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Soil and water quality status of Kadukutty region

(Final Report of Project KFRI 631/2011)

S. Sandeep
Thomas P. Thomas

Kerala Forest Research Institute
(An Institution of Kerala State Council for Science, Technology and Environment)
Peechi – 680 653, Kerala, India

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ABSTRACT OF THE PROJECT PROPOSAL

1. Project Number	:	KFRI 631/2011
2. Title of the Project	:	**Soil and water quality status of Kadukutty region**
3. Objectives		1. To study the soil quality in the Kadukutty region 2. To study the water quality in the Kadukutty region 3. To relate the soil quality with the land use of Kadukutty region
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ABSTRACT

Kadukutty in Thrissur District has a long history of industrial and agricultural development. Soil and water quality of Kadukutty region was studied and baseline information generated. It was seen that 35% of the land in the region is under mixed cultivation. Rice, coconut, banana, pepper, arecanut, nutmeg, rubber and vegetables are the main crops cultivated in the panchayat.

The pH of the soils ranged from 4.64 in vegetables to 5.42 in mixed cultivation. Soil organic carbon contents were found to be in the medium to high ranges. Heavy metal contents in soil showed that cadmium, lead and nickel were beyond the permissible limits in most of the soils in Kadukutty. To increase the information capacity (mobility/ bioavailability) of generated results a speciation analysis suggested by EU Standards, Measurement and Testing Programme called BCR process of the heavy metals in soil was conducted. The order of mobility of the metals in soil systems for the first fraction is Ni > Mn = Pb > Zn > Cd > Cu > Fe . Ni, Pb and Mn seemed to be the most mobile elements in the region. Enrichment factor values show that accumulation of these metals in soils occurred mainly due to anthropogenic activities - industrial as well as agricultural. Earthworms were abundant in sites where predominantly organic cultivation was practiced and absent in sites with high synthetic fertilizers and chemical inputs.

Water quality of the region was assessed by collecting samples from wells and prominent water courses draining the area. The pH values of Kadukutty region were found to vary between 3.70 - 5.60 and 5.20 - 6.20 in wells and water courses respectively. The values in wells were much lower than the prescribed BIS and ICMR standards especially around the industry. Heavy metal contents were found to be within the permissible limits and pesticides could not be detected in any of the analyzed water samples. All the analyzed water samples indicated high pollution levels by coliforms. Faecal coliforms were found to be present in 60 % of the analyzed well water samples. Aquatic macro invertebrates though present in water courses their community composition was seen shifted towards the tolerant taxa.

INTRODUCTION

Soil

Soils are natural bodies, covering part of the earth's surface that supports plant growth. Soil properties are a function of climate and organisms acting upon the parent material as considered by relief, over a period of time. Soils are the reservoir for many harmful constituents, elemental and biological, including heavy metals and trace metals.

A heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. Generally "heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals occur naturally in the ecosystem with large variations in concentration. However in modern times, anthropogenic activities have accentuated heavy metal concentration in the ecosystem.

In small quantities, certain heavy metals are essential for a healthy life. Some of these are referred to as trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are found naturally in foodstuffs, fruits, vegetables and commercially available multivitamin products. Heavy metals are also common in industrial applications such as manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth. Many of these products are in our homes and add to the quality of life when properly used.

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. They may enter the body through food, water, air or absorption through the skin on direct contact. Industrial exposure accounts for a common route of adult body entry. Ingestion is the most general route of exposure in children. Children may develop toxic levels from the normal hand-to-mouth activity by coming in contact with contaminated soil or actually eating objects that are not food (dirt or paint chips). Heavy metal toxicity can result in damaged or reduced mental and central nervous system function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are also common and repeated long-term contact with some metals or their compounds may even cause cancer (INECAR, 2000; Goyer and Clarkson, 2001; European Union, 2002). Through precipitation of the compounds or by ion exchange in soils and sediments, heavy metal pollutants can localize and lie dormant. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and bio magnification (Fagbote et al., 2010) causing heavier exposure for some organisms than is present in the environment.

Pollution of the natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms, when permissible concentration levels are exceeded. Anthropogenic activities have led to a rapid increase in the environmental heavy metal concentrations over the past few decades. Mining, manufacturing, and the use of synthetic products (e.g. pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge) cause heavy metal contamination of urban and agricultural soils. Heavy metals also occur naturally, but rarely at toxic levels. Potentially contaminated soils may occur at old landfill sites (particularly those that accepted industrial wastes), old orchards that used insecticides containing arsenic as an active ingredient, fields that had past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground, or in areas downwind from industrial sites.

Most heavy metals are cations, meaning they carry a positive charge. Zinc and copper, for instance, both carry a 2^+ charge. Soil particles and loose dust also carry charges. Most clay minerals have a net negative charge. Soil organic matter tends to have a variety of charged sites on their surfaces, some positive and some negative. The negative charges of these various soil particles tend to attract and bind the metal cations and prevent them from becoming soluble and dissolved in water. The soluble form of metal is thought to be more dangerous because it is easily transported and more readily available to plants and animals. By contrast, soil bound metals tend to stay in place for longer periods.

Proper evaluation of the effect of heavy metals on the natural environment is possible on the basis of knowledge about their forms and bindings with soil components. Sequential extraction could be the source of above information, enabling identification and quantitative determination of various forms of the same chemical element. The extraction procedure takes advantage of the solubility mechanisms in water, ionic exchange, oxidation and reduction processes, as well as complexation and digestion of mineral and organic soil components. Separated fractions are defined in a conventional and operational manner, and as such present a certain approximation in describing different forms of metals found.

Speciation is defined as the identification and quantification of the different defined species forms or phases in which an element occurs and is essentially a function of mineralogy and chemistry of the soil sample examined. Partial (single) and sequential extraction procedures are two techniques that have been used for determining the extractable forms of metals within soils. Partial extractions unselectively target labile metals with the degree of extraction dependent upon the severity of the reagent. In contrast, sequential extraction procedures have been applied to soils and sediments to characterize their respective metal fractions, by selectively targeting and releasing metals bound in certain geochemical phases such as carbonate, iron and manganese oxide/hydroxide, sulfide, organic matter and silicates. Although often criticized due to lack of specificity of extractants and possible readsorption of metals during extraction, sequential fractionation can provide useful information to predict the fate of heavy metal in the environment. Ideally, sequential extraction procedures selectively extract metals bound to specific soil fractions with minimal effect on the other soil components.

One of the commonly used sequential extraction procedures is the BCR (Community Bureau of Reference of the European Commission, now the Standards, Measuring and Testing Programme) procedure. The BCR procedure aims to fractionate metals into the operationally defined phases with the steps targeting exchangeable and carbonate bound metals, iron and manganese oxide/hydroxide associated metals, metals bound to sulfide and organic phases and mineral phases respectively. In this study BCR procedure was used for the determination of metal speciation in soil. The chosen extraction scheme is an operationally defined and standardised procedure in which the reagent used at each stage is intended to release metals associated with particular soil phases such as exchangeable, reducible, oxidisable, and residual.

Exchangeable fraction

Exchangeable metal ions are measures of those trace metals which are released most readily into the environment. This fraction includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes and metals that can be co precipitated with carbonates. Changes in the ionic composition influencing adsorption–desorption reactions, or lowering of pH could cause remobilization of metals from this fraction. Metals corresponding to the exchangeable fraction usually represent a small portion of the total metal content in soil, sewage sludges and sediments and can be replaced by neutral salts. Thus, this fraction generally accounts for less than 2% of the total metals present in soil.

Reducible fraction

Hydrous oxides of manganese and iron are extracted together, the well known 'sinks' in the surface environment for heavy metals. Scavenging by these secondary oxides present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of the following mechanisms: co-precipitation; adsorption; surface complex formation and penetration of the lattice. These oxides occupy a large proportion in soil and sediments, but are less abundant in sewage sludge. They are thermodynamically unstable under anoxic circumstances. Reduction of Fe (III) and Mn (IV) under anoxic conditions and their subsequent dissolution could release adsorbed trace metals.

Oxidisable fraction

The organic fraction released in the oxidizable step is not considered very mobile or available since it is thought to be associated with stable high molecular weight humic substances that release small amounts of metals in a slow manner. The trace metals may be associated through complexation or bioaccumulation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles. These metallic pollutants, associated with oxidizable phases, are assumed to remain in the soil for longer periods but may be mobilised by decomposition processes. Degradation of organic matter under oxidising conditions can lead to a release of soluble trace metals bound to this component. Heavy metals bound to sulfides might also be extracted during this step. As metals bound to organic matter and sulfides can be easily released under oxidising conditions, an oxidation process is usually applied to leach metals associated with the above mentioned phases. This fraction was one of the smallest or even negligible in the surface horizons of all soils. However, this is an important fraction, especially in polluted sediments and sewage sludge which can even dominate trace metal distribution.

Residual fraction

It largely consists of mineral compounds, where metals are firmly bonded within crystal structure of the minerals comprising the soil. The residual fraction consists of metals incorporated into the crystal structures of primary and secondary minerals. This fraction is the hardest to remove and requires the use of strong acids to break down silicate structures.

Soil biology

Macroinvertebrates in the soil play a prominent role in sustaining the soil health. Among the multitude of macroinvertebrates that inhabit the soil, earthworms are the most prominent. They not only inhabit the soil but also contribute to the physical, chemical and biological well being of the soil. They assist in the breakdown of litter, in maintaining water stable soil aggregates, proper aeration and infiltration and thus the soil air – soil moisture- soil temperature relations that favour the proliferation of all other soil biota from microbes to plant roots. The earthworm casts are richer in finer particles, humus and microbes than the soil around. Darwin (1881) documented the role of earthworms in the maintenance of soil structure (Lavelle 1998), aeration and fertility. Aristotle (cf. Shipley, 1970) referred to earthworms as the “intestines of the earth”. Earthworms are considered to have originated during the Precambrian era as evidenced by fossils from Potterne, Wiltshire, UK (Piearce *et al*., 1990).

Earthworms are considered as good indicators of soil health because a soil rich in earthworms support healthy populations of bacteria, fungi, actinomycetes, protozoans, insects, spiders, millipedes and many other organisms. All these living organisms together contribute to the living soil that maintains itself. But the advent of chemicals and its indiscriminate use as nutrients and biocides encouraged by the requirements of hybrid varieties has adversely affected these living beings in the soil. Most of them have either perished or have become scarce in most agricultural soils. The soils are either dead or dying.

High input agriculture involving cash crops and short duration crops such as paddy, banana and vegetables are known to desertify the soil as regards its faunal component. Indiscriminate application of chemicals including fertilisers, fungicides, bactericides, nematicides, insecticides and weedicides have either got rid of most living organisms or encouraged the proliferation of a few tolerant ones. Earthworms are known to succumb easily to soil acidity, moisture stress, salts, heavy metals and most of the applied chemicals though they try to accumulate heavy metals in their body to some extent.

Landuse has a direct impact on the soil since the particular crop with its specific requirements necessitate application of inputs such as nutrients and plant protection chemicals. Man's greed to get maximum profit within the shortest time lures him to adopt all practices that can increase his crop yield more often than not leading to overdose application of such inputs. Paddy, banana and vegetables are cultivated with such high levels of chemical application. Mixed cropping with coconut as the main crop is moderate in this respect. The abundance and diversity of earthworms in different landuses thus differ depending on the management practices.

Water

Apart from soil, water is one of the basic needs of life and essential for survival. Groundwater is used for domestic and industrial water supply and irrigation all over the world. In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population and the accelerated pace of industrialization. Water quality and subsequently human health is threatened by most of the industrial and agricultural development activities. Rapid urbanization, especially in developing countries like India, has affected the availability and quality of groundwater due to its overexploitation and contamination caused by improper waste disposal, especially in urban areas. According to World Health Organization (WHO), about 80% of all the diseases in human beings are caused by consumption of contaminated water. Once the groundwater is contaminated, its quality cannot be restored by stopping the pollutants from the source. It therefore becomes imperative to regularly monitor the quality of groundwater and to device ways and means to protect it. Water quality index (WQI) is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policy makers. It, thus, becomes an important parameter for the assessment and management of groundwater. WQI is defined as a rating reflecting the composite influence of different water quality parameters. WQI is calculated in this study from the point of view of the suitability of groundwater for human consumption.

Aquatic biology

Insects living in water are affected by the quality of water in which they live. Some of them are very sensitive to habitat alterations and succumb to pollution of water. There are others with adaptive mechanisms and thus capable of surviving adverse environments. May fly (Ephemeroptera) , stone fly (Plecoptera), and caddis fly (Trichoptera) commonly referred as EPT taxa are generally sensitive though variations in tolerance are also observed between their species. On the other hand, larvae of flies such as the common house fly or the mosquitoe thrive well in contaminated water. Larvae/nymphs of dragonflies and damselflies occupy a position in between the most sensitive and most tolerant groups.

Variation in tolerance to water quality deterioration has been put to effective use in monitoring water quality. Aquatic macroinvertebrates are suitable for this purpose because (i) they respond quickly to water quality changes (ii) response to stresses differs from taxa to taxa (iii) their sedentary nature permit assessment of spatial variations and (iv) their long lifecycle allow determination of temporal changes in the ecosystem (Resh, 1979., Rosenberg *et al*., 1986., Sivaramakrishnan *et al*., 1996., Barbour *et al*., 1999). A manual on the usefulness of aquatic macroinvertebrates in biomonitoring of water quality of Peninsular India has been brought out by Subramanian and Sivaramakrishnan (2007). Aquatic insects and their response to water quality was reported by Sharma *et al*.,(2008a) also. Utility of aquatic macroinvertebrates in assessing water quality has been documented by workers around the world (Resh,1979., Trivedi,1991., Sivaramakrishnan *et al*., 1996., Bath and Kaur, 1997., Dinakaran and Anbalagan, 2007., Arimoro and Muller,2010., Bio *et al*.,2011).

Water quality is impaired by several factors such as organic enrichment from domestic and municipal waste, phenolic compounds from decomposing vegetable matter, oil and grease, fertilizer and pesticide residues and industrial effluents of various kinds and other chemicals and heavy metals. Oxygen present in the water is consumed by both chemicals and microbes during aerobic decomposition process reducing the availability of dissolved oxygen to other aquatic species including insects, molluscs, fish etc. The tolerant taxa have developed alternative mechanisms to tide over the crisis and adapt to such stresses. But most other organisms that are sensitive either perish or migrate to better sites if possible. Aquatic macroinvertebrates have been studied the world over and tolerance values on a scale of 0-10 has been assigned to the common taxa of wide occurrence. Indices have also been developed at family level called family biotic index based on these tolerance values.

The study was conducted in Kadukutty region of Thrissur District. In recent times Kadukutty has been reported to face serious deterioration of environmental quality. Agriculture, which constitute >90% of the land use has been intensive with high inputs of fertilizers and pesticides and assured irrigation facilities with a wide network of canals. A major industrial establishment, NITTA Gelatin India Ltd. (NGIL) is reported to cause pollution in the region. Both these are expected to contribute their share to soil and water contamination in the area. Baseline data on pollution of soil and water is scarce in the site and hence the initiative. The present study entitled 'Soil and water quality status of Kadukutty region' was thus taken up with following specific objectives:

1. To study the soil quality in the Kadukutty region
2. To study the water quality in the Kadukutty region
3. To relate the soil quality with the land use of Kadukutty region

REVIEW OF LITERATURE

Soil

Within the terrestrial ecosystem, soils play a major role in element cycling and accumulate heavy metals in concentration orders of magnitude higher than in water and air (Ashraf et *al*., 2012). Soils receive potentially toxic elements from both natural and a wide range of anthropogenic sources, including the weathering of primary minerals; mining; fossil fuel combustion; the metallurgical, electronic and chemical industries; and waste disposal.

Soils consist of heterogeneous mixtures of organic and inorganic substances and the binding mechanisms for metals vary with the composition of the soil. The ecological effects of heavy metals in soil are closely related to the distribution of species in the solid and liquid phases of the soil (Lund *et al.,* 1990). Depending on their origin, trace elements exist in different mineral forms and chemical compounds, and in different combinations with mineral and organic components of soil and sediments which may vary according to existing conditions.

Heavy metal contamination of soil is a major concern because of their toxicity and threat to human life and the environment (Begum *et al.,* 2009). At present, the anthropogenic contribution of heavy metals into the environment far exceeds natural inputs (Nriagu *et al*., 1988). Toxic heavy metals entering the ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications (Fagbote *et al.,* 2010). Studies have shown that long-term heavy metal contamination of soils has harmful effects on soil microbial activity, especially microbial respiration and enzyme activity (Doelman and Haanstra, 1979; Brookes, 1995; Holtan-Hartwig et al., 2002; Begonia et al., 2004). Toxic effects of heavy metals on microorganisms manifests in numerous ways such as decrease in litter decomposition and nitrogen fixation, less efficient nutrient cycling and impaired enzyme synthesis (Baath, 1989). Aside from long-term metalmediated changes in soil enzyme activities, many reports have shown large reductions in microbial activity due to short-term exposure to toxic metals (Doelman and Haanstra, 1979; Hemida *et al*., 1997). The nature of effects of heavy metal pollution could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic.

The threat that heavy metals pose to human and animal health is aggravated by their low environmental mobility, even under high precipitations, and their long-term persistence in the environment (Mench *et al*., 1994; Chirenje *et al*., 2004). Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson, 2001). Cadmium is also associated with bone defects, *viz;* osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardic dysfunctions. Depending on the severity of exposure, the symptoms include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary oedema and death. Pulmonary effects (emphysema, bronchiolitis and alveolitis) and renal effects may occur following subchronic inhalation exposure to cadmium and its compounds (McCluggage, 1991; INECAR, 2000; European Union, 2002; Young, 2005). Itai-itai disease was the documented case of mass cadmium poisoning in Toyama Prefecture, Japan, starting around 1912. The cadmium poisoning caused softening of the bones and kidney failure. The disease is named after the severe pains caused in the joints and spine.

Lead is a toxic metal that can accumulate in human body and in animals and plants. Its main toxic effects are anaemia, nerve dysfunction and kidney damage. Low concentrations of lead in the body will harm normal cells, and lead molecules in the blood interfere with normal nerve cell function. Its accumulation in the brain has particularly severe impacts in early brain development (such as the embryonic period), it can lead to mental retardation and affect human brain function. Contact with excessive lead and inorganic lead compounds can cause damages to nerve, digestive, and hematopoietic systems. Lead poisoning symptoms include: headache, insomnia, bone and kidney damage, anaemia, miscarriages in women, and general systematic symptoms. Child lead poisoning causes delayed brain development or acute brain problems (Biqing *et al*., 2008). Lead poisoning also causes inhibition of the synthesis of haemoglobin; dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS). Other effects include damage to the gastrointestinal tract (GIT) and urinary tract resulting in bloody urine, neurological disorder and can cause severe and permanent brain damage. While inorganic forms of lead, typically affect the CNS, PNS, GIT and other biosystems, organic forms predominantly affect the CNS (McCluggage, 1991; INECAR, 2000; Ferner, 2001). Lead affects children by leading to the poor development of the grey matter of the brain, thereby resulting in poor intelligence quotient (IQ) (Udedi, 2003).

Iron is a heavy metal of concern, particularly because ingesting dietary iron supplements may acutely poison young children. Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption. It can cause a rusty red or brown stain on fixtures or laundry and/or cause water to develop a metallic taste. Target organs are the liver, cardiovascular system, and kidneys. Excess amount of Zn can cause system dysfunctions that result in impairment of growth and reproduction (INECAR, 2000). The clinical signs of zinc toxicosis have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anemia (Fosmire, 1990). Excess amount of Mn affects central nervous system. Symptoms of acute copper poisoning include: low blood pressure, vomiting, melena, jaundice, hemolytic anemia, and coma to death (Biqing *et al*., 2008). Uptake of high quantities of nickel can cause cancer, respiratory failure, birth defects, allergies, and heart failure. Those who get exposed to nickel dust or nickel steam will have respiratory inflammation, dermatitis, leukocytosis, nasal cancer, lung cancer and other illnesses. According to field investigation, most scholars believe that the high incidence of cancer is correlated with nickel sulfide, nickel oxide and nickel carbonyl content (Biqing *et al*., 2008).

In many cases, heavy metal contents are measured and reported to describe the pollutants' threat. One of the effective ways to understand heavy metal threat is to understand their dynamic mobility. The dynamic mobility of heavy metals cannot be reliably predicted on the basis of their total content. A comprehensive knowledge of the interaction of heavy metals and their binding to other matrix (ionic, metal oxide, organic substances and sulfides) is essential to understand their mobility behavior. In other words, chemical speciation of heavy metals allows us to identify specific chemical species or binding form and helps to determine the availability and mobility of metals. The speciation of heavy metals could explain the mobility of heavy metals into the sediment (Aryal *et al*., 2008).

Since the toxicity of heavy metals is related to the existing species, their speciation is increasingly attracting attention (Li *et al*., 2001, Davidson *et al*., 1994). Nowadays there exists a need to determine not only total concentration of elements in the examined samples, but also concentrations of various forms in which these elements could exist (Baranowski *et al* ., 2002).

Speciation is defined as "the identification and quantification of different, defined species, forms or phases in which an element occurs" and is essentially a function of the mineralogy and chemistry of the soil sample examined (Tessier *et al*.,1979). Sequential extraction provides the data concerning the type of occurrence of a given form of an element, its biological and physiochemical availability, which may be helpful in describing the migration routes of metals in their natural environment (Sutherland., 2002; Kubova *et al*., 2005). Moreover, the sequential extraction procedures are a simulation of the conditions which may occur in the environment, at the same time providing information on the potential remobilization of metals affected by changed environmental conditions (Bezak-Mazur and Rabajczyk., 2001).

Different sequential extraction techniques such as the five-step procedure of Tessier *et al*. (1979) are commonly applied to evaluate both the actual and potential mobility of metals in the environment. This extraction scheme allows the division of the total metal content into five fractions: exchangeable, carbonate bound iron/manganese oxide bound and residual fraction. The scheme was developed for sediments but many studies have used these procedures for soils (Abollino *et al*., 2002; Lu *et al*., 2003; Lu *et al*., 2004). However, this scheme may not be suitable for soils which do not contain carbonate. Rauret (1998) also elaborated that the extractants used for the fraction of metals bound to carbonates (ie acetic acid and sodium acetate) and the iron and manganese oxides (ie. hydroxylamine in acid solution) were not completely suitable. Both carbonates and oxides may not be completely attacked. Shuman (1979) proposed a scheme to study microelements in acid soils that do not contain carbonates or sulphides. This scheme included exchangeable, organic matter, iron oxide, sand, silt and clay. Another speciation scheme was developed by the EC Standards, Measurement and Testing Programme., formerly BCR (Bureau Community of Reference). This scheme proposed only four fractions: ie: exchangeable (acetic acid), reducible (hydroxylamine hydrochloride), oxidisable (hydrogen peroxide and nitric acid) and residual (aqua regia) fractions (Rauret, 1998). The BCR procedure had been tested for sediments (Thomas *et al*., 1994) and soils (Davidson *et al*., 1998).

The proposal of the European Community Bureau of Reference, usually called the BCR method (Ure *et al.*1992), seeks to minimize errors in the treatment and analysis of samples, to identify the most appropriate analytic procedure and to supply reference materials for comparison of the results between different laboratories. This method appears to be more operationally effective than others proposed previously, such as that of Tessier (Tessier *et al.*, 1979). Nevertheless, the dissolution or selective destruction of the soil components seems to be implicit in any sequential extraction technique, as does the non-specificity of the reagent or the possibility of the redistribution of metals during the extraction (Sheppard and Stephenson, 1997). Recent years have shown growing interest in the BCR method, both in polluted as well as non-polluted soils (Ure *et al*, 1993; Sahuquillo *et al.*, 1999; Barona *et al.*, 1999; Sza´kova´ *et al.*, 1999). The method has been used not only in laboratory experiments, with mineralogically uniform samples (humic acids, calcium carbonate, iron oxides or manganese, illite, montmorillonite, etc.) and with controlled quantities of added metals (Whalley and Grant, 1994), but also in natural substrates, fundamentally sediments from estuaries (Davidson *et al.*, 1994; Thomas *et al.*, 1994; Fiedler *et al.*, 1994; Sahuquillo *et al.*, 2002). The original BCR procedure has been used with good reproducibility within laboratories. The use of a sediment standard reference material showed excellent reproducibility, except for analytes that were close to detection limits (Mester *et al.* 1998; Svete e*t al.* 2001).

A common approach to estimate how much the soil is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels (Huu *et al.*, 2010). Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material (Abrahim *et al.*, 2008, Mediolla *et al.*, 2008). The EF method normalizes the measured heavy metal content with respect to a sample reference such as Fe, Al or Zn (Mediolla *et al.*, 2008). A reference element is often the one characterized by low occurrence variability. It is used to differentiate heavy metals originating from human activities and those of natural sources. (Taylor and Meclenan, 1985). To assess the extent of contamination of heavy metals, contamination factor and degree of contamination has been used (Rastmanesh *et al.*, 2010). The sum of the contamination factors of all the elements in the sample gives the degree of contamination.

Several soil arthropods particularly, collembola, snails and isopods are known to suffer mortality at known threshold levels of soil contaminants, especially heavy metals (Cortet *et.al*., 1999; Balamurali and Sanalkumar, 2010). Declining abundance with reduced soil moisture level in several species of oligocheate worms, collembolan and dipteral larvae were reported by Briones *et.al*., (1997). Earthworms, particularly Lumbricus Spp. are good bioindicators of soil quality. The influence of heavy metals in the soil on earthworms and their bioaccumulation has been the subject of many studies (Kennette *et.al*., 2002).

Earthworms in general are considered resistant to many pesticides and have been reported to concentrate the pesticides and heavy metals in their tissues. They also inhibit the soil borne pathogen and work as a detoxifying agent for polluted soils (Ireland, 1983). Earthworms may serve as bioindicator of soil contaminated with pesticides like polychlorinated hydrocarbons, polycyclic biphenyls and polycyclic hydrocarbons (Spurgeon and Hopkins,1999). Lead, cadmium, zinc and copper are accumulated and bioconcentrated in earthworms (Cortet et.al., 1999).

Water

Water quality refers to the chemical, physical and biological characteristics of water. It involves the process of evaluation of the physical, chemical and biological nature in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and aquatic system. The most common standards used to assess water quality relate to health of ecosystems, safety of human contact and drinking water. Water quality depends on the local geology and ecosystem, as well as human uses such as use of water bodies as sink (Johnson *et al.,* 1997). The parameters for water quality are determined by the intended use. Water quality tends to be focused on water that is treated for human consumption, water for industrial use, or in the environment. Water contaminants that may be present in untreated water include microorganisms such as viruses and bacteria; inorganic contaminants such as salts and metals; organic chemical contaminants from industrial processes and petroleum use; pesticides and herbicides; and radioactive contaminants. Water Quality Standards have been established to regulate substances that potentially affect human health, environment and aesthetic qualities of water. The World Health Organization (WHO) guideline for Drinking Water Standards, United

States Specification for Drinking Water and European Union Specification for Drinking Water are among the recognized water quality standards. Dissolved minerals may affect suitability of water for a range of industrial and domestic purposes. The most familiar of these is the presence of ions of calcium and magnesium which interfere with the cleaning action of soap, and can form hard sulphate and soft carbonate deposits in water heaters or boilers. Hard water may be softened by removing these ions.

Water quality standards for surface waters vary significantly due to different environmental conditions, ecosystems, and intended human uses. With the advent of industrialization and increasing populations, the range of requirements for water has increased together with greater demands for higher quality water. Water has been considered the most suitable medium to clean, disperse, transport and dispose of wastes (domestic and industrial wastes, mine drainage waters, irrigation returns, etc.). These activities have undesirable effects on the natural environment. Also, uncontrolled land use, urbanization, deforestation, accidental (or unauthorized) release of chemical substances and discharge of untreated wastes or leaching of noxious liquids from solid waste deposits have impacted negatively on the quality of water resources .

Water is a dynamic renewable natural resource. Its availability with good quality and adequate quantity is very important for human life and other purposes. In general, the quality of water is equally important as the quantity. Therefore, water quality is considered as an important factor to judge environmental changes which are strongly associated with social and economic development. It is necessary to obtain accurate and timely information to observe water quality of any water resource (Sonawane and Shrivastava., 2010). Therefore, analysis of water quality is very important and of high social relevance. Water quality must be in the standard range for drinking usage.

Aquatic macroinvertebrates are an integral part of the food chain in lotic environments and they are sensitive to changes in the environment though degrees of sensitivity differ among various groups. Communities of organisms integrate the impact of different stressors and thus provide a broad measure of their aggregate impact. Macroinvertebrates have limited migration and their assemblages are made up of species that constitute a broad range of trophic levels and pollution tolerances and thus are particularly suited for assessing site specific impacts. They are most frequently used in biomonitoring since many of them are sensitive to pollution and integrate short term and long term effects of environmental stressors (Kazanci and Dugel 2000). Many gill- breathing may fly, stone fly and caddis fly larvae can survive only where there is abundant oxygen in the water. There are other invertebrates such as tubifex worms and chironomid midge larvae that can tolerate low oxygen levels due to special adaptations in their respiratory system (Davis et al. 2001).

MATERIALS AND METHODS

Kadukutty region is located in Mukundapuram Taluk of Thrissur District. Data on land use pattern in Kadukutty was collected from secondary sources (Figure 1).

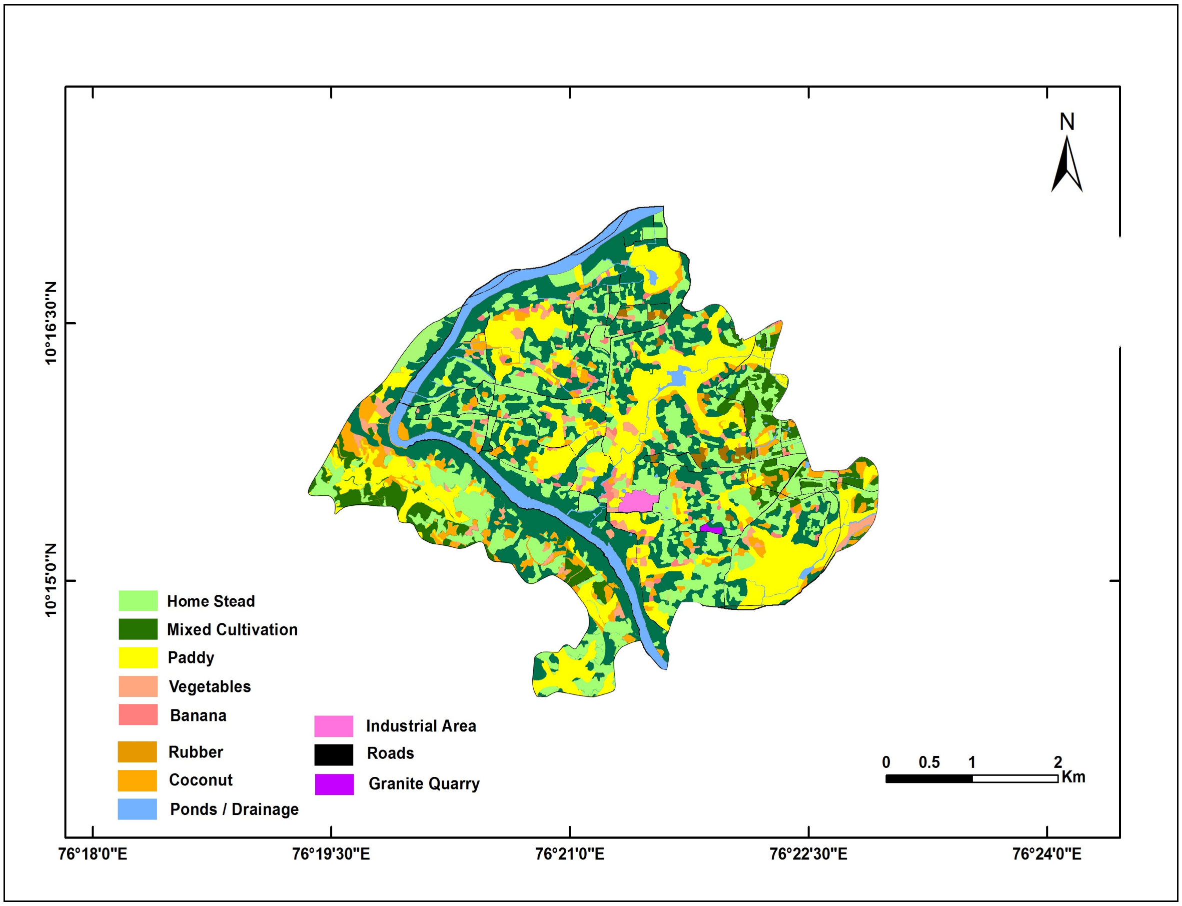

Figure 1. Map of the study area

Soil sample collection

Composite surface soil samples (0-30 cm) were collected after perambulation giving due weightage to different landuses. A total of 102 soil samples were collected from different land use sites. All the samples were air dried, finely powdered using pestle and mortar and passed through 2mm sieve for laboratory analysis (Figure 2).

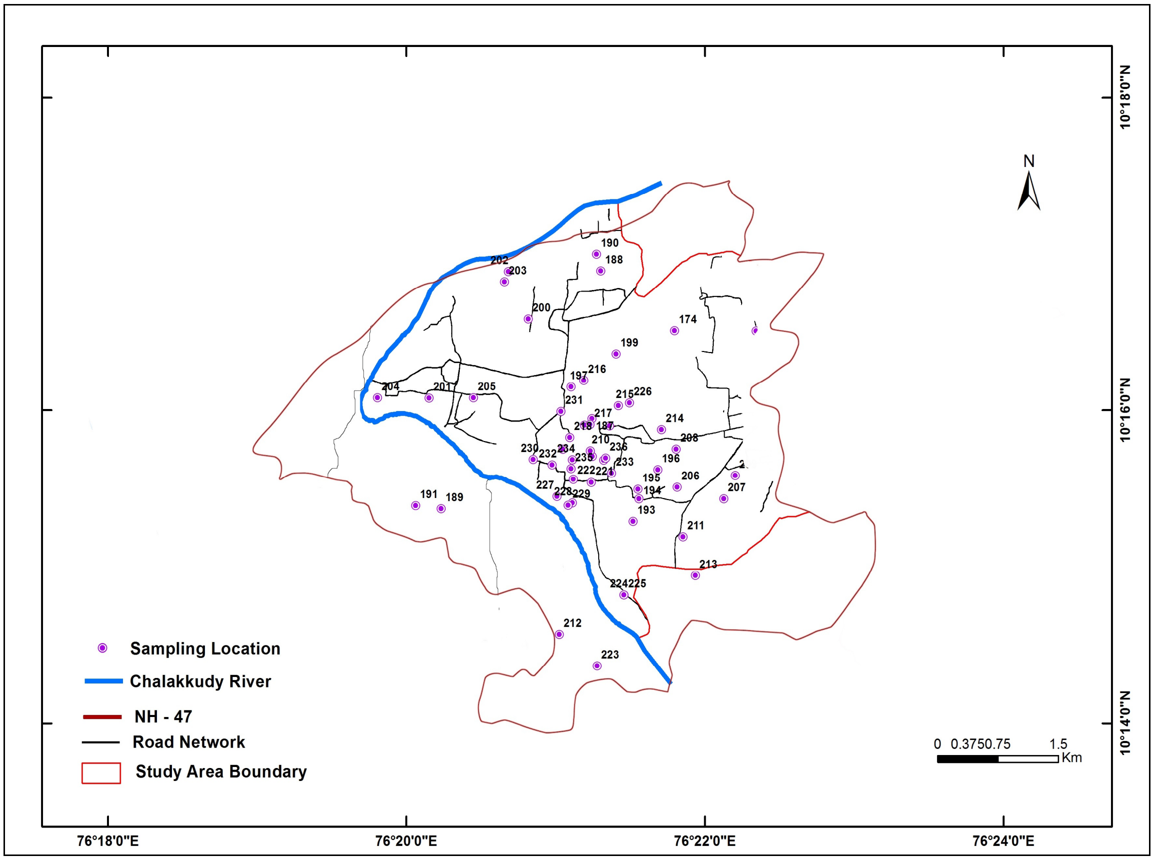

Figure 2. Soil sampling locations in the study area

Methods of soil analysis

The soil samples were first air dried, sieved and stored at room temperature . The soils were characterized with respect to salient physico-chemical properties. The protocols used for characterization of soils to realize the set objectives are detailed below.

1. Soil reaction (pH)

The pH of the soil was determined in 1:2.5 (soil: water) suspension, using combined electrode (glass and calomel) in a digital pH meter.

2. Organic carbon (OC)

Organic carbon was determined in soil samples passed through 100 mesh sieve by wet digestion method of Walkley and Black (1934) as described by Jackson (1967).

3. Heavy metals

Heavy metal contents of Cd, Cu, Cr, Mn, Ni, Pb and Zn in the samples were determined using atomic absorption spectrometer (Varian-240).

3.1 Speciation of heavy metals

Fraction 1 – Exchangeable metal fractions

Added 40 ml of 0.11 M acetic acid to 1.00 g of dry soil sample in a 50 ml polypropylene tube. The mixture was shaken for 16 hours at 22 ± 3 ^{0}C at 400 rpm. After the shaking period, the extract was separated from the solid phase by centrifuging at 3800 rpm for 20 minutes. The supernatant liquid was decanted into a 100 ml beaker and covered with a watch glass. The residue was washed again by adding 20 ml of double – distilled water, shaking for 15 minutes and then centrifuging. The second supernatant liquid was discarded without any loss of residue.

Fraction 2 – Metal forms bound to iron and manganese oxides

Added 40 ml of 0.1 M hydroxylammonium chloride (adjusted to pH 2 with 2M nitric acid) to the residue from the first step. The mixture was shaken for 16 hours at 22 ± 3 ^{0}C at 400 rpm. The extract was separated from the solid phase by centrifuging at 3800 rpm for 15 minutes. The supernatant liquid was decanted into a 100 ml beaker and covered with a watch glass. The residue was washed again by adding 20 ml of double – distilled water, shaking for 15 minutes, and then centrifuging. The second supernatant liquid discarded without any loss of residue.

Fraction 3 – Metal forms bound to organic matter

Added 10 ml of 8.8 M H_2O_2 to the residue in the centrifuge tubes in small instalments.The tube ingredients were digested at room temperature for 1 hour with occasional manual shaking. Continued the procedure for 1 hour at 85 ^{0}C and reduced the volume to a few millilitres by further heating in a water bath. A second aliquot of 10 ml of H_2O_2 was added to the residue and the digestion procedure repeated. The solution was heated to near dryness, and 50 ml of 1.0 M ammonium acetate solution (adjusted to pH 2 with nitric acid) was added to the moist residue. The sample solution was shaken, centrifuged and the extract separated as described above.

Fraction 4 – Residual metal forms

Added 6 ml of double-distilled water to the soil residue followed by addition of aqua regia (1:3 :: HNO_3:HCl v/v) solution in a sequence of 15 and 10 ml. After adding each aqua regia solution, the residue was evaporated to near dryness on a water bath. The extract was transferred by adding 1 M HNO_3 solution in small amounts on the last residue in the centrifuge tube. The tube walls were carefully washed with the same acid solution and then the washings were collected in a beaker.

Analytical reagent grade chemicals and double-distilled deionised water were used for preparing all solutions. Stock solutions containing 1000 ppm of the analytes were prepared from nitrate salts of Cd, Cu, Fe, Mn, Ni, Pb and Zn in HNO_3 (1% solution). Working standard solutions were prepared in 1 M HNO_3 by appropriate dilutions of the stock solutions.

Metal determinations in the soil extracts and digests were carried out by means of Atomic Absorption Spectrometer (Varian-240) with an air – acetylene flame.

3.2 Soil contamination indices

Degree of contamination

The sum of the contamination factors of all the elements in the sample gives the degree of contamination as indicated in the equation below:

$$C_{deg} = \sum C^i_f$$

Four categories has been defined for the degree of contamination as follows; <8: low degree of contamination, 8-16: moderate degree of contamination, 16-32: considerable degree of contamination and >32: very high degree of contamination.

Contamination factor

Cf is the single element index which is determined by the relation:

$$C^i_f = C^i_{0-1} / C^i_n$$

Where C^i_f is the contamination factor of the element of interest, C^i_{0-1} is the concentration of the element in the sample, C^i_n is the background concentration. In this study continental crustal average has been used as background concentration.

C^i_f is categorized into four groups: <1: low contamination factor, 1-3: moderate contamination factor, 3-6: considerable contamination factor and >6: very high contamination factor.

Enrichment factor (EF)

It is used to differentiate heavy metals originating from human activities and those of natural sources. This is determined by the relation:

$$EF_X = [X_S / E_S (ref)]/[X_C/E_C (ref)]$$

where EF_X is the enrichment factor for the element X, X_S is the concentration of element of interest in sample, E_S (ref) is the concentration of the reference element used for the normalization in the sample, X_C is the concentration of the element in the crust and E_C(ref) is the concentation of the reference element used for normalization in the crust.

Five contamination categories are recognized on the basis of the enrichment factor: EF< 2 states deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5-20 significant enrichment, EF = 20-40 very high enrichment and EF> 40 extremely high enrichment (Yongming *et al.*, 2006; Kartal *et al.*, 2006). The crustal abundance of heavy metals used for the calculations are given below.

Table 1. Crustal abundance of heavy metals (Compiled from various sources)

Heavy metal	Crustal abundance (ppm)
Cd	0.35
Cu	30
Ni	50
Pb	35
Zn	90
Fe	38000

3.3 Soil biology - earthworms

Earthworms were sampled in different land uses by digging soil in a 50x50cm area to a depth of 50cm and hand sorting. Morphologically dissimilar earthworms were preserved separately in 10% formalin and identified following standard keys. Specimens were further got confirmed by experts. Diversity and dominance of earthworms were calculated using the ecological software named “PAST”.

4. Water sample collection and analysis

Water samples were collected from wells as well as water courses. Samples were collected from representative water bodies during pre monsoon and post monsoon periods. Altogether 25 wells and 2 water courses were selected for the study. The details of the sampling sites are given in table 2.

Table 2. Well water sampling sites in Kadukutty			
Sl. No	**Location**	**Sl. No**	**Location**
1.	N 10^0 15’ 27.8” E 76^0 19’ 44.0”	14.	N10^0 15’ 52.2” E76^0 19’ 32.5”
2.	N 10^0 15’ 27.8” E 76^0 19’ 44.0”	15.	N10^0 15’ 2.2” E76^0 19’ 29.3”
3.	N 10^0 15’ 28.8” E 76^0 19’ 38”	16.	N10^0 15’ 1.1” E76^0 19’ 27.4”
4.	N 10^0 15’ 20.8” E 76^0 19’ 41.2”	17.	N10^0 15’ 15.3” E76^0 19’ 28.2”
5.	N10^0 15’ 19.7” E76^0 19’ 44.0”	18.	N10^0 15’ 11.5” E76^0 19’ 27.5”
6.	N10^0 15’ 12.3” E76^0 19’ 44.6”	19.	N10^0 15’ 11.6” E76^0 19’ 20.8”
7.	N10^0 15’ 08.9” E76^0 19’ 36.6”	20.	N10^0 15’ 46.1” E76^0 19’ 32.3”
8.	N10^0 15’ 04” E76^0 19’ 52.4”	21.	N10^0 16’ 18.6” E76^0 19’ 12”
9.	N10^0 15’ 1.8” E76^0 19’ 59.9”	22.	N10^0 16’ 48.7” E76^0 19’ 29.9”
10.	N10^0 15’ 4.6” E76^0 19’ 4.1”	23.	N10^0 16’ 48.8” E76^0 19’ 25.5”
11.	N10^0 14’ 52.5” E76^0 19’ 47.4”	24.	N10^0 17’ 0.8” E76^0 19’ 29.6”
12.	N10^0 14’ 49” E76^0 19’ 42.8”	25.	N10^0 16’ 19.6” E76^0 19’ 2.4”
13.	N10^0 14’ 44” E76^0 19’ 35.9”		

Perumthode and Vadakkechaal draining the region were selected for water course sampling. Samples were collected during pre monsoon and post monsoon periods.

The water samples were analyzed for pH, EC, TDS, sulphate, phosphate, sulphide, nitrate, fluoride, heavy metals (Mn, Fe, Ni, Pb, Cu, Cr, Cd, Hg, Zn, As), oil & grease, phenolic compounds, DO, BOD, COD, coliforms and pesticides (APHA, 2005).

4.2. Aquatic biology - macroinvertebrates

Sampling of macroinvertebrates was carried out using Kick net and Dip net of 500µm mesh size. The kick net was placed downstream and the stream bottom substrates 1m above kicked to dislodge specimens clinging to debris and stones into the kick net. The contents in the net were emptied into bucket and samples collected. The D frame net was employed to collect specimens clinging to vegetation, root mats etc., along the stream banks. The collected specimens were preserved in 75% ethanol for further identification.. The family biotic index (FBI), an index worked out on the basis of the abundance and tolerance level of different taxa was also worked out to indicate water quality with respect to macroinvertebrates.

$$\text{Family Biotic Index (FBI)} = \Sigma\, n_i\, tv_i / N$$

where n_i = number of specimens belonging to i^{th} taxa; tv_i = tolerance value of the particular taxa and N = total number of specimens.

Table 3. Categorization of FBI values

FBI	**Category**	**Degree of organic pollution**
0.00 - 3.75	Excellent	Organic pollution unlikely
3.76 - 4.25	Very Good	Possible slight organic pollution
4.26 - 5.00	Good	Some organic pollution probable
5.01 - 5.75	Fair	Fairly substantial pollution likely
5.76 - 6.50	Fairly Poor	Substantial pollution likely
6.51 - 7.25	Poor	Very substantial pollution likely
7.26 - 10.00	Very Poor	Severe pollution likely

RESULTS AND DISCUSSION

1. General description of the study area

The Kadukutty region lies at an altitude of 20 - 100 m above MSL and can be physiographically classified as midlands. Topography of the region ranges from flat to almost flat in the wet lands and undulating to steeply dissected in the higher elevations. The panchayat has a good network of drainage channels and the drainage pattern is dendritic.

The area enjoys a humid tropical climate with two monsoons - South West monsoon and North East monsoon with an average annual rainfall of around 2500 mm and 3 to 4 months of dry spell. The area has isohyperthermic soil temperature and ustic soil moisture regime. Bed rock in the area is gneissic charnockites. Many parts of paddy fields in the region have layers of fluvial sand deposit below the clay layer. (Geological Department, Thrissur).

Average depth of ground water table varies from 2-10 m in the study site. Irrigation in the panchayat is mainly from wells and ponds using pump sets. Canals, ponds and water courses also supplement irrigation substantially (Department of Ground Water, Thrissur).

Distribution of area under different land uses in Kadukutty is given in Table 4. Rice, coconut, banana, pepper, nutmeg, rubber and vegetables are the main crops cultivated in the panchayat. Earlier paddy was the main crop. Vegetables are raised in paddy fields during summer months.

Mixed cropping is the major cropping system in the panchayat. About 97 ha of the total area is under coconut though monoculture of coconut is almost absent. It is intercropped with crops like banana, arecanut, pepper etc. which makes mixed cropping the major cropping system in this area. Rubber is another major crop cultivated and covers an area of approximately 21 hectare. Inter cropping with ginger, pineapple etc. up to an age of 3 years is a common feature adopted by most of the farmers in the region. Cover cropping is not widely used in most of these plantations. Banana is mostly cultivated in converted paddy lands. Intensive management is practiced in banana. Irrigation is provided during dry periods. Farmyard manure including poultry castings are applied in paddy fields on a regular basis.

Table 4. Major land uses in Kadukutty region	
Land use	**Total area (ha)**
Mixed cultivation	597.5
Home stead	387.4
Paddy	305.7
Coconut	97.3
Vegetables	64.8
Banana	55.0
Rubber	21.5
Nitta Gelatin India Ltd.	8.74
Granite quarry	3.5

2. Soil quality in Kadukutty

2.1. General soil characters

Soil reaction (pH) in Kadukutty was strongly to very strongly acidic (Table 5). The pH of the soils ranged from 4.64 in vegetable sites to 5.42 in mixed cultivation sites. Vegetables grown in the region are usually short duration ones with high input of fertilizers which drastically reduces soil pH. Soils were found to be medium to high in organic carbon content. Mixed crop soils had very high (1.86%) organic carbon contents. Paddy soils also had moderate amounts of organic matter. Also due to submergence, organic carbon decomposition will be low in paddy soils. Vegetables sites recorded the lowest organic carbon content of 0.98%

Table 5 : pH and organic carbon (OC) in soils of Kadukutty under different crops					
Soil parmeters	**Banana**	**Mixed**	**Paddy**	**Rubber**	**Vegetables**
pH	4.97 (0.13)	5.42 (0.08)	5.08 (0.14)	4.88 (0.19)	4.64 (0.15)
OC (%)	1.10 (0.13)	1.86 (0.38)	1.27 (0.46)	1.21 (0.42)	0.98 (0.16)

2.2. Heavy metal content in soil

The heavy metal (Zn, Cu, Cd, Pb and Ni) concentrations of the study area are presented in Table 6. The data shows that cadmium, lead and nickel were beyond the permissible limits in most of the agricultural lands in Kadukutty. Among the different agricultural land uses, cadmium and lead contents were found to be lowest in rubber, 8.7 and 321.3 mg/ kg soil respectively. The highest values for cadmium were found in vegetable planted soils (28.2 mg/ kg soil) followed by paddy lands (18.8 mg/ kg soil). Vegetables and paddy fields are intensively managed and cadmium is essentially added in these soils through mineral fertilizers. Mixed cropping was found to have low Cd content than the other cultivated areas.

Soils collected from cultivated areas were found to have Ni slightly above permissible limits. Most of the agricultural soils in the region are maintained with huge addition of manure along with mineral fertilizers. However addition of manure, especially poultry manure (imported from neighbouring states), may be a reason for accumulation of Ni in the analysed soil samples from agricultural systems. Fertilizer application and other soil amendments such as biosolids and poultry litter have been shown to contribute to the release of heavy metals in the soil (Zhang et al. 2004; 2006).

Earlier reports also show that in agro ecosystems with a long history of urbanization and crop production, the concentrations of heavy elements in soil can be higher than those found in the parent materials. Elevated concentrations of heavy metal elements in disturbed environments may be due to the application of the elements Cu, Zn, Fe, Mn, and B to plants for correcting nutrient deficiencies or addition of Cd and Ni as impurities in fertilizers (Fageria et al. 2002). Other agricultural chemicals that result in the loading of heavy metals in soils include fungicides, insecticides, herbicides, biosolids, and other amendments. Trace metals from these sources also end up in the soil where their redistribution is dependent on the biogeochemical cycles that impact plant and animal lives (He et al. 2005). Higher standard error values observed for heavy metals Cu, Cd, Ni, Pb and Zn in soil suggests that these metals were not uniformly distributed in the study area.

Table 6 : Heavy metal content (mg/ kg) in soils of Kadukutty					
Systems	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
Banana	17.7 (2.8)	34.4 (3.6)	86.5 (8.8)	375.4 (36.1)	30.4 (5.8)
Mixed	8.7 (3.2)	17.7 (2.6)	95.3 (12.7)	321.3 (49.7)	39.8 (9.0)
Paddy	18.8 (3.2)	35.3 (3.6)	105.0 (3.7)	405.7 (8.2)	36.8 (2.5)
Rubber	10.4 (4.9)	27.4 (5.8)	100.2 (8.2)	424.6 (19.7)	52.5 (12.3)
Vegetables	28.8 (2.6)	34.4 (7.9)	93.8 (6.9)	414.0 (28.2)	19.9 (5.1)
Permissible limit (a)	3-6	135-270	75-150	250-500	300-600
Permissible limit (b)	1-3	50-140	30-75	50-300	150-300

a= Limits described by European community commission (ECC) (1986).
b =Permissible limits of Indian standards (Awashti, 2000; Sharma *et al*., 2006; Gupta *et al*., 2008). * Values in parentheses shows standard error

2.3. Heavy metal speciation in soils

Agricultural inputs by way of fertilizers and pesticides and industrial effluents pollute the soil to various levels. However, the total metal content may not be an indicator of the polluting capacity of each metal which depends on the chemical form (species) in which they are present in the soil. In the analysed samples, Cd fractions varied as F_4 (residual fraction) > F_3 (fraction bound to organic matter) > F_2 (fraction bound to Fe & Mn oxide) > F_1 (exchangeable fraction) indicating that these fractions may not be easily available to living systems (Table 7 and Figure 3). The potential source of this heavy metal may be agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants in soils (Weggler *et al* ., 2004: Bin Li *et al*., 2001). The retention of higher amounts of Cd in the cultivated soils poses a serious danger of bioaccumulation in plants as plants usually show a high preference for Cd than other studied toxic metals in the system (Amoo et al., 2005).

Cu is an element which shows an affinity towards organic matter and hence is usually retained at the site of application (Ashraf *et al*. 2012; Alloway, 1990; Lenntech, 2009). In the present study highes amount of Cu exists in the residual form and large portions of Cu was found bound to Fe and Mn oxides. The terrestrial samples had pH <5 (very strongly acidic) which greatly impairs the binding capacity of organic matter by way of organic compound dissolution.

Soils in the humid tropics are usually rich in sesquioxides (Baranowski *et al*., 2002) and the mean Fe content of the earth's crust is 35000 mg/ kg soil (Taylor and McLennan, 1995). None of the analyzed soil samples had Fe values higher than the crustal means. The Fe fractions were found to decrease in the order F_2 (fraction bound to Fe and Mn oxide) > F_4 (residual fraction) > F_3 (fraction bound to organic matter) > F_1 (exchangeable fraction). The significantly higher amounts of Fe in the exchangeable form in these sites can act as a potential danger for increased Fe absorption by food crops. In all the terrestrial samples, organic matter bound Fe fraction was found to be 8 - 9 times higher than the exchangeable fractions at all the sites. Soil organic matter has many functional groups contained in it that can serve as exchange sites. Most of the compounds in question are functional groups high in oxygen. Trace metal compounds are tied up by the highly reactive oxygen groups that hold the metals in place. The higher amount of organic bound Fe in the samples point to such a reaction. The high amount of organic matter bound Fe poses the potential danger of increased mobility and contaminating the ground water in the region.

In all the samples appreciable amount of Mn was found to exist in the exchangeable form. Mn exists as a cation in soil solution and is capable of altering the surface charge of oxides / hydrous oxides using adsorption or chemisorption. The process necessarily involves formation of short directional bonds with oxide surfaces and Mn^{2+} is capable of forming such bonds in soil systems. The association of large proportions of Mn with oxides has also been reported by Ashraf *et al.,* 2012. Exchangeable fraction is an important source of Mn to plants but, at the same time, its content in soils is known to vary by orders of magnitude within short periods of time and so its level at any particular time may not be well related to plant Mn uptake (Warden *et al*., 1991).

Ni was found to be high in the terrestrial region and was found to be present beyond permissible limits. The high content of Ni in the soil may be due to application of irrigation water contaminated with Ni. Irrigation water contaminated with sewage sludges act as a potential source for Ni. Similar observations were also made by Khurana *et al*., 2008 who reported that high concentration of Ni was observed in the sewage irrigated soils of all the industrial towns. The sampled sites were intense in agricultural activities and are irrigated by river water. There is a high possibility that the river is polluted by sewage sludge discharged from industries on its banks. The high Ni content in the river sediments also confirms such conclusions (Greeshma, 2014). Among the total Ni content, exchangeable fraction was found to predominate in all the samples. Yin *et al*. (1995) found that Cl^- ion could be an important factor enhancing non adsorption and mobility of Ni in soil. NGIL in Kadukutty using HCl to extract osein from animal bones is expected to increase chloride ions in the environment. This fact is of particular importance since the ability of Cl^- ions to maintain relatively high concentration of heavy metals in soil solution may produce favourable condition for a faster leaching of metals in the soil profile according to the soil texture or irrigation conditions. Moreover as it is an area of intense cultivation, the presence of NH_4^+, Na^+, K^+ and Ca^{2+} as cations and NO_3^-, Cl^-, SO_4^{2-} and PO_4^{3-} as anions released from applied fertilizers could be regarded to play a dominant role in mobility of Ni in soil by blocking of adsorptive sites in soils (Sherene, 2010).

Major sources of Pb pollution are exhaust gases of petrol engines, which account for nearly 80% of the total Pb in the air. Apart from minerals, sources of Pb are pesticides, fertilizer impurities, emissions from mining and smelting operations and atmospheric fallout from the combustion of fossil fuels. The study area being one with high vehicular transport, holds a high possibility of Pb contamination. The exchangeable fraction of Pb was maximum in the soil samples collected near industrial sites. The results show that a large proportion of total Pb exists as exchangeable, Fe and Mn oxides bound and organic matter bound forms and hence has got high chances to get into the agricultural crops and thereby the food chain. Moreover, the lower pH values of the soil may accelerate the Pb desorption and leaching and cause ground water pollution. The increase in Pb mobility with decreasing pH was also reported by Baranowski *et al*., 2002. Low pH and high ionic concentrations in soil solution due to intense agricultural inputs (NO_3^- ions) and industrial activity (Cl^- ions) in the region may accelerate Pb desorption and leaching (Sherene. 2010).

Zinc is one of the more mobile elements in soil (Marschner *et al*., 1995). Taylor and McLennan, (1995) reported a mean Zn concentration of 71 mg / kg in crust and in our present study the Zn concentrations were found to be much higher than this value. However, more than 75 % of Zn was found to be held in the residual fraction making it a less potential pollutant.

Table 7: Mean values of heavy metal speciation in soils of Kadukutty							
	Metals (mg/ kg soil)						
Fractions	**Cd**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Exchangeable fraction (F1)	1.1 (0.2)	3.5 (0.7)	102.4 (16.9)	69.8 (25.0)	251.9 (24.8)	153.3 (23.1)	18.6 (5.1)
Iron and manganese oxide fraction (F2)	1.5 (0.2)	6.6 (0.6)	3150.6 (808.3)	93.5 (48.4)	197.8 (25.9)	196.0 (18.6)	8.1 (2.7)
Organic matter fraction (F3)	2.5 (0.2)	3.8 (0.4)	889.0 (339.7)	17.0 (2.3)	200.5 (19.9)	185.3 (25.1)	11.4 (1.4)
Residual fraction (F4)	2.6 (0.3)	40.8 (7.5)	2558.4 (723.8)	101.7 (21.8)	188.5 (8.7)	121.1 (18.2)	82.5 (9.7)

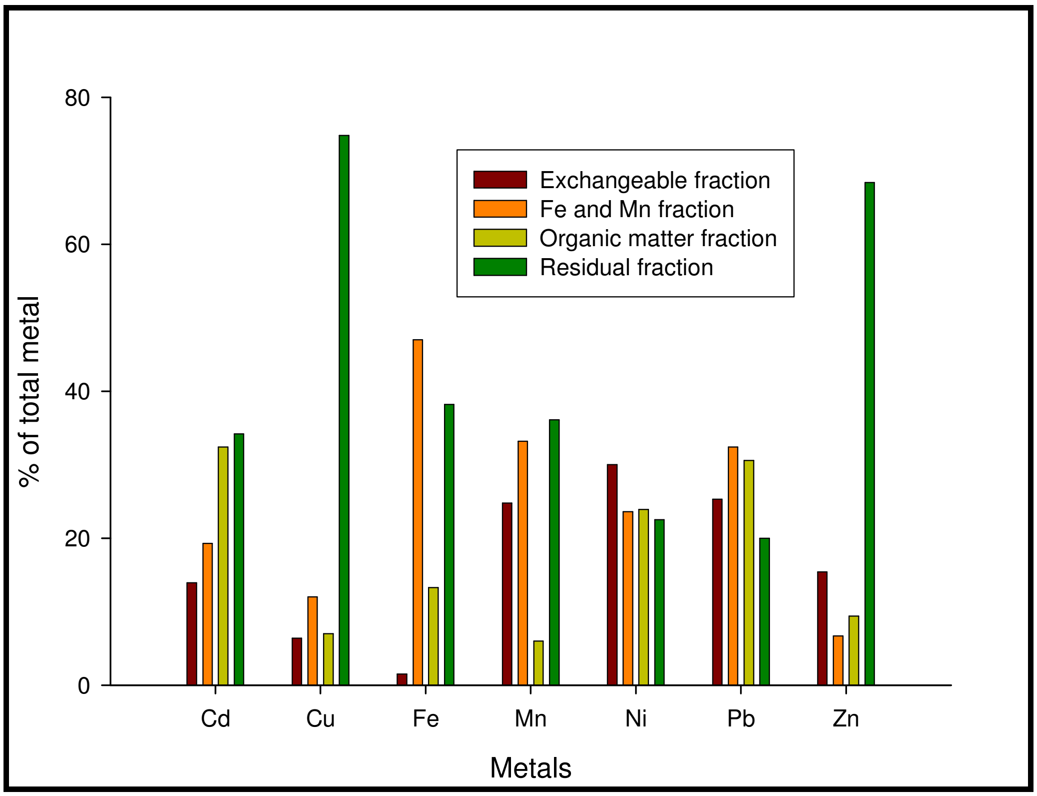

Figure 3. Speciation of heavy metals in Kadukutty soils

The distribution of heavy metals in the sample allows us to predict their mobility and bioavailability. Mean metal contents (%) for each extraction step and residual, determined using the BCR sequential extraction method, are illustrated in Figure 4 to 6. Figure 4 to 6 also includes the mobility order of the elements in each extraction stage except for the residual. Figure 4 shows the order of the most mobilisable metals in fraction 1. Ni seemed to be easily mobilised in this fraction while Fe and Cu are the minimum mobilisable elements.

The order of mobility of the metals in soil systems for the first fraction is Ni > Mn = Pb > Zn > Cd > Cu > Fe Furthermore, similar mobility orders of the elements for the second and third fraction is Fe > Mn = Pb > Ni > Cd> Cu > Zn and Cd > Pb > Ni > Fe > Zn > Cu > Mn respectively. Ni, Pb and Mn seemed to be the most mobile elements in the region. Ni, Mn and Pb were found to be maximum in the third fraction (Fe and Mn bound fraction. The extremely acidic pH of Kadukutty soils facilitates a dissolution of Fe and Mn and subsequent mobility of the associated metals. On the other hand, Cd was found mostly associated with organic matter, which binds the metal strongly with decrease in pH and hence less mobile compared to other elements. Though total Fe contents were very high in in these soils, > 90% concentration was observed in the last extraction stage i.e., residual fraction. As the soils are extremely acidic, there is a high chance that this fraction gets solubilised and leaches to the water sources polluting them. Also high available Fe content may lead to iron toxicity in field crops.

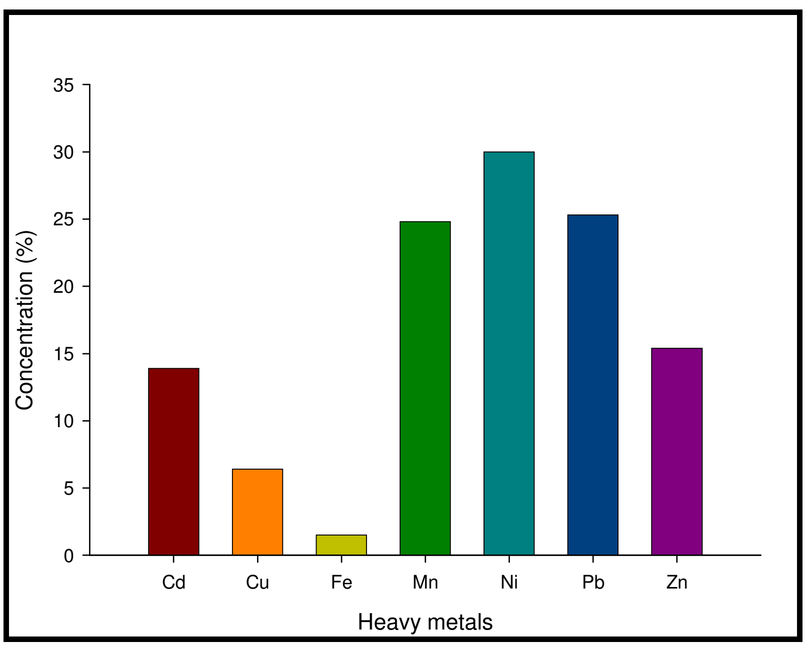

Figure 4. Extractability order of metals in first extraction stage

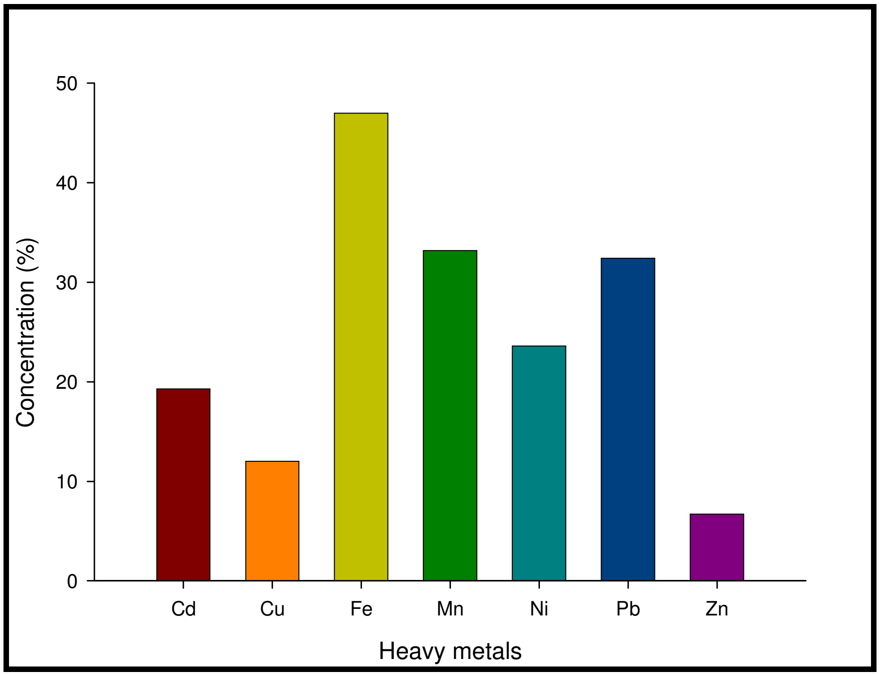

Figure 5. Extractability order of metals in second extraction stage

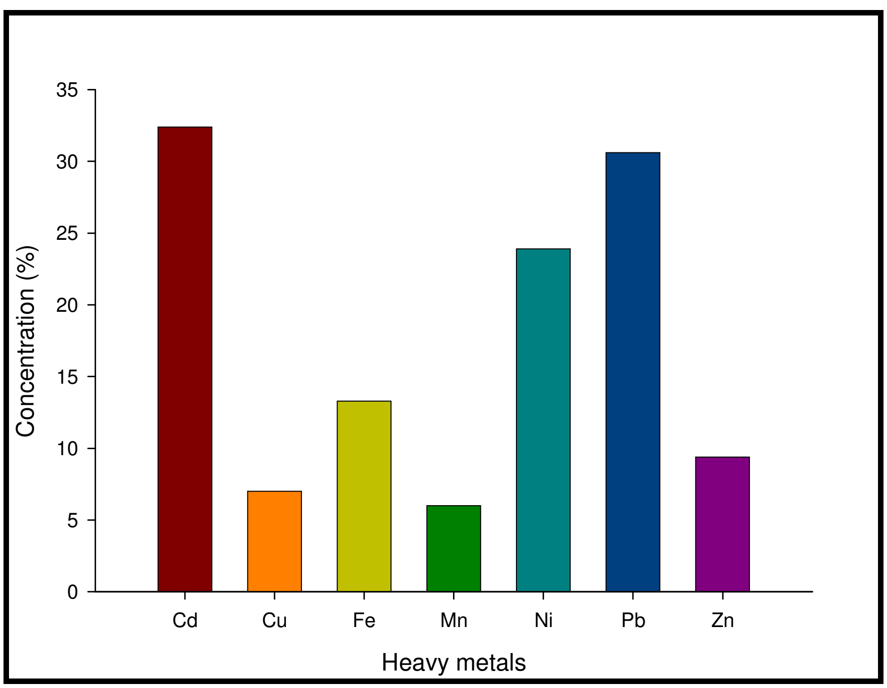

Figure 6. Extractability order of metals in third extraction stage

2.4. Soil biology - earthworms

Earthworms, rightly referred to as the farmers' friend or tiller of the soil are recognized as one of the most important soil fauna that helps in maintenance of soil structural aggregates and thereby porosity, aeration and moisture relations. It is in turn affected by the soil and its properties. Soil acidity affects earthworms adversely. Salts added as fertilizers as well as chemical pesticides also do harm this sensitive species.

Presence of earthworms itself can indicate soil health. The diversity and presence of sensitive ones add further to the knowledge. It was seen from the present study that the type of land use had an effect on the earthworm population. Areas with high inputs of chemicals to boost productivity and protect crops from pests and diseases have turned the soil barren with respect to earthworms. Presence of comparatively tolerant ones such as the Pontoscolex taxa was seen in some areas (Table 8 to 13).

Banana plots were found to have only two taxa of earthworms, namely Argilophillus sp. and Pontoscolex species, the latter one in greater numbers as compared to the former. Pontoscolex was common while Argilophillus was seen in plots where farm yard manure was provided as basal dressing

Table 8. Abundance of earthworms in banana

Earthworm taxa	S_1	S_2	S_3	S_4	S_5	(Mean±SD)
Argilophillus sp.	2	2	1	0	1	1±.84
Pontoscolex sp.	4	6	6	2	5	5±1.67

S_1, S_2…. are sampling sites; n=5

Many species of earthworms were encountered in the mixed crop plots with coconut as the major crop and their diversity was higher in plots that were predominantly supplied with organic manures. The taxa belonged to Argilophillus, Drawida, Megascolex, Microdrillus and Pontoscolex. Pontoscolex sp, was common and Drawida sp. Megascolex sp. and Microdrillus sp. were found restricted to organically farmed sites.

Table 9. Abundance of earthworms in mixed crop											
Earthworm taxa	**S_1**	**S_2**	**S_3**	**S_4**	**S_5**	**S_6**	**S_7**	**S_8**	**S_9**	**S_{10}**	**(Mean±SD)**
Argilophillus sp.	2	1	3	1	2	2	0	4	3	3	2±1.12
Drawida sp.	5	4	7	5	6	7	6	5	5	7	6±1
Megascolex sp.	10	6	9	7	5	6	7	11	9	8	8±1.9
Microdrillus sp.	3	0	4	3	4	1	5	2	5	0	3±1.8
Pontoscolex sp.	7	8	6	4	8	5	3	4	2	6	6±2.1
S_1, S_2…. are sampling sites; n=10											

Most paddy fields were practically devoid of earthworms except in sites supplied with adequate amounts of farm yard manure. Pontoscolex sp. was the only species present in such sites. High inputs of chemicals have badly affected the earthworms in paddy lands.

Table 10. Abundance of earthworms in paddy						
Earthworm taxa	**S_1**	**S_2**	**S_3**	**S_4**	**S_5**	**(Mean±SD)**
Pontoscolex sp.	1	3	5	6	4	4±1.6
S_1, S_2…. are sampling sites; n=5						

Vegetable grown lands were worser than the paddy fields with respect to the earthworm population. Most of the sites were devoid of the species though a few sites had Pontoscolex sp. present and that too scarcely. Heavy application of synthetic fertilisers and plant protection chemicals have taken a heavy toll on the soil fauna in such sites.

Table 11. Abundance of earthworms in vegetable						
Earthworm taxa	**S_1**	**S_2**	**S_3**	**S_4**	**S_5**	**(Mean±SD)**
Pontoscolex sp.	1	1	2	3	2	2±.84
S_1, S_2…. are sampling sites; n=5						

Rubber plantations, especially those near homesteads with liberal application of farm yard manure, especially cow dung, were found to favour earthworms to some extent. In such sites the species listed above in the table such as Argilophillus, Megascolex, Microdrillus and Pontoscolex were present. Pontoscolex dominated the scene here also with greater numbers and wider presence.

Table 12. Abundance of earthworms in rubber						
Earthworm taxa	**S_1**	**S_2**	**S_3**	**S_4**	**S_5**	**(Mean±SD)**
Argilophillus sp.	1	2	1	1	1	2±1.34
Megascolex sp.	1	0	1	0	1	0.6±.55
Microdrillus sp.	2	1	1	2	1	1.4±.82
Pontoscolex sp.	8	5	7	8	6	7±3.33
S_1, S_2…. are sampling sites; n=5						

Table 13. Diversity of earthworms in different land uses					
Diversity indices	**Banana**	**Mixed**	**Paddy**	**Vegetable**	**Rubber**
Earthworm taxa_	2	5	1	1	4
Individuals	6	25	4	2	14
Dominance_D	0.72	0.24	1.00	1.00	0.45
Shannon_H	0.45	1.51	0	0	0.54

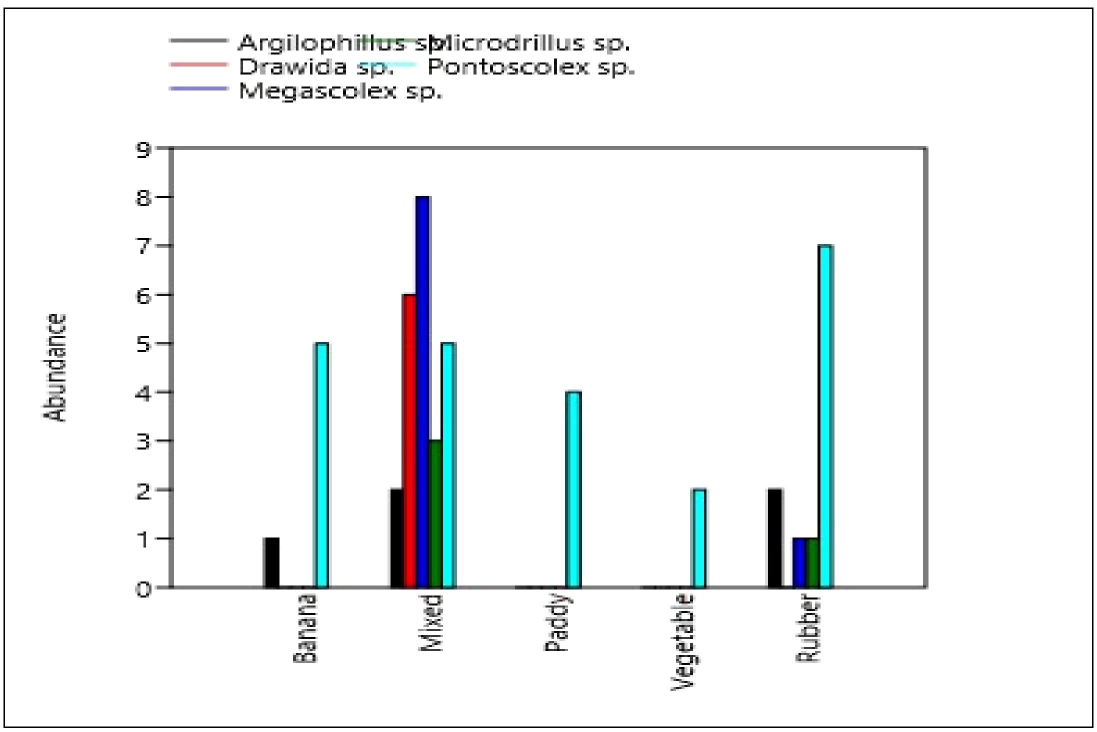

Figure 7. Abundance of earthworm taxa in different land uses

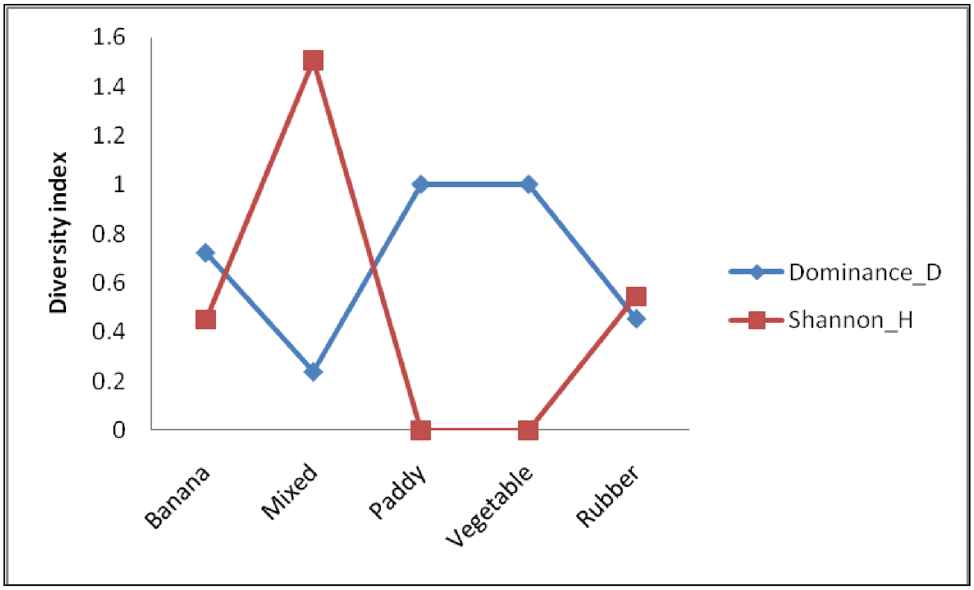

Figure 8. Diversity of earthworm taxa in different land uses

Banana, paddy and vegetable sites showed higher dominance indicating that a particular taxa dominates the scene at the cost of other taxa that are sensitive to environmental perturbations and hence unable to compete with the tolerant taxa under the changed circumstances. Dominance values were higher in paddy and vegetable (1.0) followed by banana (0.72). Mixed crop sites and rubber had lower dominance values which indicate somewhat even distribution of earthworm species compared to the other sites. Diversity of earthworms was highest in mixed crop plots (1.506) followed by banana and rubber with very low values (Figure 7 and 8).

Mixed cropping with coconut as the major crop and with many other species underneath in the homesteads and around has been shown to favour earthworms to some extent. It can be seen that there are many earthworms in some of the sites, particularly where organic manures have been given weightage over inorganic ones though some amount of synthetic fertilizers were also supplemented to provide essential nutrients.

3. Water quality in Kadukutty

3.1. Physico chemical properties

Descriptive statistics of physico-chemical parameters of water samples from the pre - monsoon and post-monsoon seasons, including minimum and maximum values, mean values and standard error (SE) of the hydrological parameters of water course and wells is presented in Tables 14 and 15.

The pH value of natural water changes due to the biological activity and chemical contamination. The pH values of Kadukutty region were found to vary between 3.70 - 5.60 and 5.20 - 6.20 in wells and water course respectively. The values in wells were much lower than the prescribed BIS and ICMR standards of 6.5 - 7.5. The lower values of pH in wells were found near the industrial unit. The water pH was found to vary more from the acceptable limits in samples collected during pre - monsoon period than during post monsoon. Low pH of water is detrimental for aquatic organisms and can also affect the solubility and toxicity of chemicals and heavy metals in the water (EPA, 2012). The majority of aquatic fauna prefer a pH range of 6.5-9.0, though some can live in water with pH levels outside of this range. As pH levels move away from this range (up or down) it can stress the fauna and affect hatching and survival rates. The further outside of the optimum pH range a value is, the higher the mortality rates. While human beings have a higher tolerance for pH levels (drinkable levels range from 4-11 with minimal gastrointestinal irritation), there are still concerns. pH values lower than 4 can cause skin and eye irritations and values below 2.5 will cause irreversible damage to skin and organ linings (Christine, 2013).

TDS values were found to be within the prescribed limits of BIS and ICMR standards in all the studied water sources. The anion contents of the water samples were analyzed with respect to SO_4^{2-}, S^{2-}, PO_4^{3-}, NO_3^- and F^- contents. Among the anions, sulphide content was found to exceed the limits in all the water bodies of the region (wells and water course). Hydrogen sulphide can result from bacterial breakdown of organic matter, human and animal wastes, industrial activities such as food processing, coke ovens, paper mills, tanneries, and petroleum products (Hollis *et al.,* 1975). It is released primarily as a gas (sulphur dioxide) and will spread in the air and in due course get deposited in nearby soil and water. Hydrogen sulphide and sulphides of the alkali and alkaline earth metals released from different sources are soluble in water. Soluble sulphide salts dissociate into sulphide ions that react with the hydrogen ions in water to form the hydro-sulphide ion (HS^-) or hydrogen sulphide (H_2S). Earlier reports by Mckee *et al.,* 1963 and USEPA, 1976 show that the relative concentrations of sulphides is a function of pH of the water; hydrogen sulphide concentrations increase with decreasing pH. In the water bodies, therefore, where the pH is acidic, the potential for hydrogen sulphide formation is more.

Oil, grease and phenolic compounds were found to be present beyond permissible limits in wells and water courses of Kadukutty. The oil and grease contents give an indication of the hydrocarbon content of water samples. In wells, the mean values of these compounds were found to be slightly lesser after monsoon as fresh inflows received after rains dilutes the concentrations.

Dissolved Oxygen (DO) is an important parameter which is essential for the metabolism of all aquatic organisms that depend on aerobic respiration. Presence of DO in water may be due to direct diffusion from air as well as photosynthetic activity of autotrophs. Oxygen can be rapidly removed from the water by discharge of oxygen demanding wastes. The DO values > 5 mg/L is prescribed by ICMR and the wells in the region were found to have values ranging from 3.7 - 6.5 and 3.2 - 7.1 during pre monsoon and post monsoon respectively. The acidic pH coupled with lower DO values may severely inhibit the metabolic activities of organisms in these water bodies.

Chemical Oxygen Demand (COD) is a parameter that is commonly used to estimate organic pollution of water samples. The permissible levels prescribed by ICMR for COD are 20 mg/L respectively. COD is a measure of oxygen equivalent to the requirement for oxidizing organic matter by a strong chemical agent. The COD test is helpful in indicating toxic conditions and the presence of biologically resistant organic substances. High organic inputs as indicated by oil, grease, phenolic compound etc., may trigger a deoxygenating process leading to depletion of dissolved oxygen and increasing the COD values. The mean COD values were found to be higher than the prescribed ICMR limits in all the analysed water bodies during pre monsoon periods indicating organic pollution. In water courses the COD values were found to be within the permissible limits after monsoon rains indicating a washing out of the toxic materials. Heavy metal contents were found to be within the permissible limits in all the analyzed samples Pesticides could not be found in the water bodies of Kadukutty.

All the wells were contaminated with coliforms with no significant seasonal difference. Total coliforms were present in the range of 23 - 2400 CFU/ 100 ml. Faecal coliforms were found to be present in 60 % of the analyzed well water samples. E - coli was not detected in any of the samples.

Table 14: Descriptive statistics of physico-chemical parameters of water in water courses in Kadukutty										
Parameters	Premonsoon				Post monsoon				Desirable limits	
	Minimum	Maximum	Mean	SE	Minimum	Maximum	Mean	SE	ICMR	BIS
pH	5.5	6.2	5.9	0.2	5.2	6	5.8	0.2	7.0-8.5	6.5 - 8.5
EC (µS/cm)	72.0	145.5	109.6	15.0	63	130	99.3	17.6	--	--
TDS (mg/L)	51.0	103.0	77.8	10.6	45	92	70.5	12.5	500	500
Sulphate (mg/L)	1.6	4.9	3.3	0.8	3.4	7.8	5.4	1.1	200	200
Sulphide (mg/L)	0.001	0.009	0.004	0.002	--	--	--	--	--	BDL
Phosphate (mg/L)	--	--	0.0	0.0	0.05	0.05	0.1	0.0	--	--
Nitrate (mg/L)	0.2	0.5	0.4	0.1	0.4	0.6	0.5	0.1	20	45
Fluoride (mg/L)	--	0.1	0.1	0.0	0.08	0.16	0.1	0.0	1	1
Oil & grease (mg/L)	11.0	67.0	32.9	12.1	1	58.8	20.5	13.0	--	--
Phenolic compounds (mg/L)	--	0.4	0.1	0.1	--	--	--	--	--	0.01
DO (mg/L)	--	--	--	--	--	--	--	--	> 5	--
BOD (mg/L)	--	--	--	--	--	--	--	--	5	--
COD (mg/L)	28.0	60.0	42.9	7.0	8	16	12.0	2.8	20	--
Mn (mg/L)	--	0.0	--	--	--	--	--	--	0.1	0.1
Fe (mg/L)	0.1	0.1	0.1	--	--	--	--	--	0.1	0.3
Ni (mg/L)	--	--	--	--	--	--	--	--	--	0.02
Pb (mg/L)	--	--	--	--	--	--	--	--	--	0.01
Cu (mg/L)	--	--	--	--	--	--	--	--	--	0.05
Cr (mg/L)	--	--	--	--	--	--	--	--	0.05	0.05
Cd (mg/L)	--	--	--	--	--	--	--	--	0.01	0.01
Hg (mg/L)	--	--	--	--	--	--	--	--	0.001	0.001
Zn (mg/L)	--	--	--	--	--	--	--	--	0.10	5
As (mg/L)	--	--	--	--	--	--	--	--	--	0.01
Lindane (µg/L)	--	--	--	--	--	--	--	--	--	2
Aldrin (µg/L)	--	--	--	--	--	--	--	--	--	0.03

Endosulfan (alpha) (µg/L)	--	--	--	--	--	--	--	--	--	0.4
Endosulfan (beta) (µg/L)	--	--	--	--	--	--	--	--	--	0.4
DDD (µg/L)	--	--	--	--	--	--	--	--	--	1
DDE (µg/L)	--	--	--	--	--	--	--	--	--	1
Dieldrin (µg/L)	--	--	--	--	--	--	--	--	--	0.03
Total coliform (CFU/100 ml)	240.0	2400.0	1375.0	593.5	2400	2400	2400.0	0.0	--	NIL
Fecal coliform (CFU/100 ml)	9.0	460.0	234.5	159.5	--	21	21	--	--	NIL
E - coli (CFU/100 ml)									--	NIL
ICMR = Indian Council of Medical Research ; BIS = Bureau of Indian Standards; BDL = Below Detectable Limits										

Table 15: Descriptive statistics of physico-chemical parameters of water in wells in Kadukutty										
Parameters	Premonsoon				Post monsoon				Permissible limits	
	Minimum	Maximum	Mean	SE	Minimum	Maximum	Mean	SE	ICMR	BIS
pH	3.7	5.6	4.8	0.1	4.3	5.5	5.0	0.1	7.0-8.5	6.5 - 8.5
EC (µS/cm)	56.5	1539.0	195.5	59.9	47.0	204.0	112.7	8.0	--	--
TDS (mg/L)	40.0	203.5	96.0	9.1	33.0	145.0	80.2	5.7	500	500
Sulphate (mg/L)	0.4	10.5	3.9	0.5	0.7	11.4	5.2	0.5	200	200
Sulphide (mg/L)	0.001	0.014	0.006	0.001	0.1	0.2	0.1	--	--	BDL
Phosphate (mg/L)	--	0.1	--	--	--	0.1	0.1	0.0	--	--
Nitrate (mg/L)	0.2	1.1	0.5	0.0	0.1	2.2	0.6	0.1	20	45
Fluoride (mg/L)	0.0	0.4	0.1	0.0	0.0	0.2	0.1	0.0	1	1
Oil & grease (mg/L)	6.0	46.3	21.8	2.5	5.2	70.0	21.7	3.3	--	--
Phenolic compounds (mg/L)	--	0.3	0.1	--	--	--	--	--	--	0.01
DO (mg/L)	3.7	6.5	5.1	0.2	3.2	7.1	5.2	0.2	> 5	--
COD (mg/L)	10.0	96.0	35.9	4.8	8.0	40.0	18.2	2.0	20	--
Mn (mg/L)	--	0.6	0.1	0.0	--	--	--	--	0.1	0.1
Fe (mg/L)	--	0.4	0.1	0.0	--	--	--	--	0.1	0.3
Ni (mg/L)	--	0.0	--	--	--	--	--	--	--	0.02
Pb (mg/L)	--	0.0	--	--	--	--	--	--	--	0.01
Cu (mg/L)	--	0.0	0.0	0.0	--	--	--	--	--	0.05
Cr (mg/L)	--	0.0	--	--	--	--	--	--	0.05	0.05
Cd (mg/L)	--	0.0	--	--	--	--	--	--	0.01	0.01
Hg (mg/L)	--	0.0	--	--	--	--	--	--	0.001	0.001
Zn (mg/L)	--	0.1	0.0	0.0	--	--	--	--	0.10	5
As (mg/L)	--	0.0	--	--	--	--	--	--	--	0.01
Lindane (µg/L)	--	0.0	--	--	--	--	--	--	--	2

Aldrin (µg/L)	--	0.0	--	--	--	--	--	--	--	0.03
Endosulfan (alpha) (µg/L)	--	--	--	--	--	--	--	--	--	0.4
Endosulfan (beta) (µg/L)	--	--	--	--	--	--	--	--	--	0.4
DDD (µg/L)	--	--	--	--	--	--	--	--	--	1
DDE (µg/L)	--	--	--	--	--	--	--	--	--	1
Dieldrin (µg/L)	--	--	--	--	--	--	--	--	--	0.03
Total coliform (CFU/100 ml)	23.0	2400.0	1315.2	169.7	7.0	2400.0	1788.8	195.8	--	NIL
Fecal coliform (CFU/100 ml)	4.0	28.0	11.2	1.8	4.0	2400.0	585.7	186.8	--	NIL
E - coli (CFU/100 ml)	--	--	--	--	--	--	--	--	--	NIL
ICMR = Indian Council of Medical Research, Kerala; BIS = Bureau of Indian Standards; BDL = Below Detectable Limits										

3.2. Aquatic biology - macro invertebrates

Macroinvertebrates in aquatic systems provide a good indicator of water quality and can be used as a ready reckoner in assessing the health of the water body. Macroinvertebrates in water were enumerated and there composition assessed at the selected sites of the stream. The results are presented below.

Macroinvertebrate composition in Perumthodu

Aquatic macroinvertebrates present in Perumthodu at the time of sampling in the post monsoon season revealed the presence of tolerant taxa in greater numbers and sensitive taxa in lesser numbers (Table 16) as can be understood from their respective tolerance values (TV). Greater numbers were obtained of Caenidae with tolerance value of 7, Libellulidae with tolerance value of 8 while Chironomidae with TV of 8 was present in even greater numbers.

Sensitive taxa such as Baetidae, Heptagenidae, Ephemeridae, Gomphidae etc., were either absent or present in insignificant numbers. The presence of pollution tolerant taxa and the absence of those that are sensitive indicate poor water quality of Perumthodu.

It was also observed that the water quality deterioration increases downstream as is indicated by the composition of aquatic macroinvertebrate taxa in the watercourse. FBI has confirmed poor water quality with FBI values of 6.6 to 7.3 table 17.

Perumthodu, is one of the prominent drainage channel in the region draining a vast area of high input agriculture. The uplands have rugged rolling topography with lower elevation and the low lands spread over a remarkable area. High input agriculture with an emphasis on cash crops is followed in the former while paddy is the main crop in the lower fields though conversion of paddy land to banana, vegetables and tapioca is on the increase. A major industry, Nitta Gelatin, functions in the area producing Ossein from animal bones using hydrochloric acid. Effluents from the agricultural as well as industrial activities contribute to pollution of air, water and soil which is reflected in the poor water quality as indicated by the composition of macroinvertebrates in Perumthodu.

Table 16: Macroinvertebrate composition with tolerance values					
Tolerance Value	Family	Perumthodu		Vadakkechaal	
		Up	Down	Up	Down
7	Caenidae	8	9	8	8
4	Baetidae	3	0	2	6
4	Heptageniidae	0	0	1	2
4	Ephemeridae	1	0	0	2
4	Hydropsychidae	2	1	6	4
0	Ryacophilidae	0	0	1	6
4	Limnephilidae	0	0	1	3
1	Gomphidae	2	0	5	7
3	Macromiidae	0	0	3	5
9	Libellulidae	8	7	6	4
5	Cordullidae	3	3	4	6
-	Platycnemidae	1	0	1	2
9	Coenagrionidae	2	2	2	0
9	Chlorocyphidae	3	3	3	2
6	Calopterigidae	1	1	1	1
5	Dytiscidae	8	7	6	8
10	Corixidae	2	2	3	0
-	Belostomatidae	1	1	1	2
5	Gerridae	1	2	2	4
8	Chironomidae	13	20	14	4
4	Tipulidae	1	0	1	3
6	Ceratopogonidae	2	1	4	0
6	Simulidae	3	4	3	0
8	Culicidae	3	3	3	0
8	Tabanidae	0	1	1	0

Table 17: Water quality of Perumthodu as indicated by FBI		
Site	**FBI**	**Water Quality**
Upstream	6.5	Poor
Downstrream	7.2	Poor

Macroinvertebrate composition in Vadakkechaal

Vadakkechaal was slightly different from Perumthodu in its size, catchment area and water quality. The macroinvertebrates and their composition indicated somewhat better quality as compared to Perumthodu but its upstream portion was more degraded than the downstream section. Tolerant taxa was more and sensitive ones less in the upper reaches compared to the lower portions (Table 18). The FBI values support the data.

Table 18. Water quality of Vadakkechaal as indicated by FBI

Site	FBI	Water Quality
Upstream	6.04	Fairly poor
Downstream	4.31	Good

The upper reach of *Vadakkechaal* was seen to trap sediments due to slow down of flow from the fields caused by the narrowing of its channel and the water devoid of sediment load was free to flow fast downwards without any stagnation resulting in comparatively better water quality. The water quality is mostly affected by agricultural effluents in this region though few small industries are also present.

4. Relation between soil quality and land use

4.1. Heavy metal contamination indices

Degree of contamination (Figure 9) gives a good indication of site specific pollution due to different heavy metals. An analysis of the data shows that all landuses in the region have a high degree of contamination (values greater than >32). Among them the degree of contamination was found to be spread between 35.01 to 94.50. The heavy metal contamination of soils varied as vegetables > paddy > banana > rubber > mixed crops (Table 19).

The study shows that Cd had a very high contamination potential in Kadukutty (Figure 8). All the soils in Kadukutty were found to be very highly contaminated with cadmium (contamination factor >6). Cd enters soils mainly *via* atmospheric deposition, fertilization, sewage sludge or compost (Umweltbundesamt, 1997) and have a very long biological half life (10-30 yr). It gets into the atmosphere from emissions by power stations, industrial production facilities, motor vehicles and domestic heating. Studies by Hackenberg and Wegener (1999) to analyze Cd balances for urban and rural districts in Germany also show that Cd accumulates in soil.

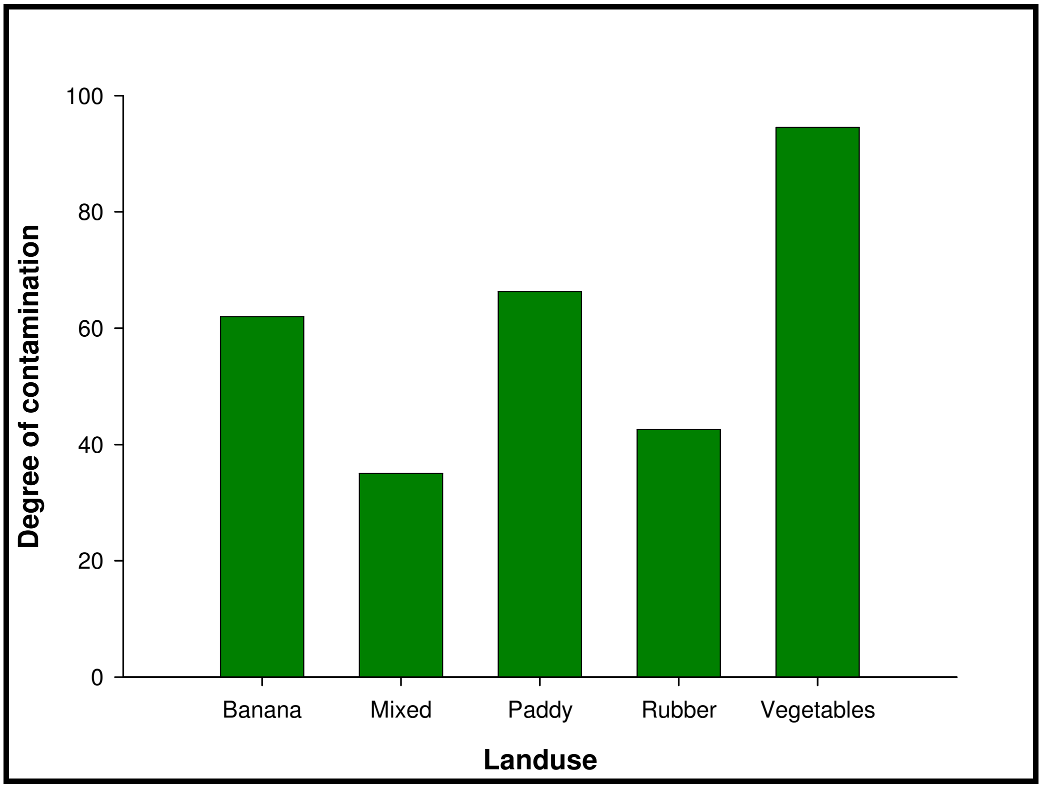

Figure 9. Degree of contamination in different land uses in Kadukutty

Earlier reports show that after entering the soil, Cd is mainly sorbed on the surface of organic compounds or clays and only a minor fraction stays in solution. However, the latter fraction is the key variable in controlling bioavailability and leaching of Cd (Allen, 1993). The relationship between sorbed and dissolved phase depends on soil properties like pH, organic carbon content, clay content etc. Cadmium with its comparatively longer half life and abundance in the mobile fractions poses a threat of getting displaced towards ground water or getting transferred to plants. Vegetable and banana cultivated soils in the region were found to be very strongly acidic and rich in organic matter. Cd adsorption in soil is spontaneous, endothermic and the system disorder increases with duration. The natural organic matter in soil is mainly responsible for Cd(II) removal at lower pH (pH < 4.2) and clay minerals contribute to a further gradual adsorption process (Yan Wang *et al.*, 2009). Vegetable, banana and paddy soils with extremely acidic reaction, high clay and organic matter contents provide a favourable soil environment for

Cd adsorption and subsequent retention. Further deterioration of soil pH by way of agricultural/ industrial activities may hence pose serious threats of Cd retention and bioaccumulation in plants grown in the region.

Table 19: Land use wise degree of contamination of sampling sites in Kadukutty

Landuse	Degree of contamination
Banana	61.98
Mixed	35.01
Paddy	66.32
Rubber	42.57
Vegetables	94.50

Ni and Pb were the other two metals found to be having very high contamination factors in the soils of Kadukutty. Nickel has been classified among the essential micro nutrients and remains associated with some metallo enzymes, but Ni is toxic at elevated concentrations in plants (Srivastava et al., 2005). Pb is not an essential nutrient for plants, but majority of lead is easily taken up by plants from the soil and accumulated in root while only a small fraction is translocated upward to the shoots (Patra et al., 2004). The effect of Pb depends on concentration, type of soil, soil properties and plant species.

Table 20: Land use wise contamination factor for different heavy metals in Kadukutty

Landuse	Contamination factors				
	Cd	Cu	Ni	Pb	Zn
Banana	50.5	1.1	**7.5**	2.5	0.3
Mixed	24.8	0.6	6.4	2.7	0.4
Paddy	53.6	1.2	8.1	3.0	0.4
Rubber	29.7	0.9	8.5	2.9	0.6
Vegetables	82.2	1.1	8.3	2.7	0.2

Atmospheric trace metals from both local and distant sources impact the environment in the form of dry and wet deposition. The leaves of plants can directly take up toxic trace metals or they are at first accumulated in the soil and reach the plants through their roots.

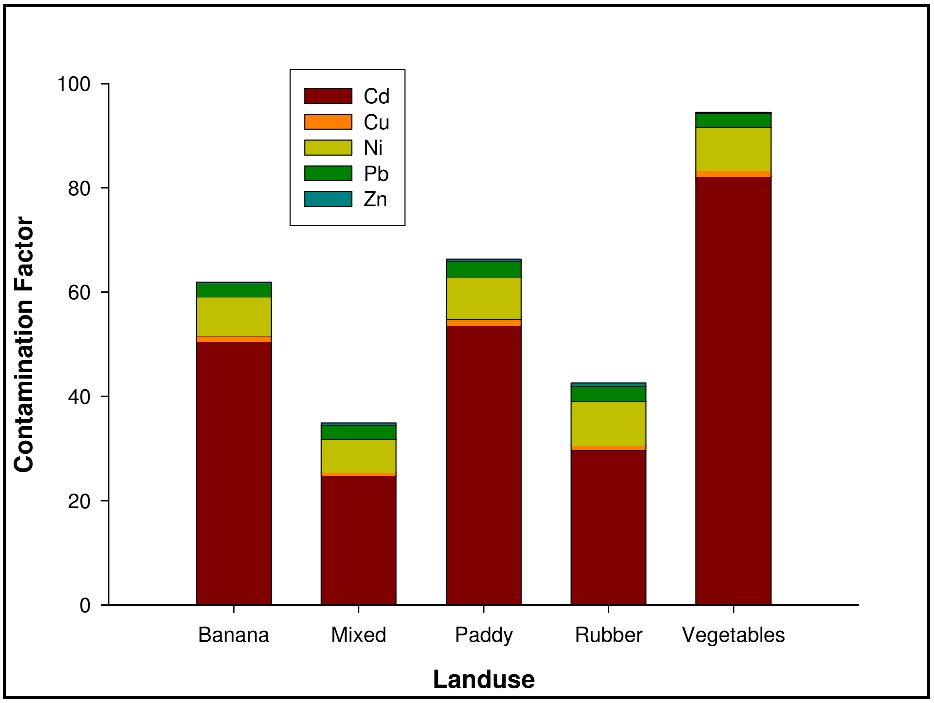

Figure 10. Contamination factors for different heavy metals in land uses of Kadukutty

The uptake of metals by the soil depends on the chemical properties of the metals and soil, especially its acidity and the content of humic substances. Some metals, such as Pb, are rather firmly bound to humic substances in the soil, whereas others, such as Cd, can easily remobilize from the soil. The fractionation of heavy metals and its associations in the present study confirms these observations. In agricultural soils which receive large amounts of organic matter by way of organic additions, a good quantity of Pb is retained by these materials, thereby reducing its mobility and bioavailability. The contamination factors for Zn and Cu was found to be in the low ranges and can be considered non pollutants in these soils (Table 20 and Figure 10).

SUMMARY

The study was conducted in Kadukutty refgion of Thrissur district to assess the landuse pattern and soil and water quality of the region. Samples were collected by giving due weightage to landuse and were analysed for physico – chemical characters and heavy metal pollution. The area enjoys a humid tropical climate with two monsoons - South West monsoon and North East monsoon with an average annual rainfall of 2500 mm and 3 to 4 months of dry spell. The area shows predominance of lateritic soil with isohyperthermic temperature and ustic soil moisture regime.

Mixed cropping is the major cropping system in the region. Rice, coconut, banana, pepper, nutmeg, rubber and vegetables are the main crops cultivated in the panchayat. Soil reaction (pH) in Kadukutty was strongly to very strongly acidic. The pH of the soils ranged from 4.64 in vegetable cultivated area to 5.42 in mixed cropping sites. Soil organic carbon contents were found to be in the medium to high in most of the sites.

Total heavy metal contents in soil showed that Cd, Pb and Ni were beyond the permissible limits in most of the agricultural lands in Kadukutty. Among the different heavy metals, Cd contents were found to be highest in vegetable lands and lowest in mixed cropping sites.

The study was modeled on the hypothesis that total heavy metal concentration *per se* may not be a sufficient indicator to suggest the bioavailability and thereby pollution caused by heavy metals. Hence the heavy metals were fractionated according to their ease of release/ mobility in the soil. The fractionation was done according to a scheme suggested by EC Standards, Measurement and Testing Programme called BCR process. This scheme divides the total heavy metal into four fractions – Fraction 1 (Exchangeable fraction), Fraction 2 (Fraction bound to Fe & Mn oxide), Fraction 3 (Fraction bound to organic matter), and Fraction 4 (Residual fraction). Elemental speciation information is crucial today because the toxicity and biological activity of many elements depend not only on their quantities, but also on their oxidation states and chemical forms. The order of mobility of the metals in soil systems for the first fraction is Ni > Mn = Pb > Zn > Cd > Cu > Fe. Furthermore, similar mobility orders of the elements for the second and third fraction were Fe > Mn = Pb > Ni > Cd> Cu > Zn and Cd > Pb > Ni > Fe > Zn > Cu > Mn respectively. Ni, Pb and Mn seemed to be the most mobile elements in the region.

From the data, we computed degree of contamination, contamination factor and enrichment factor to analyze the level of contamination of each site, to determine contamination potential of each metal and to ascertain whether these metals were derived from anthropogenic or natural sources. An analysis of the data shows that all land uses in the region have a high degree of contamination (values greater than >32). Among them the degree of contamination was found to be spread between 35.01 to 94.50. The heavy metal contamination of soils varied as vegetables > paddy > banana > rubber > mixed crops. Cadmium, nickel and lead were the major pollutants of soil in the region.

Earthworms were present in sites where cultivation was predominantly organic and absent in sites following inorganic cultivation with liberal application of synthetic fertilizers and other plant protection chemicals. Mixed crop plots were much better in earthworm population and paddy and vegetable sites extremely poor in this respect.

Water quality of the region was assessed by collecting samples from wells and water course. The pH values of Kadukutty region were found to vary between 3.70 - 5.60 and 5.20 - 6.20 in wells and water course respectively. The values in wells were much lower than the prescribed BIS and ICMR standards. Among the anions, sulphide content was found to exceed the limits in all the water bodies of the region (wells and water course). Oil, grease and phenolic compounds were found to be the other major pollutants of water in the region and present in levels above the prescribed standards in all water samples during the sampling periods.

Heavy metal contents were found to be within the permissible limits and pesticides could not be detected in any of the analyzed water samples. All the analyzed water samples indicated high pollution levels by coliforms. Faecal coliforms were found to be present in 60 % of the analyzed well water samples.

Aquatic macro invertebrates and their composition were indicative of water quality in the watercourses draining the region. It was seen that Perumthodu was poor in water quality as indicated by the predominance of tolerant taxa and the absence of most of the sensitive taxa. Vadakkechaal was slightly better as shown by the presence of some of the comparatively sensitive families. The variation in composition of the macro invertebrates was shown to reflect in the FBI values also.

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