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Impact of industrial activities on soil and water qualities in Koratty panchayat area

(Final Report of the project KFRI 561/2009)

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ABSTRACT OF THE PROJECT PROPOSAL

1. Project Number	: KFRI 561/2009
2. Title of the Project	: IMPACT OF INDUSTRIAL ACTIVITIES ON SOIL AND WATER QUALITIES IN KORATTY PANCHAYAT AREA
3. Objectives	1. Identify the different land use pattern in Koratty panchayat area 2. Generate baseline information on soil and water quality status 3. Evaluate the extent of soil and water pollution
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7. Investigators	: S. Sandeep (PI from October, 2012) Thomas P. Thomas (PI from 2009 - September, 2012) E.A.Jayson

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ABSTRACT

Soil and water are essential for sustenance of healthy life of living forms in a region. Human activities, in course of their development ventures may inflict irreparable damage to soil and water entities. Koratty panchayat in Thrissur District with a long history of industrial and agricultural activities is prone to soil and water contamination. Hence the present project was envisaged with the objective of assessing the land use pattern, generate base line information and evaluate soil and water quality in Koratty panchayat area. Land capability classification shows that 98% of the land in the region belongs to Class II and III, indicating moderate limitations for crop growth. Rice, coconut, banana, pepper, arecanut, nutmeg, rubber and vegetables are the main crops cultivated in the panchayat. Mixed cropping was the major cropping pattern identified in the region.

Heavy metals in the surface soils and in water bodies of Koratty Panchayat in Thrissur district were analyzed to assess the impact of different land uses on soil and water quality. Total heavy metal contents in soil show that cadmium in industrial sites and Cd and Ni in most of the agricultural lands in Koratty were beyond the permissible limits. 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. Though Fe was the most mobile among the different heavy metals, more than 90% of this metal was observed in the immobile residual fraction. Cd was the least mobile among the studied heavy metals in Koratty panchayat, but > 50% of this metal existed in the easily available fractions (fractions 1 and 2) thus making it a contaminant of high bioaccumulation risk by way of plant absorption. Contamination factors for Cd, Ni and Pb were very high in the soils of Koratty. Enrichment factor values show that accumulation of these metals in soils occured mainly due to anthropogenic activities - industrial as well as agricultural.

Water quality of the region was assessed by collecting samples from ponds, wells and prominent water courses draining the area. The pH values were found to vary between 4.85 - 6.85, 4.95 - 6.35 and 5.25 - 5.76 in ponds, wells and water courses respectively. The values were 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

(ponds, wells and streams). Oil, grease and phenolic compounds were found to be other major pollutants of water in the region and present in levels above the prescribed standards in all water samples during the sampling period. All the analyzed water samples from wells indicated high pollution levels by coliforms and 32 % of them by E-coli. Water quality was thus found to be impaired to various levels in Koratty panchayat.

INTRODUCTION

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 when they come in contact with humans. 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: coprecipitation; adsorption; surface complex formation; ion exchange; 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.

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. 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 due to 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.

The study was conducted in Koratty panchayat in Thrissur District. Koratty has an early history of industrialization. Government of India Press, Koratty (GIPK), Vaigai Thread Processors Ltd., Carborandum Universal (CUMI), Kerala Solvent Extractions Ltd (KSE Ltd), KINFRA Small Industries Promotion Park (KSIPP), INFOPARK etc., are the major industrial establishments in the area. Other industries include automobiles, pharmaceuticals, electroplating, fabrication, tile manufacturing etc., which are scattered throughout the study area. 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. 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 KSCSTE took up the initiative to study the quality of these important natural resources in selected sites in Kerala. Koratty in Thrissur district thus came up in the priority list alongwith Vilappilsala in Thiruvanathapuram and Cheruvannur -Nallalam in Kozhikode district. KFRI had been selected as the nodal agency to take up such investigations in Central Kerala. The present study entitled 'Impact of industrial activities on soil and water qualities in Koratty panchayat area' was thus taken up with following specific objectives:

1. Identify the land use pattern in Koratty panchayat area
2. Generate baseline information on soil and water quality
3. Evaluate the extent of soil and water pollution

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; Lenntech, 2004). 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.

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.

MATERIALS AND METHODS

Study area

Koratty panchayat located in Mukundapuram Taluk of Thrissur District spans an area of 2342 ha between $10^o13'53''$ - $10^o16'52.1''$ N latitude and $76^o19'52.54''$ - $76^o24'29.43''$ E longitude. The panchayat is bordered by Parakkadavu and Karukutty panchayats of Ernakulam district on the south, Melur panchayat on the north, Kallur Vadakkumury in the west and Kadukutty and Annamanada panchayats in the south and south -west.

Landuse

Data on land use pattern in Koratty was collected from secondary sources. Bing maps were used as base maps and land uses were delineated using Arc GIS 9.2.

I. Soil sample collection

Composite surface soil samples (0-30 cm) were collected after perambulation giving due weightage to different landuses. A total of 193 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.

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 defined according to four categories: <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:

$$EF_X = [X_S / E_S\,(\text{ref})]/[X_C/E_C\,(\text{ref})]$$

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
Cr	70
Cu	30
Mn	1100
Ni	50
Pb	35
Zn	90
Fe	38000

II. Water sample collection and analysis

The water bodies were categorized as ponds, wells and water course. Water samples were collected from these water bodies during pre monsoon and post monsoon periods. 15 ponds, 25 wells and 7 stream sites were selected for the study. The details of the sampling sites are given in table 2a - c.

Table 2a. Pond water sampling sites in Koratty

No.	Name	Locations
1	Mangattumbilli pond	N10^0 14’ 42.4” E76^0 21’ 21.2”
2	Puthenkulam	N10^0 14’ 15.3” E76^0 21’ 54.3”
3	Poottukuzhikulam	N10^0 15’ 57.3” E 76^0 23’ 32.0”
4	Perumkulam	N10^0 14’ 75.1” E76^0 22’ 65.3”
5	Chirangara temple pond	N10^0 15’ 01.5” E76^0 22’ 10.5”
6	Leprosy hospital pond	N10^0 15’ 35.2” E76^0 22’ 58.9”
7	Erattachira pond-1	N10^0 15’ 58.9” E76^0 23’ 30.1”
8	Erattachira pond -2	N10^0 15’ 57.3” E76^0 23’ 32.0”
9	Kottanchira pond	N0^0 16’ 14.1” E76^0 23’ 03.5”
10	Elavankunnu pump house	N10^0 16’ 28.3” E76^0 22’ 21.7”
11	Elavankunnu pond	N10^0 16’ 29.3” E76^0 22’ 22.9”
12	Mallanchira pond	N10^0 16’ 48.0” E76^0 20’ 17.6”
13	Vellamchira pond	N10^0 15’ 58.6” E76^0 20’ 51.8”
14	Puthenkulam pond	N10^0 16’ 21.9” E76^0 22’ 17.9”
15	Pallikkulam pond	N10^0 15’ 39.7” E76^0 20’ 33.6”

Table 2b. Well water sampling sites in Koratty

No.	Location	No.	Locations
1	N 10^0 16’ 1.3” E 76^0 21’ 12.0”	14	N 10^0 16’ 33.366” E 76^0 23’ 16.11”
2	N 10^0 16’ 1.5” E 76^0 21’ 13.0”	15	N 10^0 16’ 8.69” E 76^0 23’ 16.62”
3	N 10^0 16’ 05.3” E 76^0 21’ 18.0”	16	N 10^0 15’ 45.17” E 76^0 20’ 56.84”
4	N 10^0 16’ 5.9” E 76^0 21’ 12.9”	17	N 10^0 15’ 28.82” E 76^0 21’ 4.96”
5	N 10^0 16’ 5.6” E 76^0 21’ 31.3”	18	N 10^0 15’ 53.28” E 76^0 20’ 40.42”
6	N 10^0 16’ 11.7” E 76^0 21’ 34.3”	19	N 10^0 15’ 4.16” E 76^0 21’ 54.20”
7	N 10^0 16’ 22.3” E 76^0 21’ 34.2”	20	N 10^0 16’ 9.57” E 76^0 20’ 32.31”
8	N 10^0 16’ 20.0” E 76^0 21’ 3.5”	21	N 10^0 15’ 44.75” E 76^0 22’ 10.79”
9	N 10^0 16’ 25.70” E 76^0 21’ 21.66”	22	N 10^0 16’ 16.94” E 76^0 23’ 49.51”
10	N 10^0 16’ 25.74” E 76^0 21’ 13.42”	23	N 10^0 15’ 44.75” E 76^0 22’ 10.70”
11	N 10^0 16’ 25.37” E 76^0 22’ 10.92”	24	N 10^0 15’ 12.28” E 76^0 22’ 10.61”
12	N 10^0 16’ 33.40” E 76^0 23’ 8.53”	25	N 10^0 16’ 25.56” E 76^0 21’ 46.31”
13	N 10^0 16’ 41.36” E 76^0 23’ 16.72”		

Table 2c. Water course sampling sites in Koratty

No.	Name	Locations
1	Perumbi thodu	N10^0 15’ 28.4” E 76^0 21’ 30.6”
2	Koratty chal	N10^0 15’ 26.3” E76^0 21’ 28.0”
3	Koottalappadom thodu	N10^0 15’ 05.9” E76^0 21’ 35.3”
4	Mangalassery thodu	N10^0 14’ 12.6” E76^0 21’ 30.5”
5	Kadavanappadam thodu	N10^0 15’ 06.8” E76^0 22’ 11.8”
6	Kaithappadam thodu	N10^0 16’ 16.6” E76^0 20’ 18.7”
7	Perumbi thodu/Moodapuzha	N10^0 15’ 11.8” E76^0 22’ 23.5”

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). Water sample analysis was carried out at Water Quality Division, Centre for Water Resources Development and Management (CWRDM), Kozhikode.

Fish sampling

Fishes were collected using cast nets in the early morning hours covering the shallow and deep areas of prominent water courses draining Koratty namely Koratty chal and Perumthode. Specimens were preserved in 10% formaldehyde. Identified specimens were got analyzed for pesticide residues at Salim Ali Centre for Ornithology and natural History (SACON), Coimbatore.

RESULTS AND DISCUSSION

1. Landuse pattern in Koratty Panchayat area

1.1. General description of the study area

The Koratty panchayat area 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. Landform is almost flat in the foothills. In general, the panchayat has elevated areas towards the east with the highest elevation of 91m at Elancherykunnu and the lowest elevation in the wetlands. The panchayat has a good network of water courses. The drainage pattern is dendritic (Figure 1).

The area enjoys a humid tropical climate with two monsoons - South West monsoon and North East monsoon with an average annual rainfall of 2488 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.

The panchayat has a long history of industrialization which co existed with agriculture in the region. Majority of the holdings are marginal and fragmentation of land is a major hurdle in agricultural management. 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).

Drinking water is provided through private and public wells and ponds. Water supply in the panchayat is augmented by pipe connection provided by Kerala Water Authority. Drinking water schemes working in the panchayat are Rajiv Gandhi Drinking Water Scheme, Irattachira Drinking Water Scheme, Parakkoottam Drinking Water Scheme, Elavankunnu Drinking Water Scheme, Koratty Nalukettu Grameena Sudha Jala Vitharana Padhathy and Bore well Sudha Jala Vitharana Padhathy at Pongam and Kattappuram. In spite of these, water scarcity is experienced in elevated areas like Thirumudykunnu and Elancherykunnu during summer months.

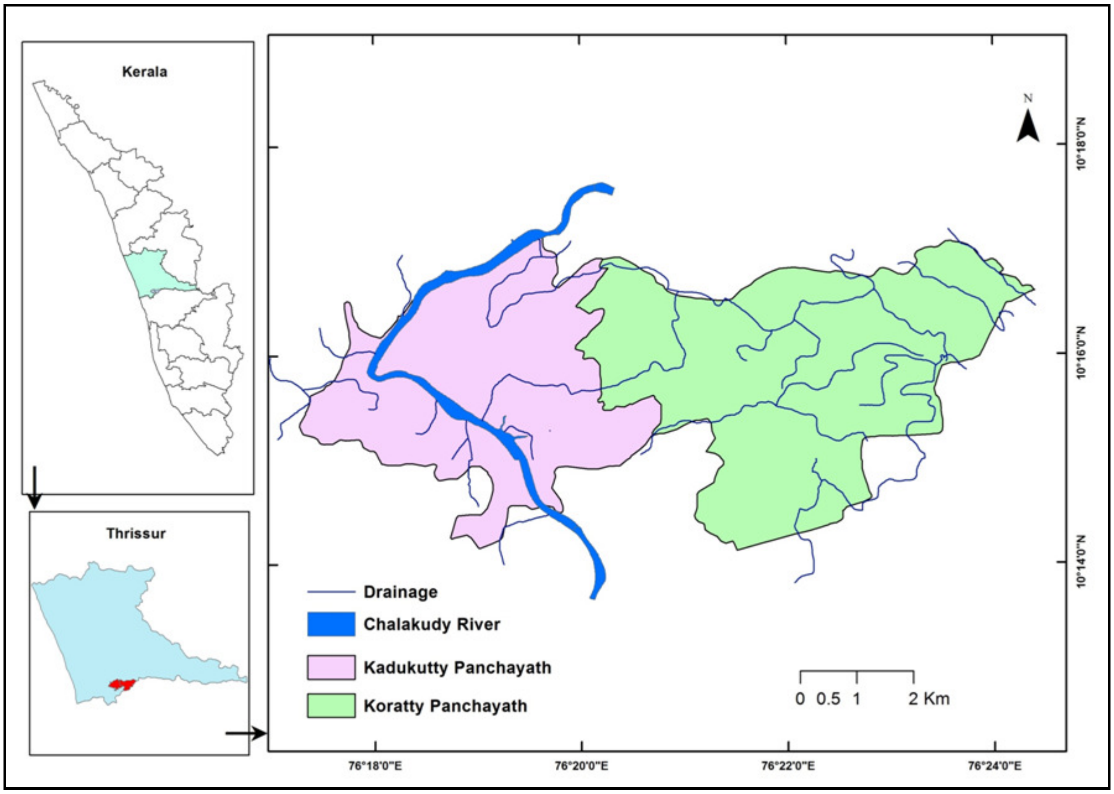


Figure 1: Map of the study area

1.2. Industries

Industrial sector is well developed in Koratty panchayat compared to other areas in Thrissur District. The area has a large number of major and minor industries, a list of which is provided in Table 3.

Table 3. List of major and minor industries in the study area

Sl. No.	Major Industries
1	Government of India Press
2	Carborundum Universal
3	Vaigai Threads
4	KINFRA Industrial Park
5	Info Park
6	**Minor Industries** Automobile workshops, Dyeing, Engineering Fabrication, Food processing, Interior designing, Drug manufacturing, Oil mills

1. Government of India Press

Government of India Press, the only Government of India owned Press in Kerala has been working in a large area with 110 acres under its possession. However in due course of time, Government has acquired a major portion of the land and at present is left with only 20 acres. This Press has been planned as a forms printing press to meet the printing requirement of various Central Govt. Departments. It went into partial production in October, 1966 and started full production in 1967. Presently its capacity is underutilized for various reasons. The Press executes the printing jobs of Postal Department, Income Tax Department, Census Department etc.

2. Carborandum Universal Ltd.

Carborandum Universal Limited has an area of 18 acres. The unit produces silicon carbide, a man made mineral of extreme hardness and sharpness. It is considered as an ideal abrasive for grinding / sanding materials of low tensile strength such as cast iron, brass, aluminum, bronze etc. Its thermal properties make it an excellent medium for use in the manufacture of refractory products and crucibles. Silicon carbide is produced by a process involving the electrochemical reaction of silica in the form of quartz with carbon in the form of raw petroleum coke. The stoichiometric mixture is reacted in an electrical resistance furnace at a temperature greater than 2200˚C to yield high quality crystals. The large crystals are then segregated, crushed, cleaned of magnetic impurities in high intensity magnetic separators and classified into narrow size fractions to suit the end use. Silicon carbide grains are also used in marble and granite polishing, manufacture of kiln furniture and as a deoxidizer in iron and steel making.

3. Vaigai Threads (Madura Coats)

The unit had 76 acres of land under its possession, of which 44 acres were acquired by the Govt. of Kerala. Sewing thread is the major product of the industry.

4. KINFRA Industrial park

One of the major industrial ventures in the region is KINFRA Small Industries Promotion Park (KSIPP), which hosts a large number of industrial units. Their vision is to create a Kerala where industry thrives in the midst of the rich greenery and where people flourish in an environment that fosters growth with the freedom to innovate. Their mission is to enable development in Kerala by identifying and promoting core competency industries in each region and wooing discerning investors from across the world. It houses manufacturing units related to ceramic products, building materials, plastic products, light and general engineering and herbal products.

5. Infopark

It's an IT park which started functioning in Koratty from 2009 and is known as Infopark Thrissur. More than 30 companies function in this park. It got the Special Economic Zone (SEZ) status from government of India in 2014.

6. Minor Industries

Several small and minor industries such as fabrication units, flour mills, wooden furniture production units, cottage industries, press, bakery, oil mills, soda making units, ice factory, dye works, electroplating units and automobile workshops also function in the region.

1.3 Land capability classes

Land capability classification is an interpretative grouping of soils to show their suitability to different kinds of uses along with management. There are eight land capability classes. Class I is the best, devoid of any limitation for intensive cultivation. Class II to VIII lands have progressively increasing limitations. 98% of the land in the region belongs to Class II and III, indicating moderate limitations for crop growth (Table 4).

Table 4. Land capability classes in Koratty Panchayat area

SI. No.	Class	Total area (ha.)	Percent of total area
1	Class 2	2106.55	89.94
2	Class 3	225.88	9.64
3	Class 4	0.96	0.04
4	Class 5	1.2	0.05
5	Class 8	1.84	0.07
6	Water bodies	5.57	0.23
	Total	**2,342.00**	**100.00**

1.4 Agricultural land uses in the region

Distribution of area under different agricultural land uses in Koratty is given in Table 5 and Figures 2a - 2c.

Table 5. Major land uses in Koratty Panchayat (Krishibhavan, Koratty)

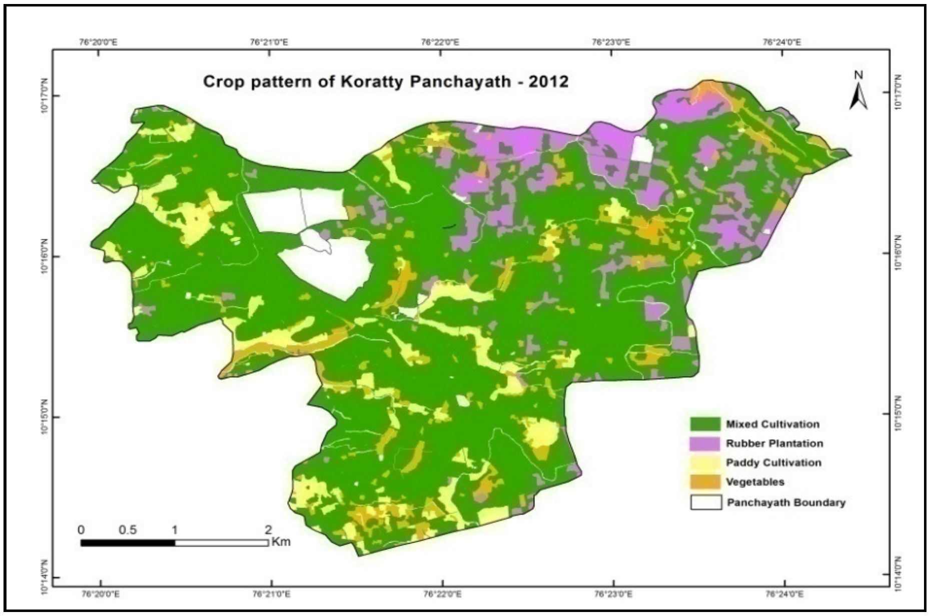
Sl No.	Land use	Total area (ha.)
1	Coconut	850
2	Rubber	250
3	Paddy	
	Virippu	60
	Mundakan	74
	Puncha	25
4	Banana	170
5	Areca nut	48
6	Pepper	30
7	Tapioca	10
8	Nutmeg	170
9	Vegetables	8

Rice, coconut, banana, pepper, arecanut, nutmeg, rubber and vegetables are the main crops cultivated in the panchayat. Earlier paddy was the main crop. Now a days due to labour scarcity most of the farmers have shifted away from paddy cultivation. Presently most of the paddy fields have been used for growing coconut, arecanut and banana and area under paddy has come down drastically. Vegetables are raised in paddy fields during summer months.

Coconut is one of the major crops in the panchayat. About 850 ha of the total area is under coconut. Coconut is mostly 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 250 ha. 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 crop management is practiced in banana. Irrigation is practiced during summer months. Manure, mostly in the form of poultry castings are applied in paddy fields on a regular basis.

2a.



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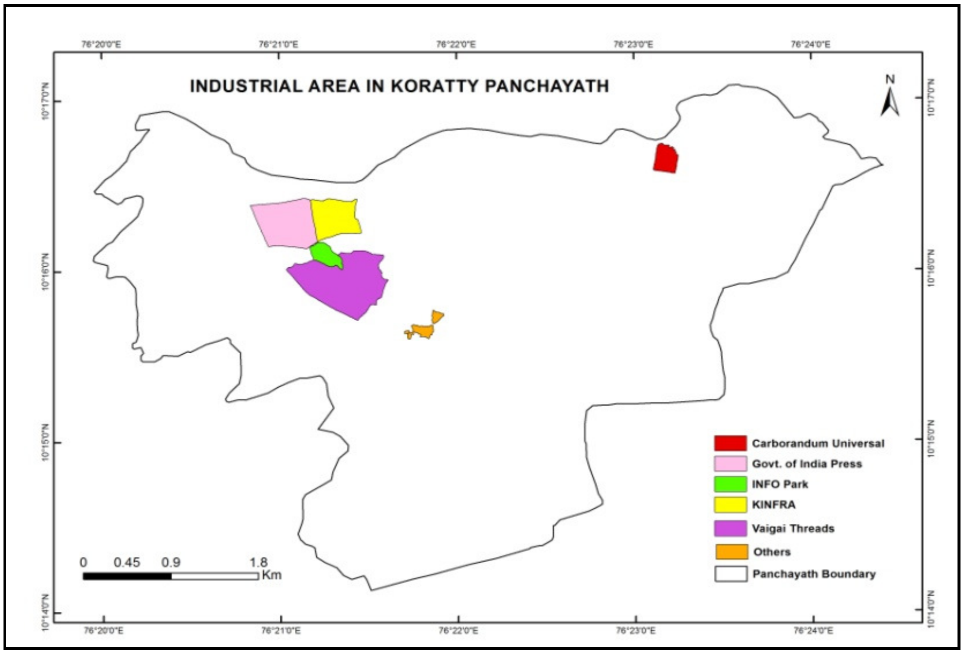

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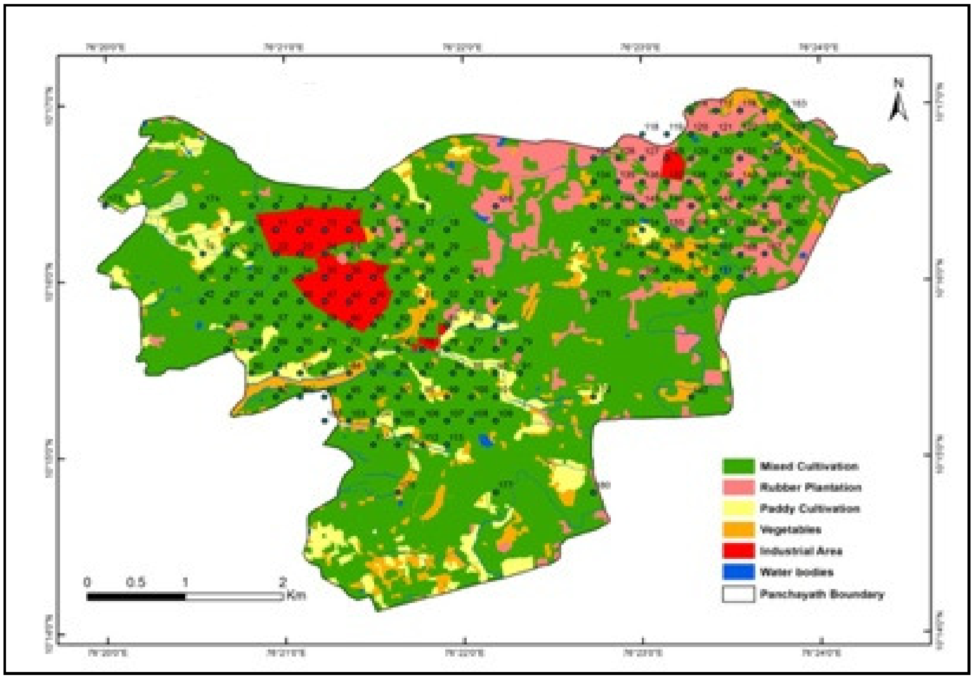

Figures 2a - 2c: Land use maps in Koratty Panchayat area 2a. distribution of major crops in Koratty Panchayat area b. Distribution of major industries in Koratty Panchayat area c. Distribution of sampling locations in the Koratty Panchayat area

In the study area, land use/cover is changing at rapid pace in the form of built-up area. There is a gradual shift towards urbanization with several major and minor manufacturing units. These anthropogenic activities pollute the soil both directly as well as indirectly. Change in land use/land cover plays an important role in changing the quality of water and soil of the area. Land use changes strongly influence soil moisture regime and soil pH which could greatly affect solubility, toxicity, bioavailability and mobility of heavy metals and cause their redistribution in soils (Bai *et al.* 2010).

2. Soil quality in Koratty

2.1. General soil characters

Soils in Koratty were moderately fine to fine textured. Gravelly sandy clay loam followed by gravelly clay loam is the predominant soil texture encountered in the panchayat. On analysis of the composite samples collected from different land uses it was found that most of the samples in the region were strongly acidic (pH 5.1 - 5.5). Soil acidity varied from 5.78 ± 0.55 in mixed plantation to 5.33 ± 0. 4 in paddy. Organic carbon content was high (> 1.5 %) in all the analyzed soil samples.

2.2. Heavy metal content in soil

The heavy metal (Mn, Zn, Cu, Cd, Pb, Ni and Cr) concentrations of the study area are presented in Tables 6 and 7. The data showed that cadmium and nickel were beyond the permissible limits in most of the agricultural lands in Koratty. Among the different agricultural land uses, cadmium and nickel contents were found to be lowest in rubber, 8.2 and 275.2 mg/ kg soil respectively. The highest values for cadmium were found in mixed plantations followed by paddy lands. Mixed plantations and paddy fields are intensively managed and cadmium finds its way to these soils through mineral as well as organic fertilizers (Zhang *et al.* 2004; 2006).

Soils collected from coconut cultivated areas were found to have cadmium within permissible limits. Most of these coconut plantations are maintained with huge addition of farmyard manure along with mineral fertilizers. Restricted use of mineral fertilizer could keep Cd contents within permissible limits in these soils. However addition of poultry manure (imported from neighbouring states) may be a reason for accumulation of Cd in all 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 trace elements in soil can be higher than those found in the parent materials. Elevated concentrations of trace 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 trace 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).

Table 6: Heavy metal content (mg/ kg) in agricultural soils of Koratty Panchayat area

Agricultural systems	**Cu**	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
Paddy	104.36 (69.82)	15.27 (16.95)	91.51 (39.82)	352.39 (100.46)	437.25 (135.81)	237.29 (10.79)	44.80 (24.36)
Coconut	144.80 (110.59)	2.36 (0.91)	33.60 (47.52)	349.10 (216.23)	401.40 (163.48)	366.00 (18.50)	68.75 (4.85)
Mixed	84.58 (50.32)	19.80 (29.05)	82.49 (43.07)	286.67 (159.80)	372.81 (168.76)	257.51 (24.18)	48.57 (27.03)
Rubber	79.50 (15.40)	8.20 (18.00)	62.90 (30.10)	255.00 (154.50)	275.20 (143.30)	216.60 (63.50)	53.00 (18.30)
Permissible limit (a)	135-270	3-6	NA	NA	75-150	250-500	300-600
Permissible limit (b)	50-140	1-3	100	NA	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; NA = Not applicable

Table 7: Heavy metal content (mg/ kg) in industrial sites of Koratty Panchayat area

Industrial sites	**Cu**	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
GOI Press	7.00 (1.50)	12.00 (1.50)	25.00 (3.00)	125.00 (22.00)	64.00 (9.00)	156.00 (18.00)	42.00 (3.50)
KINFRA	10.00 (2.00)	14.00 (1.20)	32.00 (4.00)	210.00 (34.00)	120.00 (15.00)	120.00 (14.00)	40.00 (4.00)
Infopark	20.00 (2.00)	10.00 (1.40)	15.00 (2.00)	86.00 (18.00)	87.00 (13.00)	154.00 (12.00)	45.00 (4.00)
Vaigai Threads	11.00 (0.80)	7.00 (0.90)	12.00 (2.00)	112.00 (17.00)	74.00 (14.00)	150.00 (15.00)	40.00 (3.00)
Carborandum	14.00 (3.00)	8.00 (0.80)	12.00 (2.00)	67.00 (15.00)	90.00 (14.00)	140.00 (11.00)	42.00 (5.00)
Permissible limit (a)	135-270	3-6	NA	NA	75-150	250-500	300-600
Permissible limit (b)	50-140	1-3	100	NA	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; NA = Not applicable

Higher standard error values observed for heavy metals Cu, Cd, Cr, Mn, Ni, Pb and Zn in soil suggests that these metals are not uniformly distributed in the study area. A combined map depicting the heavy metal contamination in Koratty panchayat is given in Figure 3. Soil contamination was ascertained as an integration of contaminants studied with appropriate weightage given to each of the analyzed soil property by employing the raster calculator in the GIS software. Out of the different heavy metals analyzed, only cadmium was found to slightly exceed the tolerance limits in the industrial sites. A detailed survey of the industrial sites yielded no sewage sludge disposal in these sites.

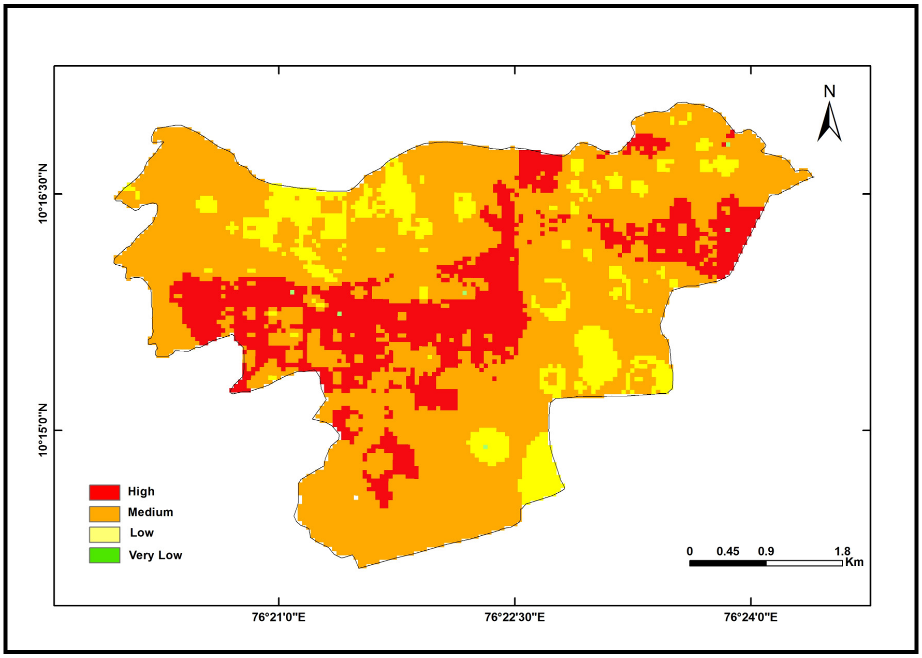

Figure 3: Distribution of heavy metal contamination in soils of Koratty region

2.3. Heavy metal speciation in soils

Heavy metal speciation was carried out in soils collected from both industrial and agricultural sites to evaluate the possible bioavailability of heavy metals at these sites.

Cadmium

In the industrial sites 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 8). 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). Samples collected from the campuses of Kerala Solvent Extraction Ltd (S_4) and Government of India Press (S_3) was found to have low Cd content in their soils indicating that these industrial units may be low dischargers of Cd. The retention of higher amounts of Cd in Fe and Mn oxides compared to organic fractions 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). The enrichment factors for Cd was > 3 for all the sites indicating high influence of anthropogenic factors rather than natural sources in increasing Cd contamination in these sites (Huu *et al.,* 2010).

Table 8: Mean values of Cd (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0 - 30 cm depth)

Fractions	**Agricultural soils**	**Industrial sites**
F1	1.16 (0.23)	1.17 (0.48)
F2	1.33 (0.14)	1.67 (0.62)
F3	0.93 (0.35)	2.24 (0.71)
F4	1.70 (0.36)	2.02 (0.47)

F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction;
F_3 = Organic matter fraction; F_4 = Residual fraction
* Values in parentheses shows standard error

Copper

The results of Cu speciation in soils (Table 9) showed that Cu was maximum in soils of industrial sites. Cu is an element with low mobility and hence accumulates at the site of application. Our study confirms the results obtained by earlier workers (Carlson *et al*., 1992, Marschner *et al*., 1995) who showed the lower mobility of Cu element among different metals. The lower mobility of Cu and its accumulation at industrial sites was also reported by Krishna and Govil, 2004. Organic matter held fraction of Cu was higher than Fe and Mn oxide bound Cu and exchangeable Cu in all the soils at both surface and subsurface levels. The affinity of organic matter towards Cu was also reported by Ashraf *et al*., 2012. According to Alloway (1990) and Lenntech (2009) when copper ends up in soils, it strongly attaches to organic matter and minerals. As a result, it does not travel very far after release.

Table 9: Mean values of Cu (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0 - 30 cm depth)

Fractions	Agricultural soils	Industrial sites
F1	1.85 (0.37)	1.00 (0.20)
F2	1.95 (0.18)	2.78 (0.26)
F3	3.05 (0.37)	3.72 (0.45)
F4	16.1 (2.34)	15.55 (2.26)
F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction; F_3 = Organic matter fraction; F_4 = Residual fraction * Values in parentheses shows standard error		

Iron

The maximum amount of Fe was found in the residual fraction. 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 38000 mg/ kg soil (Taylor and McLennan, 1995). Samples collected from industrial sites had values higher than the crustal means indicating iron pollution in these sites. In samples from cropped region, the Fe fractions decreased in the order residual fraction > Fe and Mn oxide bound fraction > exchangeable fraction > organic matter bound fraction (Table 10). The greater amount of Fe in the exchangeable form than organic matter bound forms at cultivated sites can act as a potential danger for increased Fe absorption by food crops. Moreover the exchangeable fractions become highly mobile under decreasing soil reaction (common in landuses with excessive mineral fertilizer application) leading to chances of Fe leaching into groundwater.

Table 10: Mean values of Fe (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0-30 cm depth)

Fractions	Agricultural soils	Industrial sites
F1	365.80 (97.30)	240.25 (63.9)
F2	954.50 (166.69)	804.10 (140.4)
F3	247.50 (44.50)	226.06 (40.6)
F4	33348.00 (2416.98)	41366.00 (2998.1)
F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction; F_3 = Organic matter fraction; F_4 = Residual fraction * Values in parentheses shows standard error		

Manganese

The exchangeable fraction of Mn was lower in the cropped region indicating the preferential adsorption of this element by cultivated crops. Such selective absorption will essentially reduce the metal concentration in soil. Mn as an essential micronutrient for crop growth has been reported by Hocking *et al.,* 1977. In the present study, largest amount of Mn was associated with oxides in both industrial and agricultural soils (Table 11). 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 have 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. However, oxide-Mn is readily reduced to available forms and is an important source of Mn for plants (Warden and Reisenauer, 1991).

Table 11: Mean values of Mn (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0-30 cm depth)

Fractions	**Agricultural soils**	**Industrial sites**
F1	14.40 (1.47)	59.12 (6.03)
F2	134.40 (39.53)	152.65 (44.90)
F3	7.10 (1.74)	5.82 (1.43)
F4	47.15 (6.65)	44.85 (6.32)

F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction; F_3 = Organic matter fraction; F_4 = Residual fraction
* Values in parentheses shows standard error

Nickel

Ni was found to be high in cropped regions compared to the industrial sites (Table 12). The high content of Ni in the cultivated soil may be due to application of fertilizers and irrigation water contaminated with Ni. Similar observations were made by Khurana and Bansal (2008) who reported high concentration of Ni in soils irrigated with sewage. Campel and Nikel, 2006 also showed that industrial and agricultural activities lead to Ni accumulation in surface soils.

Table 12: Mean values of Ni (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0-30 cm depth)

Fractions	**Agricultural soils**	**Industrial sites**
F1	8.60 (3.57)	3.15 (1.31)
F2	5.00 (0.98)	10.91 (2.15)
F3	70.40 (13.37)	16.10 (3.06)
F4	390.28 (32.82)	218.83 (18.40)
F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction; F_3 = Organic matter fraction; F_4 = Residual fraction * Values in parentheses shows standard error		

Lead

Industrial activities and excessive traffic leads to pollution by large amounts of Pb (Walraven *et al.,* 1997). Table 13 shows that all the fractions except organic matter bound lead was higher in industrial sites than the agricultural land. In cultivated soils, Pb is largely held by organic matter thereby restricting its free movement and hence less chance to get into the agricultural crops and thereby food chain. However the lowering of pH values in the cultivated soils may accelerate the Pb desorption and leaching in these soils and cause ground water pollution. The increase in lead mobility with decreasing pH was also reported by Baranowski *et al*., 2002. However, this aspect of lead leaching will depend on the hydraulic conductivity of soil and needs further investigation.

Table 13: Mean values of Pb (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0 -30 cm depth)

Fractions	**Agricultural soils**	**Industrial sites**
F1	5.50 (0.68)	20.81 (2.58)
F2	29.00 (1.89)	32.85 (2.14)
F3	36.25 (3.54)	18.97 (1.85)
F4	15.50 (3.86)	22.91 (5.71)
F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction; F_3 = Organic matter fraction; F_4 = Residual fraction * Values in parentheses shows standard error		

Zinc

More than 50% of the total zinc in the soils of Koratty (both industrial and agricultural soils) were held in the residual fraction (Table 14). Zn is one of the more mobile elements in soil (Marschner *et al.*, 1995). Taylor and McLennan, 1995 have reported a mean Zn concentration of 71 mg / kg soil and in our present study the Zn concentrations were found to be much lower than this value at all the sites.

Table 14: Mean values of Zn (mg/kg soil) speciation in agricultural and industrial sites of Koratty (0-30 cm depth)

Fractions	**Agricultural soils**	**Industrial sites**
F1	1.47 (0.49)	2.20(0.74)
F2	2.48 (0.63)	1.99(0.50)
F3	2.92 (0.68)	1.70(0.40)
F4	19.9 (2.26)	9.59(1.09)

F_1 = Exchangeable fraction; F_2 = Iron and manganese oxide fraction;
F_3 = Organic matter fraction; F_4 = Residual fraction
* Values in parentheses shows standard error

Heavy metal distribution

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 7 for the soils (both industrial and agricultural soils) in Koratty Panchayat. Figure 4 to 7 also gives an idea about 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. Fe seemed to be easily mobilised in this fraction while Cd and Cu are the minimum mobilisable elements. The order of mobility of the metals in the first fraction is Fe > Mn > Pb > Ni > Zn > Cu = Cd. Furthermore, similar mobility orders of the elements for the second and third fractions is Fe > Ni > Pb> Mn > Cu > Zn = Cd. Though Fe was the most mobile among the different heavy metals, more than 90% of this metal was observed in the last extraction stage i.e., residual fraction. Cd was the least mobile among the studied heavy metals but > 50% of this metal existed in the easily available fractions (fractions 1 and 2). Thus its movement from the point of origin may be restricted but still it poses a high potential risk of bioaccumulation by way of plant absorption. Pb and Ni were found to be abundant in the first three extraction stages and could be potentially dangerous by way of bio accumulation.

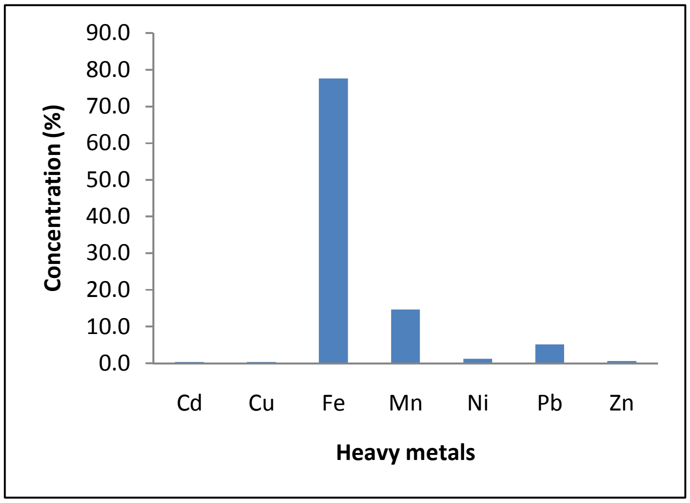

Figure 4: Extractability order of heavy metals in the first extraction stage of BCR sequential extraction procedure for the soils of Koratty

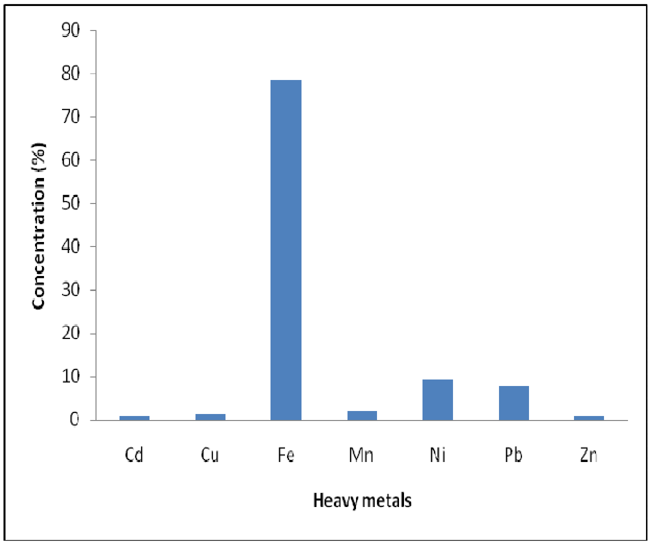

Figure 5: Extractability order of heavy metals in the second extraction stage of BCR sequential extraction procedure for the soils of Koratty

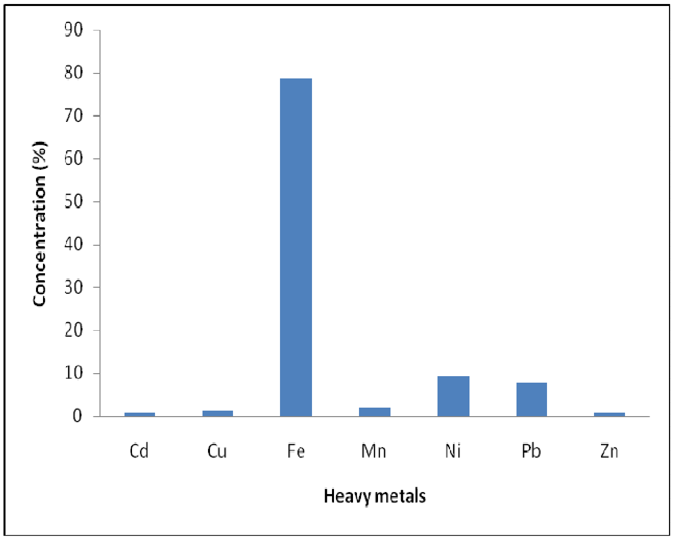

Figure 6: Extractability order of heavy metals in the third extraction stage of BCR sequential extraction procedure for the soils of Koratty

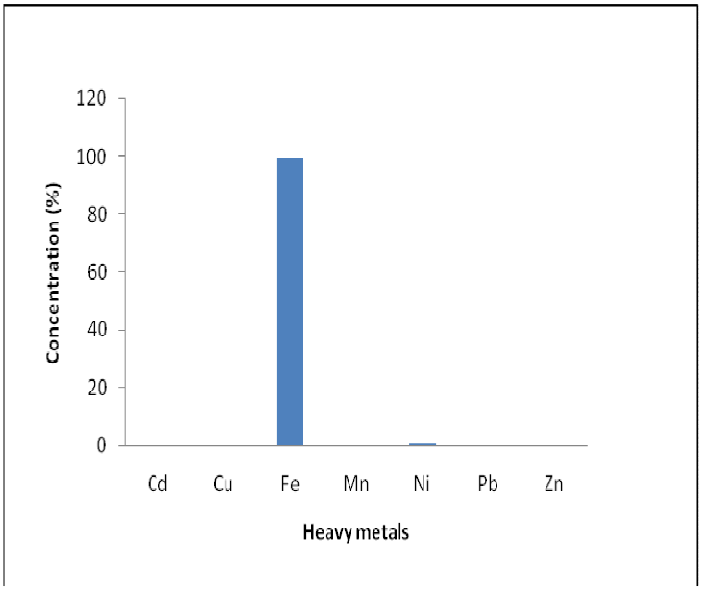

Figure 7: Extractability order of heavy metals in the fourth extraction stage of BCR sequential extraction procedure for the soils of Koratty

2.4. Heavy metal contamination indices

Degree of contamination (Figure 8) gives a good indication of site specific pollution due to different heavy metals.

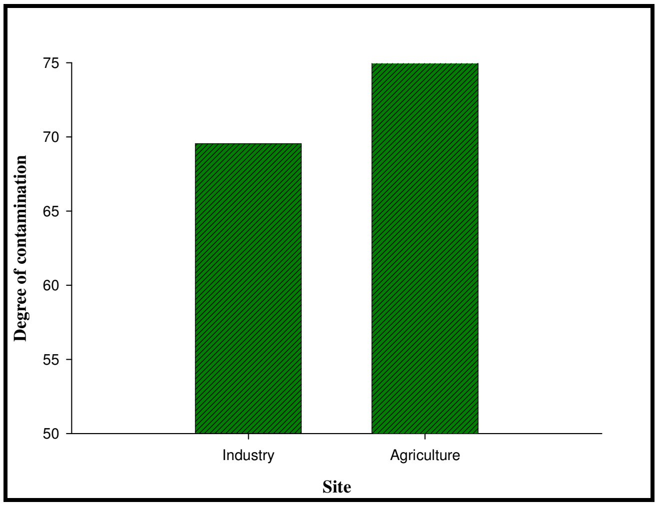

Figure 8: Degree of contamination of industrial and agricultural sites in Koratty

An analysis of the data shows that both agricultural and industrial sites in the region have a high degree of contamination (values greater than >32). The industrial and agricultural sites were further split into major industrial units and agricultural landuses, the results of which are given in Table 15.

Table 15: Land use wise degree of contamination of sampling sites in Koratty

Industry/ Agriculture	Degree of contamination
GOI press	112.50
KINFRA	99.99
VAIGAI Threads	57.56
CUMI	27.74
Infopark campus	49.96
Paddy	84.26
Coconut	51.35
Banana	95.02
Mixed	66.70
Rubber	77.49

Among the different industries, the degree of contamination was found to be spread between 27.74 to 112. 50. The heavy metal contamination of soils varied as GOI press > KINFRA > Vaigai Threads > Infopark campus > CUMI in the industrial sites. In cultivated areas of Koratty, banana fields followed by paddy lands were found to have high degrees of heavy metal contamination.

Heavy metals originating from anthropogenic and natural sources were interpreted by calculating enrichment factors for different heavy metals in the soils of the region. This technique employs normalizing of metal concentration to a texture or compositional characteristic of soil (Praveena *et al.,* 2008). In this study, the analyzed heavy metals were normalised relative to Fe since its concentration is generally not influenced by anthropogenic activities. The study shows that Cd had a very high contamination potential in both agricultural and industrial sites of Koratty (Figure 9). All the soils in Koratty were found to be very highly contaminated with cadmium (contamination factor >6). Cd in soil is characterized by a very long biological half life (10-30 yr). Cd enters soils mainly *via* atmospheric deposition, fertilization, sewage sludge or compost (Umweltbundesamt, 1997). 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 sources are higher than sinks, that is, Cd accumulates in soil. Koratty with its exhaustive agricultural and industrial network, deposits and accumulates large quantities of Cd in its soil. The heavy metal poses a serious threat as ~ 50% of the total Cd in these soils exist in easily extractable forms (exchangeable fraction and Fe and Mn fraction). Earlier reports show that after entering the soil, Cd is mainly sorbed on the surface of organic compounds or clays. 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 (OC), content, clay content etc. Cd with its long half life and abundance in the mobile fractions poses a threat of getting displaced towards ground water or getting transferred to plants.

Ni and Pb were the other two metals found to be having very high contamination factors in the soils of Koratty. 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.

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. 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 (Patra *et al.,* 2004). 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. However we couldn't find such a relationship in industrial sites of Koratty. The contamination factors for Mn and Zn were found to be in the low ranges (<1). Cu was found to be a moderate polluter in these soils (Table 16).

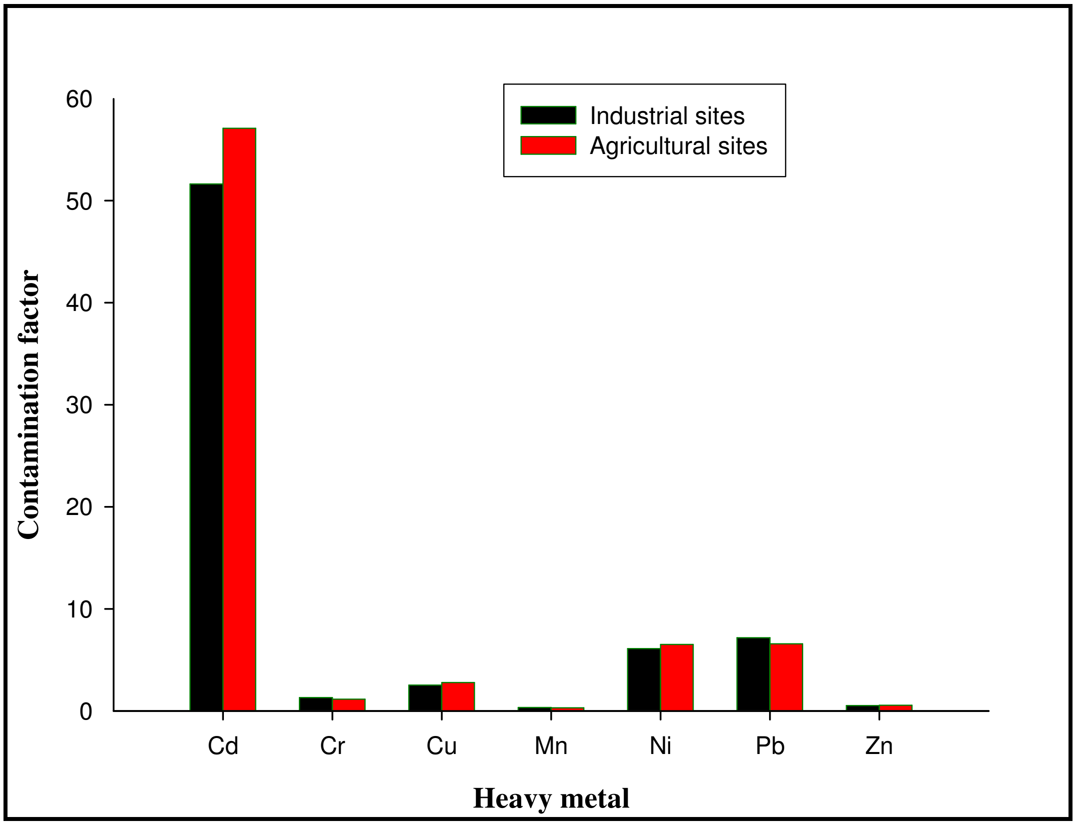

Figure 9: Contamination factors for different heavy metals in industrial and agricultural sites of Koratty

Table 16: Land use wise contamination factor for different heavy metals in Koratty

Industry/ Agriculture	**Contamination factors**						
	Cd	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
GOI	95.72	1.50	1.67	0.40	6.70	6.08	0.43
KINFRA	84.72	1.18	1.59	0.36	5.65	6.17	0.32
VAIGAI Threads	32.82	1.58	4.38	0.25	8.13	9.68	0.71
CUMI	12.97	0.81	2.96	0.23	2.80	7.08	0.91
Infopark	31.92	1.55	2.00	0.29	7.21	6.79	0.21
Paddy	62.40	1.23	3.24	0.27	8.50	8.14	0.48
Vegetable	33.28	0.90	3.14	0.24	6.46	6.72	0.60
Banana	80.84	1.52	1.91	0.42	4.83	5.15	0.35
Mixed	46.94	1.12	3.12	0.24	7.77	6.99	0.53
Rubber	62.17	0.97	2.44	0.25	5.08	5.88	0.71

Enrichment factors (EF) close to unity show crustal origin while those greater than one are related to non-crustal sources (Nolting *et al.,* 1999). Enrichment factors (Figure 10 and Table 17) of heavy metals were calculated using the continental crust average where Fe was used as reference element for normalization due to its low occurrence variability. Analysis by means of enrichment factor index reveals that the accumulated Cd, Pb and Ni in these sites have significant to extremely high enrichment. Enrichment factors for these metals indicate that these high polluters were the result of human activities rather than natural sources. The high deposits coupled with the mobility of Pb and Ni in the exchangeable fraction can make it a potential source of bioaccumulation and also poses danger of this getting leached into the ground water. Among the three major polluters, Cd has very low relative mobility in all the fractions and so chances of this polluting the ground water is the least. Hence strategies should be developed so as to prevent further loading of these three metals at these sites.

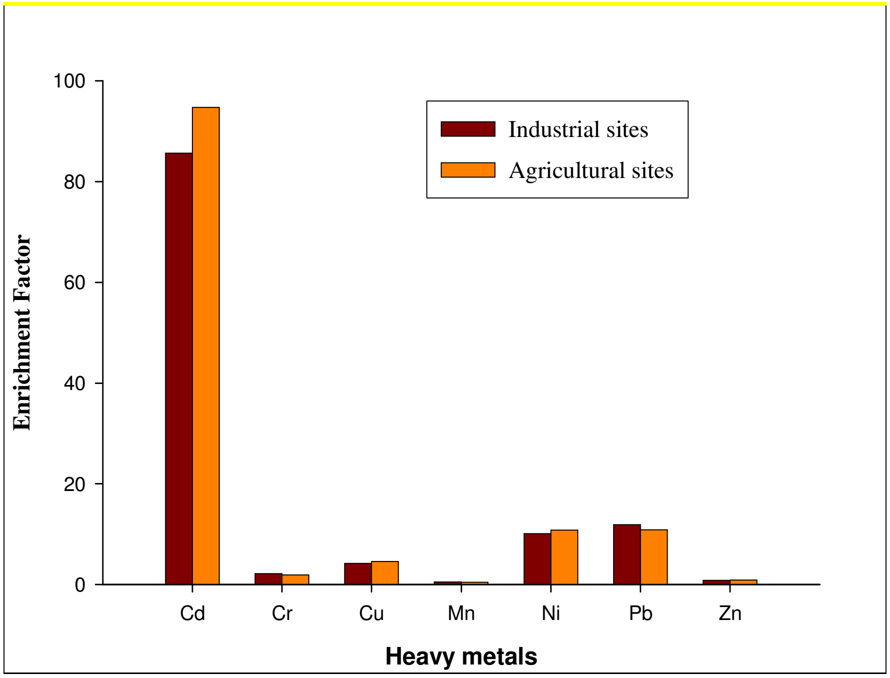

Figure 10: Enrichment factors for different heavy metals in industrial and agricultural sites of Koratty

Table 17: Land use wise enrichment factors for different heavy metals in Koratty

Industry/ Agriculture	**Enrichment factors**						
	Cd	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
GOI	158.69	2.49	2.76	0.67	11.12	10.07	0.71
KINFRA	140.46	1.95	2.64	0.60	9.36	10.23	0.54
VAIGAI	54.41	2.62	7.26	0.41	13.48	16.05	1.18
CUMI	21.50	1.34	4.91	0.38	4.64	11.73	1.50
INFOPARK	52.92	2.56	3.31	0.49	11.95	11.25	0.34
PADDY	103.45	2.04	5.38	0.44	14.09	13.49	0.80
VEGETABLE	55.18	1.50	5.21	0.40	10.71	11.14	1.00
BANANA	134.02	2.51	3.17	0.70	8.00	8.53	0.59
MIXED	77.82	1.86	5.17	0.40	12.88	11.59	0.88
RUBBER	103.07	1.61	4.05	0.41	8.42	9.75	1.17

3. Water quality in Koratty

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 ponds, wells and water course is presented in Tables 18 - 20.

The pH value of natural water changes due to the biological activity and industrial contamination. The pH values of Koratty region were found to vary between 4.85 - 6.85, 4.95 - 6.35 and 5.25 - 5.76 in ponds, wells and water course respectively. The values were lower than the prescribed BIS and ICMR standards. The water pH was found to vary more from the acceptable limits in samples collected during pre - monsoon period than during post monsoon.

TDS values were found to be within the prescribed limits of BIS and ICMR 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 (ponds, wells and water course). Hydrogen sulphide can result from bacterial breakdown of organic matter, human and animal wastes and 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 (Seinko and Plane, 1974). 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 i.e., 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 ponds, wells and water courses of Koratty. The oil and grease contents give an indication of the hydrocarbon content of water samples. In ponds and wells, the mean values of these compounds were found to be higher before 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 undertakes aerobic respiration. Presence of DO in water may be due to direct diffusion from air and photosynthetic activity of autotrophs. Oxygen can be rapidly removed from the waters by discharge of oxygen demanding wastes. The DO values > 5 mg/L is prescribed by ICMR and all the water bodies in general had acceptable levels.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are two parameters used to estimate organic pollution of water samples. The permissible levels prescribed by ICMR for BOD and COD are 5 mg/L and 20 mg/L respectively. BOD is defined as the amount of oxygen required by bacteria in stabilizing the decomposable organic matter. COD on the other hand is a measure of oxygen equivalent to the requirement of oxidizing organic matter contents 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 oils, grease, phenolic compound etc. may trigger a DE oxygenation process leading to depletion of dissolved oxygen and increasing the BOD and COD values. BOD and COD values were found to be higher than the prescribed ICMR limits in ponds and wells during both pre and post monsoon periods. Between the two sampling periods, pre monsoon had more mean COD and BOD values than post monsoon thereby confirming concentration of oxygen depleting activities/ organisms in the water bodies before rains. 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.

Among the heavy metals Fe, Mn and Ni were found to be beyond the permissible limits in ponds during both the sampling periods. Pb contents in the ponds were found to be beyond the permissible limits in the post monsoon samples. Mn and Ni contents in wells ranged between 0.01 - 0.25 mg/L and 0.01 - 0.17 mg/L and exceeded the permissible limits in certain cases. Cd content in wells and water course and Pb content in all water bodies were found to increase substantially after monsoon rains. Traces of pesticides were found in the water bodies of Koratty. Except aldrin in some ponds (premonsoon samples), none of the water bodies in the region were found to be polluted with pesticides beyond the permissible levels.

All the wells were contaminated with coliforms with no significant seasonal difference. Total coliforms were present in the range of 500 - 12000 CFU/ 100 ml. Even E- coli was present in 32% of these wells to the tune of 100 - 800 CFU/ 100 ml.

The results of fish spp. collected and pesticide residues identified are given in Tables 21 and 22. Results of pesticide residue analysis in fishes collected from major water courses draining Koratty panchayat area revealed that minute quantities (< 20 ppb) of pesticide residue were present in most of the obtained species indicating bioaccumulation. Endosulfan (α and ε) were the predominant pesiticide fractions in these samples. Though the contamination of fish by pesticides is in ppb levels, the risk associated with gradual health impairment of fish and that of higher life forms through biomagnifications has to be taken seriously.

Table 18 : Descriptive statistics of physico-chemical parameters of water in ponds during pre - monsoon and post - monsoon periods in Koratty

Parameters	Premonsoon				Post monsoon				Desirable limits	
	Minimum	Maximum	Mean	SE	Minimum	Maximum	Mean	SE	ICMR	BIS
pH	4.85	6.85	5.9	0.15	4.45	6.35	5.89	0.14	7.0-8.5	6.5 - 8.5
EC (µS/cm)	51.35	131.75	74.4	5.43	44.05	205.50	83.77	10.49	--	--
TDS (mg/L)	34.91	90.52	50.4	3.76	29.31	134.24	56.09	6.84	500	500
Sulphate (mg/L)	0.56	2.42	1.2	0.19	0.80	1.50	1.10	0.09	200	200
Sulphide (mg/L)	0.03	0.10	0.1	0.01	0.50	0.50	0.50	0.00	--	BDL
Phosphate (mg/L)	0.01	0.37	0.0	0.02	0.02	0.11	0.05	0.01	--	--
Nitrate (mg/L)	0.08	1.01	0.5	0.07	0.02	0.60	0.23	0.04	20	45
Fluoride (mg/L)	0.12	0.75	0.3	0.05	0.10	0.20	0.16	0.01	1	1
Oil & grease (mg/L)	16.80	574.00	118.3	34.91	7.40	881.20	104.95	55.89	--	--
Phenolic compounds (mg/L)	0.02	0.56	0.2	0.04	0.10	0.36	0.23	0.02	--	0.01
DO (mg/L)	3.70	6.70	5.6	0.20	4.15	6.35	5.65	0.17	5	--
BOD (mg/L)	3.55	14.30	8.3	0.89	3.55	13.25	7.01	0.79	5	--
COD (mg/L)	6.50	52.00	26.6	4.26	7.00	30.00	13.67	1.80	20	--
Mn (mg/L)	0.01	0.42	0.1	0.03	0.01	0.25	0.11	0.03	0.1	0.1
Fe (mg/L)	0.01	0.64	0.1	0.05	0.02	0.19	0.13	0.02	0.1	0.3
Ni (mg/L)	0.01	0.02	0.0	0.00	0.01	0.32	0.07	0.03	--	0.02
Pb (mg/L)	BDL	--	--	--	0.01	0.02	0.01	0.00	--	0.01
Cu (mg/L)	0.01	0.00	0.0	0.00	0.01	0.02	0.01	0.00	--	0.05
Cr (mg/L)	BDL	--	--	--	ND	--	--	--	0.05	0.05
Cd (mg/L)	BDL	--	--	--	ND	--	--	--	0.01	0.01
Hg (mg/L)	BDL	--	--	--	ND	--	--	--	0.001	0.001
Zn (mg/L)	0.02	0.07	0.0	0.00	0.01	0.02	0.01	0.00	0.10	5
As (mg/L)	BDL	--	--	--	ND	--	--	--	--	0.01
Lindane (µg/L)	0.01	0.01	0.0	0.00	0.00	0.00	0.00	0.00	--	2
Aldrin (µg/L)	0.03	0.31	0.1	0.03	0.00	0.00	0.00	0.00	--	0.03

Endosulfan (alpha) (µg/L)	0.04	0.09	0.1	0.01	0.00	0.00	0.00	0.00	--	0.4
Endosulfan (beta) (µg/L)	BDL	--	--	--	ND	--	--	--	--	0.4
DDD (µg/L)	0.00	0.04	0.0	0.01	0.00	0.00	0.00	0.00	--	1
DDE (µg/L)	BDL	--	--	--	ND	--	--	--	--	1
Dieldrin (µg/L)	0.01	0.02	0.0	0.00	0.00	0.00	0.00	0.00	--	0.03
Total coliform (CFU/100 ml)	300.00	22000.00	4584.6	1754.98	100.00	8000.00	2274.73	723.04	--	NIL
Fecal coliform (CFU/100 ml)	BDL	--	--	--	ND	--	--	--	--	NIL
E - coli (CFU/100 ml)	200.00	600.00	350.0	35.62	200.00	200.00	200.00	0.00	--	NIL
ICMR = Indian Council of Medical Research ; BIS = Bureau of Indian Standards; BDL = Below Detectable Limits										

Table 19 : Descriptive statistics of physico-chemical parameters of water in wells during pre - monsoon and post - monsoon periods in Koratty

Parameters	Premonsoon				Post monsoon				Permissible limits	
	Minimum	Maximum	Mean	SE	Minimum	Maximum	Mean	SE	ICMR	BIS
pH	4.95	6.35	5.79	0.08	4.95	6.30	5.87	0.07	7.0-8.5	6.5 - 8.5
EC (µS/cm)	31.70	146.55	76.10	6.70	46.10	149.60	77.13	5.16	--	--
TDS (mg/L)	21.30	98.11	51.25	4.52	30.85	100.17	52.13	3.47	500	500
Sulphate (mg/L)	0.42	12.26	1.41	0.46	0.72	4.68	1.87	0.20	200	200
Sulphide (mg/L)	0.01	0.13	0.04	0.00	0.02	0.11	0.04	0.00	--	BDL
Phosphate (mg/L)	0.29	0.89	0.59	0.08	BDL	--	--	--	--	--
Nitrate (mg/L)	0.06	9.165	0.96	0.37	0.14	0.86	0.37	0.03	20	45
Fluoride (mg/L)	0.10	0.4	0.24	0.02	0.10	0.20	0.14	0.01	1	1
Oil & grease (mg/L)	76.00	76	76.00	0.00	2.00	150.80	31.16	7.91	--	--
Phenolic compounds (mg/L)	0.20	0.2	0.20	0.00	0.01	16.00	2.06	0.98	--	0.01
DO (mg/L)	2.95	6.8	5.80	0.16	4.60	6.70	5.82	0.11	5	--
BOD (mg/L)	1.90	15	6.94	0.72	1.95	9.00	4.30	0.35	5	--
COD (mg/L)	6.00	53	19.36	2.27	5.00	22.50	8.29	0.68	20	--

Mn (mg/L)	0.01	0.25	0.05	0.02	0.01	0.25	0.05	0.02	0.1	0.1
Fe (mg/L)	0.00	0.1115	0.04	0.01	0.00	0.14	0.04	0.01	0.1	0.3
Ni (mg/L)	0.01	0.01	0.01	0.00	0.01	0.17	0.03	0.01	--	0.02
Pb (mg/L)	BDL	--	--	--	0.01	0.03	0.01	0.00	--	0.01
Cu (mg/L)	0.01	0.38	0.11	0.04	0.01	0.02	0.01	0.00	--	0.05
Cr (mg/L)	BDL	--	--	--	BDL	--	--	--	0.05	0.05
Cd (mg/L)	BDL	--	--	--	0.01	0.01	0.01	0.00	0.01	0.01
Hg (mg/L)	BDL	--	--	--	BDL	--	--	--	0.001	0.001
Zn (mg/L)	0.02	0.168	0.06	0.01	0.01	0.32	0.03	0.01	0.10	5
As (mg/L)	BDL	--	--	--	BDL	--	--	--	--	0.01
Lindane (µg/L)	BDL	--	--	--	BDL	--	--	--	--	2
Aldrin (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.03
Endosulfan (alpha) (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.4
Endosulfan (beta) (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.4
DDD (µg/L)	BDL	--	--	--	BDL	--	--	--	--	1
DDE (µg/L)	BDL	--	--	--	BDL	--	--	--	--	1
Dieldrin (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.03
Total coliform (CFU/100 ml)	100.00	10000	880.42	401.68	93.00	12000.00	1669.26	519.28	--	NIL
Fecal coliform (CFU/100 ml)	BDL	--	--	--	BDL	--	--	--	--	NIL
E - coli (CFU/100 ml)	100.00	700	328.57	52.55	200.00	800.00	500.00	51.64	--	NIL

ICMR = Indian Council of Medical Research, Kerala; BIS = Bureau of Indian Standards; BDL = Below Detectable Limits

Table 20 : Descriptive statistics of physico-chemical parameters of water in water courses during pre - monsoon and post - monsoon periods in Koratty

Parameters	Premonsoon				Post monsoon				Permissible limits	
	Minimum	Maximum	Mean	SE	Minimum	Maximum	Mean	SE	ICMR	BIS
pH	5.25	6.1	5.76	0.14	5.20	6.15	5.60	0.14	7.0-8.5	6.5 - 8.5
EC (µS/cm)	56.90	71.15	61.67	1.80	56.70	269.05	97.32	29.18	--	--
TDS (mg/L)	38.45	47.91	41.53	1.20	38.22	185.35	65.98	20.24	500	500
Sulphate (mg/L)	BDL	--	--	--	BDL	--	--	--	200	200
Sulphide (mg/L)	0.01	0.035	0.02	0.00	0.03	0.07	0.04	0.01	--	BDL
Phosphate (mg/L)	BDL	--	--	--	BDL	--	--	--	--	--
Nitrate (mg/L)	0.01	0.42	0.28	0.05	0.10	0.46	0.25	0.05	20	45
Fluoride (mg/L)	0.14	0.54	0.34	0.06	0.10	0.20	0.13	0.02	1	1
Oil & grease (mg/L)	43.80	312.2	128.55	41.86	23.20	132.00	57.26	13.64	--	--
Phenolic compounds (mg/L)	0.01	1.1	0.23	0.15	0.13	0.38	0.23	0.04	--	0.01
DO (mg/L)	4.55	5.6	5.11	0.15	3.55	5.55	4.81	0.28	5	--
BOD (mg/L)	4.90	14	8.76	1.09	4.85	8.90	6.79	0.56	5	--
COD (mg/L)	6.50	76	31.21	9.85	7.50	14.50	11.43	1.03	20	--
Mn (mg/L)	0.01	0.16	0.09	0.02	0.01	0.13	0.07	0.02	0.1	0.1
Fe (mg/L)	0.05	0.1575	0.11	0.01	0.09	0.26	0.16	0.03	0.1	0.3
Ni (mg/L)	0.00	0.01	0.01	0.00	0.01	0.02	0.01	0.00	--	0.02
Pb (mg/L)	0.00	0	0.00	0.00	0.01	0.02	0.01	0.00	--	0.01
Cu (mg/L)	0.01	0.1	0.04	0.02	0.01	0.01	0.01	0.00	--	0.05
Cr (mg/L)	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.05	0.05
Cd (mg/L)	BDL	--	--	--	0.01	0.01	0.01	0.00	0.01	0.01
Hg (mg/L)	BDL	--	--	--	BDL	--	--	--	0.001	0.001
Zn (mg/L)	0.02	0.341	0.13	0.07	0.01	0.06	0.03	0.01	0.10	5
As (mg/L)	BDL	--	--	--	BDL	--	--	--	--	0.01
Lindane (µg/L)	0.01	0.01	0.01	0.00	BDL	--	--	--	--	2

Aldrin (µg/L)	0.00	0.02	0.01	0.00	BDL	--	--	--	--	0.03
Endosulfan (alpha) (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.4
Endosulfan (beta) (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.4
DDD (µg/L)	BDL	--	--	--	BDL	--	--	--	--	1
DDE (µg/L)	BDL	--	--	--	BDL	--	--	--	--	1
Dieldrin (µg/L)	BDL	--	--	--	BDL	--	--	--	--	0.03
Total coliform (CFU/100 ml)	2000.00	22000	8014.29	3016.10	1000.00	8000.00	4114.29	1378.71	--	NIL
Fecal coliform (CFU/100 ml)	0.00	0	0.00	0.00	0.00	0.00	0.00	0.00	--	NIL
E - coli (CFU/100 ml)	0.00	2000	666.67	280.06	100.00	1500.00	700.00	208.85	--	NIL
ND = Not - detectable; ICMR = Indian Council of Medical Research; BIS = Bureau of Indian Standards; BDL = Below Detectable Limits										

Table 21: List of fish species analyzed for pesticide residues

Sl. No.	Common name	Scientific name
1	Climbing perch	*Anabas testudineus*
2	Common garra	*Garra mullya*
3	Common rasbora	*Rasbora dandia*
4	Gangetic leaf fish	*Nandus nandus*
5	Indian butter catfish	*Ompok bimaculatus*
6	Olive barb	*Systomus subnasutus*
7	Orange chromid	*Etroplus maculatus*
8	Striped snake head	*Channa striata*

Table 22: Pesticide residue in fish samples from Koratty

Pesticide	**Mean**	**Standard deviation**
α - HCH	0.02	0.07
β -HCH	0.00	0.00
γ - HCH	0.42	0.40
δ - HCH	0.57	0.72
ε - HCH	1.01	0.89
p,p - DDD	0.58	0.57
p,p - DDE	1.77	1.67
p,p - DDT	3.64	4.67
ε - DDT	4.56	5.73
Heptachlor epoxide	0.00	0.00
ε - Heptachlor	0.23	0.42
Heptachlor	0.23	0.42
α - Endosulfan	5.66	5.32
β - Endosulfan	4.39	4.96
Endosulfan sulfate	5.34	3.79
ε - Endosulfan	15.38	13.19
Dieldrin	1.22	1.49

SUMMARY

The study was conducted in Koratty panchayat to assess the landuse pattern and soil and water quality of the region. Samples were collected by giving due weigthage 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 2488 mm and 3 to 4 months of dry spell. The area shows predominance of laterites with a isohyperthermic soil temperature and ustic soil moisture regime.

Industrial sector is well developed in Koratty panchayat compared to other areas of Thrissur District. The area has large number of major and minor industries. Land capability classification shows that 98% of the land in the region belongs to Class II and III, indicating slight to moderate limitations for crop growth**.** Rice, coconut, banana, pepper, arecanut, nutmeg, rubber and vegetables are the main crops cultivated in the panchayat. Mixed cropping was the major cropping pattern identified in the region.

Total heavy metal contents in soil show that cadmium in industrial sites and Cd and Ni in most of the agricultural lands in Koratty were beyond the permissible limits. Pb exceeded acceptable levels in all the sites. Among the different heavy metals, cadmium and nickel contents were found to be highest in mixed crops and lowest in rubber.

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/or chemical forms. Thus, speciation analysis increases the information capacity of collected results.

The analyses were conducted in selected industrial and agricultural sites of Koratty panchayat. The order of mobility of the metals in the first fraction is Fe > Mn > Pb > Ni > Zn > Cu = Cd. Furthermore, similar mobility orders of the elements for the second and third fraction is Fe > Ni > Pb> Mn > Cu > Zn = Cd. Though Fe was the most mobile among the different heavy metals, more than 90% of this metal was observed in the last extraction stage i.e., residual fraction. Cd was the least mobile among the studied heavy metals, but > 50% of this metal existed in the easily available fractions (fractions 1 and 2) thus making it a contaminant of high bioaccumulation risk by way of plant absorption. Pb and Ni were found to be abundant in the first three extraction stages and could also be potentially dangerous by way of bio accumulation.

From the data, we computed degree of contamination, contamination factor and enrichment factor to analyse 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. Both agricultural and industrial sites in the region have a high degree of contamination (values greater than >32). Among the different industries the degree of contamination values was found to be spread between 27.74 to 112. 50. The heavy metal contamination of soils varied as GOI press > KINFRA > Vaigai Threads > Infopark campus > CUMI in the industrial sites. In cultivated areas of Koratty, banana fields followed by paddy lands were found to have high degrees of heavy metal contamination. Among the different heavy metals studied Cd, Ni and Pb were having very high contamination factors in the soils of Koratty. Enrichment factors of Cd, Ni and Pb shows that accumulation of these metals in soils occurs mainly due to the anthropogenic activities, industrial as well as agricultural.

Water quality of the region was assessed by collecting samples from ponds, wells and water course. The pH values of Koratty region were found to vary between 4.85 - 6.85,4.95 - 6.35 and 5.25 - 5.76 in ponds, wells and water course respectively. The values were lower than the prescribed BIS and ICMR standards. TDS values were found to be within the prescribed limits of BIS and ICMR in all the studied water sources and in this respect this water is suitable for drinking purposes. Among the anions, sulphide content was found to exceed the limits in all the water bodies of the region (ponds, 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.

Among the heavy metals, Pb contents in the ponds were found to be beyond the permissible limits in the post monsoon samples. Traces of pesticides were found in the water bodies. Except aldrin in some ponds (premonsoon samples), none of the water bodies in the region were found to be polluted with pesticides beyond the permissible limits. All the analyzed water samples indicated high pollution levels by coliforms and E-coli.

Literature cited

Abollino, O., Aceto, M., Malandrino, M., Mentasi, E., Sarzanini C.and Petrella, F. 2002. Heavy metals in agricultural soils from Piedmont, Italy. Distribution, speciation and chemometric data treatment. *Chemosphere.* 49: 545-557.

Abrahim, G.M.S. and Parker, P.J. 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediment from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment.* 136: 227-238.

Allen, H.E., 1993. The significance of trace metal speciation for water, sediment and soil quality criteria and standards. Science of The Total Environment. 134 (1): 23–45.

Alloway, B.J. 1990. Soil processes and the behaviour of metals. In: Heavy metals in soils, B.J. Alloway, ed. Blackie and Son Ltd.Glasgow.

Amoo, I.A., Adebayo O.T. and Lateef, A.J. 2005. Evaluation of heavy metals in fishes, water and sediments of Lake Kanji, Nigeria. *Journal of food, Agriculture and Environment.* 3(1): 209-212.

APHA (American Public Health Association). 2005. Standard methods for the examination of water and waste water. 21st Edn., Washington DC, USA.

Aryal, R.K., Furumai ,H., Nakajima, F. and Hossain, M.A. 2008. Spatial distribution and speciation of heavy metals in soakaway sediment. 11th International Conference on Urban Drainage, Edinburgh, Scotland, UK.

Ashraf, M. A., Maah, M. J. and Yusoff, I. 2012. Chemical Speciation and Potential Mobility of Heavy Metals in the Soil of Former Tin Mining Catchment. The Scientific World Journal. 2012:1-11.

Awashthi, S.K. 2000. Prevention of Food Adulteration Act no 37 of 1954. Central and State Rules as Amended for 1999, third ed. Ashoka Law House, New Delhi.

Baath, E.1989. Effects of Heavy Metals in Soil on Microbial Processes and Populations. *Water Air and Soil Pollution.* 47(3-4): 335–379.

Bai, J., Yang, Z., Cui, B., Gao, H. and Ding, Q. 2010. Some heavy metals distribution in wetland soils under different landuse types along a typical plateau lake, China. *Soil & Tillage Research.* 106: 344–348.

Baranowski, R., Rybak, A. and Baranowska, I. 2002. Speciation Analysis of Elements in Soil Samples by XRF. *Polish Journal of Environmental Studies* .11(5): 473-482.

Barona, A., Aranguiz, I. and Elias, A. 1999. Assessment of metal extraction and contamination in surface soils by 3-step sequential extraction procedure. *Chemosphere.* 39, 1911-1922.

Begonia, M.T., Begonia, G.B., Miller, G., Gilliard, D. and Young, C. 2004. Phosphatase Activity and Populations of Microorganisms from Cadmium and Lead Contaminated soils. *Bulletin of Environmental Contamination and Toxicology*.73: 1025-1032.

Begum,A., Ramaiah,M., Irfanulla,K. and Veena,K. 2009. Analysis of heavy metal concentrations in soil and litchens from various localities of Hosur Road, Bangalore, India. CODEN ECJHAO, E-J. Chem., 6(1): 13-22.

Bezak-Mazur, E. and Rabajczyk, A. 2001. A Speciation Analysis of Aluminium in the River Silnica . *Polish Journal of Environmental Studies.* 10(4): 263-267.

Bin Li., Qiuquan Wang, Benli Huang. and Shuping Li.2001. Evaluation of the Results from a Quasi Tessier's Sequential Extraction Procedure for Heavy Metal Speciation in Soils and Sediment by ICP-MS. *Analytical sciences , vol.17* The Japan Society for Analytical Chemistry.

Biqing, S., Zhaoyu, and Zhenhua, L. 2008. Environmental Pollution and Human Health, China Environmental Press.

Brookes, P, C .1995. The Use of Microbial Parameters in Monitoring Soil Pollution by Heavy Metals. *Biology and Fertility of Soils*, 19(4): 269-279.

Brown, R.M., McClelland, N.I., Deininger, R. A. and O'Connor, M.F. 1972. A Water Quality Index — Crashing the Psychological Barrier. Indicators of Environmental Quality, Environmental Science Research. 1: 173-182.

Campel, M. and Nikel, G. 2006. Nickel: A Review of Its Sources and Environmental Toxicology. *Polish Journal of Environmental Studies.* 15(3): 375-382.

Carlson, C.E.A. and Morrison,G.M. 1992. Fractionation and toxicity of metals in sewage sludge. *Environmental Technology*.13(8):751-759.

Chirenje ,T., Ma, L., Reeves, M. and Szulczewski, M. 2004. Lead Distribution in Near- Surface Soils of Two Florida Cities: Gainesville and Miami. *Geoderma.* 119: 113–120.

Davidson, C. M., Duncan, A. L., Littlejohn, D., Ure A. M. and Garden, L. M. 1998. A critical evaluation of the threestage BCR sequential extraction procedure to access the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Analytica Chimica Acta*. 363: 45-55.

Davidson, C.M., Thomas, R.P., Mcvey, S.E., Perala, R., Littlejohn, D. and Ure, A.M. 1994. Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments. *Analytica Chimica Acta*. 291: 277-286.

Doelman, P. and Haanstra, L.1979. Effects of Lead on the Soil Bacterial Microflora. *Soil Biology and Biochemistry.* 1: 487-491.

European Union. 2002. Heavy Metals in Wastes, European Commission on Environment (http://ec.europa.eu/environment/waste/ studies/pdf/heavy_metalsreport.pdf)

Fagbote E.O. and Olanipekun E.O.. 2010. Evaluation of the Status of Heavy Metal Pollution of Soil and Plant (*Chromolaena odorata*) of Agbabu Bitumen Deposit Area, Nigeria. *American-Eurasian Journal of Scientific Research.* 5 (4): 241-248.

Fageria, N.K., Baligar, V.C. and Clark, R.B. 2002. Micronutrients in crop production. Advances in Agronomy.77: 185-268.

Ferner., D.J. 2001, Toxicity and Heavy metals. *eMedicine Journal.* 2 (5):1.

Fiedler, H.D., Lo´ pez-Sa´ nchez, J.F., Rubio, R., Rauret, G., Quevauviller, Ph., Ure, A.M. and Muntau, H. 1994. Study of the stability of extractable trace metal contents in a river sediment using sequential extraction. *Analyst.* 119: 1109-1114.

Fosmire., G.J. 1990. Zinc Toxicity. *The American Journal of Clinical Nutrition*. 51(2): 225 -227.

Goyer, R.A. and Clarkson, T.W. 2001. Toxic Effects of Metals. In, Casarett and Doullis Toxicology: The Basic Science of Poisons, Sixth Edition (C.D. Klaassen, ed.) Mc-Graw-Hill, New York, pp. 811-867.

Gupta, N., Khan, D. K., and Santra, S. C. 2008. An assessment of heavy metal contamination in vegetables grown in wastewater-irrigated areas of Titagarh, West Bengal, India. Bulletin of Environmental Contamination and Toxicology. 80, 115–118.

Lund, W. 1990. Speciation analysis—why and how? *Fresenius Journal of Analytical Chemistry.* 337, 557–564.

Hackenberg, S. and Wegener, H.-R., 1999. Schadstoffeinträge in Böden durch Wirtschafts- und Mineraldünger, Komposte und Klärschlamm sowie durch atmosphärische Deposition. Regionale Frachtenmodelle zur Literature Bewertung relevanter Schadstoffeinträge. Abfall-Wirtschaft - Neues aus Forschung und Praxis. M.I.C BAEZA-Verlag, Witzenhausen, 220-223.

He, Z.L., Yang, X.E. and Stoffella, P.J. 2005. Trace elements in Agroecosystems and impacts on the environment. Journal of Trace Elements in Medicine and Biology .19:125-40.

Hemida, S.K., Omar, S.A. and Abdel-Mallek, A.Y. 1997. Microbial Populations and Enzyme Activity in Soil treated with Heavy Metals. *Water Air and Soil Pollution.* 95: 13-22.

Ho, H.H., Swennen, R. and Van Damme, A. 2010. Distribution and contamination status of heavy metals in estuarine sediments near cua ong harbor, ha long bay, Vietnam. *Geologica Belgica 13/1-2*: 37-47.

Hocking, P.J., Pate, J.S., Wee, S.C. and Mccomb, A.J. 1977. Manganese Nutrition of *Lupinus* spp. Especially in Relation to Developing Seeds. *Annals of Botany.* 41 (4): 677-688.

Hollis, J.P., Allam, A.I., Pitts, G., Joshi, M.M. and Ibrahim, I.K.A. 1975. Sulphide diseases of rice on iron-excess soils. Acta Phytopathology. 10: 329.

Holtan-Hartwig, L., Bechmann, M., Hoyas, T.R., Linjordet, R. and Bakken, L.R. 2002. Heavy Metals tolerance of Soil denitrifying Communities: N2O Dynamics. *Soil Biology and Biochemistry.* 34: 1181-1190.

Hulya, B. 2009. Utilization of the water quality index method as a classification tool, *Environmental Monitoring and Assessment*, 167: 115-124.

Huu H.H., Swennen, R. and Van Damme, A. 2010. Distribution and contamination status of heavy metals in estuarine sediments near cua ong harbor, ha long bay, Vietnam. *Geologica belgica.* 13(1-2): 37-47.

Institute of Environmental Conservation and Research (INECAR). 2000. Position Paper Against Mining in Rapu-Rapu, Published by INECAR, Ateneo de Naga University, Philippines.

Jackson, M.L. 1967. Soil Chemical Analysis. Prentice Hall of India Pvt. Ltd., New Delhi.

Johnson, L.B., Richards, C., Host, G.E., Arthur, J.W. 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biology*. 37:193–208.

Kartal, S., Aydin Z. and Tokalioglu, S. 2006. Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *Journal of Hazardous Materials.* 132: 80-89.

Khurana, M.P.S. and Bansal R.L. 2008. Impact of sewage irrigation on speciation of nickel in soils and its accumulation in crops of industrial towns of Punjab. *Journal of Environmental Biology*. 29(5). 793-798.

Krishna, A.K. and Govil, P.K. 2004. Heavy metal contamination of soil around Pali Industrial Area, Rajasthan, India. *Environmental Geology* .47(1):38 -44.

Kubova, J., Matus, P., Bujdos, M. and Medved, J. 2005. Influence of acid mining activity on release of aluminium to environment. *Analytica Chimica Acta.* 547:119–125.

Lenntech Water Treatment and Air Purification. 2004. Water Treatment, Published by Lenntech, Rotterdamseweg, Netherlands.

Lenntech, W.T. 2009. Chemical Properties, Health and Environmental Effects of Copper. Lenntech Water Treatment and Purification Holding B.V.

Li, X., Poon, C. and Liu, P.S. 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry*. 16 (1- 2): 1361‑1368

Liou, S., Lo, S. and Wang, S. 2004. A generalized water quality index for Taiwan. *Environmental Monitoring and Assessment*. 96: 35–52.

Lu, A., Zhang S. and Shan, X.2004. Time effect on the fractionation of heavy metals in soils. *Geoderma*, 125 (3-4): 225-234.

Lu, Y., Gong, Z., Zhang G. and Wolfgang, B. 2003. Concentrations and chemical speciations of Cu, Zn, Pb and Cr of urban soils in Nanjing. China. *Geoderma*, 115: 101-111.

Marschner, B., Henke,U. and Wessolek, G.1995. Effects of ameliorative additive on the adsorption and binding forms of heavy metals in a contaminated topsoil from a former sewage farm. *Journal of Plant Nutrition and Soil Science.* 158: 9.

McCluggage, D. 1991. Heavy Metal Poisoning, NCS Magazine, Published by The Bird Hospital, CO, U.S.A.

McKee, J.E. and Wolf, H.W. 1963. Water quality criteria. 2nd edition. Resources Agency of California State Water Resources Control Board.

Mediolla, L.L., Domingues M.C.D. and Sandoval, M.R.G. 2008. Environmental Assessment of Active Tailings Pile in the State of Mexico (Central Mexico). *Research Journal of Environmental Sciences.* 2(3): 197-208.

Mench, M., Didier, V., Loffler, M., Gomez, A. and Masson, P. 1994. A Mimicked in-situ Remediation Study of Metal-contaminated Soils with emphasis on Cadmium and Lead. *Journal of Environmental Quality*. 23: 58-63.

Mester, Z., Cremisini, C., Ghiara, E. and Morabito, R. 1998. Comparison of two sequential extraction for metal fractionation in sediment samples. *Analytica Chimica Acta.* 359: 133-142.

Nolting, R.F., Ramkema, A. and Everaats, J.M. 1999. The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d’Arguin (Mauritania). *Continental Shelf Research* 19: 665 – 691.

Nriagu, J.O. and Pacyna, J.M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature.* 333: 134– 139.

Olubunmi, F.E. and Olorunsola, O.E. 2010. Evaluation of the Status of Heavy Metal Pollution of Soil and Plant (*Chromolaena odorata*) of Agbabu Bitumen Deposit Area, Nigeria. *American-Eurasian Journal of Scientific Research.* 5 (4): 241-248.

Patra, M., Bhowmik, N., Bandopadhyay, B. and Sharma, A. 2004. Comparison of mercury, lead and arsenic with respect to geno toxic effects on plant systems and the development of genetic tolerance. *Environmental* and Experimental Botany.52: 199- 223.

Praveena, S.M., Ahmed, A., Radojevic, M., Abdullah, M.H., Aris, A.Z. 2008. Multivariate and geo-accumulation index evaluation in mangrove surface sediment of Mengkabong. *Bulletin of Environmental Contamination and Toxicology.* 81: 52-63.

Rastmanesh, F., Moore, F., Kopaei, M.K., Keshavarzi, B. and Behrouz, M. 2010. Heavy metal enrichment of soil in Sarcheshmeh copper complex, Kerman Iran. *Environmental Earth Sciences.* 62: 329-336.

Rauret, G. 1998. Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta*, 46: 449-455.

Sahuquillo, A., Lo´ pez Sa´ nchez, J.L., Rauret, G., Ure, A.M., Muntau, H. and Quevauviller, P.H. 2002. Sequential extraction procedures for sediment analysis. In: Quevauviller, Ph. (Ed.), *Methodologies for Soil and Sediment Fractionation Studies*, pp. 10-27.

Sahuquillo, A., Lo´ pez-Sa´ nchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M. and Ure, A.M. 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Analytica Chimica Acta* . 382, 317-327.

Said, A., Stevens, D.K. and Sehlke, G. 2004. An Innovative Index for Evaluating Water Quality in Streams. *Environmental Management*. .34 (3): 406–414.

Sharma, R.K., Agrawal, M. and Marshall, F.M. 2006. Heavy metals contamination in vegetables grown in waste water irrigated areas of Varanasi, India. *Bulletin of Environmental Contamination and Toxicology.* 77: 311-318.

Sheppard, M.I. and Stephenson, M. 1997. Critical Evaluation of Selective Extraction Methods for Soils and Sediments, Contaminated Soils. INRA (Les Colleagues, 85), Paris.

Shuman, L. M. 1979. Zinc, manganese and copperin soil fractions. *Soil Science.* 127: 10-17.

Sienko, M.J. and Plane, R.A. 1974. Chemical principles and properties. 2nd edition. McGraw-Hill Publishing Co., New York.

Sonawanea, G.H. and Shrivastavab, V.S. 2010. Ground Water Quality Assessment Nearer to the Dye user Industry. *Archives of Applied Science Research.* 2 (6): 126-130.

Srivastava, S., Mishra, S., Dwivedi, S., Baghel, V. S., Verma, S., Tandon, P. K., Rai, U. N. and Tripathi, R. D. 2005. Nickel Phytoremediation Potential of Broad Bean, *Vicia faba L.* and its Biochemical Responses. Bulletin of Environmental Contamination and Toxicology. 74: 715-724.

Sutherland, R.A. 2002. Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. *Applied Geochemistry*. 17:353–365.

Svete, P., Milacic, R. and Pihlar, B. 2001. Partitioning of Zn, Pb and Cd in river sediments from a lead and zinc mining area using the BCR three-step sequential extraction procedure. Journal of Environmental Monitoring. 3, 586-590.

Sza´kova´, J., Tlustos, P., Balı´k, J., Pavlı´kova´, D. and Vanek, V. 1999. The sequential analytical procedure as a tool for evaluation of As, Cd and Zn mobility in soil. *Journal of Analytical Chemistry.* 363, 594-595.

Taylor, S.R. and McLennan, S.M. 1985. The Continental Crust: Its Composition and Evolution. Blackwell Scientific Publications, Oxford.

Taylor, S.R. and McLennan, S.M. 1995. The geochemical evolution of the continental crust. *Reviews of Geophysics*. 33:241-265.

Tessier, A., Campbell, P. and Bisson, M. 1979. Sequential Extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*. 51, 844-851.

Thomas, R.P., Ure, A.M., Davidson, C.M., Litteljohn, D., Rauret, G., Rubio, R. and Lo´ pez-Sa´ nchez, J.F. 1994. Three-stage sequential extraction procedure for the determination of metals in river sediments. *Analytica Chimica Acta.* 286: 423-429.

U.S. Environmental Protection Agency. 1976. Quality criteria for water. Washington, DC. pp. 410.

Udedi, S.S .2003. From Guinea Worm Scourge to Metal Toxicity in Ebonyi State, Chemistry in Nigeria as the New Millennium Unfolds, 2(2): 13–14.

Umweltbundesamt, 1997. Daten zur Umwelt. Erich Schmidt Verlag, Berlin.

Ure, A.M., Quevauviller, Ph., Muntau, H. and Griepink, B. 1992. B. EUR report. CEC Brussels, 14763, 1992:85.

Ure, A.M., Quevauviller, Ph., Muntau, H. and Griepink, B. 1993. Speciation of heavy metal in soils and sediments. An account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry*. 51,135-151.

Walkley, A. and Black, I.A. 1934. Estimation of soil organic carbon by chromic acid titration method. *Soil Science*. 37: 29-38.

Walraven, N., Van Os, B.J.H., Th. Klaver, G., Baker, J.H. and Vriend, S.P. 1997. Trace element concentrations and stable lead isotopes in soils as tracers of lead pollution in Graft- De Rijp, the Netherlands. *Journal of Goechemical exploration.* 59(1): 47-68.

Warden, B.T. and Reisenauer, H.M. 1991. Fractionation of soil manganese forms important to plant availability. *Soil Science Society of America Journal*. 55, 345-349.

Weggler, K., McLaughlin, M.J. and Graham, R.D. 2004. Effect of Chloride in Soil Solution on the Plant Availability of Biosolid-Borne Cadmium. *Journal of Environmental Quality*. 33(2): 496–504.

Whalley, C. and Grant, A. 1994. Assessment of the phase selectivity of the European Community bureau of reference (BCR) sequential extraction procedure for metals in sediment. *Analytica Chimica Acta.* 291, 287- 295.

Yongming, H., Peixuan, D., Junji, C. and Posmentier, E. S. 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China, Science of the Total Environment. 355, 176–186.

Young, R.A. 2005. Toxicity Profiles: Toxicity Summary for Cadmium, Risk Assessment Information System, RAIS, University of Tennessee. (rais.ornl.gov/tox/profiles/cadmium.shtml).

Zhang, M.K., He, Z.L., Calvert, D.V. and Stoffella, P.J. 2004. Leaching of mineralsand heavy metals from muck-amended soil columns. *Soil Science*. 169: 528-40.

Zhang, M.K., He, Z.L., Calvert, D.V. and Stoffella, P.J. 2006.Extractability and Mobility of Copper and Zinc Accumulated in Sandy Soils. *Pedosphere*. 16(1): 43-9.