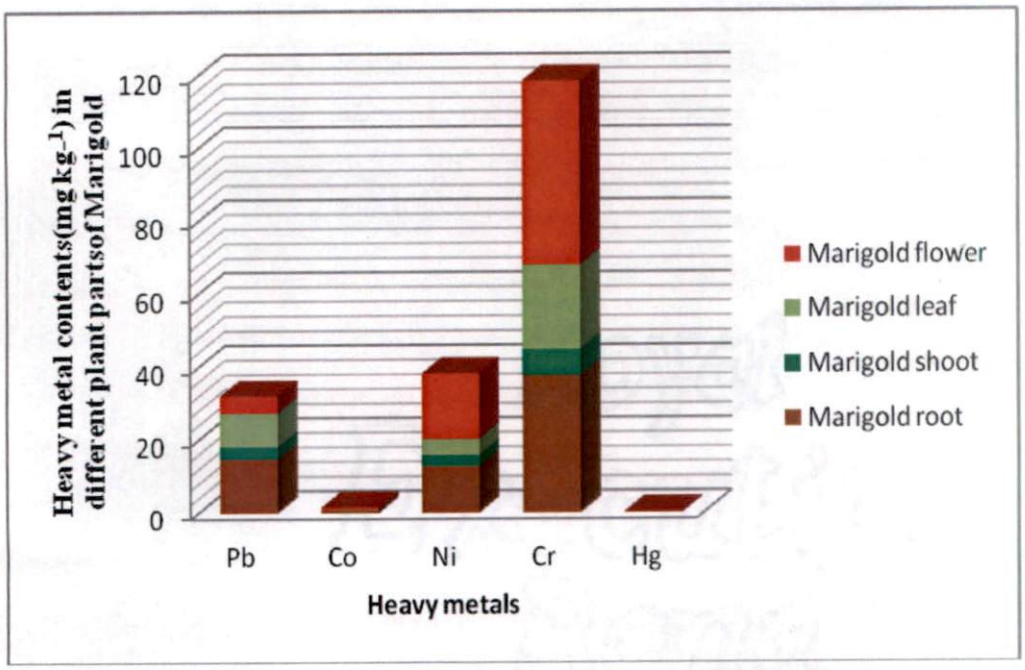

Fig.5.34. Comparison of heavy metals in the different parts of Marigold

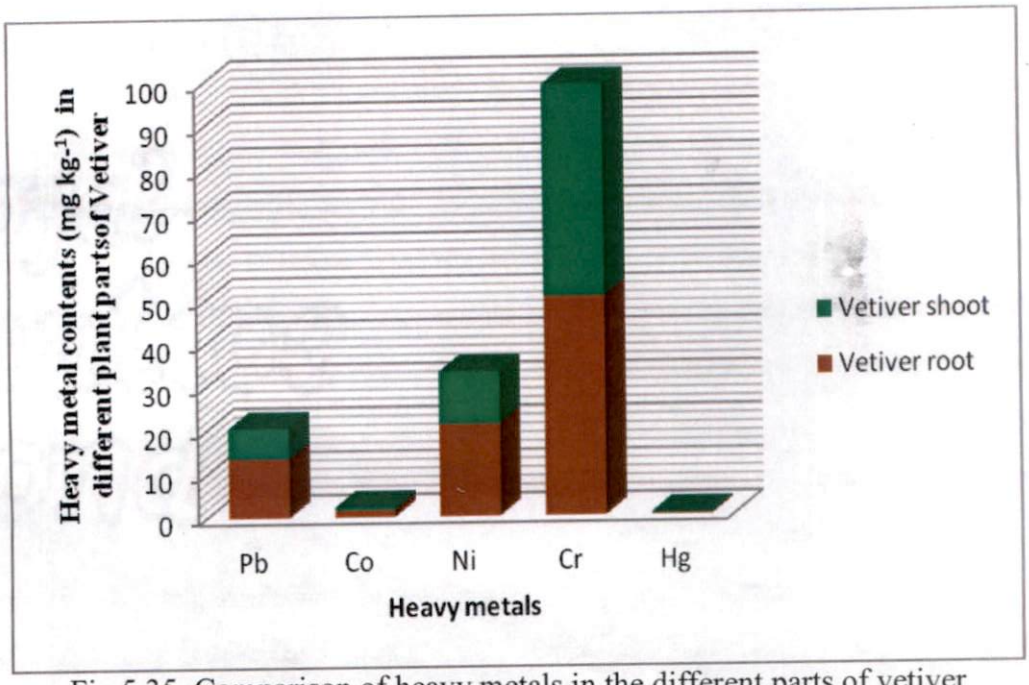

Fig.5.35. Comparison of heavy metals in the different parts of vetiver

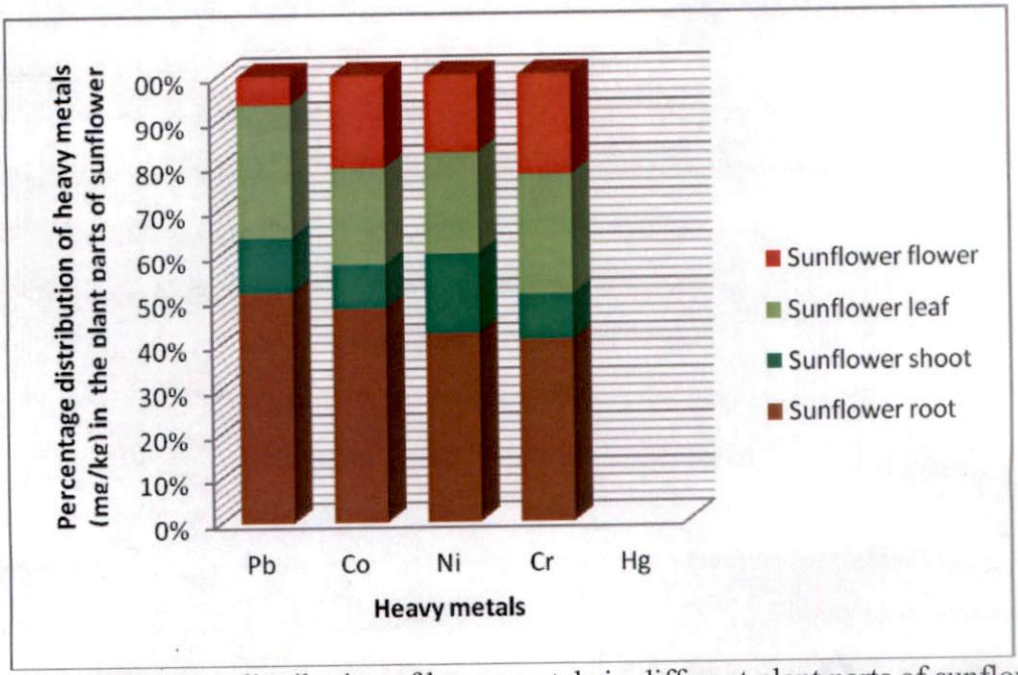

Fig.5.36. Percentage distribution of heavy metals in different plant parts of sunflower

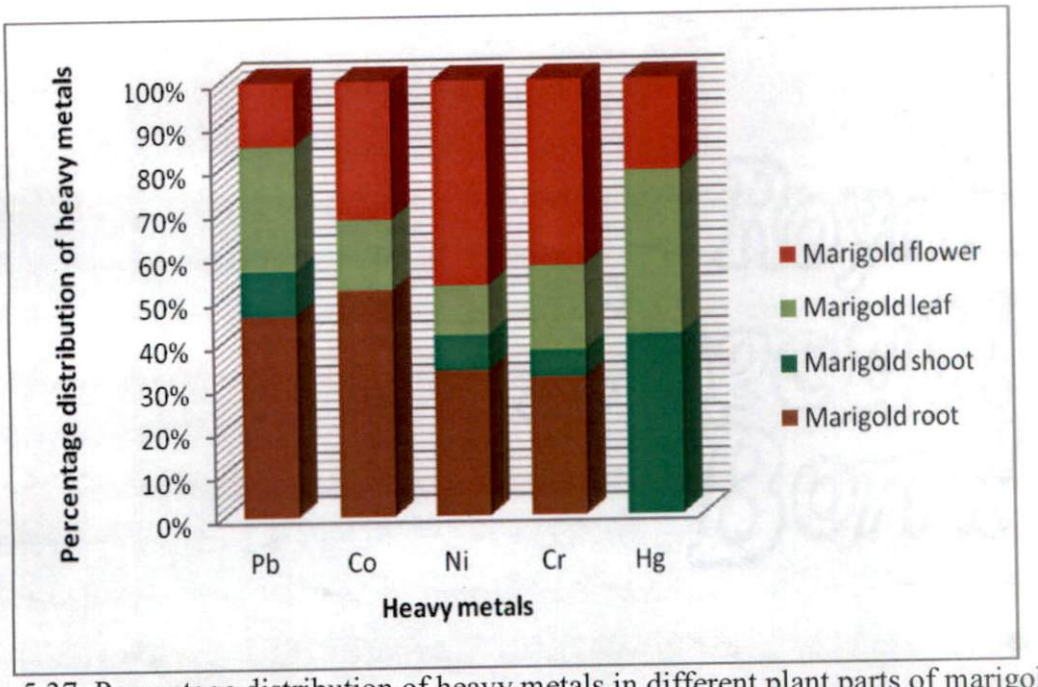

Fig.5.37. Percentage distribution of heavy metals in different plant parts of marigold

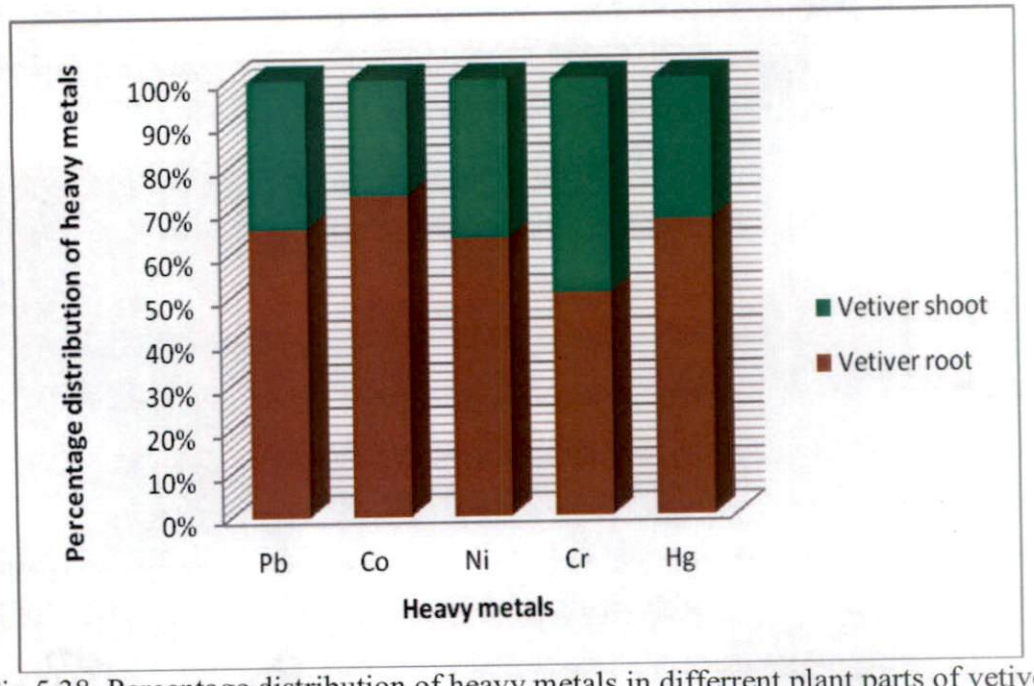

Fig.5.38. Percentage distribution of heavy metals in differrent plant parts of vetiver

5.3 Effect of aerobic and anaerobic methods of composting on the composition of heavy metals in the waste materials

As described in section 3.3 the material was collected from Laloor and subjected to aerobic as well as anaerobic methods of composting for a period of 2 months. The same sample was kept for a period of 2 months. Results of the compost analysis are presented in 4.3 of chapter 4 and the results are discussed below.

5.3.1 Effect of different methods of composting on the nutrient quality of compost and slurry

Soil reaction and electrical conductivity

It was found that there was no significant difference in the pH, which was almost in neutral range for all the three treatments with the highest for slurry. The electrical conductivity was slightly lower for slurry and it was almost same for both aerobic compost and control.

5.3.2 Effect of different methods of composting on the physico-chemical properties of the material

It was found that the total N and total C was higher in aerobic compost compared to anaerobic compost and control. This was due to the fact that during composting equal quantity of waste was treated with cowdung. There was no significant variation for total P and K for the different treatments. For total Ca, Mg and S there was no significant difference among the treatments

All the heavy metals accumulated more in control, followed by aerobic compost and the least found for slurry. There was significant difference in the heavy metal accumulation in compost and control compared to slurry. The process of composting with equal doses of cowdung and waste can promote the complexation of heavy metals (with the fractions of fulvic acid) whose mobility and availability tend to decrease (Stevenson, 1994). Also there will be dilution effect in aerobic compost as compared to control due to the addition of cowdung. In slurry only the water

soluble and easily available heavy metal concentration will be present and hence the concentration of heavy metals will be least compared to other treatments.

The variations in heavy metals under different treatments showed that except for Hg and Cr all others were below the tolerable limit. The maximum permissible level of heavy metal content in the compost is given in appendix VI.

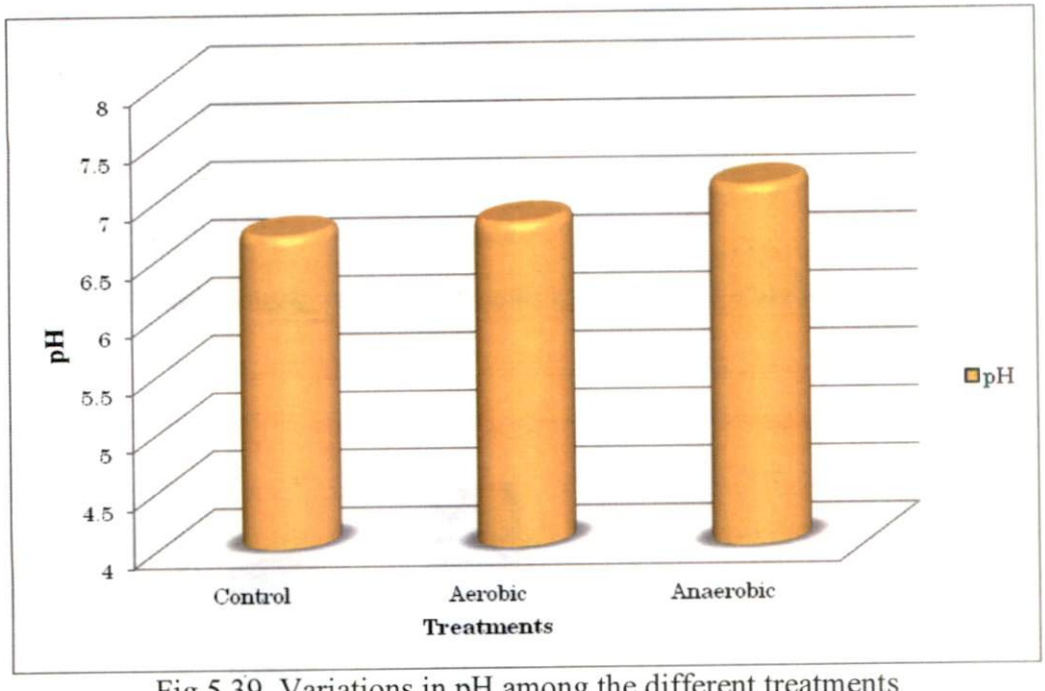

Fig.5.39. Variations in pH among the different treatments

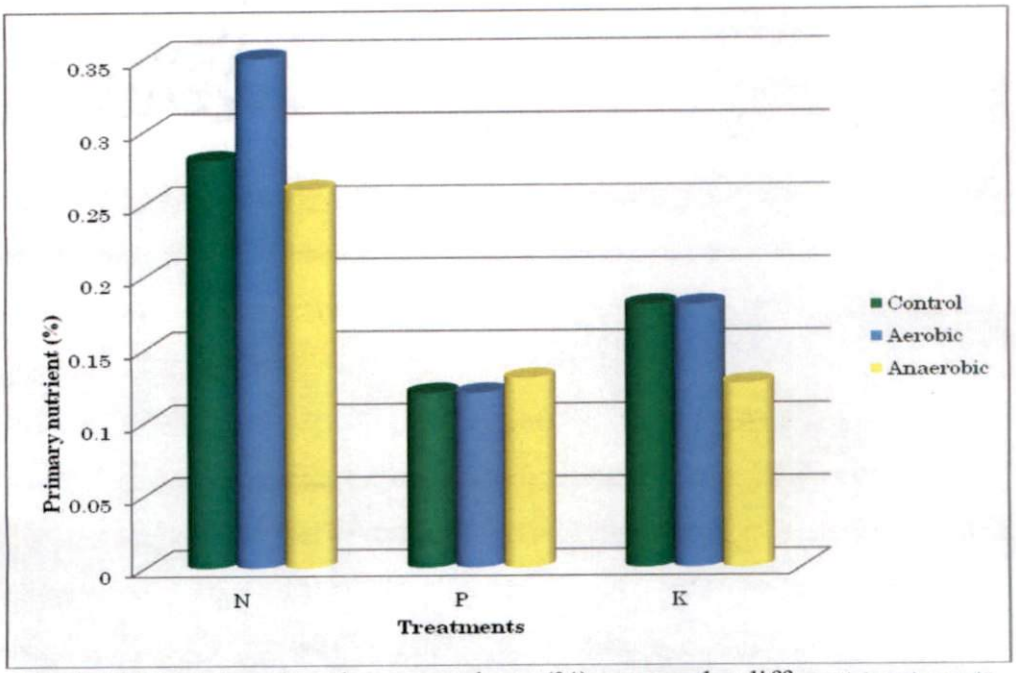

Fig.5.40.Variations in primary nutrients (%) among the different treatments

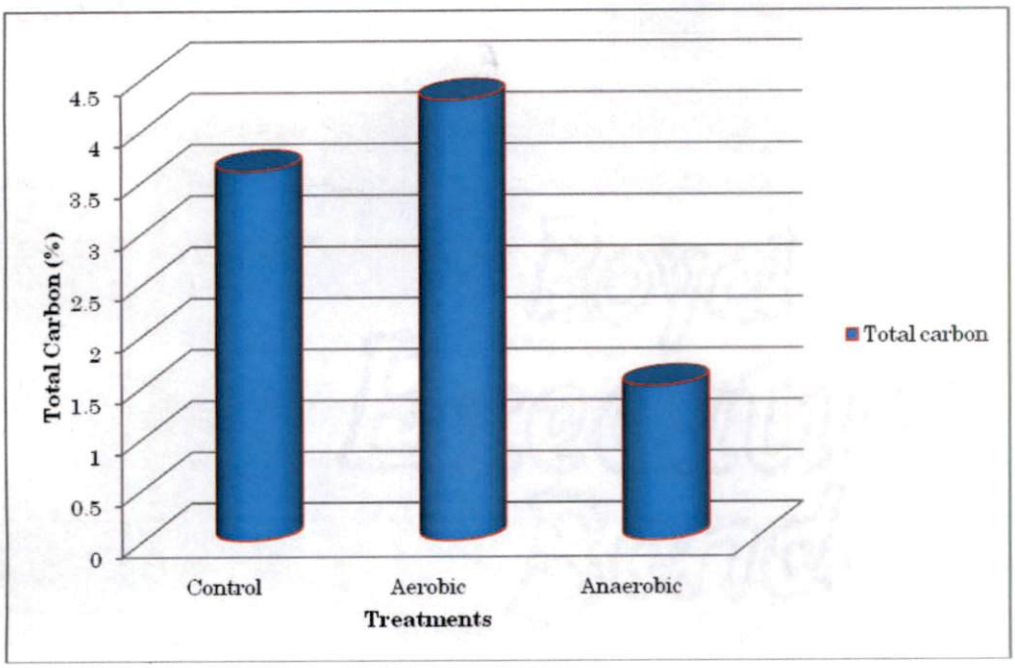

Fig.5.41. Variations in total carbon (%) among the different treatments

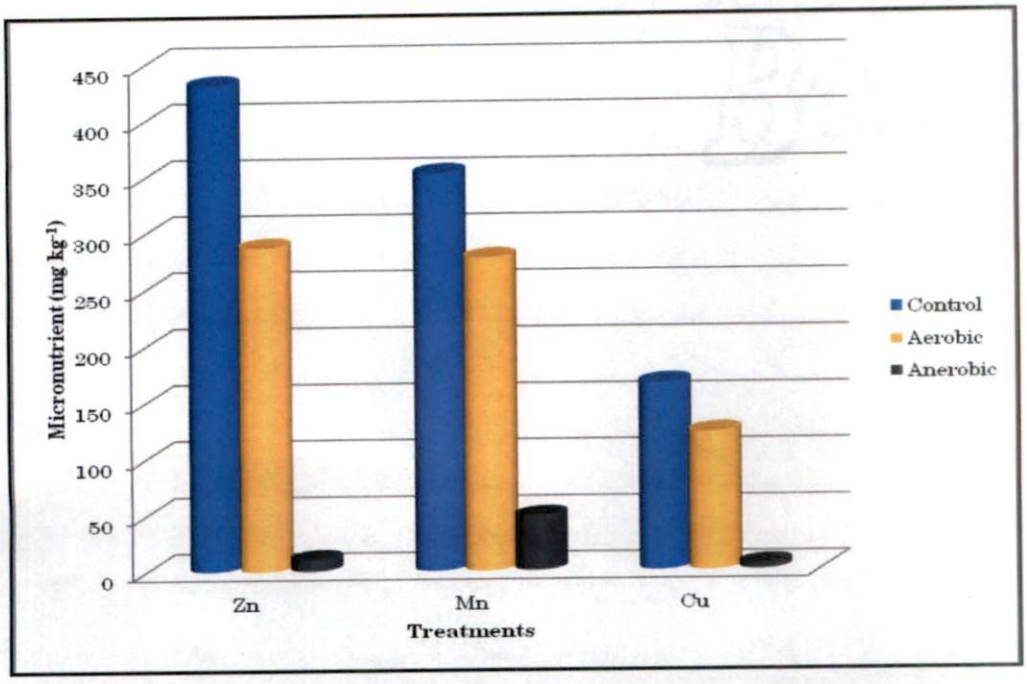

Fig.5.42. Variations in micronutrient content (mg kg^{-1}) among the different treatments

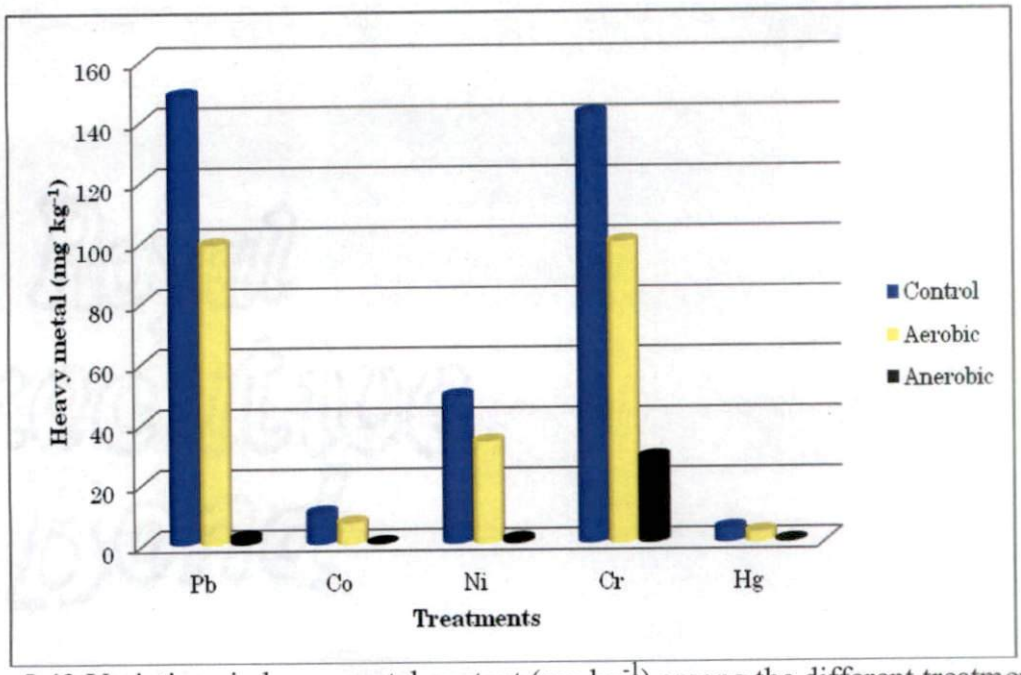

Fig.5.43.Variations in heavy metal content (mg kg^{-1}) among the different treatments

5.4 Comparative performance of amaranthus grown in soil under different methods adopted for reducing heavy metal contamination

A pot culture study was conducted with the variety Arun having duration of two months with the different treatments as mentioned in section 3.4.The result of the study was presented in 4.4 and the important findings are discussed as follows.

5.4.1. Yield and nutrient uptake of major nutrients

Maximum yield was recorded under T_6 (aerobic compost). With the aerobic compost was applied with N, P, K as 0.35 %, 0.12 % and 0.18%.This was followed by the (T_5), the waste containing N, P and K content of 0.28 %, 0.12 and 0.18 % respectively. This was followed by slurry, though nutrient content was less, frequency of application was more. However, the phytoremediated soil recorded the least yield (was less than absolute control) through the removal of almost all nutrients which is detailed in section 4.2. The uptake of the primary nutrients followed the same trend as yield with the highest in treatment with aerobic compost.

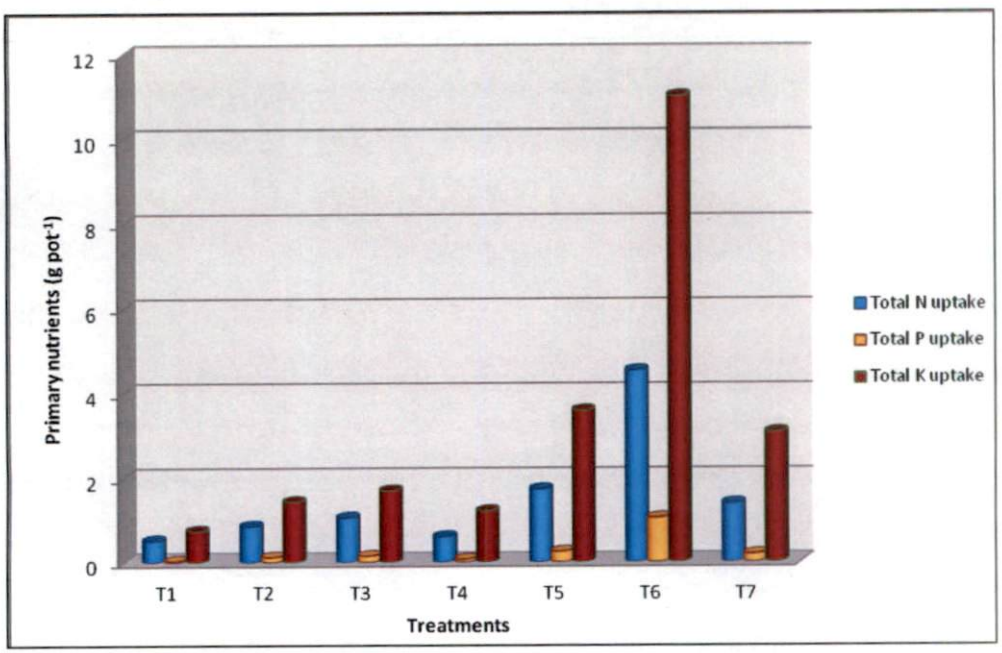

Fig.5.44 Primary nutrient uptake of amaranthus crop

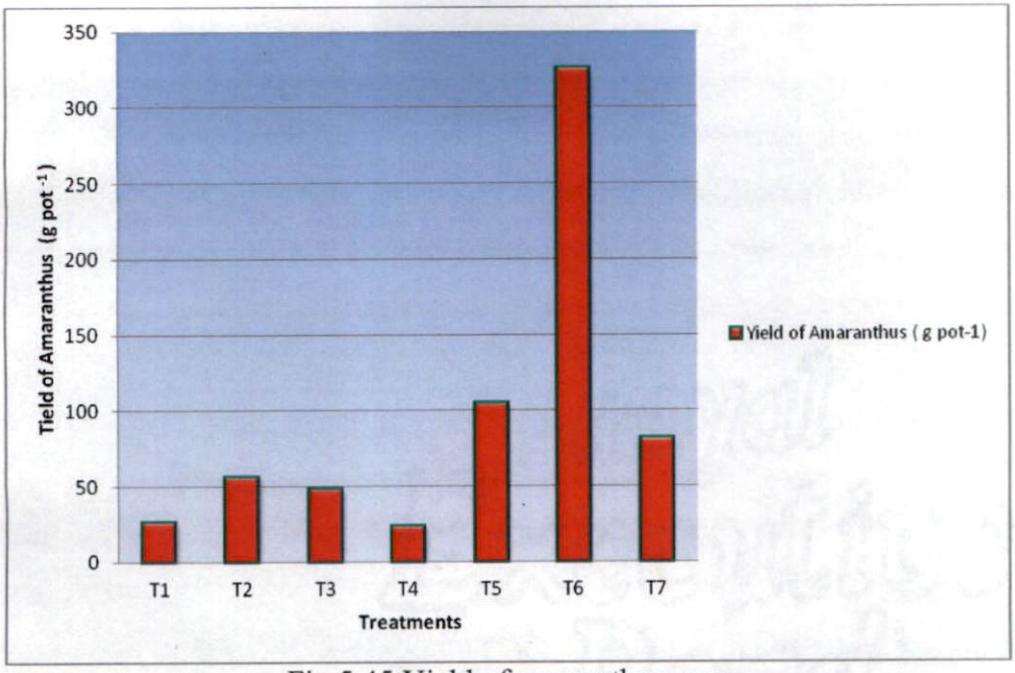

Fig.5.45 Yield of amaranthus crop

5.4.2. Micronutrient content of amaranthus root

Total Zn was the maximum in amaranthus root grown under aerobic compost T_6, followed by the phytoremediated material T_4 and then for root grown with POP recommendation T_3, almost all other treatments had a value on par with each other and the lowest Zn content was noted in roots grown under slurry. The total Mn content was also higher in the roots grown with soil under aerobic compost T_6 followed by the roots grown in soil treated with phytoremediated material T_4 then the roots grown in soil under POP T_3, slurry T_7 and FYM T_2, which were all significant from the rest and the least for roots under abs control T_1 and the root with waste material T_5 (23.77 mg kg^{-1}). The total Cu was detected only the amaranthus roots under two treatments, one under aerobic compost T_6 highest and the other for slurry T_7 and there was significant difference for Cu content for the two treatments. There was no significant difference in any of the treatments for the total Fe content in the amaranthus root.

5.4.3. Micronutrient content of amaranthus shoot

There was high variation in the total micronutrient content of the amaranthus shoot under different treatments. The Zn content was found to be higher in soil treated with POP T_3 followed by absolute control T_1, these treatments were significantly different from the rest and were on par with each other. Manganese content was higher for shoot grown under waste T_5, followed by slurry T_7 and then aerobic compost T_6, followed by absolute control T_1 and other treatments, but they were on par with each other. The total Cu was detected only the amaranthus roots under three treatments, one under aerobic compost T_6 highest, followed by waste T_5 and the other for slurry T_7. There was no significant difference in any of the treatments for the total Fe content in the amaranthus.

5.4.4. Heavy metal content of amaranthus root

Lead

The Pb content was found to be maximum in aerobic compost T_6, followed by waste T_5, phytoremediated material (T_4), FYM (T_2), POP(T_3), abs. control (T_1) and slurry (T_7). In the native soil Pb content was low and hence less in all other treatment and in roots under slurry Pb was not transmitted.

Chromium

There was no significant difference in the total Chromium content in the roots of amaranthus. This is due to the higher Cr content in the absolute control.

Nickel

The maximum Ni was reported for aerobic compost (T_6) though significant difference was observed between treatments with aerobic compost, waste (T_5), POP (T_3) and FYM (T_2). All other treatments were on par with each other.

Cobalt

Cobalt content was significantly different among treatments with aerobic compost (T_6), POP recommended treatment (T_3) and phytoremediated soil (T_4). The Co content in the materials under different treatments was very less.

Mercury

It was found maximum in aerobic compost (T_6), then waste (T_5), followed by slurry (T_7) and phytoremediated soil (T_4) and for other treatment it was only in traces.

5.4.5. Heavy metal content of amaranthus shoot

Lead

The Pb content was found to be maximum in waste (T_5) followed by aerobic compost (T_6), phytoremediated material (T_4) and slurry (T_7). The other treatment Pb content was very less and was not significantly different.

Chromium

Chromium was found to be maximum in soil treated with FYM (T_2), POP (T_3), followed by phytoremediated material (T_4) and waste (T_5) and the least in aerobic compost (T_6) and control (T_1).The native soil was also containing Cr, hence found in all treatments.

Nickel

The maximum Ni was reported for amaranthus shoot grown in absolute control (T_1), followed by FYM (T_2), waste (T_5), then phytoremediated soil (T_4), aerobic compost (T_6) and slurry (T_7). No significant difference observed between treatments. The treated soil had lower content of Ni.

Cobalt

There was no significant difference among the different treatments and the contents were found to be very less compared to other heavy metals.

Mercury

It was found maximum in waste (T5), phytoremediated soil (T_4) and compost (T_6) and in other treatment and it was only in traces.

As the heavy metal content in the upper part is considered than the underground root portion, heavy metal content in the amaranthus shoot on dry weight basis is below the

tolerable limit except for Cr. Chromium content was found to be more in amaranthus grown under all the different treatments.

5.4.6. Heavy metal content of the soil after harvest of amaranthus crop

Lead

After maximum uptake of Pb also there was more Pb content in the soil with aerobic compost (T_6), followed by waste (T_5) and phytoremediated soil (T4). In all other treatments it was in traces.

Chromium

As the native soil also contained significant amount of Cr, though it was noted maximum in treatments with aerobic compost (T_6), waste (T_5) and slurry (T_7). There was no significant difference noticed from native soil Cr content. The phytoremediated material (T_4) reported the least content.

Nickel

Nickel content was also reported to be high in aerobic compost (T_6) followed by slurry (T_7) and then waste (T_5). The other treatments Ni content was not found to be significant. From the treated soil Ni uptake was less to the plant. The least Ni content was in phytoremediated material (T_4) containing treatment.

Cobalt

Maximum content in the soil treated with POP (T_3), followed by slurry (T_7). Except for the Co content in phytoremediated material (T_4), others were on par with each other.

Mercury

As uptake of Hg was more from aerobic compost (T_6) the nutrient content reduced in soil and it was similar to that of waste material (T_5), and for all other treatments Hg was in traces.

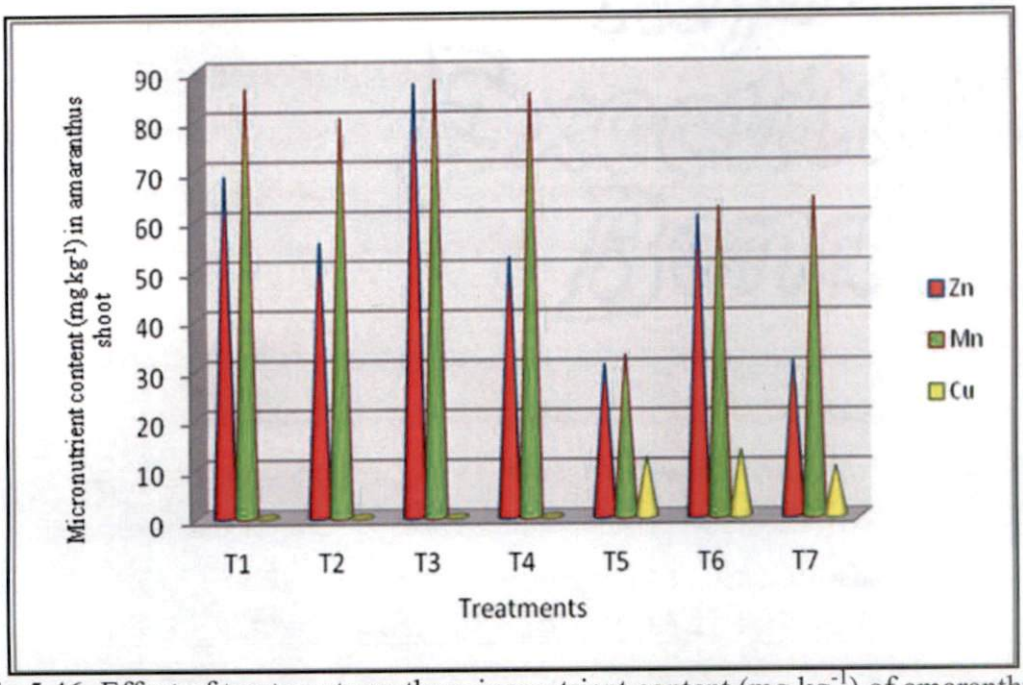

Fig.5.46. Effect of treatments on the micronutrient content (mg kg^{-1}) of amaranthus shoot

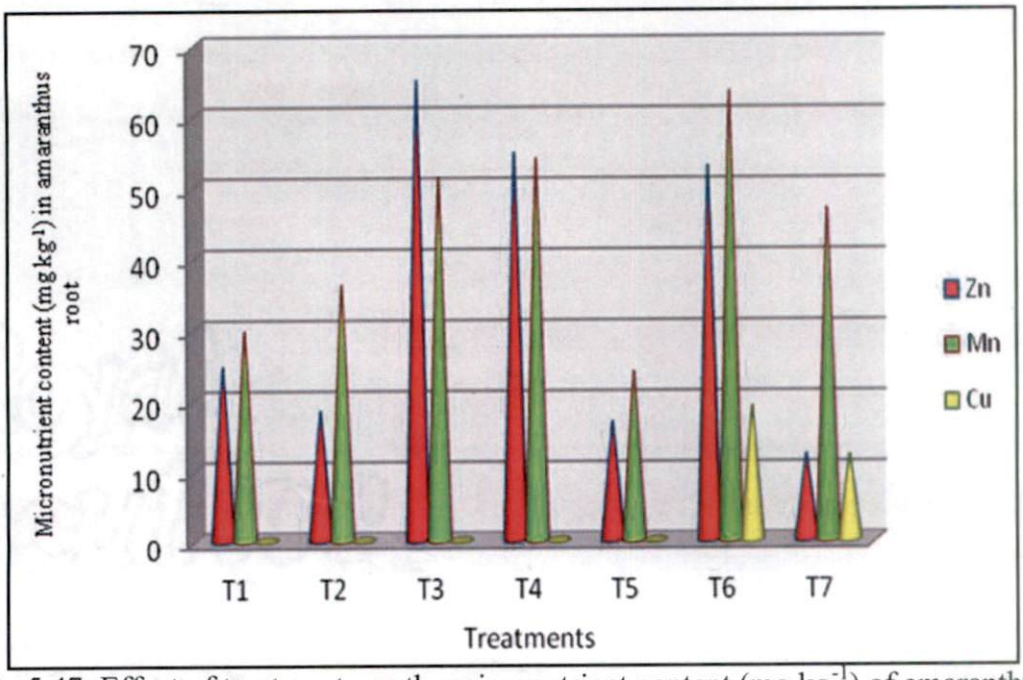

Fig.5.47. Effect of treatments on the micronutrient content (mg kg^{-1}) of amaranthus root

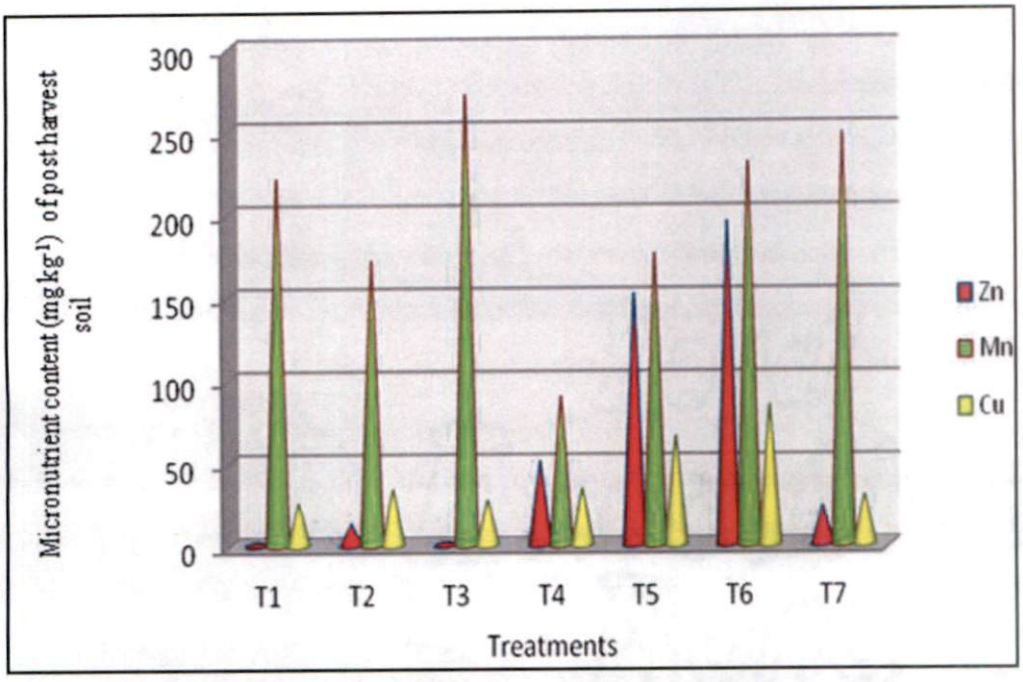

Fig.5.48.Effect of treatments on the micronutrient contents (mg kg^{-1}) of post harvest soil

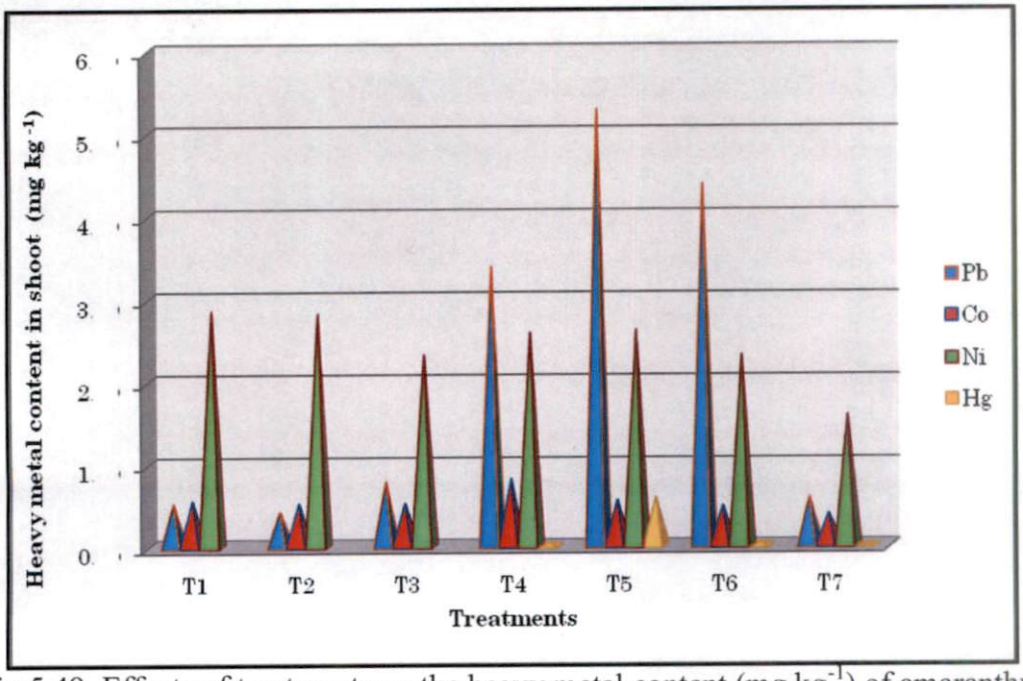

Fig.5.49. Effects of treatments on the heavy metal content (mg kg^{-1}) of amaranthus shoot

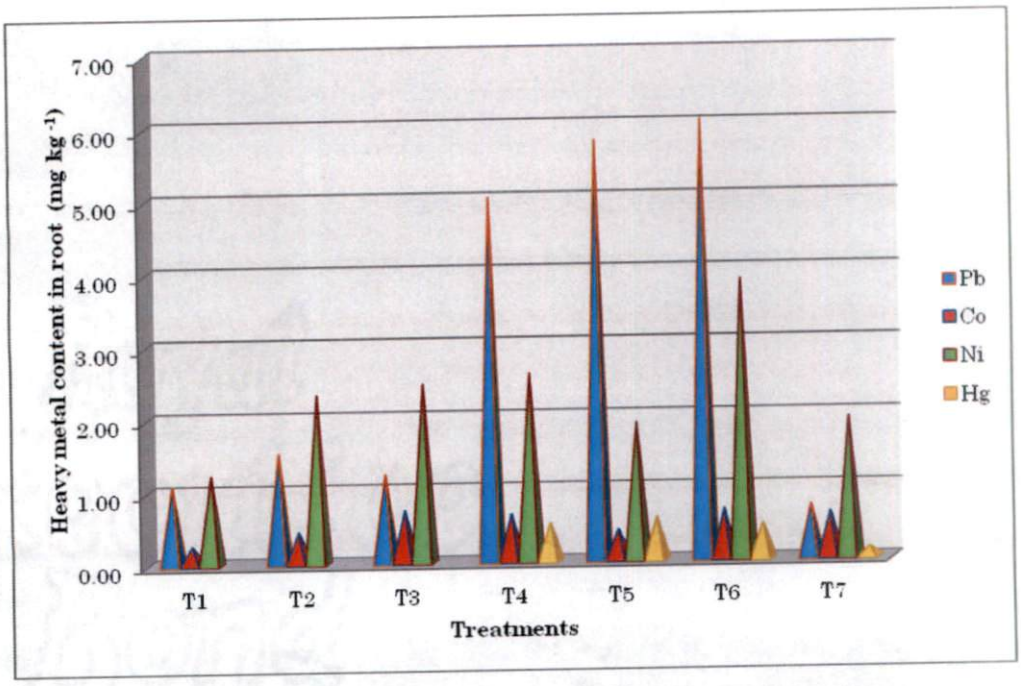

Fig.5.50. Effects of treatments on the heavy metal content (mg kg^{-1}) of amaranthus root

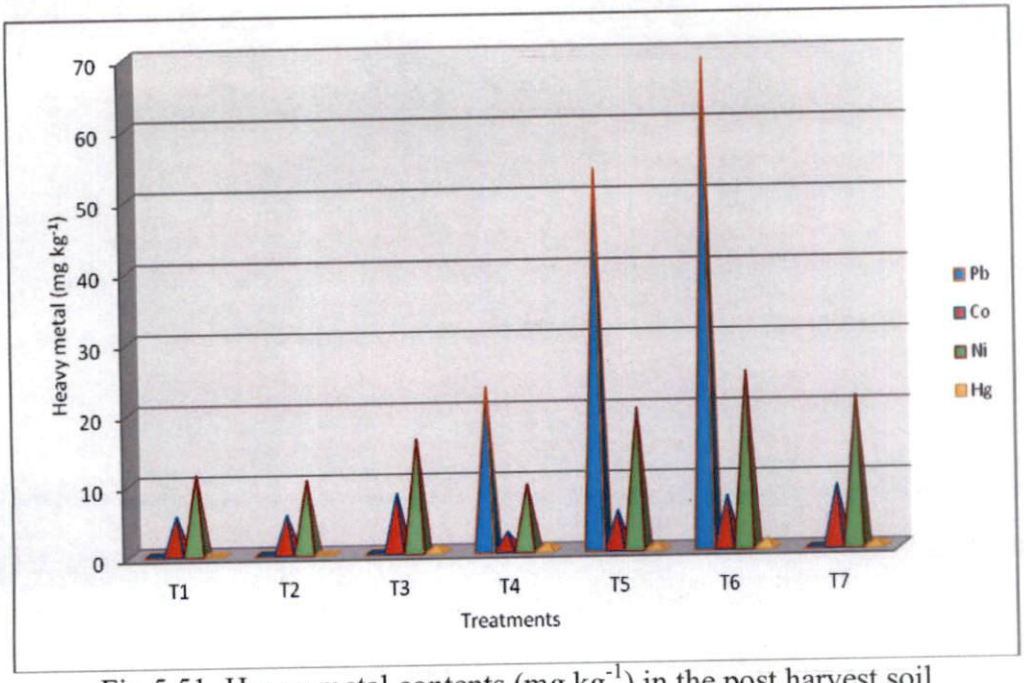

Fig.5.51. Heavy metal contents (mg kg^{-1}) in the post harvest soil

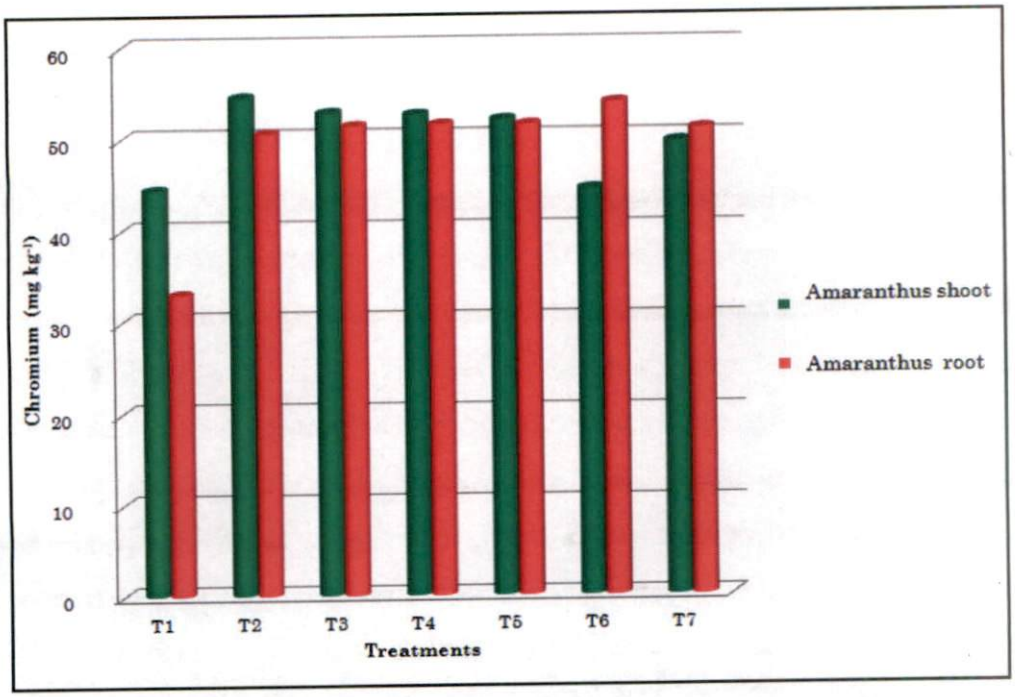

Fig.5.52. Effect of the different treatments in the chromium content (mg kg^{-1}) in the amaranthus shoot and root

All the heavy metals in the post harvest soil were found to be within the permissible limits and so it can be used for crop cultivation. The Cr content was found to be comparatively more as compared to other treatments. A number of soil processes and factors may affect the form and biomobilization potential of Cr. Chromium is present in soils mostly as insoluble $Cr(OH)_3$ or as Cr(III) adsorbed to soil components, which prevents Cr leaching into groundwater or its uptake by plants (Bartlett and Kimble, 1976). The hexa valent Cr is reduced to trivalent form during digestion of sludge, it appears that Cr applied to the soil through sewage sludge present no hazard to food chain (Bijay-Singh, 2009). Chromium accumulation and its effects on other mineral elements in *Amaranthus viridis* was studied by Zou *et al.*, (2006) showed that Cr concentration in plant tissues from a contaminated site was about 11 times higher than in those from an uncontaminated site. At both the contaminated and uncontaminated sites, Cr was accumulated primarily in its shoots, and in roots in much lower concentrations. The levels of Cr in

A. viridis tissues were as follows: leaf > root > stem. Cr occurred predominantly as Cr (III). Hence Cr present in plant species may not be toxic.

Summary

6. SUMMARY

The study entitled "Heavy metal contamination of laterites by accumulation of solid wastes" was conducted at the department of Soil Science & Agricultural Chemistry, College of Horticulture during the period 2010-2014. The salient research findings of the study are summarized experiment wise as follows

Experiment I.

- ✓ The average content of total Pb was recorded as 15.58 mg kg^{-1} and 82.84 mg kg^{-1}in the soils of Kalamassery and Laloor, respectively.

- ✓ Monitoring the Co content of the soil irrespective of different intervals and the sites of study, it was found that the average content varied from 6.06 mg kg^{-1} at Kalamassery to 7.79 mg kg^{-1} at Laloor.

- ✓ Comparatively more total Ni content was registered at Kalamassery (43.18 mg kg^{-1}) than Laloor, where the Ni content was 35.54 mg kg^{-1}, irrespective of the sampling periods and sites.

- ✓ There were little variations in Hg content of the soil with 0.56 mg kg^{-1} at Kalamassery and 0.42 mg kg^{-1} Laloor, if the sampling intervals as well as the sites of study were pooled together.

- ✓ The average contents of Cr were found to be higher for both soil types of Kalamassery and Laloor which accounted to 107.9 mg kg^{-1} and 115.67 mg kg^{-1}, respectively.

- ✓ The percentage spatial distribution of heavy metals at the different sites (including dumping and non dumping sites) of Kalamassery revealed that Cr had the highest distribution, followed by Ni, Pb, Co and Hg. In case of Laloor, Pb was found to be dominant for the major dumping sites of study where as Cr, at the non dumping site.

- ✓ The geoaccumulation index (Igeo) was worked out with the individual heavy metal content in comparison to background concentration (mg kg^{-1}) of Pb=16, Cd =0.2, Cr=100 , Hg=0.05, Ni=80 & Co=20 mg kg^{-1}, respectively.

- ✓ All sites of Kalamassery recorded Igeo value greater than one for Hg at all the sites. At the dumping sites of Laloor, the Igeo was found to be greater than one for Pb and Hg.

- ✓ Modified degree of contamination was worked out for different locations (sum of all contamination factors for a given set of pollutants divided by the number of analysed pollutants). All the sites of Kalamassery and the dumping site of Laloor registered moderate degree of contamination for all sites under study.

- ✓ The climatic (weather) conditions of the soil such as atmospheric temperature, humidity and rainfall did not influence the heavy metals content of the soil. Generally, the heavy metal contents were found to be higher during summer than rainy season except for Cr and Cd.

- ✓ The heavy metal accumulation in soil did not affect the activity of soil enzymes such as urease, phosphates and dehydrogenase. On an average the enzyme activity was reported as 1.05 to 31.50 µmol $N\text{-}NH_3 g^{-1}$ h^{-1} for urease, 6.3 to 57.81 µmol PNP g^{-1} h^{-1} for phosphatase activity and 79.10 to 1700 µmol TPF g^{-1} h^{-1} for dehydrogenase activity.

- ✓ Physico-chemical properties of soil such as pH, EC, organic matter, total content of major and micronutrients influenced the variation in the heavy metal contents of sampling location, which was closely monitored for a period of one year.

Experiment II

- ✓ The phytoremediation study with the three different crops (sunflower, marigold and vetiver) showed vetiver as a good phyto stabilizer compared to others.

- ✓ Vetiver was found to be a translocator of Cr, since Ni, Pb, Co and Hg were mostly stabilized in the root. Marigold translocated all these heavy metals from soil except Co, whereas sunflower behaved as phytostabiliser for Pb and translocated Co, Ni and Cr.

- ✓ Bioconcentration factor (the heavy metal concentration in the plant/ the heavy metal concentration in the soil) was higher for vetiver compared to sunflower and marigold.

- ✓ On the basis of removal ratio (based on heavy metal content in treated soil) vetiver was found to be the most efficient in the removal of heavy metals as per the the order Cr>Ni> Co> Pb. Marigold had removal ratio 1.02 for Cr and less than 1.00 for others. The sunflower had low removal ratio for all the heavy metals under study.

Experiment III

- ✓ Aerobic composting of the contaminated material collected from Laloor dump yard along with cowdung in the ratio 1:1, took two months for maturity.

- ✓ Compared to aerobic composting, anaerobic method was better for removal of the heavy metals.

- ✓ The heavy metal content (mg kg^{-1}), was observed to be higher in aerobic compost with an average of total Pb 99.18, Co 6.9, Ni 33.64, Cr 99.52 and Hg 0.29 mg kg^{-1} respectively and slurry it was Pb 2.16 , Co 0.24, Ni 1.2, Cr 28.06 and Hg 0.03 mg kg^{-1} respectively.

Experiment IV

- ✓ The yield of amaranthus and uptake of N, P and K was higher in the treatment (6) 325.67g pot^{-1} (soil grown with aerobic compost) followed by waste material and slurry.

- ✓ The lowest yield was reported for amaranthus (Treatment 4) under phytoremediated material, followed by absolute control (Treatment 1).

- ✓ The heavy metal contents were higher in the shoots grown with waste and the accumulation followed the order Cr>Pb>Ni>Co>Hg. The content of Pb and Hg was higher in treatment with waste material followed by treatments with aerobic compost and phytoremediated material.

- ✓ After the harvest of the crop, the heavy metal content (mg kg^{-1}) of the soil was within the threshold limit for growing crops.

- ✓ Among the different heavy metals Cr accumulated in more concentration in all the plant parts of amaranthus due to the higher presence of Cr in the laterite soil.

PRACTICAL UTILITY

- ✓ The pollution indices for waste dumping yards of Kalamassery and Laloor were worked out.
- ✓ Vetiver was found to be a good phytostabilizer for Ni, Co, Hg and Pb and hyperaccumulator for Cr.
- ✓ Anaerobic composting was proved to be better than aerobic for the effective removal of heavy metals under study.
- ✓ Decontaminated waste material can be used for crop cultivation provided the heavy metal contents are within the toxic range.

FUTURE LINE OF WORK

- ✓ Since Cr is rich in laterite soil under study, its accumulation in different crop parts are to be studied further
- ✓ Phytoremediated waste material is a good substrate for crop cultivation after the addition of necessary plant nutrients. Such studies are to be undertaken in detail

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Appendix

Appendix I. Climatic data for the survey period from July 2011 to June 2012

Month/year	Laloor			Kalamassery		
	Temp (^{0}C)	Humidity (%)	Rainfall (mm)	Temp (^{0}C)	Humidity (%)	Rainfall (mm)
Jul , 2011	24.8	85.2	605.4	25.8	88	537.6
Aug, "	25.3	85.4	605.5	26.15	87	584.6
Sept, "	27.1	82.5	527.8	26.75	85	479.7
Quarter (I)	**25.7**	**84.4**	**579.6**	**26.2**	**86.7**	**533.9**
Oct, "	28.2	77.1	156.5	27.3	78	257.7
Nov, "	27.3	70.5	123.8	27.15	68	154.3
Dec, "	26.5	65.7	34.3	26.9	62	1.8
Quarter (II)	**27.33**	**71.10**	**104.9**	**27.12**	**69.33**	**137.9**
Jan, 2012	26	62.7	7.1	27.05	58	0.1
Feb, "	27.2	63.1	18.0	28.6	54	9.3
Mar, "	28.5	69.8	43.0	29.7	67	185.4
Quarter (III)	**27.23**	**65.20**	**22.7**	**28.45**	**59.67**	**64.9**
Apr, "	28.9	76.5	401.8	29.75	73	129.8
May, "	29	76.9	100.9	28.95	76	598.1
June, "	27.1	82	414.9	27	85	337.3
Quarter (IV)	**28.33**	**78.47**	**305.9**	**28.57**	**78.00**	**355.0**

Appendix II. Quarter-wise sampling seasons

Serial No	Season	Months
S1	monsoon	July-Sept
S2	N E monsoon	Oct-Dec
S3	Summer	Jan - Mar
S4	Pre monsoon	April-june

Appendix III a. The details of biodegradable and non biodegradable waste sorted at the sampling intervals

	Quarters				
Kalamassery	**Q I**	**Q II**	**Q III**	**Q IV**	**Average**
Biodegradable	40	36	38	35	37.25
Non biodegradable (inert+bioressistant+recyclable material)	60	64	62	65	62.75
Laloor					
Biodegradable	35	39	42	37	38.25
Non biodegradable (inert+bioressistant+recyclable material)	65	61	58	63	61.75

Appendix III b. The composition of biodegradable and non biodegradable material at the sampling site

Biodegradable	Non Biodegradable		
	Recyclable	**Bioressistant**	**Inert**
food waste	Paper	Leather	stones
market waste	plastic	Rubber (tyre)	bricks
dust and dirt	metal(syringes)	Bones	ash
dry leaves and weeds	glass	Synthetic material	fine soil
	crockery		
	Iron, steel, Al		

Appendix IVa Correlation between climate, heavy metals and soil enzymes

	Temperature	Humidity	Rainfall	Cu	Zn	Fe	Al	Pb	Co	Ni	Hg	Cd	Cr	Phosphatase	Urease	Dehydrogenase
Temperature		-.516**	-.524**										-.477**	-.394*		
Humidity	-.516**		.942**			-.362*									-.354*	
Rainfall	-.524**	.942**				-.478**									-.439*	
Cu					.775**				.358*			.370*	.377*			
Zn				.775**								.475**				
Fe		-.362*	-.478**						.649**	.562**					.391*	
Al										.626**	.524**	.532**				
Pb									.385*					.350*		
Co				.358*		.649**		.385*		.638**						
Ni						.562**	.626**		.638**		.394*	.439*				
Hg							.524**			.394*		.365*				
Cd				.370*	.475**		.532**			.439*	.365*					
Cr	-.477**			.377*												
Phosphatase	-.394*							.350*								.466**
Urease		-.354*	-.439*			.391*										
Dehydrogenase														.466**		

Appendix IVb. Correlation between climate and soil properties

	Temperature	Humidity	Rainfall	Soilmoisture	Soiltemp	pH	Organic matter	N	P	K	Ca	Mg	Al	Phosphatas	Urease	Dehydrogenase
Temperature		-.516**	-.524**	-.558**						.461**	.391*			-.394*		
Humidity	-.516**		.942**		-.418*			-.358*							-.354*	
Rainfall	-.524**	.942**		.429*											-.439*	
Soilmoisture	-.558**		.429*													
Soiltemp		-.418*														
pH										.413**	.490**	.512**			-.373*	
Organicmatter								.723**	.564**	.443*						
N		-.358*					.723**		.667**	.645**	.478**	.388*				
P							.564**	.667**		.652**	.486**	.399**				
K	.461**					.413*	.443*	.645**	.652**		.705**	.652**				
Ca	.391*					.490**		.478**	.486**	.705**		.605**				
Mg						.512**		.388*	.399*	.652**	.605**		.365*			
Al												.365*				.466**
Phosphatase	-.394*															
Urease		-.354*	-.439*			-.373*								.466**		
Dehydrogenase																

Appendix IVc correlation between soil properties and heavy metals

	Soil Moisture	Soil Temperature	pH	Organic matter	N	P	K	Ca	Mg	Cu	Zn	Fe	Al	Pb	Co	Ni	Cd	Cr
Soil Moisture												-.461**						
Soil Temperature														.449**	.388*			
pH							.413*	.490**	.512**									
Organic matter					.723**	.564**	.443*			.352*								
N				.723**		.667**	.645**	.478**	.388*	.563**				.437*				
P				.564**	.667**		.652**	.486**	.399*	.743**	.579**							.360*
K			.413*	.443*	.645**	.652**		.705**	.652**	.433*								
Ca			.490**		.478**	.486**	.705**		.605**					.353*				
Mg			.512**		.388*	.399*	.652**	.605**					.365*			.373*		.541**
Cu				.352*	.563**	.743**	.433*				.775**				.358*			.370*
Zn						.579**				.775**								.475**
Fe	-.461**														.649**	.562**		
Al									.365*					-.330		.626**	.524**	.532**
Pb		.449**			.437*			.353*							.385*			
Co		.388*								.358*		.649**		.385*		.638**		
Ni									.373*			.562**	.626**		.638**		.394*	.439*
Cd													.524**			.394*		.365*
Cr						.360*			.541**	.370*	.475**		.532**			.439*	.365*	

** Correlation is significant at the 0.01 level (2-tailed).

*Correlation is significant at the 0.05 level (2-tailed).

Appendix Va

Percentage distribution of heavy metals at each sites at Kalamassery

Kalamassery	Pb	Co	Ni	Hg	Cr	Cd
	(%)					
First site	8.3	3.9	28.2	0.3	58.5	0.7
second site	9.5	3.8	25.9	0.3	60.5	0.1
Third site	10.3	2.6	20.0	0.3	66.4	0.3
Fourth site	7.2	3.9	26.0	0.4	62.6	0.0

Percentage distribution of heavy metals at each sites at Laloor

Laloor	Pb	Co	Ni	Hg	Cr	Cd
	(%)					
First site	46.84	2.42	10.88	0.14	39.62	0.09
second site	42.04	3.28	13.23	0.18	41.20	0.06
Third site	15.23	4.12	21.44	0.25	58.74	0.22
Fourth site	13.81	3.79	16.93	0.14	65.27	0.06

Appendix Vb

Geoaccumulation index of Kalamassery

Kalamassery	Pb	Co	Ni	Hg	Cr	Cd	mC_d
	Igeo calculated						
First site	-0.70	-2.11	-1.83	2.92	-0.52	2.01	3.4
second site	-0.46	-2.12	-1.25	2.80	-0.44	-1.45	2.4
Third site	-0.22	-2.51	-1.34	3.07	-0.17	1.22	3.3
Fourth site	-1.33	-2.55	-1.58	2.80	-0.85	-3.32	2.2

Geoaccumulation index of Laloor

Laloor	Pb	Co	Ni	Hg	Cr	Cd	mC_d
	Igeo calculated						
First site	2.60	-1.99	-1.25	2.55	-0.28	-0.05	3.562
second site	2.38	-1.77	-1.34	2.67	-0.45	-0.82	3.364
Third site	0.61	-1.75	-1.58	2.83	-0.23	0.68	2.950
Fourth site	0.00	-2.34	-1.79	1.00	-0.56	-1.74	1.328

Appendix Vc

Igeo class	Igeo value	Designation of quality
0	0	unpolluted
1	0 < Igeo < 1	unpolluted to moderately polluted
2	1 < Igeo < 2	moderately polluted
3	2 < Igeo < 3	moderately to strongly polluted
4	3 < Igeo < 4	strongly polluted
5	4 < Igeo < 5	strongly to extremely polluted
6	5 < Igeo	extremely polluted

(Muller, 1969)

mC_d value	Designation of quality
mCd<1.5	Nil to very low degree of contamination
1.5 > mCd < 2	Low degree of contamination
2 > mCd < 4	Moderate degree of contamination
4> mCd < 8	High degree of contamination
8> mCd < 16	Very high degree of contamination
16> mCd <32	Extremely high degree ofcontamination
m Cd > 32	Ultra high degree of contamination

(Abraham and Parker, 2008)

Appendix VI. Threshold limit of heavy metal content in compost (mg kg^{-1})

Heavy metals	Threshold Limit (mg kg^{-1})
Ni	50
Co	20
Pb	100
Cr	50
Hg	0.15

(GOI, 1985)

Appendix V1I. Total heavy metal (mg kg^{-1}) of absolute control

Heavy metal	(mg kg^{-1})
Ni	23.6
Co	9.5
Pb	4
Cr	114.6
Hg	traces

HEAVY METAL CONTAMINATION OF LATERITES BY ACCUMULATION OF SOLID WASTES

By

DIVYA VIJAYAN, V.
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ABSTRACT OF THE THESIS

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Department of Soil Science and Agricultural Chemistry
COLLEGE OF HORTICULTURE
KERALA AGRICULTURAL UNIVERSITY
THRISSUR 680 656
KERALA, INDIA

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ABSTRACT

A heavy metal is defined as a metal that has the atomic number and specific gravity greater than 20 and 5 Mg m^{-3}, respectively. Heavy metals occur naturally in the soil environment from the weathering of parent materials and also as contaminants at the waste disposing sites. Though, the soil acts as a sink for the majority of heavy metals, the excess uptake of any one of them may limit the plant growth. In this background, the research work entitled "heavy metal contamination of laterites by accumulation of solid wastes" was undertaken during the period 2010-2014.

The project aims to investigate the extent of distribution of heavy metals (As, Cd, Cr, Pb, Hg and Co) in waste dumping sites of laterite as influenced by soil and climatic conditions using geostatistical technique, to correlate the activity of major soil enzymes with the contents of heavy metals, to explore the potential of phytoremediation as well as aerobic and anaerobic methods of composting for the removal of heavy metals in solid waste and to evaluate the performance of amaranthus under different decontaminated methods adopted. In order to attain the objectives, four experiments were conducted. The effect of soil and climatic factors on heavy metal accumulation was examined with the collection of soil samples at quarterly intervals for a period of one year from two different waste disposal sites located at Laloor and Kalamassery. For the study on phytoremediation, the crops, vetiver, marigold and sunflower were experimented. Both the aerobic and anaerobic methods of composting were tried for the removal of heavy metals in another set of experiment. A pot culture study was also conducted to assess the growth of amaranthus under different decontaminated conditions.

The salient findings are summarized as follows:

The percentage distribution of Pb, Ni, Co, Cr and Hg at the different sites of Kalamassery revealed that Cr had the highest distribution followed by others. At Laloor, Pb was found to be dominant for the major dumping sites, whereas Cr at

the non dumping site. The geo accumulation index for Hg was recorded as above one for all sites at Kalamassery. The average contents (mg kg^{-1}) of Pb, Co, Ni, Hg and Cr was 15.58, 6.06, 43.18, 0.56, 107.9 at Kalamassery and 82.84, 7.79, 35.54, 0.42 and115.67 at Laloor, respectively. Heavy metal contents were found to be higher during summer than rainy season except for Cr and Cd. In general, soil enzyme activities were higher during quarter II of the sampling period. There was a positive correlation between Fe and urease (0.391*) and Pb and phosphatase (0.350*).

The phytoremediation study with the three different crops (sunflower, marigold and vetiver) proved vetiver as a good phytostabilizer compared to others. Vetiver was found to be a translocator of Cr, since Ni, Pb, Co and Hg were mostly stabilized in the root. Marigold translocated all these heavy metals from soil except Co, and sunflower translocated Co, Ni and Cr except Pb. Bioconcentration factor (the heavy metal concentration in the plant/ the heavy metal concentration in the soil) was higher for vetiver compared to sunflower and marigold. Vetiver removed the heavy metals from the waste material in the order Cr>Ni> Co> Pb. Compared to aerobic composting, the anaerobic method proved to be better for the removal of heavy metals from the waste material collected from Laloor.

The comparative performance of amaranthus grown in soil under different methods adopted for reducing heavy metal contamination showed that the yield was found to be the highest in the treatment with aerobic compost. The lowest yield was reported for amaranthus grown with phytoremediated material, followed by absolute control. The uptake of major nutrients also followed the same trend as yield. The heavy metal content was higher in the shoots of amaranthus grown with waste material and the accumulation followed the order Cr>Pb>Ni>Co>Hg. In all the treatments under study, the presence of Cr was more dominant in the post harvest soil compared to other heavy metals.