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 widespread 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 contain 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; Heitkenemper 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 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, over-exploitation, 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 petroleum-distillates 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 coarse-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 desorb 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° 55’ and 30° 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 from 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 Uttarakhand 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 km², 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.
Geologically, the valley is divided into

The lesser Himalaya Mussoorie Mountain range in NW and NE parts. It 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
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
Table -1.1: Sample Locations and their Codes

Pre and Post Monsoon Season Water and Soil Samples collection sites

<table>
<thead>
<tr>
<th>Urban Areas locating Motor Servicing Centers</th>
<th>Rural Areas, Soil &amp; Groundwater Sample locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.N. Locations</td>
<td>Sample Codes</td>
</tr>
<tr>
<td>1. Premnagar</td>
<td>DDN-1</td>
</tr>
<tr>
<td>2. Prince Chowk</td>
<td>DDN-2</td>
</tr>
<tr>
<td>4. Transport Nagar</td>
<td>DDN-4</td>
</tr>
<tr>
<td>5. Rajpur Road</td>
<td>DDN-5</td>
</tr>
<tr>
<td>6. Chakrata Road</td>
<td>DDN-6</td>
</tr>
<tr>
<td>8. Race Course</td>
<td>DDN-8</td>
</tr>
<tr>
<td>12. Kamla palace, GMS Road</td>
<td>DDN-12</td>
</tr>
<tr>
<td>17. Patel nagar</td>
<td>DDN-17</td>
</tr>
<tr>
<td>18. ISBT Majra</td>
<td>DDN -18</td>
</tr>
<tr>
<td>22. ISBT Majra</td>
<td>DDN-22</td>
</tr>
</tbody>
</table>

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.
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
Soil samples were collected in good quality zipped polythene bags from the depth of 0-15 cm by using auger. The soil samples were collected and stored in air tight zipped polythene bags by maintaining temperature range from 3-4°C. 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) × 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 ($^\circ$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 ($^\circ$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 $\mu$siemen/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 $\log_{10}$ 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**

\[
\text{Total Suspended Solids, mg/l} = \frac{A - B \times 1000 \times 1000}{\text{Volume of sample}}
\]

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:**

\[
\text{BOD, mg/l} = (D_0 - D_5)
\]

\[D_0=\text{Initial DO in the sample.}\]

\[D_5 = \text{DO after 5 days}\]

**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. K₂Cr₂O₇.

75 ml H₂SO₄ was slowly added containing AgSO₃ 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:**

\[
\text{COD mg/l} = \frac{(A-B)C \times 8 \times 100}{\text{Volume of sample}(\text{ml})}
\]

Where 

\(A\) = ml of FeSO\(_4\) (NH\(_4\))\(_2\)SO\(_4\) used for blank

\(B\) = ml of FeSO\(_4\)(NH\(_4\))\(_2\)SO\(_4\) used for sample

\(C\) = Normality of FeSO\(_4\) (NH\(_4\))\(_2\)SO\(_4\) solution determined above

**Total Hardness (CaCO\(_3\)):** 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 CaCO\(_3\) /L = A×B ×1000/ ml of sample

Where,

\(A\) = ml titration for sample

\(B\) = mg CaCO\(_3\) equivalent to 1.00 ml EDTA titrant

**Concentration of CaCO\(_3\) 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.

\[\text{CaCO}_3 = A \times B \times 1000 \text{ ml of suspension}\]
Concentration of CaCO$_3$ 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:**

\[
\text{Calcium as Ca (mg/L)} = \frac{T \times (1.05)}{\text{Sample taken, ml}}
\]

Where, \(T=\) volume of titrant, ml

\[
\text{Calcium hardness (mg/L as CaCO}_3\text{)} = \frac{T \times (1000) \times (1.05)}{\text{Sample taken, ml}}
\]

**Magnesium (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.

Magnesium concentration was determined with the help of pre determined concentration of CaCO$_3$ and Ca by adding multiplying factor 0.243 as referred in APHA, (2005).

**Calculation:**

\[
\text{Magnesium (as Mg, mg/L)} = (T - C) \times 0.243
\]

Where, \(T=\) Total hardness mg/L as CaCO$_3$

\(C=\) Calcium hardness mg/L as CaCO$_3$

**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) \( \frac{N \times V \times \text{M.W. of } \text{HCO}_3^- \times 1000}{\text{Volume of sample}} \)

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

Normality of the Acid: 0.01
M.W. of \( \text{HCO}_3^- = 61 \)
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) \( \frac{N \times V \times \text{M.W. of } \text{HCO}_3^- \times 1000}{\text{Volume of sample}} \)

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

Normality of the Acid: 0.01
M.W. of \( \text{HCO}_3^- = 61 \)
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:**

\[
\text{Chloride mg/l} = \frac{\text{ml of AgNO}_3 \times 1000 \times 35.5}{\text{ml of sample}}
\]

**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 (40\(^{0}\) or 60\(^{0}\)) or hexane or tricholoflouro ethane.

An amount of 250 ml of sample was taken in a separating funnel, 10 ml of H\(_2\)SO\(_4\) 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:**

\[
\text{Oil and grease in mg/l} = \frac{(W_2 - W_1) \times 1000 \times 1000}{\text{volume of sample taken}}
\]

Where \(W_1\) = Initial weight of dish  
\(W_2\) = 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 ml = 1.00 mg Cu

Lead: Dissolve 1.598 g 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: dissolve 1.000 g zinc metal in 20 ml 1+1 HCl and dilute to 1000 ml with water; 1.00 ml = 1.00 mg Zn

Analytical procedure for Heavy Metals:

1. Digestion of water sample: Filtered water sample were digested by adding 2 ml HNO₃

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 HNO₃.

The instrument was calibrated, for each metal to be detected, with known standard. After calibration and programming, the prepared samples were aspirated to the flame. Zero was set with double distilled water before each determination. Results were displayed in μgm/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 aspirated 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 ml = 1.00 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 ml = 1mg 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.