"ENVIRONMENTAL IMPACT OF EFFLUENTS FROM AUTO WORKSHOPS ON ECOSYSTEM OF DOON –VALLEY"

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Contents:

CHAPTER 1

LIST OF ABBRAVIATIONS

AAS (Atomic Absorption Spectrophotometer)

AC (Air Conditions)

AHB (Arobic Heterotrophic Bacteria)

APHA (Ameriacan Public Health Association)

BDL (Below Detectable Level)

BIS (Beuro of Indian Standard)

BOD (Biological Oxygen Demand)

BETEX (Benzene, Ethylebenzene, Toludene, and Xylene)

BW (Bore Well)

cm (Centimeter)

Conc. (Concentration)

COD (Chemical Oxygen Demand)

CV (Crop Value)

CGWB (Central Ground Water Board)

CFU (Colony Forming Unit)

Conc. (Concentration)

DN (Dehradun Control Sites Codes)

DDN (Dehradun Motor Workshop Sites Codes)

DO (Dissolved Oxygen)

DTW (Depth to Water Level)

DPR (Detailed Project Report)

EDTA (Ethylene Diamine Tetra Acetic Acid)

EBT (Erichrome Black-T)

EU (European Commission)

EC (Electrical Conductivity)

FOG (Fat, Oil and Grease)

G. max (Glysine Max.)

GC (Ganga catchment)

GMS (General Mahadev Singh)

gm (Gram)

hrs (Hours)

H.P. (Hand Pump)

HCl (Hydrochloric Acid)

Lube (lubricant)

ICRCL (Interdepartmental Committee for Redevelopment of Contaminated land)

Km (Kilometer)

L (leter)

Lube (Lubricant)

M (Mole)

m (meter)

Max (maximum)

Min (Minimum)

MBT (Main boundary thrust)

MBGL

mg/l (milligram/ liter)

mg/kg (milligram/ kilogram)

µg/l (microgram/ liter)

MSL (Mean Sea Level)

mm (millimeter)

M.W. (Molecular Weight)

N (Normality)

nm (Nano meter)

NW (North West)

NTU (Nephelometer Turbidity Unit)

O.N.G.C. (Oil and Natural Gas Corporation)

PMS (Premium Motor Spirit)

PA (Phenolphthalene Alkalinity)

ppm (Parts per million)

PHC (Petroleum Hydrocarbons)

S.N. (Serial Number)

SE (South East)

S.W. (Surface Water)

SEO (Spent Engine Oil)

SIR (Substrate Induced Respiration)

TA (Total Alkalinity)

T.W. (Tube Well)

TSS (Total Suspended Solids)

TDS (Total Dissolved Solids)

V (Volume)

WD (Water Divide)

LIST OF SYMBOLS

Al (Aluminium) AgNO³ (Silver Nitrate) Ba (Barium) Cl (Chloride) Cr (Chromium) Ca (Calcium) Ca CO³ (Calcium Carbonate) Cd (Cadmium) Cu (Copper) Fe (Iron) HNO³ (Nitric Acid) Hg (Murcury) HCl (Hydrochloric Acid) HCO₃ (Bicarbonate) H2SO⁴ (Sulphuric Acid) K (Potassium) KCl (Potassium Chloride) Na (Sodium) Ni (Nickel) Mg (Magnessium) µ (Micro) Mn (Manganese) Ni (Nickel) NaCl (Sodium Chloride) PbNO³ (Lead Nitrate) Pb (Lead) % (Percentage) V (Vanadium) \overline{Zn} (\overline{Zinc})

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"I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgement has been made in the text.

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THESIS COMPLETION CERTIFICATE

This to certify that the thesis entitled "Environmental impact of effluents from auto workshops on Ecosystem of Doon valley". Submitted by Ms. Mohini Singh to University of Petroleum and Energy Studies Dehradun for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by her under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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CHAPTER 1 INTRODUCTION, OBJECTIVES AND METHODOLOGY

1.1 INTRODUCTION

Increasing awareness for the environment concerns and rising demand for transportation have increased motivations for the studies of the environmental impact of motor vehicles. The rising demand for transportation have Increased the number of vehicles hence motivated a number of studies of the environmental costs of motor vehicle transportation in order to inform public policy. Most of these studies have focused on air pollution, the main environmental externality associated with road transportation, or noise. The background studies indicates that to date however little attention has been paid in the transportation and economics literature to impacts of motor vehicles on soil and water quality. With the help of this research work it is being tried to start to fill the gap for these two problems that could attract considerable scientist and researcher's attention. Unfortunately at the times over the last few years' complete treatment of wastes generated from motor vehicle servicing centers has been a difficult task and challenging steps for the workshops owners.

During the latter part of the $20th$ century there was a change in the general perception of the importance of the soil and water as an environmental component and recognition of the need to maintain or improve the soil's ability to perform the multitude of functions. At the same time there has been recognition that the soil and water are not an inexhaustible resource, and if used inappropriately or mismanaged its original quality may be lost in a relatively short time period, with very limited opportunity for regeneration or replacement, even when if the soil quality is disturbed remediation may not be possible, and its former original condition will be impossible to achieve. This changed perception of the importance of soil as an often key environmental component has arisen against a background where there has long been an understanding of the importance of water and soil in the environmental systems and how they can be damaged. Declines in the quality of these two environmental components are relatively simple to assess because we frequently evaluate them in terms of fitness to drink in the context of water of fitness to breath with air. Further soil and water quality assessments do not seek to attempt to specify a complex integration of static and functionally dynamic chemical, physical and biological factors defining an ideal state for an indefinite number of management and environmental scenarios which is the case with any assessment of soil quality. In contrast to the observed changes in air and water quality, where soil quality has declined the indications of this change may not be readily observable and the consequences of any decline in soil quality may not be experienced immediately. While most countries have national criteria for fitness to drink water and fitness to breathe fresh air, with respect to soil, expect in the most extreme cases, there are rarely such obvious criteria which can be applied and against which the quality of the soil may be judged. Moreover, while it is well known that one gallons of used motor oil are improperly discharged every year in the United States, thus polluting surface waters and coastal areas (EPA 1996).The quality of Soil and ground water has deteriorated due to discharge of industrial, sewage, domestic wastes and effluents being generating from automobile workshops. A comprehensive assessment of the impacts of motor vehicle transportation on water quality is at present too complex to be feasible. With the help of this research work an attempt has been done to focused on waste generated from the motor servicing workshops and its impact on soil and ground water quality of the study area. The extent up to which impacts are likely on existing water resources depend upon the baseline quality of the water body and quality of effluent discharge by the industry and the motor vehicle servicing centers.

Pollution makes water physically impure or foul. It alters the natural qualities of water, so that it becomes unsuitable for the uses to which it is normally put to. It can truly now said we exist in a hydrocarbon society. The paradox being that we want the mobility and convenient energy that oil provides but we also want a clean environment. Contaminants may be from a point source or from a wider, diffuse source area, a large number of point sources in an area, such as septic tanks, waste generated from automobile servicing centers, used motor oil etc can combine to give an impact that is similar to a diffuse source. The type of release (for example, spills at the surface, leakage from underground tanks or injection through bores) can affect the concentration and extant of contamination.

The soils pollution by heavy metals from automobile sources could be a serious environmental problem. These metals can be released by different operational processes of the road transport such as combustion, component wear, fluid leakage and corrosion of metals. Cadmium, Lead, copper and zinc are the major metals pollutants of the roadside soil and water system and may be released from leakage of oils, fuel burning, wear out of tiers, corrosion of batteries and

metallic parts such as radiators etc. Most of the heavy metals are toxic to the living organisms and even those considered as essential can impair important biochemical processes posing a threat to human health, plant growth and animal life (Jarup 2003., Michalke 2003., Silva et al 2005).

As population increased and technology improved and expanded, more significant and wide spread problems (environmental pollution) arose causing a continuing and accelerating decline in the quality of the environment and its ability to sustain life. However, level of these metals in the environment has increased tremendously in the past decades as a result of human inputs and activities.

The impact of pollution from automobile wastes has reached a disturbing level. Environmental contaminants are widely distributed in soils, thereby having effect on the trophic chain, plants, animals and man. These pollutants can remain in soil for a longtime. Trace metals are naturally present in the biological world in acceptable quantities, but increase of these through anthropogenic contributions.

Improper disposal of oil wastes is one of the serious causes of ground water contamination. It not only enters the subsurface and contaminates the fresh water reservoirs, but also they tend to be carried over or washed away with rain or flood thereby reaching the local water body. If they enter the water bodies then due to their toxicity they can kill the aquatic creatures and disturb the balance. These waste oils contains large variety of chemicals which tends to remaining in our ecological system for longer duration thereby continuously affecting the living organisms coming in contact with them. The most easiest way by which such waste's are disposed are, dumping them into storm water pits, or canals ,gutters, rivers. It has been observed that most of the time, shop owners just allow the waste to penetrate into ground as it cost them much to buy a special container to hold the waste due to their small operational volume.

If these compounds enter ground water, the public can be exposed in a variety of ways. The most serious risk of exposure is through the consumption of contaminated ground water, but exposure may also occur through the direct contact to the skin or by breathing in water vapor. For example, overexposure to 2-Butoxyethanol, a compound found in some cleaning solvents, often results in irritation of the skin, eyes, throat and nose, as well as destruction of red blood cells. Tetrachloroethylene and perchloroethylene (chlorinated compounds) are often found in

brake cleaning solvents. Overexposure to these compounds may result in eyes, nose, and throat irritation, nausea, dizziness, incoordination, headache, drowsiness, and liver damage. There is also evidence suggesting the carcinogenicity of these compounds. Ethylene glycol and diethylene glycol are extremely harmful compounds found in antifreeze.

Ingesting either of these compounds may result in stimulation of the CNS (Central Nervous System) followed by depression; vomiting; coma; respiratory failure; convulsions; and possibly death. In addition to these potential human health threats, motor vehicle wells also cause soil and ground water contamination that may threaten aquatic ecosystems that depend on ground water.

Regardless of the types of oil, whether it is engine oil, gear oil, or branded motor oil such as Mobil 1 oil etc. they all have one thing in common that they are hazardous once used and disposed of irresponsibly. Often, the types of waste fluids that are used to clean parts used motor oil, coolant, and other fluids can be characterized as hazardous and/or dangerous wastes. The waste fluids, if washed down a drain and into a motor vehicle waste disposal well, could pose a serious risk to human health if ground water were to become contaminated.

Soil has become the reservoir for environmental pollutants resulting from various processes such as spills, leaching and deposition (Outridge et al., 2002., Akinola and Adedeji, 2007). Important pollutants found in the soil include heavy metals which are released into the environment through natural and majorly anthropogenic sources (Jung, 2008). The concentration of these metals in the soils in a particular place are influenced by its elemental constituents and quality of heavy metal of the soil as well as the elements of the vegetation (Popa and Jitaru, 2005). Furthermore, the poor degradation and bioaccumulation strength of these metals entrench their sequestration in the environment (Ram et al., 2000., Okunola et al.,2007). Though they are less harmful at certain concentrations however, when the standard limits are exceeded, some of them may be carcinogenic, mutagenic and tetragenic to man and animals (Byrdy and Caruso, 1995; Heitkemper and Caroso, 1991., Olson et al., 1992).

Soil ecosystem is an essential component of life and man depends on it for their growth. It is also a medium for the biochemical cycling of soil nutrients. So as the soil is being contaminated with all manner of pollutants, the life process is being disturbed and hence there may be imbalance in the whole ecosystem.

Wide varieties of waste generated from human activities are dumped on soil (Adeoye et al., 2005). Soils have long being used as dumped sites for household and commercial wastes (Uchegbu, 2008). Wastes containing heavy metals, if disposed on agricultural soils or around residential areas can enter into food chain (Ademoroti, 1996). Animals that forage on the vegetation of the heavy metals polluted soils are also in danger. Soils affected by heavy metals suffer degradation due to impairment of physicochemical, biological and minarological properties., hence undermine its agricultural potential (Mbagwu, 2008).

When petroleum products are released to the environment, physical, chemical and biological processes change the contaminated site. Petroleum hydrocarbons released to the ground may move through the soil to the groundwater. (Riccardi et al. 2008., Pawlak et al. 2008., Wang et. al 2002). Individual contaminant compounds at the site may be separate from the original mixture, depending on the chemical properties of compounds. Some of these compounds evaporate into the air (Laskova et al. 2007., Paulauskiene et al.2009) and others will dissolve into groundwater and move away from release area. Other compounds will attach to particles in the soil and may stay in the soil for a long time, while other will be broken down by the organisms found in the soil (Research Triangle Institute 1999).

Petroleum hydrocarbons (PHCs) are common site contaminants but they are not generally regarded and hence regulated as hazardous wastes. Petroleum hydrocarbons indicate degradable and biodegradable properties in soil, water and sediment environment (Fedorak, Westlake 1981., Mills 1994., Prince et al. 1994., Leathy, Colwell 1990). The hydrocarbon analysis can be used for the environmental assessment of remediation (Douglas et al. 1991) or soil bioremediation (Korda et al. 1997., Jogensen et al 2000).

Growing concern about reclamation of auto-repair workshops, fuel filling stations or vehicle parking areas for residential and agricultural purpose make risk assessment of heavy metals and petroleum contaminants of the study area imperative.

Heavy metal contamination of urban topsoil has been a major concern regarding their toxicity, persistence and non-degradability in the environment. Adverse effects of elevated concentration of heavy metals to soil functions, soil microbial community composition and microbial growth have long been recognized under both field and laboratory conditions. Heavy metal contamination of urban topsoil usually derives from anthropogenic sources such as emissions from automobile exhaust, waste incineration, land disposal of wastes, use of

agricultural inputs, emission from industrial processes and wet and dry atmospheric deposits. There has been little attention vicinities.

The mobilization of heavy metals into the biosphere by human activity has become an important process in the geochemical cycling of these metals. This is acutely evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere and soil, exceeding the natural emission rates (Nriagu, 1989., Bilos et al., 2001). Soil ecosystem is an essential component of life and man depends on it for their growth. It is also a medium for the biochemical cycling of soil nutrients. So as the soil is being contaminated with all manner of pollutants, the life process is being disturbed and hence there may be imbalance in the whole system.

As per the latest estimate of Central Pollution Control Board, about 29,000 million litre/day of wastewater generated from class-I cities and class-II (study area belongs to class II) towns out of which about 45% (about 13000 mld) is generated from 35 metro-cities alone. The collection system exists for only about 30% of the wastewater through sewer line and treatment capacity exists for about 7000 million litre/day. Thus there is a large gap between generation, collection and treatment of wastewater. A large part of un-collected, un-treated wastewater finds it way to either nearby surface water body or accumulated in the city itself forming cesspools. In almost all urban centres cesspools exist. These cesspools are good breeding ground for mosquitoes and also source of groundwater pollution. The wastewater accumulated in these cesspools gets percolated in the ground and pollute the groundwater. Also in many cities/towns conventional septic tanks and other low cost sanitation facilities exists.

Pollutants are being added to the groundwater system through human activities and natural processes. Waste disposals from motor servicing centers are being dumped near the automobile workshop, and are subjected to travel with surface runoff and may percolate into aquifers. The percolating water receives a huge amount of dissolved contaminants and reaches the aquifer system and finally contaminates the groundwater. The problem of groundwater pollution in several parts of the country has become so acute that unless urgent steps for abatement are taken, groundwater resources may be damaged.

The quality of groundwater depends on a large number of individual hydrological, physical, chemical and biological factors. Generally higher proportions of dissolved constituents are found in groundwater than in surface water because of greater interaction of ground water with various materials in geologic strata. The water used for drinking purpose should be free from any toxic elements, living and nonliving organism and excessive amount of minerals that may be hazardous to health. The contamination of groundwater by heavy metals has assumed great significance during recent years due to their toxicity and accumulative behavior. These elements, contrary to most pollutants, are not biodegradable and undergo a global ecobiological cycle in which natural waters are the main pathways. The determination of the concentration levels of heavy metals in these waters, as well as the elucidation of the chemical forms in which they appear is a prime target in environmental research today.

A vast majority of groundwater quality problems are caused by contamination, overexploitation, or combination of the two. Most groundwater quality problems are difficult to detect $\&$ hard to resolve. The solutions are usually very expensive, time consuming $\&$ not always effective. An alarming picture is beginning to emerge in many parts of our country. Groundwater quality is slowly but surely declining everywhere. Groundwater pollution is intrinsically difficult to detect, since problem may well be concealed below the surface $\&$ monitoring is costly, time consuming & somewhat hit-or-miss by nature. Many times the contamination is not detected until obnoxious substances actually appear in water used, by which time the pollution has often dispersed over a large area. Essentially all activities carried out on land have the potential to contaminate the groundwater, whether associated with urban, industrial or agricultural activities. Large scale, concentrated sources of pollution such as industrial discharges, landfills $\&$ subsurface injection of chemicals $\&$ hazardous wastes, are an obvious source of groundwater pollution. The only solution to diffuse sources of pollution is to integrate land use with water management. Once pollution has entered the sub-surface environment, it may remain concealed for many years, becoming dispersed over wide areas & rendering groundwater supplies unsuitable for human uses.

Fats, oil and grease, also called FOG in the wastewater business can have negative impacts on wastewater treatment systems. Blockages in the wastewater collection system are serious, causing sewage spills, manhole overflows, or sewage backups in homes and businesses. These repairs cost money and may lead to higher local wastewater rates, thereby affecting the company's profit margin. There is a combination of four forms in which oil and grease can exist namely, oil dissolved in water, chemically emulsified oil, free oil which is a liquid that floats to the surface of water, and mechanically emulsified oil. Used oil is any oil that has been refined from crude oil or any synthetic oil made from coal, shale or polymer-based starting material. As the name implies, it must have been used, and as a result of such use, it is contaminated with physical impurities (like metal fines, sawdust or dirt) or chemical impurities (like fuel, solvents, halogens or water). Common uses include lubricants and heat transfer fluids. Used oil does include: engine oil, transmission fluid, compressor oil, metalworking oils, hydraulic oil refrigeration oil, and electrical insulating oil. Used oil does not include: vegetable oil or animal oil, even when used as lubricant, virgin (unused) oil, bottom clean-out waste from virgin oil storage tanks, petroleum-derived products like antifreeze or kerosene, and petroleumdistillates used as solvents.

Biological health of soils may be affected both by specific toxic petrochemicals and/or general, physico-chemical alterations to the soil environment wrought principally by high MW hydrocarbons -- for example, hydrophobicity and inhibition of water and soil gas movements. In addition to these confounding constraints, ecotoxicological literature on petrochemicals is limited by 1) the enormous range of organisms that could be potentially be affected, and 2) the preponderance of coarse-scale field studies that involve complex petrochemical mixtures. The following section thus addresses only a few of the better documented effects.

A toxic response in soil is a function of both the inherent toxicity of the contaminant and it's bioavailability. Bioavailability expresses the frequency and intensity of exposure, which, in turn, are regulated by the mobility of both the contaminant and the organism.

Therefore, it is expected that factors regulating *in situ* toxicity of chemicals to soil dwelling organisms will vary with the relative mobility of the organism. Creatures with limited capability for movement in soil (e.g. most microorganisms, plants) tend to be most susceptible to chemicals that can move in the vapour or dissolved phases. Thus toxic chemicals with high water solubility or vapor pressures, for example, BTEX species; tend to affect poorly mobile soil organisms. Chemicals with poor mobility in soil may pose a lesser threat to sessile organisms because 1) exposure may not occur, and if exposure does occur, local detoxification is possible. On the other hand, toxicity to mobile soil organisms (e.g. microarthropods, earthworms) is less affected by contaminant mobility and more affected by structure-activity relationships such as lipid solubility, which is a strong determinant of a chemical's bioaccumulation potential.

Motor servicing workshops and fuel filling stations from the point of view of environmental concerns every site is unique and information on the site's history helps to focus a more detailed investigation. Garages and fuel filling stations are widely distributed throughout the country. Sites range from the small urban and rural petrol stations, with just one or two petrol pump, to large garages with comprehensive workshops offering a complete repair and maintenance service. The larger premises tend to be concentrated along the trunk road network and on the edges of built-up areas, along by-passes and at major road junctions. Specialist repair shops tend to be sited in urban areas. Many private bus companies, road haulage contractors and other large businesses maintain their own repair facilities and fuel storage depots. In addition to activities associated with storage and retail of petrol and diesel, 'added – value' services including car washes are found at most service stations. Petrol filling stations are unlikely to generate significant quantities of waste since their major commodity; petrol is sold on for direct use. However there may be spent oil containers and sludge from petrol storage tanks left on site.

Waste from repair garages may include any, or all of the materials mentioned above. There may be small quantities of used batteries, asbestos from brake linings and spent oil or solvent containers.

Contaminants on a site is largely depend on the history of the site and on the range of materials present there. It is most unlikely that any one site will contain all of the contaminant therefore contamination associated with petrol filling stations and garage repair sites is possible due to the storage and garage repair sites is possible due to the storage, spillage, leakage and disposal of raw materials or waste products. In the past contamination of the ground from spillage was common due to overfilling of faulty pipes or caps etc. Today strict precautions are taken when fuel is delivered and the number of spills has been reduced. However all filling stations are susceptible to spillage occurring due to operator error or equipment failure. Spills may also occur when motorists overfill vehicle tanks.

Ground adjacent to car washes, where these are present on filling stations may be contaminated by the run-off of water which contains oil and greases and some other chemicals used for cleaning. In the past, waste oil and other fluids are likely to have been disposed of down nearby drains or thrown on to open ground. Combustible materials may have been burned on- site along with some of the waste oils.

Petrol and diesel are highly mobile and may migrate to contaminate a wide area. Free product released at the surface or leaking from an underground structure may migrate through ground,

vapor may diffuse into the soil and migrate as a vapor front ahead of free products. Chlorinated hydrocarbons, used as degreasing solvents have low viscosities and are highly mobile. The risk to groundwater from petroleum hydrocarbons and solvents depends on the depth of the water table and the properties of soil. Normally higher the organic matter and clay content within the soil the greater the adsorption of organic compounds and the lower their mobility. Conversely the greatest migration of contaminants will occur in course- grained sands and gravels with little organic contents. The less soluble compounds which become adsorbed on to clay or organic matter may cause water pollution long after the original source has been removed, as a result of the chemical continuing to desorbs into soil-water. Organic compounds may pose a threat to current and potential potable water supplies. Less soluble solvents and spillages of oil hydrocarbons will tend to migrate to the water table. These compounds are usually less dense than water and float on the water table surface whereas denser than water tends to migrate to the bottom of aquifers. They are persistent chemicals and can render groundwater unsuitable for public supply at low concentration. The soluble hydrocarbons may contaminate surface water via run- off or surface discharge of contaminated groundwater.

The movement of metals through soil is significantly retarded by the presence of clay minerals and organic matter. The solubility of some metals (for example copper, zinc, and lead) may increase under acidic conditions.

Vehicle washing areas may also pose a threat of potential contamination if a catchment pit with an interceptor is used. Inadequate drainage systems and spillage of detergents may release potential contaminative chemicals on to the land, surface water and groundwater.

An auto repair workshop is an area of open land allocated to automobile repair workers in the vicinity of an urban center. A typical city has usually 5-6 authorized motor vehicle workshops in proportion to its population and activities, but nowadays some cities have more. Although there has been an increased recognition of the importance of the need to measure and monitor the nature of the soil to derive measures of soil quality.

Contaminated groundwater may be unfit for certain uses and may become harmful to humans, vegetation and property. Treatment of groundwater is usually expensive, and sometimes a contaminated water supply must be abandoned and a new supply located. Preventing contamination before it occurs is the best solution because groundwater contamination can

have such serious consequences, many citizens, as well as local state and federal agencies are taking action to protect groundwater resources.

Petroleum hydrocarbons are common sites contaminants, but they are not generally regarded and hence, regulated as hazardous wastes. PHCs indicate degradable and non-degradable properties in soil, water and sediment environment. Re-refined petroleum products, e.g. gasoline, diesel fuel, used engine oil constitute a major class of contaminants from the point of view of environmental concerns.

The production and use of petroleum has given rise to several environmental problems. Toxic crude oil can be spilled on land or in water, poisoning plants and animals. The burning of fuels derived from petroleum releases toxic gases that pollute the air. Some scientists even believe that the burning of petroleum fuels contributes to global climate change. Spills and seeps. Petroleum can spill during many stages of its production, transportation, and consumption. Petroleum can leak from wells on land or in the sea. Pipelines can break, causing petroleum to spill during transportation. Oil tankers may collide or sink, releasing huge loads of crude oil into the water. Accidents or disasters can cause toxic petroleum products to spill from power plants, refineries, and even gasoline stations. Some petroleum also seeps naturally from openings in the sea floor.

Spills and seeps release about 15 million barrels of crude oil into the environment each year. This makes up only about (1/5) of the oil consumed in one day. About 10 percent of this oil seeps naturally from the ocean floor. Petroleum companies spill about 28 percent of this oil during production and transportation. The remaining 62 percent is released in spills during industrial and private consumption. Gasoline and other petroleum products can enter soils and aquifers from leaking pipelines or storage tanks and from accidents involving tank, trucks, road cars. Most groundwater contamination cases are caused by underground tanks from gasoline stations. The potential contaminants entering groundwater formations from leaking depends on the type of effluent disposed. The main problem of petroleum contamination of ground water is taste. Toxicity is not a problem because the water is already undrinkable due to taste and odour well before concentrations reach to toxic levels.

Many streams receive these disposed wastes. Seepage of such water into underlying groundwater may adversely affect groundwater quality. Urban runoff may infiltrate directly into the ground through pavements after it has reached a stream, or via recharge pits or "dry

wells" constructed for disposal of storm runoff. Movement of contaminated or saline water in inland aquifers, sea water intrusion due to excessive withdrawals in coastal aquifers and recharge of water contaminated by air pollution may also adversely affect groundwater quality.

Protection of natural soil and groundwater quality and management of waste generated from various sources is emerging great public concern in India. People are becoming more conscious about the nature of ground water and its usage with concern for its future utility when affected not only by our waste disposal activity but also by its current uses of extravagance and overexploitation especially in urban areas. An important aspect of urbanization is the increase in demand and creation of potential with possibility of pollution of groundwater.

There has been a tremendous increase in the demand for fresh water due to growth in population. The rapid growth of urban areas has affected the groundwater quality due to overexploitation of resources and improper waste disposal practices. Hence there is always a need for the concern over the protection and management of groundwater quality. It is absolutely necessary to ascertain the potability of water before it is used for human consumption. Thus constant monitoring of groundwater quality is needed so as to record any alteration in the quality and the outbreak of health disorders.

Further, the importance of groundwater in the doon valley can be understood from the situation that 76 % of the total supply of domestic water comes from the groundwater and so far more than 200 tubewells and 250 dugwells have been drilled in the entire Doon valley for the augmentation of drinking and irrigation water supply. Overexploitation of groundwater may lower the water table and reduce the saturated thickness of the aquifers.

Therefore the study of soil and groundwater quality with special reference to waste generated from automobile workshops is being undertaken to understand the geochemical evolution of soil and water and aspects of petroleum product contamination.

A lubricant (sometimes referred to as "lube") is a substance (often a liquid) introduced between two moving surfaces to reduce the friction between them, improving efficiency and reducing wear. They may also have the function of dissolving or transporting foreign particles and of distributing heat. One of the single largest applications for lubricants, in the form of motor oil, is to protect the internal combustion engines in motor vehicles and powered equipment.

According to current statistics, the lube market in India is in the order to 1 million tons per annum, with a prevailing annual growth rate of 3.5%. Since lube oil is the highest-value component of a barrel of crude oil and most of the lube oil gets used only once, it becomes one of the world's largest bulk pollutants for soil, water and air thereby highly contributing to the low quality of life.

Therefore, there is an urgent need to systematically carry out a study to conserve it and use it scientifically, so that emissions are within the prescribed limits $\&$ no suspended particulate matters are ejected in the atmosphere which poses serious environment pollution & wastage of high value lubricants. The automobile industry in India is the ninth largest in the world with an annual production of over 2.3 million units in 2008. In 2009, India emerged as Asia's fourth largest exporter of automobiles, behind Japan, South Korea and Thailand.

Following economic liberalization in India in 1991, the Indian automotive industry has demonstrated sustained growth as a result of increased competitiveness and relaxed restrictions. Several Indian automobile manufacturers such as Tata Motors, Maruti Suzuki and Mahindra and Mahindra, expanded their domestic and international operations. India's robust economic growth led to the further expansion of its domestic automobile market which attracted significant India-specific investment by multinational automobile manufacturers. In February 2009, monthly sales of passenger cars in India exceeded 100,000 units.

A Motor Servicing Centre performs lots of activities which includes all kind of Cleaning, Mechanical, Electrical Work & Denting / Painting. Taking care of Private / Passenger Cars involves heavy utilisation of water resources and the washed away water becomes the source of contaminants in local water bodies. AC servicing and other servicing is also the source of contaminants. Car Wash may be Interior or Exterior Cleaning. Every Motor Company has their own Servicing Centre and the effective utilisation of water resources differs from company to company servicing station. The effluent of the washed water is either disposed to local water bodies or goes underground.

Present study was conducted in Doon valley of Uttarakhand state. Dehradun (Doon valley) is the capital city of Uttarakhand, which is lying between latitudes 29^0 55' and 30^0 30' and longitudes 77° 35' and 78° 24'. Deforestation, urbanization, industrialization have adversely affected geohydrological regime and environment of the NW-SE trending intermontane Doon valley in the sub Himalayan region. The quality of water has severely deteriorated at various

paces of Dehradun. The city has witnessed tremendous growth in the last twenty years (DPR, 2009). After the formation of Uttarakhand state, increase in population rate, urbanization, introduction of new industries and immigration of people for employment has been increased in Uttarakhand especially in Doon valley. Pollutants are increasingly added in soil and water system. Untreated discharge of effluents being generated form motor servicing centres is continuously adding pollutants in the soil and groundwater system. This Waste water generating from motor servicing centres that includes heavy metals, oil and greases and other toxic compounds may deteriorate the ground water quality and also may enter in the food chain through soil and plants and may cause adverse effects on human health.

Dehradun has been tourist place since long time; more than 80% drinking water supply is being taken from ground water resources. After the formation of capital of Uttarkhand state many people came from various state of the country. As per census 2001, Dehradun district had a total population of 12.80 lakh (Census of India 2001). After the formation of capital of uttarakhand the district itself saw a population boom. Dehradun is also a famous township city and hence arrival of tourist in the city have increased from 4.6 lakh in 2000, 9.3 lakh in 2003. This floating population of the city is estimated at 35,000 person per day. After the formation of capital population of the city has drastically changed due to various employments and business purposes which ultimately increased the vehicular populations in the city.

1.2 OBJECTIVES

The present study will be carried out with following objectives:

- Physicochemical assessment of waste water generated from motor servicing centers
- Analyzing pre and post monsoon quality of soil and water chemistry
- To Understand Environmental impact of waste generated of the study area

1.3 METHODOLOGY

Present research work is based on the soil and water quality of in and around the areas of motor servicing workshops in pre and post monsoon seasons. Waste water generated from motor servicing workshops were collected and analysed. Soil samples were also collected and analysed to study the impact of waste on soil quality of the study area. Beside these, some samples from control sites (away from motor servicing workshops) also being collected and analyzed for the reference.

The samples of soil, ground water, waste water being generated from motor workshops and soil of nearby locations of motor workshops are the real representatives of their origin. These samples were collected at a frequency where the important variations, contaminants etc are not lost or over induced. Sampling were done as per standard way by following up methodology of Trivedi and Goel (1986), Ghosh et al., (1983) and standard method APHA (1995).

To identify the major pollutants in soil, drinking water and waste water different samples in contrast sampling seasons i.e. Pre monsoon and postmonsoon were collected and analyzed. Number and locations of sampling sites were selected on the basis of population, vehicular loads, location and source of contamination.

Samples of tubewell and handpump were collected after pumping of sufficient time to flush out any deposited or left over mud, rust or contaminant present in pipes and sampling bottles were fully filled with samples leaving no air space which were kept sealed to prevent any leakage. Each bottle was clearly labeled with the name and address of the sampling locations, sample description and date of sampling. Samples were preserved immediately after the collection by following up standard methods APHA (1995) and Trivedi and Goel.

Soil samples were collected separately with the help of Auger. Every time 500 gm soil was collected from a depth of 0-15 cm from each place of the site and placed in the clean zipped polythene bag (Figure:1.6 and 1.7) and brought to the laboratory for the analysis. A contrasting pair of samples i.e control sites and motor workshops were taken indicating two sapling seasons.

Methodology includes following steps:

- **Field work**
- **Laboratory work**

1.3.1 FIELD WORK

Field work is based on the identified problems and objectives of the research which includes survey of study area and sample collections. Survey were done on the basis of vehicular loads, amount of waste being discharge by motor servicing workshops and number of motor workshops present in the vicinity.

SELECTION OF STUDY AREA

Present study is carried out in Doon valley of Uttarakhand state which is known as an educational hub of the country. Between 1981 to 1991 change in population of doon valley was 21.33% and 21.85% respectively, but it was found after the survey that a sudden jump from 21.85% to 39.73, an increase by 18% in 10 years (from 1991 to 2001) has been seen. The fact behind this was formation of new state in this decade and due to this reason many new departments has been introduced and many people came here from across the country. Dehradun is also known as a famous township city and hence the arrival of tourist in this city has increased from 4.6 lakh in 2000 to 9.3 lakh in 2003.

Doon valley described here conforms to the Dehradun tehsil of Dehardun district having a geographical area of 2245 km^2 , maximum east-west length of the valley is approximately 80 km and the width varies from 2.5 km in the extreme west, 25 km in the central part to nearly 45 km in the east. The terrain is undulating and the altitude range from 315 m to 2,500 m. Dehradun the largest centre among all the urban settlements of hill district of Uttarakhand state and Mussoorie, also known as Queen of hills, have centres of all developmental activities in the region. Availability of infrastructure in these two urban settlements has given impetus to the development of regional linkages and played a vital role in the development of the region. The natural beauty and climate of Doon valley have also provided the potential for a prosperous tourist industry.

The longitudinal valley is drained by the spring fed perennial rivers the Suswa and Asan which contribute to the Ganga and Yamuna forming the eastern doon and the western doon respectively. The drainage pattern is observed in the Suswa and Asan where fanglomerates, doongravels, diluvial terraces, elongated ridges and isolated hillocks have been evolved. Various terraces and uneven terrain are eroded and gullied by fast flowing torrents with higher gradients. The valley forms a geomorphic unit with a geological structure of the lesser Himalaya and the Shivalik mountain ranges separated by a synclinal trough. The valley forms a part of the sub mountain region of the Himalaya and its outer ranges are known as Shiwalik.

Fig 1.1: Study Area Map

Geologically, the valley is divided into

The lesser Himalaya Mussoorie Mountain range in NW and NE parts. I comprises Shimla slates, Jaunsar group and Mussorie group. The synclinal trough comprising Pleistocene and Holocene gravels, doon gravels and Doon valley in the center. The Shivalik range in the south, comprising the lower, middle and upper Shivalik and conglomerates, sandstones shale's and clays.The Dehradun valley is divided into two intra- basins, viz Asan basins and Suswa basins (Western and eastern doons) by the Dehra Asharori low water divide with gradient varying from 10.3 m/106 km to 12.7 m /1.6 km owing to considerable elevation varying 318 m to 242 m. The swift drainage has incised the valley evolving dissected and ravine topography. Doon valley has a humid subtropical climate, its elevations keeps the temperature low, while the wooded Shiwalik hills check the heat waves and dust storms of plain from the south and the lesser Himalaya checks the cold waves from the north. The mountain ranges have temperate and valley has warm climate May to June are the hottest and December to January are the coldest and annual rainfall is 215.9 cm and vegetation in the valley is wide in range – tropical, subtropical and temperate about 50% of the total area lies under the forest.

There are two major drainage lies in the valley viz lesser Himalayan drainage line and Shivalik drainage line. They contribute their water through 23 drainage basin to Asan and Suswa in the western and eastern doons respectively. Suswa rises very nearly opposite Asan river to the left of Saharanpur – Mussoorie highway and flows in the south-easterly direction to discharge. Song rises in the Saklana area of Tehri district near Surkanda peak on Mussoorie chamba ridge. It flows westwards along the northern face of Ladwakot – Paled - Maidan ridge and forms the boundary between Tehri and Dehradun Forest Divisions. In the centre of the valley the doon aquifer zone occurs. The streams contributing their water to Asan are Jiwangarh, Sitla, Swarna, Kalikad, Kalota, Tons, Bhitarli, Kaikurli, Nun, Nimmi, Arnigad, and Chorkhala from northwest part of the lesser Himalayan Drainage line. The Asan meets the Yamuna in eastern doon, the NE lesser Himalayan drainage line gives rise to Bindal, Baldi, Bandal, Rispana, Song, Jakhan, Lalpani, Chandrabhaga and Dholani.

SAMPLE COLLECTION

Sample of soil, ground water and waste water generating from auto workshops were collected in two comparative seasons i.e. Premonsoon and post monsoon. Sampling design has been grouped in three categories:

- 25 Ground water samples
- 25 Soil samples from nearby locations of ground water resources
- 25 Waste water samples generating from motor servicing workshops
- 25 Soil samples from nearby locations of motor servicing workshops

Fig1.2 Map of Motor Servicing Workshops in the Dehradun City

Ground water samples were collected from tubewells, handpumps and borewell. Waste water samples were collected from discharge point of the motor servicing workshops (figure-2) Soil samples were collected from nearby locations of motor servicing workshops and rural areas of the Dehradun district mostly closed to the ground water resources.

Fig. 1.3: Satellite Image of Study Area Showing Motor Servicing Workshops and Sampling Sites

Pre and Post Monsoon Season Water and Soil Samples collection sites					
	Urban Areas locating		Rural Areas, Soil &		
Motor Servicing Centers			Groundwater Sample locations		
S.N.	Locations	Sample	S.N.	Locations	Sample
		Codes			Code
1.	Premnagar	$DDN-1$	1.	Sellaqui (B.W. water)+ Soil	$DN-1$
2.	Prince Chowk	$DDN-2$	2.	Sellaqui $(B.W.) + soil$	$DN-2$
$\overline{3}$.	Majra	$DDN-3$	$\overline{3}$.	Sahashtradhara H.P. Water + soil	$DN-3$
4.	Transport Nagar	$DDN-4$	4.	Dhool Kot (H.P water) + soil	$DN-4$
$\overline{5}$.	Rajpur Road	$DDN-5$	5.	Fateh pur (H.P water)+soil	$DN-5$
6.	Chakrata Road	$DDN-6$	6.	Nanda ki chowki (H.P.water) + soil	$DN-6$
$\overline{7}$.	Haridwar Road	$DDN-7$	$\overline{7}$.	Vasant Vihar (T.W)+ Soil	$DN-7$
8.	Race Course	$DDN-8$	8.	Badowala H.P.+ Soil	$DN-8$
9.	Rajpur Road	$DDN-9$	9.	Prem nagar T.W+Soil	$DN-9$
$\overline{10}$.	Kargi Chowk	$DDN-10$	$\overline{10}$.	Jaintanwala H.P.+Soil	$DN-10$
11.	GMS road	$DDN-11$	11.	Bhuddi chowk H.P. +Soil	$DN-11$
$\overline{12}$.	Kamla palace, GMS	$DDN-12$	$\overline{12}$.	Pithuwala H.P.+Soil	$DN-12$
	Road				
$\overline{13}$.	Transport Nagar	$DDN-13$	13.	Ratanpur H.P.+ Soil	$DN-13$
14.	Transport Nagar	DDN-14	14.	Dandi pur H.P.+Soil	$DN-14$
$\overline{15}$.	Mohabbewala	$DDN-15$	$\overline{15}$.	Sahastradhara crossing T.W+Soil	$DN-15$
16.	Mohabbewala	$DDN-16$	$\overline{16}$.	Bidholi (T.W.Water)+Soil	$DN-16$
17.	Patel nagar	$DDN-17$	17.	Sellaqui (H.P.Water)+ soil	$DN-17$
18.	ISBT Majra	DDN-18	18.	ISBT H.P+ SOIL	$DN-18$
19.	ISBT, Majra	DDN-19	19.	GMS road H.P.+ Soil	DN-19
$\overline{20}$.	Haridwar road	$DDN-20$	20.	Kargi chowk T.W+Soil	$DN-20$
21.	Saharanpur Road	$DDN-21$	$\overline{21}$.	Dharampur chowk T.W+ Soil	$DN-21$
22.	ISBT Majra	$DDN-22$	$\overline{22}$.	Vidhan Sabha (H.P.)	$DN-22$
23.	Saharanpur road	$DDN-23$	23.	Patel Nagar (H.P)+Soil	$DN-23$
24.	Majra	$DDN-24$	24.	Ballupur Chowk (T.W.)	$DN-24$
$\overline{25}$.	Majra	$DDN-25$	$\overline{25}$.	O.N.G.C(T.W.)	$DN-25$

Table -1.1: Sample Locations and their Codes

Water samples (grab) were collected in 500 ml "Torson marked" polyethylene bottles. Prior to their use for sampling all the bottles were soaked with nitric acid (1 M) and were ringed many times with double distilled deionised water. All the sample bottles were stored in ice box till brought to laboratory for the analysis.

Figure 1.4 Discharge of waste water

Figure: 1.5 Terrain Map of Study Area showing Sampling Locations and their Codes

Soil samples were collected in good quality zipped polythene bags from the depth of 0- 15 cm by using auger .The soil sample were collected and stored in air tight zipped polythene bags by maintaining temperature range from $3 - 4$ ⁰C. Two sets of soil samples were collected i.e. Soil samples from nearby locations of motor servicing workshops and soil samples from nearby locations of groundwater resources which were considered as control site. Total number of 25 samples was collected from each site in both the sampling seasons.

Figure: 1.6 Soil Samples Collection

Figure 1.7 Collection of Soil Sample

Figure 1.8 Discharge of Oil in Stream Chanel (a & b)

Samples were analyzed for temperature with the help of Soil thermometer by taking triplicate readings, Conductivity of the soil sample were measured by preparing soil suspension in the ratio 1:2.5 with the help of conductivity probe.

On site analysis of temperature, conductivity, total dissolved solids (TDS), pH, dissolved oxygen (DO) was performed with the Help of multi parameter water analysis kit immediate after the collection. Water samples were preserved at pH<2 in separate 300 ml polyethylene bottles by adding concentrated $HNO₃$ for the analysis of heavy metals.

pH of soil was measured by using digital pH probe in prepared suspension of 1:2.5, Concentration of Bicarbonate (HCO₃) Calcium (Ca), Calcium carbonate (CaCO₃) and Chloride was measured by titration method. Whereas concentration of Sodium (Na) and Potassium (K) was analyzed by using flame photometer. Oil and greases present in soil samples were analysed gravimetrically by organic solvent method. Heavy metals were estimated by using atomic absorption Spectrophotometer (Perkin Elmer A Analyst 300). Soil samples were air dried and crushed in a mortar pestle and sieved with the 0.25 pore size sieve and digested by wet digestion method and then analyzed for the study of parameters viz. Zn, Cu, Pb, Mn, Zn,Cd and Ni.

Biological oxygen demand (BOD), chemical oxygen demand (COD), Total hardness, Ca Concentration, Alkalinity, Chloride concentration were analysed by titrimetric methods. Whereas concentration of oil and greases, Total suspended solids (TSS) were analysed by gravimetric method by following up standard method (APHA, 2005). Concentration of Magnesium was calculated by using formula Total hardness ($CaCO₃$ mg/l – Ca hardness mg/l) \times 0.244 as per standard method (APHA, 1980)

Temperature: The parameters of temperature are basically important for its effects on the chemical and the biological reactions in water and soil. A rise in temperature in water and soil leads to speeding up chemical reactions which reduce the solubility of gases and amplifies the taste and odours. The temperature is also very important in the` determination of various other parameters such as pH, conductivity, saturation of gases and various forms of alkalinity etc.

Procedure: Calibrated centigrade thermometer was used to record the temperature of water sample. Thermometer was dipped into water up to a desirable depth for 5-7 minutes and reading was noted down displayed on the display unit. Probe of thermometer should not be taken out while taking readings. Temperature was taken in degree centigrade $({}^{0}C)$.

While soil temperature was measured by inserting soil thermometer on sampling site at a desirable depth and triplicate readings of each sites were taken in degree centigrade $({}^{0}C)$.

Electrical Conductivity (EC): Electrical conductivity is the ability of a substance to conduct the electrical current in water. It is mainly caused by the presence of various ionic species. It is generally measured with the help of conductivity meter, having a conductance cell containing electrodes coated with Platinum black or carbon.

Procedure: Probe of conductivity was dipped into the test solution and the conductivity was noted in µsiemen/cm.

Total dissolved solids (TDS): Total dissolved solids denotes mainly the various kinds of minerals present in the water. In natural water dissolved solids are composed mainly of carbonates, bicarbonates, Chlorides Sulphates, Phosphates and Nitrates of calcium, magnesium, sodium, potassium, iron and manganese etc.

Procedure: The TDS was measured by using TDS meter. Probe of TDS metre was dipped into the test solution and the TDS was noted down in mg/l.

Hydrogen Ion Concentartion (pH): pH is one of the most important parameter used for the study of water and soil chemistry. pH is generally measured on a log scale and equals to negative log₁₀ of hydrogen ion concentration.

pH= - log_{10} $[H^+]$

pH is the measure of the intensity of acidity or alkalinity and measure the concentration of hydrogen ions in water. It does not measures total acidity or alkalinity, in fact the normal acidity or the alkalinity depends upon excess of hydrogen ions or hydroxyl ions over the other, and measures in normality or gram equivalents of acids or alkali.

Procedure: Electrode was calibrated against standard buffer solutions with known capacity i.e. Buffer solution 4, buffer solution 7 and buffer solution 9.2 capacity. Electrode was rinsed by using deionised distilled water and electrode was dipped in sample water, reading displayed on digital screen was noted down.

Soil pH: Soil pH was taken by preparing soil suspension of 1:2.5 ratios. pH electrode was dipped in soil suspension and reading was noted down.

Dissolved Oxygen (DO): Dissolved Oxygen (DO) level in natural water and wastewater depend on the physical, chemical and biochemical activities in the water bodies. The analysis of DO is a key test in water pollution and waste treatment process control. DO is a measure of Oxygen concentration of oxygen reflects whether the process undergoing is aerobic or anaerobic.

Procedure: Probe of DO meter was inserted into test solution (sample) and DO was noted down.

1.3.2 LABORATORY WORK

Laboratory work includes preparation of samples for analysis i.e drying and sieving of soil samples and their digestion for analysis. Following parameters were analyzed in the laboratory for the study of soil and hydrochemistry.

Total suspended solids (TSS): Solids refers to matter suspended or dissolved in water or waste water. Solids may affect water or effluent quality adversely in a number of ways. Total suspended solid is a term applied to the material residue left in a vessel after filtration of a sample and its subsequent drying in an oven at a defined temperature.

Procedure: A 50 ml washed and dried beaker was taken. A filter paper (Whatman No. 42) has been taken and weight. 20 ml of unfiltered sample was filtered through filter paper. The final weight of filter paper was taken after drying of sample.

Calculation

Total Suspended Solids, mg/l =

A-B×1000×1000 Volumeof sample

Where,

A=Final weight of Filter paper in gm

B= Initial weight of Filter Paper in gm

Turbidity (NTU): Turbidity was measured by using turbidity meter. The instrument was calibrated accordingly for the measurement of turbidity by preparing known standards of 0 NTU, 1 NTU and 10 NTU. Sample filled tube was inserted into the instrument and turbidity displayed was noted down in Nephelometric Turbidity Unit.

Biological Oxygen Demand (BOD): The biological oxygen demand determination is empirical tests in which standardized laboratory procedure are use to determine the relative oxygen requirement of waste water effluents and polluted water. The test measure the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic sulphide and ferrous ions. In other words biological oxygen demands (BOD) represent the amounts of oxygen for the microbial decomposition of the organic matter in the water. The BOD procedure, which is used extensively in monitoring water quality and biodegradation of waste material, is designed to determine how much oxygen microorganisms consume during oxidation of the organic matter in sample.

Procedure: Samples were collected in two BOD bottles of 300 ml capacity from each site. One set of the bottle were kept in BOD incubator at 20° C for 5 days and the DO constant was determined in another set immediately after the compilation of 5 days incubation, the DO first set was determined and BOD was calculated in mg/l with the help of following formula.

Calculation:

BOD, $mg/l = (D_0 - D_5)$ D_0 = Initial DO in the sample. D_5 = DO after 5 days

Chemical Oxygen Demand (COD): Chemical Oxygen Demand determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. COD test is widely used for measuring the pollution strength of waste waters.

Procedure: Reflux Method

0.4 g Hg SO⁴ was placed in a reflux flask, 50 ml sample or an aliquot of sample diluted to 50 ml was added with distilled water and pumic stone or glass beads was Added followed by 25 ml std. $K_2Cr_2O_7$.

75 ml H2SO⁴ was slowly added containing AgSO⁴ by mixing thoroughly. This slow addition along with swirling prevent fatty acid to escape out due to high temperature. Then it was thoroughly mixed. This slow addition along with swirling prevent fatty acid to escape out due to high temperature.

Mix well. If color turns green either take fresh sample with lesser aliquot or add more dichromate and acid.

Connect the flask to condenser. Mix the content before heating, improper mixing will result in bumping and sample may be blown out.

Reflux for a minimum 2 hrs. Cool then wash down the condenser with distilled water.

Dilute the mixture to about 300ml and titrate excess of dichromate with standard ferrous ammonium sulphate using ferrion indicator. The color will change from yellow to green blue and finally red. Record the ml of titrant used. Reflux the blank in the same manner using distill water instead of sample.

Calculation:

COD mg/l $=\frac{(A-B)C X 8 X 100}{Volume of sample(ml)}$

Where $A = mI$ of FeSO4 (NH4)₂SO4 used for blank

 $B = ml$ of FeSO4(NH4)₂SO4 used for sample

C= Normality of $FeSO_4(NH4)_2 SO_4$ solution determined above

Total Hardness (CaCO3): Water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present.

Procedure: 10 ml of sample was taken in a conical flask and add a pinch of EBT indicator and 1 ml of buffer solution, the solution turns wine red, titrate it against EDTA until wine red colour changes to blue.

Calculation:

Hardness (EDTA) as mg CaCO₃ /L = A×B ×1000/ ml of sample

Where,

A= ml titration for sample

 $B=$ mg CaCO₃ equivalent to 1.00 ml EDTA titrant

Concentration of CaCO3 in soil sample: A soil suspension of 1: 2.5 was prepared by taking 10 gram soil and 25 ml of distilled water. A quantity of 10 of soil suspension was taken and 1 pinch of EBT indicator + 1 ml of buffer solution was added, a wine red appearance occurred then it was titrated with EDTA Solution red colour turned into blue colour.

 $CaCO₃ = A \times B \times 1000$ ml of suspension

Concentration of $CaCO₃$ was calculated in mg/kg

Calcium Concentration (Ca) and Ca Hardness: A known volume (50ml) of the sample was pipetted into a clean conical flask, to which 1ml of sodium hydroxide and 1ml of isopropyl alcohol is added. A pinch of muroxide indicator is added to this mixture and titrated against EDTA until the pink colour turns purple.

Calculation*:*

Calcium as Ca $(mg/L) = \frac{T (400.5) \times (1.05)}{S_{cmn}log t_{elton}}$ Sample taken,ml

Where, T= volume of titrant, ml

Calcium hardness (mg/L as CaCO₃) = $\frac{T(1000) \times (1.05)}{\text{Sample taken m}}$ Sample taken,ml

Magnessium (Mg) concentration: Magnesium is a relatively abundant element in the earth's crust, ranking eighth in abundance among the elements. It is found in all natural waters and its source lies in rocks, generally present in lower concentration than calcium.

Magnessium concentration was determined with the help of pre determined concentration of CaCO₃ and Ca by adding multiplying factor 0.243 as referred in APHA, (2005).

Calculation*:*

Magnesium (as Mg, mg/L) = $(T - C) \times 0.243$

Where, $T = Total hardness mg/L as CaCO₃$

 $C =$ Calcium hardness mg\L as CaCO₃

Total Alkalinity: Alkalinity of water is its acid neutralizing capacity. It is the sum of all the titrable bases.

Procedure: 10 ml of sample was taken and 2-3 drops of phenolphthalein indicator was added if pink colour appears then carbonate is present (usually carbonate concentration is absent in water sample), if solution remains colourless then phenolphthalein alkalinity is absent (PA=0) and total alkalinity was determined by titrating against 0.1 N HCL until colour disappears this is phenolphthalein alkalinity (PA). Then 1-2 drops of methyl orange indicator was added and titrated against 0.01 N HCL until yellow colour changes to pink at the end point this is called total alkalinity (TA).

Calculation:

Bicarbonate (Alkalinity) $\frac{N x V X M W \text{ of } HCO3 X 1000}{N M G}$ Volume of sample

N= Normality of the Acid, V=Volume of the Acid (Titrant)

Normality of the Acid: 0.01 M.W. of $HCO₃ = 61$ Volume of Sample =10

Soil alkalinity: Alkalinity of soil was analysed by preparing soil suspension of 1:2.5 (soil: distilled water)

10 ml of sample was taken in a conical flask, 1-2 drops of methyl orange indicator was added yellow colour appeared then it was titrated against 0.01 N HCL then yellow colour changes to pink colour end point reading was noted down.

Alkalinity was calculated by using following formula:

Bicarbonate (Alkalinity) $\frac{N x V X M W \text{ of } HCO 3 X 1000}{V_{\text{obs}} + S \text{ (s)} \text{ (s)}}$ Volume of sample

N= Normality of the Acid, V=Volume of the Acid (Titrant)

Normality of the Acid: 0.01 M.W. of $HCO₃ = 61$ Volume of Sample =10

Chloride (Cl): The chloride concentration is higher in wastewater than in raw water because sodium chloride (NaCl) is common article of diet and passes unchanged through the digestive system.

Procedure: 50 ml of sample was taken in a conical flask and 2 ml of potassium chromate was added to it, then solution was titrated against silver nitrate solution and persistent red tinge appeared.

Chloride concentration of Soil: Chloride concentration of soil was analysed by preparing soil suspension of 1: 2.5

Procedure: 50 ml of test solution was taken and 2 ml of potassium chromate was added to it, then solution was titrated against silver nitrate solution and persistent red tinge appeared.

Calculation:

Chloride mg/l = $\frac{\text{ml of AgN03 x 1000 x 35.5}}{\text{ml of sample}}$ ml of sample

Sodium and Potassium: Standard solution and standard Curve

Sodium (Na): 2.54 gram of NaCl was dissolved and diluted to 1000 ml with distilled water. 1 ml of this solution is equal to 1 mg of Na. Standard solution of 1.0 to 10.0 has been prepared and analyzed emission for Na at flame photometer at 589 nm.

Potassium (K): 1.907 gm of KCl has been dissolved in 1000 ml of distilled water. 1 ml of this solution is equal to 1 mg of Na. Standard solution of 1.0 to 10.0 has been prepared and analyzed emission for Na at flame photometer at 766 nm.

Oil and greases: Dissolved or emulsified Oil and Grease is extracted from water by intimate contact with petroleum ether $(40⁰$ or $60⁰)$ or hexane or tricholoflouro ethane.

An amount of 250 ml of sample was taken in a separating funnel, 10 ml of H_2SO_4 and 30 ml petroleum ether was added to the sample by shaking it. After some time separate two distinct layer appeared. Lower layer were discarded and petroleum ether was filtered into preweight dish from water bath and petroleum ether was evaporated with the help of water bath. Weight of disc was taken.

Calculation:

 Oil and grease in mg/l $=\frac{(W2-W1) \times 1000 \times 1000}{\text{m} \cdot \text{m} \cdot \$ volume of sample taken **Where W1 = Initial weight of dish W2 = Final Weight of dish V = Volume of sample taken**

Standard solution and Standard Curve for heavy metals

Copper: Dissolve 1.000 g copper metal in 15 ml of $1+1$ HNO₃ and dilute to 1000 ml with water; $1.00 \text{ ml} = 1.00 \text{ mg Cu}$

Lead: Dissolve 1.598 g lead nitrate $(PbNO₃)₂$ in about 200 ml water, add 1.5 ml conc. HNO₃ and dilute to 1000 ml with water; 1.00 ml = 1.00 mg Pb

Zinc: dissolve 1.000 g zinc metal in 20 ml $1+1$ HCl and dilute to 1000 ml with water; 1.00

Analytical procedure for Heavy Metals:

- 1. Digestion of water sample: Filtered water sample were digested by adding 2 ml HNO_3
- 2. Digestion of soil samples: A suspension of 1: 2.5 ratio (10 gm soil: 25 ml distilled water) were prepared and digested by adding 2 ml HNO_3 .

The instrument was calibrated, for each metal to be detected, with known standard. After calibration and programming, the prepared samples were aspired to the flame. Zero was set with double distilled water before each determination. Results were displayed in μ gm/l from which the actual concentration in water sample was calculated. It was the total content of water sample, which was expressed in mg/l (ppm).

Heavy metals: Heavy metals present in soil and water was analyzed by using atomic absorption spectrophotometer (AAS).

Operational method: In AAS, a sample is aspired into a flame and atomized and a light beam is directed through the flame, into a monochromometer onto a detector that measures the amount of light absorbed by the atomized element in the flame. Each metal has its own characteristics wavelength absorbed in the flame is proportional to the concentration of elements in the sample.

Instrument operation: Heavy metals are analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300. In general, install a hollow cathode lamp for the desired metal in the instrument and roughly set the wavelength. Turn on the instrument, and let instrument warm up until energy source stabilizes. Install suitable burner head position. Turn on air and adjust flow rate that specified by manufacturer to give maximum sensitivity for the metal being measured Turn on acetylene, adjust flow rate to value specified and ignite flame. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Atomize a standard (usually on near the middle of the

linear working range) and adjust burner both up and down and sideways to obtain maximum response. Absorbance is recorded when freshly prepared sample is aspirated with a new hollow cathode lamp.

Standard Solution and Standard Curve for Heavy metals:

Copper (Cu): Dissolve 1.000 gram Copper metal in 15 ml of 1+1 HNO³ and dilute to 1000 ml with water; $1 \text{ ml} = 1.00 \text{ mg}$.

Lead (Pb): Dissolve 1.598 gm lead nitrate, $Pb(NO₃)₂$ in about 200 ml water, add 1.5 ml conc. $HNO₃$ and dilute to 1000 ml with water 1.00 ml = 1.00 mg Pb

Zinc (Zn): Dissolve 1.000 gm zinc metal in 20 ml 1+1 HCL and dilute to 1000 ml with water; 1.00 ml = 1.00 mg Zn

Manganese (Mn): Dissolve 1.000 gm Manganese metal in 10 ml conc. Mix with 1 ml conc $HNO₃$. Dilute to 1000 ml with distilled water 1 ml solution = 1 mg Mn

Nickel (Ni): Dissolve 1 gm Ni metal in 10 ml hot conc. HNO₃, cool and dilute it to 1000 ml with distilled water $1 \text{ ml} = 1 \text{ mg Ni}$

Chromium (Cr): Dissolve 1.923 gm CrO₃ in water when solution is complete acidify with 10 ml concentrated HNO₃. And dilute to 1000 ml with water 1 ml = 1 mg Cr

Cadmium (Cd): Dissolve 1.000 gm cadmium metal in 4 ml Conc. HNO₃ and dilute to 1000 ml with water, 1.00 ml = 1 mg Cd.

CHAPTER -2

REVIEW OF LITERATURE

The ground water quality varies from place to place because of various processes and reactions act on the water from the moment it condensed in the atmosphere to the time it is discharged. Therefore ground water quality plays an important role to examine the suitability of water for a particular uses like public water supply, irrigation, industrial application, fish culture and power generation.

The newly built state of Uttarakhand has a total geographic area of 51,125 km², of which 93% is mountainous and 64% is covered by Forest. Most of the northern parts of the state are part of Greater Himalaya ranges, covered by the high Himalayan peaks and glaciers, while the lower foothills were densely forested. Two of India's mightiest rivers, the Ganga and the Yamuna take birth in the glaciers of Uttarakhand, and are fed by myriad lakes, glacial melts and streams in the region. Besides this, ground water also plays a vital natural resource in the state. The ground water quality varies from place to place because of various processes and reactions that act on the water from the moment it condensed in the atmosphere to the time it is discharged. Therefore ground water quality plays an important role to examine the suitability of water for a particular uses like public water supply, irrigation, industrial application, fish culture and power generation.

A large number of studies on groundwater contamination have been carried out by different workers for various places. Few studies on ground water quality for the state of Uttarakhand has been carried out by National Institute of Hydrology, Roorkee (Jain et al., 1996, 1997, 1999; Ali et al., 1999).

People in the villages of district Hardwar were suffering from stomach problem like dysentery, diarrhea, stomach pain, vomiting etc. and were solely depends on ground water either from Jal Nigam hand pumps or their private hand pumps. Keeping in view of this aspect, soil and ground water quality of Dehradun is being assessed for the research purpose with reference to oil contents and extent of contamination.

Doon Valley is located between the rivers Yamuna and Ganga. Doon valley, existing in the Siwalik range of outer Himalaya, is a synclinal depression between the Lesser Himalayan Mountains in the north and Sub-Himalayan Siwalik hills in the south.

The climate of the valley is salubrious almost throughout the year. The total annual rainfall is about 1800 mm of which bulk precipitates in the months of July-August. Geological structure of Doon valley is characterized by two major faults, crustal and fractures along which rock slabs of mountain mass have been uplifted and moved southward. Geohydrologically, Doon valley is divided into three zones namely Lesser Himalayan zone, Synclinal Central zone and Siwalik zone. The springs are potential source of water in the Doon valley. The depth of water table varies from 3 to 90 m below ground level whereas it is shallowest in the central part of the valley (Asan river) and deepest close to the water divide of Asan and Song rivers and near Kaulagarh. Perched conditions of shallow water table of local extent are also present in the valley.

Dehradun is the administrative centre and the interim capital of the new state of Uttarakhand. Dehradun is situated at the Himalayan foothills in the fertile Doon Valley. The valley is well known for its salubrious climate and natural beauty. It is due to this reason Dehradun has been one of the favourite residential cities. Dehradun is also one of the most beautiful resort centers in India, it is well known for its scenic natural beauty, beautiful forests, waterfalls and surroundings. It is also an important educational centre of the country. India's some of the best public schools and convents are located here. The Indian Military Academy, Forest Research Institute, ONGC and many more offices of Central and State Govt. are located here.

Dehradun is well linked with rail, road and air routes to all the parts of the state and the country. Main languages spoken in the district are Hindi, Garhwali Sindhi, Punjabi, and Urdu. Doon Valley has the Himalayas to its north, the Shivalik range to its south, the sacred river Ganga to its east and the river Yamuna to its west. The city of Dehradun is surrounded by river Song on the east, river Tons on the west, Himalaya ranges on the north and Sal forests in the south. Doon Valley is situated between the two most important rivers of India. i.e. Ganga and Yamuna, located in a picturesque setting. Dehradun is surrounded by dense forest all around and number of streams and canals dissect the city in the north-south direction. The high hills in the east and north and Shivaliks in the south give an interesting topographical setting to the city. All the hill ranges around Dehradun (except the Shivaliks) are rich in lime stone reserves.

Nestled in a wide and thickly forested valley of the Shivalik ranges, Dehradun is famous for its fruit orchards such as Leechis and Mangoes. Forest products play an important role in the economy of the Dehradun district.

As per the latest estimate of Central Pollution Control Board, about 29,000 million litre/day of wastewater generated from class-I cities and class-II towns (study area belongs to class II city) out of which about 45% (about 13000 mld) is generated from 35 metro-cities alone. The collection system exists for only about 30% of the wastewater through sewer line and treatment capacity exists for about 7000 million litre/day. Thus there is a large gap between generation, collection and treatment of wastewater. A large part of un-collected, un-treated wastewater finds it way to either nearby surface water body or accumulated in the city itself forming cesspools. In almost all urban centres cesspools exist. These cesspools are good breeding ground for mosquitoes and also source of groundwater pollution. The wastewater accumulated in these cesspools gets percolated in the ground and pollute the groundwater. Also in many cities/towns conventional septic tanks and other low cost sanitation facilities exists. Due to non-existence of proper maintenance these septic tank become major source of groundwater pollution. In many urban areas groundwater is only source of drinking. Thus, a large population is at risk of exposed to water borne diseases of infectious (bacterial, viral or animal infections) or chemical nature (due to fluoride or arsenic). Water born diseases are still a great concern in India.

Pollutants are being added to the groundwater system through human activities and natural processes. Solid waste from industrial units is being dumped near the factories, and is subjected to reaction with percolating rainwater and reaches the groundwater level. The percolating water picks up a large amount of dissolved constituents and reaches the aquifer system and contaminates the groundwater. The problem of groundwater pollution in several parts of the country has become so acute that unless urgent steps for abatement are taken, groundwater resources may be damaged.

The quality of groundwater depends on a large number of individual hydrological, physical, chemical and biological factors. Generally higher proportions of dissolved constituents are found in groundwater than in surface water because of greater interaction of ground water with various materials in geologic strata. The water used for drinking purpose should be free from any toxic elements, living and nonliving organism and excessive amount of minerals that may be hazardous to health. Some of the heavy metals are extremely essential to humans, for

example, Cobalt, Copper, etc, but large quantities of them may cause physiological disorders. The contamination of groundwater by heavy metals has assumed great significance during recent years due to their toxicity and accumulative behavior. These elements, contrary to most pollutants, are not biodegradable and undergo a global eco-biological cycle in which natural waters are the main pathways. The determination of the concentration levels of heavy metals in these waters, as well as the elucidation of the chemical forms in which they appear is a prime target in environmental research today.

A vast majority of groundwater quality problems are caused by contamination, overexploitation, or combination of the two. Most groundwater quality problems are difficult to detect $\&$ hard to resolve. The solutions are usually very expensive, time consuming $\&$ not always effective. An alarming picture is beginning to emerge in many parts of our country. Groundwater quality is slowly but surely declining everywhere. Groundwater pollution is intrinsically difficult to detect, since problem may well be concealed below the surface $\&$ monitoring is costly, time consuming $\&$ somewhat hit-or-miss by nature. Many times the contamination is not detected until obnoxious substances actually appear in water used, by which time the pollution has often dispersed over a large area. Essentially all activities carried out on land have the potential to contaminate the groundwater, whether associated with urban, industrial or agricultural activities. Large scale, concentrated sources of pollution such as industrial discharges, landfills & subsurface injection of chemicals & hazardous wastes, are an obvious source of groundwater pollution. These concentrated sources can be easily detected $\&$ regulated but the more difficult problem is associated with diffuse sources of pollution like leaching of agrochemicals & animal wastes subsurface discharges from latrines & septic tanks & infiltration of polluted urban run-off & sewage where sewerage does not exists or defunct. Diffuse sources can affect entire aquifers, which is difficult to control $\&$ treat. The only solution to diffuse sources of pollution is to integrate land use with water management. Once pollution has entered the sub-surface environment, it may remain concealed for many years, becoming dispersed over wide areas $\&$ rendering groundwater supplies unsuitable for human uses.

A lubricant (sometimes referred to as "lube") is a substance (often a liquid) introduced between two moving surfaces to reduce the friction between them, improving efficiency and reducing wear. They may also have the function of dissolving or transporting foreign particles and of distributing heat. One of the single largest applications for lubricants, in the form of motor oil, is to protect the internal combustion engines in motor vehicles and powered equipment.

According to current statistics, the lube market in India is in the order to 1 million tons per annum, with a prevailing annual growth rate of 3.5%. Since lube oil is the highest-value component of a barrel of crude oil and most of the lube oil gets used only once, it becomes one of the world's largest bulk pollutants for soil, water and air, thereby highly contributing to the low quality of life. Therefore, there is an urgent need to systematically carry out a study to conserve it and use it scientifically, so that emissions are within the prescribed limits $\&$ no suspended particulate matters are ejected in the atmosphere which poses serious environment pollution & wastage of high value lubricants.

The impact of hydrocarbon contamination from automobile wastes reaching day by day at an alarming rate. Environmental contaminants can be distributed in soils, thereby having effect on the trophic chain, plants. These contaminants can remain in soil for a long time. Trace metals are naturally present in the biological world in acceptable quantities, but increase of these through anthropogenic contributions has since the last century been known to affect microbial growth, numbers, survival, biomass and abundance.

It has been observed that some chemicals found in used motor oil such as heavy metals and other toxic contaminants, tend to persist and accumulate, not break down like many natural substances. For this reason, although the exact amount of time is not known for sure, motor oil contaminants can remain in the ground or water system for a number of years, if not hundreds. These hazardous materials also have been known to find their way into organisms such as fish, as well as cause mutations, birth defects and cancer.

It has been noticed that a large body of literature is available concerning automobile exhaust emission and air or noise pollution but there has been little attention given to soil and water pollution in the vicinities of auto mechanic workshops, which are also liable to pollution arising from gasoline combustion exhausts, lubricating oil spills and other chemical inputs to automobile operations.

Liu et al., (1981) Studied on Soil of Shenfu irrigation area located between Shenyang and Fushum cities of China. The area was continuously being irrigated by petroleum containing waste water since 1940s and in the year 1960 a 70 km long irrigation channel was constructed

after the channelization irrigation area was extended to 10,000 hectare. After going though the study of soil quality of this area it was found that soils of the irrigation area have been seriously contaminated by the petroleum products.

Indiscriminate disposal of spent engine oil (SEO) into water drains, gutters or an open vacant plots and farms has become a common practice in Nigeria especially by auto mechanic workshops. This oil also called spent lubricant or waste engine oil which is usually obtained after the process of servicing and subsequently draining from automobile and generator engines servicing centers and much of this oil is drained in nearby streams which can ultimately enter into the soil and ground water.

Whisman et al (1974) Studied the chemical properties of engine oil and found that large amount of heavy metals such as V, Pb, Al, Ni, and Fe which were found below detection limit in fresh (unused) lubricating oil. But after going through the study of used engine oil they found a rising concentration of these heavy metals.

These pollutants can pollute not only the surface water and soil system of the affected areas but also they can enter in ground water regime and can pollute the ground water resources of the areas. As 97% of total drinking water supply in Dehardun district comes from ground water resources, it becomes necessary to evaluate ground water quality of the area with reference to its suitability for the drinking purpose.

A study was conducted by Jain, (1996). In this study ground water quality of doon valley has been studied during the year 1996-97 to examine the suitability of ground water for drinking purposes. In this study they have taken twelve water samples representing the shallow ground water of the area and water of the study area were analysed for various constituents viz., pH, Conductance, Total dissolved solids, Alkalinity, Hardness, Chloride, Sulphate, Phosphate, Sodium, Potassium, Calcium and Magnesium. The data was analysed with reference to BIS and WHO Standards. Hydro chemical faces were determined and water types were identified. The results of the study provides information needed for the ground water quality management in Doon valley.

The surface water quality is being deteriorated due to discharge of industrial, sewage, motor workshops waste water and domestic effluents directly into water bodies like stream and river which can percolate into ground water system and can contaminate the quifers as well as

surface water of the area. A study indicating seasonal variation on physico-chemical parameters of surface and ground water of Doon valley by Kumar, M., et al., (2010). The study evaluated surface water and ground water of eastern Doon valley. The study was conducted to analyse various water samples of Raipur block for physicochemical characteristics. The water quality parameters such as pH, DO, alkalinity, hardness, BOD, COD, TS, TSS, Mg, Mn, and some toxic elements like Pb and Fe in ground water and Rispana river of Doon valley have analysed to determine the pollution status. The study reveals that ground water of the area were hygienic and safer in all senses of use for drinking purpose but the surface water of Rispana river need some treatment before use.

Though the study area (Doon valley) is bestowed with plenty of surface water resources, groundwater is the main source for fulfilling the drinking requirements in the area. It becomes necessary to examine the ground water parameters to know the scientific attributes of the groundwater bearing formations.

Similar study has considering ground water parameters of Doon valley has been conducted by Rawat, M. et al., (2011). In this study they have analysed 20 samples and obtained hydrochemical data indicating the ground water quality of the area. The findings of the research indicates that 95% samples falls alkaline in nature and only 5% were alkaline to week acids.The data suggest that the groundwater in Doon Valley is potable and Suitable for domestic use.

Presence of crude oil in soil can change the physicochemical properties of soil and can make the soil condition unsatisfactory for the growth of plants (De Jong E.1980), due to rise in toxic level of these trace elements such as iron and zinc and reduction in the level of available plant nutrient, growth of plants may suffer because plants are highly susceptible to oil exposure and these toxic compounds may kill them within a few weeks to several months.

Environmental consequences of oil pollution has become common for inhabitants of Delta states. Due to oil spills most agricultural lands in the state have degraded and productive areas have turned into wastelands. Due to the destruction of soil microorganisms, and dwindling agricultural productivity, and increasing soil infertility formers have been forced to abandon their land, to seek non–existent alternative means of livelihood. It has been found that aquatic life is also being destroyed by means of traditional pollution, fishing grounds which lead to exacerbating hunger and poverty in fishing communities.

A similar study was also made by Wang et al., (2000) they found that a relatively large amount of hydrocarbons and highly toxic polycyclic aromatic hydrocarbons were present in the used engine oil.

Chindah and Braide, (2000) Conducted a study on the effect of oil spill on crop production in the Niger Delta and reported that oil spill on crops causes great damage to the plant production due to high retention time of oil occasioned by limited flow. It was also stated that these oil contamination can hamper proper soil aeration due to formation of oil film on the soil surface which acts as a physical barrier between air and soil. Because oil pollution affects the physicochemical properties of the soil such as temperature, structure, nutrient status and pH.

Worgu (2000) Studied on economic impact of oil pollution on crops varieties and concluded that due formation of oily layer on stomata, blockage of stomatal tissues may occur and shoots of some crop varieties like pepper and tomatoes may wilt and die off. Because oily layer can inhibits photosynthesis, transpiration and respiration.

Purohit et al., (2000). Studied on soil samples of Doon valley and investigated concentration of heavy metals (Cr, Cu, Ni, Pb, and Zn). On comparison of heavy metals and contamination threshold values they concluded that most of the soil samples of Doon valley varied from uncontaminated to slightly contaminated by heavy metals but in case of Cr and Ni, some samples exceeded the contamination of threshold value 250 and 100 mg/kg and their background value was 109 and 52 mg/kg respectively. The high concentration of Cr and Ni was found mostly in and around the area of Ganga catchment including undisturbed forest land. The background concentration of Pb was found low as compared to nearby locations of highways.

It has been studied by (Quinones et al in 2003) They concluded that there are several vegetal species which can grow in such soils which are being polluted with hydrocarbons and they can participate in degradation through the rhyzosphere, part of the root, which can favor the growth of several microorganisms.

Nixon and Saphores (2003). Conducted study on the impacts of motor vehicle transportation on non-point source and on groundwater pollution and estimated the value of costs for cleaning up leakage. This work also suggests that the effective policies should combine economic incentives, information campaigns and enforcements measures coupled with preventive environmental measures.

Dominguez-Rosado and Pichtel (2004) Stated that used mineral based crankcase oil known as spent engine oil is subjected to high temperature and high mechanical pressure. This spent engine oil is a common and toxic environmental contaminant which is not naturally found in the ecosystem. Large amounts of these spent engine oil is liberated into the environment during the process of oil change which ultimately dispersed into gutters, nearby water channels, open vacant plot and form lands

Dioka et al (2004) Made a study on some toxicological effects of petroleum products on occupational health. This evaluation study was carried out to find out the effect of petroleum products (especially petrol which contains tetraethyl lead) by using the following biochemical markers: like urea, uric acid, creatinine, electrolytes, inorganic phosphorus, zinc and blood lead, as well as the activities of alanine and aspartate aminotransferases and alkaline phosphatase. The result of the study showed that occupational exposure of human subjects to lead in petrol increases the concentrations of uric acid and phosphate in exposed subjects. The results concluded that occupational exposure to lead in petrol may harm to liver and renal function.

Richert et al (2004) Analyzed used oil and sludge samples for total metal and leaching with the help of TCLP technique. Results showed that concentration of lead in four oil samples exceeded the 5 ppm toxicity level and is considered as toxic waste substance. Six samples of contaminated sludge were found to contain high concentration of total lead, chromium and barium, but TCLP test showed toxicity below regulatory limit. With the help of this work the content of benzene, ethylebenzene, toluene and xylene (BETEX) in used oil were also evaluated. The objective of the research was to determine if contaminated engine oil and sludge sample exceed the regulatory of toxicity characteristics concentration.

Chen et al (2005). Investigated the concentration of potentially harmful heavy metals in the soil of urban parks. In order to evaluate the potential risks to residents and tourist they assessed the soil samples from 30 urban parks in Beijing. The study reveals a clear accumulation of Cu and Pb. The concentration of Ni in the urban park soils were found similar to the soil background concentrations but one of the 30 parks had middle or high IPIs. They also emphasized that the more attention should be paid to heavy metal pollution of the parks soils in Beijing.

A similar work has been done by Zhang et al. (2005) In this investigation an effect of petroleum contamination on diversities and enzymatic activities of bacteria in paddy soils were assessed in the Shenfu irrigation area, the largest area irrigated by oil containing wastewater for more than 50 yrs in northeastern china. Peroxidase, dehydrogenase, urease hydrogen polyphenol oxidase, and substrate induced respiration (SIR) were measured to assess the study effects of Petroleum waste water irrigation on soil biochemical characteristics. Results of the analysis showed that paddy soil TPH concentration decreased along the gradient of the irrigation channel from up to downstream. According to current pollution level the paddy soil TPH concentration was found positively correlated with the colony forming units (CFU) of aerobic heterotrophic bacteria (AHB). With the help of this study they evaluated the long- term effect of petroleum-containing wastewater irrigation on bacterial diversities and soil enzymatic activities. The diversity of microbial communities and enzymatic activities in the soil ecosystem could be changed under the pollution stress.

They also concluded soil enzymatic activities and soil microorganisms are sensitive biological indicators of soil pollution. It was also suggested that the petroleum pollution in the Shenfu irrigation area resulted in the increase of the number of AHB and the diversities of *eubacteria* at the present pollution level. The activities oxidoreductases were increased due to the presence of TPH. It was predicted that the decrease in activity of urease can be taken as a sensitive indicator of degradation of soil quality.

Amusan et al (2005) found that values of Zn concentrations were 63.20 microgram / gram in Bode- Osi (rural community) and 102.11 microgram/ gram in municipal waste dump sites soils of Niegeria.

Aiyesanmi, (2005). Studied on oil field in Niger delta area of Nigeria. They analyzed Soil samples for some heavy metals, including, Cu, Hg, Ni, Pb,Ba, Cd, Cr and Zn and the results were used to evaluate the degree of contamination of the soil of oil field. The soil reaction in this study was found acidic pH range, while moderate to high organic matter contents were recorded. Heavy metals measured in soil showed varying concentrations among sample locations within the field. Some levels of significant difference $(p<0.05)$ were observed for nickel and mercury concentrations between the wet and dry seasons, while other metals showed no significant difference. The results however, revealed that the soils were predominantly slightly contaminated with these metals.

A study has been made by Onweremadu et al (2007) They studied on seasonal changes of heavy metal concentration in soils. The study investigated temporal variations in concentration of heavy metals in three towns having automobile service centers in Imo State. From this investigation heavy metals were found in both arable and automobile soils, but more concentration were recorded on the latter (automobile soils). Results from the study shows that mean values of Cd, Cr, Ni, Hg and Pb were 6.2 mg/kg, 4.7 mg/kg, 6.5 mg/kg, 0.02 mg/kg and 71.9 mg/kg respectively in the dry season while 2.9 mg/kg Cd, 2.2 mg/kg Cr, 1.9 mg/kg Ni, 0.01 mg/kg Hg and 51.9 mg/kg Pb were recorded during the rainy season of the experimental period. Study reveal that higher values of heavy metals concentration were found in automobile soil as follows: 18.1 mg/kg Cd, 12.0 mg/kg Cr, 16.3 mg/kg Ni, 4.8 mg/kg Hg and 312.8 mg/kg Pb in rainy season, and 15.1 mg/kg Cd, 8.1 mg/kg Cr, 11.9 mg/kg Ni, 2.7 mg/kg Hg and 267.9 mg/kg Pb. However, Cd showed highest variability in arable soils during the dry season ($CV = 79\%$) while Hg varied widely in automobile soils in the rainy seasons ($CV =$ 54%).

The chance of heavy metal accumulation may reach to the toxic levels as a result of long- term application of untreated wastewaters. They can be considered as soil contaminants due to their widespread occurrence, acute and chronic toxicity. Some study on heavy metal concentration and its accumulation were also conducted by some workers.

Aydinalp and Marinova (2003). Conducted the study on "Distribution and forms of heavy metals in some agricultural soil and found concentration of Ni as 157.8 mg/kg in agricultural soil and Karatas et al (2006) Made a study on "Heavy metal accumulation in irrigated soil with waste water" and Assessed Cr concentration in waste water irrigated soil. In their study they determined Cr concentrations as 22 mg/kg and 32 mg/kg in wastewater irrigated soil with pump 2 and 3 respectively at Konya (Turkey).

From the investigation of above data it was concluded that the heavy metals influenced, soil properties especially soil pH, aluminum saturation, base saturation and effective cation exchange capacity. Moderate and high variations in heavy metals were encountered in both arable and automobile soils irrespective of seasons. These variability influence crop growth, however with the exception of Cd and Pb all other investigated heavy metals were below critical levels of toxicity.

Bishnoi and Arora (2007). Worked on potable ground water quality in some villages of Haryana. In this study they evaluated various water quality parameters such as pH, electrical conductivity, total dissolved salts, total hardness, total alkalinity, sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride and sulphate along with fluoride concentration. On the basis of this study they concluded that ground water and dug well water quality varied spatially. Water at most of the locations is not suitable for drinking purpose as per WHO guidelines. Hardness and fluoride were major health related issues. It was suggested by them some kind of treatment for hardness, fluoride and salinity removal is immediately required to avoid water borne diseases.

Onweremadu et al (2008) Investigated soil characteristics of crude oil contaminated soils of a town within an oil exploration zone of southeastern Nigeria in 2006.Target sampling technique was used in collecting soil samples, which were later prepared for various laboratory analyses. Cassava sludge was obtained from waste water disposal pit and composted using Aerated pile method. Five temporal treatments namely 30, 60, 90, 150 and 180 days were observed when 0.5 kg composed Cassava sludge was applied on 5 kg soil set up in completely randomized design. Result showed difference in chemical composition of sludge and its compost. There were significant (P=0.05) variation in the removability of priority pollutants using composted Cassava sludge: with greater efficacy at 120 and 180 days for total cadmium and nickel. There study reveals that the anionic forms of contaminants become more available in the pedosphere thereby creating greater chances of uptake by crops consumed by humans. It was also concluded that composted *cassava sludge* exhibited least efficiency in the removal of TPH which is attributed to possible precipitation of organic substances contained in the compost by Ca and Mg. It has been observed that this research work may not be conclusive as further investigations need to be conducted relating Cd to other heavy metals as well as soil properties.

Omosun et al (2008) Studied the effect of crude oil concentrations on growth and anatomy of *Amaranthus Hybridus*. They investigated the changes in growth and anatomy of *A. hybridus* grown in a crude oil contaminated soil and possible use of this changes in anatomy as a phytomonitoring technique of crude oil pollution. The response of the growth and anatomy of *A. Hybridus* in provoked crude oil contaminated soil was investigated using 1-4% v/w crude oil and a control (0%). Some growth parameters were studied like plant height, number of leaves, leaf area plant fresh weight and plant dry weight, the mean value obtained were higher for contol (0%) and progressively decreased from 1-4%. The 4% was lethal to the *A. hybridus* grown on it as they all died within 10 days after planting. *A. hybridus* grown in higher concentrations (2-3%) exhibited greater sinuosity in their epidermal cell walls than those grown in 0 and 1% stomatal index of leaves of *A. hybridus* progressively decreased as the crude oil concentration of soil increased.It was also noticed that the thickness of walls of the cortical cells was more prominent in A. hybridus grown in crude oil polluted soil than in the control. It was also investigated that the cortical cells of the roots and stems of *A. hybridus* in 2-3% polluted soil were flattened tangentially and smaller in size compared to that grown in control which had round polygonal cells that appeared larger. It was also found that these changes in anatomy of *A. hybridus* due to contaminated by crude oil were discussed as possible pollution indicator.

This study also reveals that these visible significant anatomical changes seen in all the *A. hybridus* grown in the crude oil contaminated soil could be employed as an index of monitoring environmental pollution. It also suggested that this investigation can also be done in other plant species to ascertain their possible use in phytomonitoring.

Pawlak et al (2008) The laboratory methodology used by researcher was based on modern instrumentation and experimental investigation and petroleum contaminated soil samples were analyzed for oil and grease content, total petroleum hydrocarbons and volatile aromatic compounds. The results show that total petroleum hydrocarbon fraction accounted for oil and grease content. Based on their work they highlighted that how used petroleum oil and grease enter in groundwater or to the drain which can ultimately become environmental and economic problem to the country.

The study highlighting the phytoremediation or bioremediation of petroleum contaminated soil was conducted by Njoku et al (2008b) The main objective of this investigation was to evaluate the suitability of G.*max* for use in remediation of crude oil polluted soil. The findings of this study indicate that growth of G. *max* in crude oil contaminated soil affects the physicochemistry of the soil enhancing the degradation of crude oil. For instance, the significant effect that the growth of G. *max* produced on the pH and moisture content of the soil with 75g crude oil indicates that G. *max* affects the physico-chemistry of crude oil contaminated soil.

It can also be inferred from the findings of this study that the growth of G. *max* in crude oil contaminated reduces the toxicity of crude oil in the soil. This is going by the sprouting of weeds in the soils with G. *max* and none of such soils without G. *max*. They further suggested that soil augments like cow dung should be added to crude oil contaminated soil to enhance the increase the efficacy of using G. *max* in remediating crude oil contaminated soils. It was suggested by Njoku et al. (2008a) have reported that addition of cow dung to crude oil contaminated soils enhances the growth of G. *max* in such soil.

Ilemobayo and Kolade (2008) Studied on soil samples taken from five automobile workshops in Akure, Nigeria Analyzed heavy metals and pH and found that Fe and Zn were of high concentration in all the sites considered. And also concluded that mechanic workshops situated within the metropolis are anthropogenic sources of heavy metals in soil. They may pose serious threat to the underground water plume which will ultimately affects public health. Also suggested that stricter environmental laws is to be observed in this regards to curb this menace and all stakeholders involved in the use of auto mechanic workshops need to be alerted of the impending dangers looming from indiscriminate heavy metals dumping. They pointed out that auto-mechanic workshops soil should be heavily cemented and proper drainage for used oils lubricants and spilled gasoline constructed.

Achuba and Clarke (2008) In this research work the effect of spent engine oil on soil pH as well as activity of selected enzymes (catalase and dehydrogenase) was studied. The result from the study reveal that spent engine oil caused a slight change in soil pH relative to the control. There was a significant decrease $(p<0.05)$ in catalase activity in contrast to a significant increase (p < 0.05) observed in dehydrogenase activity. On the whole the data suggest that spent oil alters soil biochemistry.

Similar study has been made by Akoachere et al (2008) The main objective of the study was isolation and characterization of bacteria capable of effectively degrading and cleaning waste engine oil in Buea and also to ascertain the influence of some environmental factors on the rates of degradation of these isolates. Seventy two soil sample collected from lubricating oil dump sites (3 auto-mechanic workshops and 3 petrol stations, comprising impacted soils) and uncontaminated plots (non-impacted soils/controls) were analyzed for oil degrading and heterotrophic bacteria following standard microbiological and biochemical methods.

Apart from this the ability of cultures to degrade lubricating oil was also tested individually and in mixed bacterial consortium at different temperatures and nutrient concentrations. On the basis of this study they concluded that oil-degrading bacteria are abundant in soils in Buea.

This can be exploited for large oil spill clean-up campaigns. This study also provides information on the physico-chemical requirements of optimum degradation by these bacteria.

Ipeaiyeda and Dawodu (2008) Conducted study on heavy metals contamination and its dispersion in topsoil of reclaimed auto repair workshops in Nigeria. Their study was aimed at ascertaining the dispersion of contaminated Zn, Ni, Cr, Hg and Pb within the soil profile. They have analyzed 75 soils samples collected from auto mechanic workshops and 18 samples from control sites. From study of these soil samples a significant level of contamination were found in view of elevated levels of these metals above background concentrations in control sites. They also concluded that Pb was the most significant contaminants and the degree of contamination was highest for Pb followed by Hg. The detailed levels of total metal contamination for Pb and Hg exceeded international threshold for agricultural use.

The water samples containing petrochemical effluents were evaluated for elemental contaminants along a kilometer distance in Ubeji Creek, a tributary of Ubegi river in the Niger delta of Nigeria. The work has been done by Achudume (2009) twenty water samples were collected from six sites at various times. The water samples were analyzed several physicochemical parameters. Results fro the analysis showed variations in temperature, pH, BOD COD, Dissolved and suspended solids as well as conductivity. The entire environment starting from the end of- pipe source was coated with black oily residue result from the analysis reveal that water quality were found very poor.

The absence of fish and other aquatic lives the high levels of Zn (2.4), Cr (0.24), Fe (63.44). Hg (4.24) , Mn (2.49) and Pb (0.76) levels $(\mu\text{g/l})$ confirm the toxic nature of Ubegi Creek. At the lower reaches, the mixing of effluent with brackish waters was not enough to support aquatic life, partly because of diminishing oxygen and toxic shock. Nevertheless, the study provides evidence to suggest that the water in Ubegi Creek is toxic. It also provides graphic data to suggest point source where effluents could be held for treatment or neutralization before being discharged into the aquatic environment.

Pathak, C et al (2010) Studied on heavy metals contamination in waste –water irrigated agricultural soil and brought out the conclusion that due to waste water irrigation concentration of heavy metals such as Zn, Pb, Ni, Cu, Cd and Hg has found increased in soil being irrigated by waste water as compared to natural water irrigated soil. The study also highlighted that the concentration of Zn was higher and concentration of Cr was found minimum in both the natural soil and impacted areas soil. They concluded that increase of these heavy metals in soil of Dehradun is alarming and may also occur in agricultural crops which may cause some health hazards by entering in human body through food chain.

Charles and Victor (2010) Study has conducted for the estimation of heavy metals contamination in relation to microbial counts in soils of auto mechanic workshops. In which soil samples from six different locations in the Port –Harcourt Metropolis in Nigeria. They made a relationship between heavy metals contamination and soil microbes with respect to soil depths from automobile workshops. And found the concentration of Pb, Cd, Ni, Hg and V. The presence of these heavy metals was mainly due to waste from automobile workshops activities. And four species of fugi such as *fusarium sp, Trichderma sp, Aspergillus sp, Rhizoctonia sp* were identified. While the bacteria were mainly Bacillus *sp.* These species except Rhizoctina *sp* responded to the presence of heavy metals pollution levels and used in bioremediation of polluted soils in the Niger Delta areas.

Nwachukwu et al (2010) worked on automobile wastes management and found the metals concentration in the order of Pb>Mn>Cu in soil samples taken from the depth of 100 of profile and suggested that mechanic villages should have emission testing facilities, concrete floor workshops, toilet facilities, tarred roads and drainage channeled to one or more three phase storm water treatment facilities. They also recommended infiltration method in the sandy areas and the detention method in the shale areas. They further recommended extended producer responsibility (EPR) for used motor oil, the use of local phyto-remediation plants sensitive to Pb, Mn, and Cu, installation of groundwater monitoring wells, comprehensive waste management plan, standard guidelines for establishment of mechanic villages, code of practice and continuous education for the mechanics.

A similar study has been conducted by Nkwocha and Daru (2010) The main objective of the study was to determine the effects of oil pollution on local plant species in terms of abundance and composition and to investigate the levels of contamination in two local food crops. Four impacted and two reference sites were identified; observations were made for a period of fifteen months and samples collected for analysis. Results from the analysis showed that local plant species were greatly affected at the impacted sites, and the leaves of the two crops contained significant levels of the contaminants examined. At the control sites, the distribution frequency of plants ranged between 13.5% and 93.4% while at the impacted sites it ranged between <2% and 39%. A total of 43 species distributed into 20 families of plants of heavy metals were relatively higher in the leaves of food crops at the polluted sites than those at the control sites. The high values recorded on heavy metals were associated crop species, soil types and age of crops but most importantly due to the acidic nature of the soils resulting from oil pollution. Results shoed that oil pollution constitute a potential danger to the food chain, food security and general health of the local population. The results of the case examined showed that oil pollution not only led to the extinction of the most vulnerable plant species but also drastically reduced their distribution frequencies at the impacted sites, it raised the acidic level of soils, reduced the level of their essential minerals, and increased their levels of heavy metals.

The most outstanding results of this study concluded that oil pollution leads to the contamination of local food chain. It is most probable that the source of traces of heavy metals found in the leaves of food crops at the polluted sites was from oil pollution. The levels of contamination observed in cassava and pumpkin leaves at the polluted sites, which are essential components of the local staple food is more worrisome. If the high level of contamination observed in this study was occasioned by just an incidence of oil spill, urgent and serious studies are therefore required to assess the levels of contamination in the entire food crops in many rural communities that have been experiencing frequent oil spills in the region. Another important observation was that oil pollution provoked systemic changes among local animal and plant species; while some were endangered, others became more vulnerable, rare and even extinct.

The result of this study are sufficiently compelling to warrant future studies in the area to obtain regular information on the general and specific effects of oil pollution on plant biology, plant community and especially on food crops, as this area remains the major food basket of Imo state. This will also help in understanding the level of danger and various health implications of regularly consuming such crops and the precautionary measures to be taken by the local population to ensure food security both in present and in the future.

Nawachukwu (2010) Worked on three automobile mechanic villages (Okigwe, Nekede and Orji) in Nigeria. In which three samples from each mechanic villages were collected for the study of metals concentration and concluded that the degree of mechanic activity or population of mechanics and their workshops density affects the degree of metal enrichment in the

mechanic village soil. Orji mechanic village has the slope and drainage area with less workshop density, which supports dispersion of metal contaminants from the mechanic village thereby reducing metal concentration in the soil.

Adewole and Uchegbu (2010) Investigated the properties of soil and maize plants sampled from the vicinity of selected auto mechanic workshops in Ile-Ife, Nigeria. The results from the study shows that the oldest automobile workshop had the highest accumulation of Fe> Zn>Pb>Hg, in that order, when compared with the youngest. The control site (Non automobile workshops) had metal concentrations typical of agricultural soils. It was also recommended that any attempt to cultivate an open vacant land near automobile workshops to edible crops, specially maize should be discouraged. It was also suggested that these heavy metals if ingested may affect the health of man.

Odoh et al (2011) The determination of trace metals in soils within motor parks in some selected local government areas of Benue state of Nigeria were carried out with the help of Flame Atomic Absorption Spectrophotometric technique and were found a positive correlation among the metals determined. Metals such as Pb. Cd, Cu, and Zn showed a high degree of contamination, while Co, Mn, and Ni shows low degree of contamination in the study sites.

Adelekan and Abegunde (2011) Worked on soil and groundwater samples of 7 automobile mechanic village of Ibadan, Nigeria and analyzed samples for the metals like Cd, Cu, Pb, Cr and Ni and same metals were analyzed in samples taken from the control sites. The results of both types of samples compared to establish limits sets for soils in some countries. The values measured in the groundwater samples were found higher than these limits in several cases .The values measured in this study were higher than those limits for the heavy metals with exception of Cu where all the values were higher than the limits. The recommendation from this study include execution of some form of phyto-remediation measures at the villages. It was also suggested for the strict compliances to the regulatory limits in sludge to be released from these villages into the environment and the enforcement of the environmental protection regulations to arrest the ongoing buildup of these metals of those metals.

A similar kind of work has been done by R.C. John et al (2011). On the basis of this work it has been focused. The effect of crude oil on the growth of legum and fate of nitrogen- fixing bacteria was investigated by using standard cultural techniques. The results from the investigation revealed observable effects of soil on physico-chemistry, plant growth and nodulation as well as on densities of heterotrophic, hydrocarbonoclastic and nitrogen fixing bacteria. The effects however varied with different levels (0.5%, 1%, 5%, 10%, 15%, and 20%) of pollution.

It was noticed that ammonium and nitrate levels were high in the unpolluted soil but decreased with increase in pollution levels. Nitrite was not detected in contaminated soil probably due to the reduction in numbers of nitrogen fixers, from $5.26 \pm 0.23 \times 10^6$ cfu/g in soils to $9.0 \pm 0.12 \times 10^5$ and $2.2\pm0.08\times10^5$ in soils with 5% and 20% levels of pollution respectively. The contaminated soil also exhibited gross reduction in the nodulation of legumes. It was also noticed that a range of 13-57 nodules was observed in legumes from polluted soil against 476 nodules recorded for plants cultured on unpolluted soils. This investigation reveals that symbiotic nitrogen fixing bacteria associated with legumes in wetlands are very sensitive to crude oil pollution. This study has also revealed that although diazotrophs are generally inhibited by oil pollution, some tolerant species even in small densities could enhance oil degradation in wetland soil.

The contamination of soil due to heavy metals in developing countries is steadily increasing by the disposal of sewage water and industrial waste. Most of the industrial and sewage waste are disposed and being used for growing crops like fruits, vegetables etc. These effluents may contain not only organic matter and other nutrients but also huge amount of heavy metals in soil, ground water and even in food chain also. These heavy metals may accumulate in the soil at an alarming rate and may persist for a long term in food chain by accumulating in plants and animals and ultimately get consumed by human.

A study highlighting concentration of heavy metals in vegetables being grown on waste water irrigated soil was conducted by Chopra and Pathak (2012). Study investigated the heavy metals concentration in vegetables irrigated by waste water. The findings of the study indicates that the variation in concentration of heavy metals in the crops varieties depending on the interaction of heavy metals in different parts of plants like shoots, roots stems, leaf etc. It was also found that concentration of Cr was found higher than the prescribed limit set by WHO in waste water irrigated soil. The Cd concentration was also found higher than the prescribed limit of Indian standard. It was also concluded that the more accumulation of heavy metals in vegetables may pose a potential threat to human health.

Water quality is the degree of potability which is determined by the amount and kinds of suspended and dissolved substances. Water is being deteriorated by environmental pollution

and also by some other factors. In recent years, because of continuous growth in population, rapid industrialization and the and the accompanying technologies involving waste disposals, the rate of discharge of the pollutants into the environment is far higher than the rates of their purification. The physico-chemical investigation of water samples of Kangra district of Himachal Pradesh was done by Kumar et al (2012). They analysed seven water samples for various parameters like temperature, turbidity, pH, dissolved oxygen, and chemical oxygen demand. The result of the analysis showed that the temperature was within limit and the water samples were found not highly turbid which indiacting that water from different sampling sites was not much polluted. The low COD values was the indication of lesser amount of water pollution in the sampling sites. The observation of the study also suggest that unsuitable development in surrounding area could lead in environmental damage by changing the hydrological chractreistics.

Motor vehicle servicing centers popularly known as mechanic workshops are sources of automobile wastes and these automobile wastes are becoming a visible problem especially in developing countries. Therefore the usual improper disposal of these wastes now demands attention in order to protect the soil for agricultural purpose.

An understanding of the nature of soils in natural and human influence ecosystems is essential if progress is to be made in the determination and monitoring of soil quality. The change circumstances and the recognition of the often crucial role that soils play within these systems has resulted in a demand for measures soil quality, similar to those used in the characteristics of water and air.

Automobile wastes are hazardous wastes with serious agronomic and environmental implications. Soil properties varied widely and temporally in automobile soils. Heavy metals are naturally present in soils, but anthropogenic activities have resulted in high concentrations in the environment. Motor vehicle servicing centers may be sources of automobile wastes in urban and semi urban areas. In these areas fossil fuels products are used leading to excess accumulations of various forms of heavy metals. These accumulations deteriorate nearby farms and cause non-point-source pollution. But these heavy metals vary with seasonal changes.

In soils, petroleum hydrocarbon creates condition lead to the unavailability of essential plant nutrients such as nitrogen, and the availability of some toxic elements such as arsenic and lead to plants. Crude oil in soil makes the soil condition unsatisfactory for plant growth, due to the reduction in the level of available plant nutrient or a rise in toxic levels of certain elements such as iron and zinc plants are highly susceptible to oil exposure and this may kill them within a few weeks to several months. There are several vegetal species that are capable of growing in soils polluted with hydrocarbons and they participate in their degradation through the rhizosphere, part of the root, which favors the growth of several microorganisms and increase biomass and microbial activity, accelerating degradation processes. The main objective of this study was to investigate the changes in growth and anatomy of *A. hybridus* grown in a crude oil contaminated soil and possible use of these changes in anatomy as a phytomonitoring techniques of crude oil pollution.

The result of this research work reveal that these visible significant anatomical changes seen in all the *A. hybridus* grown in the crude oil contaminated soil could be employed as an index of monitoring environmental pollution. This investigation can also be done in other plant species to ascertain their possible use in phytoremediation.

The findings of this research work showed that spent engine oil adversely affected soil properties. Maize plants that survived in contaminated soils became stunted. Consequently, the need to encourage the protection of farmlands and their surroundings against indiscriminate disposal of the oil cannot be overemphasized.

The used oil from a single oil change may look as harmless as dirty dishwater, but nothing could be further from the truth. A single gallon of used oil can contaminate a million gallons of freshwater, an amount equal to a year's supply of drinking water for 50 people. Even a little as a single pint of oil can create an oil slick the size of a football field. Once we realize how little it takes to caused widespread contamination, it is easy to see that you must properly dispose of this extremely hazardous and highly common waste. Dumping oil in sewers is not an option; sewers lead to waste treatment plants, which will have a difficult – not to mention expensivetime removing the oil from water intended for humans. Dump the oil on the ground and eventually it will find its way to sever grates, and from there to the waste treatment plant. Storm drains lead to stream, rivers and lakes in our communities, potentially poisoning these waters for fish and other wildlife.

The wetland is an environment at the interface between terrestrial ecosystem and aquatic systems. This makes them different from each yet highly dependent on both (Mistsch and Gosslink 1986). They are generally richer in mineral salts due to water supply from the surroundings via runoff and/or ground water. Nitrogen is a common soil nutrient element required in large quantities by plants. The growth of higher plants in many ecosystems is limited by nitrogen supply. Nitrogen is largely made available to plant in form of ammonium or nitrate ion by activities of soil microorganisms through the process of nitrogen fixation. These microorganisms are the nitrifying bacteria.

Therefore contamination of soil may crude oil could lead to a depression of microbial density and activities even in case of relatively light contamination (Odu, 1972 a,b). The extent of effect depends on the original soil properties and the plant exposed to contaminated soil. Hence if leguminous plants is planted on a crude oil contaminated soil, the activities of the nitrogen fixing bacteria may be retarded. These oil can also inhibits the action of the enzyme "nitrogenase" Thereby disrupting the process of protein synthesis.

With an ever increasing world's population, there is a concomitant increase in the demand for petroleum and petroleum products, which apparently constitutes a source of environmental pollution (Raven et al., 1993). Oil pollution is a major environmental concern in many countries, and this has led to concerted efforts in studying the feasibility of using oil- degrading bacteria or bioremediation. The discharge of used engine oil from vehicles is the main source of oil pollution in the environment of Buea. The soil is the habitat to many living organism; any change in their number or form may upset or cause a total collapse of the ecosystem. The effect of oil spill leads to an enrichment of the oil degrading microbial population. However a decrease in microbial population exposed to crude oil and its products have also been documented. Beside this some other work has also done concern with crude oil contamination and soil and water microorganism. Atlas (1981) Suggested that certain crude oils contain toxic component that are bacteriostatic. These inhibitory effects have also been reported to depend on concentrations. (Benka-Coker, 1989). No single micro degrade a petroleum hydrocarbon molecule. However different species or strains of the same species may be capable of degrading different groups of hydrocarbon, found in oil (Facundo et al., 2001). Pollution control strategies involving physico-chemical methods have often aggravated the problem rather than eliminated it (Walker and Crawford, 1997). Beside these Dinkla et al., 2001 reported that biodegradation is an attractive method for the remediation contaminated sites because of its economic viability and environmental soundness.

The physical, chemical and thermal processes are the common techniques that have been involved in the cleaning up of oil contaminated sites (Frick et al., 1999). These techniques however have some adverse effects on the Environment and are also expensive (Frick et al., 1999, Lundstedt, 2003).

Recently biological techniques like phytoremediation are being evaluated for the remediation of sites contaminated with petroleum. Phytoremediation is the use of plants and/or associated microorganism to remove, contain or render harmful material harmless (Cunninghum et al., 1996; Schwab and Banks, 1999; Merkl, 2005). It has been shown to be effective for different kinds of pollutants (contaminants) like heavy metals, radionuclide's and broad range of organic pollutants (Schroder et al., 2002; Schnoor, 2002).

According to Pivetz (2001), plant for phytoremediation should be appropriate for the climatic and soil conditions of the contaminated sites .Such plants should also have ability to tolerate conditions of stress (Siciliano and Germida, 1998a) Njoku, et al., (2008a) demonstrated that G.*max* germinates and grows in crude oil polluted soils. Also Frick et al., (1999) included G.*max* in the list of plants that can grow and remediate petroleum hydrocarbon contaminated sites. However no record has shown that G. *max* can remediate crude oil polluted soils. It is therefore important to study the ability of G.*max* to affect the phsico-chemistry (pH, moisture and organic contents and the crude oil content of soil polluted with crude oil.

The incidence of oil pollution has been extensively studied in many parts of the world. Most importantly various publications on oil spillage containing relevant information and new understanding on its effect on specific environmental components have been made. By taking as an example, in one of the studies in a community in the Niger Delta Region, Osugi, et al (2004) observed that hydrocarbons and heavy metals from crude oil negatively affected flora and fauna, enhanced the absorption and bioaccumulation of heavy metals in plants cells. It has also been reported that acute exposure to oil spills can potentially affect clean-up crews, regulatory and emergency officials, coastal residents and member of scientific team investigating the spills causing various diseases such as vomiting, abdominal pains skin irritation, and some cancers (National research council, 2004).Some report had been made that constant exposure to high concentration levels of lead from oil may be associated with elevated high blood pressure (Martin et al 2006).

Alade et al (2012) were worked on environmental impact of vehicle service centers on soils in Ogbomosho Nigeria and characterized to conclude the level of heavy metals present in soil samples of diesel and petrol service centers and concluded that soils samples from both petrol engine vehicle service centers and diesel engine vehicle servicing centers are polluted with Pb, Zn, Cr, Cd and Ag. The metals concentrations measured in the collected samples from both the sampling locations were higher than European Union (EU) and federal Environmental Protection Agency limits while the concentration of all the metals detected were below these limits. The conclusion of the study suggests that Premium motor spirit (PMS) used in Nigeria may contain lead (Pb) and may be one of the source through which environment of these vehicle services centers are contaminated with heavy metals.

Dwivedi et al., (2013). Investigated Total dissolved solids, total solids and total suspended solids. In this research work they analysed various water samples collected from Mohand rao river of doon valley in three different seasons and found an overall increase in percentage of total solids during summer season, similar trend was found in rainy season as compare to winter season. They also pointed out the impact of catchment characteristics such as soil type, vegetation, geology and topography on water quality of the study Mohand rao catchment area.

Shekhon and Singh (2013). Made a study for the determination of heavy metals (Cd, Cr, Ni, Al, Pb, Se) in drinking water of district Patiala. In this study the ground water samples collected from 100 localities during July 18 to 28, 2012. During this study they observed that the Ni and Al levels were high in most of the samples whereas concentration of Cr, Pb, As and Se levels were found to be below the permissible limits of WHO, and level of Cd was found 0.006 mg/l to be above the permissible limit of 0.005 mg/l. They also concluded that high concentrations of Ni and Al warrant to identify and evaluate natural and anthropogenic sources responsible for distribution of heavy metals in ground water.

Ramola and Singh (2013). Investigated heavy metals concentrations such as Cd, Cr, Pb, Ni, Zn, and Cu. in effluents of pharmaceutical industries of Dehradun district and determination of contaminants were performed by using atomic absorption spectrophotometer. The concentration of heavy metals were found in varying range. Among the heavy metals highest range was found for Fe (10.80 mg/l). The highest concentration of Pb was found as 0.26 mg/l while 0.55 mg/l for Cd. The study reveals that concentration of heavy metals were found above the permissible limit as recommended by WHO standards.

Therefore, the present study of soil and groundwater quality of petroleum contamination prone areas has been undertaken to understand the geochemical assessment of soil and groundwater water and aspects of contamination, if any in dehradun district.
The present research work will discuss detailed account of chemical composition of soil and groundwater of nearby locations of motor servicing workshops with the help of elemental and physico-chemical analysis with reference to suitability of water for various uses and also suitability of soil for agriculture purpose.

CHAPTER -3

GEOHYDROLOGYOF STUDY AREA

Doon valley is situated in Uttarakhand state of India and southwest of Himalaya Shiwalik region and extends for a length of about 80 km with its average width of 20 km occupying an area of about 2245 km². The area lies between longitude 77^0 35'E to 78^0 19'E and latitude in the north –western limit of state Uttarakhand and adjoining the state of Himachal- Pradesh. The valley is bounded in the northeast by lesser Himalayan belt and Shiwalik region on the south west. Two important rivers of north India Yamuna and Ganga demarcate the south -eastern and north –western boundaries of Doon valley. Maximum east-west length for the valley is approximately 70 km and the width varies from about 2.5 km in the extreme west, 25 km in the central part of nearly 45 km in the east.

The valley comprises of mainly 6 sub watersheds: Asan (left), Asan (right), Suarna Tons, Song, Ramau and Chandrabhaga. A north- south divide divide roughly corresponding to Mussorie- Saharanpur road bifurcates the valley into the major subwatersheds of Song and Asan which flow to their master systems in the east and west respectively.

3.1 CLIMATE

The climate of Dehradun is more temperate and humid than that of the adjoining districts, the maximum day and night temperatures being 3 to 6° C lower throughout the year. Only the the months of May and June are hot though they are seldom oppressive.

The valley enjoys a salubrious climate almost throughout the year. The summer maximum and minimum temperature vary from 36.6° C to minimum range between 23.4° and 5.2° C respectively. The total annual rainfall is about 1800 mm of which bulk precipitates in the month of July- August.

The district has within its limits lofty peaks of the Outer Himalayas as well as the Dun Valley with climatic conditions nearly similar to those in the plains. The temperature depends on the elevation. The climate of the district, in general, is temperate. In the hilly regions, the summer is pleasant but in the Doon Valley, the heat is often intense. The temperature drops below

freezing point not only at high altitudes but also even at places like Dehradun during the winters, when the higher peaks are under snow.

The summer starts by March and lasts up to mid of June when the monsoon sets in. Generally, the month of May and early part of June is hottest with mean temperatures shooting upto 36.2°C at Dehradun and 24.8°C at Mussoorie. The maximum temperature rises to over 42°C at Dehradun while at Mussoorie it doesn't exceed 32°C. Winter starts from November and continue upto February. The highest maximum temperature recorded at Dehradun was 43.9°C on June 4, 1902 and that at Mussoorie was 34.4° C, on May 24^{th} 1949. The mean daily maximum temperature during winter is 19.1°C at Dehradun and 10.2°C at Mussoorie. The mean daily minimum temperature in January is 6.1°C at Dehradun and 2.5°C at Mussoorie. In Mussoorie the temperature drops to about -6^oC to -7^oC when snow fall occurs. The lowest minimum temperature at Dehradun during winter was -1.1° C, on February 1st, 1905 and January 1945 while at Mussoorie it was -6.7 \degree C, on February 10th, 1950. Monsoon starts by the mid of June and lasts upto September.

Frost is quite common in winter nights. Severe frost occurs in January and February and cause damage to young *sal* regeneration. There are many places especially in the low grasslands and within two miles on each sides of the Suswa and Song rivers, where the night temperature during October to April are several degrees lower than those at Dehradun. In these places frost occurs as early as the first week of November.

The prevailing wind come from the west and are generally of moderate velocity, except when severe storms occur during the hot weather, in April and May. In the evening there is always a light breeze coming down the hills generally from the north. The hot 'loo' rarely manages to cross the Shiwalik ridge. Nightly dews prevail uninterrupted throughout the year except for April, May and part of June. (Kumar, 2004)

The monsoon generally breaks out by the end of June and the rains continue until about the middle of September, the heaviest falls normally occurring in July and August. Occasional showers may continue in September and October after which, there is usually little rain until about the end of December. Some rain usually falls in January and February after which there is very little rain except for occasional thunderstorms until the break of the monsoon. Few months, however, pass without any rain at all; however, bad drought years are rare in Doon valley.

The district receives an average annual rainfall of 2073.3 mm. Most of the rainfall is received during the period from June to September, July and August being the wettest months. The region around Raipur gets the maximum rainfall, while the southern part receives the least rainfall in the district. About 87% of the annual rainfall is received during the period June to September. The climatic average data for last 25 years of Doon Valley is summarized below.

Table 3.1.1 Climate Data of Doon Valley

3.2 PHYSIOGRAPHY

In the shiwalik range of outer Himalaya, there are a number of longitudinal valleys, called the Duns. One of the largest is the Doon valley (Dehradun). The Doon valley is a synclinal depression between the lesser Himalayan mountains in the north and sub- Himalayan hills in the south. Aligned parallel to the general trends of Himalaya, it is a veritable intermontane valley, bottom of which is filled up with thick detritus shed from overlooking hill slopes. Broadly the Doon valley can be divided into three different slopes; northeastern slopes of the Shiwalik, Doon valley proper and southwestern slopes of Shiwaliks are quite steep in higher reaches and have easy gradient lower down. These are cut by a large number of shorts, shallow and boulder streams which carry their discharge into Asan, Suswa and Song rivers. The southwestern slopes are very steep and carry poor vegetation.

3.3 GEOLOGY

Geological structure of Doon valley is characterized by two major faults, crustal and fractures along which rock slabs of mountain mass have been uplifted and moved southward. The doon valley and Shiwalik range is principally composed of the rocks of the Shiwalik groups. The rocks of the Shiwalik groups are classified into the lower, the middle and the upper Siwaliks. The southern limb of the Doon -valley and the Shiwalik.

Rishikesh and some parts of Mohand is found in Doon valley, within the Himalayan ranges of mountain in the outer (Sub) Himalayan division. The southernmost zone of the outer Himalaya consists of 9500m thick piles of Tertiary sedimentary rocks (conglomerate, sandstone, mudstone, phyllites, shale, limestone ranging in age from Paleocene to lower Pleistocene (Thakur 1992). The breakdown of the rising central Himalaya has resulted in deposition of the Shiwalik group in the form of Molasses deposits, overlain by late Pleistocene Doon gravels (Parkashetal,1980)

In the Shiwalik region a number of longitudinal valleys occur, of which one of the largest is in the Doon valley having 80 km length and 20km width (Nossion, 1971). The Doon valley and its environ were studies as one hydrogeologic system to understand the ground water recharge, movement, storage and discharge on the regional hydrogeologic context. The valley having more than 1600 km² area enjoying up to 2800 mm rainfall during rainy season from June – September. Knowledge of this regional geology and hydrogeology of the areas played a lot on selection of specific sites for Vertical electrical resistivity sounding and Seismic refraction profile as well as hydrogeological interpretation of the geophysical data.

District Dehradun is situated in NW corner of Uttarakhand state and extends from N Latitude 29°58' to 31°02' 30" and E Longitude 77°34' 45" to 78°18' 30". It falls in Survey of India Toposheets Nos. 53E, F, G, J and K. The district is bounded by Uttarkashi district on the north, Tehri Garhwal and Pauri Garhwal districts on the east and Saharnpur district (UP) on the south. Its western boundary adjoins Sirmour district of Himachal Pradesh separated by Rivers Tons and Yamuna.

The total area of Dehradun district is 3088 km² with an average altitude of 640 m above MSL. The district comprises of six tehsils, namely Dehradun, Chakrata, Vikasnagar, Kalsi, Tiuni and Rishikesh. Further, it is divided into six developmental blocks, viz: Chakrata, Kalsi, Vikasnagar, Sahaspur, Raipur and Doiwala.

Geologically, Doon valley is a synclinal trough within the Shiwalik system. The limbs of the syncline consist of the middle and upper Shiwalik rocks followed by the northerly dipping pretertiary formations of Lesser Himalaya in the north. On basement of Shiwalik rocks, Dun gravels are deposited.

Geologically Doon valley can be categorized as

3.3.1 LESSER HIMALAYA

The lesser Himalayan zone can be represented by the rocks of Pre – Tertiary and Tertiary age. The Pre- Tertiary rocks have come in contact with the Tertiary rocks by the NW-SE trending Main Boundary Thrust (MBT) and with the Eocene rocks by the Krol Thrust Towards the east of Yamuna River the Krol belt directly override the Shiwalik Group along MBT with the overlapping of intervening zone of Lower Tertiaries.

3.3.2 SHIWALIKS

Middle Shiwalik sandstone and upper Shiwalik boulder beds are exposed in the south of Main Boundary Thrust. The middle Shiwalik is represented by conglomerates, which show an upward – coarsening succession in the alluvial fan system.

MIDDLE SHIWALIK

It is composed of grey, salts and peeper textured poor to moderately sorted, fine to coarse grained multistoried sandstones with subordinate amount of mudstone. Multistory sandstone complex of Middle Shiwalik exhibits vertical facies variation from sandstone –mudstone to sandstone to mudstone –conglomerate. A very characteristics feature of the multistoried sandstone is the repetitive occurrence of selective cementation layers of varying thickness and sharp contacts with the under and overlying friable sandstone.

UPPER SHIWALIKS

The Upper Shiwalik is predominantly made up of thick succession of Pre Tertiary clasts derived from the Lesser Himalaya with subordinate sandstone and mudstone facies represented by Boulder Conglomerate Formation.

3.3.3 DOON GRAVELS

The valley areas are filled by the alluvium belonging to Holocene to Plestocene age which overlie the Shiwaliks. There are primarily gravels and are known as the Doon Gravels. On the basis of lithology and structural framework the Doon gravels are further categorized into three units $(A, B, and C)$

UNIT–A: It is mainly composed of clast derived from Lesser Himalayan limestone, shale, slate, and Lower Tertiary purple and buff coloured green sandstone. The clasts are sub – angular to sub rounded granular to pebble size, embedded in fine grained matrix.

UNIT –B: It is predominantly composed of rounded to sub- rounded boulders and pebbles mainly of quartzite together with sandstone and phyllite. This composition of clast indicates that Unit- B is derived from the upper Shiwalik Boulder Conglomerate along with Middle Shiwalik sandstone and Lesser Himalayan phyllite and quartzite.

UNIT–C: This unit consist of poorly sorted angular to sub-angular granules and pebbles interlayered with large pebbles and sometimes boulders. Unit- C gravels is widely distributed along the south of Santaurgarh thrust and represent the youngest gravel unit of fan away from the thrust clast size decreases the mud and silt content increases.

Figure 3.1: Geological Map of Study Area

3.4 DRAINAGE

District Dehradun is drained by Ganga, Yamuna and their tributaries. The two basins are separated by a ridge starting from Mussoorie and passing through Dehradun. The easterly flowing rivers join River Ganga and the westerly flowing rivers join River Yamuna. Ganga River enters the district near Rishikesh where Chandrabhaga River joins it. Song and Suswa are two main tributaries of the Ganges. Suswa flows SE, draining the eastern Doon along with its ephemeral tributaries like Bindal Rao, Rispana Rao etc. and joins River Song SE of Doiwala. Song River has its origin from the adjoining Tehri district. Initially it runs parallel to the Mussoorie Mountain chain in NW direction for few kilometers and then takes a sudden turn in SE direction and joins Suswa River south of Doiwala.

Figure 3.2 Drainage map of Study area

Yamuna River emerges from Yamnotri, which falls in district Uttarkashi. It enters Dehradun district at the point called Khat Bhondar which is about 20km east of Deoban. Tons is the main tributary of Yamuna which has its emerging point in the north of Yamnotri and receives water from Supin and Rupin (tributaries of Tons). River Tons separates Uttarakhand from Himachal Pradesh. The western part of Doon Valley is drained by Asan and its tributaries; it joins

Yamuna near Rampur Mandi. Yamuna River roughly divides the district in two halves, the hilly region in the north and Doon valley in the south.

Both surface and subsurface sources are being developed for irrigation purpose. The perennial rivers/ springs/ gadheras are being developed by constructing canals and guls. Canals in District Dehradun run for a length of 786 km. There are four main canal systems namely Bijapur, Rajpur, Kalanga and Jakhan. These canal systems were developed during the British period and now being maintained by the state irrigation department. The Rajpur canal system, Jakhan canal system, Kalanga canal system, and Bijapur canal system have 7, 5, 7 and 10 number of canals, respectively. Canal system, Jakhan canal system, Kalanga canal system, and Bijapur canal system have 7, 5, 7 and 10 number of canals, respectively.

Sub surface water is developed through tubewells. There are 118 functional Irrigation tubewells in District Dehradun (as on 31.3.2009). Most of these tubewells are located in the intermontane Doon Valley tapping the Doon Gravels. Besides the canals and tubewells, there are other irrigation practices like pump sets, hydrum, hauz, tanks etc.

3.5 GEOMORPHOLOGY: GEOMORPHIC DIVISIONS

Dehradun district may be divided into four geomorphological units namely alluvium, piedmont fan deposits, structural and denudational hills and residual hills.

3.5.1 ALLUVIM

This unit is represented by unconsolidated and loose admixture of sand, gravel, pebbles, silt and clay of varied grades deposited in the form of terraces along Asan, Song, Tons, Yamuna, Ganges etc. and in the intermontane valley as well. These are represented by unconsolidated material like sand, gravel, silt and clay. The terraces are formed by river cuttings followed by deposition of eroded and transported material in step like features along the river.

3.5.2 PIEDMONT FAN DEPOSITS

The area comprising of Dun gravels formed of numerous coalesced fans constitute this unit. The older Dun gravels belong to the upper realm of principal Doon fans whereas the younger and youngest duns belong to lower realm of principal Doon fans and dip controlled pedimont fans respectively.

3.5.3 DENUDATIONAL AND STRUCTURAL HILLS:

The denudational and structural hills comprise Siwalik and Lesser Himalayan Ranges. The Shiwaliks are exposed as a narrow band all along the southern boundary of Doon Valley and also in isolated patches. These hills have undergone severe denudation, weathering and erosion, making steep to moderate slopes.

3.5.4 RESIDUAL HILLS:

The residual hills are mostly formed by erosion and are the remnants of post Upper Siwalik deposits. These are called Older Doon Gravels or Langha Boulder Beds. Boulder beds, shales and red clay represent this unit. The residual hills are present in Doiwala and Vikas Nagar blocks.

Figure 3.3: Geomorphological Map of Study area

3.6 SOIL TYPES

Due to wide variation in topography, intensity of erosion, parent material and other factors, the soils show wide variation in many characteristics specially textures, depth, stoniness, colour, drainage, moisture status, organic matter contents and cation exchange capacity. In fact soil are the products of original geological formations hence three geological zones exhibit difference

in their soil types. On the basis of geological belts soil types of Doon valley has been categorized in three main categories:

3.6.1 LESSER HIMALYAN BELT

The Himalayan belt contains only a small bit of the tract especially in Nahan formation of the sub Himalayan series. It consist principally of loose sandstone and hence soil is arenaceous in nature. It is well suited to forest growth by providing a good foothold to trees even where there is no soil.

3.6.2 SHIWALIK BELT

The Shiwalik belt consist of sansstone and conglomerates, which are often soft and friable. Bands of clay are interceded with these sandstone and conglomerates, giving cohesionto the soil and therby improving its physical qualities. The soil resulting from the Shiwalik sandstone is a sandy loam, with sometimes a large proportion of clay. In higher regions with steep slopes the soil is very shallow and dry. Consequently the vegetation as a whole is more xerophytic. It is however, deep on northerly aspects and in lower slopes. The best soil occur on the lowest slopes where the proportion of clay is large and the drainage is adequate. But such conditions do not prevail over large areas.

3.6.3 THE BOULDER BELT OF THE VALLEY

The boulder belt is characterized by underlying beds of boulders and shingles of great thickness. Thin bands of clay are also intruded in these deposits causing swamps where they crop out. The soil, overlying the boulder mass, is very variable both in depth and richness and is altogether absent in rau beds. It is generally, sandy and poor with varying proportions of clay locally. Because of great thickness of underlying boulders, the water table is at a great depth.

Soils of Lachhiwala, in the south of the valley in Eastern Doon are generally silty loam to silty clay in texture and acidic to near neutral in reaction containing a high amount of organic carbon. The higher percentage of base saturation indicates adequate level of available nutrient in them. Non -calcarious soils are acidic to neutral and the texture varies from loam to loamy sands.

The soils of Jhajra in western Doon differ considerably due to physiography and relief. The soils are highly eroded. Soil cover is thin; texture is very coarse and nutrient status very poor. The soils however, at the lower portion of gentle slopes are fine loamy to coarse loamy in texture and acidic in nature. The soils of Barkot range in the Golatappar area in Eastern Doon do not exibit abrupt change in texture. These are acidic to near neutral in nature and fine loamy in texture.

The nature and soil type play an important role in agriculture and have direct relation with groundwater recharge. Physiography, climate, drainage and geology of the area are the factors responsible for the nature and type of soil and soil cover. The soil type also depends upon the slope and rate of erosion.

Figure 3.4 Soil Type map of study area 3.7 LAND –USE /LAND COVER

The forests are predominant land –use in the valley covering approximately 56 per cent of the valley. Cultivation is the second major land – use in the valley (27 per cent). About 19 per cent of this cultivation is practiced on hill slopes and rest being done on gentle slopes or in plains. Sal forests are predominant forest type in the valley, Shiwalik belt, valley proper and residual hills. The southern slopes of Lesser Himalayan region as covered with pine forests at lower altitudes and banj-oak forests at higher altitudes, found mixed at places with rhododendron, fir and pine. The gravelly alluvium of streams and river is covered with Khair – sissoo forests. The degraded forests cover much as 29 per cent area of the valley. The distinct topographic,

climatic and edaphic factors of Doon valley, characterized by their vicinity to tropics in the south and Himalayan highlands in the north, has bestowed the region with rich biological diversity.

Figure 3.5 Land use map of Study area

3.8 HYDROGEOLOGY:

WATER BEARING FORMATIONS:

The hydrogeology of the district is mainly controlled by the geology and geomorphology. A wide variation in the geology and land forms, in the area, gives rise to different hydrogeological conditions. Broadly Dehradun district is divided into three hydrogeological units, viz. (1) Himalayan Mountain Belt (2) Siwalik zone and (3) Doon Gravels

3.8.1 HIMALAYAN MOUNTAIN BELT:

Groundwater, in this unit, occurs as disconnected local bodies both under confined and unconfined conditions. Quartzite, schist, shale, slate, phyllite, compact sandstone, limestone and dolomite of Jaunsar, Baliana, Krol and Tal Groups are the main rock types. The rock

formations are characterized by fissures, fractures, veins and joints which provide the secondary porosity. The secondary porosity and permeability help forming the local bodies of groundwater. The weathered veneers found on hill tops, ridges, spurs etc. give rise to large groundwater repositories, under perched conditions. The alluvial deposits of fluvial and colluvial origin in the lower reaches of streams/ rivers in the form of fans and terraces are highly porous and permeable and hold promising areas for ground water exploration.

The springs and seepages are the main source for hilly areas. The springs show wide variation in discharge ranging from 1400 to 1507000 liters/ day (Bartarya, 1995)

3.8.2 SHIWALIK ZONE

Groundwater occurs under confined and unconfined conditions in this unit. The water levels are comparatively deep. In spite of the boulder- conglomerate bed of Upper Siwalik Formation being highly porous and permeable most of the water goes as run off due to steep slopes and the sediments forming piedmont fans dipping into the Intermontane valley. About 70 gravitational type springs have been reported which have a varying discharge from less than a liter per second to 113 liters/second $(0.002 \text{ m}^3/\text{min})$. The fresh water bearing zones are present in the Upper Siwaliks due to the presence of pebble–gravel–conglomerate–boulder beds and act as good groundwater reservoirs when underlain by the Bhabar or Dun gravels. Exploration has revealed that the pebble - boulder and gravel - sand beds of Siwalik are capable of yielding copious quantities of water.

3.8.3 DOON GRAVELS

The intermontane valley portion, of district Dehradun, is underlain by alluvial fan deposits. The sediments descend from the Lesser Himalayan front as well as the North facing Siwalik hill slopes. These fan deposits are called as 'Doon Gravels' and characterized by boulders and pebbles embedded in sandy and silty matrix. The clasts are mainly composed of quartzite, sandstone and phyllite, which are mainly derived from the Krol belt of the Himalayas Pebbles from Siwalik conglomerates are also present in the Doon Gravels.

Doon Gravels are highly porous and they have a significant permeability. Groundwater occurs under unconfined and semi confined conditions. The saturated granular zones occur in a depth range between 35.50 and 138.68 mbgl. The piezometric head ranges from 20.0 to 125.0 mbgl. Transmissivity varies from 1648.0 to 3500.0 m²/day while the field permeability ranges from 5.86 to 104.0 m/day. The discharge from the tubewell varies from 600 to 3000 lpm for a tapped thickness of 30 to 50 m with a drawdown of 2 to 7 m. The hydraulic conductivity, in the district, varies from 13 to 583 m/day.

3.9. DEPTH OF WATER LEVEL

There are 19 hydrograph stations located in the southern half of the district. The northern part is hilly where continuous water table is lacking and hence no hydrograph stations in this part. Using the data of these hydrograph stations Depth to Water maps for pre-monsoon, 2006 and Post monsoon, 2006 are prepared. Depth to Water, in the southernmost part of the district, ranges between 5 and 10 m. The area close to the hills is represented by water table >15 mbgl. The intermediate part has DTW in the range between 10 and 15 mbgl. During the post monsoon period the 5-10 m and 10-15 m ranges of DTW increased and the >15 m group is reduced.

A comparison of the shallow water levels of May, 2006 with the decadal average of May have been made. This comparison reveals that larger part of the Doon Valley shows a rise in water levels between 0 and 2 m. A small area in the SE part of the Valley close to the foot hills shows water level decline between 0 and 2 m. The decadal fluctuation map shows that by and large the area has groundwater potential with low development of shallow aquifers

3.10 GROUND WATER RESOURCES:

There are six developmental blocks in District Dehradun. Two blocks (Chakrata and Kalsi) fall in mountainous terrain where the slopes are high and water resources are not estimated for these blocks. Water Resources are estimated, using GEC 1997 methodology, for Raipur, Doiwala, Sahaspur and Vikas Nagar blocks as the topography is by and large plain, in these blocks. The block areas are divided into command and non-command. Draft for all uses and recharge from all sources are calculated for command and non-command areas.

CHAPTER-4

SOIL, WATER AND WASTE WATER CHEMISTRY OF THE STUDY AREA

District Dehradun which is also the capital of Uttarakhand state is located in the valley of foothills. Dehradun district is rapidly growing city not only in Uttarkhand state but also in Himalayan region and northern India with respect to urban and industrial development especially after the formation of the capital of the state. Since 2000 about 114% growths in urban population has been taken place, after the declaration of new industrial development policy for the Uttarakhand state in the year 2003 lead to the establishment of various types of industries.

With the emergence of various types of industries and departments many people arrived here for running their business which has impacted on population density of the district and which also have increases the number of vehicles and ultimately enhanced the number of motor servicing workshops in the district.

GEOLOGY AND GEOMORPHOLOGY OF THE STUDY AREA

Doon valley is an intermontane valley and has a distinct geological attributes with a wide spectrum of rocks varieties ranging in the age from Proterozoic to Quarternary (Thakur, 1981), located at the northern periphery of Shiwalik foreland basin in area of north western Garhwal Himalaya. Doon valley is a broad synclinal depression situated between the lesser Himalayan Hills in the north and the very young topographic relief of the Shiwalik ranges in the southern part of valley and is connected by the rivers Ganga in the eastern part and Yamuna in the western part (Mundepi, 2013).

Dehradun can be divided into Shiwalik range, Doon valley and Himalayan front. Nossin (1971). Sangeetha (2000) identified the Doon valley as five geomorphic units. The major geomorphic units in Asan watershed are denude- structural hills, residual hills, Piedmont zone, River terraces, Flood plains, Lineaments and settlements (Sangeeta, 2000). Residual hills of Doon Gravels control the drainage pattern in the area. River terraces of Asan Sitla Rao, Suarna streams are gentle to flat in nature.

Shiwalik group of rocks are thrusted over Indo- Gangetic plain sediments along the Himalayan Frontal Fault forming the Dehradun valley as a piggyback basin (Ori and Friend, 1984; Gupta, 1993). The boundaries of the valley is a quadrilaterals 72 km in length and 24 km in width, along the NW-SE regional Himalayan trend (Nossin, 1971; Nakata, 1972; Williams, 1992).

Geologically Dehradun can be divided into three major units; Lesser Himalayan formations, Shiwalik formation and the Alluviam covered valley depression. Proterozoic to lower Cambrian rocks of Lesser Himalayan Formation, Shiwalik formation and the alluvium covered valley depression. Proterozoic to Lower Cambrian rocks of Lesser Himalaya are the thick alluvium deposits that fills synclinal depression consist of three major fans (eastern, central and western) descending from the Lesser Himalayan hills, occupying a major part of the area as surficial deposits. The coalescence of these fans resulted in a piedmont plain (or fan surface). The near horizontal to slightly dipping piedmont plain and other fluvial deposits (fan conglomerate) are named as the "Doon Gravel" by Medilicott (1864) due to the preponderance of gravel in these deposits (Rao, 1986).

Lesser Himalayan Region: The surrounding Lesser Himalayan rock comprise of the Jaunsar (Chandpur phyllites and Nagthat quartzite) and Mussoorie Group (shale, sandstones, greywacke, calcarious slates, dolomite and sandstone of the Blaini – Krol Tal sequence) of Proterozoic- Cambrian. The Lesser Himalaya can be represented by the rocks of Pre -Tertiary and Tertiary age. The Pre –Tertiary rocks have come in contact with the Tertiary rocks by the NW –SE trending Main- Boundary Thrust (MBT) and with the Eocene rocks by the Krol Thrust.

The western fan is drained by the streams like Surna nadi and Koti nadi, which are originated from lesser Himalayan range and joining the river Yamuna. The collision and merging of the central fan with the western fan is drained by the streams like Surna nadi, Sitla Rao, Mauti nadi and Koti nadi originating from Himalayan range and joining the river Yamuna. The collision and merging of the central fans with the western fan results in a higher elevation and the formation of a water divide (WD) between the Yamuna and Ganga catchments. The Tons river forms the boundary of the western and central fans. The Bindal nadi, Song and Jakhan rivers drain the central and eastern fans and join the river Ganga. The area lying towards the southeast sector, henceforth, is referred to as the Ganga Catchment (GC), and of the northwest sector as the Yamuna Catchment (Mundepi, 2013).

Shiwaliks: Middle Shiwalik sandstone and Upper Shiwalik boulder beds are exposed in the south of Main Boundary Thrust. The Middle Shiwalik is dominated by friable grey coloured sandstones and Upper Siwalik is represented by conglomerates, which show an upward coarsening succession in the alluvial fan system.

Doon Fan gravel Terrace: Gravels descend from the Lesser Himalayan front as well as the north facing Shiwaliks slopes called as "Doon Gravels" characterized by very coarse boulders embedded in sandy and siltybmatrix. The clasts are mainly composed of quartzite, limeston, sandstone and phyllite which are derived mainly from the Krol belt of the Himalayas. Pebbles from Shiwalik conglomerates are also present in Doon gravels. The Doon gravels are composed of three units namely Older, Younger and Youngest Doon gravels.

The Doon Fan Gravel Terraces are medium to large and gently sloping terraces, developed on either side of the streams, consisting gravels, pebbles, boulders, sand clay and rock fragments. These terraces are formed by the erosional phenomenon of the streams flowing down from the lesser Himalaya and are also called fan cut terraces and extensively used for agriculture. At places these fans show differential and subsequent faulting.

Doon Fans Gravels Dissected Hills: The southern slope of the lesser Himalaya is characterized by a number of alluvial fans forming low lying dissected hills. The Doon Fan Gravel Dissected Hills are represented as an elongated feature tapering towards south with variable slope and very gentle towards south. It is highly dissected by streams and gullies running down from the lesser Himalaya and characterized by thick vegetation.

Sub Recent Fan Terrace: Sub Recent Fan Terraces are very much conspicuous on either side of the Asan River. They are a bit higher in elevation from valley floor containing recent alluvium. This unit comprise of boulders, gravels, pebbles, sand and clay, deposited on lower part of the piedmont dissected slope as well as on the lower part of Doon Fan Gravel Terraces.

Moderately Dissected Structural Hill: Moderately Dissected Structural Hills are mainly confined to the middle Shiwalik in Doon valley, with moderate to steep dip towards NW and having moderate to high relief. These hills are characterized by compact, massive, medium to coarse grained friable sandstone which is at places folded and faulted with gentle to steep dip, and moderately dissected. This unit forms a distinct water divide in Doon valley.

Piedmont Dissected Slopes: The Piedmont zone extends from Shiwalik water divide in the south to the synclinal axis of the Doon valley in the north. It consists of boulder, gravel, clay and pebbles derived from the upper Shiwalik formations. In the southern part it shows steeper gradient and has parallel to sub parallel Drainage pattern.

HYDROGEOLOGY

The area is broadly divided into three hydrological units namely, the Himalayan mountain belt, the Shiwaliks and the Doon alluvial fill (Doon gravels). Doon valley is drained by two drainage systems separated through Mussorie, Dehradun and Mohand anticline in the south. Asan river system flows towards North –West and it merge with Yamuna River at Dhalipur. In the South- East part of doon valley another drainage system flows which is called as Song river system is a major stream and finally merges with Ganga river at Rishikesh. Asan river is situated in the western part of doon valley between 77° 38' E and 78° 06'E longitudes and 30° $14'N$ and $30⁰31'N$ latitudes. In the western part of the study area Asan River bifurcates into many tributaries and streams, narrow in the upper reaches of the valley widening as soon as they enter into the upper level of the gravel terrace. Length of Asan river catchment is about 40 Km and width is 18 Km and is of third order stream and a huge amount of water with rainfall enters as surface runoff and flash floods. The drainage system of Asan river is controlled by this unit has lowest relief and consist of soft saturated sediments.

Asymmetrical synclinal valley drained by Asan watersheds flows in North- Westwards and ultimately joins the Yamuna river. Though the area is blessed with rich amount of surface water resources, yet groundwater is one of the major source of water being for drinking purpose and irrigation requirements. The bed consists of reworked Doon fan gravel, older Doon gravel mixed with boulders and pebbles, derived from Lesser Himalayan rocks.

The springs and seepages are the main source of water for hilly areas. The springs of the study area show wide variations in their discharge from 1400 to 15, 07,000 liters per day (CGWB, 2009). About 70 gravitational type springs have been reported from Dehradun district which have a discharge varying from less than a liter per second to 113 liter per second (0.002 m^3) $/min$).

In Himalayan mountain belt ground water zones occurs as disconnected local bodies under both confined and unconfined conditions. Quartzite, schist, shale, phyllite, compact sandstone, limestone and dolomite of Jaunsar, Baliana, Krol and Tal groups have secondary porosity and permeability. The formations are characterized by fissures, veins, fractures and joints. The zone of lineament, fault and main boundary thrust shows areas of high secondary porosity.

The weathered veneer found on hilltops, ridges, spurs etc. give rise to large ground water repositories under perched conditions. Significant variations in the yield for short distances are common. The alluvial deposits of fluvial origin in the lower reaches of the streams /rivers in form of fans and terraces are highly porous and permeable and hold promising areas for ground water exploration.

Ground water occurs in Shiwalik zones as both confined and unconfined conditions and the depth to water level is comparatively deep. Though boulder – conglomerate belt of upper Shiwaliks formations is highly porous and permeable, much of the water runs -off due to steep slopes and sediment forming piedmont fans dip into the intermontane valley. Pebble gravel conglomerate- boulder beds in the upper Shiwaliks, when underlain by the Bhabhar or Doon Gravels, act as good groundwater resources and serve as fresh water bearing zones. Exploration revealed that these are capable of yielding copious volume of water.

Gravels descend from the Lesser Himalayan front as well as the north facing Shiwaliks slopes called as "Doon- Gravels" characterized by very coarse boulders embedded in sandy and silty matrix. The clasts are mainly composed of quartzite, limestone, sandstone and phyllite, which are derived mainly from Krol belt of the Himalayas. Pebbles from Shiwalik conglomerates are also present in Doon gravels. The older Doon Gravels are characterized by the matrix represent debris flow deposits. The Younger Doon Gravels is Chractreized by rounded clasts of quartzite, limestone, sandstones, phyllite and shale derived from the Lesser Himalayas and Shiwalik provinces. Calcification is prominent due to the availability of carbonate material from the Krol belt. The Youngest of Doon gravels consist of very large boulders representing debris flow and braided river system. Recent alluvial deposits formed by rivers overlie this unit.

River Terraces: In Doon valley the River terraces are relicts of former flood plain levels that have undergone cyclic uplift and subsequent erosion under the influence of different physical and climatic conditions. The river terraces are formed by down cutting of fan materials (Piedmont) and shifting of river courses constitute older alluvial formation consisting of river born detritus deposits of varying dimensions. The sediments matrix of terrace consists of clay, silt, sand, gravel, pebbles and boulder.

Channel Bar: These geomorphic features of low relief are mostly observed all along the sitla rao river and its tributaries. The river in the study area flow through unconsolidated materials like boulder, pebble, sand, silt and clay and develop channel bars are found in the Asan, Sitla Rao, Mauti Nadi, Gauna Nadi, Koti Nadi and Chor Khala.

SOILS OF THE STUDY AREA

Different types of soil are found on different landforms. The surface soils of Doon fans have formed on mudflow and on over bank deposits in the middle and distal zones of the fans respectively. Particle size data indicates that the Doon Soils are mostly medium (sand, sandy loam silty loam) to moderate fine / textured (sandy clay loam, silty loam sandy clay) loamy soils.

The lower river terraces and young floodplains show weakly developed soil profiles. These soils are characterized by A –bw- C type horizons. The solum thickness about 90 cm with B horizons of about 60 cm thickness. (Singh, 1998). The colour of the B horizon is dark brown whereas that of the C- horizon (or parent material) is grayish brown.

A Study was conducted for highlighting the impact of waste water generated from motor servicing centers in Doon valley is a direct concern to health of local public of district Dehradun

RESULTS AND DISCUSSION

Results obtained and analyzed for Temperature, Conductivity, Total Dissolved Solids(TDS), Total Suspended Solids(TSS), Turbidity, Hydrogen Ion Concentration (pH), Dissolved Oxygen(DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand,(COD) Oil and Grease concentration, anions such as Chloride (Cl) and Bicarbonate $(HCO₃)$, Cations like Sodium(Na), Potassium(K), Calcium (Ca) and Magnessium (Mg), Total Hardness, Calcium Hardness, and Heavy metals like Lead (Pb), Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr) and Manganese (Mn) are being discussed in subsequent sections.

4.1 **TEMPERATURE** (⁰C)**:**

Temperature was taken by using Calibrated centigrade thermometer. Probe of thermometer was dipped into water up to a desirable depth for 5-7 minutes and reading was noted down displayed on the display unit. Temperature was taken in degree centigrade (^{0}C) . While soil temperature was measured by inserting soil thermometer on sampling site at a desirable depth and triplicate readings of each sites were taken in degree centigrade (^{0}C) .

Temperature data of all the samples is presented in Annexure: 4.1 with minimum, maximum and standard deviation in ground water, Soil and Waste water. Graphical representation of the results for temperature is being presented by Sigma plot in figure number: 4.1

Ground water: In ground water samples temperature varied from min $32.10⁰C$ to Max 34.90 ⁰C with an average of 32.75 ⁰C in Pre monsoon season. While it varied from 30.60 ⁰C to 32.60 ⁰C with an average value of 31.54 ⁰C in post monsoon season. Higher value of temperature (i.e. 34.90 $^{\circ}$ C) during pre monsoon season was found in Hand pump of Sahastradhara and in Post monsoon season it was observed on west side of Dehradun city as $32.60⁰C$ in a Hand pump of General Mahadev Singh road. Although in most of the samples temperature variations were found in a similar trends, as the temperature is an interdependent parameter which depends on depth of the source, weather condition, rainfall and seasonal variations of the area. The variability in temperature is due to seasonal temperature range of the study area.

Soil: Temperature of Soil samples were analyzed and has been observed that it varies from 30.90 $^{\circ}$ C to 33 $^{\circ}$ C with an average value of 32.02 $^{\circ}$ C, in pre monsoon, the maximum temperatures of 33 $\mathrm{^{0}C}$ was observed in the soils of Dharampur, as the area is densely populated and bisected by the Haridwar road the vehicular load could be seen very high in this area. It has also been observed that this area has some commercial sales and service center of automobiles, similar observation was also observed on the west side of Doon in and around Shimla bye pass road that the soil temperature in post monsoon resulting similar increase as in the soil temperature of 32.50 $\mathrm{^{0}C}$ in the village of Dandipur.

In contrast of baseline study of soil chemistry, soil sample were collected in and around the motor servicing workshops. The temperature of the soil samples varied from a minimum value of 31.30 $\mathrm{^0C}$ to a maximum value of 32.50 $\mathrm{^0C}$ with an average of 31.90 $\mathrm{^0C}$ and standard deviation of 038 in pre monsoon season while it varied from a minimum value of 32.30 $\rm{^0C}$ to a maximum value of 34.20 0 C with an average value of 32.87 0 C and standard deviation of 0.57 ${}^{0}C$ in post monsoon season.

Waste water: Temperature of waste water generated from motor servicing workshops varies from minimum 32.20 ^oC to maximum 36.30 ^oC with an average value of 33.94 ^oC and standard deviation of 1.03 °C in pre monsoon season, while in post monsoon season it varies from a minimum value of 31.30 0 C to a maximum value of 36.50 0 C with an average 33.65 0 C and 1.46 $\mathrm{^0C}$ standard deviation. Maximum temperature was found in a branded two wheeler servicing center in the Prem Nagar. In post monsoon season it was noticed that temperature range varied from 32.20 °C minimum to 36.30 °C maximum.

4.2 TURBIDITY (NTU):

Turbidity was measured by using turbidity meter. The instrument was calibrated accordingly for the measurement of turbidity by preparing known standards of 0 NTU, 1 NTU and 10 NTU. Sample filled tube was inserted into the instrument and turbidity displayed was noted down in Nephelometric Turbidity Unit. Turbidity of the samples in annexure :4.2 and graphical representation of results of the samples is being presented in Figure 4.2

Ground Water: Turbidity of ground water ranges from a minimum 1 NTU to maximum 2 NTU with an average value of 1.56 NTU and 0.51 standard deviation in pre monsoon season while it varied from a minimum 1 NTU to a maximum 3 NTU with an average value of 2.08 NTU and 0.76 NTU standard deviation in post monsoon season. Turbidity of all the ground water samples was found within desirable limit of drinking water as prescribed by Indian Standard of Drinking water.

Waste Water: Turbidity of waste water varied from minimum 24.58 NTU to maximum 67.49 NTU with an average value of 43.12 NTU and 11.93 NTU in pre monsoon season while it varied from a minimum 21.00 NTU to a maximum value of 35.00 NTU with an average value of 26.92 NTU and 526NTU standard deviation. From the analysis of the result it was noticed that all the samples are exceeding the minimum and maximum prescribed limit (5 to 10 NTU) of Indian standard of drinking water as prescribed by CPCB. It was observed that all the samples were highly turbid and reaching at an alarming rate which is prone to contaminate ground water system of the study area.

4.3 ELECTRICAL CONDUCTIVITY (EC)

(EC): Probe of conductivity was dipped into the test solution and the conductivity was noted in µsiemen/cm. Conductivity data in annexure-4.3. Plot representation of the results for conductivity is being presented by Sigma plot in figure number: 4.3.

Ground water: In ground water samples conductivity varied from minimum 200 µSiemen/cm to maximum 876.67 µSiemen/cm in pre monsoon season with an average value of 528.48 µSiemen/cm and standard deviation of 190.174 µSiemen/cm in pre monsoon season while it varied from a minimum 485.00 μ Siemen/cm to maximum 876.98 μ Siemen/cm with an average value of 659.98 µSiemen/cm and standard deviation of 127.645 µSiemen/cm in post monsoon season. Although limits of conductivity has not been recommended WHO and Indian standards specifications of drinking water but as per European Commission (EC) of drinking water Electrical conductivity of potable water should be below 1500 µSiemen/cm. The rain water mixes with the automobile waste and then infiltrates down in the groundwater system , Since the amount of rainfall is less in the premonsoon season therefore the conductivity of the groundwater samples could be seen less as compared to the postmonsoon where the conductivity is more and the amount of rainfall and wet spell is high.

Soil: In soil sample conductivity was measured from a minimum value of 172.00 µSiemen/cm to 1750. 00 µSiemen/cm with an average value of 517.00 and standard deviation 421.65 µSiemen/cm. in pre monsoon season while it varied from a minimum value of 256.00 µSiemen/cm to maximum 1287.00 µSiemen/cm with an average value of774.00 µSiemen/cm and standard deviation 300 µSiemen/cm in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied. In pre monsoon season conductivity of the soil sample of motor workshops varied from a minimum value of 234.00 μ Siemen/cm to a maximum value of 1453 μ Siemen/cm with an average value of 728.89 μ Siemen/cm and standard deviation of 310.56 μ Siemen/cm. While in post monsoon season it varied from a minimum level of 452.98 µSiemen/cm to maximum 1234.00 µSiemen/cm with an average value of 787.41 µSiemen/cm and standard deviation of 238.30 µSiemen/cm. Results of the soil analysis shows that conductivity ranges of control sites soil samples were found more as compared to soils of motor workshops which indicate the more ionic movement in the soil samples of control sites. It was also noticeable

that conductivity of post monsoon samples was found high as compared of premonsoon soil samples this is due to high dissolution of ions in soil system.

Waste water: Conductivity of waste water samples varied from minimum 654.00 µSiemen/cm to maximum 1634 µSiemen/cm with an average value of 1127.92 µSiemen/cm and standard deviation 272.45 µSiemen/cm in pre monsoon season while it varied from minimum 287.42 µSiemen/cm to a maximum level of 1145.00 µSiemen/cm with an average value of 662.01 µSiemen/cm and standard deviation of 242.96 µSiemen/cm in post monsoon season.

As indicates from the above stated results it was found that EC of waste water was found low in pre monsoon season and high in post monsoon season whereas reverse results were observed in case of soil samples which gives a clear understanding of solute transfer from waste water to soil system in post monsoon season.

4.4 TOTAL DISSOLVED SOILDS (TDS):

The TDS was measured by using TDS meter. Probe of TDS metre was dipped into the test solution and the TDS was noted down in mg/l. TDS data in annexure-4.4 with minimum, maximum and standard deviation in ground water and Waste water. Results for TDS is being presented by preparing Sigma plot in figure number: 4.4.

Ground water: Total dissolved solids concentration varied from a minimum value of 134.11 mg/l to a maximum value of 581.33 mg/l with an average value of 354.33 mg/l and standard deviations of 137.23 mg/l in pre monsoon season while it varies from a minimum value of 306.17 mg/l to a maximum value of 587.57 mg/l with an average value of 442.50 mg/l and standard deviation of 90.97 mg/l in the post monsoon season. The results were compared with Indian standard of drinking water which indicates that most of the samples excepting few samples of Dhoolkot area which are of shallow depth, rest all were within the desirable limit (500 mg/l) in both the seasons and all the samples were found below the maximum permissible limit (2000 mg/l) as per guidelines of Indian standard.

Waste water: TDS of waste water sample varies from a minimum level of 438.18 mg/l to a maximum value of 1094.78 mg/l in the Premnagar area with an average value of 756.48 mg/l standard deviation of 182.56 mg/l in pre monsoon while it varied from minimum value of 192.56 mg/l to a maximum value of 767.15 mg/l with an average value of 446.23 mg/l and

162.78 standard deviation in post monsoon season. The results of the investigations shows that most of the waste water samples in pre monsoon season accepted two samples of Transport Nagar and one sample of Majra are within the desirable limit of WHO and Indian standard. Samples collected from the other parts of the study areas results that they have crossed the desirable limits but falls under the maximum allowable limits of the BIS and WHO. Samples when repeated during the post monsoon shows that maximum samples are well within the desirable limits in the area of Race course, Kargi Chowk and Rajpur road and only few samples were categorized under the maximum allowable limits which shows the dilution processes during the monsoon period, Concentration of the pollutants got dissolved and carried away in the flow of water.

4.5 TOTAL SUSPENDED SOLIDS: (TSS)

TSS was measured by taking a 50 ml washed and dried beaker. A filter paper (Whatman No. 42) has been taken and weight. 20 ml of unfiltered sample was filtered through filter paper. The final weight of filter paper was taken after drying of sample. TSS data is presented in annexure-4.5with minimum, maximum and standard deviation in ground water and Waste water. Graphical representation of the results for TSS is being presented by Sigma plot in figure number: 4.5.

Ground water: TSS of ground water of study area varies from minimum 8 mg/l to maximum 50 mg/l with an average value of 24.32 mg/l and 10.30 mg/l in pre monsoon season while it varies from a minimum range of 10 mg/l to a maximum range of 40 mg/l with an average value of 20.64 mg/l and 7.08 mg/l standard deviation.

Waste water: TSS of waste water varies from a minimum 25 mg/l to 48 mg/l with an average range of 38.52 mg/l and 7.1 mg /l standard deviation in pre monsoon season while it varies from a minimum range of 30 mg/l to 63 mg/l maximum range with an average value of 48.08 mg/l and 9.44 mg/l standard deviation in post monsoon season. The observations indicate that value of total suspended solids were found lower in ground water samples and higher in waste water samples because of many pollutants comes out during the process of vehicle servicing and washing. It was also observed that in post monsoon the value was found higher than that of pre monsoon season because, during the monsoon season solids gets dissolved with rainwater and enters into the ground water regime.

4.6: HYDROGEN ION CONCENTRATION (pH)

Electrode was calibrated against standard buffer solutions with known capacity i.e. Buffer solution 4, buffer solution 7 and buffer solution 9.2 capacity. Electrode was rinsed by using deionised distilled water and electrode was dipped in sample water, reading displayed on digital screen was noted down. pH data is presented in annexure-4.6 with minimum, maximum and standard deviation in ground water, soil and Waste water. Results for pH are being presented by preparing Sigma plot in figure number: 4.6.

Ground water: pH of ground water of the study area varies from a minimum range of 6.3 to a maximum range of 7.2 with an average value of 6.6 and 0.29standard deviation in pre monsoon season while it varies from a minimum range of 6.2 to 7.2 maximum range with an average value of 6.8 and 0.29 standard deviation in post monsoon season. Although it was not found very much variations in pH ranges between pre monsoon and post monsoon season and most of the samples were found within the desirable to maximum permissible limit (i.e. 6.5 to 8.5) of BIS and WHO.

Soil: pH : From the available literature neither a high pH more than 8.4 nor a low pH below 5.0 is favourable for crops yield. It has been also suggested through various research that most of the plants prefer neutral pH (7) range. The sample collected and analysed varies from a minimum range of 6.8 to maximum range of 7.7 with an average value of 7.3and 0.30standard deviation in pre monsoon season while it varies from a minimum range of 6.8 to a maximum range of 8.9 with an average value of 8.04 and 0.509standard deviation. The findings of the results shows that in pre monsoon all the soil samples are showing pH range higher than 5.0 and most of the samples are showing pH value lower than 8.4 excepting some samples which are slightly higher than 8.4. As it is evident that value higher than 5.0 in post monsoon season are seems too favourable for soil health and most of the samples were found slightly alkaline in nature.

In contrast of baseline investigations of study area soil chemistry of motor workshop were also studied. pH of motor workshops of study area varies from a minimum range of 6.3 to a maximum range of 8.4 with an average value 7.4 and 0.5 standard deviation in pre monsoon season while it varies from a minimum range of 6.8 to maximum range of 8.2 with an average value of 7.3 and 0.37 standard deviation in post monsoon season. The results of the analysis indicate that most of the soil samples are within the allowable (7) pH range for soil and plant growth.

Waste water: pH of waste water samples varies from a minimum range of 5.7 to a maximum range of 6.8 with an average value of 6.13 and 0.2 standard deviations in pre monsoon season while it varies from a minimum range of 5.4 to a maximum range of 6.4 with an average value of 5.92 and 0.29 standard deviation in post monsoon season. In the present study pH range of most of the samples are showing below the desirable limit $(6.5 - 8.5)$ as prescribed by BIS which indicates acidic nature of the water.

4.7 DISSOLVED OXYGEN: (DO)

Data of dissolved oxygen is presented in annexure-4.7 with minimum, maximum and standard deviation in ground water and Waste water. Plot representation of the results for DO is being presented by Sigma plot in figure number 4.7. Probe of DO meter was inserted into test solution (sample) and DO was noted down.

Ground water: DO of ground water varies from a minimum range of 5.8 mg/l to a maximum range of 8.1 mg/l with an average value of 6.5 and 0.54 mg/l standard deviation in pre monsoon season while it varies from a minimum range of 5.1 mg/l to a maximum range of 8.1 mg/l with an average value of 6.4 mg/l and 0.7 mg/l standard deviations in post monsoon season. The amount of dissolved oxygen present in high quantity are in potable water supply are good because it makes drinking water taste better. However high DO levels speed up corrosive nature in water pipes, for this reason industries prefer to use least possible demand of DO. The dissolved oxygen in all the ground water samples of the study area showing good range of dissolved oxygen i.e > 5 mg/l which indicates that ground water samples of the study area are having rich supply of DO.

Waste water: DO of waste water varies from a minimum range of 2.8 mg/l to a maximum range of 6.91 mg/l with an average value of 5.8 mg/l and 0.8 mg/l standard deviation in pre monsoon season while it varies from a minimum range of 5.8 mg/l to a maximum range of 8.1 mg/l with an average value of 6.54 mg/l and 0.51 standard deviation. The variations of DO value in the study area indicates that waste water of samples of auto workshops are loaded with

various organic and inorganic pollutants which tends to decrease DO concentration when it infiltrates and enters into the aquifers.

4.8 ALKALINITY

(HCO3): Alkalinity data is presented in annexure-4.8 with minimum, maximum and standard deviation in ground water, soil and Waste water. Graphical representation of the results for alkalinity is being presented by Sigma plot in figure number: 4.8. Alkalinity was done by titrating 10 ml of sample with 0.01 N HCL solution and 2-3 drops of phenolphthalein and 1-2 drops of methyl orange indicator.

Ground water: Alkalinity of ground water varies from a minimum range of 30.5 mg/l to a maximum range of 146.4 mg/l with an average value of 86.62 mg/l and 24.93 mg/l standard deviation in pre monsoon season while it varies from a minimum range of 79.3 mg/l to maximum range of 256.2 mg/l with an average value of 151.52 mg/l and 48.63 mg/l standard deviation in post monsoon season. The value of alkalinity in both the sampling season was near the desirable limit of BIS and WHO and was found under the maximum prescribed limit of 600 mg/l.

Soil: Alkalinity of soil samples varies from a minimum range of 73.2 mg/kg to a maximum range of 152.5 mg/kg with an average value of 115.7 mg/kg standard deviation of 24.93 mg/kg in pre monsoon season while it varies from a minimum range of 41.5 mg/kg to a maximum range of 207.4 mg/kg with an average value of 104.7 mg/kg and standard deviation 36.79 mg/kg in post monsoon season. Soil alkalinity is associated with presence or absence of sodium carbonate (Na₂CO₃) in the soil, either as a result of natural mineralization of the soil particles or brought in by irrigation.

In contrast of baseline study of soil samples of study area, soil chemistry of motor workshops were also studied. Alkalinity of motor workshops soil samples varied from minimum 79.3 mg/kg to a maximum range of 146.5 mg/kg with an average value of 146.5 mg/kg and 36.25 standard deviation in pre monsoon season whereas in post monsoon season it varied from a minimum range of 36.6 mg/kg to a maximum range of 134.20 mg/kg with an average value of 79.97 mg/kg and 30.93 mg/kg standard deviation. The results obtained from analysis shows that alkalinity of soil samples in both the study locations (control sites and motor workshops) are showing similar trend in both the seasons.

Waste water: Alkalinity of waste water varies from a minimum range of 67.1 mg/l to a maximum range of 594.00 mg/l with an average value of 291.7 mg/l and 141.2 mg/l standard deviation in pre monsoon season while it varies from a minimum range of 61.00 mg/l to a maximum range of 594.00 mg/l with an average value of 298.08 mg/l and 138.19 mg/l standard deviation in post monsoon season. The investigation results shows that most of the samples are within the desirable limit of BIS and all the samples taken for the analysis was found below the maximum prescribed limits suggested by BIS.

4.9 TOTAL HARDNESS:

Total hardness was calculated with the help of titration method. 10 ml of sample was taken in a conical flask and add a pinch of EBT indicator and 1 ml of buffer solution, the solution turns wine red, titrate it against EDTA until wine red colour changes to blue. Total hardness data is presented in annexure-4.9 with minimum, maximum and standard deviation in ground water and Waste water. Graphical representation of the results for total hardness is being presented by Sigma plot in figure number: 4.9

Ground water: Total hardness of ground water varies from a minimum value of 95.00 mg/l to a maximum value of 270.00 mg/l with an average value 177.03 mg/l and standard deviation 50.00 mg/l in pre monsoon season while it varies from a minimum range of 85.00 mg/l to a maximum range of 250 mg/l with an average value of 163.33 mg/l and 51.86 mg/l standard deviation in post monsoon season. Since hardness is depend on concentration of Ca and Mg salts and desirable limit of hardness for drinking water is prescribed as 300 mg/l. Data obtained after the analysis indicates that all the ground water samples are within the desirable and permissible limits of Indian standards.

Waste water: Total hardness of waste water varies from a minimum range of 100 mg/l to a maximum range of 420.00 mg/l with an average value of 274.25 mg/l and 93.93 mg/l standard deviation in pre monsoon season while it varies from a minimum range of 230.00 mg/l to a maximum range of 540.00 mg/l with an average value of 316.48 mg/l and 95.76 standard deviation. Results of the study indicates that 40 % of the samples collected shows hardness value higher that desirable limit (i.e. 300 mg/l) .

4.10 CALCIUM (Ca):

Ca concentration was calculated with the help of titration method. A known volume (50ml) of the sample was pipetted into a clean conical flask, to which 1ml of sodium hydroxide and 1ml of isopropyl alcohol is added. A pinch of muroxide indicator is added to this mixture and titrated against EDTA until the pink colour turns purple.Calcium concentration data is presented in annexure-4.10 with minimum, maximum and standard deviation in ground water, soil and Waste water. Graphical representation of the results for temperature is being presented by Sigma plot in figure number: 4.10

Ground water: Ca concentration in ground water samples varies from a minimum range of 21.02 mg/l to a maximum range of 79.89 mg/l with an average value of 47.56 mg/l and 18.31 standard deviation in pre monsoon season while it varies from a minimum range of 8.41 mg/l to a maximum range of 71.48 mg/l with an average value of 40.17 mg/l and 20.47 mg/l standard deviation in post monsoon season. The level of Ca in ground water was found within desirable limit of Indian standard and WHO excepting two samples i.e. Buddi Chowk area and Dharampur chowk which are showing slightly higher range than desirable value (75 mg/l). It was also noticed that concentration of Ca in pre monsoon ground water sample of the study area is higher that post monsoon season this is due to the dilution of the ions in post monsoon season because of the reason that carbonate rocks in the form of dolomite and limestone of Krol formation are tends to get diluted with rain water which ultimately lowers the concentration of ions.

Soil: Calcium concentration of soil samples varies from a minimum range of 46.25mg/kg to a maximum range of 105.03 mg/kg with an average value of 64.83 mg/kg and 15.68 mg/kg standard value in pre monsoon season while it varies from a minimum range of 42.05 mg/kg to a maximum range of 75.69 mg/kg with an average value of 56.22 mg/kg and 11.43 mg/kg standard deviation in post monsoon season. The observation of the study indicates that in soil samples of study area Ca concentration is showing similar trend as ground water which also concludes that infiltration processes allows to interact with the groundwater system. The distribution of Ca ions due to weathering of the carbonate rocks during the monsoon season has decreased the concentration of calcium in post monsoon season and leaching effect of dolomite and limestone in soil system which ultimately decreases the Ca concentration in soil of the study area during pre-monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied. Calcium concentration of the motor workshops soil samples varied from a minimum range of 63.07 mg/kg to a maximum range of 159.79 mg/kg with an average value 91.72 mg/kg and 32.84 mg/kg standard deviation in pre monsoon season whereas in post monsoon season it varied from a minimum range of 50.46 mg/kg to 235.49 mg/kg with an average value of 101.85 mg/kg and 59.46 mg/kg standard deviation. Similar trend was observed in soil samples of motor workshops of study area. Results of the analysis indicates that Ca concentration in motor workshops soil samples was more than control sited soil system this is due to anthropogenic activities as these workshops are located in urban areas of the study area and shows a clear comparison between urban and rural areas soil chemistry.

Waste Water: The investigations indicates that Ca concentration varies from a minimum range of 33.64 mg/l to a maximum value of 73.05 mg/l with an average value of 55.75 mg/l and 10.61 mg/l standard deviations in post monsoon season while it varied from a minimum range of 8.41 mg/l to a maximum range of 71.48 with an average value of 40.20 mg/l and 19.27 mg/l of standard deviations. The observations of the data indicates that values of all the samples were found lower in waste water than ground water samples because of interaction of Ca ions with the lithology of the study area.

4.11 CALCIUM HARDNESS:

Ca hardness in ground water and waste water samples were determined with the help of titration method. A known volume (50ml) of the sample was pipetted into a clean conical flask, to which 1ml of sodium hydroxide and 1ml of isopropyl alcohol is added. A pinch of muroxide indicator is added to this mixture and titrated against EDTA until the pink colour turns purple.Calcium hardness data is presented in annexure-4.11 with minimum, maximum and standard deviation in ground water and Waste water samples. Graphical representation of the results for Ca hardness is being presented by Sigma plot in figure number: 4.11

Ground water: Ca hardness in ground water samples varied from a minimum range of 52.5 mg/l to a maximum range of 189.00 mg/l with an average value of 114.87 mg/l and 41.79 mg/l standard deviation in pre monsoon season whereas in post monsoon season it varied from a maximum range of 14.82 mg/l to a maximum range of 178.5 mg/l with an average value of 96.49 mg/l and 54.53 mg/l standard deviations. The investigation report shows that values of Ca hardness are more in pre monsoon season as compared to postmonsoon season due to dilution effect of Ca ions during infiltration and ultimately decreases the concentration monsoon season.

Waste water: Ca hardness of waste water samples varied from a minimum range of 14.82 mg/l to a maximum range of 89.30 mg/l with an average value of 53.63 mg/l and 16.59 mg/l standard deviation in pre monsoon season while it varied from a minimum range of 126.00 mg/l to 336.00 mg/l with an average value of 193.31 mg/l and 68.42 mg/l standard deviation. The observation of the data indicates that Ca hardness value is less in pre monsoon season and more in post monsoon season due to the Ca ions leaches in the soil system of the study area which ultimately decreases the concentration of the Ca

4.12: MAGNESIUM (Mg)

Magnesium concentration was determined with the help of pre-determined concentration of $CaCO₃$ and Ca by adding multiplying factor 0.243 as referred in APHA, (2005).

Magnesium concentration data is presented in annexure: 4.12 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical plot representation of the results for Magnesium hardness data is being presented by Sigma plot in figure number: 4.12

Ground water: In ground water samples magnesium varied from a minimum range of 5.1 mg/l to a maximum range of 30.98 mg/l with an average value of 15.57 mg/l and 8.24 standard deviations in pre monsoon season. Whereas in post monsoon season it varied from a minimum range of 2.79 mg/l to a maximum range of 30 .86 mg/l with an average value of 15.56 mg/l and 8.46 mg/l standard deviation.

Soil: In soil samples magnesium concentration varied from a minimum range of 6.07 mg/kg to a maximum range of 42.16 mg/kg with an average value of 21.11 mg/kg and 10.85 mg/kg standard deviation in pre monsoon season whereas in post monsoon season it varied from a minimum range of 10.56mg/kg t a maximum range of 27.71 with an average value of 18.56 mg/kg and 5.2 mg/kg standard deviation.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied. Magnessium concentration of motor workshop soil samples varied from a minimum range of 0.84 mg/kg to a maximum range of 42.52 mg/kg with an average value of 15.01 mg/l and 11.67 mg/kg standard deviation in pre monsoon season whereas in post monsoon it varied from a minimum range of 14.33 mg/kg to a maximum range of 59.29 mg/kg with an average value of 38.44 mg/kg and 12.20 mg/kg standard deviation.

Waste water: Magnessium concentration varied from a minimum range of 6.43 mg/l and maximum 93.07 with an average value of 53.71 mg/l and 24.57 mg/l in pre monsoon season while it varied from a minimum range of 3.03 mg/l to a maximum range of 98.04 mg/l with an average value of 33.82 and 28.55 mg/l standard deviation in post monsoon season.

4.13 SODIUM: (Na)

Sodium concentration was determined with the help of flame photometer. 2.54 gram of NaCl was dissolved and diluted to 1000 ml with distilled water. 1 ml of this solution is equal to 1 mg of Na. Standard solution of 1.0 to 10.0 has been prepared and analysed emission for *Na* at flame photometer at 589 nm.

Sodium concentration data is presented in annexure: 4.13 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for Sodium hardness data is being presented by Sigma plot in figure number: 4.13

Ground water: Sodium concentration in ground water varied from a minimum range of 5.1 mg/l to a maximum range of 10.1 mg/l with an average value of 6.07 mg/l and 1.66 mg/l standard deviation in pre monsoon season while it varied from a minimum range of 2.3 mg/l to a maximum range of 4.3 mg/l with an average value of 3.34 mg/l and 0.67 standard deviation in post monsoon season.

Soil: Sodium concentration in soil samples varied from a minimum range of 2.00 mg/kg to a maximum range of 29.00 mg/kg with an average value of 20.73 mg/kg and 5.71 mg/kg standard deviation in pre monsoon season whereas it varied from 10.87 mg/kg to a maximum range of 26.90 mg/kg with an average value of 16.82 mg/kg and 4.51 mg/kg standard deviation.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied. Sodium concentration of the motor workshops soil samples varied from a minimum range of 3.8 mg/kg to a maximum range of 25.45 mg/kg with an average value of 18.35 mg/kg and 5.58 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 10.70 mg/kg to a maximum range of 27.8 mg/kg with an average value of 20.66 mg/kg and 4.59 mg/kg standard deviation.

Waste water: Sodium concentration of waste water samples varied from 10.2 mg/l to a maximum range of 29.3mg/l with an average value of 20.73 mg/l and 5.71 mg/l standard deviation in premonsoon season while it varied from a minimum range of 10.87 mg/l to a maximum range of 26.90 mg/l with an average value of 16.82 mg/l and 4.5 mg/l standard deviation in post monsoon season.
4.14 POTASSIUM: (K)

Potassium was determined with the help of flame photometer by dissolving 1.907 gm of KCl in 1000 ml of distilled water. 1 ml of this solution is equal to 1 mg of Na. Standard solution of 1.0 to 10.0 has been prepared and analyzed emission for Na at flame photometer at 766 nm.

Potassium concentration data is presented in annexure: 4.14 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for Potassium concentration data is being presented by Sigma plot in figure number: 4.14

Ground water: In ground water samples concentration of potassium varied from a minimum range of 5.00 mg/l to a maximum range of 7.8 mg/l with an average value of 5.8 mg/l and 0.8 mg/l standard deviation in pre monsoon season while it varied from a minimum range of 2.1 mg/l to a maximum range of 4.2 mg/l with an average value of 2.8 mg/l and 0.61 mg/l standard deviation in post monsoon season.

Soil: In soil samples concentration of potassium varied from a minimum range of 4.2 mg/kg to a maximum range of 27.00 mg/kg with an average value of 11.54 mg/kg and 6.98 mg/kg standard deviation in pre monsoon season whereas it varied from a minimum range of 5.2 mg/kg to a maximum range of 28.9 mg/kg with an average value of 14.11 mg/kg and 7.00 mg/kg standard deviation in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration.

From the obtained data of potassium concentration of motor workshop soil samples it was found that concentration of potassium in motor workshop soil samples varied from a minimum range of 2.3 mg/kg to a maximum range of 20.9 mg/kg with an average value of 7.7 mg/kg and 5.7 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 2.5 mg/kg to a maximum range of 18.5 mg/kg with an average value of 7.1 mg/kg and 4.9 mg/kg of standard deviation in post monsoon season.

Waste water: Potassium concentration in waste water samples varied from a minimum range of 5.5 mg/l to a maximum range of 37.10 mg/l with an average value of 15.94 mg/l and 8.28 mg/l standard deviation in pre monsoon season whereas it varied from a minimum range of 4.3

mg/l to a maximum range of 35.90 mg/l with an average value of 14.15 mg/l and 8.30 mg/l in post monsoon season.

4.15 CHLORIDE (Cl)

Chloride concentration was determined with the help of Argentometric titration method as described in APHA (2005). 50 ml of test solution was taken and 2 ml of potassium chromate was added to it, then solution was titrated against silver nitrate solution and persistent red tinge appeared.

Chloride concentration data is presented in annexure: 4.15 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for Chloride concentration data is being presented by Sigma plot in figure number: 4.15

Ground water: In ground water samples concentration of Chloride varied from a minimum range of 9.92 mg/l to a maximum range of 74.44 mg/l with an average value of 30.43 mg/l and 18.72 mg/l standard deviation whereas from the analysis of the post monsoon ground water samples it was found that chloride concentration of ground water samples varied from a minimum range of 14.88 mg/l to a maximum range of 158.81 mg/l with an average value of 68.00 mg/l and 39.90 mg/l standard deviation.

Soil: Chloride concentration in soil samples varied from a minimum range of 183.63 mg/kg to a maximum range of 307.76 mg/kg with an average value of 235.51 mg/kg and 32.65 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 109.18 to a maximum range of 332.52 mg/kg with an average value of 201.43 mg/kg and 64.20 mg/kg standard deviation in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration. Chloride concentration in motor workshop soil samples varied from a maximum range of 173.71 mg/kg to a maximum range of 471.48 mg/kg with an average value of 375.72 mg/kg and 70.15 mg/kg standard deviation in pre monsoon season whereas it was noticed that in chloride concentration in post monsoon motor workshop soil samples ranges minimum 292.81 mg/kg to maximum 461.55 mg/kg with an average value of 384.19 and 51.54 mg/kg standard deviation.

Waste water: Chloride concentration in waste water samples varied from a minimum range of 79.41 mg/l to a maximum range of 208.44 mg/l with an average value of 127.61 mg/l and 35.86 mg/l standard deviation in pre monsoon season whereas it varied from a minimum range of 24.81mg/l to a maximum range of 248.15 mg/l with an average value of 90.97 mg/l and 59.84 mg/l standard deviation in post monsoon season.

4.16 OIL AND GREASE:

Oil and greases concentration was determined with the help of organic solvent extraction method as described in APHA, (2005) .Dissolved or emulsified Oil and Grease was extracted from water by intimate contact with petroleum ether $(40⁰$ or $60⁰)$ or hexane or tricholoflouro ethane.

An amount of 250 ml of sample was taken in a separating funnel, 10 ml of H_2SO_4 and 30 ml petroleum ether was added to the sample by shaking it. After some time separate two distinct layer appeared. Lower layer were discarded and petroleum ether was filtered into preweight dish from water bath and petroleum ether was evaporated with the help of water bath. Weight of disc was taken and concentration of oil and greases in water and soil sample was calculated.

Oil and greases concentration data is presented in annexure 4.16 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for oil and greases data is being presented by Sigma plot in figure number: 4.16

Ground water: In ground water samples oil and greases concentration varied from a minimum 2.00 mg/l to a maximum range of 6.7 mg/l with an average value of 4.00 mg/l and 1.58 mg/l in premonsoon season while it varied from 1.4 mg/l to a maximum range of 2.9 mg/l with an average value of 2.1 mg/l and 0.31 mg/l standard deviation in post monsoon season. Since the oil and grease is discharged on the surface and because of volatile properties it gets transpired into the air shows desirable limits in the premonsoon season. During the postmonsson season it gets mixed with the rain water and gets soluble and infiltrate to subsurface and contributes to the groundwater system and hence the value observed is well under the desirable condition. Rapid expansion of the city and vehicle probably might increase the amount in the coming years.

Soil: Concentration of oil and greases present in soil samples of the control sites of study area varied from a maximum range of 1.2 mg/kg to a maximum range of 2.4 mg/kg with an average value of 1.8 mg/kg and 0.3 mg/kg standard deviation in pre monsoon season whereas it varied from a minimum range of 1.3 mg/kg to a maximum range of 2.5 mg/kg with an average value of 2.01 mg/kg and 0.34 mg/kg in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration.

From the analysis of soil samples of motor workshop it was noticed that oil and greases concentration varied from a minimum range of 18.6 mg/kg to a maximum range of 53.00 mg/kg with an average value of 32.48 mg/kg and 10.95 mg/kg whereas in post monsoon season it varied from a minimum 12.1 mg/kg to a maximum range of 34.00 mg/kg with an average value 23.61 mg/kg and 5.91 mg/kg standard deviation. During the post monsoon interaction of surface water, precipitation and soils dilutes the concentration of the oil and grease.

Waste water: Oil and greases concentration of waste water samples varied from a minimum range of 240 mg/l to a maximum range of 612 mg/l with an average value of 455.89 mg/l and 105.58 mg/l standard deviation whereas it varied from a minimum 200 mg/l to a maximum range of 480 mg/l with an average value of 346.51 mg/l and 84.07 standard deviation.

4.17 BIOLOGICAL OXYGEN DEMAND (BOD):

BOD was determined by collecting samples in two BOD bottles of 300 ml capacity from each site. One set of the bottle were kept in BOD incubator at 20° C for 5 days and the DO constant was determined in another set immediately after the compilation of 5 days incubation, the DO first set was determined and BOD was calculated.

BOD data is presented in annexure: 4.17 with minimum, maximum and standard deviation in ground water and Waste water samples. Graphical representation of the results for BOD data is being presented by Sigma plot in figure number: 4.17

Ground water: BOD of ground water varied from a minimum range of 1.1 mg/l to a maximum range of 2.3 mg/l with an average value of 1.48 mg/l and 0.44 standard deviation in pre monsoon season while it varied from a minimum range of 1.1 mg/l to a maximum range of 2.2 mg/l with an average value of 1.5 mg/l and 0.38 mg/l standard deviation in post monsoon season.

Waste water: BOD of waste water varied from a minimum range of 5.6 mg/l to a maximum range of 13.4 mg/l with an average value of 9.7 mg/l and 2.6 mg/l standard deviation in pre monsoon season while it varied from a minimum range of 2.4 mg/l to a maximum range of 6.8 mg/l with an average value of 4.7 mg/l and 1.3 mg/l standard deviation.

4.18 CHEMICAL OXYGEN DEMAND: (COD)

COD of ground water and waste water samples were determined with the help of open reflux method followed by titrating with standard ferrous ammonium sulphate using ferrion indicator.

COD data is presented in annexure 4.18 with minimum, maximum and standard deviation in ground water and Waste water samples. Graphical representation of the results for COD data is being presented by Sigma plot in figure number: 4.18

Ground water: COD of ground water samples varied from a minimum range of 3.4 mg/l to a maximum range of 5.3 mg/l with an average value of 4.3 mg/l and 0.56 mg/l standard deviation in pre monsoon season while it varied from a minimum range of 2.3 mg/l to a maximum range of 4.4 mg/l with an average value of 3.2 mg/l and 0.70 mg/l standard deviation in post monsoon season.

Waste water: COD of waste water varied from a minimum range of 5.6 mg/l to a maximum range of 13.4 mg/l with an average value of 9.7 mg/l and 2.6 mg/l standard deviation in pre monsoon season whereas it varied from a minimum range of 4.3 mg/l to a maximum range of 11.3 mg/l with an average value of 8.3 mg/l and 2.1 standard deviation in post monsoon season.

4.19 COPPER: (*Cu***)**

Cu concentration was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by Dissolving 1.000 gram Copper metal in 15 ml of $1+1$ HNO₃ and diluted to 1000 ml with water; $1 \text{ ml} = 1.00 \text{ mg } Cu$, and were analysed.

Cu data is presented in annexure 4.19 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Plots of the results for *Cu* data is being presented by Sigma plot in figure number: 4.19

Ground Water: The presence of *Cu* concentration in ground water were found in negligible amount (below detectable limit) in most of the samples as experienced in both sampling seasons viz. pre monsoon and post monsoon season.

Soil: The presence of *Cu* concentration in soil of the study area varied from a minimum range of 26.45 mg/kg to a maximum range of 54.89 mg/kg with an average value of 37.78 mg/kg and 7.7 mg/kg standard deviation in pre monsoon season whereas it showed a lower concentration from the minimum range of 7.34 mg/kg to a maximum range of 34.24 mg/kg with an average value of 16. 93 mg/kg and 7.52 mg/kg in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration.The investigation of the soil samples taken from the nearby locations of motor workshops showed the presence of *Cu* concentration in the range of minimum 18.89 mg/kg to a maximum range of 54.89 mg/kg with an average concentration of 34.15 mg/kg and 13.24 mg/kg standard deviation in pre monsoon season while it varied from a maximum range of 12.34 mg/kg to 36.23 mg/kg with an average value of 19. 84 mg/kg and 6.88 mg/kg in post monsoon season.

Waste Water: The examination of waste water samples showed a rising amount of *Cu* concentration as compared to ground water samples. The value of the *Cu* in waste water samples ranges from a minimum 1.2 mg/l to a maximum range of 3.7 mg/l with an average amount of 2.1 mg/l and 080 mg/l standard deviation in pre monsoon season whereas it varied from a minimum range of 1.1 mg/l to a maximum amount of 3.2 mg/l with an average value of 2.2 mg/l and 0.66 mg/l standard deviation in post monsoon season.

4.20 ZINC: (*Zn*)

The concentration of *Zn* was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by dissolving 1.000 gm zinc metal in 20 ml 1+1 HCL and dilute to 1000 ml with water; 1.00 ml = 1.00 mg Zn.

Zn data is being presented in annexure4.20 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for *Zn* data is being presented by Sigma plot in figure number: 4.20

Ground Water: The analysis of the samples of ground water showed a negligible amount of Zn concentration in both the seasons. As recommended by BIS and WHO limit of *Zn* is 5 mg/l as desirable and 15 mg/l as maximum permissible limit.

Soil: Minimum to maximum limit of *Zn* for soil has been recommended by Interdepartmental Committee for redevelopment of Contaminated land (ICRCL) as 25 mg/kg and minimum 300 mg/kg to 600 mg/kg maximum as permissible limit of Indian Standards, Awasthi (2000). In soil samples of study area concentration of *Zn* varied from a minimum range of 123.76 mg/kg to a maximum range of 216.65 mg/kg with an average value of 162.35 mg/kg and 26.19 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 124.87 mg/kg to a maximum range of 156.87 mg/kg with an average value of 117.81 mg/kg and 20.48 mg/kg standard deviation in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration.The investigations of the soil samples of the nearby locations of the motor workshops samples showed a declined range of Zinc concentration in contrast of control sites soil samples. It ranges from a minimum value of 65.2 mg/kg to a maximum value of 178.40 mg/kg with an average of 126.51 mg/kg and 38.20 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 49.58 mg/kg to a maximum range of 134.45 mg/kg with an average value of 98.33 mg/kg and 29.63 mg/kg standard deviation in post monsoon season. The observation of the results shows that *Zn* concentration of control sites soil samples were found higher than motor workshops areas. The higher concentration in controls sites is due to addition of *Zn* added compost because controls sites soil samples belongs to agricultural areas and *Zn* is a necessary nutrient for plant growth hence its additional amount is usually added in farm soils. Whereas soil samples of motor workshops belong to urban areas hence concentration of *Zn* is lower than rural areas soil samples in both the sampling seasons.

Waste Water: The results from the analysis of the waste water showed a minimum range of Zn concentration from 1.2 mg/l to a maximum range of 2.3 mg/l with an average value of 1.8 mg/l and 0.3 mg/l standard deviation in pre monsoon season while it varied from a minimum range of 2.3 mg/l to a maximum range of 2.1 mg/l with an average value of 2.02 mg/l and 0.50 mg.l standard deviations in post monsoon season. *Zn* is one of the heavy metal which is mainly associated with automobile source and is derived from mainly during the process of servicing of vehicles and also is the component of tyres mesh, rim and engines and can be release during the abrasion, wears and tear. The prescribed limit for *Zn* recommended by WHO and BIS 5 mg/l as desirable and 15 mg/l as maximum permissible limit. And same ranges have been decided for discharge of waste water /effluent by CPCB. Although results are below the prescribed limit but on comparing with ground water it is slightly higher than ground water samples.

4.21 LEAD: (*Pb***)**

The concentration of *Pb* was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by dissolving 1.598 gm lead nitrate, $Pb(NO_3)$ ₂ in about 200 ml water, added 1.5 ml conc. HNO₃ and dilute to 1000 ml with water 1.00 ml = 1.00 mg *Pb*

Pb data is being presented in annexure 4.21 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for *Pb* data is being presented by Sigma plot in figure number: 4.21

Ground Water: The analysis of ground water samples indicates that most of the ground water samples showed negative results of *Pb* concentration (below detectable limit) but in some samples it was detected in a very small amount. The concentration of *Pb* in ground water of study area varies from a minimum range of 0.01 mg/l to a maximum range of 0.013 mg/l with an average value of 0.01 mg/l and 0.001 mg/l standard deviation in pre monsoon season and ground water samples of post monsoon were also showed the variation of results in same manner as pre monsoon seasons. The range varied in post monsoon season were found a minimum 0.01 mg/l to a maximum 0.011 with an average value of 0.010 and 0.00057 standard deviation. The observations of the results indicates that all the samples are well within the desirable limit (0.05 mg/l) of BIS and WHO.

Soil: The observations of the soil samples data indicates that *Pb* concentration in soil samples of control sites varied from a minimum range of 4.6 mg/kg to a maximum range of 53.60 mg/kg with an average value of 23.30 mg/kg and 14.66 mg/kg standard deviation in pre monsoon season whereas it varied from a minimum range of 12.37 mg/kg to a maximum range of 23.76 mg/kg with an average value of 18.59 mg/kg and 3.48 mg/kg standard deviation in post monsoon season. Investigations of the data shows that all the samples of the control sites soil are well within the permissible limit of Indian standard (250 mg/kg-500 mg/kg) but while comparing these results with interdepartmental Committee for Redevelopment of Contaminated land (ICRCL) it was found that some samples have crossed the prescribed limit (50 mg/kg)in pre monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration.The results of the samples taken from nearby locations of motor workshops were showed an increasing concentration of *Pb* as compared to control sites samples. Concentration of *Pb* in motor workshops samples varied from a minimum 26.87 mg/kg to a maximum 56.45 mg/kg with an average value of 40.94 and 9.17 mg/kg in pre monsoon season whereas it varied from a minimum 12.23 mg/kg to a maximum 24.67 mg/kg with an average 17.77 mg/kg and 3.6 mg/kg standard deviation in post monsoon season. Data indicates that same pattern was found in the areas of motor workshops and *Pb* concentration was found higher in pre monsoon season as compared to post monsoon season due to dilution of *Pb* ions with infiltration.

Waste Water: The results of the analysis of the waste water samples showed that all the the samples were fount contaminated with *Pb.* The concentration of *Pb* in waste water samples varied from a minimum 2.1 mg/l to a maximum 5.8 mg/l with an average value of 4.1 mg/l and 1.1 mg/l standard deviation in pre monsoon season and approximate same variations were observed in post monsoon seasons also i.e *Pb* concentration of waste water samples in post monsoon season varied from a minimum range of 2.1 mg/l to a maximum range of 5.4 mg/l with an average value of 3.2 mg/l and 0.90 mg/l standard deviation.

The recommended value of *Pb* for drinking water is 0.05 mg/l as per BIS and WHO. Studies carried out for waste water has been considered and the results have been compared with general standards for discharge of waste water/ effluents recommended by CPCB. It was noticed that all the samples are crossing the prescribed limits i.e.0.1 to 2.0 mg/l.

4.22 MANGANESE (*Mn***)**

The concentration of *Mn* was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by dissolving 1.000 gm Manganese metal in 10 ml conc. Mixed with 1 ml conc $HNO₃$. Diluted to 1000 ml with distilled water 1 ml solution = 1 mg Mn

Mn data is being presented in annexure: 4.22 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for *Mn* data is being presented by Sigma plot in figure number: 4.22

Ground Water: The results from the analysis showed that most of the samples in both the sampling season were showed concentration of *Mn* with similar trends i.e few samples in both the seasons were showed negligible amount (below detectable level) of *Mn* but in most of the samples it was observed in small amount i.e it varied from minimum 0.01 mg/l to a maximum 0.012 mg/l with an average value of 0.013 mg/l and 0.00035 mg/l standard deviation in pre monsoon season. Whereas it varied from a minimum 0.01 mg/l to a maximum level 0.017 mg/l with an average value of 0.01 mg/l and 0.0022 mg/l standard deviation in post monsoon season.

Soil: In soil samples the concentration of *Mn* varied from a minimum 0.012 mg/kg to maximum range of 0.015 mg/kg with an average of 0.083 mg/kg and 0.82mg/kg standard deviation in pre monsoon season. Whereas it varied from a minimum range of 0.12 mg/kg to a maximum range of 1.2 mg/kg with an average value of 0.48 mg/kg and 0.53 mg/kg standard deviation in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration. In Soil samples of the motor workshops the concentration of *Mn* varied from a minimum 0.01 mg/kg to a maximum value of 1.5 mg/kg with an average value of 0.4 mg/kg and 0.56 mg/kg standard deviation in premonsoon season while it varied from a minimum 0.01 mg/kg to a maximum 2.4 mg/kg with an average value of 0.60 mg/kg and 0.06 standard deviation in post monsoon season.

Waste Water: In waste water samples *Mn* varied from a minimum range of 0.11 mg/l to a maximum range of 2.7 mg/l with an average value of 0.89 mg/l and 0.82 mg/l standard deviations in pre monsoon season. While it varied from a minimum range of 0.01 mg/l to a maximum range of 1.2 mg/l with an average value of 0.53 mg/l and 0.45 mg/l standard deviation in post monsoon season.

4.23 NICKEL (Ni)

The concentration of *Ni* was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by dissolving 1 gm *Ni* metal in 10 ml hot conc. HNO3, cool and dilute it to 1000 ml with distilled water 1 ml = 1mg *Ni*

Ni data is being presented in annexure: 4.23 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for *Ni* data is being presented by Sigma plot in figure number: 4.23

Ground Water: In ground water samples concentration of *Ni* varied from a minimum range of 0.01 mg/l to a maximum range of 0.016 with an average value of 0.013 and 0.0018 standard deviation in pre monsoon season while it varied from a minimum range of 0.012 mg/l to a maximum range of 0.041 mg/l with an average value of 0.022 mg/l and 0.0095 mg/l standard deviation in post monsoon season.

Soil: Investigation of soil samples shows that *Ni* concentration varies from a minimum 6.13 mg/kg to a maximum 19.91 mg/kg with an average value of 13.96 mg/kg and 3.96 mg/kg standard deviation in pre monsoon season whereas it varied from a minimum range of 9.56 mg/kg to a maximum range of 23.28 mg/kg with an average value of 15.098 mg/kg and 3.99 mg/kg standard deviation in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration. Results from the study indicate slightly rising concentration of *Ni* in soil samples of motor workshops as compared to control sites soil samples. Concentration range varied from a minimum range of 12.34 mg/kg to a maximum 45.34 mg/kg with an average value of 23.83 mg/kg and 8.18 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 12.67 mg/kg to a maximum range of 35.78 mg/kg with an average value of 22.34 mg/kg and 6.22 mg/kg standard deviation in post monsoon season.

Waste Water: The analysis of the waste water samples shows that Ni concentration in waste water samples varied from a minimum range of 0.012 mg/l to a maximum range of 2.3 mg/l with an average value of 0.62 mg/l and 0.80 mg/l in pre monsoon season while it varied from a minimum range of 0.01 mg/l to a maximum range of 1.09 mg/l with an average value of 0.22 mg/l and 0.34 mg/l standard deviation in post monsoon season.

4.24 CADMIUM: (*Cd***)**

The concentration of *Cd* was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by dissolving 1.000 gm cadmium metal in 4 ml Conc. HNO₃ and diluted to 1000 ml with water, 1.00 ml = 1 mg *Cd*.

Cd data is being presented in annexure: 4.24 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for *Cd* data is being presented by Sigma plot in figure number: 4.24

Ground water: The results of the ground water samples indicate that concentration of cadmium was found nil (not detectable) in all the 25 samples in both the sampling seasons.

Soil: The analysis results done for soil samples of control sites indicate the presence of cadmium concentration in all the 25 samples. Concentration of *Cd* varied from a minimum range of 0.02 mg/kg to a maximum range of 1.9 mg/kg with an average value of 0.31 mg/kg and 0.45 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 0.023 mg/kg to a maximum range of 1.02 mg/kg with an average value of 0.41mg/kg and 0.35 mg standard deviation in post monsoon season.

In contrast of baseline study of soil samples of study area soil chemistry of motor workshop were also studied for the consideration. The results of the analysis of the samples indicates that *Cd* concentration in soil samples of motor workshops varied from a minimum 0.023 mg/kg to a maximum range of 3.23 mg/kg with an average value of 1.16 mg/kg and 0.91 mg/kg standard deviation in pre monsoon season while it varied from a minimum 0.12 mg/kg to maximum range of 2.13 mg/kg with an average value of 1.25 mg/kg and 0.669 mg/kg standard deviation in post monsoon season.

Waste Water: Waste water analysis result shows that concentration of *Cd* in all the 25 samples was present in both the sampling seasons. In pre monsoon season it varied from a minimum range of 0.012 mg/l to a maximum range of 1.92 mg/l with an average value of 0.599 mg/l and 0.56 mg/l standard deviation while in post monsoon season it varied from a minimum range of 0.01 mg/l to a maximum range of 0.67 mg/l with an average value of 0.23 mg/l and 0.15 mg/l standard deviation.

4.25 CHROMIUM:(*Cr***)**

The concentration of *Cr* was analysed with the help of Atomic absorption spectrophotometer model no Perkin Elmer A Analyst 300 by dissolving 1.923 gm $CrO₃$ in water when solution is complete acidify with 10 ml concentrated HNO₃. And dilute to 1000 ml with water 1 ml = 1 mg *Cr*

Cr data is being presented in annexure: 4.25 with minimum, maximum and standard deviation in ground water, soil and Waste water samples. Graphical representation of the results for *Cr* data is being presented by Sigma plot in figure number: 4.25

Ground Water: It was observed that in most of the ground water samples Cr concentration was found absent but it some samples Cr concentration was detected. The range of *Cr* concentration in ground water samples varied from minimum 0.012 mg/l to maximum range of 0.071 mg/l with an average value of 0.020 mg/l and 0.020 mg/l standard deviation in pre monsoon season whereas it varied from a minimum 0.01 mg/l to a maximum range of 0.031 mg/l with an average value of 0.014 mg/l and 0.0068 mg/l standard deviation.

Soil: In soil samples *Cr* concentration varied from a minimum range of 1.2 mg/kg to a maximum range of 3.2 mg/kg with an average value of 3.2 mg/kg and 2.05 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 1.1 mg/kg to a maximum range of 2.6 mg/kg with an average value of 1.62 mg/kg and 0.46 mg/kg standard deviation in post monsoon season.

The soil study of motor workshops were also undertaken and results shows that *Cr* concentration was found in and around the areas of motor workshops varied from a minimum range of 12 mg/kg to a maximum 37.23 mg/kg with an average value of 20.60 mg/kg and 6.64 mg/kg standard deviation in pre monsoon season while it varied from a minimum range of 11.23 mg/kg to maximum 27.87 with an average value of 18.65 mg/kg and 5.50 mg/kg standard deviation during the post monsoon season.

Waste Water: In waste water samples *Cr* concentration varied from a minimum 0.01 mg/l to a maximum 1.50 mg/l with an average value of 0.37 mg/l and 0.51 mg/l standard deviations in post monsoon season whereas it ranges from a minimum 0.01 mg/l to a maximum 1.13 mg/l with an average value of 0.25 mg/l and 0.38 mg/l standard deviation in post monsoon season. The concentration of *Cr* was low in post monsoon season as compared to pre monsoon season due to dilution of the metals.

	Parameters	Limits (a) mg/kg	Limits (b) mg/kg
S. No.			
	$\text{Zinc}(\text{Zn})$	$300 - 600$	
٠.	Lead (Pb)	250-500	
	Nickel (Ni)	75-150	
	Copper (Cu)	135-270	

Table- 4.1 Heavy Metals Concentration limits in Soil as per Indian Standards

Limits-a Permissible limits of Indian Standards, Awasthi (2000)

Limits –b- Mean of heavy metal limits in soil used for agricultural and recreation recommended by interdepartmental Committee for Redevelopment of Contaminated land (ICRCL)

Table: 4.2 BIS Standards for Drinking Water

S. No.	Parameters	Standards				
		Inland Surface	Public	Land for \vert	Marine	
		Water	Sewers	Irrigation	Coastal Areas	
1.	Temperature ${}^{0}C$	Not to exceed	\mathbf{r}	$\frac{1}{2}$	Not to exceed	
		5^0 C above the			5^0 C above the	
		receiving water			receiving	
					water	
2.	pH	$5.5 - 9.0$	$5.5 - 9.0$	$5.5 - 9.0$	$5.5 - 9.0$	
3 ₁	Oil and Grease	10 mg/l	20 mg/l	$\overline{10}$ mg/l	20 mg/l	
	mg/1					
4.	Biological	30 mg/l	350 mg/l	100 mg/l	100 mg/l	
	Oxygen					
	Demand (BOD)					
5.	Chemical	250 mg/l				
	Oxygen					
	Demand (COD)					
6.	Lead (Pb)	0.1 mg/l	1.0 mg/l	\overline{a}	2.0 mg/l	
7.	Cadmium (Cd)	2.0 mg/l	1.0 mg/l	\blacksquare	$2.0 \text{ mg}/1$	
8.	Chromium (Cr)	2.0 mg/l	2.0 mg/l	\blacksquare	2.0 mg/l	
9.	Copper (Cu)	3.0 mg/l	3.0 mg/l	\blacksquare	3.0 mg/l	
10.	$\text{Zinc}(\text{Zn})$	5.0 mg/l	15 mg/l	$\frac{1}{2}$	15 mg/l	
11.	Nickel (Ni)	3.0 mg/l	3.0 mg/l	\blacksquare	3.0 mg/l	
$\overline{12}$.	Manganese	2 mg/l	2 mg/l	$\frac{1}{2}$	2 mg/l	
	(Mn)					

Table: 4.3 General Standards for discharge of Waste Water/ Effluents

Figure 4.1 Temperature Pre and Post Monsoon

- 3. Pre Monsoon Motor Workshop Waste Water
- 4. Pre Monsoon Motor Workshop Soil
-
- 7. Post Monsoon Motor Workshop Waste Water
- 8. Post Monsoon Motor Workshop Soil

Figure 4.2 Turbidity (NTU) Pre and Post Monsoon

Figure 4.3 Conductivity Pre and Post Monsoon

Figure 4.4 Total Dissolved solids (TDS) Pre and Post Monsoon

3.Post Monsoon Control Sites Ground Water

4. Post Monsoon Motor Workshop Waste Water 2. Pre Monsoon Motor Workshop Waste Water

Figure 4.5 Total Suspended Solids (TSS) Pre and Post Monsoon

Figure 4.6 Hydrogen Ion Concentration (pH) Pre and Post Monsoon

Figure 4.7 Dissolved Oxygen (DO)

Figure 4.9 Total Hardness Pre and Post Monsoon

Figure 4.10 Calcium (Ca) Pre and Post Monsoon

Figure 4.11 Calcium Hardness Pre and Post Monsoon

Figure 4.13 Sodium (Na) Pre and Post Monsoon

Figure 4.14 Potassium (K) Pre and Post Monsoon

Figure 4.15 Chloride (Cl) Pre and Post Monsoon

Figure 4.17 Biological Oxygen Demand (BOD) Pre and Post Monsoon

Figure 4.18 Chemical Oxygen Demand (COD) Pre and Post Monsoon

Figure 4.19 Copper (Cu) Pre and Post Monsoon

Figure 4.20 Zinc (Zn) Pre and Post Monsoon

Figure 4.21 Lead (Pb) Pre and Post Monsoon

Figure 4.22 Manganese (Mn) Pre and Post Monsoon

Figure 4.23 Nickel (Ni) Pre and Post Monsoon

Figure 4.24 Cadmium (Cd) Pre and Post Monsoon

Figure 4.25 Chromium (Cr) Pre and Post Monsoon

CHAPTER 5

CONCLUSION

The research thesis is an attempt to find the environmental impact of effluents from auto workshops on ecosystem of Doon valley. Doon valley is situated in Uttarakhand state of India and southwest of Himalaya- Shiwalik region and bounded in the north east by Lesser Himalayan belt and by Shiwalik ranges on the south – west.

Climate: The climate of Dehradun is more temperate and humid than that of other districts of Uttarakhand. The maximum and minimum day and night temperatures being $3^{0}C$ to $6^{0}C$ lower through out the year. Only the month of May and June are hot though they are seldom oppressive. The temperature as recorded in the Forest Research Institute observatory during the last decade varied from $3^{0}C$ in December to about $38.2^{0}C$ in May. The lowest temperature was on January 16, 1946 and February 28, 1956 when it fell to -1.1° C and Frost is quite common on winter night severe frost occur in January and February and cause damage to young *sal* regeneration. There are many places especially in the low grasslands and within temperature during October to April are several degrees lower than those at Dehradun.

The prevailing winds come from the west and are generally of moderate velocity, except when severe storms occur during the hot weather, in April and May. In the evening there is always a light breeze coming down the hills generally from the north. The monsoon generally breaks out by the end of June and the rains continue until about the middle of September the heaviest rain fall normally occurring in July and August. Occasional showers may continue in September and October after which, there is usually little rain until about the end of December. Doon valley is an intermontane valley located at the northern margin of Shiwalik foreland basin in Garhwal Himalaya. Dehradun district may be divided into four geomorphological units namely alluvium, piedmont fan deposits, structural, denudational hills and residual hills.

Soil: Due to wide variation in topography, intensity of erosion, parent material and other factors, the soils show wide variation in many characteristics specially textures, depth, stoniness, colour, drainage, moisture status, organic matter contents and cation exchange capacity. In fact soil are the products of original geological formations hence three geological zones exhibit difference in their soil types. On the basis of geological belts soil types of Doon valley has been categorized in three main categories: Lesser Himalayan Belt, Shiwalik Belt and the Boulder belt of the valley.

District Dehradun is drained by Ganga, Yamuna and their tributaries. The two basins are separated by a ridge starting from Mussoorie and passing through Dehradun. The easterly flowing rivers join River Ganga and the westerly flowing rivers join River Yamuna. Ganga River enters the district near Rishikesh where Chandrabhaga River joins it. Song and Suswa are two main tributaries of the Ganges. Suswa flows SE, draining the eastern Doon along with its ephemeral tributaries like Bindal Rao, Rispana Rao etc. and joins River Song SE of Doiwala. Song River has its origin from the adjoining Tehri district. Initially it runs parallel to the Mussoorie Mountain chain in NW direction for few kilometers and then takes a sudden turn in SE direction and joins Suswa River south of Doiwala.

Dehradun is the largest center among the all the urban settlements of hill districts of Uttarakhand state. Availability of infrastructure in doon valley settlements has given impetuous to the development of the region. The natural beauty and climate of Doon valley have also provided the potential for a prosperous tourist industry. After the formation of the capital it has been recorded that many people came here to establish their business, new departments were introduced with new developments. As the population of the area got increased the number of vehicles was also rise which ultimately increased the number of motor vehicles workshops in the valley. A number of authorized and unauthorized motor workshops are being operated by different agencies. On the basis of research survey it has been noticed that about 200 motor servicing workshops are present in the valley.

Thus keeping this in the mind Soil and water chemistry of Dehradun district with the reference to waste being generated from motor servicing workshops were studied. A total of 100 soil and water samples were collected from the study area representing the Ground water system, soil, Motor workshops waste water and soil of the nearby locations of the motor servicing workshops during the pre and post monsoon season. The impact of waste generated from motor servicing workshops on ground water and soil system of the area were also highlighted. The research has been undertaken by keeping following objectives in mind

With the following objectives:

- Physicochemical assessment of waste water generated from motor servicing centers
- Analyzing pre and post monsoon quality of soil and water chemistry
- To Understand Environmental impact of waste generated of the study area

Following methodology were adopted to achieve these objectives

- Preparation of Study area Map representing geological, morphological, drainage map and soil type map. Topographic map of Dehradun (Study area) digitized in Arch GIS to show the motor servicing workshops was also prepared
- Terrain map of Dehradun (study area) to show motor workshops and sampling locations of soil and ground water.
- Soil, water and waste water chemistry of the study area was done by sampling and physico- chemical analysis of the samples in HSE lab of University of Petroleum and Energy Studies Dehradun.
- The sampling program, preservation of samples and analytical work has been designed as per the guidelines of standard method APHA (2005), Trivedi and Goel (1986) Ghosh et al (1983)
- Soil of the study area (Taken from control sites) were found well within the Indian standards and ICRL (1987) whereas soils taken from in and around the areas of motor workshop are the indication of an increased concentration of oil and greases and other pollutants.

The conclusive points observed during the research work are being described in this chapter.

Ground water data indicates that parameters studied during the research work are very much agree with the desirable and maximum permissible limit of drinking water as prescribed by BIS and WHO. Temperature of ground water samples were found in an agreeable range in both the sampling season but while comparing these ranges with waste water samples it showed a little rising trend in temperature. Soil temperature of the Dharampur area was found higher during the study this is due to the heavy vehicular load in this area. Similar observation was also observed on the west side of Doon in and around Shimla bye pass road that the soil temperature in post monsoon resulting similar increase as in the soil temperature.

Turbidity of the ground water samples were within the desirable limit as prescribed by BIS (1991) but in the waste water samples it was observed that turbidity range was quite high (maximum 67.49 NTU) due to mixing of pollutants in water huge amount of waste discharge are drained which makes the water turbid. Electrical conductivity of the ground water samples was high in pre monsoon season as compared to post monsoon season the reason is due to the mixing and movement of ionic compounds in water while in soil samples taken from control sites conductivity was observed as high in comparison to soil of motor workshops. TDS of the ground water samples are well within the desirable limit whereas in case of waste water it was noticed that most of the waste water samples in pre monsoon season accepted two samples of Transport Nagar and one sample of Majra are within the desirable limit Samples when repeated during the post monsoon shows that maximum samples are well within the desirable limits in the area of Race course, Kargi Chowk and Rajpur road and only few samples were categorized under the maximum allowable limits which shows the dilution processes during the monsoon period, Concentration of the pollutants got dissolved and carried away in the flow of water.

The observations for the TSS indicate that value of total suspended solids were found lower in ground water samples and higher in waste water samples because of many pollutants comes out during the process of vehicle servicing and washing. It was also observed that in post monsoon the value was found higher than that of pre monsoon season because, during the monsoon season solids gets dissolved with rainwater and enters into the ground water regime. Although it was not found very much variations in pH ranges between pre monsoon and post monsoon season and most of the samples were found within the desirable to maximum permissible limit (i.e. 6.5 to 8.5) of BIS and WHO. Hydrogen Ion concentration of the ground water samples was not found very much variable in pH ranges between pre monsoon and post monsoon season and most of the samples were found within the desirable to maximum permissible limit (i.e. 6.5 to 8.5) of BIS and WHO whereas the findings of the results soil of control sites all the soil samples are showing pH range higher than 5.0 and most of the samples are showing pH value lower than 8.4 excepting some samples which are slightly higher than 8.4. As it is evident that value higher than 5.0 in post monsoon season are seems too favourable for soil health and most of the samples were found slightly alkaline in nature. While pH of motor workshops of study area varies from a minimum range of 6.3 to a maximum range of 8.4 with an average value 7.4 and 0.5 standard deviation in pre monsoon season while it varies from a minimum range of 6.8 to maximum range of 8.2 with an average value of 7.3 and 0.37 standard deviation in post monsoon season. The results of the analysis indicate that most of the soil samples are within the allowable (7) pH range for soil and plant growth.

In the present study pH range in waste water showing below the desirable limit $(6.5 - 8.5)$ as prescribed by BIS which indicates acidic nature of the water.

The dissolved oxygen (DO) in all the ground water samples of the study area showing good range of dissolved oxygen i.e > 5 mg/l which indicates that ground water samples of the study area are having rich supply of DO. Whereas the variations of DO value in the study area indicates that waste water of samples of auto workshops are loaded with various organic and inorganic pollutants which tends to decrease DO concentration when it infiltrates and enters into the aquifers. The value of alkalinity in both the sampling season in both types of samples like ground water and waste water was near the desirable limit of BIS and WHO and was found under the maximum prescribed limit of 600 mg/l. Alkalinity of soil of control sites and motor workshops sample were found good for soil health. The total hardness of ground water was within the desirable limit whereas in waste water it was abobe the desirable limit (300 mg/l). The level of Ca in ground water was found within desirable limit of Indian standard and WHO excepting two samples i.e. Buddi Chowk area and Dharampur chowk which are showing slightly higher range than desirable value (75 mg/l). Whereas the observations of the data indicates that values of all the samples were found lower in waste water than ground water samples because of interaction of Ca ions with the lithology of the study area. The study indicates that in soil samples of study area Ca concentration is showing similar trend as ground water which also concludes that infiltration processes allows to interact with the groundwater system. The distribution of Ca ions due to weathering of the carbonate rocks during the monsoon season has decreased the concentration of calcium in post monsoon season. Results of the analysis indicates that Ca concentration in motor workshops soil samples was more than control sited soil system this is due to anthropogenic activities as these workshops are located in urban areas of the study area.

The investigation report shows that values of Ca hardness are more in pre monsoon season as compared to postmonsoon season due to dilution effect of Ca ions during infiltration and ultimately decreases the concentration monsoon season. Whereas the observation of the waste water samples the data indicates that Ca hardness value is less in pre monsoon season and more in post monsoon season due to the Ca ions leaches in the soil system of the study area which ultimately decreases the concentration of the Ca. Magnessium (Mg) concentration was found in lower range in ground water, soil and waste water due to geological conditions of study area. Potassium (K) concentration was also found in low concentration in both the ground water and soil system. Whereas Sodium was found higher in ground water and soil samples as it is found in the form of $Na₂CO₃$ and NaCl in geology of the study area.

Chloride concentration in ground water, soil and waste water found well within the desirable level. Whereas Oil and grease concentration was found well within the desirable limit in case of ground water and soil samples (control sites) of the study area whereas in case of motor workshops samples the concentration was quite higher as compare to control sites samples. The data shows that oil and grease concentration in waste water samples are heavily loaded with oil and grease concentration in both the sampling seasons and crossed the desirable limit of WHO, BIS and CPCB Guidelines for discharge of waste water. Soil of nearby locations of motor workshops was also polluted with oil and grease.

Biological oxygen demand (BOD) and Chemical oxygen demand was found higher in waste water samples as compare to ground water samples. Heavy metals analysis of the ground water, soil and waste water samples shows a clear difference between control sites and affected areas. The data shows that *Cu* concentration was found as negligible amount in ground water in most of the samples whereas in waste water samples the maximum range found as 3.7 mg/l. Similarly the in soil samples of control sites area *Cu* concentration was found lower as compared soil of motor workshops samples. The *Zn* concentration of ground water samples and waste water samples was found well within the desirable limit of BIS and WHO, but it was little higher in waste water samples as compared to ground water sampled. Whereas in soil samples *Zn* concentration was higher in control sites soil samples as compare to soil of motor workshops due to addition of *Zn* added compost in soil rural areas. Lead (*Pb*) concentration in ground water was found below the detectable limit in most of the ground water samples whereas in waste water samples the concentration of *Pb* was higher than desirable limit of BIS and WHO. The investigation of soil samples gives same idea about the concentration of *Pb* which shows that in soil of control sites are well within the permissible limit of Indian standard (250 mg/kg-500 mg/kg) but while comparing these results with interdepartmental Committee for Redevelopment of Contaminated land (ICRCL) it was found that some samples have crossed the prescribed limit (50 mg/kg) in pre monsoon season. Concentration of *Pb* in motor workshops samples varied from a minimum 26.87 mg/kg to a maximum 56.45 mg/kg it was higher than control sites soil samples which indicates that Pb concentration is due to discharge of effluents from motor workshops in the study area.

The Manganese (*Mn*) concentration in ground water was found below the detectable limit in most of the samples but in waste water samples it was found high maximum range was 2.7 mg/l, and similar trend was observed in soil chemistry of the study area. Data indicates that *Mn* concentration was higher in motor workshops area soil samples as compare to control sites soil samples. Nickel concentration of ground water samples was found low as compared to waste water samples and Ni concentration of soil of control sites area and motor workshops area was also found in same manner. Cadmium (*Cd*) concentration of ground water as nil in all the samples whereas in waste water samples the presence of *Cd* indicates that waste water is contaminated with *Cd* and can be associate with ecosystem in the future and soil study also give the same idea about the *Cd* concentration. The maximum range of *Cr* was found as 0.071 mg/l in ground water samples whereas it goes to higher level as 1.5 mg/l in waste water samples which indicates that waste water being generating from motor workshops are highly contaminated with heavy metals. And soil samples of the study also give same idea for the concentration of Cr.

The research thesis outlined the ground water, waste water, soil and soil chemistry of nearby locations of motor servicing workshops and on the basis of obtained results it was concluded that ground water is of good quality and can be use drinking, irrigation and industrial purposes. All the data studied for phisico-chemical analysis was found within the prescribed limit. Soil samples of the rural areas (control sites) were also well within the desirable limit but in case of waste water maximum parameters gives negative results for the Ecosystem of the study area. Parameters such as Turbidity, Oil and grease and heavy metals concentration are an indication of pollution load in waste water which has ultimately increased the pollutants concentration of nearby locations of the servicing centres. The study also suggest that if proper management of is not done then these contaminates can be associates with the Ecosystem of the Doon valley because of percolation of other hydrocarbons which are associated with Oil and grease of used oil can percolate in ground water and also can enter in soil system also. If proper step does not arise these pollutants will be a part of our food chain also.

REFERENCES

Abass O. Alade, Oluwatoyin A. Okelana, Dauda O. Araromi and Oladipo O. Ogunleye. (2012) Environmental Impact of Vehicle Service Centers on Soils in Ogbomosho Nigeria. Research Journal of Environmental Science 6 (1): 45-50, 2012.ISSN 1819-3412/DOI: 10.3923/rjes. 2012.45.50

A.C. Achudume (2009) The Effect of Petrochemical Effluent on the Water Quality of Ubegi Creek in Niger Delta of Nigeria. Bull Environ Contam Toxicol (2009) 83:410-415 DOI 10.1007/s00128-009-9736-2

Adewole, M.B. and Uchegbu, L.U. (2010) Properties of soils and plants uptake within the vicinity of selected automobile workshops in Ile-Ife Southwestern, Nigeria.Ethopian Journal of Environmental Studies and Management Vol. 3 No. 3 2010

Aiyesanmi, A.F. Assessment of Heavy metal contamination of Robrtkiri oil field's soil (2005) Nigerian Journal of Soil Science 15/2005

APHA, AWWA, and WEF, (2005) Standard Method for Examination of Water and Waste Water, 21st Ed. American Public Health Association, Washington DC

Atlas, R.M. (1981) Microbial degradation of petroleum hydrocarbons: an environmental perspective, Microbiol. Rev., 45:180-209

Avasthi, S.K. (2000) 'Prevention of Food Adulteration Act No. 37 of 1954. Central and State rules as amended for 1999' 3rd Ed. (Ashoka Law House) New Delhi

B.A.Adelekan and K.D. Abegunden (2011) Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria. Int. J. of the physical sciences Vol. 6(5), pp.1045-1058, 4 March, 2011

Bartarya, S.K. (1995) Hydrogeology and Water Resources of Intermontane, Doon valley. Jour. Him. Geol., 6 (2), 17-28

Benka –Coker M. (1989) Studies on the effects of crude oil and heavy metal contamination of soil and water on the microbial population at the Kokori flare site, Bendel State Nigeria. Ph.D thesis submitted to the University of Benin Nigeria, p 137

BIS (1991) Indian Standard for drinking water –specification (First Revision) IS – 10500:1991. BIS, New Delhi, India

Bishnoi, M. and Arora, S. (2007) Potable groundwater quality in some villages of Haryana, India : Focus on fluoride pp, Journal of Environmental Biology, Triveni Enterprises, Lucknow (India) 28 (2) 291- 294 (2007)

Chopra, A.K. and Pathak, C. (2012) Bioaccumulation and translocation efficiency of heavy metals in vegetables grown on long –term waste water irrigated soil near Bindal river, Dehradun. Pp Agric Res (April- June 2012) 1 (2):157-164 DOI 10.1007/s 40003-012-0016-8

C.E. Dioka, O.E. Orisakwe, F.A.A. Adeniyi and S.C. Meludu (2004) Liver and Renal function tests in artisans Occupationally exposed to lead in mechanic village in Nnewi, Nigeria. *Int. J. Environ. Res. Public Health* 2004, 1, 21- 25

CGWB, Central Ground Water Board , Dehradun (2009) Ground water Management Studies, Dehradun Uttarkhand, 22

Chindah A.C., Braide S.A.,(2000) "The impact of oil spills on the Ecology and Economy of the Niger Delta" In Proceedings of workshop on Sustainable Remediation Development Technology held at the Institute of Pollution Studies, Rivers State University of Science and Technology, Port Harcourt, 2000.

Cunningham, S.D., Anderson, T.A.., Schwab, A.P. and Hsu, F.C. (1996) Phytoremediation of oil contaminated with organic pollutants. *Adv. Agron*. 56, 55-114

De Jong, E., (1980) Effects of crude oil spill on cereals. Environmental Pollution, 22: 187-307 Environmental Protection Agency (1991) Final reports of heavy metals contents in Taiwan Agricultural Soils 4 Vols. Tapei, Taiwan, ROC

E.U. Onweremadu and C.I.Duruigbo (2007) Assessment of Cd concentration of crude oil polluted arable soils. Int. J. Environ, Sci. Tech., 4(3): 409-412, 2007, ISSN: 1735-1472

Facundo JM-R, Vanesa H-R, Teresa ML (2001) Biodegradation of diesel oil in soil by a microbial consortium. Water Air Soil Pollut. 128:313-320

F.I. Achuba and B.O. Peretiemo-Clarke (2008) Effect of spent engine oil on soil catalase and dehydrogenase activities *Int. Agrophysics,* 2008, 22, 1-4

Frick, C.M., Farell, R.E. and Germida, J.J. (1999) Assessment of Phytoremediation as an in situ technique for cleaning oil-contaminated sites.

Ghosh A.B., Bajaj, J.C., Hassan, R and Singh, D.(1983) Soil and water testing methods, A laboratory manual, IARI. New Delhi. 1983 31-3

Gupta, S. (1993) Fluvial response to thrust tectonic in a modern piggyback basin, western Himalaya . 5th Internationtl. Conf. Fluvial Sediments, Brisbane, 48 (Abstract). University of Queensland, Brisbane

H. Li, Y. Zhang, C.G. Zhang and G.X. Chen (2005) Effect of petroleum – containing wastewater irrigation on bacterial diversities and enzymatic activities in a paddy soil irrigation area. J Environ.Qual. 34 : 1073-1080 (2005). doi: 102134/jeq 2004.0438

Hilary Nixon and Jean- Daniel Saphores. (2003) The Impacts of motor vehicle operation on water quality: A preliminary Assessment, Ph.D thesis school of Social Ecology, Economics and Civil and Environmental Engineering Departments, University of California, Irvine 92697 USA.

ICRCL. (1987) Inter-developmental Committee for the redevelopment of contaminated land, guide on assessment and redevelopment of contaminated land. Paper 59/83 2nd ed. *Development of the Environment, London.*

Jain, C.K., (1996-97) Ground water quality district Dehradun., Natioanal Institute of Hydrology, Jal Vigyan Bhawan, CS (AR) 10/96-97

Jane –Francis T.K. Akoachere, Theresa N. Akenji, Felicitas N. Yongabi, Gerald Nkwelang and Ronald N. Ndip (2008) "Lubricating oil-degradation bacteria in soils from filling stations and auto-mechanic workshops in Buea, Cameroon: occurrence and characteristics of isolates. African Journal of Biotechnology Vol. 7(11), pp.1700-1706, 3 June, 2008.

Kumar, M., Pandey, I.P. and Agarwal, V.(2010) The Seasonal Variation Impact on the Physico- Chemical Parameters of Rispana River and Underground Water in the Eastern Doon Valley. IJEP 30 (10): 853-856 (2010)

Kumar, A., Rawat, S., Srivastava, M. and Bhushan, V. (2012) Physicochemical analysis and isolation of bacteria from water samples of Maharana Pratap Sagar, Kagra District of Himachal Pradesh. Journal of applied Sciences in Environmental Sanitation, 7 (3): 161- 166

Kumar, P (2004) "Economics of Soil Erosion: Issues and Imperatives from India" Cocept Publishing Company A/15-16, Commercial Block, Mohan Garden New Delhi-110059

Liu, R.T., and J.Z. Xu, (2002) Present situations problems and counter measures of sewage irrigation in China (In Chinese.) China water Resour. 10: 123-125

Liu, Q.S., E.S. Qi, C.G.Zhang, G.F.Yong, L.X.Xu and Q.N.Jiang.(1981) Study on the microbial ecology in petroleum –wastewater irrigation area and the degradation of Petroleum (In Chinese) Environ Sci. 2:161-166

Lundstedt, S. (2003) Analysis of PAHs and their transformation products in contaminated soil and remedial processes. Solfjodern Offset AB, Umea, Sweden, 55pp

M.A. Nawachkwu, H. Feng and J. Alinnor (2010) Assessment of heavy metal pollution in soil and their implications within and around mechanic villages. *Int. J. Environ. Sci. Tech.,* 7 (2), 347-358

Maria R., Teresa R., Doug H. and Pawlak, Z (2004) The toxicity characteristics of leaching procedure (TCLP) extraction in evaluation of heavy metals and total organic volatile contaminants in used engine oil and sludges XIXth ARS Separatoria- Zloty Potak Poland 2004.

Mark, R. (2004) Wastewater used in urban agriculture : Assessing current research and options for national and local governments. P 18-19. *In* cities Feeding People Program series report. Int. Development Res. Center Germany

Martin, D.,Glass, T.A., Todd, A.C.Shi, W. et al (2006) Association of blood and tibia lead with blood pressure and Hypertention in a community of older adults. *Am J Epidemiol* 163 (5),467- 478

Medlicott, H. (1964) The geological structure and relations to the southern portion of the Himalayan ranges between river Ganga and Ravee. Mem Geol. Survey India, v.3, pp 87-93

Merkl, N. (2005) Phytoremediation of petroleum- contaminated soil Margraf Publisher Wiekershim, 125 pp

Mitsch, W.J and Gosslink J.G (1986) Wetland. Van Nostrand Rienhold, New York, p 539

Michael A. Nwachukwu, Haun Feng and Kennedy Achilike (2010) Integrated study for automobile wastes management and environmentally friendly mechanic villages in the Imo River basin, Nigeria. African Journal of Environmental Science and Technology Vol. 4 (4),pp. 234-249, april 2010

Mundepi, A.K. (2013) Seizmic Mirozonatio Study in Doon valley, Northwest Himalaya, India J.Geological Society of India Vol. 81, June 2013, pp 767-773

Nossin JJ (1971) Outline of the geomorphology of the Doon Valley, Northern UP, India, *Zeitschrift fuer Geomorphologie- Balogh Scientific Books* 12 Berlin Stuttgart 18-50

Nakata, T. (1972) Geomorphic history and crustal movements of the foothills of the Himalaya. Rep Tohoku Univ. Japan, $7th$ Ser (Geog), v.22, pp.39-177

Nakata, T. (1972) Geomorphic history and crustal movements of foothills of the Himalaya. Rep Tohoku Univ. Japan, 7^{th} Ser (Geog), v.22, pp. 39-177.

National Research Council (NRC) (1985) Oil in the sea, inputs, fates and effects. National academy Press, Washington, DC

Njoku, K.L., Akinola, M.O.and Oboh, B.O. (2008). Germination and performance of *Glycine max* L. (Merrill) in crude oil contaminated soil augmented with cow dung. Nat Sci. 6(1).48-58

Njoku, K.L.,Akinola, M.O. and Oboh, B.O.(2008). Germination, survival and growth of accessions of *Glysine max* L. (Merrill) (Soyabean) and *Lycopersicon esculantum* L. (Tomato) in crude oil polluted soil. R. *Journ*. *Environ*. *Toxicol*.2 (2):77-78

Nossin, J.J. (1971) Outline of geomorphology of the Doon valley northern U.P. India Z. Geomorph, NF Suppl. Bd, v.12, pp18-50

Njoku, K.L., Akinola, M.O. and Oboh, B.O (2009) Phytoremediation of crude oil contaminated Soil: The effect of growth of *G.max* on the physico-chemistry and crude oil contents of soil. In: Nature and Sciene 2009; 7 (10)

Nkwocha, E. and Duru, P.O (2010) "Micro- Analytic Study on the effects of oil Pollution on local plant species and food crops" Advances in bioresearch, Vol 1 (1) June 2010:189-198, Society of Education, India

Odoh, R., Agbaji E.B. and Kagbu J.A. (2011) Assessment of Trace metals Pollution in Auto-Mechanic Workshop in some selected local government Area of Benue State, Nigeria. Int. J. Chemistry Vol. 3. No. 4: December 2011 doi:10.5539/ijc.v3n4p78

Odu C.T.I. (1972) Microbiology of soil contaminated with petroleum hydrocarbons I. Extent of contamination and some soils and microbial properties after contamination. J Inst. Petrol (London) 20(I): 2-8

Odu C.T.I. (1972) Microbiology of soils contaminated with petroleum hydrocarbons II Natural reclamation and rehabilitation of soils affected. J Inst. Petrol (London) 20 (1):77-92

Oguntimehin, Ilemobayo and Ipinnmoroti, K (2008) Profile of Heavy metals from automobile workshops in Akure, Nigeria. Journal of Environmental Science and Technology 1 (1): 19-26, 2008 ISSN 1994-7887

Okonokhua, B.O., Ikhajiagbe., Anoliefo, G O and Emede, T. O (2007) The Effects of Spent Engine Oil on Soil Properties and growth of maize (Zea mays L.) J. Appl. Sci. Environ. Manage. September, 2007 Vol. 11 (3) 147-152

Ori, G.G and Friend, F.P. (1984) Sedimentary basin formed and carried piggyback on active thrust sheet. Geology, v 12, pp. 475-478

Osu C. I, Okereke, Victor, C. (2010) Heavy metals contamination in relation to microbial counts in soils of Automobile mechanic workshops, port Harcourt Metropolis, Rivers States, Nigeria Journal of American science 2010. 6(9)

Osugi, L.C. and Onojake, C (2004) Trace heavy metals associated with crude oil: A case study of Ebocha-8-oil spill polluted site in Niger Delta, Nigeria. *Journal of chemistry and biodiversity* 1(2), 1569-1577

Oyodele Rotimi Ipeaiyeda and Modupe Dawodu (2008) Heavy metals contamination of topsoil and dispersion in the vicinities of reclaimed Auto-repair workshops in IWO, Nigeria Bull. Chem. Soc. Ethiop.2008, 22(3), 339-348 ISSN 1011-3924

Pathak, C., Chopra, A.K., Kumar, V. and Srivastava, A. (2010) Heavy metals contamination in waste –water irrigated agricultural soil near Bindal river Dehradun, India. pp in Poll Res. 29 (4): 583-587 (2010)

Pivetz., B.E. (2001) *Phytoremediation of Contaminated Soil and Ground water at Hazardous waste sites.* Man Tech Environmental Resources Services Corporation, Ada, Ok,36pp

Quinones-Aquilar, E.E., R. Ferra-Cerrato, R.F.Gavi, L.Fernandez, V.R.Rodriguez and A. Alarcom (2003) Emergence and growth of maize in a crude oil polluted soil. Agroscienia, 37: 585-594

Ramola, B. and Singh A.(2013). Heavy metal concentrations in pharmaceutical effluents of ndustrial area of Dehradun (Uttarakhand), India in J Environ Anal Toxicol 3: 173 doi: 104172/2161 -05251000173

Rao, D.P. (1986) An approach to the quantitative estimates of rates of recent movements, the Sub –Himalaya example. Roy Soc. NZ Bull., v.24, pp.541-564

Rawat, M., Sharma, H., Singh, M., Kedareswaru, U. and Singh, R.P. (2011). Evaluation of aquifer parameters and groundwater quality in Doon Valley, Uttarkhand. J. Ind. Geophys. Union (July 2011) Vol. 15, No. 3, pp. 125-136

R.C. John, A.Y. Itah, J.P. Essien and D.I.Ikpe (2011) Fate of Nitrogen-Fixing Bacteria in crude oil contaminated Wetland Ultisol. Bull Environ Contam Toxicol (2011) 87:343-353 DOI 10.1007/s00128-011- 0320-1

Sangeeta Guha (2000) Geological and Hydrogeomorphological studies of Asan Watersheds, Garhwal Himalaya, U.P. Unpublished thesis, submitted to Department of Geology, University of Delhi 287

Schnoor, J.L. (2002) Phytoremediation of Soil and Groundwater: Technology Evaluation Report TE-02-01.Groundwater remediation Technologies Analysis Center (GWRTAC)

Schroder, P., Harvey, P.J. and Schwitguebel, J.P. (2002) Prospects for phytoremediation of organic pollutants in Europe. *Environ. Sci.Pollut. Res*. 9 (1), 1-3

Schwab, A.P. and Bank, M.K. (1999) Biologically Mediated Dissipation of Polyaromatic Hydrocarbons in the root zone. In: *Bioremediation through Rhizosphere Technology*, pp 132- 141. American Chemical Society, Washington DC

Sekhon, G.S. and Singh, B. (2013) Estimation of heavy metals in the ground water of Patiala District of Punjab, India. pp Scknow Publications Ltd. Earth resources ER, 2013, 1(1): 1-4

Siciliano, S.D. and Germida, J.J. (1998) Biolog analysis and fatty acid methyl ester profiles indicate that Pseudomonas inoculants that promote phytoremediation alter the root- associated microbial community for *Bromus bieberstenii.Soil Biol. Biohem.*30, 1717-1723

Thakur, V.C. (1981) An overview of thrusts and nappes of Western Himalaya. In Thrust and Nappe Tectonics, price NJ and McClay KP (edition), Geological Society London (Specific Publication) 287-392.

Tong, B. C., Yuan, M. Z., Mei L., Ze, H., Hang, T. W and Qin, Z. T. (2005) Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China Chemosphere 60 (2005) 542-551 doi:10.1016/j.chemoshphere.2004.12.072

Trivedi, R.K. and Goel, P.K.(1986) Analysis of soils and aquatic sediments. In chemical and Biological methods for water pollution studies. Environmental Publication Karad. 1986. 97- 112

Udo, E.J. and A.A.A Fayemi, (1995) The effect of oil pollution on soil germination, growth and nutrient uptake of corn. Journal of Environmental Quality, 4: 537-540

Wang, J; Jiq, C.R; Wong, C.K; Wong, P.K. (2000) Characterization of polycyclic aromatic hydrocarbons created in lubricating oils. Water, Air and Soil Pollution, 120; 380-396

Walker M.V., Crawford R.L., (1997) Overview :Biotransformation and Biodegradation. In: Hurst CJ, Kundsen GR, Mcinerney MJ, Statzenbach LD, Walter WM (eds). Manual of Environmental Microbiology, American Society of Microbiology Press, Washington, D.C. pp 707-708

WHO (1978) Health Hazards for Drinking Waters. Report of the working group, London. 26- 30 September 1977. WHO Copenhagen. WHO (1983) International Standards for drinking water quality, World Health Organization, Geneva pp186

Whisman, M.L., Goetzinger, J. W., Cotton, F. O. (1974) Waste lubricating oil research In: An Investigation of several Re-fining Methods. Beureau of mines, Bartlesville, Energy Research Center.

Williams, G.R.C. (1992) Memoirs of Dehradun. Natraj Publications, Dehradun Dun

Worgu, S.O., Hydrocarbon exploitation. Environmental Degradation and Poverty in the Niger Delta region of Nigeria, Lund University Lumes Programme, Lund, Sweden, 2000, 2-11pp