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# STUDIES ON THE QUALITY OF RAINWATER AT VARIOUS LAND USE LOCATIONS AND VARIATIONS BY INTERACTION WITH DOMESTIC RAINWATER HARVESTING SYSTEMS

A Thesis

Submitted by

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# Certificate

Certified that this thesis entitled "Studies on the Quality of Rainwater at Various Land Use Locations and Variations by Interaction with Domestic Rainwater Harvesting Systems" submitted to Cochin University of Science and Technology, Kochi for the award of Ph.D Degree, is the record of bonafide research carried out by Mr. Roy M Thomas, under my supervision and guidance at School of Engineering, Cochin University of Science and Technology. This work did not form part of any dissertation submitted for the award of any degree, diploma, associate ship or other similar title or recognition from this or any other institution.

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#### **DECLARATION**

I, Roy M Thomas hereby declare that the work presented in the thesis entitled "Studies on the Quality of Rainwater at Various Land Use Locations and Variations by Interaction with Domestic Rainwater Harvesting Systems", being submitted to Cochin University of Science and Technology for the award of Doctor of Philosophy under the Faculty of Engineering, is the outcome of the original work done by me under the supervision of Dr. Benny Mathews Abraham, Professor of Civil Engineering, School of Engineering, Cochin University of Science and Technology, Kochi. This work did not form part of any dissertation submitted for the award of any degree, diploma, associate ship or other similar title or recognition from this or any other institution.

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#### "In His time He makes all things beautiful" (The Bible-Eccl 3:11)

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#### ABSTRACT

In many parts of the world, the amount of water being consumed has exceeded the annual level of renewal, thus creating a non sustainable situation. As per the international norms, if per-capita water availability is less than 1700m³ per year then the country is categorized as water stressed and if it is less than 1000m³ per capita per year then the country is classified as water scarce. In India per capita surface water availability in the years 1991 and 2001 were 2309 and 1902m³ and these are projected to reduce to 1401 and 1191m³ by the years 2025 and 2050 respectively. Hence, there is a need for proper planning, development and management of the greatest assets of the country, viz. water and land resources for raising the standards of living of the millions of people, particularly in the rural areas.

The enormity of the water crisis and the need for water conservation can hardly be over emphasised. Government agencies across the globe are introducing policies to promote increased use of directly captured rainwater, as an supplementary source of drinking water. The Government of Kerala has introduced legislation making roof top rainwater harvesting mandatory in all newly constructed buildings in the state. The quality of harvested rainwater depends upon many factors such as air quality, system design and maintenance, materials used, rainfall intensity, length of time between rainfall events, social context as well as water handling.

In this context, the studies on quality of rainwater are of relevance. The present study focused on the quality of rainwater at various land use locations and its variations on interaction with various domestic rainwater harvesting systems. Sampling sites were selected based upon the land use pattern of the locations and were classified as rural, urban, industrial and sub urban. Rainwater samples were collected from the south west monsoon of May 2007 to north east monsoon of October 2008, from four sampling sites

namely Kothamangalam, Ernakulam, Eloor and Kalamassery, in Ernakulam district of the State of Kerala, which characterized typical rural, urban, industrial and suburban locations respectively. Rain water samples at various stages of harvesting were also collected The samples were analyzed according to standard procedures and their physico-chemical and microbiological parameters were determined.

The variations of the chemical composition of the rainwater collected were studied using statistical methods. It was observed that 17.5%, 30%, 45.8% and 12.1% of rainwater samples collected at rural, urban, industrial and suburban locations respectively had pH less than 5.6, which is considered as the pH of cloud water at equilibrium with atmospheric CO<sub>2</sub>. Nearly 46% of the rainwater samples were in acidic range in the industrial location while it was only 17% in the rural location. Multivariate statistical analysIs was done using Principal Component Analysis, and the sources that influence the composition of rainwater at each locations were identified ,which clearly indicated that the quality of rain water is site specific and represents the atmospheric characteristics of the free fall

The quality of harvested rainwater showed significant variations at different stages of harvesting due to deposition of dust from the roof catchment surface, leaching of cement constituents etc. Except the micro biological quality, the harvested rainwater satisfied the Indian Standard guide lines for drinking water. Studies conducted on the leaching of cement constituents in water concluded that tanks made with ordinary portland cement and portland pozzolana cement could be safely used for storage of rain water

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# **ABBREVIATIONS**

ADR - Average Daily Runoff

BCM - Billion Cubic Meter

Cfu - Colony Forming Unit

CUSAT - Cochin University of Science & Technology

DRWH - Domestic Rainwater Harvesting

EC - Electric Conductivity

GEO - Global Environment Outlook

ICI - Interstructure Compromise infrastructure

LPCD - Litre Per Capita Demand

MDGs - Millennium Development Goal

MPN - Most Probable Number

NSSF - Non Sea Salt Fraction

NTU - Nephelometric Turbidity Units

OPC - Ordinary Portland Cement

PCA - Principal Component Analysis

PPC - Portland Pozzolana Cement

RWH - Rainwater Harvesting

SSF - Sea Salt Fraction

TCLP - Toxcity Charecteistic Leaching Procedure

TDS - Total Dissolved Solid

UNEP - United Nationals Environment Programme

WHO - World Health Organization

# INTRODUCTION

The importance of water is obvious to everyone. We cannot imagine existence of life in the form of flora and fauna without water. At present, space scientists are vigorously engaged in searching for water on other planets. Existence of life on other planets is not conceivable for the human mind, unless there is evidence of water.

More than 2000 million people would live under conditions of high water stress by the year 2050, according to the United Nations Environment Programme (UNEP) which warns water could prove to be a limiting factor for development in a number of regions in the world. About one-fifth of the world's population lacks access to safe drinking water and with the present consumption patterns, two out of every three persons on the earth would live in water stressed conditions by 2025. Around one-third of the world population now lives in countries with moderate to high water stress where water consumption is more than 10% of the renewable fresh water supply, said the Global Environment Outlook (GEO), 2000, the UNEP's Millennium Report. According to the report pollution and scarcity of water resources and climate change would be the major emerging issues in the next century.

Providing access to safe drinking water is one of the most effective means to improve public health. Globally, more than 1.1 billion people do not have access to what the World Health Organization (WHO) considers to be an "improved water supply which includes a household water collection (WHO 2005). Despite major efforts to deliver safe, piped, community water to the world's population, the reality is that water supplies delivering safe water will not be available to all people in the near future. In an effort to bring global attention to this problem, the UN, as part of its Millennium Development Goals (MDGs) has set a target of having the proportion of people without access to safe drinking water by 2015 (Sachs 2005). It is clear that all possible approaches must be tried to mitigate the problem of drinking water, maximizing the control of households with regard to their own water security.

The reality of water crisis cannot be ignored. In spite of higher average annual rainfall in India (1,170 mm) as compared to the global average (800 mm), it does not have sufficient water. The projections of India becoming a water stressed country by 2025 can be proved wrong only if we are able to utilize a substantial portion of the surface runoff, which is currently lost as runoff to sea or through evaporation. It is in this context, that rainwater harvesting gain importance.

India still has an enormous amount of water, theoretically as much as 173 million hectare-meters, that could be captured as rain or as runoff from small catchments in a nearby villages or towns. Therefore, the theoretical potential of water harvesting for meeting household needs is enormous. Rain captured from 1-2% of India's land could provide India's population if 950 million with as much as 100 litres of water per person per day (Agarwal, 1998). There is no village in India which could not meet its drinking water needs through rainwater harvesting. As there is a synergy between population density and rainfall levels, less land is required in more densely populated areas to capture the same amount of rainwater. And in

such areas there are usually more non-porous surfaces like rooftops, which have improved runoff efficiency. Water harvesting means capturing the rain where it falls. There are a variety of ways of harvesting water, such as capturing runoff from rooftop, local catchments, capturing seasonal flood waters from local streams and conserving water through watershed management.

Rainwater harvesting is often considered to be traditional method of water collection and storage. The practice of rainwater harvesting can be traced back many countries, especially in country like India where rainwater harvesting is mentioned in ancient inscriptions as far back as 5<sup>th</sup> century Before Christ (BC). However, types and methods of rainwater harvesting have changed over time and many different systems are now available all over the world. After a relatively long period in oblivion, domestic rainwater harvesting is currently making an impact in many countries (especially in the developing world) as an alternative household water supply option. A number of reasons can be attributed to this resurgence, the more important of which are (1) decrease in the quantity and quality of both ground water and surface water, (2) failure of many piped water schemes due to poor operation and maintenance of infrastructure, (3) improvement in roofing material from thatched to more impervious materials like concrete, tiles, corrugated iron sheets and asbestos, (4) increased availability of low cost rainwater harvesting techniques, (5) shift from more centralized to decentralized management and development of water resources, and (6) increase in competition between different water sections and the global trend towards rural to urban migration.

During the past two decades significant development in rainwater harvesting has taken place both in the developed and developing countries. The growth in uptake of rainwater harvesting in the developing countries has been most significant in Thailand. Sri Lanka, Kenya, India, Ethiopia, Uganda and Brazil (Gould and Nissen-Petersen, 1999). In the arid regions of China, rainwater harvesting is seen as the only solution for providing domestic and productive water (Zhu and Liu, 1998). In all these countries, rainwater harvesting has been developed as a means of increased household water security, mostly for the rural communities. This is quite obvious as rural poor are the most vulnerable in water scarcity situations.

By 2025, it is estimated that about two thirds of the world's population ie. about 5.5 billion people will live in areas facing moderate to high water stress (UNPF, 2002). For fast growing urban areas, water requirements are expected to double from 25.0 billion cubic meters (BCM) in 1990 to 52.0 BCM in 2025. It has also been indicated that industrial water demand would increase from 34 BCM of 1990 to 191 BCM by the year 2025. Agriculture, the largest consumer of water resources in India, will probably require 770 BCM by the year 2025 to support food demand in India. The total estimated demand of 1013 BCM by the year 2025 would be close to the current available annual utilizable water resource (1100 BCM) of India (Vasudevan and Pathak, 2000)

Water is the need of the hour and with failing monsoons year after year, there is a need to solve the crucial problem of water by conserving rainwater. There is no choice but to adopt better water management technique, such as rainwater harvesting to recharge the underground aquifers. The simple technique of rainwater harvesting is to save and store the water running off from a roof and using it for indoor needs. Artificial recharge is a process of augmenting the underground water tables by artificial infiltration of rainwater and surface runoff. In areas where water

supply is problematic or water resources are scarce, rainwater harvesting is a good solution.

Water quality issues when using harvested rainwater is of relevance, since world wide rain is harvested from many surfaces including roof tops and ground surfaces.

The quality of harvested rainwater depends upon many factors such as air quality, system design and maintenance, materials used, rainfall intensity, length of time between rainfall events, social context as well as water handling. Due to rapid economic development and consequent increase in energy consumption, concerns about air pollution have emerged to be an important social and scientific issue in developing countries. Rainwater is the most effective scavenging factor for removing particulate and dissolved organic gaseous pollutants from the atmosphere. The scavenging of the atmospheric pollutants affect the chemical composition and the pH of the rainwater. The context of acidification or neutralization of precipitation, very much depends on the environment through which the raindrops travel. It is reported that the raindrops immediately coming out of the cloud possess relatively low pH, but when they reach the earth's surface, the pH is increased (Khemani et. al. 1987).

Regular networks to observe atmospheric deposition of anthropogenic substances have been established in Europe, North America and parts of Asia in response to a concern about ecological and other effects. During the last decade, a number of studies on the chemical composition of precipitation have been carried out in parts of North India. Precipitation studies to investigate into the atmospheric deposition have not been reported from Kerala. The present study attempts to find the chemical

composition as well as quality of rainwater at various locations-rural-urban, industrial and sub-urban in Ernakulam district in the State of Kerala.

Water quality is also affected by the rainwater catchment system components. A number of studies have investigated into the quality of roof collected rainwater with only a few studies on the quality of harvested rainwater at various system components. A part of this study focuses on their aspect. UNEP and others suggests that 'the type of roofing material should be carefully considered'. Another concern is centered on the cementitious materials used for the construction of storage tanks. This stems from the known presence of most of the naturally occurring trace of toxic metals in the raw materials used in the manufacture of cement. The practical importance of this problem lies in the fact that leaching of hardened cement paste adversely affects the quality of drinking. This study attempts to address the concern over the health risk involved while using harvested rainwater stored in cement tanks.

The contents of various chapters of this thesis are briefly described below:

Chapter 1 introduces the importance of rainwater harvesting, its need and potential in India. The quality issues associated with the use of harvested rainwater from the source to the point of delivery is also outlined briefly.

Chapter 2 critically reviews the earlier efforts in the related fields in the literature. The precipitation studies, quality assessment of rainwater and harvested rainwater in terms of physical, chemical and microbiological aspects is also covered in detail. The scope of the work and objectives are also discussed.

Chapter 3 gives an account of the various materials and methods used in the study. A detailed account of the construction of rainwater storage tank made for the study is also given.

Chapter 4 presents the results of the investigations of the precipitation studies carried out at various locations. A detailed report on the quality of rainwater at these sites is also given.

Chapter 5 deals with the quality of harvested rainwater at various system components. The leaching studies on cement mortar in contact with water is also presented.

Chapter 6 presents the conclusions derived from the detailed investigations carried out.

# REVIEW OF LITERATURE

#### 2.1 Introduction

Where there is water on earth, virtually no matter what the physical conditions, there is life. This colourless, odorless and tasteless liquid is essential for all forms of growth and development—human, animal and plant. Also water is a fundamental basic need for sustaining human economic activities. While water is a renewable resource, its availability in space (at a specific location) and time (at different periods of the year) is limited, by climate, geographical and physical conditions, by affordable technological solutions which permit its exploitation, and by the efficiency with which water is conserved and used.

The limits of sustainable use in each climatic region are determined by local climate, hydrological and hydro-geological conditions. In many parts of the world, the amount of water being consumed has exceeded the annual level of renewal, creating a non-sustainable situation. The International Drinking Water Supply and Sanitation Decade and other international declarations have clearly recognized that access to water is a fundamental right of people. Notwithstanding some impressive records in activities related to the UN Drinking Water and Sanitation Decade (WHO 1990), the provision of water at affordable cost and of acceptable quality is emerging as a major environmental challenge. It is clear that all possible approaches must be tried to mitigate the

immediate problem of drinking water, maximizing the control of the house-holds with regard to their own water security. This chapter deals with a brief description of the present drinking water scenario in India, an introduction to rainwater harvesting, the relevant literature regarding the quality of rainwater, roof harvested rainwater etc. This chapter also throws light into relevant literature on the leaching of the heavy metals in water stored in cement tanks.

# 2.2 Drinking water-Current problem and perspective

The lives of women and children as well as the environment have been seriously threatened by water shortages in the country.

- As a result of excessive extraction of ground water, drinking water is not available during the critical summer months.
- About 5 percent of the rural population does not have access to regular safe drinking water and many more are threatened by less and less access to safe drinking water in the not so distant future. Water shortages in cities and villages have led to large volumes of water being collected and transported over great distance by tankers and pipelines.
- High levels of fluoride, arsenic and iron, lead to major environmental health problems and in the case of iron, people simply do not like to drink the water because of its smell/taste.
- Ingress of sea water into coastal aquifers as a result of over extraction
  of ground water has made water supplies more saline, unsuitable for
  drinking and irrigation.
- Pollution of ground and surface waters from agro-chemicals and from industry poses a major environmental health hazard, with potentially significant costs to the country.

- The World Bank has estimated that the total cost of environmental damage in India amounts to US \$9.7 billion annually, or 4.5 percent of the gross domestic product. Of this, 59 percent results from the health impacts of water pollution.
- It has been recently estimated that by 2017 India will be 'water stressed' per capita availability will decline to 1600 cum. Cities generate 2000 crore litres of sewage but treat only 10% of it. Poor drinking water and sanitation infrastructure will lead to high levels of water related diseases and death. It is estimated that 60% of irrigation water is wasted by seepage through unlined field channels and due to over application.

# 2.3 Overall per capita availability of water resources at present and in future

About 85% of the rural drinking water supply and 33% of the urban water supply is met from groundwater. 50% of the irrigation also comes from groundwater. As per the norms of the National Drinking Water Mission, the present per capita need in rural areas is 40 LPCD for humans and an additional 30 LPCD for cattle. The norms for urban population vary between 130-150 LPCD. However, the consumption in Delhi is 240 LPCD, which is the highest in the country and higher than that for many cities in the Western world.

As per the international norms, if per-capita water availability is less than 1700m<sup>3</sup> per year then the country is categorized as water stressed and if it is less than 1000m<sup>3</sup> per capita per year then the country is classified as water scarce. In India per capita surface water availability in the years 1991 and 2001 were 2309 and 1902m<sup>3</sup> and these are projected to reduce to 1401 and 1191m<sup>3</sup> by the years 2025 and 2050 respectively. Hence, there is a need for proper planning, development and management of the greatest assets of the

country, viz. water and land resources for raising the standards of living of the millions of people, particularly in the rural areas.

Food self-sufficiency is difficult at a runoff level of less than 1700m<sup>3</sup> per person and India will reach this stage by 2025 AD. Per capita availability of water at less than 1700m<sup>3</sup>/annum leads to water stress and when it goes down to 1000m<sup>3</sup>/annum, it gives rise to water scarcity. In certain areas of Tamil Nadu, it has already reached a level of 400m<sup>3</sup>/person (Sharma S.K, 2000). India is at the threshold of a water scarcity situation. Six of the country's major basins are already classified as those with less than 1000m<sup>3</sup> of water available per head per year.

About one-third of the country's area, comprising the states of Rajasthan, Gujarat, Andhra Pradesh, Madhya Pradesh, Maharashtra, Tamil Nadu and Karnataka is drought-prone. The area needing immediate attention for drought proofing is about 12% of the total area (Chaddha and Kapoor, 2000).

India's average annual surface water potential is estimated as 1869 km<sup>3</sup> and out of this only 37% can be harnessed using the currently practiced schemes of minor, medium and major irrigation projects. It is obvious that the projection of India's becoming a water-stressed country by 2025 can be proved wrong only if we are able to utilize a substantial portion of the remaining 63% of surface runoff, which is currently lost as runoff to sea or through evaporation.

# 2.4 Rainwater harvesting

#### 2.4.1 Definition and relevance

Frazier (1983) has defined the term 'water harvesting' as the process of collecting and storing water from an area that has been treated to increase

precipitation runoff. A "water harvesting system" is described as the complete facility for collecting and storing precipitation run-off.

Rainwater harvesting primarily consists of the collection, storage and subsequent use of captured rainwater as either the principal or as a supplementary source of water. Both potable and non-potable applications are possible (Fewkes, 2006). Examples exist of systems that provide water for domestic, commercial, institutional and industrial purposes as well as agriculture, livestock, groundwater recharge, flood control, process water and as an emergency supply for fire fighting (Gound & Nissen-Peterson, 1999; Koning, 2001; Datar, 2006). The concept of RWH is both simple and ancient and systems can vary from small and basic, such as the attachment of water but to a rainwater downspout, to large and complex, such as those that collect water from many hectares and serve large numbers of people (Legett et al., 2001).

## 2.4.1.1 Contemporary relevance of rainwater harvesting

Rainwater harvesting matters more today than any other time. There are several reasons, as Jackson et al. note (1) over half of the accessible fresh water runoff globally is already appropriated for human use, (2) more than  $1x10^9$  people currently lack access to clean drinking water and almost  $3x10^9$  people lack basic sanitation services, (3) because the human population will grow faster than increases in the amount of accessible fresh water, per capita availability of fresh water will decrease in the coming century, (4) climate change will cause a general intensification of the earth's hydrological cycle in the next 100 years, with generally increased precipitation, evapotranspiration, occurrence of storms and significant changes in bio geochemical processes influencing water quality. Humanity now uses 26% of the total terrestrial evapotranspiration and 54% of the runoff that is geographically and temporally accessible. New dam construction could increase accessible runoff

by about 10% over the next 30 years, whereas the population is projected to increase by more than 45% during that period. Under such circumstances, harvesting rain shall be crucial.

#### 2.4.2 Components of rainwater harvesting systems

The fundamental processes involved in rainwater harvesting are demonstrated in Fig.2.1.



**Fig.2.1:** Flowchart demonstrating fundamental rainwater harvesting processes

All rainwater harvesting systems share a number of common components (Gould & Nissen-Peterson, 1999).

- A catchment surface from which runoff is collected, e.g. a roof surface.
- A system for transporting water from the catchment surface to a storage reservoir.
- A reservoir where water is stored until needed.
- A device for extracting water from the reservoir.

# 2.4.3 A brief history of rainwater harvesting

Gould & Nissen-Peterson (1999) provide a detailed history of rainwater harvesting systems. The authors state that, whilst the exact origin of RWH has not been determined, the oldest known examples date back several thousand years and are associated with the early civilizations of the Middle East and Asia. In India, evidence has been found of simple stone-rubble structures for impounding water that date back to the third millennium BC (Agarwal & Narain, 1997). In the Negev desert in Israel, runoff from hillsides has been

collected and stored in cisterns to be used for agricultural and domestic purposes since before 2000 BC. There is evidence in the Mediterranean region of a sophisticated rainwater collection and storage system at the Palace of Knossos which is believed to have been in use as early as 1700 BC (Hasse, 1989). In Sardinia, from the 6<sup>th</sup> century BC onwards, many settlements collected and used roof runoff as their main source of water (Crasta et al., 1982). Many Roman villas and cities are known to have used rainwater as the primary source of drinking water and for domestic purposes (Kovacs, 1979).

There is evidence of the past utilization of harvested rainwater in many areas around the world, including North Africa (Shata, 1982), Turkey (Ozis, 1982; Hasse, 1989), east and southeast Asia (Prempridi & Chatuthasry, 1982), Japan, China (Gould & Nissen-Peterson, 1999), the Indian sub-continent (Kolrkar et al., 1980; Ray, 1983; Pakianathan, 1989), Pakistan and much of the Islamic world (Pacey & Cullis, 1986), sub-Saharan Africa (Parker, 1973), Western Europe (La Hire, 1742; Hare, 1900; Doody, 1980; Leggett et al., 2001a), North and South America (McCallan, 1948; Bailey, 1959; Moysey & Mueller, 1962; Gordillo et al., 1982; Gnadlinger, 1995), Australia (Kenyon, 1929) and the South Pacific (Marjoram, 1987).

During the twentieth century the use of rainwater harvesting techniques declined around the world, partly due to the provision of large, centralized water supply schemes such as dam building projects, groundwater development and piped distribution systems. However, in the last few decades there has been an increasing interest in the use of harvested water (Gould & Nissen-Peterson, 1999) with an estimated 100,000,000 people worldwide currently utilizing a rainwater system of some description (Heggen, 2000).

In the developed world the use of RWH to supply potable water is mostly limited to rural locations, mainly because piping supplies from centralized water treatment facilities to areas with low population densities is often uneconomic. The development of appropriate groundwater resources can likewise be impractical for cost reasons (Fewkes, 2006). Perrens (1982) estimates that in Australia approximately one million people rely on rainwater as their primary source of supply. The total number of Australians in both rural and urban regions that rely on rainwater stored in tanks is believed to be about three million (ABS, 1994). In the USA it is thought that there are over 200,000 rainwater cisterns in existence that provide supplies to small communities and individual households (Lye, 1992). Harvesting rainwater for potable use also occurs in rural areas of Canada and Bermuda (Fewkes, 2006).

## 2.5 Quality of rainwater.

Precipitation is the main process by which trace gases and aerosols are scavenged from the atmosphere in temperate climates. Atmospheric aerosol particles and gases play a major role in the chemistry of rain water by in cloud and below cloud scavenging processes. As a result, the following chemical species are typically found in rainwater: ammonium, sodium, potassium, calcium, magnesium, hydrogen, sulphate, chloride, nitrate, bicarbonate and carbonate ions. Among these chemical species, hydrogen ion concentration (or pH) is very important for acid rain assessment.

Absolutely neutral precipitation would have a pH of 7. However presumed that pure water is in equilibrium with global atmospheric CO<sub>2</sub> and yield the natural acidity to the rain water with pH 5.6. This pH value 5.6 has been taken as the demarcation line for acidic precipitation. Howe ever in the absence of common basic components, such as NH<sub>3</sub> and CaCO<sub>3</sub>, rain water pH would be expected to be about 5 due to natural sulphur compounds (Charlson and Rodhe, 1982).

The pH value as low as around 3 have been found on occasions in rural parts of Europe (W.M.O., 1978). The pH value below 5 were observed in the

Silent Valley forest, India (Praksa Rao et al., 1993). Mukherjee (1975) found that monsoon rain water at Calcutta dissolves little CO<sub>2</sub> and the dissolved gas is not in equilibrium with atmospheric CO<sub>2</sub>. Hence monsoon rainwater is neutral at Calcutta. Mukherjee and Nand (1981) suggested that the neutral pH precipitation would be higher than 5.6 in tropic due to the lower dissolution rate of CO<sub>2</sub> in prevailing high temperature. Apart from the mineral acids resulting from oxidation of SO<sub>2</sub> and NO<sub>3</sub> organic acids are also found to be contributing acidity to the precipitation (Chan et.al., 1987, Ayer, 1989, Durama, 1992).

Possibility of occurrence of acid rain at Visakhapatanam if the emissions were controlled was discussed by Varma (1986). Alkaline pH values were observed for precipitation samples collected over Minicoy and Portblair (Mukherjee, 1986). Chemical analysis of monsoon rain water at Udipur was carried out by Gupta and Kothari (1991). They observed that the rain water had a high content of chloride and sulphate, first spell of rain was rich in nitrate and electrical conductivity of rain water decreased successively from May to August, but thereafter increased.

Potassium originates mainly from rural areas from soils and vegetation (Gatz, 1991). Sodium and chloride and to some extent magnesium are from maritime origin (Mukherjee et al., 1985); Ezcurra et al., 1988, Ahmed et al., 1990 and Yamaguehi et al. 1991). Calcium sulphate is only slightly soluble in water and separates quickly from water to form a stable aerosol. Therefore in the atmosphere, calcium and sulphur derived from sea water will be present largely as CaSO<sub>4</sub> but CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> will remain in solution and will be precipitated (Mukherjee, 1957).

Ravichandran and Padmanabhamurthy (1994) in their study in Delhi found that in two consecutive months during monsoon, the samples were found to acidic. They observed that although cations and anions decreased

considerably, the hydrogen ion concentration increased with increase of precipitation amount during these months due to the wind from industrial areas located in the east/southeast of Delhi.

Main reason for alkaline pH values for rainfall is that the cation neutralize the acidity of rainfall (Khemani et al., 1987, Kukhopadhyay et al., 1992). Verma (1989) in his study based on soil characteristics concluded that rainfall with low pH may be expected in southeast Indian coastal belt. The atmospheric carbon dioxide dissolves and attains equilibrium with rain drops, forming carbonic acid, thus, even in an environment free of all pollutants, the rainwater is still acidic (Mukherjee, 1992).

Statistical methods are quite often being used in water quality studies. The generally used methods are correlation and regression analysis besides the common variability studies. Correlation studies provide a straight relationship between the attributes regression analysis provided the type of relationship. Kumar et al. (1994) and Jain et al. (1999) studied correlations among the water quality parameters of ground water samples from different parts of India and developed linear regression equations to predict ground water quality.

A high SO<sub>4</sub><sup>2-</sup> value is expected to give a low pH value in the rainwater (Patel and Tiwari, 1991). Correlation studies are site specific and the correlation coefficient can vary considerably from location to location. (Bhargava et al. (1978), Brar et al. (1984), Gupta (1981), Handa (1975).

Well waters have been known to have very high nitrate content (Ozha et al., 1993). The nutrients in entrapped water also increase due to seepage of effluents from industry and due to storm water run-off (Gangal and Zutshi, 1990). The level of contamination of entrapped water may be different for a residential area when compared to an industrial area (Gangal and Zutshi, 1990).

The quality of water from different entrapped sources in an urban area is affected sufficiently by the adjoining environment. The trace metal content of the water samples is also shown to have sufficient enrichment (Bhattacharya et al., 1996).

Water quality index may be defined as rating, reflecting the composite influence on the overall quality, of a number of individual quality characteristics of water of individual quality parameters, which is being regarded as one of the most effective way to communicate water quality (Bharati, Krishna and Murthy, 1990).

A number of studies on time trend analysis in precipitation chemistry have been reported from Central and Western Europe. North America and recently from South East Asia. Purbaum et. Al. (1998) have taken a compare pensive account of such studies from USA, Netherland, Denmark, Spain, Canada, and Germany. Most of the studies have reported decrease in SO<sub>4</sub> concentrations along in the increase in pH that could be directly related with the decrease in the emissions of SO<sub>2</sub>. Nilles and Conley (2001) also reported rainfall composition data for a period 1981 – 1998, from about 144 sites of National Atmospheric Deposition Program of USA. About 35% decrease in SO<sub>4</sub> has been reported. No significant trends were observed for NO<sub>3</sub>, NH<sub>4</sub>, and Ca, although, about 64 sites showed decreasing trend for Ca and 30 sites showed increasing trend for NH<sub>4</sub>. Fujita et at (2001) have reported trends in chemical composition of precipitation at six rural stations in western Japan during 1987 – 1996. There was no significant change in the concentrations of non-sea salt fraction of SO<sub>4</sub>, ie, nss SO<sub>4</sub> and no sea salt fraction of Ca, ie, nss Ca, whereas, concentration of NO<sub>3</sub> and NH<sub>4</sub> showed increasing (45%) trends.

The ratio of neutralizing potential (NP) to acidic potential (AP) showed 24% increase Lee et al. (2001) have reported changes in chemical composition

of precipitation at four sites in South Korea during 1993- 1998. Concentration of nss SO<sub>4</sub>, NH<sub>4</sub> and Ca showed decreasing trends at statistically significant level whereas, NO<sub>3</sub> did not show much variation. Overall, pH did not show any significant trends.

Acid precipitation has been a growing problem in China, especially in its southern parts. About 73% of its energy is produced by coal burning, resulting in substantial increase in sulfur emission. Natural alkaline dust naturalizes much of the acidity in north but in south the problem of acidity is more severe. pH values reported are between 4 and 5 with sometimes well below 4 also (2 has etal. 1988 : Q in and Huang, 2001). However, due to some recent policies in fuel changes and other restrictions, growth of sulfur emissions has been decelerated, but the increase in NO<sub>3</sub> emissions is still substantial (streets et.al 2001). According to Hedin et.al. (1994), the lowering of pH in precipitation make take place in Asia in future due to the decrease in alkaline dust owing to mobilization and urbanization.

Satai. et.al. (2004) has presented the data a chemical composition of precipitating of bulk precipitation sample that has been collected during 1984–2002 Pune-a trophical urban location in India. Data form these studies were used to analyse the long term trends in the major chemical constituents of precipitation. Significantly increasing trends were observed for SO<sub>4</sub>, and NO<sub>3</sub> which could be at tributed to the rise in industrial and vehicular activities during this period, also Ca, the chief neutralizing constituent, showed decreasing trend, mainly due to the rapid urbanization that reduced the availability of open land which is the major source for Ca. This has resulted in the overall decrease in trend of pH. However, the average pH value is still in the alkaline range due to the dominance of neutralizing potential of precipitation over the acidic potential.

# 2.6 Quality of roof harvester rainwater

# 2.6.1 Factors affecting roof runoff quality

Quality of any water is determined by the quality of source water, its exposure to contaminants during collection, treatment and storage and when it reaches the consumer (Heijnen 2001). In a roof top rainwater harvesting system, which consists of a collection system (roof), a conveyance system (gutters or pipes) and a storage system (tank or cistern), contamination of water can occur at any of these states. Rainwater is generally considered as non-polluted, or at least not significantly polluted, but may be acidic, contain traces of lead, pesticides, etc., depending on the locality and prevailing winds. Contamination occurs when it falls on the roof, collects dirt, dissolves some heavy metals in the case of metal surfaces, and then flows into storage. Changes may occur during storage also depending on the material used.

There are several factors, which influence the quality of roof runoff. These can be summarized as (Forster 1996).

- Roof material chemical characteristics, roughness, surface coating,
   age, weatherability, etc.
- Physical boundary condition of the roof-size, inclination and exposure,
- Precipitation event intensity, wind, pollutant concentration in the rain;
- Other meteorological factors season, weather characteristics, antecedent dry time;
- Chemical properties of the substance vapour pressure, solubility in water, Henry'c sonstant, etc;
- Concentration of the substance in atmospheric boundary layer emission, transport, half-life, phase distribution, etc;

• Location of the roof – its proximity to pollution sources.

It is well known that most substances show a distinct "first-flush phenomenon" – the concentrations are extremely high in the first minutes of a rain event, and decrease later towards a constant value (Martinson and Thomas 2005). Generally these dynamic effects are observed in the first 2 mm of runoff height. The first-flush effect is caused by one or a combination of the following three processes (Zinder et al. 1998):

- Matter deposited on the roof during the preceding dry period is washed off by the falling rain.
- Weathering and corrosion products of roof cover are washed off.
- Concentrations in the falling rain itself are decreasing with increasing rainfall depth due to scavenging of particles, aerosols and gases by rain droplets.

It is clear that by diverting the first flush the quality of collected rainwater can be improved significantly. However, in many situations, not much care is taken to do this due to a variety of reasons. A properly maintained first-flush device alone would improve the quality of collected rainwater to a great extent.

# 2.6.2 Microbial and physico-chemical quality

Microbial quality of roof-collected rainwater has been the subject of many investigations. Table 2.1 lists some of the recent studies on rainwater harvesting systems reported from different parts of the world.

Table 2.1: Microbiological quality of roof-collected rainwater

S.	Location/ Country	Samples Collected	No. Of samples	Parameters tested	Salient findings	References
			analysed			
<del> </del>	Rural areas of	Water faucet	125	HPC, TC, FC, ENT,	56% samples exceeded microbiological	Simmons et al. (2001)
	Auckland, New			Salmonella, Aeromonas,	criteria for drinking water. Aeromonas	
	Zealand			Cryptosporidium, etc.	found in 16% samples, Salmonella in one	
					sample, Cryptosporidium in two samples	
2	Port Harcourt,	Roof catchments	:	HPC, Pseudomonas,	High HPC. Pseudomonas present in all	Uba & Aghogho
	Nigeria			Salmonella, Shigella, Vibrio	except Zn roof. High number of pathogenic	(2000)
					bacteria like Salmonella present	
<sub>ب</sub>	Rural areas of South	Rainwater tanks	100	HPC, TTC, FS, TC, E. coli	59% samples contaminated with TTC.	Plazinska (2001)
	Australia				84% contaminated with FS. High HPC	
4.	Palestine	Roof catchments and water		TC, FC	All samples contaminated with TC and FC.	Ghanayem (2001)
		tanks			Less bacterial contamination from metal	
					roofs	
5.	Thailand	Roof catchments and point	602	FC, FS	76% samples exceeded the WHO	Appan (1997)
		of consumption			standards	
6.	New Delhi, India	Roof runoff	54	FC, TC, HPC, FS	All indicator bacteria were present. Rough	Vasudevan et al.
					surfaces carried more contaminants. 13%	(2001)
					met WHO standards for all the indicator	
					bacteria and 25-30% met the relaxed	
					standards	
7.	US Virgin Island	Rainwater systems	13	Giardia, Cryptosporidium	45% samples positive for Giardia. 23%	Crabtree et al. (1996)
					positive for Cryptosporidium	
ю	Kerala, India	Rainwater tanks	30	FC	93% samples contaminated with FC.	Pushpangadan &
					FL > 500 MPW/100 mL in 13%	Sivanandan (2001)

HPC - heterotropic plate count, TC - total coliforms, FC - faccal coliforms, TTC - thermotolerant coliforms, FS - faccal streptococci,

ENT - enterococci.

Water samples for these analyses were collected either directly from roof or from storage systems. Direct comparison between these studies is difficult because of variation in design, sampling and analytical procedures. However, these studies along with numerous other studies reported in the literature (Yaziz et al. 1989; Pinfold et al. 1993; Thomas and Greene 1993; Ariyananda and Mawatha 1999; Pushpangadan and Sivanandan 2001; Pushpangadan et al. 2001; Handia 2005) clearly show that rainwater harvesting systems do not often meet the microbiological drinking-water quality standards. Various sources have been attributed to the frequent presence of faecal contamination but, mostly, pollution is of animal origin as the faecal coliform/faecal streptococci ratio is less than unity (Appan 1997).

Microbiological quality of collected rainwater depends on several factors. These include the quality of roof materials and contamination of roofs. The bacteriological quality of rainwater from metallic roofs is generally better than that from other types of roof (Yazis et al. 1989; Vasudevan et al. 2001; Ghanayem 2001). The dry heat typical of a metal roof under bright sunlight especially in tropical countries will effectively kill many of the organisms. The characteristics of a rainfall event also influence the microbial quality. Yazis et al. (1989) reported that contamination of rainwater increased with longer dry periods between rainfall events as a result of increased levels of deposition on roofs. They also found that rainfall intensity affected the quality of runoff.

There have been studies on the influence of storage time on the microbiological quality of rainwater. While some studies showed bacterial population declined with storage, some other investigators found that the numbers of bacteria increased with storage. A study by Lye (1989) revealed that certain bacterial strains of Pseudomonas and Aeromonas were able to grow from low initial levels (1 CFU/ml) to higher concentrations (100

CFU/ml) during storage of collected rainwater. Additional studies by Lye (1991) showed that long term storage of rainwater did not cause a decrease in levels of certain bacterial strains. However, Vasudevan et al. (2001) reported that faecal coliforms, total coliforms and faecal streptococci decline rapidly in rainwater storage tanks. These reported differences are presumably linked to the availability of nutrients and suitability of environmental conditions for growth in rainwater storage tanks. Plazinska (2001), based on a survey of over 100 rainwater tanks used by indigenous communities in rural Australia, reported that the most prominent factor influencing the microbiological quality was the tank capacity, with smaller tanks showing higher levels of bacterial contamination. None of the tanks had any mechanical deices for protecting the water quality, and thus for the same catchment area, tanks of lower capacity received a relatively greater share of contaminating microorganisms Further, in smaller tanks, there was a higher probability that sludge accumulated at the bottom of the tank might become agitated and mixed with standing water. This study thus indicated that installation of some first-flush devices alone would result in considerable improvement in microbiological water quality.

Traditional indicators such as total coliforms and faecal coliforms are generally used for assessing the microbial quality of rainwater. In addition to these organisms, some studies determined the presence of specific pathogenic and opportunistic organisms in harvested rainwater. Table 2.1 shows that bacterial pathogens such as *Salmonella spp.*, *Vibrio spp.*, *Aeromons sp.* and *Legionella spp.* and protozoan pathogens such as *Giardia spp.* and *Cryptosporidium* are frequently detected in roof-collected rainwater. Concern has been expressed on the suitability of traditional indicators for assessing the possible health risks associated with the consumption of collected rainwater which may be contaminated with a variety of opportunistic and pathogenic

microorganisms (Lye 2002). A recent study reported from rural areas of New Zealand showed a positive association between the presence of *Aeromonas* and the various indicator organisms in roof-collected rainwater (Simmons et al. 2001). Households reporting at least one member with gastrointestinal symptoms in the month prior to sampling were more likely to have *Aeromonas* spp. Identified in their water supply than those households without symptoms. Further research is required on the suitability of the *Aeromonas* group as an indicator of microbial quality and health risk with respect to roof-collected rainwater supplies. Studies are also needed to monitor the level of viruses in rainwater.

While microbial quality of rainwater is often suspect, it should be emphasized that collected rainwater still represents the best option in many situations in terms of microbiological quality. A study conducted in Thailand (Pinfold et al. 1993) showed that traditional rain water was superior in terms of microbiological quality. Other surveys by Ariyananda and Mawatha (1999), Pushpangadan et al. (2001) and Handia (2005) in Sri Lanka, India and Zambia, respectively, also revealed that microbial quality of stored rainwater is often better than that of other sources of drinking water such as shallow groundwater. Suitable interventions can still improve the quality of harvested rainwater in many situations.

Many studies have been reported in the literature on the physicochemical characteristics of roof-collected rainwater, and these studies from different parts of the world reveal that, in general, physico-chemical quality meets the drinking-water quality guidelines with the notable exception being pH (Ghanayem 2001; Pushpangadan et al. 2001; Simmons et al. 2001; Chang et al. 2004). Wide variations, however, are seen in the concentrations of major ions like calcium, magnesium, sodium, potassium, chlorides, sulphates and nitrates. Variation reflects differences in roofing material and its treatment,

orientation and slope of roof, air quality of region, characteristics of precipitation, etc. (Forster 1996; Wu et al. 2001; Chang et al. 2004).

pH of rainwater usually ranges from 4.5-6.5 but increases slightly after falling on the roof and during storage in tanks. Water sampled from ferrocement tanks, which is the most commonly used material for storing collected rainwater in developing countries, was significantly more likely to be alkaline (Simmons et al. 2001; Pushpangadan and Sivanandan 2001; Handia 2005), pH value declines with age of tank and period of storage. Chemical analyses by Forster (1996) revealed pH differences between various roofing materials (Concrete, fibrous cement, pantile, zinc and tarfelt). A shift towards alkaline values for fibrous cement was attributed to dissolution of roof material and not to the deposited aerosols. The above finding was contradicted by studies by Gromaire et al. (2001) and Moilleron et al. (2002). They found dissolution of roof covering material negligible. Studies by Vasudevan et al. (2001) reported no significant differences in chemical quality with roof material and design of roof, gutter and storage types. Uba and Aghogho (2000) and Polkowska et al. (2002) found pH of roof runoff within acceptable limits. Runoff from a wood shingle roof had a pH lower than that of rainwater (Chang et al. 2004). Roughness and cracks of wood shingle, trap water which allow wood rotting organisms to penetrate deeper into wood, plants to grow and organic matter to decay, and as a consequence additional H<sup>+</sup> ions are released due to weathering and decomposition of organic matter. This makes the care and maintenance of wood shingle very important with respect to quality of roof runoff.

Zobrist et al. (2000) detected cat ions like sodium, potassium and calcium, and anions like chlorides, sulphates and nitrates in all samples, and among the cat ions, sodium and calcium had the highest concentration. The greatest increase of macro ion concentration during passage over roof surface

was found for potassium and sodium (Forster 1998). The differences within roofs clearly indicated that the ions originated from roof material; fibrous cement having greater calcium, and concrete tiles having greater potassium and calcium were susceptible to weathering, whereas dry deposition was of minor importance. But roof contribution of acidic ions like sulphates and nitrates was different, and they were transported by deposition. Study by Zobrist et al. (2000) found that a tile roof acted as a slight source of suspended particles and alkalinity, and weathering of a gravel roof produced calcium and alkalinity. The high particle load found in a zinc roof was attributed to its strong weathering in combination with smooth surface that has low resistance to particle wash off (Forster 1996).

Another study was conducted by Forster (1998) to investigate the influence of location as well as to uncover seasonal behaviour of pollutants in runoff. Differences in concentrations of ions like NH4<sup>+</sup> and Cl deposited via atmosphere could be observed with change of season, and roofs receiving local emission showed elevated concentration of suspended particles. Influence of antecedent dry time, precipitation intensity and roughness of material in the concentration profile of suspended solids and inorganic ions was also studied by Forster (1999). Typical run-off profile started with a high pollutant load and showed a decreasing trend while a modification was found when rain intensities were low and surfaces rough. Suspended solid concentration for tar felt showed an increase within the course of an event. Gromaire et al. (1998) also found a good linear relationship between suspended solid concentration from roof runoff and the following rain event characteristics, viz. dry weather duration, intensity and duration of rain.

J.E. Gould (1984) has discussed bacteriological analysis (total coliform, faecal coliform and faecal streptococci) from roof tank water. Accepted water quality standards of Botswana is also tabulated. Generally high quality of

properly stored rainwater is seen. Periodic chlorination is the most economic solution as suggested by the author. However the factors which will determine whether a water source is used or not are more likely to be related to taste, colour and odour, rather than necessarily directly to quality as stated in the paper.

Gould and McPherson (1987) have described bacteriological analysis of water samples from thirteen roof tanks and eight ground catchment tanks in Botswana. The results show that rainwater collected from corrugated iron roofs and stored in covered tanks is of high quality compared with traditional water sources. Water from roof catchment systems in Botswana presents a serious health hazard.

Mayo and Mashauri (1991) have given the bacteriological (total and faecal coliform and faecal streptococci), chemical (pH and total hardness) and physical (turbidity and colour) analyses of water samples from rainwater cistern system at the University of Dar es Salaam in Tanzania between October, 1988 and December, 1989. The results showed that 86% of samples were free from faecal coliform. However, faecal streptococci were obtained in 53% of the samples and 45% of the samples tested for total coliforms were positive. About 54% of the consumers raised objections over the taste of water. The pH range was found out to be 9.3 - 11.7 which is above standard limits.

Otieno (1994), Kenya has established from a study that except or the initial rainfall, the quality of rainwater is quite high, comparing favorably with river waters He has tabulated comparison of rainwater from roof catchment with river water and WHO standards.

Bambrah and Haq (1997) have discussed the suitability of using untreated rainwater for human consumption in Kenya. They have reviewed

existing literature on rainwater quality in their country. Guidelines for drinking water quality and various physical and chemical treatments have been described for disinfecting the stored water.

Feasibility of using roof rainwater catchment systems in West Bank Palestine as supplementary water source have been investigated by Sharekh (1995). From the Physico-chemical and bacteriological test results tabulated it was found that, rainwater stored in cisterns can be used for drinking and domestic purposes. Level of total coliform contamination were found 27%>0 coliform. Concentration of major constituents were well within the prescribed limits.

Water shortage in various regions in Japan is taken care by utilizing rainwater as an alternative as reported by Kitamura et al. (1997). Although rainwater quality is acceptable, variations take place during storage. No bacteriological studies were reported. Stored rainwater pH were almost constant except for the last 3 weeks duration. Turbidity varied during first two weeks.

Ammonia nitrogen varied decreasing storage, which was probably caused by the bacterial activities. Bird droppings and insect carcasses were stored together with collected rainwater. It was a sanitary problem.

Physico-chemical quality along with bacteriological quality has been tabulated for three selected sites in Sri Lanka by Heijen and Mansur (1998). Colour/turbidity are a bit higher than expected. Dirt on the roof and the non-application of a first flush device or a simple filter were the likely causes. E-coli count was consistent low, though 21% of samples shown 100 colonies/100 ml of total coliform.

National Water Supply and Drainage Board, Sri Lanka (1998) has tabulated all chemical and bacteriological analysis (total coliform, E.coli and

faecal streptococci) report. No chemical pollution has been found, bacterial contamination was there and the board recommended boiling of stored rainwater before consumption.

P.K.Sivanandan (1999) has reported chemical analysis of water sample from open wells in Adimalathura area, Kerala. Samples from all around villages were collected and chemical testing was done. Parameters studied were pH, EC, DO, chloride, total hardness, Ca hardness, Mg, total alkalinity, bicarbonates and carbonates. Results indicated that chemical quality of water had potable status.

Mitraniketan (1999) Kerala in a project report tabulated rainwater analysis. Chemical parameters included pH, alkalinity, chloride, iron, nitrate, nitrates, sulphate, total solids and hardness. Bacterial examination was also done and the results revealed that the stored water had potable status

# 2.7 Leaching of heavy metals and quality of water in rainwater storage tank

There is a growing interest in the environmental impacts of cement-based materials, especially for the materials in which industrial by-products are contained. Organic components in cement and in concrete admixtures, such as fly ash, slag and silica fume, are at a very low level because they have been burned away during their formation processes. The main aspect in respect of the environmental impacts of cement-based materials, therefore, is the leaching of inorganic compounds when they are contact with environmental waters, eg. rain or ground water. Studies show that both cement and fly ash contain trace amounts of heavy metals and other toxic inorganic components.

Concerns have been aired over the type of materials coming into contact with water for human consumption. These concerns surround the potential of materials to leach inorganic constituents, with possible resulting contamination of drinking water. One of these materials presently causing great concern is

"concrete", which accounts for the largest bulk of man-made material coming into contact with water. The concern is centered on the cementitious materials used in the production of concrete. This stems from the known presence of most of the naturally occurring trace toxic metals in the raw materials used in the manufacture of cement. This is especially true for coal, which contains toxic metals in widely varying concentrations, depending on the rank and geological origin of the coal This concern over cementitious materials is further fuelled by results from a past leaching investigation involving its unhydrated form by the CA Kiln Dust Task Force (1992). This investigation conducted a Toxicity Characteristic Leaching Procedure (TCLP) with acetic acid on cement samples from 97 cement plants in North America. The results showed As, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Th leached in detectable concentrations.

This recent concern over cementitious materials in concrete has seen three research teams, Kanare and West (1993), Rankers and Hohberg (1991) and Germaneau et al. (1993), conducting leaching investigations on hydrated cementitious materials during the 1990s. Kanare and West investigated the leaching of harmful trace metals from eight portland cement concretes, made from four cements and two aggregates, using the TCLP with two different The first test used the traditional TCLP leachant of acetic acid, leachants. whereas the second test replaced this leachant with de-ionised water. Results for the acetic acid test showed that Cr, Hg, Ni, and Pb were leached, whereas results for the de-ionised water test showed partial leaching of Cr, Hg, and Ni. Rankers and Hohberg undertook various leaching tests on cement mortars. The tests used included two agitated extraction tests (similar to the TCLP), a flow around dynamic test (called a column test), and a serial batch test (called a tank test). The first agitated extraction test used was from a German standard (DIN 38414-S4). This test involved placing a crushed sample into agitated de-ionised water for 24hr, similar to the TCLP. Their second agitated test determined the

maximum leachability of the crushed samples, by subjecting a very small sample to agitated nitric acid, maintained at pH 4, for 5 hr. The third test involved placing the crushed samples into a polyethylene column and then percolating mineralized water adjusted to pH 4 using nitric acid. The fourth test involved uncrushed cubes in a tank-leaching test and was carried out over a substantial period of time in dilute nitric acid, which was renewed at increasing periods. Results showed that Cd, Cr, and Pb leaching occurred with the second agitated test, but leaching with the first test gave metal solutions too dilute for their concentrations to be established. No results were given for the last two tests, but the paper inferred leaching did take place. Germaneau et al. carried out a 5-day serial batch test with de-ionised and natural mineral water to investigate the preconditioning of water supply mains. Their work showed traces of Cr, Ni, and Pb were leached from iso-rilem mortar prisms containing a range of commercial binders. The results from these three research teams detected the presence of some trace toxic metals in the leachates taken.

Most extensive study on quality aspects of water stored in domestic rainwater tanks has been given by Fuller et al. (1981). Water samples from three different areas (Vineyard and Orchard areas: 7 cities), industrial areas: 4 cities, and residential areas: 2 cities) were colleted which reflected conditions in water stored in domestic rain water tanks through South Australia. Galvanised iron tanks within the range of 10,000 to 25,000 liter with closed tops were selected. Tanks which had catchments of unpainted galvanized iron were chosen. Also householders were asked to answer a series of question regarding use and maintenance of their tanks. Microbiological parameters, heavy metals (Pb, Zinc, Cd), pesticides and other physico-chemical tests were conducted. The results of the study are summarized

Coliform bacteria: coliform bacteria were present in 12 of 41 tanks,
 up to 500 coliforms/100 ml were recorded.

- E.coli: E.coli was detected in 6 tanks 15% of 41 tanks levels up to 200 E.coli/100 ml were recorded.
- Plate counts gave an indication of the general level of microbiological contamination of water. Plate counts in most rainwater tanks were in excess of 1000/ml.
- Heavy metals:

Concentrations of lead in rainwater from tanks in Port Pirie were significantly higher (0.061 and 0.072 mg/l) than other sites. This could be a result of dust from surroundings country sides washed from roof tops with each rainfall.

Zinc concentrations were found to be excess of 15 mg/l.

- i) Pesticides were not detected in the majority of samples.
- ii) Concentrations of Suspended solids were negligible in all samples.
- iii) The range of pH values were 6.1 to 9.2 low. pH values can accelerate corrosion problems in domestic appliances while high pH is an indication of undesirable biological activity in the tank.
- iv) Only samples taken from 2 rainwater tanks had T.D.S. concentrations in excess of 100 mg/ml (caused by sea spray).

Hillier etal (1999) investigated the long leaching of toxic trace metals from various Portland cement mortars in an a famous environment. Test samples were subjected to a leaching procedure based on criteria detailed by the Netherlands "diffusion" method. The leachates generated were analysed for various toxic metals using atomic absorption spectroscopy. The analytical results revelated only vanadium leached in detectable fualities from poorly cured concrete, and its removal was restricted from the surface only.

Xijing et al. (1995) from China have analysed and assessed water quality of the catchment and storage rainwater physico-chemical testing result have been discussed. pH, Cu, Pb, Se, Zn, K, nitrites, total alkalinity have higher values in the rainwater contained in concrete water cellars with cement or grey tile catchment surfaces. The indices of As, Fe, Ca2+, Mg2+, total hardness have higher values in the rainwater contained in soil water cellars. Total coliform become fewer in rainwater contained in concrete cellars with tile surfaces. The author emphasized that the problem could be solved through changing the building materials of catchment surfaces and water cellars, improving hygienic conditions and taking some effective disinfectant measures.

Kita and Kitamura (1995) from Japan have described fluctuation in the quality of rainwater stored in container during storage. The results are:

- pH and COD remains constant
- NH<sub>4</sub> first increases then decreases and finally remains zero
- Color and turbidity remain constant
- Results of coliform group of bacteria were positive throughout the periods.

Adam Neville (2001) has studied the effect of cement paste on drinking water. When water conducts are made of concrete or are lined with cement motor, the cement paste can be leached by water. This occurs to a significant degree if the water remains in prolonged contact with the cement paste. The consequences of leaching are an increase in pH and in the content of CaCO<sub>3</sub>. He concluded that the actual levels of various chemical species in different of these species need to be established so that a safe use of cement in conducts can be assured.

Qijeen Yu etal (2005) conducted studies on the effects of mix proportion, leachant pH, curing age, carbonation and specimen making method etc. On the leaching of heavy metals and Cr (VI) in flyash cement mortars and cement – solidified fly ashes. The results mainly indicated that the leachability of some heavy metals is greatly dependant on leachant pH, the amount of heavy metals leached from cement – solidified fly ashes depends more on the kind of fly ash than their contents in fly ash.

#### 2.8 Scope of work

A critical review of the literature reveals that, during the last decade, a number of studies on the chemical composition of precipitation, have been carried out in North India. These studies have revealed that the nature of rainwater in India is generally alkaline due to the contribution of soil derived particles in the atmosphere. Precipitation studies to investigate in to the atmospheric deposition have not been reported from Kerala. In the context of the relevance of rainwater harvesting, as a solution to the impending water crisis, the quality of rainwater is of prime importance, especially if it is to be used as potable water. The study of the quality of rainwater is important as rainwater is an effective scavenging factor for removing the atmospheric deposition, which varies from location to location. Water quality is also affected by the rainwater catchment system components. This study also focuses on the quality of rainwater at various land use locations and its interactions with various rainwater catchments system components. In addition to traditional methods, ferrocement tanks are widely used in Kerala for the storage of rainwater. Concerned with the safety of the stored rainwater, number of questions arises from the society. Whether the rainwater stored in the cent tank is safe up to the next summer? Whether this storage creates any health problem to the users? This study also attempts to find an answer to the above concerns.

## 2.9 Objectives

- 1 To investigate the atmospheric deposition of pollutants through precipitation studies at various places in Kochi.
- 2 To assess the chemical composition and the quality of rainwater in the study area.
- 3 To assess the quality of harvested rainwater at various stage of harvesting and storage and compare it with the recommended drinking water standard.
- 4 To study the leaching of cement constituents during storage of rainwater.
- 5 To evaluate health risk associated with rain water stored in Portland Pozzolana Cement and Ordinary Portland Cement tanks.

# MATERIALS AND METHODS

#### 3.1 Introduction

A critical review of the available literature points to the need for study of the quality of rainwater and harvested rainwater and harvesting systems at individual locations in order to ascertain the health risks, if any involved. The sampling and analytical methods adopted for the purpose described in this chapter.

# 3.2 Site description

The sites were classified with regard to how they may be influenced by their surroundings. The classification is based on reported information, and supplemented with our own knowledge of the locations. The sampling stations with in the city limits in cities are termed urban and the stations located in the outskirts of a city, as suburban. These stations are thought to be affected both by local emissions, including the extra dust, which is stirred up in this environment and those emissions constituting the regional levels. Sites without any important anthropogenic emissions in the neighbourhood (within about 10km) are denoted as rural and are considered to be representative of the surrounding countryside although spatial gradients undoubtedly occur. Emission of dust from soil is apparently variable both in time and space, especially in arid and agricultural environments. A rural location therefore does not prelude strong local

#### 3.2.2 Ernakulam

The site selected is Kacheripady, located at the heart of the city, which represents a typical urban area. The site is located about 100 m from the nearest busy road (traffic density 1000 to 1500 vehicles per day) which is further connected to a very busy state highway at around, 5km away from the sampling site. The traffic density on this highway is around 80000 to  $1.5 \times 10^5$  vehicles per day. There is no industrial activity in the surrounding area.

#### **3.2.3** Eloor

Eloor is an industrial area. The sampling site is located about 18 km away from Kochi city. The site is situated around 200m away from the nearest road (traffic density 50000 to 90000 vehicle/day). A busy high way (traffic density10<sup>5</sup> to 1.6 x 10<sup>5</sup> vehicles/day) passes through a distance of 6km from the sampling site. The industries located in this area include fertilizer, pesticide, chemical and aluminum.

## 3.2.4 Kalamassery

Kalamassery is a residential cum commercial area. The sampling site is located in the Cochin University campus, about 12 km away from the city and 2.5 km away from a highway (traffic density  $10^5$  to  $1.6 \times 10^5$  vehicle/day). The site located in the outskirts of the city represents a typical suburban site.

## 3.3 Sample collection

#### 3.3.1 Rainwater

The state of Kerala is blessed with an average annual rainfall of 3000 mm, the bulk of which (70%) is received during the South West monsoon which sets in by last week of May and extends up to September.

It also gets rains from the North East monsoons during October to December. Even though the State receives intermittent summer showers, the state experiences severe summer especially from middle of February to May.

Rainwater samples were collected during the southwest monsoon of May 2007 to the northeast monsoon of October 2008. A total of 377 samples were collected from the different sampling sites under consideration. Rainwater samples were collected in polyethylene bottles previously rinsed with double distilled water, kept on the terraces of the buildings at a height of 1.5m above the roof surfaces. These collectors were mounted just before rain and removed immediately after the rain event is over. Meteorological parameters like amount of precipitation and temperature were also noted for each location.

#### 3.3.2 Harvested rainwater

In order to study the quality of harvested rainwater at various stages, rainwater falling on the concrete roof of the laboratory block of School of Engineering (Cochin University) was taken. A ferrocement tank of capacity 20,000 litres was constructed in the campus. The details regarding sizing of the tank is given in Chapter 5. Harvested rainwater stored in tanks were also collected from the locations mentioned in Sec.3.2. The harvested rainwater samples were collected in polyethylene containers previously rinsed with double distilled water.

## 3.3.2.1 Construction details of ferrocement tank in the campus

Ferrocement is the technology of choice for many rainwater harvesting programmes, the tanks are relatively inexpensive and, with little maintenance, last indefinitely. Ferrocement construction, has several advantages over conventional reinforced concrete, principally because the

reinforcement is well distributed throughout the material and has a high surface area to volume ratio. In particular cracks are arrested quickly and are usually very thin resulting in a reliable water tight structure.

- It has high tensile strength
- Within reasonable limits, the material behaves like a homogeneous, elastic material
- No shuttering or moulds or vibrator is needed.

A circular area 4m in diameter is cleared near the laboratory block in the School of Engineering campus for the construction of the rainwater harvesting tank. Excavation is done along the circumference to a depth of about 60cm. A layer of sand 10cm in thickness is spread evenly over the excavation. Solid blocks are laid to a depth of 50cm below G.L. and 40cm above ground level. Weld mesh(2" x 2), 12 gauge are laid in a circular shape, for the tank height at the site near to the excavated area. L-shaped 6mm diameter steel rods are fastened with steel wire at 45cm c/c spacing along the periphery of the weld mesh. A dome with reinforcement details, as shown in figure 3.2 is constructed to cover the tank. The arrangement of reinforcement, of the dome is carried out on level ground at the site. It is then placed and secured properly with the tank reinforcement. The whole assembly is then placed inside the solid block.

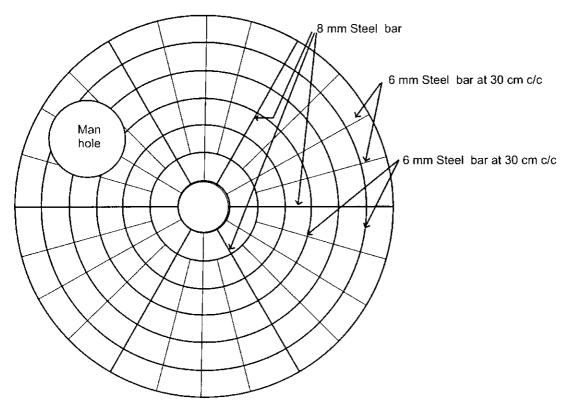


Fig: 3.2 Reinforcement details of the dome

Cement concrete (1:2:4) is laid over the floor reinforced with steel rods of diameter 6mm at 10cm c/c spacing in both direction. Chicken mesh is tied to the weld mesh, both from inside and outside. Plastering is done on the outside and inside in two layers with cement mortar 1:3 and 1:2.5 respectively. The surface area finished smooth with a wooden float. Water proofing compound is added to the cement mortar for the inside surface. A 5cm thick layer of cement mortar 1:2.5 is laid on the floor with slope towards the centre in order to facilitate cleaning of the tank. In order to seal any minor holes, the inside of the tank is coated with a cement slurry of thick consistency. Provision is made for the overflow and outlet from the tank. In the dome provision is made for the filter and man hole. The various stages of construction of the storage tank and the cross sectional elevation are shown in Fig: 3.3 and Fig 3.4 respectively. The estimation of the tank is given in appendix I.



(a)





(c)



(d)



(e)



(f)



(g)



(h)



(i)



(j)

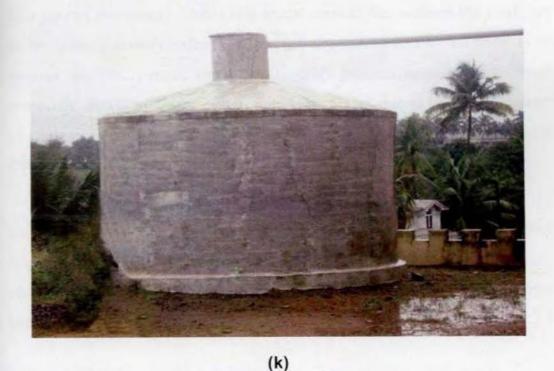


Fig: 3.3 Various stages in the construction of rainwater storage tank

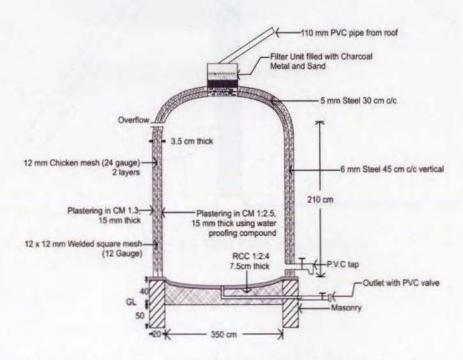


Fig: 3.4 Cross sectional elevation of the storage Tank

Contaminants washed from a roof are usually concentrated in the first part of the runoff. After this initial run-off has washed the roof, the water is considerably safer, so a useful alternative to fine filtering is to remove the first part of the rainfall. This process is called first flush diversion. RWH system deal with the 'first flush' due to the high chances of contamination it would cause. The arrangement adopted in the present RWH system is as shown in Fig.3.5

Filtering before the storage cistern is necessary. The choice of the filtering system depends on construction conditions. Low maintenance filters with a good filter output and high water flow re preferred. The sand charcoal-stone filter which is often used for filtering rainwater entering a tank is the one adopted here. The details of the filter is depicted in Fig.3.6

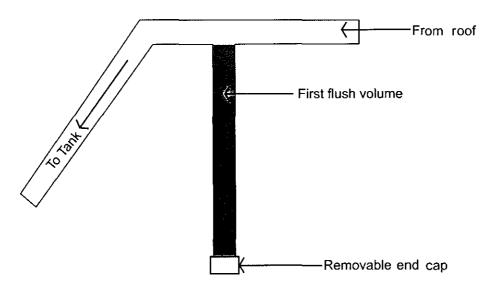


Fig: 3.5 First flush arrangement

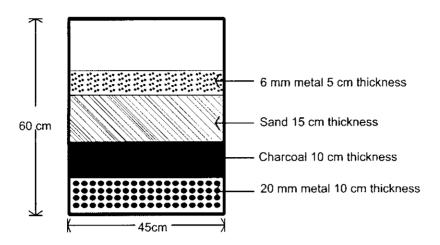


Fig: 3.6 Filtering unit

#### 3.3.2.2 Details of the tanks from other locations

Water samples were collected from the rain water storage tanks at the locations selected. Details of the tanks are shown in Table 3.1. Samples were collected during January 2008, after the northeast monsoon season.

Volume of Roof Material of the Type of SI.No. Location material rainwater tank tank (1 ) treatment 1. Govt.L.P.Shool Sand filter Concrete Ferrocement 10,000 Kothamangalam Town Hall 2. Sand filter ACC Ferrocement 50,000 Ernakulam 3. Ayurveda Dispensary Eloor Panchayath Concrete Ferrocment 20,000 Sand filter Eloor 4. C-SiS 10,000 NIL Concrete Brick CUSAT

Table 3.1: Details of the roof water harvesting systems of the study

# 3.3.3 Well water and tap water

Traditionally, the people of Kerala depend upon well water (over 4.5 million open cut wells). Due to increase in population and change in land use

and water use pattern, community water supplies are also widely depended upon to meet the water requirements. Since well water and tap water are used by majority of the people in the state, it was also decided to compare the quality of these water with that of harvested rainwater. Samples were collected from individual wells and community water supplies in pre-cleaned polyethylene containers, from the locations selected for the study.

#### 3.4 Sample storage

All the collected samples mentioned in section 3.3 were filtered through Whatman 41 filter papers and refrigerated at 4°C in laboratory till the analysis was carried out. Great care was taken to ensure the integrity of the samples. For heavy metal analysis, the samples were acidified using concentrated nitric acid.

## 3.5 Studies on leaching of cement with stored water

#### 3.5.1 Materials used

In order to conduct the leaching studies cement mortar cubes were prepared using cement and sand in the proportion 1:3. Ordinary Portland cement 53 Grade of Zuari Cements make and Portland Pozzolano cement of Coromondel Cements make used for the study were procured from the local market. River sand used for making cement mortar cubes were obtained from the banks of Periyar river, Kerala. Plastic tanks of capacity 500litres, procured from the local market was used to store rainwater samples collected at Kalamassery, the suburban sampling site.

## 3.5.2 Preparation of test specimens

Cement mortar cubes (of cross sectional area 50 cm<sup>2</sup>) were prepared with cement (both PPC and OPC) and sand in the proportion 1:3 and water cement ratio 0.5. Mixing was done using a mechanical mixer until a uniform

mix was obtained. This mix was placed in already oiled moulds and compacted using vibrator at 1200 rpm for 2 minutes. The cement mortar cubes were de moulded after 24 hours and cured for 28 days by immersing in clean fresh water.

### 3.5.3 Test procedure

Twenty one numbers of cement mortar cubes made up of PPC and OPC as explained above were kept in two plastic tanks of capacity 500 litres. The cubes were arranged in such a way that there is constant contact with water on all the sides of the cubes when the tank is filled with rainwater. The arrangement of the cubes shown in Fig.3.7 is believed to simulate the condition of storage of rainwater in cement tanks. The same procedure was repeated with 21 numbers of PPC and OPC cement mortar cubes in two more tanks for the sake of replication. All these tanks were filled with rainwater and kept in closed condition for restricting the algal growth. One tank of 500 litre capacity was filled with rainwater alone, to serve as the control. For periodic analysis, water was taken from each tank into bottles, after stirring with a plastic rod without causing disturbance to the arrangement of cubes. The temperature of the water was also recorded.

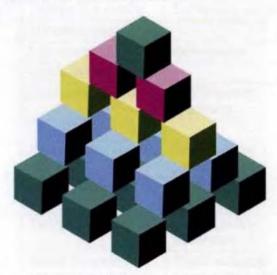


Fig: 3.7 Arrangement of cement mortar cubes

## 3.6 Chemical analysis.

The analytical determination of the different physico-chemical parameters was carried out within the holding time of each parameter according to Standard methods (APHA, 1998). Methods used for the analysis along with the instrument used and manufacturer are given in Table 3.2. Samples were analysed in the Environmental Engineering Laboratory of School of Engineering, CUSAT.

The analysis of water samples for heavy metals concentration using spectroscopic methods were done at the Sophisticated Test Instrumentation centre (STIC) CUSAT. The constituents of PPC and OPC were also analysed. The method adopted for the analysis of heavy metal concentration in cement sample is outlined as follows. 0.25 gram of cement samples were taken in a TFM vessel and digested with 15ml hydrochloric acid (HCl) 2ml nitric acid (HNO<sub>3</sub>) and 1 ml hydrochloric acid in a microwave digester. The digested solution was made up to 250ml using HPLC grade water. The filtered sample solution was analysed with ICP-AES system used certified standards.

**Table 3.2** Details of chemical analysis

SI. No	Parameter	Method	Instrument Name	Manufacturer
1	pН	Electrometric method	pH meter	Systronics
2	Conductivity	Electrometric method	Conductivity meter	Electronics India Ltd
3	Alkalinity	Tritrimetric method		
4	Turbidity	Light scattering	Nephelometer	Elico
5	Chloride	Mohr's method		
6	Nitrate	Diazotization method	UV-VIS spectro photometer	Systronics
5	Hardness	EDTA method		
6	Iron	Phenanthroline method	UV-VIS spectro photometer	Systronics
7	Sodium, potassium	Flame ionization	Flame photometer	Systronics
8	Sulphate	Turbimetric method	UV-VIS spectro- photometer	Systronics
9	Heavy metals	Atomic absorption spectroscopic methods	Atomic absorption spectrophotometer	Thermo electron corporation

#### 3.7 Microbiological analysis

All samples were tested for bacterial indicator, viz total coliforms. The concentration of total coliforms was estimated by a multiple tube fermentation method (most probable number method) by employing Lauryl tryptose broth (Hi Media Laboratories, Mumbai). The inoculated samples were incubated at 37°C for 48h. The result is expressed as most probable number per 100ml (MPN/100ml). The test was conducted in accordance with the techniques described by American Public Health Association (APHA 1998).

## 3.8 Statistical Analysis

#### 3.8.1 Univariate Data Analysis

Prior to focusing the data analysis in a multivariate way, univariate descriptive statistics (mean and standard deviation) for the measured variables were studied for each sampling point. Pearson's correlation coefficient was estimated to assess the degree of association between different parameters in rainwater at each location and between the various sites.

## 3.8.2 Multivariate data analysis

A starting data matrix with rows representing the different precipitation events and columns corresponding to the chemical variables measured was constructed. In order to avoid the effect of different size variables, the data were autoscaled to produce new variables with zero mean and a unit standard deviation. The multivariate statistical procedure used is principal component analysis (PCA). PCA was used to provide a data structure study in a reduced dimension, retaining the maximum amount of variability present in the data.

In sample PCA, one is supposed to have n independent observations from a p variable random variable collected in a data matrix  $X_{n,p}$ . The matrix of the eigen vectors derived by a covariance (or correlation) matrix computed

on X contains all useful information to describe the relationship among the observed *p* variables.

By collecting observations concerning the concentration of pollutants in rainwater, in all the stations of a network, a data matrix for each station can be defined. Let  $K = \{1, 2, ..., K\}$  be the set of the stations belonging to the network, where we use the same notation for a set and for its cardinality. If  $n_k$  is the number of observations from the station k, then we have a set of K data matrices  $X_k, k = 1, 2, ..., K$ , where  $X_k$  has  $n_k$  rows and p columns. In such a case, the station is a classification criterion for the observations belonging to the whole network.

#### 3.8.2.1 Between and within variance related to a classification criterion:

If  $S_k$  is the covariance matrix of  $X_k$ , and S is the covariance matrix of

$$X = \begin{pmatrix} X_1 \\ X_2 \\ \dots \\ X_k \end{pmatrix}$$

then a strong property of S is given by the well known decomposition:

$$S = W + B$$
,

where W is the within-groups covariance matrix and B is the between-groups covariance matrix. W represents the part of the variance common to all the elements of the classification criteria while B represents the part of the variance due to the differences among the mean values in the groups.

For the total variance tr(S), the same additive decomposition:

$$tr(S) = tr(W) + tr(B)$$

can be written. So the ratio:

$$\frac{tr(B)}{tr(S)}$$

gives the measure of the importance of the considered classification criterion.

#### 3.8.2.2 Comparing PCAs

Suppose that  $1/n_k$   $1'_k X_k = 0$ , where  $1'_k = (1,1,...,1) \in \mathbb{R}^{nk}$ ,  $\forall k$  and  $0 \in \mathbb{R}^p$ . Clearly, it is possible to perform PCA in each of the K data matrix  $X_k$ , considering the set of the covariance matrices  $S_k = 1/n_k X_k' X_k$ . An interesting question, at this point, is to evaluate how different are the principal components in several stations and what kind of differences there are.

Exploratory statistical ways to answer this question belong to a class of exploratory techniques, named 'multiway data analysis', essentially because they have been built for data which can be classified in several ways. One of the methods of multiway data analysis, named interstructure-compromise-infrastructure (ICI), provides a framework to compare two or more PCAs, of the same variables, when these variables have been measured on different occasions, i.e. in this case, 'stations'. This method, as the name suggests, consists of three steps.

The first step, interstructure, provides an analysis of the similarities between the K structures of relationship among variables. This is a global comparison of the PCAs of single occasions. A KxK similarity matrix C, termed interstructure matrix is defined, whose generic element is  $c_{kh} = tr(S_kS'_h), k, h = 1, 2, ..., K$ . A normalized interstructure matrix Z is also defined with element:

$$z_{kh} = \frac{c_{kh}}{\sqrt{c_{kk}c_{hh}}} k, h = 1, 2, ..., K.$$

Z is a matrix correlation index. It results  $0 \le z_{kh} \le 1$ , where if  $z_{kh} \to 1$ Then PCAs in occasions k and h are very similar, and if  $z_{kh} \to 0$  then such PCAs are very different.

Therefore, Z allows a better reading of the interstructure. A graphical representation of the first eigenvectors of C is the tool for describing, in a global framework, the similarities between structures.

The second step, compromise, provides a summarizing structure of all the K considered structures. The pxp compromise matrix S is obtained as a linear combination of the covariance matrix  $S_k$ .

$$\overline{S} = \sum_{k=1}^{K} a_k S_k$$

where coefficients  $a_k$  are defined by the elements of the first eigenvector of matrix C. In this way, compromise S has particular optimal statistical properties. A graphical representation of the first eigenvectors of S describes the compromise structure thus obtained.

The goal of the third step of ICI, intrastructure, is to describe how single structures differ from one another. If  $\Gamma$  is the matrix of the eigenvectors, with unitarynorm, and A is the diagonal matrix of the eigenvalues of  $\overline{S}$ , then each structure can be projected into the space spanned by the columns of  $\Gamma$  by means of the projection:

$$P_k = \sqrt{a_k S_k \Gamma A^{-1}} \quad k = 1, 2, ..., K.$$

So, with a single graphical representation, it is possible to describe the different role of each variable in each considered structure.

# QUALITY OF RAINWATER IN VARIOUS LAND USE LOCATIONS

#### 4.1 Introduction

India is at the threshold of a water scarcity situation. It is projected that by the year 2025, India would become a water stressed country, hence it is pertinent to shift the thrust of the policies from 'water development' to 'sustainable water development'. A vital element of this shift in strategy is the increasing importance of rainwater harvesting and recharge of ground water. Several state governments in India has introduced legislation that makes it obligatory to incorporate roof top rainwater harvesting systems in newly constructed buildings in urban area. In this context the quality of rainwater becomes significant, since it depends upon many factors-the most important being the land use pattern of the location where the rainwater is harvested. This chapter deals with the chemical composition and the quality of rainwater at different land use locations in Ernakulam district. The variables influencing the rainwater composition found out using statistical method are also incorporated in this chapter.

## 4.2 Rainfall during the period of study

The major rainfall season for Kerala is the southwest monsoon period from June to September. Next to the southwest monsoon, the other principal rainy season is the northeast monsoon. Kerala receives summer showers from March to May. The rainfall data from May 2007 to December 2008 is given in Table 4.1.

**Table 4.1:** Rainfall received in Ernakulam district during May 2007 to December 2008

			,	Year: 2007	1			_
Month	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Rainfall (mm)	403	721	899	372	735	424	538	12
-\I	<u>-</u>	<u></u>		Year: 2008				
Month	Jan.	Feb.	March	April	May	June	July	Aug.
Rainfall (mm)	0	23	284	150	199	386	520	235
				Year: 2008	<u> </u>			
M	lonth		Sept.	Oct.	T	Nov.		Dec.
Rainf	all (mm)		546	298		24		27

It can be seen from Table 4.1 that 85% of the total rain is received during the two monsoon seasons, ie. June to December, while the summer rains ie. from March to May constituted 14.5% of the total rain. Only 23 mm of rainfall is received during January to February 2008, which accounts for only 0.5% of the total rain. The rainfall received during the period of study is shown in Fig:4.1. From the above it is quite evident that the rainwater received during June to December is the major source for the coming months. Any failure in the southwest monsoon or northeast monsoon will result in scarcity of water. This will also affect the availability of drinking water, electricity production and agriculture. All efforts should therefore be made to plan and manage the use of water with utmost care so that even when the monsoon fails, water scarcity is not felt. Collection of rainwater during the rainy season both for drinking and other purposes would hence be most useful.

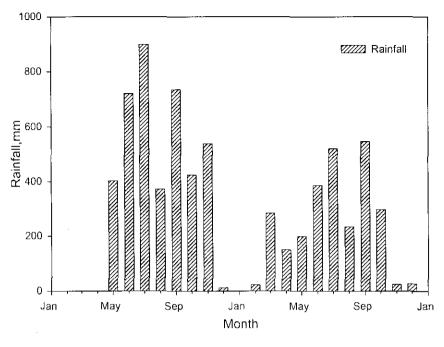


Fig: 4.1 Rainfall Variation during May 2007 - October 2008

In terms of water security, it may be noted that among the 35 Meteorological sub-divisions in India, Kerala receives the maximum annual rainfall. Considering the area and population, around thirteen thousand litres of water is available per head per day out of which only one or two percent is sufficient for meeting the daily needs of a person. Thus water security in terms of quantity especially in the high rainfall areas of Kerala, is very good. This state is hence highly suitable for testing DRWH in terms of economic viability and water quality vis-à-vis other alternatives for providing water (Padma Vasudevan and Namrat Pathak, 1999).

# 4.3 Chemical composition of rainwater

All the samples collected during the period of study were analyzed for the ionic components. All the concentrations are reported in  $\mu eql^{-1}$  so that a simple arithmetic procedure can be used to obtain comparisons between various data sets. The pH value of water indicates the logarithm of reciprocal of hydrogen ion concentration present in water. Thus pH is a measure of

hydrogen ion concentration  $[H^+]$  mmol/l  $H^+$ .

$$pH = -\log_{10} \lceil H^+ \rceil.$$

is approximately equal to  $mg/l H^+$ .

Due to the highly alkaline nature of soil in India, the role of  $HCO_3^-$  becomes very important. Since no direct method is available for the measurement of  $HCO_3^-$ . There are two sources of bicarbonate ( $HCO_3^-$ ) and carbonate ( $HCO_3^-$ ) ions in rainwater. One of the atmospheric carbon dioxide ( $HCO_3^-$ ) that dissolves in rainwater to form bicarbonate ion ( $HCO_3^-$ ) and carbonate ion ( $HCO_3^-$ ) as well as  $H^+$ . The other is the atmospheric aerosol particles of calcite ( $HCO_3^-$ ) reacting as strong bases with  $H^+$  to give ( $HCO_3^-$ ). These reactions occur according to the following equations:

$$CO_2 + H_2OCO_2.H_2O,$$
 (1)  
 $K_H = 3.4x10^{-2} \, mol \, l^{-1} \, atm^{-1} \, (at \, 298 \, K),$   
 $CO_2.H_2O \rightleftharpoons H^+ + HCO_3^-$  (2)  
 $K_1 = 4.6x10^{-7} \, mol \, l^{-1} \, (at \, 298 \, K).$   
 $HCO_3 \rightleftharpoons H^+ + CO_3^{2-},$  (3)  
 $K_2 = 4.5x10^{-11} \, mol \, l^{-1} \, (at \, 298 \, K),$ 

where  $K_H$  is Henry's coefficient;  $K_1$  is  $CO_2$ ,  $H_2O$  dissolution coefficient; and  $K_2$  is  $HCO_3^-$  dissolution coefficient. Then the equilibrium relations are

$$K_H P_{co_2} = [CO_2.H_2O], \dots$$
 (4)

$$K_1[CO_2 + H_2O] = [H^+][HCO_3^-].$$
 (5)

$$K_2[HCO_3^-] = [H^+][CO_3^{2-}],$$
 (6)

where  $P_{CO_2}$  is the atmospheric  $CO_2$  partial pressure. Thus, in rainwater the  $HCO_3^-$  and  $CO_3^{2-}$  concentrations following from the dissolution of  $CO_2$  as well as carbonate aerosol particles is

[HCO<sub>3</sub>]=[CO<sub>2</sub>.H<sub>2</sub>O]K<sub>1</sub>/[H<sup>+</sup>]=
$$K_H P_{ev_2} K_1/+[H+]$$
 .....(7)  
= 5.5/[H<sup>+</sup>](µmol 1<sup>-1</sup>),

$$[CO_3^{2-}] = [CO_2.H_2O]K_1K_2/[H^-]^2 = K_H P_{co_2} K_1K_2/+[H^+]^2$$

$$= 0.00025/[H^+]^2 (\mu mol 1^{-1}),$$
(8)

where the atmospheric CO<sub>2</sub> concentration is assumed to be equal to 350 ppm. Since CO<sub>3</sub><sup>2</sup> concentration is very low, generally, it is neglected (Losno et al., 1991; Warneck, 1988).

When pH is above 5.6 and the sample in equilibrium with atmospheric carbon dioxide, the concentration of HCO<sub>3</sub> in mole/l is calculated as follows:

$$[HCO_3] = 10^{-11.2 + pH}$$

The above equation could underestimate the concentration of HCO<sub>3</sub> (Granat, 1972).

Prior to focusing the data analysis in a multivariate way, univariate descriptive statistics (mean and standard deviation) for the measured variables were studied for each sampling point and the details is as given in Table 4.2. In general, rainwater collected from the different sampling sites had a pH in the 5.62-6.00 μeql<sup>-1</sup> range, while the H<sup>+</sup> ion concentration was in 163-4.43 μeql<sup>-1</sup> range. K<sup>+</sup> concentration varied from 4.02 μeql<sup>-1</sup> for the Eloor (industrial location) to 7.28 μeql<sup>-1</sup> for Kothamangalam (rural). The corresponding values obtained for Ernakulam (urban) and Kalamassery (suburban) are 6.94 μeql<sup>-1</sup> and 4.77μeql<sup>-1</sup> respectively. It can be seen that K<sup>+</sup> concentration is lowest in the industrial location, slightly higher in sub urban and still higher in the urban location. K<sup>+</sup>

concentration is highest in the rural location. This trend shown in the present study is in good agreement with that reported by Kulshrestha et al. (2005) in a review of precipitation monitoring studies in India. The trend shown in the variation of  $Ca^{2+}$  ion concentration is similar to that of (Kulshretra et al, 2005), with the lowest value (37.35  $\mu eql^{-1}$  for industrial, slightly higher one for urban and suburban location with the highest value (44.10  $\mu eql^{-1}$ ).  $Mg^{2+}$  concentration is lowest at Kalamassery suburban location, while it is highest in Eloor industrial location.

Sampling Site		PH	H+	HCO3	Ca²⁺	Mg <sup>2+</sup>	Fe <sup>2+</sup>	Cu <sup>2+</sup>	Na⁺	K+	S04 <sup>2</sup> ·	No <sup>3-</sup>
	Mean	5.97	2.06	10.79	38.36	39.36	1.71	2.13	24.76	7.28	0.00	0.00
1	SD	0.49	3.05	13.67	33.61	19.53	2.45	2.37	27.42	7.73	0.00	0.00
•	Mean	6.00	1.98	13.35	37.82	38.01	1.29	1.56	13.67	6.94	0.00	0.00
2	SD	0.58	2.10	18.62	34.00	7.74	2.01	1.71	13.39	4.60	0.00	0.00
	Mean	5.62	4.43	6.70	37.35	43.48	1.16	2.01	23.92	4.02	0.00	0.00
3	SD	0.58	4.08	11.01	30.10	49.46	1.57	2.17	34.25	5.08	0.00	0.00
	Mean	5.99	1.63	9.21	44.10	35.67	1.86	1.62	31.38	4.77	0.00	0.01
4	SD	0.40	2.09	7.84	30.30	15.27	2.38	1.94	38.42	4.93	0.00	0.01
<b>-</b>	Mean	5.91	2.38	10.25	39.53	38.69	1.55	1.84	24.96	5.81	0.00	0.01
Total	SD	0.52	3.01	13.47	31.96	24.90	2.18	2.07	30.83	5.90	0.00	0.01

Table 4.2 Descriptive Statistics of data

The relationships between various ionic species in rainwater at different locations were determined by correlation analysis. Table 4.3 shows the Pearson's coefficient ® for rainwater collected from Kothamangalam (place1). Good positive correlation was found between Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> at 0.01 significance level. The Pearson's coefficient table for rainwater samples at the other locations are also given in Tables 4.4 to 4.6. Very strong positive correlation exist between Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup> and NO<sub>3</sub><sup>-</sup>, Fe<sup>2+</sup> and Ca<sup>2+</sup> at Ernakulam (Place 2). NO<sub>3</sub><sup>-</sup>, has a good positive correlation with pH and also H<sup>+</sup> at places 3 and 4. the correlation between Na<sup>+</sup> and Ca<sup>2+</sup> and Mg<sup>2+</sup> for place 3 and that between Ca<sup>2+</sup> and Na<sup>+</sup>, K<sup>+</sup> was found to be very good.

<sup>1-</sup> Kothamangalam(Rural), 2- Ernakulam(Urban), 3- Eloor(Industrial), 4- Kalamassery(Suburban) Except pH, all concentrations are in  $\mu$  eql<sup>-1</sup>

Table 4.3 Pearson Correlation Coefficient for rainwater (Place 1)

		Н	+ =	HCO3.	Ca2+	Mg2+	F82+	Cu2+	Na+	¥
	Pearson Correlation	-	.782(**)	.822(**)	.342(*)	.382(*)	.378(*)	.331(*)	.146	.158
Ŧ	Sig. (2-tailed)		000	000	.031	.015	910	.037	.634	909.
	2	40	40	37	40	40	40	40	13	13
	Pearson Correlation	.782(**)	-	397(*)	011.	215	.205	.174	310.	.271
÷	Sig. (2-tailed)	000		.015	.499	.182	.205	.283	.962	.370
	į	40	40	37	40	40	40	40	13	13
	Pearson Correlation	.822(**)	.397(*)	-	.541(**)	.259	392(*)	.391(*)	180.	.021
HC03-	Sig. (2-tailed)	000	.015		100.	.122	.016	710.	.823	.954
	2	37	37	37	37	37	37	37	10	10
	Pearson Corrolation	.342(*)	011.	.541(**)	-	.245	.200	.236	.664(*)	044
Ca2+	Sig. (2-tailed)	.031	499	100		128	216	.142	.013	.886
	2	40	40	37	40	40	40	40	13	13
	Pearson Correlation	.382(*)	.215	.259	.245	-	.239	011.	.425	.169
Mg2+	Sig. (2-tailed)	.015	.182	.122	.128		.137	.498	.147	.581
	2	40	40	37	40	40	40	40	13	13
1	Pearson Correlation	.378(*)	.205	.392(*)	200	.239	-	178	325	720.
Fe2+	Sig. (2-tailed)	.016	.205	.016	.216	.137		.272	.278	.802
	Z	40	40	37	40	40	40	40	13	13
	Pearson Correlation	.331(*)	.174	.391(*)	.236	.110	.178	-	082	.153
Cu2+	Sig. (2-tailed)	.037	.283	710.	.142	.498	272		.789	.618
	2	40	40	37	40	40	40	40	13	13
	Pearson Correlation	.146	.015	.081	.664(*)	.425	.325	082	-	.103
Na+	Sig. (2-tailed)	.634	.962	.823	.013	.147	.278	.789		.737
	2	13	13	10	13	13	13	13	13	13
	Pearson Correlation	.158	.271	.021	.044	.169	7.70.	.153	.103	-
K+	Sig. (2-tailed)	909.	370	.954	.886	.581	.802	.618	.737	
	N	13	13	10	13	13	13	13	13	13

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

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

Table 4.4 Pearson Correlation Coefficient or rainwater (Place 2)

		Æ	<del>+</del>	HCO3-	Ca2+	Mg2+	Fe2+	Cu2+	Na+	κ +	No3-
	Pearson Correlation	-	854(**)	(**)898.	1507.	.334	172.	.258	.048	.141	800.
표	Sig. (2-tailed)		000	000	.004	100.	.148	.168	916.	.763	.992
	N	30	30	29	30	30	30	30	7	1	4
	Pearson Correlation	.854(**)	-	554(**)	308	.270	.215	.248	.100	890°	237
±	Sig. (2-tailed)	000		.002	760.	.150	.255	187	.832	.885	763
	2	30	30	29	30	30	30	30	7	7	4
	Pearson Correlation	(**)698.	554(**)	-	.728(**)	.130	.340	.146	.064	.197	206
HC03-	Sig. (2.tailed)	000	.002		000	.500	170.	.449	.904	607.	794
	2	29	29	29	29	29	29	29	9	9	4
	Pearson Correlation	11205	.308	728(**)	1	.033	.6381**)	.231	.476	.271	177
Ca2+	Sig. (2-tailed)	-004	.097	.000		.864	000	.219	.281	.556	729
	2	30	30	29	30	30	30	30		7	4
	Pearson Correlation	.334	.270	.130	.033	-	.154	760'	164	070.	943
Mg2+	Sig. (2-tailed)	1.70.	.150	.500	.864		.417	119.	726	.881	790'
-7	N	30	30	58	30	30	30	30	7	7	4
	Pearson Correlation	271	.215	.340	1. 1829.	.154	1	.265	369	.709	. 189
Fe2+	Sig. (2-tailed)	.148	.255	.071	000	.417		.157	.415	.074	.811
	N	30	30	29	30	30	30	30	7	1	4
	Pearson Correlation	.258	248	.146	.231	760.	.265	-	.255	.522	.842
Cu2+	Sig. (2-tailed)	.168	.187	.449	.219	119.	.157		.580	.230	.158
	2	30	30	29	30	30	30	30	7	7	4
	Pearson Correlation	.048	100	.064	.476	.164	369	.255	-	.580	(a)
ha+	Sig. (2-tailed)	919	.832	.904	.281	.726	.415	.580		.172	
	22	7	7	9	7	7	7	1	7	7	0
	Pearson Correlation	-141	068	.197	172.	0.070	.709	.522	.580	-	(e)
÷	Sig. (2-tailed)	.763	.885	.709	.556	.881	.074	.230	.172		-
	2	7	7	9	7	7	7	1		7	0
	Pearson Correlation	800:	237	.206	.271	.943	. 189	842	(a)	(a)	-
No3.	Sig. (2 tailed)	.992	.763	794	.729	.057	118.	.158		·	
	2	4	4	4	4	4	4	4	0	0	7

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

Table 4.5 Pearson Correlation Coefficient or rainwater (Place 3)

		H	±	HCO3-	Ca2+	Mg2+	Fe2+	Cu2+	Na+	¥	No3-
	Pearson Correlation	1	.884(**)	.844(**)	.367	311.	.462(*)	.228	.014	.161	.560
Ŧ	Sig. {2:tailed}		000	000	870.	.593	.023	.283	.973	.731	.191
1	2	24	24	22	24	24	24	24	8	1	7
	Pearson Correlation	.884(**)	-	.561(**)	.219	.152	.337	102	.242	.335	.701
<del>+</del>	Sig. (2-tailed)	000		700.	.304	479	701.	.636	.563	.463	.080
	2	24	24	22	24	24	24	24	8	7	7
	Pearson Correlation	.844(**)	.561(**)	-	.334	074	.392	.429(*)	660.	.093	.466
HC03.	Sig. (2-tailed)	000.	700.		.129	.743	.071	.047	.852	.882	.352
	Z	22	22	22	22	22	22	22	9	9	9
	Pearson Correlation	.367	.219	.334	-	.185	.115	.353	779(*)	.437	.029
Ca2+	Sig. (2-tailed)	9/0.	304	.129		.386	.592	160.	.023	.327	.951
	N	24	24	22	24	24	24	24	8	7	7
	Pearson Correlation	115	152	.074	185	,	168	- 005	(**)086	. 168	170.
Mg2+	Sig. (2-tailed)	.593	.479	.743	.386		.432	.983	000	718	.880
	2	24	24	22	24	24	24	24	80	7	7
	Pearson Correlation	.462(*)	.337	392	115	168	ļ	.178	.376	479	.270
Fe2+	Sig. (2-tailed)	.023	.107	1,00.	.592	.432		.406	.358	.276	.558
	2	24	24	22	24	24	24	24	8	1	7
	Pearson Correlation	.228	.102	.429(*)	.353	900:	178	1	.236	.329	.305
Cu2+	Sig. (2-tailed)	.283	.636	.047	160.	.983	.406		.573	.471	.505
	2	24	24	22	24	24	24	24	8	7	7
	Pearson Correlation	.014	.242	660.	(*)877.	()086	.376	.236	-	760	.319
₩ +	Sig. (2-tailed)	.973	.583	.852	.023	000	.358	.573		.836	.793
	2	80	8	9	8	8	89	80	80	7	3
	Pearson Correlation	181.	335	.093	.437	168	479	328	.097	-	.(a)
<b>*</b>	Sig. (2-tailed)	.731	.463	.882	.327	.718	.276	.471	.836		000
	R.	7	· ·	5	7	7	7	7	7	7	3
	Pearson Correlation	.560	.701	.466	.029	.071	.270	305	.319	(a)	
No3.	Sig. (2-tailed)	.191	.080	.352	.951	.880	.558	.505	.793	000:	
	2	7	7	9	7	7	7	7	m	m	7

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

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

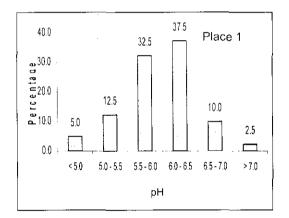
Table 4.6 Pearson Correlation Coefficient or rainwater (Place 4)

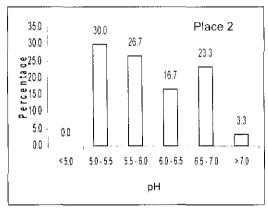
		£	÷	HC03.	Ca2+	Mg2+	Fe2+	Cu2+	- e2	<b>*</b>	No3.
	Pearson Correlation	-	.828(**)	885(**)	.334	.044	.072	.376(*)	196	389	705
E	Sig. (2-tailed)		000.	000.	.058	.810	169.	.031	.502	158	160.
	2	33	33	31	33	33	33	33	14	14	8
!	Pearson Correlation	828(**)	-		.173	.022	150	.192	.254	.151	938(**)
±	Sig. (2-tailed)	000		.004	334	906	777	284	381	909	100.
	2	33	33	31	33	33	33	33	14	14	88
	Pearson Correlation	(**)388.	.504(**)		.382(*)	.082	070.	.434[*)	.102	.565	445
HC03:	Sig. (2-tailed)	000	.004		.034	099	709	.015	.753	.056	.376
	2	31	31	31	31	31	31	31	12	12	9
Ì	Paarson Correlation	.334	.173	.382(*)	-	289	.217	.168	.659(*)	(,)	.542
Ca2+	Sig. (2-tailed)	.058	334	.034		.103	.225	349	010	010.	166
	2	33	33	31	33	33	33	33	14	14	osc.
	Pearson Correlation	.044	.022	.082	.289	-	124	.195	.130	487	,424
Mg2+	Sig. (Z-tailed)	.810	905	099	.103	!	492	277	657	720	.296
	2	33	33	31	33	33	33	33	14	14	80
	Pearson Correlation	.072	150.	070.	.217	.124	-	164	242	024	.517
Fa2+	Sig. (2-tailed)	.691	TTT	.709	.225	492		.363	.404	.936	190
	2	33	33	31	33	33	33	33	14	14	8
!	Pearson Correlation	.376(*)	.192	.434(*)	168	195	.164	  -	.020	474	360
Cu2+	Sig. (2-tailed)	.031	284	.015	.349		363		.947	180	380
	2	33	33	16	33	33	33	33	14	14	æ
	Pearson Correlation	196	.254	.102	.659(*)	130	242	.020	-	221	.431
₽ + *	Sig. (2-tailed)	.502	.381	.753	010.	/ 99'	404	947	į	447	695
		14	41	12	41	<u> </u>	14	14	14	4	4
	Pearson Correlation	398	151	.565	1.)199	.487	.024	474	.221	-	000
<b>K</b> +	Sig. (2-tailed)	.158	909	056	010		936	780.	.447		1.000
	2	14	14	12	14	14	14	41	4	14	4
	Pearson Correlation	705	(**)8£6	.445	542	424	517	.360	.431	000	-
No3-	Sig. (2-tailed)	.051	100	.376	166	. 296	061.	380	569	1.000	
	2	80		9	80	, ao	80	œ	4	4	٥

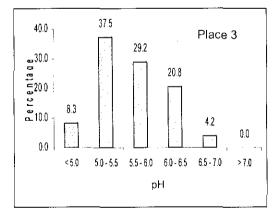
\*\* Correlation is significant at the 0.01 level (2-tailed).
\* Correlation is significant at the 0.05 level (2-tailed).

### 4.3.1 pH variation of rainwater with land use

Fig: 4.2 shows the presentage frequency distribution of pH of rain water samples collected at different locations during the monsoon of the years 2007 and 2008. The reference level commonly used to compare acidic precipitation to natural precipitation is pH 5.6, the pH that results from the equilibration of atmospheric CO<sub>2</sub> with precipitation. It may be observed from the Fig: 4.2 that about 45% of the total rain events at Eloor reflects that pH of rainwater is acidic, while it is only 17% in the case of Kothamangalam. The frequency distribution of the pH for the study period at different locations is tabulated in Table 4.7. It can be seen that 82.5%, 70%, 54.2% and 87.9% of rainwater samples collected at places 1, 2, 3 and 4 respectively have pH greater that 5.6.







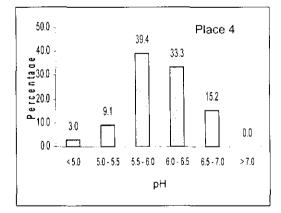


Fig: 4.2 Frequency distribution of pH in rainwater at different land use locations

**Table 4.7** Frequency distribution of pH of rainwater at different land use locations

			Frequency Distri	bution (%)	
L	ocation	Kothamangalm (1)	Ernakulam (2)	Eloor (3)	Kalamassery (4)
La	and use	Rural	Urban	Industrial	Sub urban
	< 5	5	0	8.3	3
	5.5.5	12.5	30	37.5	9.1
	5.5-6	32.5	26.7	29.2	39.4
of pH	6.0-6.5	37.5	16.4	20.8	33.3
Range of	6.5-7	10	23.3	4.2	15.2
_	>7	2.5	3.3	0	0
	< 5.5	17.5	30	45.8	12.1
	5.5 -> 7	82.4	70	54.2	87.9

The reason for the pH of 45.8% of rainwater samples of Eloor being acidic, can be attributed to the vicinity of industries near the sampling site. The table clearly points out that 87.9% of pH of rainwater samples of reflects alkaline nature of rainfall.

The average H<sup>-</sup> concentration and pH in rainwater samples at different stations in India reported by Khemani. et.al, 1989, Kulashrestha.et.al, 2005 and from the present study is shown in Table 4.8.

The pH values obtained in the present study are mostly in agreement with those obtained for different land use locations at various stations in India.

**Table 4.8** Average pH values and H<sup>+</sup> concentration of rain water samples

	Station	рН	H <sup>+</sup> in μ eql <sup>-1</sup>
stal	Alibag	7.2	0.063
Coastal	Colaba	7.1	0.079
<del></del> -	Kalyan	5.7	2
trial	Chembur	4.8	15.85
Industrial	Indraprastha	5.0	10
	Eloor*	5.62	2.40
	Pune	6.3	0.50
Urban	Delhi	6.1	0.79
_	Ernakulam*	6.0	1.0
	Sirur	6.7	0.20
sub urban	Kalamassery*	5.99	1.02
Rural	Kothamanglam*	5.97	1.07
e.	Industrial	6.1	0.794
Kulshreshtha et.al (2005)	Urban	6.4	0.398
shreshtha (2005)	Sub urban	6.7	0.2
춫	Rural	6.5	0.316

<sup>\*</sup> present study (others as reported by Khemani et. al, 1989)

The frequency distribution of  $H^+$  ion concentration is given in Table 4.9 and Fig: 4.3 for the various land use locations. The  $H^+$  ion concentration corresponding to equilibrium pH of 5.6 in  $2.5\mu eql^{-1}$ .

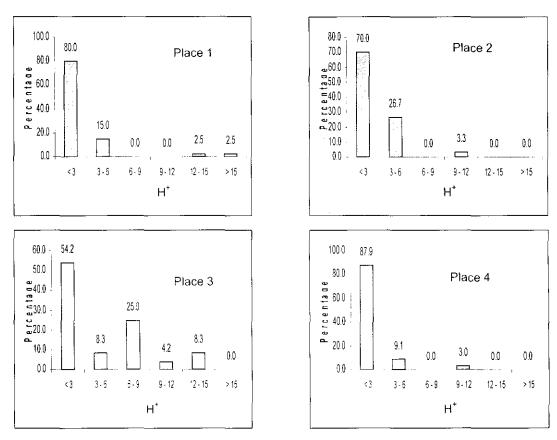


Fig: 4.3 Frequency distribution of H<sup>+</sup> in rain water at different locations

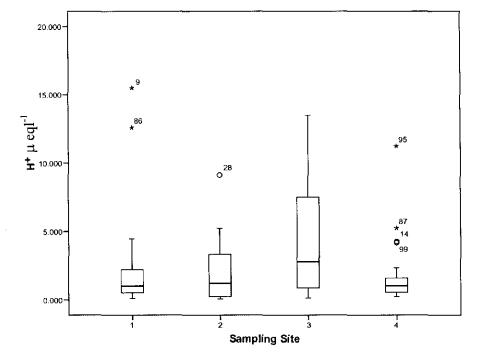


Fig: 4.4 Box and whisker plot for H<sup>+</sup> concentrations at different location

**Table 4.9** Frequency distribution of H<sup>+</sup> ion concentration

		Frequency d	istribution (%)	
Range of H <sup>+</sup> ion µ eql <sup>-1</sup>	Rural	Urban	Industrial	Sub urban
< 3	80	70	54.2	87.9
3-6	15	26.7	8.3	9.1
6-9	0	0	25	0
9-10	0	3.3	4.2	3
12-15	2.5	0	8.3	0
> 15	2.5	0	0	0

The highest percentage of  $H^+$  ion concentration in the category <3  $\mu$  eql<sup>-1</sup> is 87.9%, for the sub urban location, compared to 80% for the rural location. The suburban sampling site at Kalamassery is located inside the Cochin University campus with lot of vegetation cover.

The Box and Whisker charts are a great tool for a quick look at how several processes compare. A box and whisker plot is a picture of how a set of data is spread out and how much variation there is. It is sometimes called a box plot. It does not show all the data. Instead it highlights a few of the important features in the data. These important features are the median, the upper (75<sup>th</sup>) quartile, the highest value, the lower (25<sup>th</sup> quartile) and the smallest value. Box and Whisker plots are ideal for comparing multiple processes because the centre, the spread and overall range are immediately apparent from the chart.

The Box and Whisker plot provides a lot of information despite being a simple tool. The length of the box provides an indication of the spread or variation in the data. If the median is not in the centre of the box, it is an

indication that the data is skewed. If the median is closer to the bottom of the box, the data are positively skewed. If the median is closer to the top of the box, the data is negatively skewed. Figs.4.4 shows the box and whisker plot according to the sampling site for different ion concentrations in µeql<sup>-1</sup>.

# 4.3.2 Variation of Ca2+, Mg2+ and other ionic components.

Table 4.10 gives the descriptive statistics of the entire data set. It can be seen that the concentration of the ionic species as the following order.

 $Ca^{2^{+}} > Mg^{2^{+}} > Na^{+} > HCO_{3}^{-} > K^{+} > H^{+} > Cu2^{+} > Fe^{2^{+}} > NO_{3}^{-}$  thus  $Ca^{2^{+}}$  is the major contributing factor in the rainwater composition. Coarse mode Ca aerosols are contributed by soil dust in the ambient air in India. Therefore  $Ca^{2^{+}}$  aerosols seems to be a major component for neutralization of rainwater acidity in most of the Indian site (Khemani et al., 1989, Saxena et al. 1991, Kulshrestha et. al, 1996)

Table 4.10 Descriptive statistics of rainwater samples

	Mean	SD
рН	5.91	0.5238
H⁺	2.38	3.0117
HCO <sub>3</sub>	10.25	13.4733
Ca <sup>2+</sup>	39.53	31.9646
Mg <sup>2+</sup>	28.35	24.4590
Fe <sup>2+</sup>	1.55	2.1786
Cu <sup>2+</sup>	1.84	2.0720
Na⁺	24.96	30.8316
K <sup>+</sup>	5.81	5.8960
\$04	0.00	0.0000
NO <sub>3</sub>	0.01	0.0068

Fig: 4.5 to Fig: 4.12 show the frequency distribution of various ionic constituents of rainwater. In case of  $HCO_3^-$ , more than 75% of rainwater samples at all locations showed concentrations below 15  $\mu$  eql<sup>-1</sup>. More than 58% samples showed concentrations for  $Mg^{2+}$  below 50  $\mu$  eql<sup>-1</sup>, where as only more than 45% samples showed concentrations for  $Ca^{2+}$  below 50 $\mu$  eql<sup>-1</sup>. Higher concentration of all ionic components were rarely found in the rainwater samples.

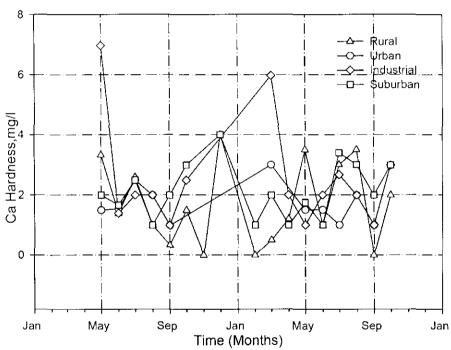


Fig: 4.5 Variation of Ca Hardness of rainwater collected from different locations

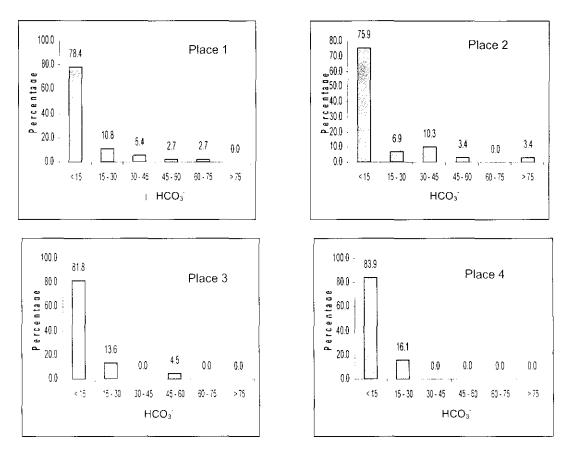


Fig: 4.6 Frequency distribution of HCO<sub>3</sub> in rainwater at different locations

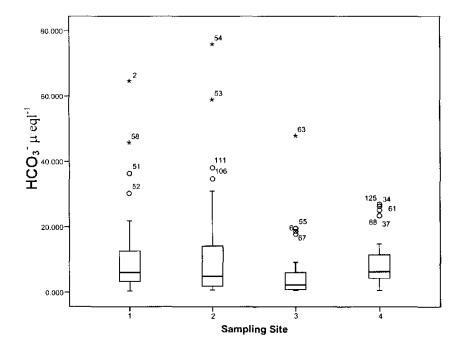


Fig: 4.6 (a) Box plot for HCO<sub>3</sub> concentrations at different locations

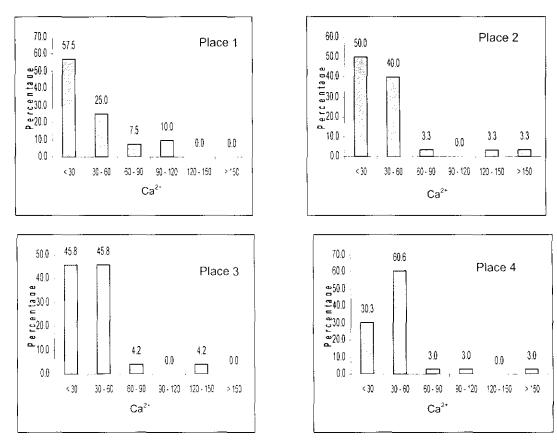


Fig: 4.7 Frequency distribution of Ca<sup>2+</sup> in rainwater at different land use locations

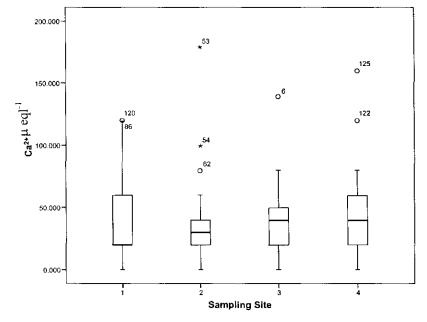
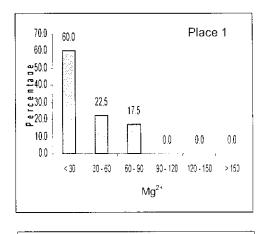
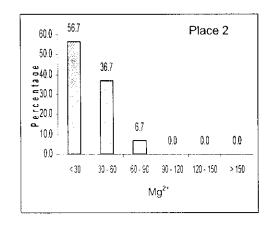
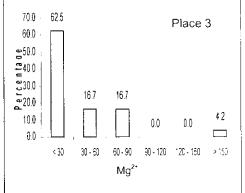


Fig: 4.7 (a) Box plot for Ca2+ concentrations at different locations







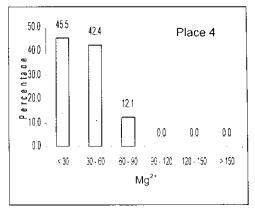


Fig: 4.8 Frequency distribution of Mg<sup>2+</sup> in rainwater at different land use locations

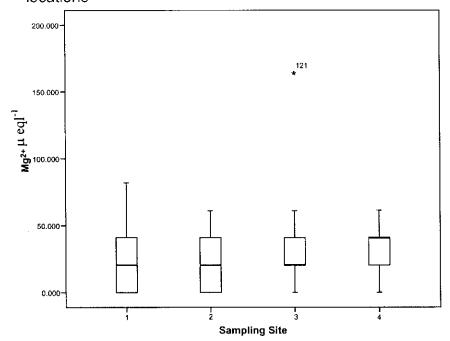


Fig: 4.8(a) Box plot for Mg<sup>2+</sup> concentrations at different locations

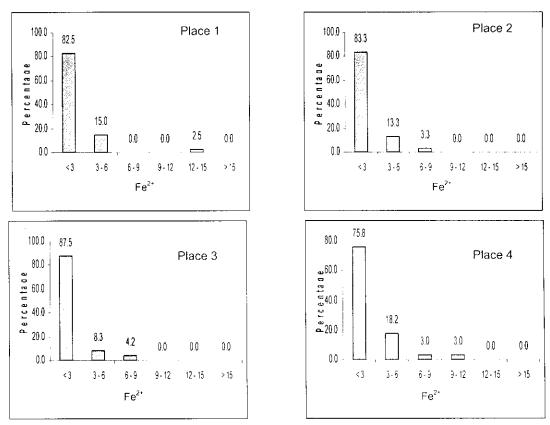


Fig: 4.9 Frequency distribution of Fe<sup>2+</sup> in rainwater at different land use locations

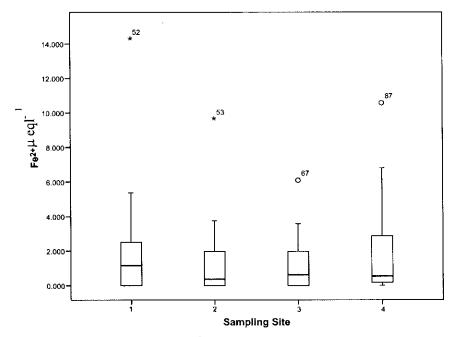


Fig: 4.9 (a): Box plot for Fe<sup>2+</sup> concentrations at different locations

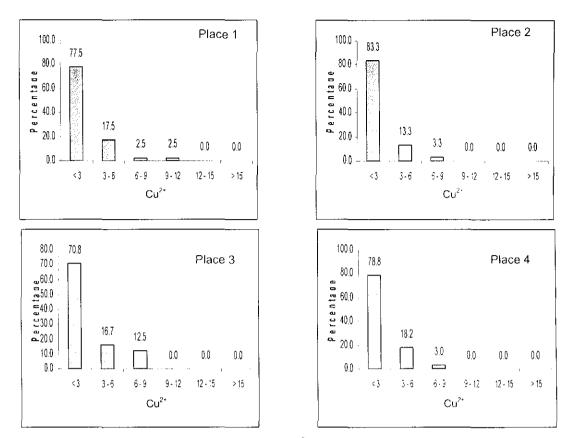


Fig: 4.10 Frequency distribution of Cu<sup>2+</sup> in rainwater at different land use locations

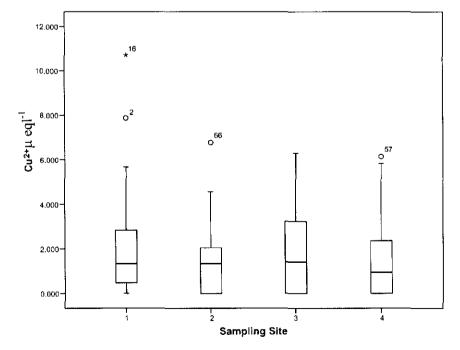


Fig: 4.10 (a): Box plot for Cu<sup>2+</sup> concentrations at different locations

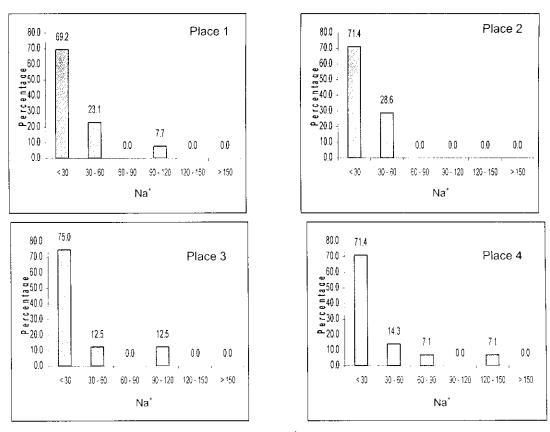


Fig: 4.11 Frequency distribution of Na<sup>+</sup> in rainwater at different land use locations

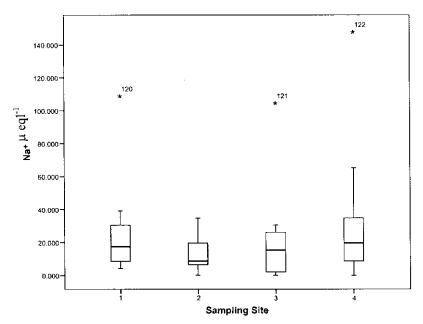


Fig: 4.11(a) Box plot for Na<sup>+</sup> concentrations at different locations

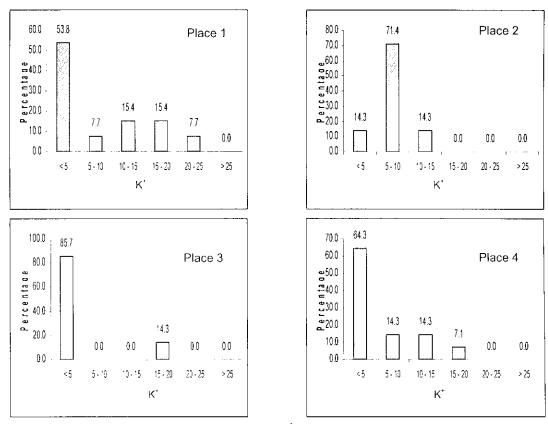


Fig: 4.12 Frequency distribution of K<sup>+</sup> in rainwater at different land use locations

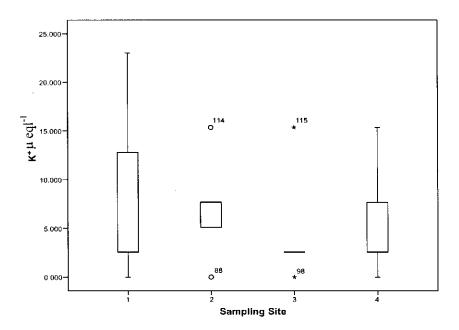


Fig: 4.12(a): Box plot for K<sup>+</sup> concentrations at different locations

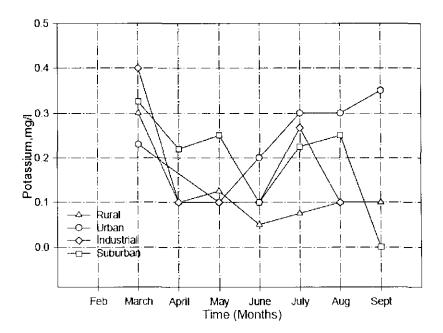


FIG: 4.13 Variation of potassium of rainwater collected from different locations

Fig: 4.13 to 4.15 shows the variation of Ca Hardness, copper concentration and iron concentration in rainwater samples collected from different locations.

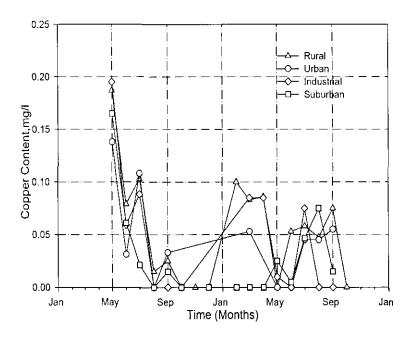


Fig: 4.14 Variation of Copper content present in rainwater collected from different locations

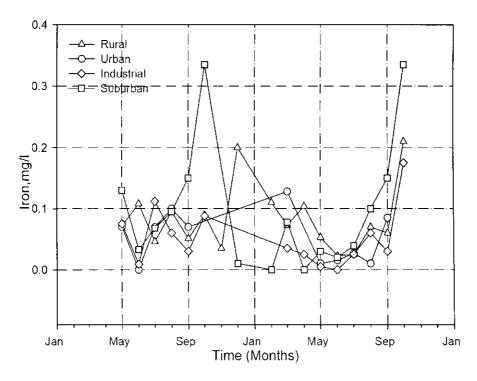


Fig: 4.15 Variation of iron in rainwater collected from different locations

#### 4.3.3 Marine contribution

In order to estimate the marine and non-marine contributions, different ratios like sea salt fractions and enrichment factors have been calculated. For this, Na has been taken as reference element assuming that all sodium is of marine origin (Kulshrestha et a., 1996). Table 4.11 shows the ratios of K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> with respect to Na<sup>+</sup>. All ratios have been found to be higher at all the sites than the recommended sea water ratios. These elevated values may be due to the contribution of anthropogenic and crustal sources. Similarly high ratios of these components with respect to Na<sup>+</sup> suggest a non-marine origin for these components (Khemani, 1993; Kulshrestha et al., 1996). The sea salt fraction (SSF) and non-sea salt fractions (NSSF) of the various components have been calculated using the following equations

$$\% SSF = \frac{100(Na)(X/Na^+)sea}{X}$$

where X is the component of interest.

$$% NSSF = 100 - SSF$$

Enrichment factor (EF) of rainwater samples were calculated using the formula

$$EF = \frac{(X/Na)rain}{(X/Na)sea}$$

Table 4.11 Shows that all ionic components eg: Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> appear to be of non-marine contribution at all places of study. The enrichment factors of different species calculated with respect to Na showed that all components are enriched showing significant influence of local sources other than marine influence at the site.

Table 4.11 Comparison of seawater ratios with rain water components

Place code		K+	K⁺/Na⁺			Ca <sup>2+</sup> /Na <sup>+</sup>	Na⁺			Mg <sup>2</sup> -	Mg <sup>z+</sup> /Na <sup>+</sup>	
	-	2	m	4		2	က	4		2	က	4
Seawater ratio	0.0218	0.0218	0.0218	0.218	0.0439	0.0439	0.0439	0.0439	0.227	0.227	0.227	0.227
Ratio in rain water	0.294	0.5076	0.168	0.152	1.5492	2.766	1.56145	1.405	1.0714	1.79	1.3511	0.9936
SSF%	7.41	4.29	1.2976	14.34	2.8337	1.5871	2.811	3.123	21.185	1.268	1.680	22.846
NSSF	92.59	95.71	98.7024	85.66	97.1663	98.4129	97.189	96.876	78.814	98.732	98.319	77.153
ΕF	13.406	23.288	7.706	6.97	35.289	63.0068	35.53	32.011	4.720	7.885	5.951	4.377

### 4.3.4 Principal Component Analysis

The differences among the precipitation data were studied using multivariate procedure – Principal Component Analysis (PCA). In order to describe the total rainfall characteristics, PCA was applied to the complete autoscaled data matrix. By retaining the first three principal components or eigenvectors, 82.38% of the total variance of the total data set was explained. This meant reducing, the dimensionality of the total data from 9 to 3 (66% reduction) loosing only the 17.62% of the information contained in them. Selection of any additional eigenvectors did not supply relevant additional information. The contribution of the chemical variables to each principal component can be evaluated by studying the loadings of the variables in the first three eigenvectors.(See Table 4.12).

Table 4.12 Rotated Component Matrix for the total data set

	Eigenvector 1	Eigenvector 2	Eigenvector 3
H <sup>+</sup>	-0.306	-0.179	0.748
HCO <sub>3</sub>	0.178	0.144	-0.969
Ca <sup>2+</sup>	0.186	0.918	-0.213
Mg <sup>2+</sup>	-0.494	0.583	0.201
Fe <sup>2+</sup>	0.949	0.141	-0.191
Cu <sup>2+</sup>	-0.469	-0.605	0.227
Na⁺	0.215	0.935	-0.033
K <sup>+</sup>	0.585	0.330	0.639
No <sub>3</sub> ·	0.864	0.210	-0.164
Eigenvalue (%)	43.096	21.510	17.778

The interpretation was made on the basis of the different rainwater components defined by Sequeira and Lai (1998): the sea salt base (SSB) component, the partially neutralized acid (PNA) component, anthropogenic activity component (AAC) and total acidity component (TAC). For a principal component (PC), a physical interpretation of sources is possible by comparing the elements having high correlation in a particular PC with elements associated with known possible sources. The variables contributing mainly to the first eigenvector were Fe<sup>2+</sup>, NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>. The PCI has negative high loading for Mg<sup>2+</sup>, Ca<sup>2+</sup> and H<sup>+</sup>. This PC is associated with anthropogenic sources (high loadings for NO<sub>3</sub><sup>-</sup> and Fe<sup>2+</sup>). PC2 has high loadings for Na<sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> with negative loading for Cu<sup>2+</sup> and H<sup>+</sup>. Soil could be identified as a source for this PC2. PC3 has high loadings for H<sup>+</sup> and K<sup>+</sup>. In this eigenvector, the potassium contribution could be considered a vegetation or waste water related component caused by biomass burning or waste-incineration source.

With the aim of reaching a deeper knowledge about the influence of the sampling site localization on the composition of rainwater collected, a second multivariate study was also conducted over the data obtained in each sampling station. For achieving this goal, the approach used consisted of preparation of 4 autoscaled subsets of samples, one for each sampling site. Once the data matrix has been prepared, the next step was application of PCA to each of the 4 data matrices to describe the rainwater composition for each sampling site based on the loadings obtained. The results of PCA achieved for each of them (the loadings for the chemical variables in the first three eigenvectors as well as the total variance retained) are presented in Table 4.13 to Table 4.16 Three principal components or eigenvectors have been considered to be sufficient to represent the chemical data because in all the cases the percentage of the explained variance was higher than 75%.

Table 4.13 Rotated Component Matrix of rain water samples at Place 1

	Eigenvector1	Eigenvector 2	Eigenvector 3
H+	-0.553	0.182	0.726
HCO3-	0.961	0.101	-0.127
Ca2+	0.032	0.893	0.191
Mg2+	0.698	0.511	0.143
Fe2+	0.852	-0.252	0.339
Cu2+	-0.164	-0.114	-0.603
Na+	-0.019	0.927	-0.147
K +	0.065	-0.125	0.729
Eigenvalue (%)	31.658	25.351	19.992

At Kothamangalam, (place 1) total three PCs have been extracted which explain 77% of variance as shown in Table 4.13 PCI has high loadings HCO<sub>3</sub>, Fe<sup>2+</sup> and Mg<sup>2+</sup>. This PCI is attributed to terrigenous dust, because the soil in the area is mostly laterite, which are rich in oxides of iron. HCO<sub>3</sub>, suggests that atmospheric CO<sub>2</sub> is present in the location, while Mg<sup>2+</sup> concentration suggests soil as a source. PC2 has high loadings Ca<sup>2+</sup> and Na<sup>+</sup>, which again suggests soil as a source. The variables contributing to the third eigenvectors are H<sup>+</sup> and K<sup>+</sup> in almot equal loadings. This PC suggests biomass burning as a source and an acid component.

Table 4.14 Rotated Component Matrix of rainwater samples at Place 2

	Eigenvector 1	Eigenvector 2	Eigenvector 3
H+	-0.115	-0.850	-0.021
HCO3-	-0.030	0.968	0.043
Ca2+	0.453	-0.048	-0.791
Mg2+	0.187	0.139	0.695
Fe2+	0.557	-0.396	0.704
Cu2 +	0.769	0.486	0.330
Na+	0.831	0.159	-0.107
K +	0.905	-0.153	0.087
Eigenvalue (%)	36.038	25.765	19.726
			i

Similar to Kothamangalam, three PCs or eigenvectors have been extracted for Ernakulam, (place 2) which explains 81.53% of the variance. As given in Table 4.14, the PCI has high loadings for K<sup>+</sup>, Na<sup>+</sup>, Cu2+ and Ca<sup>2+</sup>. It is interesting to note that PC2 has high loading for *HCO*<sub>3</sub> and negative loading for H<sup>+</sup>. PC3 has high loading to Mg<sup>2+</sup> and Fe<sup>2+</sup>. Similar to previous discussion, PC1 and PC3 can be attributed to the waste incineration and terrigenous dust particles, while PC2 is mostly a total acidity component (TAC) as a source.

Table 4.15 Rotated Component Matrix of rain water samples at Place 3

	Eigenvector1	Eigenvector 2	Eigenvector 3
H+	.0.083	-0.973	0.159
HC03-	-0.294	0.895	0.257
Ca2+	0.681	-0.400	0.604
Mg2+	0.965	-0.156	0.208
Fe2+	-0.481	0.691	-0.538
Cu2+	0.532	0.185	0.825
Na+	0.972	-0.072	0.224
K+	-0.135	0.081	-0.966
Eigenvalue (%)	59.548	25.407	13.793

The three eigenvectors extracted for Eloor (place 3) explains 98.75% of the variance as given in Table 4.15 Compared to other places, the total variance retained is almost equal to 100. The variables contributing to the first eigenvector are Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, which suggest soil as a source. PC2 has loadings for Fe<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, suggesting soil and atmospheric CO<sub>2</sub> as possible sources respectively. PC3 has high loadings for Cu<sup>2+</sup> and a low loading for H<sup>+</sup>, which again suggests soil as a source due to spraying of chemicals.

Table 4.16 Rotated Component Matrix of rainwater samples at Place 4

	Eigenvector1	Eigenvector 2	Eigenvector 3
H+	-0.544	-0.158	0.202
HC03-	0.805	0.264	-0.128
Ca2+	0.502	0.826	-0.05
Mg2+	0.335	0.162	-0.853
Fe2+	0.067	0.219	0.923
Cu2+	0.818	-0.288	0.161
Na+	-0.001	0.888	0.102
K+	0.710	0.315	0.148
Eigenvalue (%)	38.763	21.113	15.170

Similar to other sampling sites, three PCs have been extracted for Kalamassery (place 4), which explains 75.05% of variance. As given in Table 4.16, PC1 has high loadings for HCO<sub>3</sub>-, K<sup>+</sup> and Cu<sup>2+</sup>, and moderate loading for Mg<sup>2+</sup> while PC3 has high loading for Fe<sup>2+</sup> and a low loading for H<sup>+</sup>. These two PCs can be attributed to soil as a source.

From the ongoing discussion on PCA of the complete data and individual sampling sites, the high loadings of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and Fe<sup>2+</sup>, which are soil oriented ions, suggests a significant influence of terrigenous dust on the composition of rainwater. This could be due to the boom in the construction activities in the cities as well as in country side, during the year 2007-2008. The second major source of influence is the atmospheric CO<sub>2</sub>, which is mostly contributed by the increase in vehicular population of Ernakulam district. Waste

incineration and biomass burning has an influence on the chemical composition of rainwater, characterised by  $K^+$  ions concentrations especially in the urban and suburban areas of Ernakulam. It is also clear that PCA is an effective statistical tool for identifying the sources that influence the composition of rainwater.

Table 4.17 Mean and range of parameters for free fall ratio at different land use

Parameters	Rural	Urban	Industrial	Suburban	IS 1050 (1991
рН	5.76 (4.65·7.01)	6.03 (5.04-7.08)	5.66 (4.87-7.14)	5.94 (4.90-6.63)	6.5-8.5
Alkalinity (mg/l as CaCO3)	10 (8-12)	8 ((6-20)	20 (15-30)	10 (5-20)	200
Turbidity (NTU)	0.2 (0·0.4)	0.8 (0·0.9)	1.3 (1.4)	0.8 (0-1)	5
Total hardness (mg/l as CaCO3)	2.94 (0-90)	3.02 (0-9.95)	3.72 (1-12.94)	3.68 (0-10.40)	300
Conductivity	14.21 (1.4-7.01)	17.06 (4.9-39.30)	14.29 (2-31.80)	14.82 (4.5-38.30)	
Calcium hardness (mg/l.)	1.66 (0-6)	2.99 (1.4.98)	2.199 (0-10.95)	2.16 (0·8)	75
Sulphate (mg/l)	0	0	0	0	200
Nitrate (mg/l)	0	0	0.0003 (0-0.0004)	0.01 ((0.0.02)	45
lron (mg/l)	0.061 (0-0.40)	0.044 (0-0.27)	0.0364 (0-0.180)	0.055 (0.0.34)	0.3
Copper (mg/l)	0.0623 (0-0.34)	0.049 (0-0.22)	0.0588 (0-0.20)	0.0404 (0-0.20)	0.05
Sodium (mg/l)	0.627 (0-0.34)	0.35 (0-0.80)	0.554 (0-2.4)	0.656 (0-3.40)	500
Potassium (mg/l)	0.282 (0-1.20)	0.26 (0·0.60)	0.191 (0-0.60)	0.189 (0-0.60)	
Cadmium (mg/l)	BDL	BDL	BDL	BDL	0.01
Cobalt (mg/l)	BDL	BDL	BDL	BDL	0.01
Nickel (mg/l)	BDL	BDL	BDL	BDL	0.02
Lead (mg/lit.)	BDL	BDL	BDL	BDL	0.01
Mercury (mg/l)	BDL	BDL	BDL	BDL	0.001
Zinc (mg/l)	0.02 (0.01-0.03)	0.02 (0.01-0.03)	0.03 (0.01-0.06)	0.07 (0.04-0.09)	5
Total coliform MPN/100ml	230 (<3.760)	460 (5-1100)	45 (0-120)	460 (0-570)	0

Table 4.18 Mean and range of parameters for free fall rain at selected sites

Parameters	This study (sub-urban)	Trichur, Kerala	lle-lfe, Nigeria <sup>b</sup>	Kefalonia, Island Greece°	Selanfor, Malaysia <sup>d</sup>
рН	5.94 (4.90-6.63)	6.52 (6.12-6.77)	6.68 (6.45-7.15)	(7.63-8.80)	5.90 (5.00-6.60)
Alkalinity (mg/l as CaCO3)	10 (5-20)	20.89 (16-24)	3.20 (0.50-7.00)	(6.00-48.00)	
Turbidity (NTU)	0.8 (0-1)	4.3 (0-23.0)	6.3 (1.7-9.5)		3 (2.0-5.0)
Total hardness (mg/l as CaCO3)	3.68 (0-10.40)	22.0 (12.0-40.0)	2.5 (1.7-3.9)	(24.0-74.0)	
Conductivity	14.82 (4.5-38.30)	20.89 (16.00-24.00)	10.40 (15.70-16.50)	(56.00- 220.00)	13.70 (6.60-33.00
Calcium hardness (mg/l)	2.16 (0-8)	15.5 ( < 0.12·42.4)	0.77 (0.53-1.1)	(10.62-19.2)	••
Sulphate (mg/l)	0	6.50 (0.00-20.00)	0.50 (0.00-1.27)	(1.00-13.00)	
Nitrate (mg/l)	0.01 (0.0.02)	3.83 (0.75-11.34)	0.86 (0.00-2.77)	(5.28-13.02)	
lron (mg/lit.)	0.055 (0-0.34)	< 0.050		(0.006-0.040)	
Copper (mg/l)	0.0404 (0-0.20)	<.01		( < 0.006- 0.040)	
Sodium (mg/lit.)	0.656 (0·3.40)	0.44 (0.00-2.80)	0.21 (0.10-0.34)	(2.00-11.00)	
Potassium (mg/l)	0.189 (0-0.60)				
Cadmium (mg/l)	BDL	< 0.001		{ < 0.0001· 0.00019}	
Cobalt (mg/l)	BDL				
Nickel (mg/l)	BDL				
Lead (mg/lit.)	BDL	< 0.01			0.20 (0.04-0.52)
Mercury (mg/l)	BDL				
Zinc (mg/l)	0.07 (0.04-0.09)	0.060 (0.058-0.062)		( < 0.010- 0.077)	0.034 (0.015- 0.060)
Total coliform MPN/100ml Meera V (2007	460	239 (( < 3.750)		(0-570)	<3

<sup>&</sup>lt;sup>a.</sup> Meera, V. (2007), <sup>b.</sup> Adeniyi & Olabanfi (2005), <sup>c.</sup> Sazakli et. al. (2007, <sup>d.</sup> Yaziz et al. (1989).

## 4.4 Quality of rainwater

As stated earlier, the quality of rainwater is important as it is the source water in all dometic rainwater harvesting systems. The physico-chemical characteristic and the microbiological quality of rainwater collected from the different sampling sites were analysed. Analysis of the rainwater samples collected during June to August 2007 showed that the concentration of Cadmium, Cobalt, Nickel, Lead and Mercury were below the detection limits, at all locations of study. The concentration of Zinc with in permissible limits at all locations hence further analysis for heavy metal concentration was not conducted. The test results are tabulated and the mean values are reported in Table 4.17.

Comparison with IS 10500 (1991) drinking water quality guidelines indicate some departure, for parameters pH and bacteriological quality for rainwater collected from all locations of study. As per IS 10500 (1991), the pH of potable water should be in the range 6.5 to 8.5 and the total coliforms should be zero. It can be seen from table 4.17 that the pH of the rain water samples are less than the described range and that total coliforms are present in all the four locations. pH varied between 6.03 (for urban) to 5.66 (for industrial), the pH at the industrial location being more acidic than the others. This highlights the importance of rain water quality studies at different land use locations. The copper concentration in rural and industrial location are 0.0623 mg/l and 0.0588 mg/l respectively, slightly greater than the desired limit (0.05 mg/l). The site in the rural area is located near rubber plantation, where pesticides in the form of copper sulphate are used seasonally. Many industries including a pesticide factory is located within 3.5 km radius of the sampling site selected. This could be a possible reason for the high copper concentrations in the rural and industrial site. However, both the rainwater samples have concentrations within 1.5 mg/l, which is given as the permissible

limit in the absence of alternate source, as per IS 10500 (1991).

Table 4.18 shows the concentration of different parameters in free fall rain observed in the present study (suburban location) and that reported by other researchers. The values are comparable except for heavy metals concentration. In the present study, heavy metal concentration was below detectable limits. The studies conducted by Yaziz et.al. are much in agreement with the present study except for heavy metals and total coliform.

The study revealed that the rainfall chemistry as well the quality were a true representation of the characterisation of the land use pattern of the sampling site. It can also be concluded, that raw rainwater deviates from the standards for drinking water and hence it is advisable to treat the rainwater before using it for potable purpose.

# VARIATIONS IN RAINWATER QUALITY BY INTERACTION WITH DOMESTIC RAINWATER HARVESTING SYSTEMS

#### 5.1 Introduction

The studies on rainwater samples at different land use locations reveal that the quality of rainwater deviates from the Indian Standard for drinking water quality for some parameters. Rainwater scavenges the atmospheric aerosols contributing to the variation of the quality of rainwater as it reaches the place of collection. This rainwater interacts with the different materials in the process of domestic rainwater harvesting. In Kerala, for the storage of rainwater, in addition to traditional methods, ferrocement tanks are widely used, for the construction of which Ordinary Portland cement (OPC) and Portland Pozzolano Cement (PPC) are used. During the storage of rainwater in cement tank for a long period of time, there is a chance of leaching of cement constituents and heavy metals. This chapter outlines the variation in the quality of rainwater from catchment surface to the storage tank. The results of the experimental investigation carried out to find out the safety of using cement water tank for storing rainwater, is also dealt with.

#### 5.2 Quality of rainwater at various stages of harvesting and storage

Rainwater catchment systems are open to environmental hazards because of the nature of the catchment area. There are several ways contaminants can enter the rainwater system and compromise the water quality. For instance, chemical contaminants may dissolve during precipitation and leach due to characterestics of the rainwater system components while microbial risks can be introduced through bird droppings, or poor collection and storage design.

#### 5.2.1 Rainwater quality from roof catchment

Rainwater samples collected from the PVC down pipe attached to the roof of the Laboratory Block of School of Engineering, Cochin University were analysed and the results are as reported in Table 5.1.

Table 5.1 Quality of rainwater from the roof catchment at sub urban location

Parameters	Mean Value
рН	7.11
Conductivity, μs/cm	36.61
Total Hardness, mg/l as CaCO <sub>3</sub>	7.24
Calcium Hardness, mg/l	6.42
Iron, mg/l	0.05
Zinc, mg/l	0.02
Copper, mg/l	0.04
Sodium, mg/l	0.50
Potassium, mg/l	0.45
Turbidity, NTU	0.8
TDS, mg/l	55
Alkalinity, mg/l as CaCo <sub>3</sub>	10
Sulphate, mg/l	0.6
Nitrate, mg/l	0.001
Total Coliform, MPN/100ml	1000
	<u> </u>

A comparison with Table 4.17 shows that, on interaction with the roof catchment surface (concrete), there is a drastic change in the quality of rainwater with an increase being noticed in almost all parameters. pH has

increased from 5.76 to 7.11 and conductivity from 14.21 µs/cm to 36.61 µs/cm (2.6 times). Measure of conductivity is an indication of the amount of dissolved solids in the water sample, hence it is obvious that the increase in dissolved solids is from the interaction with the roof catchment surface. Analysis of water samples from the roof catchment showed that all physico-chemical quality parameters met the IS guide lines. A large increase in total coliform from 230 MPN/100 ml to 1000 MPN/100 ml is noticed, which indicates that the microbial quality of the roof harvested rainwater has deteriorated and does not meet the IS guide lines

### 5.2.2 Quality of stored rainwater.

A rainwater harvesting tank was constructed near the sampling site No-4 (CUSAT campus, Kalamassery), with a view to assess the quality of harvested rainwater upon storage and to act as a supplementary source of non-potable water (for WC flushing in the toilets of laboratory Block)

#### 5.2.2.1 Sizing of the tank

The tank used to store water in a roof water harvesting system is usually its most expensive component .Sizing a tank means choosing the best compromise between good performance and low cost. In calculating the performance of a DWRH system (and how it varies with size of tank), we need to first decide what demand is going to be put on the system. The three most common demand strategies are

Constant demand- a fixed amount, which we can call 'standard' demand, is drawn each day until the tank runs dry

Adaptive demand- a fixed ('standard') amount is drawn whenever the tank is between 1/3 and 2/3 full. This demand is increased by one third whenever the tank is more than 2/3 full, but is reduced by one third whenever the tank is less than 1/3 full.

Seasonal-varied demand-a large amount might be withdrawn in traditionally wet months and a lower amount in traditionally dry months.

Of these three demand patterns, the second ('adaptive') is usually the best from an economic point of view. Hence this was chosen.

The method for tank sizing is based on a procedure as given below (Thomas et.al.2007). It is assumed that the users manage their water with an adaptive strategy-drawing more, when the tank is nearly full than when it is nearly empty.

• The average daily run-off (ADR) is calculated as follows

ADR in litres/day= (roof area in m 2) X (local annual rainfall in mm)/430 (the number 430 takes into account days in a year and 0.85 roof runoff coefficient.ADR worked out to be 1422.63 l/day.

• A suitable climate zone is selected.

Zone A-Uniform rainfall zone

Zone B-bimodal rainfall zone

Zone C-unimodal rainfall zone

Zone D-Monsoon zone

The climate of the area under consideration falls under zone –B category with two wet seasons each year and not more than three successive dry months.

• Design objective is to be decided.

Design objective III is selected which gives 85% satisfaction and medium cost

 A recommended tank size N (which is listed in days) is read off from the Table 5.2 (Thomas et.al.2007). The tank size V in litres is worked out as ADR x N . The basis of design in column 1 is to get the highest satisfaction for the money spent. The basis of design in column II to IV is to achieve

some particular level of demand satisfaction. This is the fraction (of the water the user chose to demand of the roof water system) that the user actually gets in an average year. Based upon that, the volume of the tank is 19916.79 litres. This method, based on adaptative strategy is much more realistic than the constant demand method.

Table 5.2: R	ecommended tank size, N in days (Thomas et.al.,2007)
Climate zone	Objective of design

Climate zone  Zone A  Uniform humid	Objective of design						
	l shortest pay back	II Low coast satisfaction = 70%	IIII Medium cost satisfaction = 85%	IV High cost satisfaction 97%			
	N < 5 days	N < 5 days	N= 5days	N = 15days			
Zone B Two dry seasons	N < 5 days	N = 6 days	N = 14 days	N = 60 days			
Zone C One dry season	N < 5 days	N = 8 days	N = 40 days	N = 160 days			
Zone D Monsoon	N < 5 days	N = 13 days	N = 80 days	N = 220 days			

## 5.2.2.2 Quality of the rainwater in storage tank

A ferrocement storage tank of capacity 20,000 litres was constructed in the School of Engineering Campus, the details of which are given in Sec3.3.2.1. The tank, which was properly cured, received the first southwest monsoon, six months after construction. The first flush was diverted and the rainwater falling on the roof was collected and analysed for various physicochemical and micro biological parameters. The results of the quality of roof harvested rainwater are reported in Table 5.3.

A comparison of Table 5.3 and 5.2 reflects the changes in the quality of the roof harvested water on interaction with the storage material of the tank. The conductivity increased from 36.6 µs/cm (for roof harvested water)=to-

 $104.65~\mu s/cm$  (for roof harvested stored water), clearly indicating that the leaching of cement constituents into water has increased the concentration of dissolved solids. The pH of stored water showed a slight increase 7.11 to 7.4. Significant variation was observed for alkalinity, hardness, zinc and total coliforms. The increase may be attributed to the dissolution of cement from the newly constructed ferrocement tank Table 5.3 also brings out that physicochemical quality of harvested rainwater has improved upon storage and were within the prescribed limits of potable water.

**Table 5.3** Quality of roof harvested rainwater in the new storage tank at CUSAT

	Mean	Value	
Parameters	6 Months after construction	7 Months after construction	
рН	7.4	6.8	
Conductivity, µs/cm	104.65	80.52	
Total Hardness, mg/l as CaCO3	13.00	2.00	
Calcium Hardness, mg/l	3.2	0.32	
Iron, mg/l	Traces	Traces	
Zinc, mg/l	0.06	0.03	
Copper, mg/l	NIL	Nil	
Sodium, mg/l	0.1	0.65	
Potassium, mg/l	0.6	0.18	
Turbidity, NTU	0.75	0.50	
TDS, mg/l	74.18	52.0	
Alkalinity, mg/l as CaCo <sub>3</sub>	46	8.0	
Sulphate, mg/l	NIL	Nil	
Nitrate, mg/l	Traces	Nil	
Total Coliform , MPN/100ml	460	300	

Microbial quality was found to improve on storage, as is evident from the total coliform count given in Tables 5.2 and 5.3. The total coliform decreased from 1000 MPN/100ml for roof harvested rainwater to 300 MPN/100ml upon storage. According to Spinks et al, (2003) the improvement in water quality upon storage was attributed to a number of processes that operate in a tank, including accumulation of microorganisms at the surface air-water interface (the water surface micro layer), flocculation and settlement in the tank, and the action of bio films.

# 5.2.3 Quality of harvested rainwater from different land use locations

In order to evaluate any significant variations in roof harvested rain water stored in tanks that are put into use in the field, at different land use locations, rain water samples were collected as per the details given in Sec. 3.3.2.2 and analysed. The results are as reported in Table 5.4. It can be seen from Table 5.4 that the quality of roof harvested rainwater on storage shows a deviation from the Indian Standards only for bacteriological quality. The conductivity of the harvested rainwater in urban and industrial locations were 112.5μs/cm and 124.5μs/cm compared to 42.9 μs/cm for sub urban and, 61.40 μs/cm for rural location respectively. Alkalinity, total hardness and turbidity also showed the same trend. The tank at the urban location is near to a state highway, while that the industrial location has industries in the vicinity (within 4-5km)

Table 5.4 Quality of harvested rainwater at various land use locations

	Land	use pattern		
Parameter	Rural	Urban	Industrial	Sub urban
рН	7.49	7.43	8.47	7.68
Conductivity, µs/cm	61.40	112.5	124.5	42.9
Total Hardness, mg/l as CaCO3	24.0	47.0	35.0	14.0
Calcium Hardness, mg/l	21.0	47.0	30.0	11.0
lron, mg/l	0.03	0.09	0.04	0.05
Zinc, mg/l	0.02	0.02	0.03	0.07
Copper, mg/l	0.07	0.035	0.045	0.05
Sodium, mg/l	2.40	2.10	6.80	0.10
Potassium, mg/l	1.0	1.60	6.40	0.60
Turbidity, NTU	NIL	NIL	0.8	0.8
TDS, mg/l	91.0	76.82	88.0	64.0
Alkalinity, mg/l as CaCo₃	35.0	54.0	60.0	8.0
Sulphate, mg/l	NIL	NIL	0.8	NIL
Nitrate, mg/l	0.0005	NIL	Traces	Traces
Total Coliform, MPN/100ml	1100	3	20	1100

# 5.3 Comparison of quality of harvested rainwater with other conventional sources

Table 5.5 shows the quality of water collected from open wells and piped water supply from different locations. A comparisons of Table 5.4 and 5.6 shows that the physico-chemical quality of harvested rainwater at all locations compare well with the important sources of drinking water-well and piped water supply. One interesting observation is that the pH value of well water at all locations was less than 6.5.

**Table 5.5** Quality of water collected from open wells and piped water supply at different locations

		Open cut well				Piped water supply			
Parameter	Rural	Urban	Industrial	Sub urban	Rural	Urban	Industrial	Sub urban	
рН	5.72	6.29	5.17	4.7	6.51	6.26	6.93	6.68	
Conductivity, µs/cm	90.7	41.8	125.3	167.5	55.0	56.2	75.5	47.3	
Total Hardness, mg/l as CaCO₃	19.0	19.0	38.0	19.0	23.0	21.0	21.0	11.0	
Calcium Hardness, mg/l	8.0	14.0	30.0	9.0	10.0	14.0	18.0	6.0	
Iron, mg/l	0.015	0.03	NIL	NIL	0.13	0.20	0.02	0.10	
Zinc, mg/l	0.03	0.02	0.03	0.07	0.02	0.03	0.03	0.06	
Copper, mg/l	0.03	0.075	0.085	NIL	0.045	0.04	NIL	0.03	
Sodium, mg/l	7.6	2.0	5.7	6.4	2.3	0.20	3.50	2.90	
Potassium, mg/l	3.1	1.1	4.5	3.1	1.20	1.0	0.90	8.90	
Turbidity, NTU	0.1	0.08	1.8	0.1	0.30	0.07	0.06	1.1	
TDS, mg/l	20.0	36.0	110.0	70.0	30.0	54.0	64.0	85.0	
Alkalinity, mg/l as CaCo <sub>3</sub>	18.0	8.0	30.0	16.0	24.0	20.0	22.0	40.0	
Sulphate, mg/l	NIL	Traces	NIL	Traces	NIL	NIL	NIL	NIL	
Nitrate, mg/l	0.0002	0.002	0.002	NIL	Traces	NIL	NIL	0.004	
Total Coliform, MPN/100ml	460	1100	7	460	460	NIL	NIL	NIL	

## 5.4 Studies on leaching of cement constituents

## 5.4.1 Effect of leaching on the pH

One important, perhaps the most important, effect of leaching is a rise in the value of the pH. The variation in pH of water in which OPC and PPC cement mortar cubes were immersed, with time is shown in Fig.5.1 and Table 5.6. All the samples showed pH above 10, which slightly increased and fluctuated with time. Cement upon hydration becomes gelled silica, alumina, calcium hydroxide and various components derived from them. Calcium hydroxide, being the major component that could be leached, the pH of the medium increases with increasing leaching from the samples. It can also be seen that the variation of pH among PPC and OPC immersed in water samples is not appreciable. However, the pH of PPC samples is slightly higher than that of OPC samples.

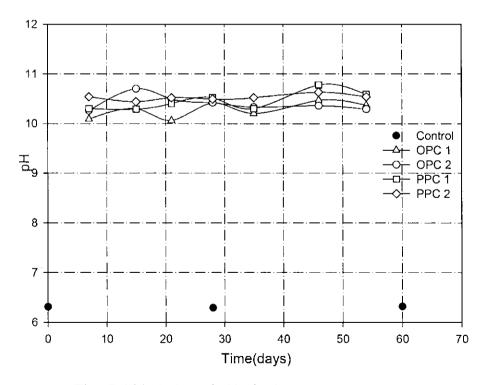


Fig: 5.1 Variation of pH of rainwater on storage

It can also be observed from the Fig.5.1 that the pH of both samples were in between 10 and 11, and that of the raw water is around 6.5. In a solution saturated with calcium hydroxide, the pH would be above 11. This means that the medium is not saturated with respect to hydrated lime solubility is probably limited by the dissolution of surface bound lime.

pH value OPC-2 Elapsed time Control OPC-1 PPC-1 PPC-2 (days) 6.31 0 7 10.09 10.26 10.3 10.54 10.7 10.29 15 10.3 10.44 21 10.06 10.49 10.4 10.52 28 6.29 10.42 10.42 10.52 10.49 35 10.2 10.33 10.3 10.52 46 10.47 10.36 10.78 10.63 54 10.37 10.29 10.59 10.54 60 6.32

**Table 5.6** Variation of pH with time

It is generally accepted that, for health reasons, the value of pH at the point of delivery should not exceed 9.5, but values well in excess of 10, or sometimes even more, have been found. Occasionally, there have been complaints about skin irritation developed by contact with such water (Douglas et al., 1996).

#### 5.4.2 Electrical conductivity as a measure of leachability

Figure 5.2 shows the variation of electrical conductivity with time for the control as well as the duplicate samples. The control did not show any significant variation in conductivity. It can be seen from the figure that water in which PPC samples were immersed showed higher electrical conductivity compared to that of OPC samples. This is probably due to the

higher proportion of refractory materials in PPC derived from fly ash. The variation of conductivity with time is tabulated in Table 5.7. As already stated, cement upon hydration becomes gelled silica, alumina, calcium hydroxide and various complex components derived from them. Of these calcium hydroxide readily dissolves and raises the electrical conductivity of the medium. Rate of leaching depends on temperature, surface area exposed to water and turbulence. The variables have been the same in all the experiments. Conductivity is a good estimator of TDS because TDS in mg/l is proportional to the conductivity in micromhos. Based upon that, it can be estimated that TDS of water containing PPC samples was higher than OPC samples, indicating that leachability of PPC is more than that of OPC.

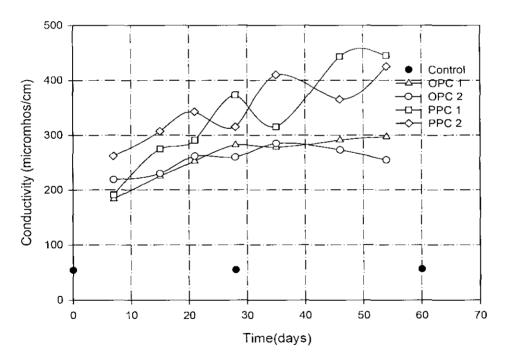


Fig: 5.2 Variation of Conductivity of rainwater with storage

Table 5.7 Variation of electrical conductivity with time

	Electrical conductivity ( µs/cm)						
Elapsed time (days)	Control	OPC-1	OPC-2	PPC-1	PPC-2		
0	54.4						
7		184	219	191	262		
15		225	230	275	307		
21	- I - I - I - I - I - I - I - I - I - I	253	262	291	343		
28	55	282	260	373	315		
35		278	285	315	410		
46		291	273	443	365		
54		297	255	445	425		
60	56.5						

#### 5.4.3 Variation of alkalinity with storage

Variation in alkalinity of water in which OPC and PPC samples were separately immersed is given in Fig.5.3 and Table 5.8. The calcium carbonate alkalinity of the water in which PPC and OPC samples are immersed increased from 17.04 mg/l as CaCO<sub>3</sub> (control) to 55.38 and 57.51 respectively, after a week. The rainwater with alkalinity of 17 can be considered as very low alkaline water. It can also be seen from Table 5.8 that after a period of 54 days, the alkalinity of water in which PPC and OPC mortar cubes are immersed were 85.2 and 108.6 mg/l as CaCO<sub>3</sub> respectively, a five fold and six fold increase compared to the control. Eventhough the alkalinity of water containing PPC is 108.6 mg/l as CaCO<sub>3</sub>, it is well within the limiting value of 200 mg/l.

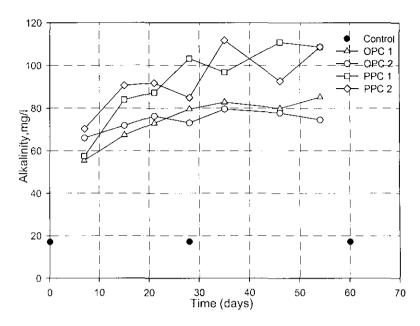


Fig: 5.3 Variation of Alkalinity of stored rainwater with time

Table 5.8 Rate of leaching of PPC and OPC samples with reference to alkalinity

Elapsed time (days)	Alkalinity (mg/l as CaCO3)		Percentage in the previous	
Ziapoda (imo (adrjo)	PPC	OPC	PPC	OPC
0	17.04	17.04		
7	55.38	57.51	225	238
28	79.55	103.2	43.6	79.4
54	85.2	108.6	7.1	5.2

Another interesting observation is that with increase in time, the rate of leaching decreases. It is evident from Table 5.8 that the increase in alkalinity of water due to leaching of cement mortar cubes is more pronounced in the initial stage (ie., the filling of water for the first time after construction of tank).

### 5.4.4 Effect of storage on hardness of water

Tables 5.9 and 5.10 give the variation of calcium hardness and total hardness with time. It can be seen that, though there is an increase in the hardness of the samples, the total hardness is within the limit the effect of storage on Ca hardness and total hardness of water is given in Fig.5.4. According to the hardness alkalinity relationships, if the alkalinity is less than the total hardness, then the alkalinity equals the temporary hardness. If the alkalinity is greater than the total hardness, then all hardness is temporary. It is quite evident from discussion that, the alkalinity of the water containing submerged PPC and OPC blocks is higher than the total hardness and hence all hardness is temporary, which is due to bicarbonates.

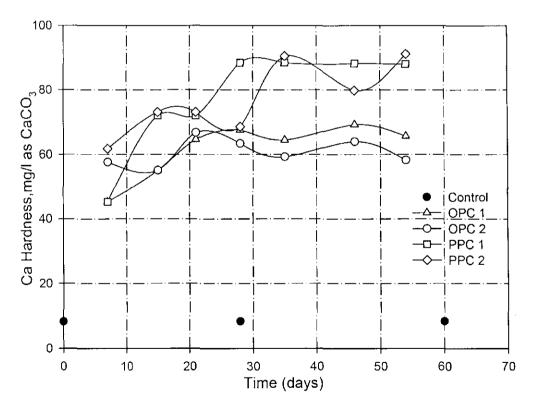


Fig: 5.4 Variation of Ca Hardness of rainwater on storage

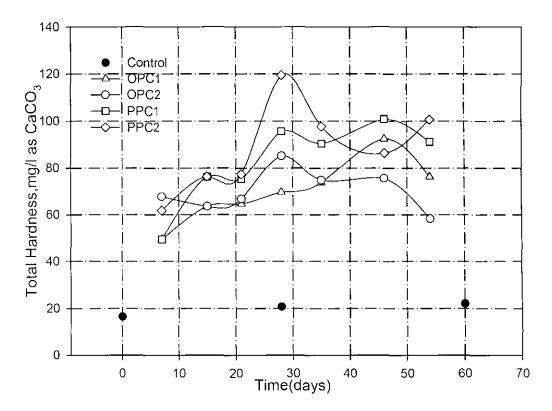


Fig: 5.5 Variation of Total Hardness with Time

Table 5.9 Variation of Calcium Hardness with time

Ca Hardness (mg/l as CaCO <sub>3</sub> )						
Elapsed time (days)	Control	OPC-1	OPC-2	PPC-1	PPC-2	
0	8.24					
7		45.32	57.68	45.32	61.8	
15		55.12	55.12	72.08	73.14	
21		64.66	66.78	72.08	73.14	
28	8.32	67.6	63.44	88.4	68.64	
35		64.46	59.28	88.4	9.48	
46		69.3	64.04	88.2	79.8	
54	· · · · · · · · · · · · · · · · · · ·	65.72	58.3	87.98	91.16	
60	8.32				-	

Total hardness (mg/l as CaCO₃)						
Elapsed time (days)	Control	OPC-1	OPC-2	PPC-1	PPC-2	
0	16.48					
7		49.44	67.80	49.44	61.8	
15		63.6	63.6	76.32	76.32	
21		64.66	66.78	75.26	77.38	
28	20.80	69.68	85.2	95.25	119.44	
35		73.84	74.88	90.48	97.76	
46		92.4	75.59	100.80	86.35	
54		76.32	58.3	91.16	100.7	

Table 5.10 Variation of total Hardness with time

### 5.4.5 Variation of sulphate upon storage

22.1

60

Sulphate is derived from the minerals used in the manufacture of cement. Gypsum is added to control the setting time. The variation of sulphate of the water in which OPC and PPC cement mortar cubes are immersed is given in Fig.5.6 and Table 5.11.

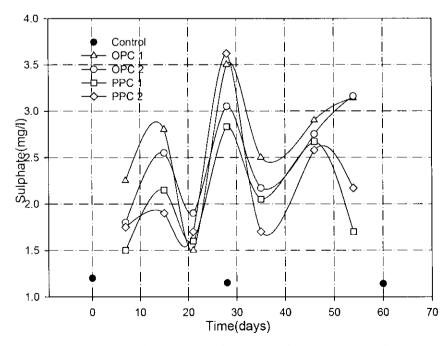


Fig: 5.6 Variation of Sulphate Content of rainwater with storage

Table 5.11 Variation of sulphate concentration with time

Sulphate concentration (mg/l)					
Elapsed time (days)	Control	OPC-1	OPC-2	PPC-1	PPC-2
0	1.3				
7		2.25	1.8	1.5	1.75
15		2.8	2.55	2.15	1.9
21		1.5	1.9	1.6	1.7
28	1.15	3.5	3.05	2.83	3.62
35		2.5	2.17	2.05	1.7
46		2.9	2.75	2.67	2.58
54		3.14	3.16	1.7	2.17
60	1.14			<u> </u>	

#### 5.4.6 Leaching of heavy metals

The concentration of heavy metals in the sample as well as in the leachate are shown in Tables 5.12 and 5.13. ICP-AES was used to measure three typical heavy metals, namely copper, mercury, lead. Detection limits for the three elements are also shown in the table. Twice the detection limit is considered as quantification limit. It is clear from the table 5.12 the concentration of heavy metals are much higher in OPC than that of PPC. This higher concentration in OPC may be attributed in their origin from the minerals used in the manufacture of cement. Interestingly, PPC shows lower concentration of copper and lead, though it contains fly ash.

0.113

0.039

Elements	Sample detection limit (ppm)	Ordinary Portland cement (ppm)	Portland pozzolano cement (ppm)
Cd	0.01	0.907	0.145
Hg	0.1	0.05	0.05

0.05

Ph

Table 5.12 Concentration of heavy metals in the cement used

The cements were leached with dilute hydrochloric acid to extract the metals. Normal cementatious materials dissolve in warm dilute hydrochloric acid. During the manufacture of cement, the temperature in the furnace exceeds 950°C, metals are converted to their oxides which combines with more silica, which is acidic in nature. The metal oxides dissolves in silica forming microbeeds of silica, which is glassy and refractory and cannot be decomposed with warm dilute hydrochloric acid. This is a possible explanation to the low amount of heavy metals present in PPC.

Table 5.13 Concentration of heavy metals (in ppm) in the leachate

Elements	Sample detection limit	Control	OPC-1	OPC-2	PPC-1	PPC-2
Copper	0.01	0.002	0.002	0.002	0.003	0.001
Mercury	0.1	0.01	0.05	0.04	0.06	0.03
Lead	0.05	0.023	0.025	0.025	0.029	0.023

Table 5.13 gives the concentration of heavy metals present in the water in which the cement samples were submerged as well as in the raw water. It is seen that the concentration of the three metals is low in the raw water (control). The concentration in PPC were comparable with that of OPC. Eventhough a slight leaching is evident compared to control water, they are well within the safe limit for drinking water.

#### 5.5 Treatment of harvested rainwater

From the on going discussions, it is clear that the quality of rainwater changes according to land use pattern of the location and interaction with various harvesting systems. The physico-chemical quality of harvested rainwater in the storage tank is well within the prescribed limits, but the bacteriological quality fails to meet the standards laid down by IS. 10500(1991). Hence the harvested rainwater should be treated for making it suitable for drinking purpose. The methods commonly adopted at the household level are boiling and chlorination. A simple method, which is now gaining popularity, is treatment with silver. Silver is known to improve the bacteriological quality of water. The roof harvested rainwater was treated by immersing a silver foil in the water vessel.

The harvested water was left in the container for eight hours and the treated water was tested for bacteriological quality. The total coliform count of the harvested rainwater decreased to zero from 1000 MPN/100ml, thus making the water 100% bacterial free. The silver foil & the experimental arrangement is shown Fig -5.7 and Fig 5.8.



Fig: 5.7 Silver foil



Fig: 5.8 Experimental setup

The advantages of this treatment is outlined as follows

- Provide 100% bacteria free drinking water
- Simple and a safe method for treating water
- No electricity or chemical required
- · No normal side effects and does not impart any odour
- · An in expensive and affordable method
- An environmental friendly method
- · No recurring cost and maintenance
- Suitable for urban as well as rural condition

# 5.6 Quality of rainwater at various stages of harvesting

It is clear from the physico-chemical, microbiological and statistical analysis of rainwater samples that there is significant variation in the quality of rainwater from free fall as it interacts with the various components of harvesting system. The quality of rainwater at various stages of domestic rainwater harvesting at the suburban sampling site is tabulated in Table 5.14.

The pH of the free fall is 5.94 while at the point of exit from the harvesting storage tank it is 6.8. At various stages of harvesting and storage in between these, the pH of rainwater is 7.11, 10.52 and 7.4. The increase of pH from 7.11 to 10.52 is due to the leaching of cement constituents in water. It can be seen that the pH of stored water in the tank is greater if the tank is put to use, soon after curing. It is evident from Table 5.14 that inorder to have a pH with in6.5-8.5, the rainwater storage tank may be put to use, preferably four months after construction. The same trend is seen with all the other parameters also.

Table 5.14 Quality of rainwater at various stages of domestic rainwater harvesting at a suburban location

Parameter	Freefall	Roof harvested rainwater	Soon after curing*		six months after construction	
			1 month of storage	2 months of storage	1 month of storage	2 months of storage
рН	5.94	7.11	10.52	10.54	7.40	6.8
Conductivity µs/cm	14.82	36.61	373	475	104.65	80.52
Total hardness mg/l as CaCo <sub>3</sub>	3.68	7.24	95.25	91.16	13.00	2.00
Alkalinity mg/l as CaCO3	10.00	10.00	79.55	85.20	46.00	8.00
Total coliform MPN/100ml	460	1000	-		460	300

<sup>\*</sup> Results from leaching studies

The study showed that the quality of rainwater satisfied all the physicochemical parameters for potable water at various stages of harvesting except when cement tank is put for storage soon after the curing period. Proper treatment of harvested rainwater is required to improve the bacteriological quality of water. A simple treatment of immersing a silver foil for eight hours in harvested rainwater is found to be make the sample meet the bacteriological quality guidelines of IS 10500 (1991) The study also concluded that tanks made with PPC and/or OPC are safe for storage of rainwater.

# SUMMARY AND CONCLUSIONS

#### 6.1 Introduction

In many parts of the world, the amount of water being consumed has exceeded the annual level of renewal, thus creating a non sustainable situation. The enormity of the water crisis and the need for water conservation can hardly be over emphasised. Government agencies across the globe are introducing policies to promote increased use of directly captured rainwater, as an supplementary source of drinking water. The Government of Kerala has introduced legislation making roof top rainwater harvesting mandatory in all newly constructed buildings in the state. One of the myths about rainwater is that it is considered contamination free, but the fact is that the quality of rainwater depends on many factors such as air quality, rainfall intensity, interval between rainfall events etc. In this thesis, an attempt has been made to study the quality of rainwater at various land use locations and its interaction with domestic rainwater harvesting systems

# 6.2 Conclusions of the study

Rainwater samples were collected from the south west monsoon of May 2007 to north east monsoon of October 2008, from four sampling sites namely Kothamangalam, Ernakulam, Eloor and Kalamassery, in Ernakulam district of the state of Kerala, which characterised typical rural, urban, industrial and

suburban locations respectively. A total of 377 samples were collected, during this period from the sampling sites, taking utmost care in sampling and storage

The samples were analysed according to standard procedures and their physico-chemical and microbiological parameters were determined. Univariate data analysis were conducted for each component for the entire data set and for each sampling site.

The percentage frequency distribution of the pH of rainwater collected at the various land use sampling sites gave interesting results. It was observed that 17.5%, 30%, 45.8% and 12.1% of rainwater samples collected at rural, urban, industrial and suburban locations respectively had pH less than 5.6, which is considered as the pH of cloud water at equilibrium with atmospheric CO<sub>2</sub>.Nearly 46% of the rainwater samples were in acidic range in the industrial location while it was only 17% in the rural location. The sampling site at the sub urban location is within CUSAT campus, where there is a lot of vegetation. In the sub urban location, only 12% of the rainwater samples were in the acidic range, clearly indicating that the quality of rainwater is site specific.

The concentration of ionic species in rainwater had the following order in the entire data set.

$$Ca^{2+} > Mg^{2+} > Na^{+} > HCO^{3-} > K^{+} > H^{+} > Cu^{2+} > Fe^{2+} > NO_{3}^{-}$$

It could be concluded that Ca<sup>2+</sup> is the major contributing factor in the rainwater composition. This is in agreement with the findings of Khemani et.al, (1989), Saxena et.al, (1991) and Kulshrestha et.al, (1996). ie Ca<sup>2+</sup> aerosols seems to be a major component for neutralization of rainwater acidity in most of the Indian sites.

The differences among the precipitation data were studied using multivariate procedure-Principal Component Analysis. The concentration of

the chemical variables to each principal component could be evaluated by studying the loading in the eigen vectors. The high loading of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and Fe<sup>2+</sup>, which are soil oriented ions, confirms a significant influence of terrigenous dust on the composition of rainwater. This could be due to the boom in the construction activities in cities as well as in the country side during the year 2007-2008. The second major source of influence is the atmospheric CO<sub>2</sub>, which is mostly contributed by the increase in vehicle population of Ernakulum district. Waste incineration and biomass burning has an influence on the chemical composition of rainwater, (characterised by K<sup>+</sup> concentration) especially in the urban and sub urban areas of Ernakulam. It is clear that PCA is an effective statistical tool for identifying the sources that influence the composition of rainwater.

The rainwater samples collected at all land use locations satisfied the guidelines of drinking water, as per IS 10500(1991), except for pH and bacteriological quality. Copper concentration in rural and industrial locations were 0.0623 mg/l and 0.0588 mg/l,which is slightly greater than the desired limit of 0.05 mg/l,but within 1.5 mg/l,which is the permissible limit in the absence of alternate source. The site in the rural area is located near rubber plantation, where pesticides in the form of copper sulphate are used seasonally. Many industries including a pesticide factory is located within 3.5 km radius of the sampling site selected. This could be a possible reason for the high copper concentration in the rural and industrial site.

It could be clearly concluded that the quality of rainwater is not contaminant free, It is site specific and represents the atmospheric characteristics of the location of the free fall. The directly captured rainwater could be used for drinking only after proper treatment.

Analysis of rainwater samples harvested from a roof catchment surface and collected from a ferrocement tank constructed in the CUSAT campus showed that these samples satisfied all the physico-chemical parameters (including pH) of drinking water standards as per relevant IS. The microbial quality did not meet the standards pointing to the need of proper treatment of harvested water. A simple treatment of immersing silver foil in the harvested rain water for eight hours proved to be effective in making the water 100% bacteria free and hence potable.

These observations on the leaching of cement constituents in water are quite interesting. When Ordinary Portland Cement and Pozzolanic Portland cement storage tanks are new, there is an increase in pH to 10.5.

Due to leaching of cement constituents, an increase in calcium content and alkalinity was observed, but the concentrations were within limits as per relevant IS .With increase in time, the rate of leaching is found to decrease.

The pH remained almost constant (10.5) for nearly three months, but decreased to 7.2 and 6.8 at the end of six and seven months respectively after construction. If these tanks are put to use, preferably four months after construction, the pH of the harvested rain water will be in the range of 6.5 to 8.5

Another health concern was the leaching of heavy metals from cement. The concentration of heavy metals in water containing PPC and OPC mortar blocks were within the permissible limits. Hence tanks made with PPC and/or OPC are safe for storage of rainwater.

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Estimate of the construction of the rainwater tank at Kalamassery

Capacity-20,000 liters

Diameter-350cm

Height- 210 cm

Wall thickness-3.5 cm

Material/Labour	Quantity	Rate(Rs)	Amount(Rs)	
Cement	25 bags	280	7000/-	
Steel	80 kg	35	2800/-	
Sand	135 cft	45	6075/-	
Gravel	100 cft	20	2000/-	
Metal	40cft	20	800/-	
Charcoal	½ bag	500	250/-	
Solid Block	140 Nos	18	2520/-	
Binding Wire	2 kg	60	120/-	
Chicken Mesh(24 gauge)	5 Roll	580	2900/-	
Weld Mesh (12 gauge)	2 Roll	1600	3200/-	
White Cement	12 kg	20	240/-	
Mason	9 Nos	400	3600/-	
Helper	15 Nos	350	5250/-	

TOTAL <u>Rs: 36,755/-</u>



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