INVESTIGATION ON THE TRANSPORT OF POLLUTANTS TO AQUATIC ENVIRONMENT WITH SPECIAL REFERENCE TO GROUNDWATER

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Degree of Doctor of Philosophy in Chemistry

BY

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CERTIFICATE

This is to certify that the Thesis entitled **Investigation on the transport of pollutants to aquatic environment with special reference to groundwater** herewith submitted by Shri. A. Shahul Hameed in partial fulfilment of the requirements of the Ph. D. degree in chemistry of the University of Calicut, is an authentic record of the research work carried out by him under our supervision and guidance in the Department of Chemistry, University of Calicut and Central Water Analysis Laboratory of CWRDM, Kozhikode and, that no part thereof has been presented before for any other degree

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DECLARATION

It is hereby declared that the Thesis herewith enclosed is an authenticated and bonafide record of the research work carried out by me under the supervision of Dr. N Thankarajan, Professor and Head (Retd.), Department of Chemistry, University of Calicut, and Dr K. Vasu, Scientist-E1 and Head-in-Charge, Nuclear Hydrology Division, CWRDM, Kunnamangalam, Kozhikode, and that the work has not been presented for any other Degree or Diploma. All sources of help received by me during the study have been duly acknowledged

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ABBREVIATIONS

In this Thesis, for the sake of brevity, symbols and formulae have been freely used instead of names. Since ions involved are familiar ones, their ionic charges are not generally indicated. Other abbreviations used are:

Alk	alkalinity
BGL	below ground level
BIS	Bureau of Indian Standards
BOD	biochemical oxygen demand
DWL	depth to water level
EC	electrical conductivity
MS	mild steel
MSL	mean sea level
ND	non-detectable
OC	organic carbon
OD	outer diameter
r	linear correlation coefficient
TH	total hardness
Tg	tera gram (10^{12} g)

PART I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

General

Needless to say that water is an essential commodity for the existence and sustenance of life on earth. It covers over 70% of the earth's surface, out of which about 97% is in the salty ocean and more than 2% is in glaciers and ice caps leaving around 1% as utilisable freshwater (World Book, 1997). Most of this water is underground, and the remainder includes the water in rivers, lakes, springs, pools and ponds. The freshwater requirement for a variety of uses like drinking and domestic purposes, fish culture, recreation, agriculture and industry is to be met from this limited freshwater potential.

Of all the beneficial uses, water for drinking and domestic purpose is of prime concern. Surface systems like rivers and streams, and sub-surface systems like wells form the major drinking water sources. Water supply schemes based on rivers are mainly concentrated in cities and municipal towns. Sub-surface systems which are generally exploited in the form of open dug wells, bore wells and tube wells serve as major drinking water sources for the rural population.

Water quality and its relevance

In order to satisfy the water needs, besides its quantity, its quality is also very important, as the quality decides its suitability for any desired use. Water that occurs in nature is commonly found to carry a wide variety of substances. Water reaching the surface of the earth through precipitation collects a number of substances on travel, and subsequently attains changes in quality on reaching the ground. The water passing downward finally reaches the aquifer zone, an underground stratum capable of holding and transmitting water. Hydrochemical factors generally influence changes in the quality of water under the ground. The degree of mineralisation and change in other constituents of water attain an equilibrium depending on the geology of the particular area with which the water is in contact.

Water scarcity and deterioration of its quality are of growing concern for countries all over the world. According to FAO (IAEA,1998), the global demand for freshwater is doubling every 20 years. Man's influence on the quality of water is quite apparent, and of late, water quality deterioration due to human polluting interventions are on the increase leading to heavy stress on fresh water availability. The sources of pollution generally fall under two main categories viz.

point sources and non-point sources. Point sources include municipal and industrial waste waters and other sources for which specific points of entry can be identified. Non-point sources are diffused sources like urban run-off, agricultural run-off etc.

Kerala State with a total area of 38,864 sq. km has three distinct physiographic zones: lowland, midland and highland which are <7.5, 7.5-75 and >75 metres respectively, above mean sea level (STEC, 1998). Though the State receives the second highest average rainfall among the States of India, a number of factors contribute to the potable water scarcity in certain areas, especially during the 6 to 7 months preceding monsoon. The uneven distribution of rainfall, the narrow width and steep slope of the land between the origin and end of the rivers causing quick run-off to the sea, porous sub-stratum and deforestation tendencies in the high ranges, are some of the major factors contributing to severe temporal imbalance of water availability in the State. The fast pace of development and uncontrolled exploitation of natural resources lead to water and air pollution, which further limits freshwater availability.

In Kerala, only about 300, among the 1001 panchayaths have been provided with protected water supply; the remaining 70% depends on local water sources. People depend mainly on groundwater sources for their domestic needs in these areas, and open dug wells are the major extraction structure in the State. On an average, the density of dug wells per sq. km is 200 in coastal belt, 150 in midlands and 70 in the highlands (CWRDM, 1995).

Importance of pollution studies

Groundwater represents a significant and in many places predominant proportion of the available water source. It is the sole source of drinking water especially in rural areas, where protected water supply schemes are scanty. The groundwater sources which were considered to be relatively free from pollution are gradually becoming contaminated as a result of both natural and human interventions. Increased use of groundwater in an uncontrolled manner inevitably leads to falling of groundwater levels and to undesirable consequences such as salt water intrusion, especially in coastal belt. Besides, disposal of solid wastes and sewage on land, agricultural activities, indiscriminate discharge of untreated industrial effluents etc. lead to pollution of sub surface aquatic systems. Pollution of surface water may be mitigated by concerted prevention and control, but it is more serious when pollutants enter the groundwater. Polluted groundwater may remain in aquifers for centuries and is very difficult, if not impossible, to clean it up.

Types of pollutants altering the quality of water are of diverse nature. Depending on the origin of the wastes, the nature of chemicals present in them, and the transformations that could occur during their transport, the pollutants differ in their characteristics.

An important aspect of pollution is the urge to understand the fate and transport of the pollutants introduced into the soil/water environment. The pollutants are not stationary, they move along with the medium in all possible directions. Moreover, they are not inert in nature. They are, in, most of the cases, chemically active substances. Further, the environment, through which these substances move also is biologically and bio-chemically very active. Though chemical quantification of pollutants gives a clear picture of the quality status and fitness to potability of water, it does not give any idea about the vulnerability of the water sources over time and space to the incoming pollutants from different sources. It does not provide any idea about how far and how fast a pollutant migrates in the given environment. Hence, understanding the fate and transport of the pollutants by quantifying the movement or transport in the media is of great importance.

The homestead system of living in Kerala, where the residential buildings are located within the agricultural farms, renders the groundwater sources, especially open dug wells, susceptible to threat from agricultural runoff and domestic wastes as the pollutants present in them in soluble form may percolate down to reach the groundwater. When a community sewage treatment system (stabilization pond) is also located in the vicinity of residential area, it enhances the susceptibility of water to contamination due to possible leaching of pollutants through soil strata. Besides, as these dug wells are shallow, their vulnerability to contamination is increased. In a similar situation, an industry located in the midst of the residential area too poses threat to the quality of groundwater sources.

Scope of the present Investigation

Survey of literature (Part II) reveals that transport of pollutants through the soil hasn't received the type of special attention it deserves in the context of groundwater pollution. Hence, this investigation has been so designed as to enable a detailed and extensive study of this phenomenon, choosing two different pollution sources in Kerala State, India.

Influence of pollutants from the sewage stabilization ponds of Kozhikode Medical College, on the quality of water in the domestic wells in and around the residential campus of the college, was examined in detail during the period, 1993 -95.

Transport of pollutants from effluents discharged by a clay mining industry at Madayi in Kannur District, and its effect on the quality of well water in the surrounding areas during the period 1996-97 was also examined.

Apart from evaluating the extent of pollution of well water due to transformation and transport of pollutants, analysis of temporal and spatial trends of the spread of pollutants was also envisaged. Identification of actual source of pollutants, from among potential sources, using isotope technique, was another important objective of this investigation.

In view of the health hazards of water pollution, results of this investigation could be of vital significance. Hopefully, this investigation would attract further work and interest in this field and might provide valuable pointers to sanitary and/or environmental engineers to devise remedial measures to alleviate, and wherever possible, eliminate the threat of pollution spreading to groundwater.

PART II

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Groundwater pollution

Groundwater pollution is one of the most important problems of many developed and developing countries. Stephen Foster (1996) of British Geological Survey, who conducted groundwater surveys in 30 countries, reports that the groundwater sources are becoming increasingly polluted in recent times. He observed that indiscriminate disposal of liquid effluents and solid wastes coupled with inadequate sanitation arrangement, and the leakage of stored chemicals into the ground from industrial units are the main reasons for groundwater pollution in urban areas. In the rural areas, dominated by agricultural activities, pesticides and fertilisers used are the major pollutants.

The type of pollutants altering the quality of water is diverse in nature depending on their origin, chemical content, and transformations that occur during transport to the water resources. The most common sources of pollutants are sewage treatment plants, industrial houses, coal mines, urban and agricultural run-off, animal feed lots and, land fills (Philip Cohen, 1985).

Studies on groundwater pollution has been given a major thrust in many parts of the world. In Australia, water quality deterioration due to salinity or because of the presence of ions such as fluoride or nitrate has been reported by many researchers (Hart, 1974 ; Peck et al., 1983 ; German, 1983 ; Lawrence,1983). Groundwater pollution in most urban environments, especially in large cities such as Sydney, Melbourne, Adelaide, Perth and Canberra, has been studied in detail (Lawrence and Hughes, 1981 ; Jacobson,1983).

Septic tanks and drains, which are of widespread use in rural, recreation and suburban areas contribute filtered sewage effluent directly into groundwater. Robertson et al., (1991) have observed that septic system located near shallow unconfined aquifers is a potential source of large scale contamination of groundwater in Ontario.

Among multifold threat to groundwater in industrial societies, the impact of waste sites have caused growing concern during the past decades. Groundwater contamination around the vicinity of several waste sites in Berlin (Friessel et al.,1986), and around the conventional sub-surface waste water disposal system in Long Island (Andreoli et al.,1975) is well documented. Robinson and Maris (1979) identified a wide range of polluting substances in leachate from domestic landfill sites of various ages in UK. Pollution of groundwater due to crop land, urban run-off, and leakage from disposal sites has been studied by many authors (Alexander, 1976; WRI, 1990; Andrzej Tonderski, 1996). Changes in chloride (1.3-41 mg/l) and nitrate (0.4-10.5 mg/l) concentrations in the groundwater underlying the Boise-Namba area in south-west Idaho basin, affected by waste disposal and land-use practices, were reported by United State Geological Society (USGS) in its survey (Johnson and William, 1987). The concentrations showed wide fluctuations, rising and falling trends, over the long term period of 10 years. In this area, housing developments are not connected to central sewer systems. Here, septic systems are the probable sources of chloride. In the case of nitrate, the sources include barnyard and feedlot wastes, closely spaced septic systems, and commercial fertilisers (Johnson and William, 1987). Nitrate is observed to be a predominant pollutant arising from many pollution sources. A brief discussion on nitrogen cycle and its hydro-chemical behaviour would be relevant in this context.

Nitrogen cycle and its hydro-chemical behaviour

Nitrogen and its compounds are essential building blocks for ecosystem and human survival. Lithosphere holds far more nitrogen in storage than the other locations combined (Table 1).

Table 1 Major areas of nitrogen storage in ecosystem (Smil, 1985; Warneck, 1988) (estimated amount on a global scale)

Location	Nitrogen storage, Tg
Lithosphere	2.6×10^6
Soil	85×10^3
Continental bio-mass	10×10^3
Atmosphere	3.8×10^3
Surface litter	1.5×10^3
Marine biomass	380
Ocean storage	23
Human beings	5.5

The dominant position of nitrate in the nitrogen cycle is clearly brought out by the flow sheet in Fig.1. The figure reveals the sources and pathways leading to nitrate in the environment.

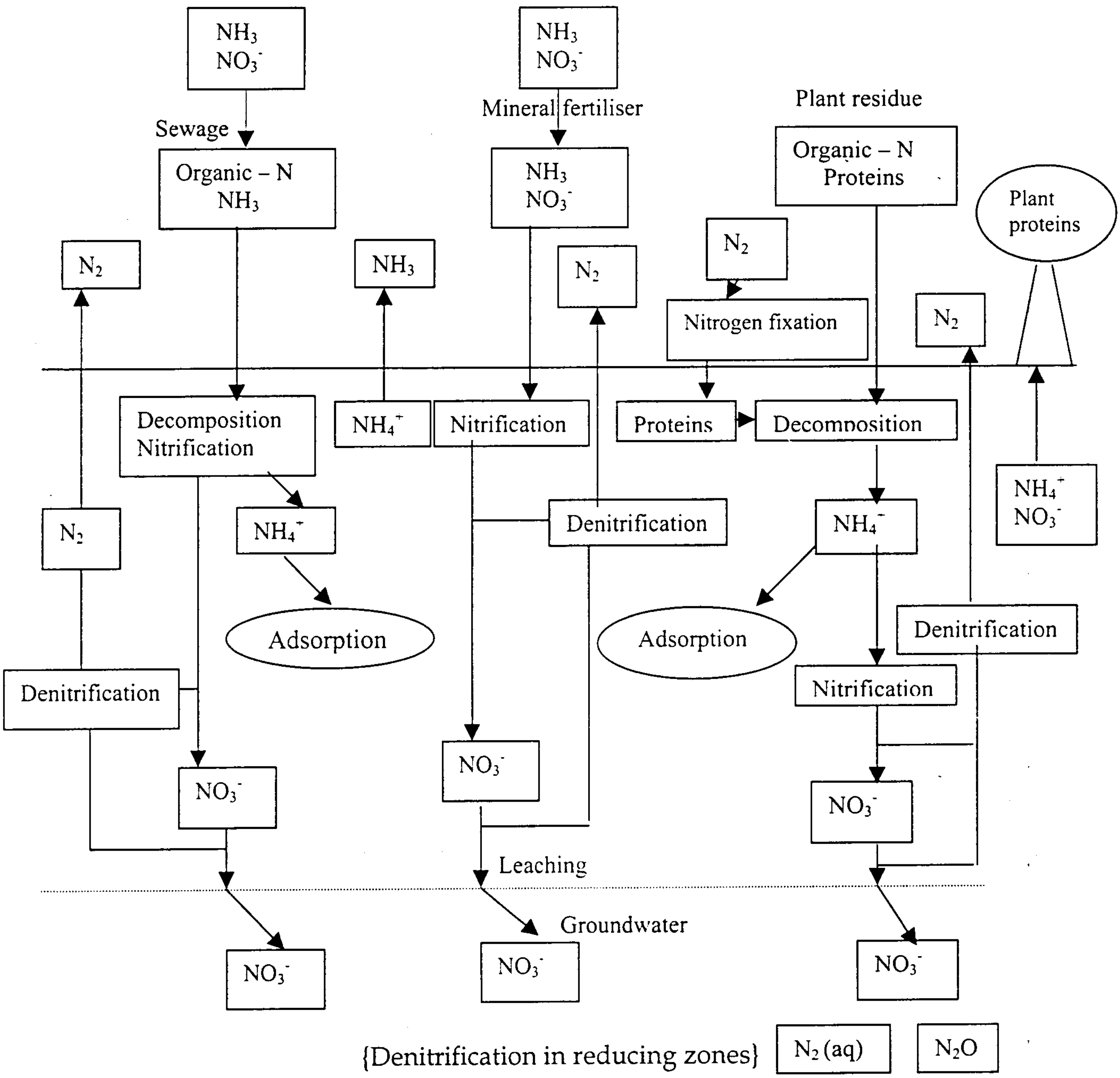


Fig. 1 Nitrogrn cycle in the environment

The major active zone of nitrogen use and transfer is the soil and biosphere on the continents, with minor activity in aquatic ecosystem. For the use of plants, nitrogen is made available through the process of 'fixation' which converts mainly inert, inactive N_2 to the active form through bacterial processes. Most of the N_2 made available for fixation comes from the atmosphere and from the decay of free-living organisms. Nitrogen is then given to the plants in an assimilable form through mineralisation to ammonia (NH_3) and then to nitrate (NO_3) under aerobic conditions, called nitrification. The cycle in the soil is completed by the return of oxidised nitrogen to an inert condition through denitrification under anaerobic conditions.

Aerobic processes also lead to the formation of nitrogen dioxide (NO_2), much of which is released to the atmosphere. Anaerobic processes create nitric oxide (NO), nitrous oxide (N_2O) and N_2. All of these pathways and processes depend on environmental conditions such as soil acidity ($pH<6$ inhibits denitrification), water content, soil type and plant type (Bridgman, 1990). Temperature is crucial because biochemical activity increases exponentially with increasing temperature.

Nitrogen in aquatic systems

The nitrogen content in ocean and continental surface water is much less than in the biosphere or atmosphere. Over 95% of nitrogen stored in ocean is inactive, in molecular form (Smil, 1985). Only nitrate (about 2.5% of total ocean nitrogen) and organic matter (1.5%) have a small active role. Oceans gain nitrogen through river run-off from continents, and wet and dry deposition to bottom sediments, and release to the atmosphere in areas of biological activity.

Nitrogen transformations in groundwater

Nitrate is the most common form of dissolved nitrogen identified in groundwater. Nitrate in groundwater generally originates from nitrate sources on the land surface in the soil zone, where nitrogen rich wastes are buried. During periods of active water flow also, some of the nitrogen is leached by run-off or infiltration to the groundwater.

Nitrogen transformation reactions that occur in shallow aquifers include the following (Freeze and Cherry, 1979; Stumm and Morgan, 1981).

Ammonification

$$-CH_2O(NH_3) + O_2 \rightarrow NH_4^+ + HCO_3^- \text{ --------------------------- } 1$$

Nitrification

$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ ------------------------------ 2

Denitrification

$4NO_3^- + 5CH_2O \rightarrow 2N_2(g) + 5HCO_3^- + H^+ + 2H_2O$ -----------3

Dissimilatory nitrate reduction

$NO_3^- + H_2O + 2CH_2O \rightarrow NH_4^+ + 2HCO_3^-$ ---------------------4

Ammonification and nitrification commonly occur above the water table, whereas the last two (3 & 4) which are citrate reduction reactions, generally occur beneath the water table under oxygen deficient conditions (Freeze and Cherry, 1979).

Concentrations of nitrate in the range commonly reported in groundwater are not limited by solubility constraints. Because of this and because of its ionic form, NO_3^- is very mobile in groundwater. In groundwater that is strongly oxidising, nitrate is the stable form of dissolved nitrogen. Very shallow groundwater in highly permeable sediment or fractured rock commonly contains considerable dissolved oxygen. It is in this hydrologic environment that nitrate commonly migrates large distances from input areas (Freeze and Cherry, 1979).

Health effects of excess nitrate

The severe health risk associated with the consumption of water containing excess nitrate has been well recognised. Nitrate present in water can be reduced to nitrite by bacteria present in stomach. Infants, yet to develop normal gastric acidity, are likely to harbour nitrate reducing bacteria in their stomach. Nitrites act on haemoglobin in the blood to form methemoglobin, thereby reducing oxygen in the blood and leading to methemoglobenemea (Robert and Ebba Lund, 1981). This is also referred to as blue baby syndrome which generally affects infants under 6 months of age. Cases have been reported apparently caused by concentrations of 11-40 mg of NO_3/l (Irving , 1974).

Nitrites are also suspected to cause cancer by reaction with organic amines to form N-nitroso amines. Nitrate in water may be converted to N-nitroso compounds that act directly as carcinogenic agents.

Nitrates → nitrites → N-nitroso compounds

Other possible health effects associated with the ingestion of nitrates in water for extended periods have also been detected in animal studies including changes in heart blood vessels and behavioural effects (Shuval and Gruener, 1977). Nitrate, nitrite and secondary amines are precursors of nitrosamines. Nitrosamine precursors may be converted to nitrosamines in the stomach of mammals (Sander et al., 1968), thus presenting a possible additional health risk due to nitrate in drinking water and food. A series of experiments conducted in late 50's and early 60's which were reviewed by Magee and Barnes, 1967, revealed that many nitrosamines are carcinogens in various species of laboratory animals. Epidemiologically correlation has been found to occur between nitrates in drinking water and stomach cancer (Hill et al., 1973; Bawsworth et al., 1975; Mirvish,1977).

Nitrate- a potential pollutant

Prevalence of excess nitrate in shallow groundwater sources in the areas of extensive human development, cultivation, livestock or septic tank has been reported in many places. The intensive use of nitrogen fertilizers on irrigated crop lands has led to building up of nitrate in groundwater sources of eastern Sandhills of Nebraska, as reported by Adelman and Tabidian (1996). Another study in Nebraska (Muir et al., 1973, 1976) led to the conclusion that nitrogen fertilizers contributed substantially to groundwater nitrate contamination only for sites with intensive irrigation development, very sandy soils and shallow groundwater tables. High concentrations of nitrate have been delineated in extensive areas in many parts of the world, including Israel (Saliternik, 1972), England (Foster and Crease, 1972), Germany (Groba and Hahn,1972), California (Calif. Bureau Sanitary Engg., 1963; Nightingale, 1970), Nebraska (Spalding et al., 1978), Southern Ontario and Southern Alberta (Freeze and Cherry, 1979). Tester and Carry (1985) observed that 20% of the potable water supply bore holes located in the Great House Chalk aquifer had nitrate concentrations exceeding 11.3 mg/l. These were located generally in arable farming areas of the Chalk out-crop where unsaturated zone was relatively thin. Presence of nitrate exceeding 10 mg/l in over 163 well water samples collected from parts of Buffalo and Merric Counties in Nebraska has been reported by Gormly and Spalding (1979).

Nitrate concentration of a large regional carbonate-rock aquifer in England is reported to be widespread (Freeze and Cherry, 1979). Analysis of the occurrence and movement of nitrate in this aquifer is complicated by the fact that nitrate is carried in groundwater flowing in a network of joints and solution channels, while some of the nitrate is lost from the active flow regime as a result of diffusion into the porous matrix of the limestone (Young et al., 1977). The transport velocity differs for each contaminant depending on the interactions like adsorption, chemical equilibrium with the solid soil particles (Jain Hocks, 1981).

Information on fate, transformation and transport of pollutants within the soil/water environment is important to understand the interaction of the pollutants. Prediction of pollutant migration and their fate in sub-surface environment requires the knowledge of spatial and the temporal variability of parameters which are used as input data for transport models. Solute transport in porous media has been studied by many workers (Fried and Combarnous, 1971; Mc Mohan and Thomas, 1974; Metry, 1976; Basak and Murthy, 1979; Young and Warith, 1990).

In many agricultural areas, shallow groundwater has become contaminated locally as a result of extensive use of fertilizers, and leaching of nitrate from storage, or disposal of livestock and fowl wastes on land (Freeze and Cherry, 1979). The conversion of organic nitrogen in these wastes to nitrate takes place through biochemical processes. Specific cases of groundwater contamination from animal wastes are reported by Gillham and Webber (1969) and Hedlin (1972). Although extensive nitrate concentration of shallow groundwater can often be attributed to leaching of fertiliser, the nitrate in shallow groundwater in large areas in Southern Alberta (Grisak, 1975), Southern Saskatchewan, Montana (Custer, 1976), and Texas (Kreitler and Jones,1975) seems to be caused by other means. In these cases, most of the nitrate is observed to be derived by oxidation and leaching of natural organic nitrogen in the soil. The greater abundance and deeper penetration of oxygen into the soil might have occurred as a result of cultivation. The contribution of selected chemical from irrigation return flow to sub-surface aquatic systems have been recognised in early seventies. Excess chloride and nitrates in groundwater were reported in Central Wisconsin (Saffigna and Keeney, 1977) and in other places (Burwell et al., 1976).

In India, as in many other parts of the world, the quality of both surface and sub-surface fresh water systems continues to deteriorate due to many human activities. The groundwater sources, a potential source for majority of the population and hitherto considered to be well protected, are facing severe threat of pollution from domestic, agricultural and industrial activities in the country.

In Madhya Pradesh, the groundwater quality of around 98 villages was observed to be affected by either excess nitrate, excess fluoride, high concentration of dissolved solids or hardness. Out of

114 water samples collected from these places, over 53 samples contained nitrate ranging from 0 to 112 mg/l (Nawlakhe et al.,1995). High concentration of nitrate in dug wells of entire Nagaur District of Rajasthan was reported by Gupta (1992). Over 80% of water samples in Churu District and 65% in Barmer District of Rajasthan had nitrate values more than 50 mg/l. It was observed that nitrate increased with total hardness, and decreased as the depth of water table increased. In sandy soils with low water holding capacity and high permeability, movement of pollutants like chloride and nitrate is much quicker than in clayey soils (Ozha et al., 1993).

High levels of iron in groundwater, both in open dug wells and bore wells have been reported in many parts of the country. In India, 14 states (Andhra Pradesh, Assam, Arunachal Pradesh, Bihar, Kerala, Madhya Pradesh, Maharashtra , Manipur, Meghalaya, Nagaland, Orissa, Tamil Nadu , Tripura and West Bengal) have been reported to contain excess iron in drinking water (Das et al.,1992; Pandeya and Shrivastava, 1992; Tak et al., 1992; Prasad, et al., 1994). In general, iron originates from rocks and minerals by dissolution in natural waters. Magnetite (FeO), Ilmenite ($TiFeO_3$), Pyrite (FeS_2) and Iron silicate ($FeSiO_3$) present in granites, gneisses, charnockites are the main sources of iron in the groundwater systems (Chandrasekharan et al., 1981). Contamination of groundwater with iron can also result from acid mine discharges , land fill leachates and iron related industries. The influence of refuse dumps on the quality of groundwater around Amberpet and Golkonda landfill sites at Hyderabad was studied by Jeevan Rao and Shantaram (1995).

Pollution threat from industrial activities

Industrial activities also pose severe threat to fresh water sources through indiscriminate discharge of their effluents. The influence of industrial effluents on deterioration of water quality of wells in the vicinity of industrial locations has been studied by many workers. Pollution of freshwater bodies due to major industries like pulp & paper mills, tanneries, and sugar and textile industries is well documented. Groundwater sources in industrial towns like Faridabad, Ludhiana, Kanpur, Lucknow, and Varanasi are reported to be affected due to wanton discharge of industrial effluents. Increased level of dissolved solids, nitrate and sulphate, together with falling pH level, observed in the case of shallow groundwater, are noticeable in some deeper aquifers also (Lakshmanan et al.,1986; Sahgal et al., 1989; Shankar and Narayan, 1989; Vijay Kumar et al., 1992). Discharge of tannery effluents containing high concentrations of total solids, calcium, magnesium, chloride and chromium, on nearby lands/streams has been reported to cause severe pollution of drinking water wells in the towns of Ambur, Ranipet and Vaniambadi of North Arcot District and in many villages in and around Dindigul of Tamil Nadu (Apparao and Karthikeyan, 1990). Disposal of untreated effluent from bleaching and dyeing units in Trippur of Tamil Nadu resulted in high salinity, hardness and sulphate content of groundwater (Prakash Nelliyat, 1995). Similarly, discharge of waste effluents through open drains from textile mills in Kannur, Kerala has led to building up of chloride and sulphate in the well waters, and polluting over 42% of domestic wells in the area (Shahul Hameed et al., 1997). Monitoring of water quality of wells in selected locations of Kerala indicated high concentration of dissolved solids and chloride in the coastal region; high levels of chloride, fluoride and iron in the midlands, and iron and bacterial contamination in a few highland regions (STEC, 1998).

Clay mining, which does not involve any chemical process, too fall in this category causing degradation of both terrestrial and aquatic environment in a local and regional scale. Pollution of aquatic environment and deterioration of the quality of drinking water due to mine discharge have been observed around the mining area in certain parts of the world (Martin and Crawford, 1987; Gray, 1996). The investigations on the effect of coal mining on water quality revealed that acidity and concentration of sulphate, iron, manganese, aluminium and dissolved solids were generally higher around the mining areas. The overflowing water from water-filled mines and open pits in pyrites and coal mined areas is acidic and is severely polluted by metals and sulphate (Christensen et al., 1996).

In spite of the fact that pollution of groundwater sources has been monitored in many parts of our country including Kerala, most of these studies pertained to point sources of pollutants, especially to effluents of major industries. Groundwater contamination due to diffused sources, like waste dumps, sanitary land fills, agricultural run-off, septic system, feed-lot wastes etc., are yet to be studied in detail. Though sporadic studies have been conducted in certain parts of India, where the pollutants such as nitrate, chloride and sulphate were identified, sufficient effort does not seem to have been made to ascertain the actual origin of the pollutants from possible sources. Where the pollutants are formed through transformation processes, it is essential to know from which ingredients of the main source, or from elsewhere, the pollutants are derived. Such discrimination would have probably helped to evolve suitable strategies for abatement of water pollution. Although possible modes of transport of pollutants through soil have been indicated (Metry, 1976; Alfoldi Laszlo, 1983; Young and Warith, 1990; Simmons et al., 1992) further work seems necessary, in view of their extreme usefulness in containing groundwater pollution. Information on health hazards of pollutants are available (Bawsworth et al., 1975; Shuval and Gruener, 1977; Chambon et al., 1983). Desirable limits of pollutants in drinking water have been reported and recommended by appropriate agencies (USEPA, 1976; UNESCO, 1978; MSSC, 1979) including Bureau of Indian Standards (BIS), and Indian Council of Medical Research (ICMR).

PART III

MATERIALS, INSTRUMENTS AND METHODS

CHAPTER I

Transport of Pollutants from the Sewage Stabilization Pond of Kozhikode Medical College

CHAPTER II

Transport of Pollutants from Effluents Discharged by A Clay Mining Industry at Madayi in Kannur District

MATERIALS, INSTRUMENTS AND METHODS

Materials

Chemicals used for analytical purposes are Analar Grade (Glaxo or E.Merck) purchased from local dealers at Kozhikode.

Samples for analyses were collected in clean plastic containers after proper washing and rinsing, and were preserved wherever necessary.

Instruments

Instruments used in this investigation are:

1. 'Systronics' Model-305 Conductivity Meter
2. 'Systronics' Model-335 Digital pH Meter
3. 'Systronics' Model-131 Turbidity Meter
4. 'Elico' Model-SL171 Spectrophotometer
5. `OPTIMA' Mass Spec (micromass) with NA 1500 NC elemental analyser

Methods

Standard methods reported in the literature were used for analyses (APHA, 1985). Total alkalinity was estimated by titration against standard acid, and total hardness by complexometric titration against EDTA using Eriochrome Black-T as indicator. Calcium hardness was estimated by complexometric titration against EDTA using ammonium purpurate (Murexide) as indicator. The difference between total hardness and calcium hardness was taken as magnesium hardness. From the values of calcium hardness and magnesium hardness which are expressed as $CaCO_3$, the level of calcium and magnesium were calculated. Determination of chloride was done by titration against standard silver nitrate solution, and of sulphate by turbidimetric method after precipitation of sulphate as barium sulphate. Nitrate, after reduction with cadmium in a column, and subsequent diazotization, was determined colorimetrically. Iron was also determined colorimetrically using 1,10-phenanthroline. Fluoride was estimated by colorimetric method based on the reaction between fluoride and a zirconium-dye lake. Phosphate was determined by the reaction with ammonium molybdate forming molybdophosphoric acid which was further reduced to intensely coloured complex, molybdenum blue by stannous chloride and estimated colorimetrically. Total dissolved solids in water was estimated by standard procedure (APHA, 1985). A well mixed sample was filtered through 0.45 micron glass fibre filter and a definite volume of the filtered sample was evaporated to dryness on a pre weighed dish in an hot air oven at 103°-105° C to constant weight. From the weight of the dried residue, the total dissolved solids per litre of water was calculated.

Standard calibrated glassware and double distilled water was used for analyses. Analyses were carried out in triplicate, and their average was taken. The results are expressed in mg/l except pH, EC and isotope variations. pH is expressed in pH units, EC in micromhos/cm at 25°C, $\delta^{15}N$ and $\delta^{34}S$ in per mille (‰).

Water samples for isotopic analysis were filtered through 0.45 micron glass fibre filter discs and then evaporated to dryness in hot air oven at 103°-105° C. The dry residue was scrapped off from the dish and taken in aluminium foil. These residues were forwarded to International Atomic Energy Agency, Vienna for isotopic analyses. Measurement of $\delta^{15}N$ was carried out on a classical double inlet, double collector mass spectrometer. The abundance of $\delta^{15}N$ in the form of diatomic nitrogen (N_2) is measured in the mass spectrometer with atmospheric nitrogen as standard.

For the sulphur isotope analyses, the sulphate in water samples was precipitated as $BaSO_4$ by the addition of $BaCl_2$. The solution was filtered and the precipitate was dried in oven at 103-105°C to remove moisture and the same was then taken in aluminium foil. This precipitate was forwarded to Atomic Mineral Division, Hyderabad for $\delta^{34}S$ analysis.

The isotopic composition is usually reported as δ value, the deviation from universally accepted reference standard and expressed in per mille (parts per thousand) as shown below:

$$\delta\ (‰) = \frac{R_{\text{Sample}} - R_{\text{Standard}}}{R_{\text{Standard}}} \times 1000$$

Where, R denotes the ratio of heavier to lighter isotope.

CHAPTER I

TRANSPORT OF POLLUTANTS FROM THE SEWAGE STABILIZATION POND OF KOZHIKODE MEDICAL COLLEGE

INTRODUCTION

The fast pace of progress in recent years in India has led to an increased awareness of hygiene among the people, and consequently to proliferation of septic systems. Reports of pollution of groundwater caused by such stabilization ponds, prompted a detailed and comprehensive investigation of various aspects relating to transformation and transport of pollutants from the ponds to the surrounding areas. This extensive study carried out during the period from July 1993 to June 1995, using 23 observation wells envisaged identification of pollutants and determination of their concentration levels, together with spatial and temporal trends in their occurrence. In this connection, it was of interest to examine trends in migration of a few selected ions in soil. Pin-pointing of actual origin of major pollutant from possible precursors using tracer technique, was an important objective of the investigation.

Nature of the location and type of the stabilization pond were examined in detail at the outset. As a prelude to the investigation proper, sewage and soil of the study area were analysed.

DESCRIPTION OF THE STUDY AREA

Location, Physiography and Climate

The residential area around the Kozhikode Medical College campus, where the sewage treatment system (which is known variously as sewage lagoon, oxidation pond or stabilization pond) is also located, was selected for this investigation. The site lies between 75° 49′ and 75° 53′ East longitude and, between 11° 16′ and 11° 18′ North latitude (Fig.2). It is a region of high rainfall with humid tropical climate. The annual precipitation is around 3500 mm, and temperature variation is from 22 to 33°C. More than 75% of the annual rainfall is received during the south-west monsoon months of June to August. About 15% of the rainfall is received during the north-east monsoon between September and November. The rest of the precipitation occurs as summer or pre-monsoon showers during the months of December to May.

The area is a part of high grade granulitic terrain of precambrian age. It is covered with laterite soil and crystalline bedrock which are

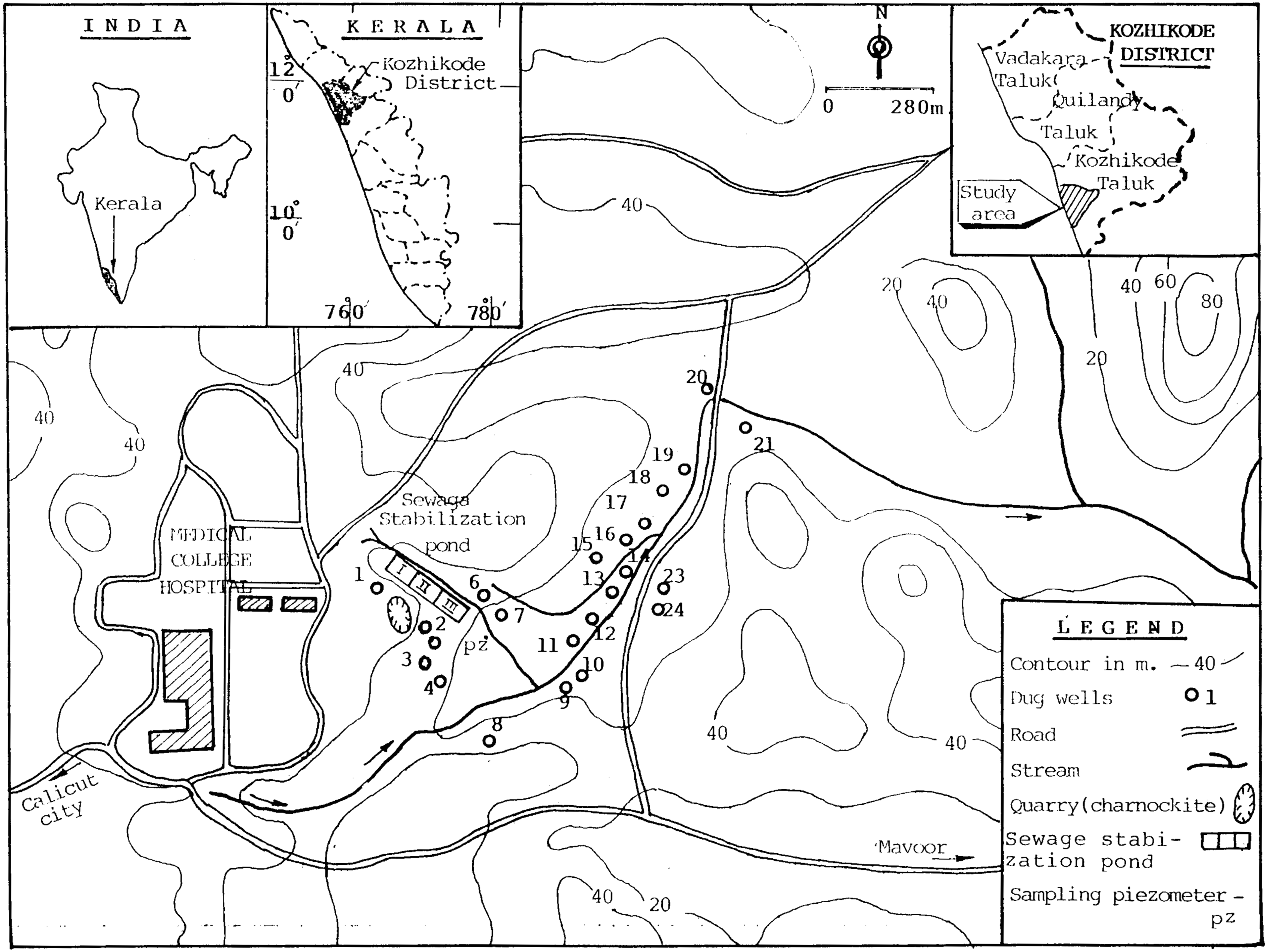


Fig.2 STUDY AREA SHOWING THE LOCATION OF OBSERVATION WELLS

exposed at a few places. The bedrock in the area is gneissic charnockites and exhibits medium grained granulitic texture. Observations made on the exposed bedrock show two sets of vertical and one set of oblique joints. The vertical joint planes trend N 85° E and N 15° W respectively. The mineral foliation in the rock trends NW-SE and has a dip of 80° E. The crystalline rocks are intensely deformed during more than one phase of orogeny. The overburden in the area is laterite formed by the weathering of crystalline basement rocks. The laterites are of residual and fairly matured type. The overburden thickness above the basement rocks varies from place to place owing to the irregular topography. On an average, it is about 9 m as observed from the existing open dug wells.

Physiographically, the study area forms part of the midland region of Kerala with elevation between 7 and 75 m above MSL. The terrain is undulating in nature with gently sloping residual hills separated by valley fills. The sewage stabilisation pond is situated on the slope of a hillock and is also at the side of a seasonal stream course.

Soil and groundwater

The soils in the study area are underlain by laterite formation which is separated from the basement rocks by a lithomarge zone.

The soils are red laterite type containing a high proportion of gravel. Clay content of the soil increases with depth. The soils in the upper valley portions are well-drained and are reddish brown in colour. In the middle and lower slopes, the water table is shallow, the drainage poor, and the soils dry out less frequently. This is reflected in increasing degree of hydration of iron. These soils have brownish yellow colour. The lithomarge clay in the valley portion has an average thickness of four metres which is much higher than the clay horizons in the slopes.

Groundwater in the area occurs under water table condition. Most of the dug wells extends up to the lithomargic clay zone. Some of the wells situated on the upper hill slopes have encountered hard rock at the bottom.

Sewage stabilization pond

A stabilization pond consists of a large shallow earthen basin in which waste water is retained long enough for natural purification processes to provide the necessary degree of treatment. In these ponds, at least part of the system must be aerobic to produce an acceptable effluent. Although some oxygen is provided by diffusion of air, the bulk of the oxygen in ponds is provided by photosynthesis.

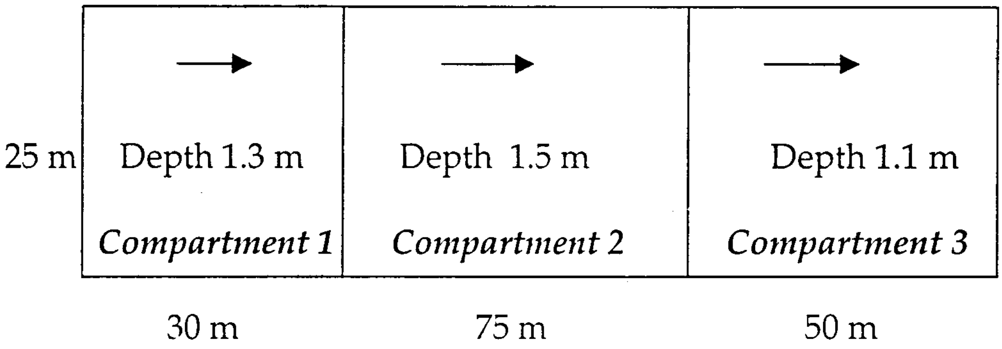
These ponds generally have a depth of 1.25 m with a loading of 100 kg BOD/acre /day, and have a retention time of around 20 days. The raw sewage is treated entirely by natural processes involving algae and bacteria. A special relationship exists between the bacteria and algae in the aerobic zone. Here, the bacteria use oxygen as an electron acceptor to oxidize the waste water organics to stable end products such as CO_2, NO_3 and PO_4. The algae in turn use these compounds as material source and, with sunlight as energy source, produce oxygen as an end product. The oxygen is then used by the bacteria, in a symbiotic relationship with the algae.

Description of the sewage stabilization pond of the study area

The sewage stabilization pond of the Kozhikode Medical College is located on the eastern side of the college campus (Plate I).

Plate :1 A view of the sewage stabilization pond

The system consists of earthen embankments with three compartments and the raw sewage is led into the first compartment , and after about 7 - 10 days of retention time, the stabilized waste is discharged into the nearby land from the third compartment. The description of the pond is given below:



EXPERIMENTAL PROCEDURE

Survey and water sampling

Twenty three private owned wells in the Medical College Campus were selected for observation. The total depth of the wells ranged from 6.9 to 10 m in the upper hill slope and from 1.3 to 5.6 m in the valley portions. Periodic monitoring of groundwater level was carried out in these wells. Levelling survey with respect to a bench mark was carried out for finding groundwater levels in the wells.

Based on the results, a groundwater contour map of the study area was prepared.

Water quality in the observation wells was assessed by drawing samples at bimonthly intervals from July, 1993 to June, 1995. Electrical conductivity, pH, and concentrations of various substances present in the samples were determined.

Depth-wise water sampling

A suction-type multilevel point sampler (Fig.3) was installed 25 m away from the sewage stabilization pond. For this, a bore hole was drilled at the site to a depth of 10 m. A casing pipe made of PVC, 110 mm OD with openings of 4 mm diameter made at regular intervals of 1 m was lowered. In order to draw water samples at different depths, nylon tubes of 4 mm OD were directly connected to the main pipe at the openings. The space between the soil and the outer surface of the casing pipe was filled with sand and the openings in the pipes were covered with nylon filter cloths to prevent the entry of sand and other solid soil particles into the nylon sampling tubes. Water samples drawn at a depth interval of 1 m from the multilevel point sampler were subjected to physico-chemical analyses to study the vertical movement of the pollutants.

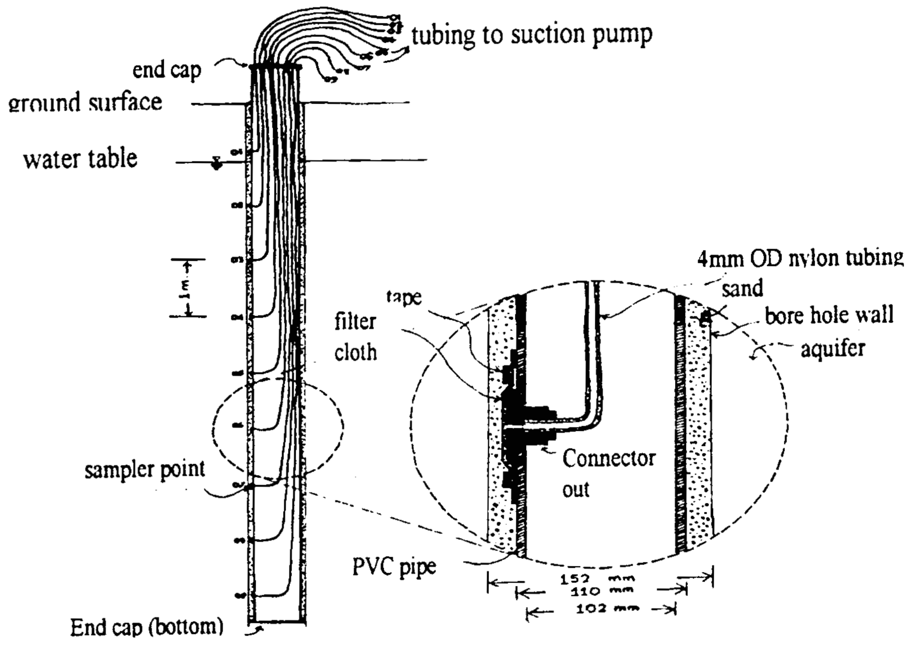


Fig. 3 Suction type multilevel point sampler

Analyses of sewage and soil

Sewage and soil analyses were carried out. The quantum of wastes entering the stabilization pond was found to be of the order of 50,000 litres/day. These comprised mostly of wastes of organic nature, human excreta, washings, residues, drugs and pharmaceuticals, and those of similar nature. Random samples of the influent sewage were collected at weekly intervals for ten weeks and analysed. Similarly, the effluent left out from the pond after stabilization, was also collected from the outlet and analysed. Analyses were carried out on a representative soil sample collected from the region, and on samples collected from different depths of the soil around the stabilization pond after air drying and sieving (2 mm). For estimating soil organic carbon, a 0.5 mm sieved soil sample was used (Jackson, 1958; Chopra and Kanwar, 1976).

Isotope technique

Isotope technique was used to fix the origin of nitrate present as a pollutant in the well water. Two stable isotopes of nitrogen occur naturally: ^{14}N, which has a natural abundance of 99.632 percent, and ^{15}N, which represents the balance. Although this value is essentially constant in atmospheric N_2 (Junk and Svec, 1958), it varies among other forms of nitrogen as a result of chemical and physical fractionation effects. These variations are commonly expressed as δ, deviations from a standard. For nitrogen, usually atmospheric N_2 is taken as standard.

$\delta^{15}N$ is an expression of difference between the $^{15}N/^{14}N$ of a sample and the $^{15}N/^{14}N$ of a standard (Kreitler, 1979). In isotopic terminology it is expressed as:

$$\delta^{15}N(‰) = \frac{(^{15}N/^{14}N)_{\text{Sample}} - (^{15}N/^{14}N)_{\text{Standard}}}{(^{15}N/^{14}N)_{\text{Standard}}} \text{ X } 1000$$

Transport of pollutants-Soil column experiment

Soil column experiment was conducted to compare movement of pollutant ions (chloride, nitrate and phosphate) through soil. A 1 m glass column, 9.1 cm in diameter, having a funnel shaped bottom was packed to field bulk density for a depth of 60 cm, with representative soil of the study area. A perforated plastic disc was provided at the bottom of the column over which the soil was filled. The funnel shaped portion was filled with gravel as a support to the disc which held the soil column. The column was fixed on a MS stand. The experimental set up is shown in Fig.4. Aqueous solutions of sodium chloride, potassium nitrate and sodium di-hydrogen phosphate (100 ppm of chloride, nitrate and phosphate) were used. The solutions were taken separately in a constant head device and dispensed over the soil surface.

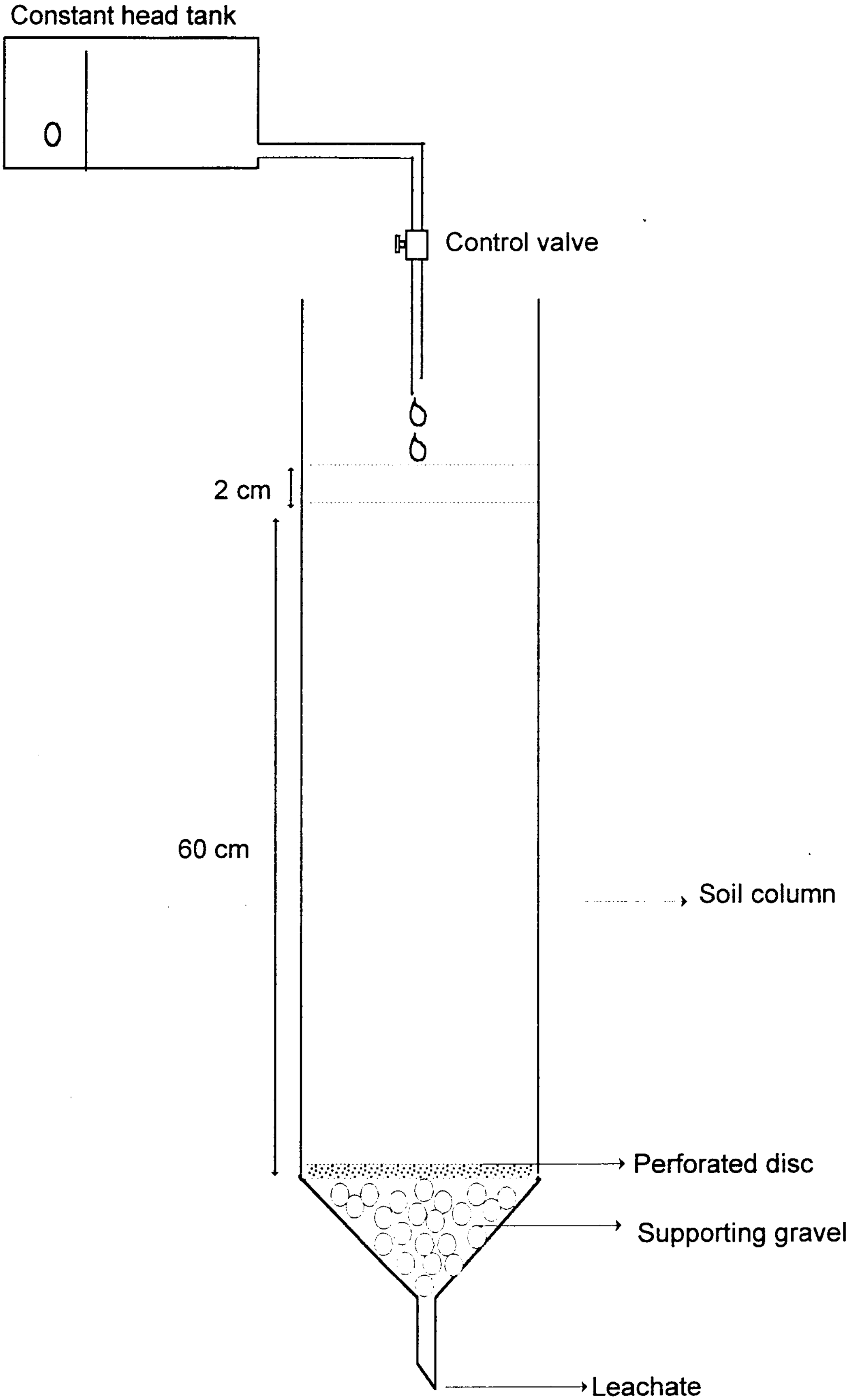


Fig. 4 Experimental setup for soil column studies

A depth of 2 cm was maintained over the soil surface in the column adjusting the flow rate from the constant head device. The solutions were leached through the three columns individually for each ion of interest and the leachate was collected at definite intervals till an uniform concentration of the particular ion was reached for few successive collections.

RESULTS AND DISCUSSION

Sewage analyses

Results of analysis of raw sewage is brought out in Table 2. These results indicate that the input falls under weak strength category of sewage, as per Peavy et al., 1985. Analytical data of sewage effluents let out after stabilization are presented in Table 3.

Table 2 Physico-chemical characteristics of the raw sewage

Source	Settleable Solids	BOD	pH	E C	Alk	Cl	SO_4	Free ammonia	NO_3	PO_4-P
Raw Sewage	4.5	127	6.9	662	156	43	28	7.5	ND	4.4

Table 3 Physico-chemical characteristics of stabilized effluent of the sewage stabilization pond

Period	pH	EC	Cl	SO_4	NO_3	PO_4-P	F	Ca	Mg	Fe
Pre monsoon 1995	6.6	550	55.7	10.2	204	5.4	0.7	13.8	6.7	0.5
Monsoon 1995	7.8	671	45.0	20.0	168	6.4	0.6	11.2	6.6	0.4

The chemistry of the stabilized effluents clearly indicates that except nitrate, all other species like chloride and sulphate are present at very low concentrations. In view of the high nitrate content, its transport from the effluents to the surrounding wells, especially those located in the close vicinity, appeared possible.

Soil analyses

Physico-chemical data of the representative soil of the region are presented in Table 4, and those of the soil samples collected from the area adjoining the sewage stabilization pond in Table 5.

Table 4 Physico-chemical data of representative soil of the study area

Sl. No	Depth (cm)	pH	OC %	N %	P (P_2O_5) %	K (K_2O) %	Sand %	Silt %	Clay %
1	0-30	6.5	0.52	0.05	0.05	0.16	43.5	19.6	31.7

Table 5 Physico-chemical data of soils surrounding the stabilization pond

Sl. No	Depth (cm)	pH	EC	OC %	N %	P (P_2O_5) %	K (K_2O) %	Sand %	Silt %	Clay %
1.	0-30	4.5	90	1.00	0.10	0.18	0.16	49.8	22.8	27.2
2.	30-60	4.5	68	0.83	0.09	0.16	0.17	44.8	22.0	30.6
3.	60-90	4.5	60	0.63	0.06	0.14	0.16	36.0	25.0	36.6
4.	90-120	4.4	82	0.61	0.07	0.14	0.16	37.3	23.4	37.2

From soil chemistry point of view, the soil at the site of investigation around the stabilization pond is fairly rich in organic carbon and plant nutrients like nitrogen and phosphorus as compared to representative soil. This indicates the influence of the sewage stabilization pond on the nutrient level of the surrounding soil.

Pattern of flow of groundwater

Based on the results of levelling survey, a contour map (Fig. 5) of the study area was prepared in order to understand clearly the flow pattern of groundwater in the region. It is observed that the general flow pattern of groundwater in the study area is from the west, north and south hill slopes with respect to the stabilization pond.

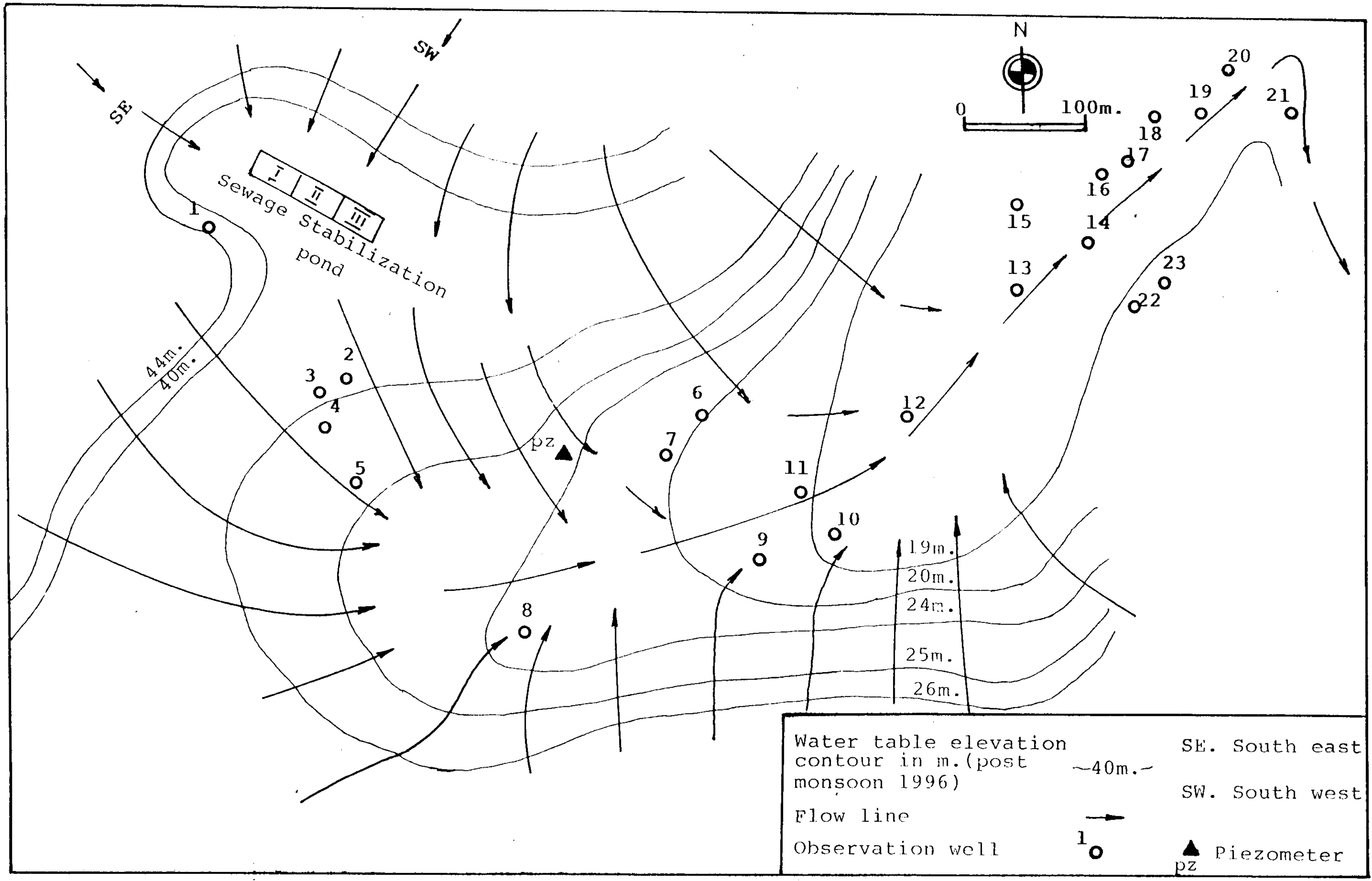


Fig.5 GROUNDWATER CONTOUR MAP OF THE STUDY AREA

It discharges into the central valley portion, and is then drained out of the area in the north eastern direction, which is the principal groundwater flow direction in the area. The sewage stabilization pond is situated on the upper valley slope in the west from where groundwater flow is towards south-west and south-east directions and finally drains out of the area towards north-east. The spacing between the groundwater table contours is wider in the lower region and closer along the slopes indicating that the hydraulic gradient of the aquifer in the valley region is less compared to that of the slopes.

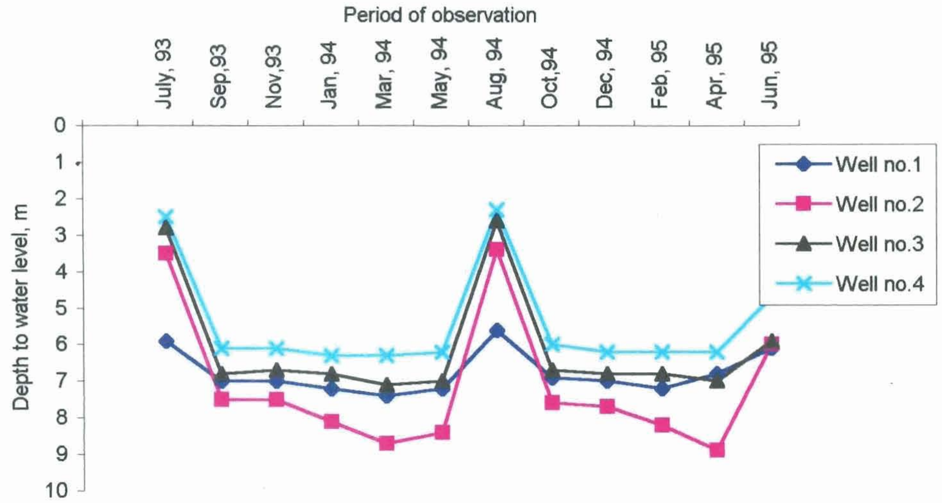
The following observations have been made with respect to fluctuation of water table in the wells :

1. The observation wells can be grouped into three types based on the physiographic set-up, as upper hill slopes, valley portion in the higher elevation and valley portions in the lower elevation.
2. The depth to water level varies from 2.3 to 8.9 m below ground level in the hill slopes, and between 0.2 to 3.7 m in the valley portions according to seasons (Table 6).

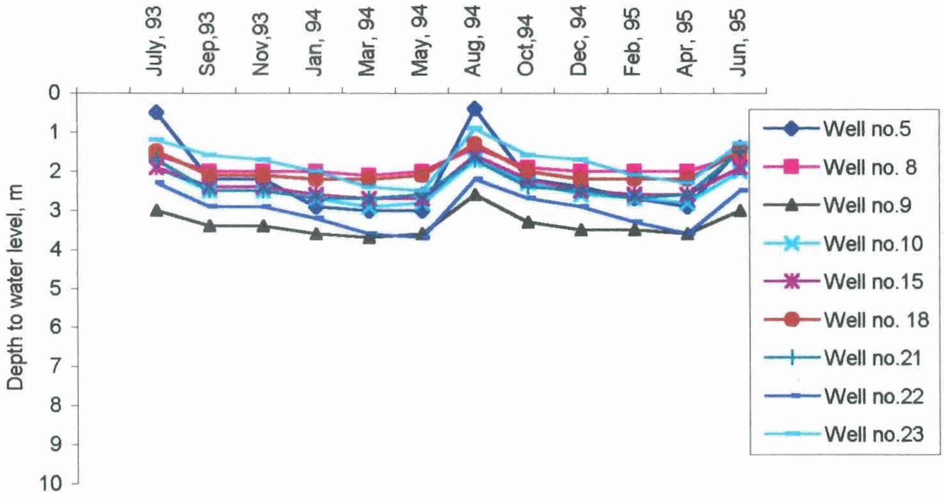
Table 6 Depth to groundwater in different physiographic regions in the study area

Group	Site description	Range of depth to groundwater level (BGL) in metres	
		Min	Max
I	Upper hill slopes	2.3 to 5.6	6.3 to 8.9
II	Valley portion in higher elevation	0.4 to 2.6	2.1 to 3.7
III	Valley portion in lower elevation	0.2 to 1.5	0.7 to 2.0

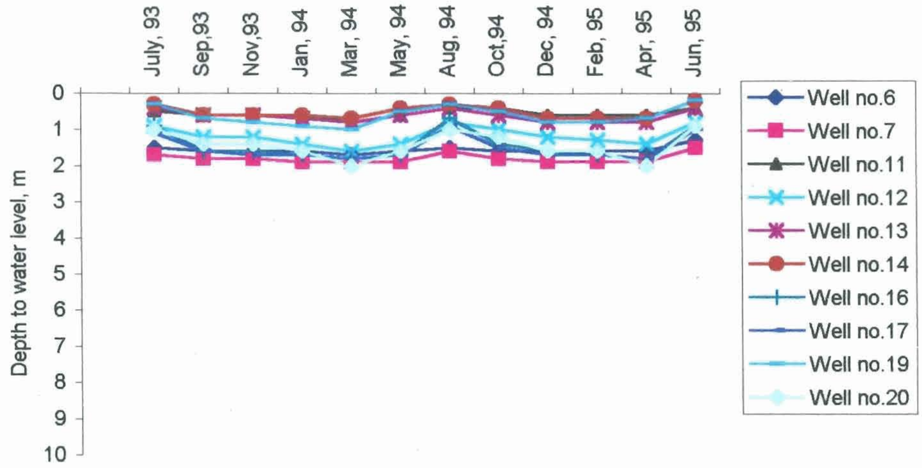
3. The minimum depth to groundwater was recorded during the highest rainfall months, viz. July-August period, and the maximum depth to groundwater was recorded during summer, viz. March-May period.
4. The water table fluctuation is directly influenced by rainfall intensity and duration.
5. The depth to water level rises very sharply during July-August and drops very sharply during September-October period. During pre-monsoon (Feb-May) and post-monsoon periods (Oct-Jan), the water table fluctuation is minimum and the same is reflected in the groundwater level hydrographs. Figure 6 (i to iii) depicts the groundwater hydrographs for the three different physiographic regions, namely the upper hill slopes, valley portions in the higher elevation, and valley portions in the lower elevation, respectively.



(i) Upper hill slopes



(ii) Valley portions in higher elevation



(iii) Valley portions in lower elevation

Fig. 6 Groundwater hydrographs

General quality status of well water

Significant variations in the level of different contaminants in water could be observed during the period of investigation. The minimum and maximum values of the physico-chemical data are presented in Table 7.

Table 7 General quality (ranges) of well water in the study area

Sl. No.	Characteristics	Range		Desirable limits	
		Minimum	Maximum	BIS	ICMR
1.	Electrical conductivity	40	600	--	--
2.	pH	5.3	7.6	6.5 to 8.5	7.0 to 8.5
3.	Total alkalinity (as $CaCO_3$)	2	99	200	--
4.	Total Hardness (as Ca CO_3)	8	97	300	300
5.	Chloride	8	81	250	200
6.	Sulphate	ND	18	200	200
7.	Nitrate	ND	50	45	20
8.	Phosphate	ND	0.18	--	--
9.	Fluoride	ND	ND	1.0	1.0
10.	Iron	ND	0.78	0.3	0.1
11.	Calcium	1.6	28	75	75
12.	Magnesium	0.5	10.9	--	50

Pre-monsoon, monsoon and post-monsoon seasons representing the months, February to May, June to September, and October to January respectively are the three main seasons of Kerala State. Considering the above periods, the overall quality of the well water between 1993 and 1995 was assessed and the results are summarised in Tables 8-14. Since all the observation wells are mainly used for domestic purpose, the compliance of each constituent with the desirable limit for potability as specified by Bureau of Indian Standards (BIS,1991) was examined.

It was observed that electrical conductivity (an indirect measure of total dissolved solids), total alkalinity, total hardness, chloride, sulphate, fluoride, calcium and magnesium are well within the desirable limit of potability. Though pH appears to be on the lower side, below 6.5, it is generally expected in groundwater samples, and may not pose any serious health hazard. Rain water and melted snow in non-urban and non-industrial areas have pH normally between 5 and 6.

Table 8 Physico-chemical data of the well water during monsoon period, 1993

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	5.4	138	6	11	22	1.2	13.4	ND	0.02	2.4	1.2
2	5.6	348	20	61	38	3.8	42.6	0.03	0.02	15.2	5.6
3	5.9	152	19	24	18	1.3	10.3	ND	0.02	5.2	2.7
4	5.6	131	8	24	21	0.4	6.9	ND	0.02	5.2	2.7
5	5.5	141	6	13	19	ND	14.4	ND	0.02	2.8	1.5
6	6.0	166	11	12	27	5.6	8.0	ND	0.07	2.8	3.9
7	5.8	176	15	18	25	6.9	9.9	ND	0.01	4.4	1.7
8	5.6	114	9	10	18	1.9	8.2	ND	0.01	2.0	1.2
9	5.6	104	9	11	18	0.5	7.2	0.01	0.01	2.4	1.2
10	5.4	114	12	13	16	1.5	7.4	ND	0.01	2.8	1.5
11	6.5	452	73	74	37	9.8	13.9	ND	0.04	22.0	4.6
12	6.5	269	59	47	25	3.9	4.0	0.01	0.20	14.4	2.7
13	6.3	210	40	61	17	4.3	3.7	ND	0.04	16.4	4.9
14	6.3	490	35	55	81	11.8	6.2	ND	0.11	14.8	4.4
15	5.3	86	10	13	14	3	1.2	ND	0.02	2.0	1.9
16	5.4	90	14	15	15	3.2	3.7	ND	0.01	2.8	1.9
17	5.4	117	13	16	16	2	3.2	ND	0.03	3.6	1.7
18	5.6	148	10	32	16	2	6.2	0.10	ND	10.0	1.7
19	6.7	193	50	53	13	10.8	1.5	0.02	0.14	16.0	3.2
20	6.2	169	27	32	17	4.5	3.2	ND	0.07	8.8	2.4
21	5.7	124	19	23	16	1.3	0.8	ND	0.09	5.2	2.4
22	5.4	93	10	9	15	0.9	3.7	ND	0.03	2.0	1.0
23	5.5	104	10	11	14	1.8	2.2	0.01	0.03	2.0	1.4

Table 9 Physico-chemical data of the well water during post-monsoon period , 1993

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	5.8	141	6	33	28	ND	18.1	0.02	ND	3.6	5.9
2	6.1	107	15	38	16	0.8	3.8	0.01	0.08	4.8	6.3
3	6.4	121	16	35	18	ND	5.0	0.01	ND	5.6	4.6
4	5.5	121	4	31	25	ND	12.6	0.01	ND	2.4	6.1
5	5.8	128	3	28	25	ND	29.3	0.01	0.08	4.8	3.9
6	5.5	141	9	30	30	1.3	17.1	0.02	0.09	2.4	5.8
7	5.7	221	11	29	39	2.8	19.6	0.02	ND	5.6	3.4
8	5.6	138	12	19	31	0.3	11.9	0.03	0.06	2.0	3.4
9	6.1	79	5	30	22	0.3	10.1	0.02	ND	2.0	6.1
10	6.2	83	6	25	20	2.8	12.0	0.03	0.05	4.8	3.2
11	6.7	376	64	43	28	3.3	8.4	0.03	0.34	12.0	3.2
12	6.6	266	44	67	27	3.5	10.5	0.03	0.15	11.6	7.8
13	6.7	186	32	57	20	4.5	4.4	0.02	0.23	11.6	6.8
14	6.4	595	37	89	67	5.3	4.4	0.03	0.54	17.6	10.9
15	6.0	86	10	26	17	0.9	5.5	0.03	0.01	2.0	3.9
16	5.9	83	12	28	18	1.8	3.5	0.03	0.12	2.8	3.4
17	6.0	133	16	29	17	4.3	3.1	0.02	0.20	3.6	4.8
18	6.0	107	15	32	20	0.8	14.2	0.04	ND	4.4	5.1
19	6.9	269	57	61	18	3.5	3.5	0.03	0.13	13.6	6.6
20	6.7	159	40	54	21	2.8	3.3	0.02	ND	10.0	7.1
21	6.2	138	28	48	20	2.0	2.7	0.03	0.09	7.2	7.6
22	6.0	74	17	26	22	0.3	8.7	0.03	0.08	3.2	3.2
23	5.9	112	12	33	17	0.8	4.4	0.03	0.02	2.4	6.6

Table 10 Physico-chemical data of the well water during pre-monsoon period, 1994

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	5.7	114	11	19	23	0.5	15.4	0.02	0.40	4.0	1.9
2	6.2	107	27	34	18	2.5	7.2	0.03	0.13	9.6	3.9
3	6.2	117	32	33	18	1.5	7.6	0.02	0.13	7.2	3.6
4	5.9	100	12	13	23	0.5	12.8	0.01	0.13	2.8	3.4
5	5.7	173	9	17	25	0.8	25.5	0.02	0.70	6.8	2.7
6	5.9	141	13	20	26	1.8	28.2	0.01	0.22	6.4	5.8
7	6.1	279	20	35	42	7.0	23.4	0.01	0.21	6.0	5.6
8	5.6	128	17	22	28	1.0	13.0	0.04	0.23	4.0	4.1
9	5.6	72	9	12	21	1.0	15.9	0.02	0.18	2.8	2.9
10	5.8	83	9	18	21	2.6	19.9	0.02	0.19	4.0	2.2
11	6.6	366	69	73	37	8.8	15.1	0.01	0.17	20.4	4.6
12	6.7	366	71	59	46	3.8	14.4	0.02	0.40	15.6	2.5
13	6.7	162	42	50	23	6.0	11.3	0.01	0.78	14.4	3.4
14	6.5	342	49	76	80	13.5	8.6	0.01	0.16	17.6	8.0
15	5.7	55	13	21	13	2.0	11.5	0.01	0.60	7.6	2.7
16	5.9	83	14	17	12	2.0	7.3	0.01	0.16	2.8	3.4
17	5.8	77	18	21	15	2.5	7.8	0.01	0.18	4.4	5.3
18	5.7	58	11	14	14	1.5	10.9	ND	0.64	16.4	2.4
19	6.8	283	71	85	20	9.5	13.3	0.03	0.28	18.8	10.9
20	6.6	162	38	47	24	8.8	12.2	0.02	0.24	9.2	6.3
21	6.4	124	27	36	21	2.8	19.5	0.01	0.18	5.6	4.1
22	5.9	45	10	23	16	0.8	10.2	0.01	0.56	4.4	8.5
23	5.9	40	11	23	16	1.0	7.6	0.03	0.16	8.4	4.9

Table 11 Physico-chemical data of the well water during monsoon period, 1994

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	6.1	152	14	16	18	1.0	13.5	0.01	0.18	6.4	4.9
2	5.7	552	26	74	48	14.0	39.2	0.01	0.10	17.6	7.3
3	5.6	131	20	32	14	4.0	7.5	0.01	0.10	4.8	4.9
4	5.5	166	22	18	22	ND	10.2	ND	0.21	5.6	1.0
5	5.5	145	16	18	20	1.0	24.4	0.01	0.14	6.4	0.5
6	5.6	186	24	28	22	10.0	10.0	0.01	0.18	6.4	2.9
7	5.6	159	18	26	18	10.0	10.2	0.01	ND	8.0	1.5
8	5.3	117	18	14	24	2.0	4.9	0.01	0.10	4.0	1.0
9	5.6	83	16	36	12	2.0	14.6	0.03	0.14	4.0	6.3
10	5.5	104	16	24	18	4.0	14.6	0.01	0.12	5.6	2.4
11	6.7	600	64	90	38	18.0	15.5	0.01	0.23	28.0	4.9
12	5.9	393	80	60	20	16.0	13.7	0.01	0.16	20.0	2.4
13	6.1	400	50	56	18	17.0	17.7	0.02	0.38	18.4	2.4
14	6.0	179	26	30	20	2.0	13.3	0.02	0.45	6.4	3.4
15	5.3	83	14	20	18	7.0	12.0	0.03	ND	7.2	0.5
16	5.5	138	24	26	16	4.0	12.8	0.02	0.11	5.6	2.9
17	5.3	179	22	30	20	7.0	15.1	ND	ND	7.2	2.9
18	5.4	104	20	20	16	11.0	15.1	0.01	0.01	4.8	1.9
19	5.8	235	48	50	14	3.0	2.7	0.03	0.12	19.2	0.5
20	5.7	173	28	40	12	5.0	6.6	0.01	0.01	11.2	2.9
21	5.6	131	26	24	16	1.0	4.4	0.01	ND	5.6	2.4
22	5.5	97	12	16	18	6.0	16.4	0.02	ND	5.6	4.9
23	5.6	90	12	14	16	3.0	10.2	0.01	ND	4.0	1.0

Table 12 Physico-chemical data of the well water during post-monsoon period, 1994

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	6.2	95	7	15	20	0.8	25.8	0.01	0.38	3.2	1.9
2	6.4	64	24	16	12	3.0	5.1	ND	0.23	4.8	1.0
3	6.5	85	24	28	20	1.3	10.6	0.01	0.24	6.4	2.7
4	6.4	71	7	12	20	1.0	23.0	0.01	0.45	4.4	1.5
5	6.0	90	5	17	18	0.5	38.3	0.02	0.17	4.4	1.5
6	5.7	95	6	18	23	3.0	28.6	0.02	0.22	3.6	2.2
7	6.6	130	12	20	30	6.5	9.0	0.01	0.14	4.8	1.9
8	6.2	67	6	11	18	6.0	13.7	0.03	0.31	4.8	1.2
9	6.6	55	7	12	16	0.8	18.8	0.03	0.09	2.0	1.7
10	6.9	65	9	13	17	1.8	13.5	0.02	0.07	2.4	1.7
11	6.9	235	74	68	20	4.0	4.9	0.01	0.24	18.8	5.1
12	7.2	160	40	45	27	1.9	8.1	ND	0.10	12.8	3.2
13	7.2	113	38	46	16	4.1	4.5	0.01	0.73	12.4	3.6
14	6.9	265	52	58	40	12.5	6.4	0.01	0.22	16.0	4.4
15	7.1	48	7	14	13	3.3	4.0	0.01	0.43	3.2	1.5
16	6.1	65	9	21	14	1.8	4.2	0.01	0.13	5.6	1.0
17	6.4	65	17	15	14	2.5	2.1	0.01	0.02	3.2	1.4
18	6.9	80	52	22	16	2.3	13.6	0.01	ND	4.8	1.2
19	7.6	140	60	65	11	5.0	5.0	0.01	0.16	16.0	2.4
20	6.6	95	30	32	13	4.3	3.5	0.01	0.02	9.2	2.2
21	6.8	73	24	24	15	2.3	ND	0.02	0.03	5.2	2.7
22	6.6	63	18	9	18	1.3	7.2	ND	0.05	4.4	1.2
23	6.8	48	19	14	8	1.0	5.0	0.04	0.09	3.6	1.7

Table 13 Physico-chemical data of the well water during pre-monsoon period, 1995

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	6.0	93	10	14	22	ND	12.2	0.01	0.05	2.6	1.7
2	6.3	80	24	20	13	1.0	5.5	0.01	0.05	4.6	1.9
3	6.6	105	32	30	19	ND	11.1	ND	0.10	6.8	3.2
4	5.9	90	7	12	23	ND	11.1	0.01	0.28	2.6	1.2
5	5.7	140	4	22	25	ND	50.0	0.01	0.12	5.0	2.3
6	5.7	110	5	14	21	0.8	27.3	0.01	0.03	2.8	1.7
7	6.0	175	6	26	37	3.3	25.8	ND	0.02	6.2	2.6
8	5.4	85	6	13	21	ND	21.0	0.06	0.03	2.4	1.6
9	5.5	60	8	10	20	ND	17.2	0.03	0.03	1.6	1.2
10	5.6	75	9	11	17	0.5	17.7	0.02	ND	1.8	1.3
11	6.7	230	47	34	34	1.0	8.4	0.06	0.14	8.4	2.9
12	6.8	250	52	56	35	2.5	24.4	ND	ND	14.2	4.9
13	6.7	135	39	45	23	2.5	6.6	ND	0.03	10.6	4.5
14	7.0	335	62	70	45	2.5	15.1	ND	0.27	16.0	7.2
15	6.0	45	10	8	12	1.0	4.7	0.18	ND	2.0	0.7
16	5.9	45	11	8	11	1.0	1.7	ND	0.03	1.6	1.0
17	6.2	50	15	17	14	1.3	1.1	0.01	0.03	2.4	2.3
18	5.9	60	10	13	12	0.5	6.4	ND	ND	2.8	1.3
19	7.3	235	99	97	11	3.0	3.9	0.02	0.08	18.2	3.7
20	6.3	100	33	39	14	4.5	2.4	ND	0.03	6.2	4.4
21	6.5	115	24	24	17	1.0	1.1	0.01	0.03	4.8	2.2
22	5.7	55	8	11	15	ND	10.1	ND	0.03	2.2	1.3
23	6.2	40	12	11	9	ND	8.2	0.01	0.05	1.6	2.2

Table 14 Physico-chemical data of the well water during monsoon period, 1995

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
1	6.2	114	8	14	19	0.5	19.5	0.03	0.24	2.8	1.7
2	6.7	128	18	31	17	2.0	14.2	0.04	ND	5.6	4.1
3	6.9	150	21	30	19	1.0	14.2	0.06	0.12	6.8	3.2
4	6.3	89	8	10	17	1.0	12.4	0.05	0.05	2.0	1.2
5	5.5	122	2	15	17	ND	17.7	0.03	0.26	3.2	1.7
6	5.8	150	6	18	24	2.0	8.9	0.05	ND	2.0	3.2
7	5.9	204	5	23	29	5.0	16.8	0.07	0.12	4.4	2.9
8	5.6	104	6	12	18	1.0	4.4	0.04	ND	1.6	1.9
9	6.8	92	9	13	16	0.5	9.7	0.08	ND	1.6	2.2
10	7.0	104	8	15	18	1.0	14.2	0.08	ND	2.4	2.2
11	7.1	244	40	51	29	4.0	8.9	0.08	ND	12.0	5.2
12	7.2	281	54	42	29	6.0	6.6	0.06	0.10	12.0	2.9
13	7.0	214	37	55	25	10.0	4.9	0.10	0.14	15.2	4.1
14	7.2	85	34	41	39	9.5	2.7	0.08	0.16	10.0	3.9
15	6.6	79	10	16	13	2.0	3.3	0.10	ND	2.8	1.9
16	6.4	79	13	15	12	2.0	2.5	0.07	ND	3.2	1.7
17	6.1	89	16	17	13	2.5	2.3	0.08	ND	4.0	1.7
18	6.2	85	18	14	14	1.5	6.6	0.06	0.18	2.8	1.7
19	7.4	162	54	39	8	6.0	0.7	0.05	0.28	9.2	3.9
20	7.0	128	24	32	14	7.5	2.3	0.10	0.17	8.0	2.9
21	6.4	73	18	20	19	2.5	1.4	0.08	0.22	3.2	2.9
22	6.3	172	9	13	15	ND	5.8	0.10	ND	2.0	1.5
23	7.1	79	25	8	17	ND	4.9	0.08	ND	2.4	0.5

In general, the major ionic species of dissolved inorganic carbon present in significant amount in groundwater is HCO_3^- resulting in the pH level of 5 to 6 (Freeze and Cherry, 1979) for non-saline water. Moreover, the soil has a capability to generate acidity and to consume much or all the available dissolved oxygen in the water that infiltrates it. Geo-chemically, the most important acid produced in the soil zone is H_2CO_3, formed from CO_2 and H_2O. The CO_2 is generated by the decay of organic matter and by respiration of plant roots (Freeze and Cherry, 1979). Thus, the lower level of pH is what is expected, and does not pose any health risk. Iron content in a few cases is a little higher than the desirable limit of 0.3 mg/l , but in all cases it is less than the maximum permissible limit of 1 mg/l, and hence potability is not affected. The level of phosphate is also very low and no limit has been specified in BIS for phosphate. The level of fluoride in all the samples is found to be below the detection limit. Among all the constituents, nitrate is present in appreciable quantity in many wells during the period of investigation

The minimum and maximum level of nitrate observed in each well during different seasons of each year of observations (1993, 1994 and 1995) and the average of all observations were compiled and presented in Table 15. In order to understand the variations in the level of nitrate, the coefficient of variation (C.V.) was also computed. The coefficient of variation reveals the homogeneity or otherwise between any two populations. When it is less for a particular population, that population is considered to be homogeneous and stable. In the present investigation, from the table it can be seen that some of the wells have significantly high coefficient of variation compared to the nearby wells. For example, if we consider the wells 1 and 2, the well No.2 has high C.V. of 100.2, revealing its heterogeneity; or in other words, the variation of nitrate with respect to seasons in this well is high compared to that of well No.1. Similarly, well No.17 (as compared to No. 18) and well No.21 (as compared to No.20) are subjected to high variation in the level of nitrate with respect to seasons. Location of these wells either close to the pond, or to the open drain carrying the liquid effluent, may be the reason for this observed high fluctuations.

Considering the potential health hazard of excess nitrate in drinking water, its extent, variation and spatial distribution in the wells were determined in detail, and are discussed in the following sections.

Table 15 Levels of nitrate concentration in the monitored observation wells

Well No.	Average Conc. of Nitrate, mg/l	Coefficient of variation (C.V.)	Minimum mg/l	Maximum mg/l
1	16.8	28.2	12.2	25.8
2	16.8	100.2	3.8	42.6
3	9.5	31.6	5.0	14.2
4	12.7	39.2	6.9	23.0
5	28.5	42.8	14.4	50.0
6	18.3	52.5	8.0	28.6
7	16.4	42.0	9.9	25.8
8	11.0	52.6	4.9	21.0
9	13.4	32.7	7.2	18.8
10	14.2	28.3	7.4	19.9
11	10.7	38.1	4.9	15.5
12	11.7	57.6	4.0	24.4
13	7.6	67.7	3.7	17.7
14	8.1	56.4	2.7	15.1
15	6.0	68.4	1.2	12.0
16	5.1	75.2	1.7	12.8
17	5.0	99.7	1.1	15.1
18	10.4	38.0	6.2	14.2
19	4.4	96.1	0.7	13.3
20	4.8	74.0	2.3	12.2
21	4.3	161.0	0.0	19.5
22	8.9	45.7	3.7	16.4
23	6.1	44.7	2.2	10.2

Nitrate, the major pollutant in the study area

Nitrate is a major groundwater pollutant from the point of view of general health, especially among infants (Comly, 1945; Joshi et al., 1989 ; Ozha and Jain, 1993). In India, it is estimated that 20 to 50% of the wells produce nitrate above 50 mg/l in areas of high population density, causing health hazard (Joshi et al., 1989). High concentrations of nitrate are common in village wells than in irrigated wells situated in the fields (Jacks and Sharma, 1983). Kerala State with groundwater as the major source of drinking water has about 250 open dug wells per sq. km, and a population density of around 750 persons per sq. km (CWRDM, 1995). Urban sewage, domestic wastes and agricultural residues are the major sources of pollution of groundwater in the region.

Record of season-wise variation in nitrate content of well water during the period of investigation reveals that the desirable limit (45 mg/l) of nitrate in potable water specified by BIS is exceeded only once. However, in view of the grave health hazards involved, the limit specified by ICMR (20 mg/l) is considered for discussion. The nitrate levels as compared to the desirable limits specified by both BIS and ICMR are shown in Fig.7(i) and 7(ii). It may be seen that if the limit of 20 mg/l is considered, more wells fall in this category indicating the prevalence of nitrate content in different seasons during the period of observation. Hence, the extent of nitrate pollution in different seasons was evaluated.

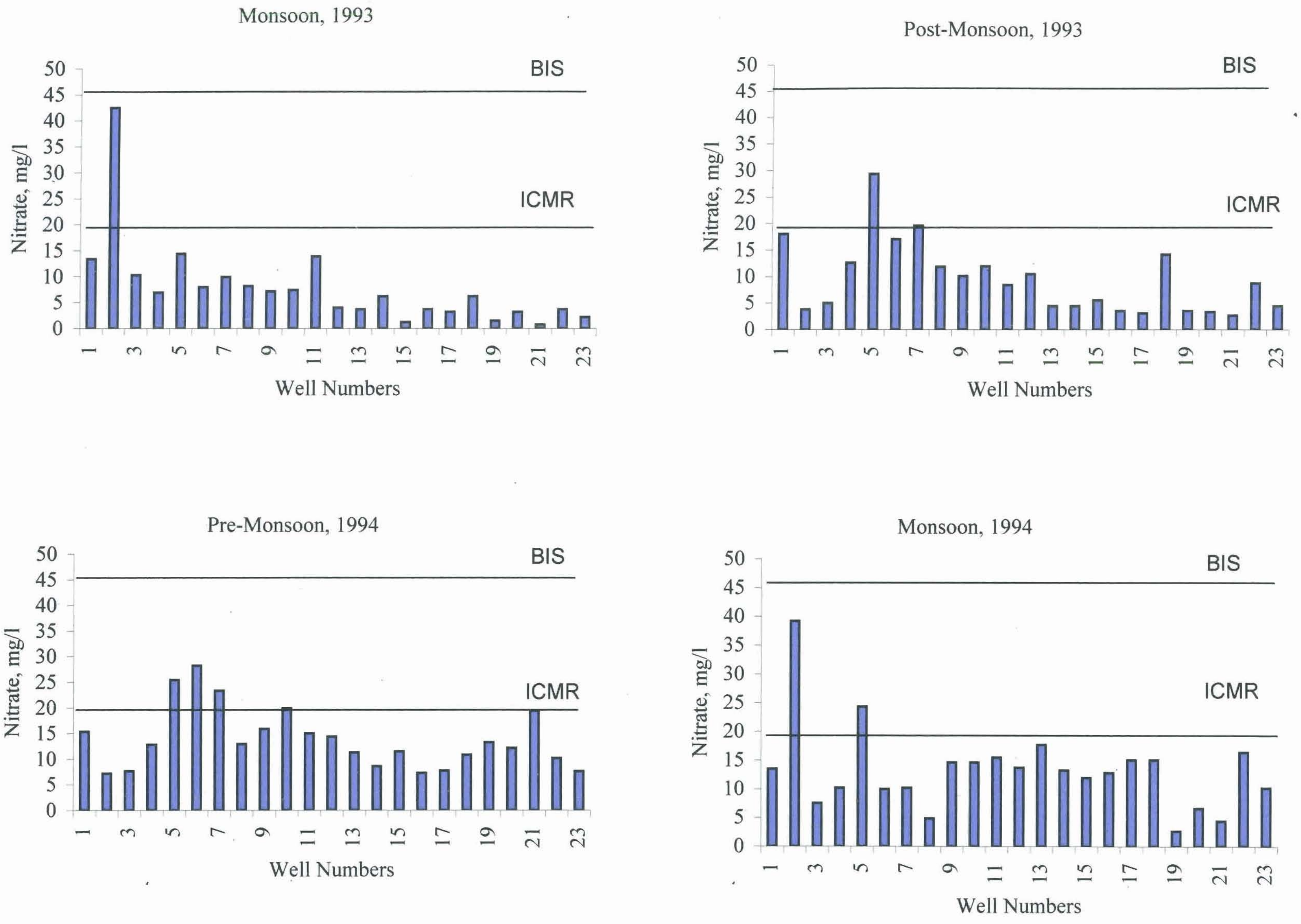


Fig. 7(i) Nitrate levels as compared to desirable limits for drinking water

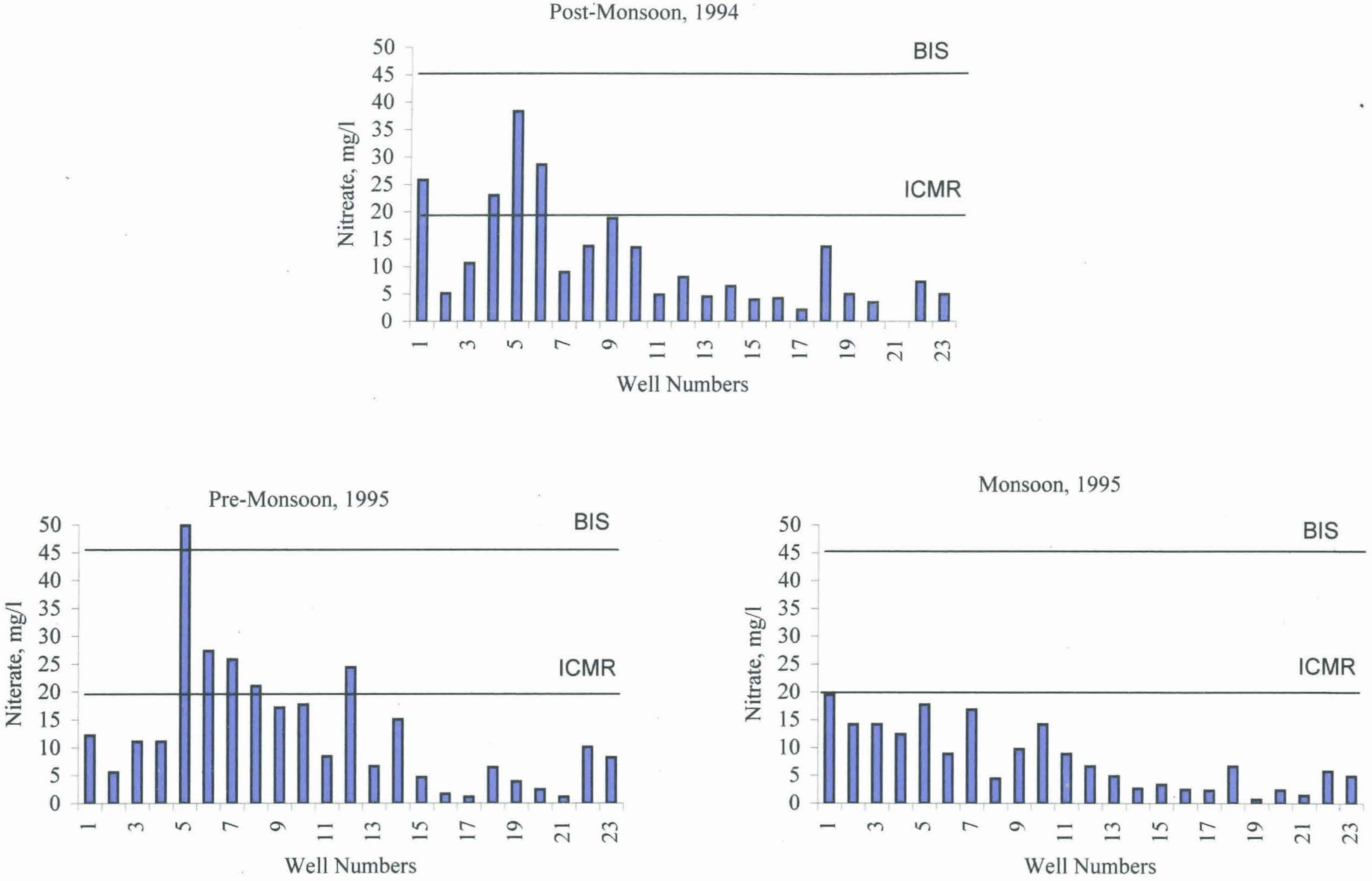


Fig. 7(ii) Nitrate levels as compared to desirable limits for drinking water

Extent of nitrate pollution and percentage distribution

The extent of pollution of wells due to nitrate at different levels, namely less than 10 mg/l, 10-20 mg/l and greater than 20 mg/l, during different seasons in each year of observation is presented in Fig.8. It was observed that during monsoon 1993, around 79% of wells had nitrate less than 10 mg/l level, 17 % of wells had of nitrate pollution during the year 1994. However, during the following year, i.e.1995, the percentage of wells having nitrate greater than 20 mg/l increased to 22% nitrate within the range of 10-20 mg/l and 4% had greater than 20 mg/l level. In the same year, during post-monsoon season, the percentage of wells having nitrate less than 10 mg/l had come down to 57% while the percentage falling within 10-20 mg/l had increased to 39%. In the next year, 1994, the number of wells with nitrate level within 10-20 mg/l had considerably increased during pre-monsoon and monsoon periods. Similarly, the percentage of wells having nitrate above 20 mg/l also had increased to 13%, 9% and 17% during pre-monsoon, monsoon and post-monsoon periods respectively. This indicates the higher level during pre-monsoon season, while no well was observed to contain nitrate at this level during monsoon of 1995.

In this context, if we compare the rain-fall pattern during these three years (Fig.9), the year 1994 had higher rainfall compared to the other two years, indicating the possibility of spread of nitrate to more wells and to higher concentrations.

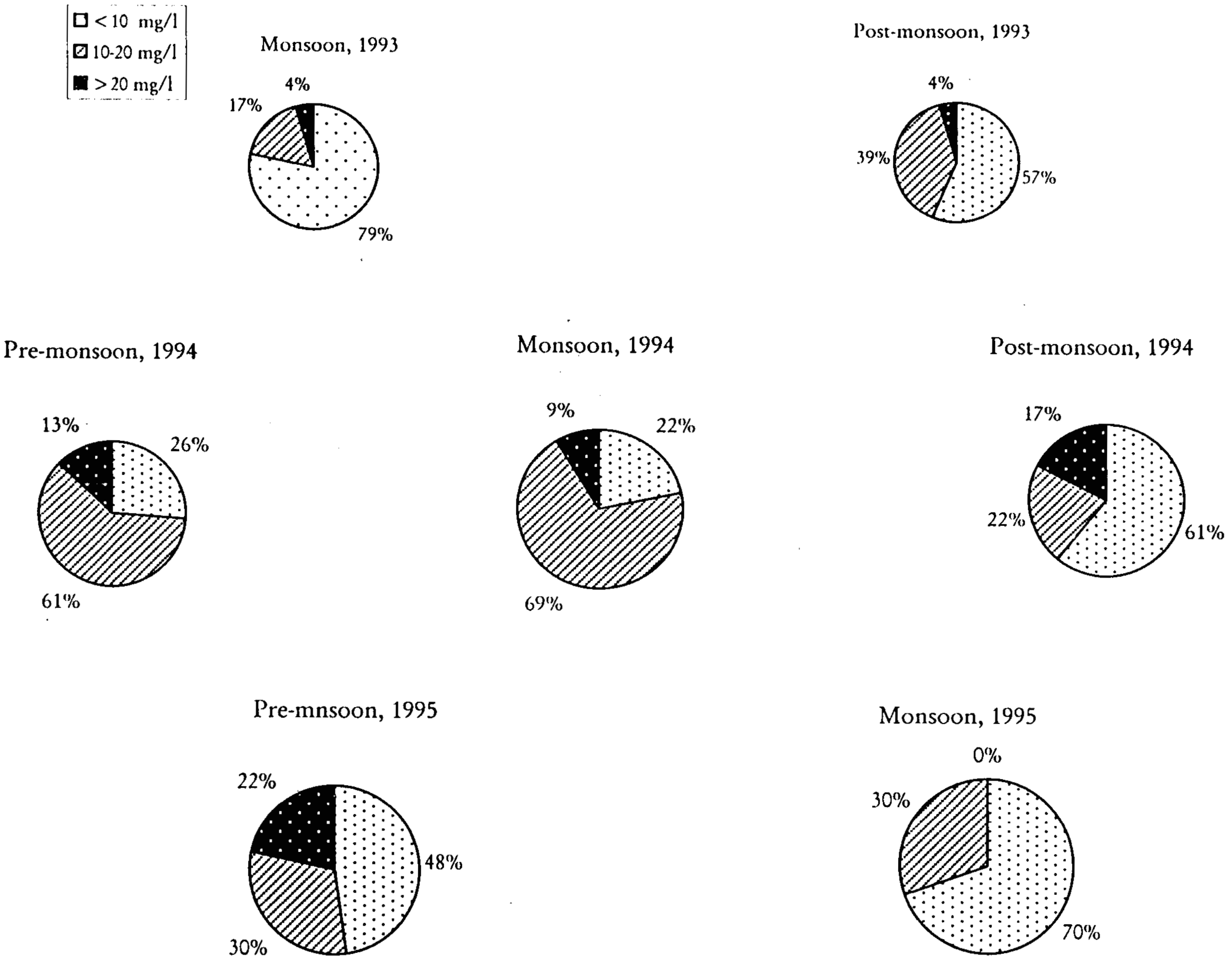


Fig. 8 Extent of nitrate pollution and percentage of affected wells

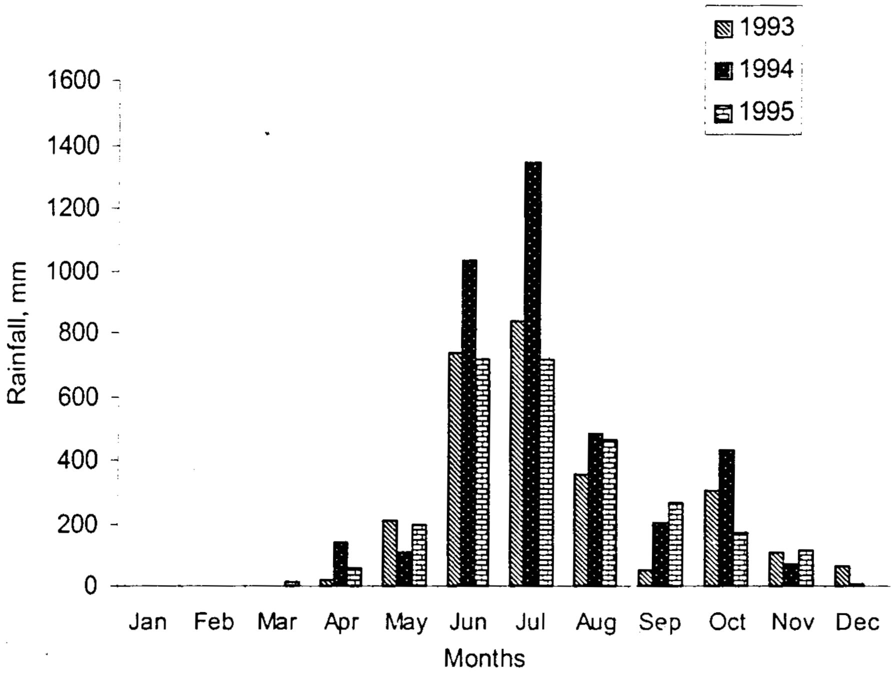
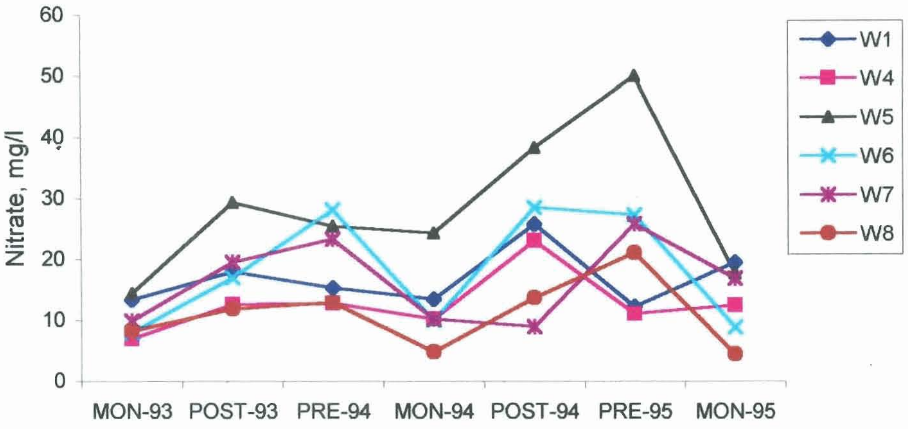


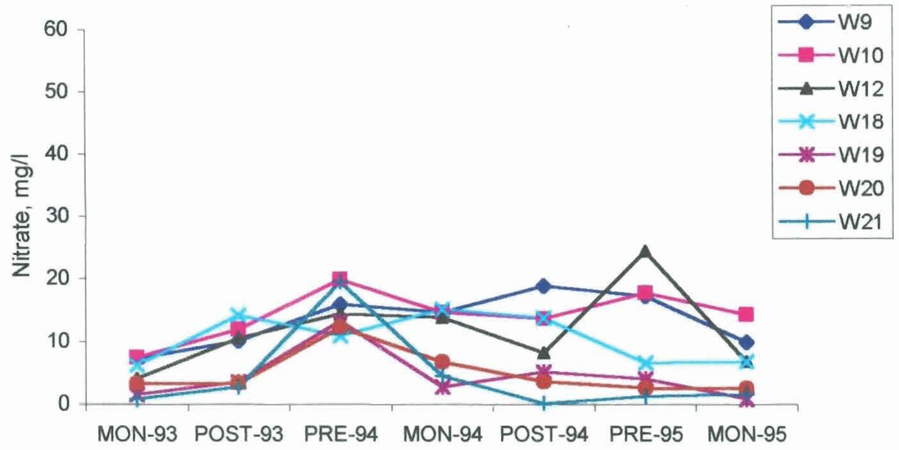
Fig. 9 Monthly rainfall during the period of study

Temporal trends and spatial distribution of nitrate in the wells

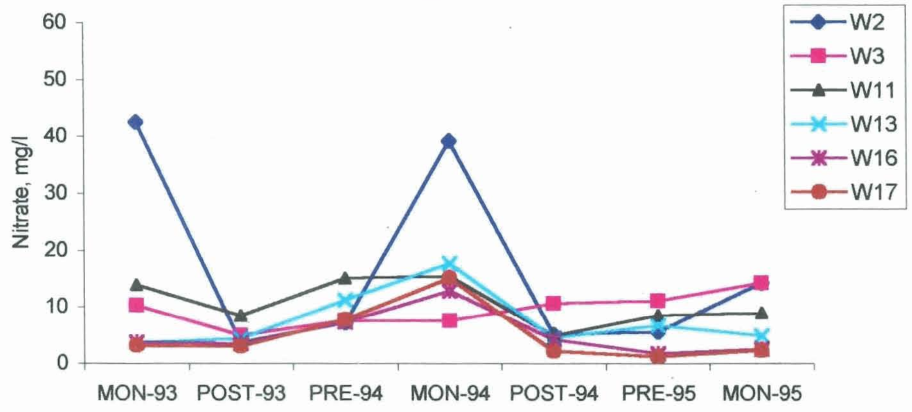
The temporal variation of nitrate content in the wells in each year of observation was analysed. In wells with Nos.1, 4, 5, 6, 7, 8, 9, 10, 12, 18, 19, 20 and 21, the level of nitrate was observed to be higher during pre-monsoon and post-monsoon periods as compared to monsoon period (Fig.10 i & ii). This pattern is expected since during monsoon, with increase in volume of well water, dilution of constituents should occur.


Higher level of nitrate during pre- and post- monsoon seasons

(i)



(ii)


Higher level of nitrate during monsoon season

(iii)

Fig.10 Temporal variation of nitrate during each season in different years (Wells of similar trends are grouped)

However, in wells bearing Nos. 2,3,11, 13, 16 and 17, the level of nitrate was high during monsoon period contrary to the general trend (Fig.10 iii). This phenomenon is uncommon and is attributed to an inflow of nitrate from external sources to these wells through soil infiltration along with the rain water during this season. Probably migration of nitrate to the wells from the stabilized sewage effluent could have occurred. Wells bearing Nos. 2 and 3 are situated close to the stabilization pond while wells with Nos. 11, 13, 16 and 17 are along the drain originating from the sides of the stabilization pond which carries the over-flow during monsoon. This could very well be the reason for the higher amount of nitrate in these wells.

The spatial trends in nitrate levels with respect to three physiographic regions were examined. The ranges of nitrate present in the wells in three seasons of each year of observation (1993-95) with respect to three regions, namely upper hill slopes (Group I), valley portions in higher elevation (Group II) and valley portion in lower elevation (Group III), in the study area are presented in Table 16.

It may be noted that the minimum observed levels of nitrate in the upper hill portion are higher compared to those of the lower valley portions. The wells located in the upper hill portion are closer to the stabilization pond than those in the lower valley regions.

Table 16 Ranges of nitrate concentration in three physiographic regions

Sl. No.	Period of observation	Level of nitrate , mg/l Group I		Group II		Group III	
		Min	Max	Min	Max	Min	Max
1.	Monsoon-93	6.9	42.6	0.8	14.4	1.5	13.9
2.	Post-monsoon-93	3.8	18.1	2.7	29.3	3.1	19.6
3.	Pre-monsoon-94	7.2	15.4	7.6	25.5	7.3	28.2
4.	Monsoon-94	7.5	39.2	4.4	24.4	2.7	17.7
5.	Post-monsoon-94	5.1	25.8	ND	38.3	2.1	28.6
6.	Pre-monsoon-95	5.5	12.2	1.1	50.0	1.1	27.3
7.	Monsoon-95	12.4	19.5	1.4	17.7	0.7	16.8

Among the wells in the upper hill region, well No.2, situated close to the pond was found to have significantly high level of nitrate especially during rainy months (July-August) in all the years (Fig. 10 iii), indicating regular supply of nitrate through infiltration from some external sources. It was reported that, in periods and areas of poor precipitation, when the water exchange between the first aquifer and the soil ceases, the nutrient lost from the ecosystem will accumulate in the soil. However, during rainy periods, these nutrients will be released through infiltration into the groundwater (Alfoldi Laszlo, 1983). A similar situation could be visualised in the present case, where nitrate, temporarily stored in soil, could have been leached through precipitation to this well, thus increasing its nitrate concentration.

Studies on the vertical movement of nitrate in the soil

In general, all water that infiltrates into natural groundwater flow systems passes through the soil zone. Pollutants once deposited on the surface of the soil move downward along with water as a medium. Though nitrogen present in sewage in the organic form do not directly pose any threat to groundwater, stabilization through enzyme catalysed biochemical transformation of these compounds into more water soluble inorganic forms like nitrites and nitrates can result in their fast movement. Under oxidising conditions nitrate is the stable form (Freeze and Cherry, 1979). Mobility of nitrate is enhanced by its solubility in water, and it moves easily with the medium. However, the influence of humic substances present in the soil, in fact, retards its downward movement by adsorption/chemisorption at the protonated sites of certain functional groups like $-NH_2$, -COOH and -OH. Hence, in terms of quantity, nitrate level is always observed to be more in the surface or in the immediate subsurface layers of the soil. In the deeper aquifer, it is expected to be very low. This is what is observed in the samples collected from the multilevel point sampler at different depths. However, in the areas where the soils are clayey and devoid of organic matter and humus, more and more nitrate can be expected in the groundwater. Compared to nitrate, other ions like chloride and sulphate do not show such significant decrease with depth (Fig.11). They remain almost at the same level as observed from the piezometer samples. Nitrate is found to be high in the surface layers.

Figure 12 brings out the temporal trends of nitrate distribution at different depths as indicated by analytical data of the samples collected at different periods of observation. High variation of nitrate in top layers (up to 6 m depth) especially during monsoon (July-August) is quite conspicuous, supporting the migration of nitrate from some external sources through infiltration during precipitation. During December, which is a dry period, the depth-wise variation of nitrate is observed to be minimal.

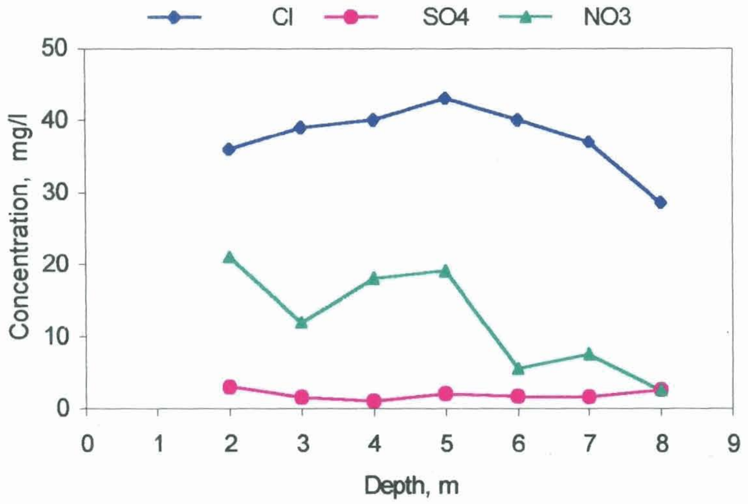


Fig .11 Depth-wise distribution of nitrate as compared to chloride and sulphate in the site of investigation during 1995

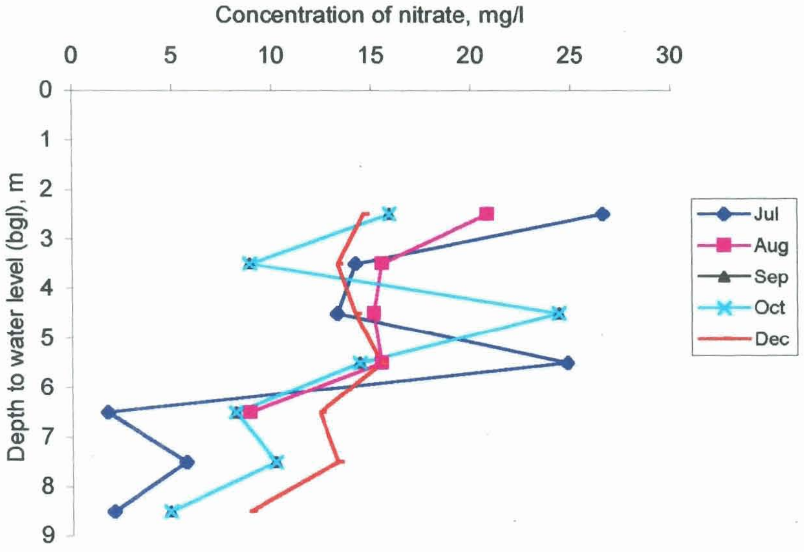


Fig. 12 Temporal trends of nitrate at different depths in piezometer

Wells with very shallow depth and pollution risk

Wells with Nos. 11, 12, 13, 14 and 19 were found to have electrical conductivity of the order of 300 micromhos/cm as compared to the normally observed level of 100-150 micromhos/cm in the region. These were noted especially during monsoon period when lower levels were expected, due to dilution. This feature is attributed to the fact that these wells are very shallow with depth varying between 1.3 and 3.5 m. During monsoon, the water rises almost to the ground, bringing well water level on par with surface water (Table 17), thereby increasing susceptibility to contamination. Moreover, as these wells are located adjacent to a natural drain which collects liquid wastes from nearby hotels, along with storm run-off, influence of these wastes could also enhance the deterioration of the water quality.

Table 17 Wells with high risk of pollution

Sl. No.	Well No.	Total depth of the well (m)	Depth to water level (BGL) during monsoon (m)
1.	11	2.5	0.4
2.	12	3.5	0.8
3.	13	1.3	0.4
4.	14	1.4	0.3
5.	19	2.3	0.2

Interrelationship of nitrate with other minor pollutants

Presence of nitrate in groundwater and its relationship with other contaminants present have been studied in Medchal block of Andhra Pradesh. Nitrate concentration was found to increase with increase in hardness, chloride, sulphate and total dissolved solids, while decrease in pH and alkalinity ; fluoride and water table did not lead to any significant effect on nitrate content (Vijay Kumar et al., 1992). The study by Ozha et al., (1993) revealed that nitrate concentration increased with increase in total hardness, calcium and magnesium, but decreased with increase in water table. In the present study, the overall mean of nitrate content in the wells was found to increase with increase in electrical conductivity, total hardness, chloride and iron content. However, nitrate content showed decrease with increase in pH, alkalinity, sulphate and phosphate.

According to Ozha et al., (1993), nitrate concentration decreases with increase in water table indicting that when the level of water increases the nitrate present in the system gets diluted, which is a common phenomenon. In the present investigation, it was observed that the groundwater table fluctuation is directly influenced by the rainfall pattern as referred in section on groundwater flow (page 47). In this context, the relationship between the concentration of nitrate and depth to water level in each well was explored, considering every observation. The correlation coefficient(r) indicated both positive and negative relationships (Table 18a and 18b).

In well Nos.1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 18, 20, 21, 22 and 23, as the depth to water level from the ground increased (ie. water table decreased), the level of nitrate increased. In well Nos.2, 3, 13, 16, 17 and 19, as the depth to water level decreases (ie. water table increases), the level of nitrate increases. In order to understand the significance of the observed correlation coefficient, the 't' test for testing the significance of an observed correlation coefficient (Indrani Gupta et al., 1997) was calculated. The test indicated that only Well no. 2 and 5 are best correlated at 95% confidence limit.

In well No.2, when the depth to water level decreases (i.e. Water table increases), the concentration of nitrate increases, which indicates that nitrate gets transported into this well during rainy seasons. In well No.5, the reverse is the trend. Figure 13 displays the trend of nitrate with respect of depth to water level of wells 2 & 5. However, a similar correlation analysis with pH did not give any significant relationship.

Table 18(a) Correlation between nitrate and depth to water level (BGL)

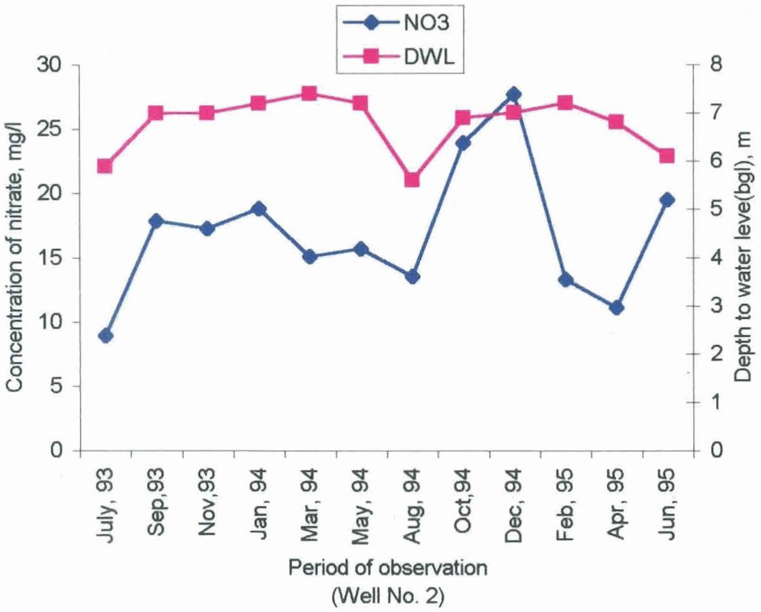
Period	Well Number 01		Well Number 02		Well Number 03		Well Number 04		Well Number 05		Well Number 06	
	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL
July, 93	8.9	5.9	83.1	3.5	15.6	2.8	5.4	2.5	9.9	0.5	3.7	1.5
Sep,93	17.9	7	2.0	7.5	5.0	6.8	8.4	6.1	18.9	2.2	12.2	1.6
Nov,93	17.3	7	3.1	7.5	4.7	6.7	11.1	6.1	24.4	2.2	14.8	1.6
Jan, 94	18.8	7.2	4.4	8.1	5.3	6.8	14.2	6.3	34.3	2.9	19.3	1.6
Mar, 94	15.1	7.4	6.6	8.7	11.5	7.1	17.7	6.3	24.4	3	21.3	1.7
May, 94	15.7	7.2	7.8	8.4	3.8	7	8.0	6.2	26.6	3	35.2	1.6
Aug, 94	13.5	5.6	39.2	3.4	7.5	2.6	10.2	2.3	24.4	0.4	10.0	1.5
Oct,94	23.9	6.9	6.6	7.6	11.1	6.7	26.6	6	34.6	2.2	28.4	1.6
Dec, 94	27.7	7	3.5	7.7	10.2	6.8	19.5	6.2	42.1	2.4	28.8	1.6
Feb, 95	13.3	7.2	6.6	8.2	13.3	6.8	11.1	6.2	44.3	2.7	23.6	1.6
Apr, 95	11.1	6.8	4.4	8.9	8.9	7	11.1	6.2	55.4	2.9	31.0	1.6
Jun, 95	19.5	6.1	14.2	6	14.2	5.9	12.4	4.7	17.7	1.4	8.9	1.3
r	0.31		-0.86		-0.32		0.40		0.59		0.56	

Period	Well Number 07		Well Number 08		Well Number 09		Well Number 10		Well Number 11		Well Number 12	
	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL
July, 93	8.4	1.7	9.9	1.6	5.9	3	5.9	1.9	14.9	0.5	6.5	0.9
Sep,93	11.4	1.8	6.5	2	8.4	3.4	8.9	2.5	12.9	0.6	1.5	1.2
Nov,93	11.7	1.8	6.9	2	6.9	3.4	9.3	2.5	4.4	0.6	10.3	1.2
Jan, 94	27.5	1.9	16.8	2	13.3	3.6	14.6	2.7	12.4	0.6	10.6	1.4
Mar, 94	14.6	1.9	6.6	2.1	14.2	3.7	16.8	2.9	8.9	0.8	8.0	1.6
May, 94	32.1	1.9	19.3	2	17.7	3.6	23.0	2.8	21.3	0.6	20.8	1.4
Aug, 94	10.2	1.6	4.9	1.4	14.6	2.6	14.6	1.7	15.5	0.4	13.7	0.8
Oct,94	14.4	1.8	12.4	1.9	22.2	3.3	11.5	2.3	2.7	0.4	0.7	1
Dec, 94	3.5	1.9	15.1	2	15.5	3.5	15.5	2.6	7.1	0.6	15.5	1.2
Feb, 95	11.8	1.9	26.6	2	16.6	3.5	17.7	2.7	11.5	0.6	26.6	1.3
Apr, 95	39.9	1.9	15.5	2	17.7	3.6	17.7	2.8	5.3	0.6	22.2	1.4
Jun, 95	16.8	1.5	4.4	1.6	9.7	3	14.2	2	8.9	0.4	6.6	0.8
r	0.32		0.46		0.29		0.54		0.02		0.38	

Table 18(b) Correlation between nitrate and depth to water level (BGL)

Period	Well Number 13		Well Number 14		Well Number 15		Well Number 16		Well Number 17		Well Number 18	
	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL
July, 93	5.9	0.4	7.9	0.3	0.0	1.9	5.9	0.9	5.4	1.1	2.0	1.5
Sep,93	1.5	0.6	4.5	0.6	2.5	2.4	1.5	1.6	1.0	1.6	10.4	2.1
Nov,93	4.4	0.6	4.4	0.6	4.4	2.4	2.7	1.6	1.8	1.7	15.9	2.1
Jan, 94	4.4	0.7	4.4	0.6	6.6	2.6	4.4	1.7	4.4	1.7	12.4	2.2
Mar, 94	6.2	0.8	6.6	0.7	12.4	2.7	5.8	1.8	6.6	1.8	9.7	2.2
May, 94	16.4	0.6	10.6	0.4	10.6	2.7	8.9	1.7	8.9	1.7	12.0	2.1
Aug, 94	17.7	0.4	13.3	0.3	12.0	1.6	12.8	0.7	15.1	0.9	15.1	1.3
Oct,94	2.5	0.6	1.3	0.4	0.6	2.2	5.3	1.4	2.5	1.5	0.7	2
Dec, 94	6.6	0.8	11.5	0.7	7.3	2.5	3.1	1.6	1.8	1.7	26.6	2.2
Feb, 95	8.0	0.8	9.7	0.7	5.8	2.6	2.2	1.7	1.8	1.7	9.7	2.2
Apr, 95	5.3	0.8	20.4	0.7	3.5	2.6	1.1	1.8	0.4	1.8	3.1	2.2
Jun, 95	4.9	0.4	2.7	0.2	3.3	1.9	2.5	0.9	2.3	1	6.6	1.5
r	-0.24		0.29		0.21		-0.49		-0.48		0.21	

Period	Well Number 19		Well Number 20		Well Number 21		Well Number 22		Well Number 23	
	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL	NO_3	DWL
July, 93	2.0	0.3	5.0	1	1.5	1.7	2.5	2.3	4.4	1.2
Sep,93	1.0	0.7	1.5	1.4	0.0	2.5	5.0	2.9	0.0	1.6
Nov,93	2.7	0.8	2.2	1.4	0.9	2.5	5.5	2.9	4.4	1.7
Jan, 94	4.4	0.9	4.4	1.6	4.4	2.7	12.0	3.2	4.4	2
Mar, 94	0.0	1	2.2	2	17.7	2.7	7.5	3.6	3.3	2.4
May, 94	26.6	0.5	22.2	1.6	21.3	2.6	12.8	3.7	12.0	2.5
Aug, 94	2.7	0.3	6.6	1	4.4	1.7	16.4	2.2	10.2	0.9
Oct,94	7.3	0.5	1.6	1.2	0.0	2.4	2.4	2.7	3.1	1.6
Dec, 94	2.7	0.8	5.3	1.6	0.0	2.5	12.0	2.9	6.9	1.7
Feb, 95	5.5	0.8	2.7	1.6	1.8	2.7	14.2	3.3	3.5	2.1
Apr, 95	2.2	0.7	2.2	2	0.4	2.6	6.0	3.6	12.8	2.3
Jun, 95	0.7	0.2	2.3	0.9	1.4	1.5	5.8	2.5	4.9	1.3
r	-0.13		0.04		0.27		0.18		0.21	



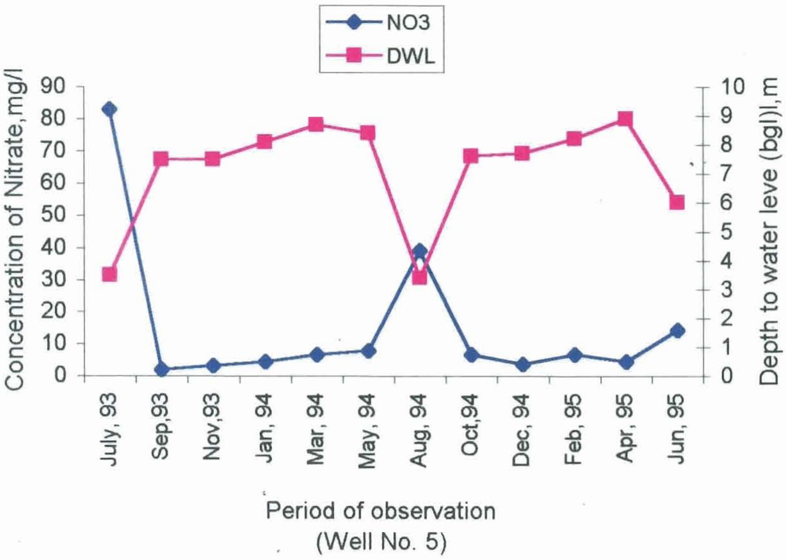


Fig.13 Variation of nitrate with respect to depth to water level in the wells

Isotopic investigation for discrimination of source of nitrate

Pollutants like nitrate, sulphate and phosphate originate from more than one source, thus necessitating discrimination of actual source from among potential sources. Nitrate, the major pollutant in the observation wells, can originate, apart form sewage effluents, from a wide variety of materials like soil organic nitrogen, cattle manure, animal feed lots, synthetic fertilizers etc. All circumstantial evidences strongly pointed to sewage effluents as the possible source of origin of excess nitrate in well water. For concrete evidence, isotopic technique based on environmental stable isotope was used as a foolproof method. Isotope ratic of nitrogen, $^{15}N/^{14}N$, was determined for the purpose.

In recent years, many researchers have had success in identifying the sources of nitrates in groundwater by studying the ratio of ^{15}N and ^{14}N (Kreitler et al., 1978; Gormly and Spalding, 1979). Isotopic composition of nitrogen compounds is controlled, in part, by biological processes, except nitrification; the lighter isotope, ^{14}N is used preferentially, resulting in enrichment of ^{15}N (Ritter et al., 1986). A more positive value of $\delta^{15}N$ indicates enrichment of ^{15}N and conversely, a more negative value indicates depletion of the ^{15}N isotope.

The $\delta^{15}N$ values of nitrate are good indicators of origin of nitrates from different sources like inorganic fertilizers, organic manure, human and animal wastes etc. Values of $\delta^{15}N$ are reported to be indicative of nitrate formed by nitrification of mineral fertilizers (range - 4 to +2‰) or manure (range +6 to +16‰). The artificial fertilizers normally have a $\delta^{15}N$ values ranging between 0 and 5‰ (Deseo et al., 1996). According to Aravena et al., (1993) $\delta^{15}N$ values of commercial fertilizers vary between -2 and +4‰.

In the study area, no sample has $\delta^{15}N$ value less than 10 ‰ indicating the absence of nitrate arising from inorganic fertilizers. The $\delta^{15}N$ values in the sample are in the range of 11.8 to 27.4‰ which are indicative of the nitrate originating from human and animal wastes. According to Flipse and Bonner (1985), $\delta^{15}N$ of nitrates of the soils from animal feed-lots ranges from 10 to 20, and in shallow aquifers the $\delta^{15}N$ values range between 12.1 and 21.3‰. Further, according to Freyer and Aly (1974), $\delta^{15}N$ of nitrates originated from human and animal wastes varies between 10 and 20‰ .

The $\delta^{15}N$ values of nitrate of water samples of a few selected wells are given in Table 19. The $\delta^{15}N$ values of nitrate of water samples of the wells do not indicate contamination due to fertilizers or soil organic nitrogen.

Table 19 Nitrate content and $\delta^{15}N$ values of well water samples

Sl. No.	Well No.	Nitrate (mg/l)	$\delta^{15}N$ ‰
1	1	5.1	27.3
2	2	10.6	15.1
3	3	38.3	12.8
4	5	8.8	27.0
5	6	9.0	26.4
6	7	18.8	14.2
7	11	25.8	12.8
8	12	23.0	11.8

The data clearly indicate that nitrate observed in these wells has had its origin from the organic matter like human and animal wastes. In the present context, the pollutant has originated from the sewage stabilization pond, as well as from the leach pits/cattle sheds attached to the individual households. Thus, the $\delta^{15}N$ values of nitrate observed in the wells pin-point its source.

Identification of actual origin of pollutants and their mode of migration in the terrestrial environment are essential for devising proper strategy for pollution abatement.

Transport of pollutants in the soil environment

Pollutants arising from various pollution sources pass through different geologic formations as they migrate through soil to the sub-surface aquatic environment. Their transport to groundwater is complicated by geo-chemical reactions as well as by hydrologic dispersion phenomena. Information on the fate, transformation and transport of pollutants within the soil/water environment is important to understand the interaction of the pollutants with the medium. This will not only give a qualitative measure of the pollutant in question, but also provide quantitative information on the movement with respect to time and area of spreading. By means of laboratory soil column experiments, breakthrough (BT) curves are constructed from which quantitative information on the rate of pollutant movement and mechanism of interaction with the soil particles can be predicted.

Results of relative concentration (C/C_0) at different time intervals in the column experiments are presented in Table 20.

Table 20 Soil column experiment - results of C/C_0 at different time interval {C_0 (Nitrate, Chloride, Phosphate) : 100 mg/l each}

Sl. No.	Time interval min	C/C_0 for nitrate	C/C_0 for chloride	C/C_0 for phosphate
1	0	0	0	0
2	60	0	0	0
3	120	0.037	0	0
4	180	0.142	0	0
5	240	0.345	0	0
6	300	0.652	0	0
7	360	0.832	0.062	0
8	420	0.940	0.213	0.006
9	480	0.990	0.415	0.008
10	540	0.990	0.599	0.013
11	600	0.990	0.686	0.02
12	660	0.990	0.757	0.025
13	720	0.990	0.825	0.025
14	780	-	0.899	0.025
15	840	-	0.932	0.025
16	900	-	0.932	0.025
17	960	-	0.932	0.025

The BT curves developed for nitrate, chloride and phosphate are presented in Fig. 14. Whereas in the case of nitrate and chloride, the curves are perfectly S-shaped, the curve for phosphate is almost parallel to X-axis. This indicate that nitrate and chloride have little interaction with the soil particles. However, it is evident from the curve of phosphate that it is rendered immobile in the soil column, presumably through formation of insoluble aluminium and iron phosphates.

The hydrodynamic dispersion coefficient (D_L), which is generally determined by using one dimensional dispersion equations gives an idea of the spread of any solute in porous media (Jong Tae Jeong and Kun Jai Kee, 1992). Two commonly used methods for determining the values of the dispersion coefficients from the experimental data are those of Fried and Combarnous (1971) and of Kirkham and Powers (1972).

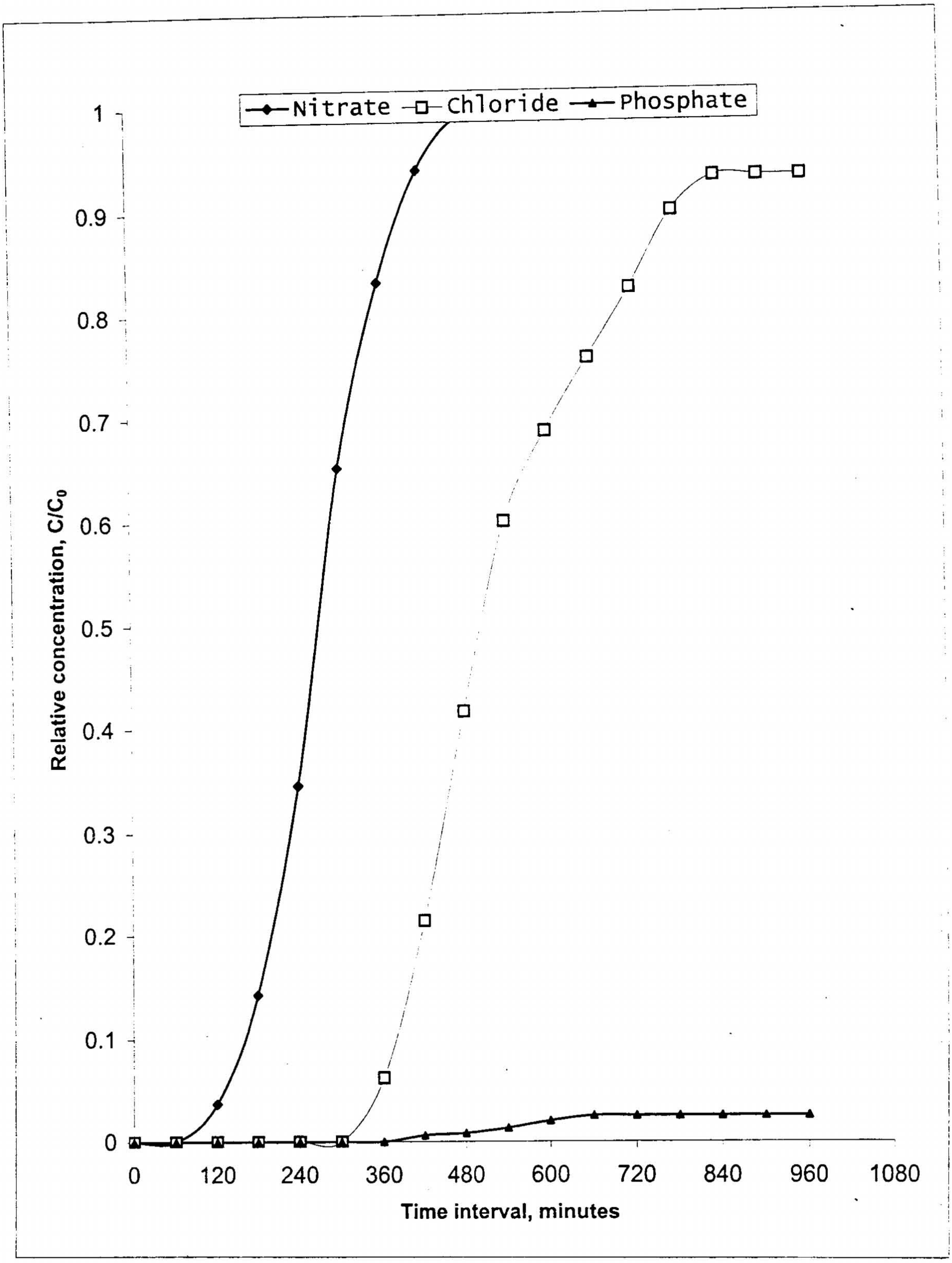


Fig. 14 Breakthrough curve for soil-ion interaction

In the modified method proposed by Fried and Combarnous (1971) the following expression was suggested for the determination of hydrodynamic dispersion coefficient (D_L).

$$D_L = \frac{1}{8}\left[\frac{x - ut_{0.16}}{\sqrt{t_{0.16}}} - \frac{x - ut_{0.84}}{\sqrt{t_{0.84}}}\right]^2$$

where, $t_{0.16}$ and $t_{0.84}$ are the times required for $C/C_0 = 0.16$ and $C/C_0 = 0.84$ to reach a particular distance x in the soil column.

In the present investigation, an attempt was made to find out the dispersion coefficients for nitrate and chloride based on the values obtained from the BT curves. Hydrodynamic dispersion coefficients (D_L) obtained for nitrate and chloride are 108 and 114 cm^2/hr respectively (Appendix I). The values indicate that there is very little difference in the rate of spreading of the two chemical species in the medium. The shape of BT curves also support this result.

CONCLUSION

Nitrate derived from sewage effluent has been clearly identified as the major pollutant of well water in the vicinity of the stabilization pond. At the same time, it should be underscored that nitrate is an important source of plant nutrient as well. Isotope data having revealed that the source of nitrate could be of human and animal origin, they may arise from, besides the sewage stabilization pond, the leach pits and animal feed lots of the residences. Hence, necessary correction steps like local containment with proper treatment must be encouraged. Tailoring of technology to treat pond effluents effectively before releasing to the surrounding is called for to prevent pollution arising from it.

CHAPTER II

TRANSPORT OF POLLUTANTS FROM EFFLUENTS DISCHARGED BY A CLAY MINING INDUSTRY AT MADAYI IN KANNUR DISTRICT

INTRODUCTION

Kerala is rich in clay minerals and clay based industries abound in the State. Clay mining does not involve any chemical process. Probably for this reason, no pollution study of the clay mine effluents has been reported. However, in the process of mining, other underlying minerals might get exposed. Weathering of such minerals and their subsequent leaching could lead to pollution of the surrounding area. Since this aspect has been totally ignored so far, a brief study of possible pollution of well water by clay mine effluents in Madayi, Kannur District was undertaken as a part of ` Present Investigation'.

DESCRIPTION OF THE STUDY AREA

Location, Physiography and Climate

The study area, Madayippara (Madayi) is located 29 kms north-west of Kannur city (Fig.15). It lies between 75° 15′ 0″and 75° 15′ 50″ East longitude and between 12° 0′ 13″ and 12° 0′ 51″ North latitude.

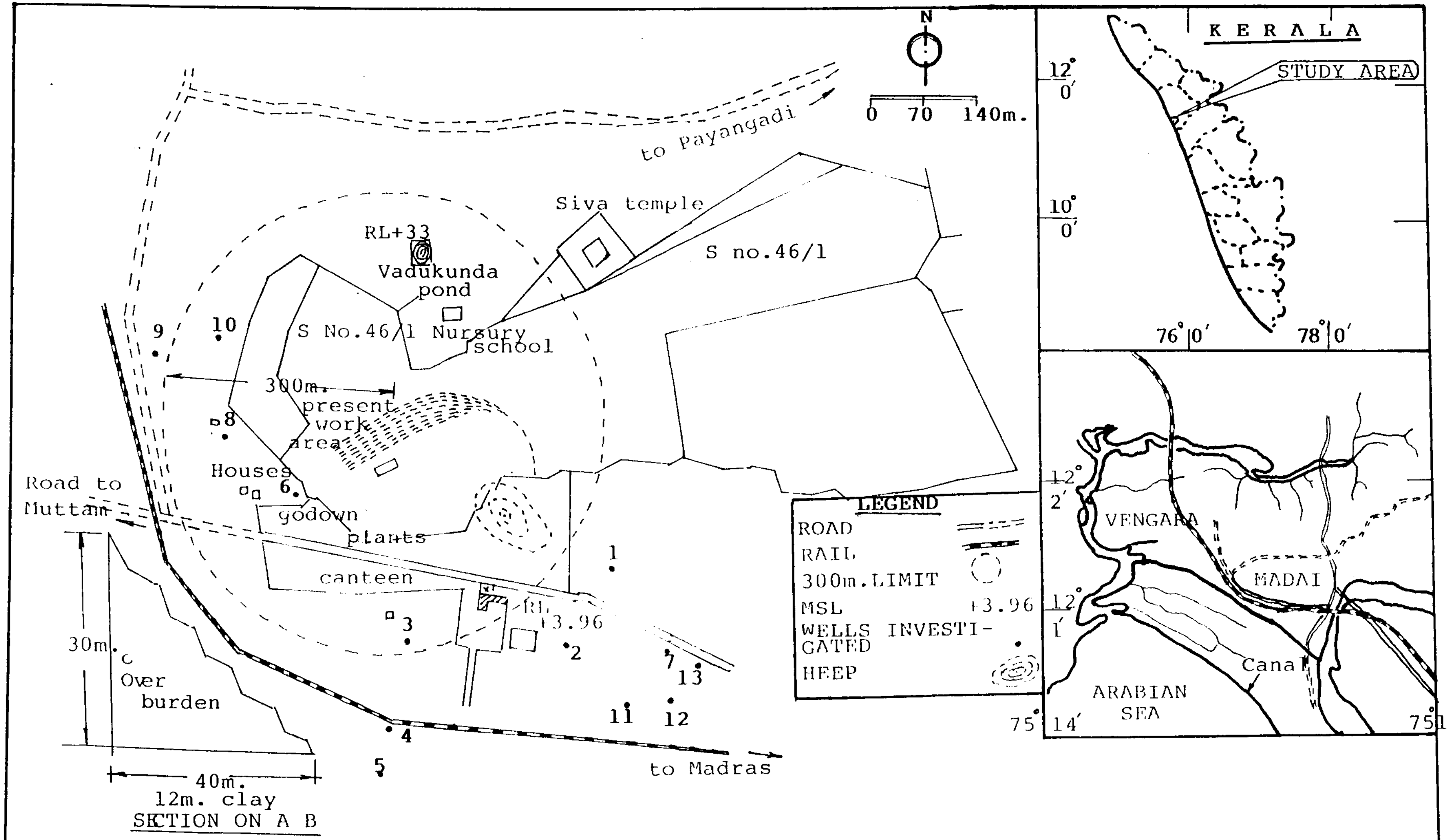


Fig.15 LOCATION MAP OF THE STUDY AREA AT MADAI, KANNUR

The mining area comprises mostly of flat topped or gently undulating hills of laterite with a maximum elevation of 41 m above MSL. The general gradient of Madayippara plateau falls from northern to southern side. The study area receives an average annual rainfall of 3308 mm, of which 81.2% is obtained during south-west monsoon alone. The mean daily temperature is 25.4°C. The month of May is the hottest with the maximum recorded temperature of 34.2°C.

Mining process

The Kerala Clays and Ceramic Products Ltd. has been carrying out mining operations at Madayi since 1952. The mining land comprises of hard laterite to a depth of 10 m followed by high aluminium laterite to 2 m, alternate layers of ball clay and lignite to 10 m and finally the China clay to a depth of 10.5 m. Clays are extracted by open-cast mining by digging the clay dry and washing with water to remove impurities. The water carrying the clay, sand and impurities are conveyed into shallow channels called sand pits. The sand gets deposited at the bottom, and overflow containing the clay is conveyed through channels and led to settling tanks. The settled clay slurry is pumped off to the pressing unit where it is filtered and the pure clay is removed as cake. The same water is re-circulated a few times for initial washings and then discarded. Fresh water is pumped-in to make up the water lost due to evaporation or spillage or drainage during the process. Plate 2 shows a view of the mining area and Plate 3, the pool of water accumulated in the mined open pit.

EXPERIMENTAL PROCEDURE

A network of 13 wells designated as MDY 1 to MDY 13, were selected around tha mining area (Fig.15) for water quality monitoring. Samples from these wells were collected in July and October, 1995 and, January and April 1997. The water samples and the mine discharge samples were analysed for their Physico-chemical characteristics.

RESULTS AND DISCUSSION

Quality of mine discharge

The physico-chemical characteristics of the mine discharge are presented in Table 21.

Table 21 Physico-chemical data of the mine discharge

Period	pH	EC	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
July, 1996	2.4	5820	600	20	2800	2.8	ND	360	176	35.4
October, 1996	2.5	6000	1100	20	2860	5.8	ND	350	364	46.4

Plate : 2 A view of Madayi clay mining area

Plate : 3 Pool of water in the mined pit

Drainage (effluent) from the mine area was observed to be highly acidic, with pH ranging from 2.4 to 2.5, and was rich in sulphate and iron. Sulphate ranged between 2800 and 2860 mg/l and iron content between 350 and 360 mg/l during the period of observation. On close scrutiny it was found that during mining sulphide mineral, iron pyrites (FeS_2), gets exposed to the atmosphere. Its exposure to water and oxygen in the tracts results in the production of sulphuric acid and iron sulphate (Powell and Larson,1985 ; Blevins, 1989) as per the following equation :

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2SO_4^{2-} + 4H^+$$

These effluents when discharged untreated, could very well lead to pollution of groundwater sources, as observed around the area. Plate 4 and 5 show the mode of disposal of mine effluents through the open drains.

Quality of well water

The physico-chemical data of well water at different periods of observation during 1996-97 are presented in Table 22-25. These results show that high acidity in a few wells, and high sulphate content in most of the wells, are the main causes for the water quality deterioration. Water in over 61% of the observation wells is nonpotable

Plate : 4 & 5 Discharge of mine effluents through natural drains

Table 22 Physico-chemical data of the well water (July, 1996)

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
MDY1	7.8	312	12	52	56	63	12.7	ND	0.05	14.4	3.9
MDY2	4.1	222	0	56	36	60	8.4	ND	1.00	14.4	4.9
MDY3	8.1	294	44	96	52	63	6.8	ND	0.29	30.4	4.9
MDY4	8.2	312	90	100	14	25	11.6	ND	ND	36.8	2.0
MDY5	8.5	264	116	80	28	13	1.4	ND	ND	27.2	2.9
MDY6	2.7	2160	0	612	28	1000	9.1	ND	1.65	196.8	29.3
MDY7	8.0	1200	110	356	228	163	12.0	ND	ND	112.0	18.5
MDY8	7.7	2340	180	428	560	106	8.9	ND	ND	124.8	28.3
MDY9	7.7	780	112	220	76	70	10.8	ND	ND	73.6	8.8
MDY10	7.7	594	148	156	48	33	9.0	ND	ND	48.8	8.3
MDY11	6.8	264	68	76	20	40	2.6	ND	0.10	25.6	2.9
MDY12	7.9	960	128	280	84	300	8.5	ND	1.40	91.2	12.7
MDY13	7.6	324	92	112	28	16	3.6	ND	ND	36.8	4.9

Table 23 Physico-chemical data of the well water (October, 1996)

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
MDY1	8.0	291	44	84	34	38	9.1	ND	0.22	21.6	7.3
MDY2	3.9	258	0	68	16	89	2.8	ND	0.09	14.4	7.8
MDY3	8.0	414	46	170	22	125	2.2	ND	0.11	37.6	18.5
MDY4	8.4	269	104	136	16	30	2.0	ND	0.15	36.8	10.7
MDY5	8.5	174	70	58	8	1	1.6	ND	0.07	15.2	4.9
MDY6	3.6	672	0	252	52	150	4.7	ND	0.60	65.6	21.5
MDY7	8.2	543	62	234	28	61	2.4	ND	0.60	67.2	16.1
MDY8	8.4	1456	168	402	234	78	12.8	ND	0.42	116.0	27.3
MDY9	8.4	672	130	200	68	31	2.4	ND	ND	70.4	5.9
MDY10	8.5	414	88	140	32	15	2.8	ND	0.35	43.6	7.6
MDY11	8.5	302	90	130	16	36	1.1	ND	0.06	32.8	11.7
MDY12	8.5	672	62	266	52	128	7.0	ND	0.08	68.8	22.9
MDY13	8.4	246	90	94	20	10	1.4	ND	ND	24.0	8.3

Table 24 Physico-chemical data of the well water (Januray, 1997)

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
MDY1	6.9	540	22	130	66	95	9.3	ND	0.32	42.4	5.9
MDY2	3.3	780	0	168	16	313	2.8	ND	0.38	60.8	3.9
MDY3	6.1	720	48	264	36	275	0.8	ND	0.15	94.4	6.8
MDY4	8.2	1560	116	644	14	500	1.0	ND	0.10	235.2	13.7
MDY5	7.9	120	44	44	8	8	1.4	ND	0.20	12.8	2.9
MDY6	3.9	2160	0	700	100	850	10.8	ND	0.15	256.0	14.6
MDY7	8.0	1980	64	608	354	313	7.6	ND	0.09	188.8	32.2
MDY8	8.1	1680	154	516	230	105	3.2	ND	0.14	145.6	37.1
MDY9	8.0	960	104	348	92	63	3.0	ND	0.49	118.4	12.7
MDY10	8.1	720	116	172	56	36	5.2	ND	0.34	56.0	7.8
MDY11	7.5	240	24	80	10	69	2.4	ND	0.9	24.0	4.9
MDY12	8.3	720	82	308	42	100	2.6	ND	0.23	99.2	14.6
MDY13	7.6	174	60	64	12	11	3.4	ND	0.12	20.8	2.9

Table 25 Physico-chemical data of the well water (April, 1997)

Well No.	pH	EC	Alk	TH	Cl	SO_4	NO_3	PO_4-P	Fe	Ca	Mg
MDY1	7.0	1680	65	520	30	438	9.7	ND	0.64	152.0	34.2
MDY2	2.5	3900	0	520	16	1875	2.0	ND	1.70	60.0	90.3
MDY3	6.0	780	48	340	36	288	0.8	ND	ND	88.0	29.2
MDY4	7.7	960	104	500	16	281	4.6	ND	0.28	156.0	26.8
MDY5	7.9	420	68	250	28	53	1.4	ND	0.29	68.0	19.5
MDY6	3.4	2460	0	830	108	1100	1.6	ND	1.00	172.0	97.6
MDY7	7.6	1560	96	380	202	38	6.8	ND	ND	108.0	26.8
MDY8	7.8	1860	142	390	540	173	5.6	ND	ND	92.0	39.0
MDY9	7.9	900	146	330	86	54	4.4	ND	ND	108.0	14.6
MDY10	8.2	840	150	200	76	40	8.2	ND	ND	61.6	11.2
MDY11	8.1	552	96	230	18	145	3.4	ND	0.85	68.0	14.6
MDY12	7.8	1440	158	490	90	294	6.6	ND	ND	144.0	31.7
MDY13	7.9	240	80	100	16	4	1.4	ND	0.40	32.0	4.9

due to the presence of high concentration of sulphate and chloride, and in some cases due to very low pH also. The wells, MDY2 and MDY6, situated at close vicinity to the mine boundary, are observed to be highly polluted with very low pH, and very high sulphate content. The extent of pollution is observed to decrease as the distance from the mine area/drains increases. Moreover, some of the wells in low lying area are already observed to be under the influence of sea water intrusion, especially during summer months. The low lying lands surrounding the terrace is a sea regressed area and many layers of sea shells could be seen beneath the sandy and clay layers (Anonymous, 1992). This may be the reason why the wells in the area have pH in the alkaline range. The wells, MDY8, MDY9 and MDY10, located on the western side of the mining area are suspected to be intruded by sea water as evidenced by the higher level of chloride than sulphate in these wells. In well MDY7 also, except during October '96, higher level of chloride than of sulphate is conspicuously present. However, in all these cases, the ratio of SO_4/SO_4+Cl, an index generally used to discriminate the source of sulphate (Robinson and Bottrell, 1995) is found to be greater than 0.12, the value for sea water (Table 26), which confirms that sulphate, originating from elsewhere is also present. The other sources are undoubtedly the mine effluents. Thus, these wells have the polluting influence of both sea water and the mine drainage.

Table 26 Index of SO_4/SO_4+Cl during different periods of observation

Sl.No.	Well No.	SO_4/SO_4+Cl			
		July, 1996	October, 1996	January, 2000	April, 2000
1	MDY1	0.53	0.52	0.59	0.94
2	MDY2	0.63	0.85	0.95	0.99
3	MDY3	0.55	0.85	0.88	0.89
4	MDY4	0.64	0.65	0.97	0.95
5	MDY5	0.31	0.11	0.50	0.65
6	MDY6	0.97	0.74	0.89	0.91
7	MDY7	0.42	0.69	0.47	0.16
8	MDY8	0.16	0.25	0.31	0.24
9	MDY9	0.48	0.31	0.40	0.38
10	MDY10	0.40	0.32	0.39	0.34
11	MDY11	0.67	0.69	0.87	0.89
12	MDY12	0.78	0.71	0.70	0.77
13	MDY13	0.36	0.33	0.48	0.20

Temporal variations in water quality

Temporal trends in concentrations of selected water quality determining parameters viz. TDS,. chloride and sulphate, in the observation wells are presented in Fig.16a, 16b and 16c.

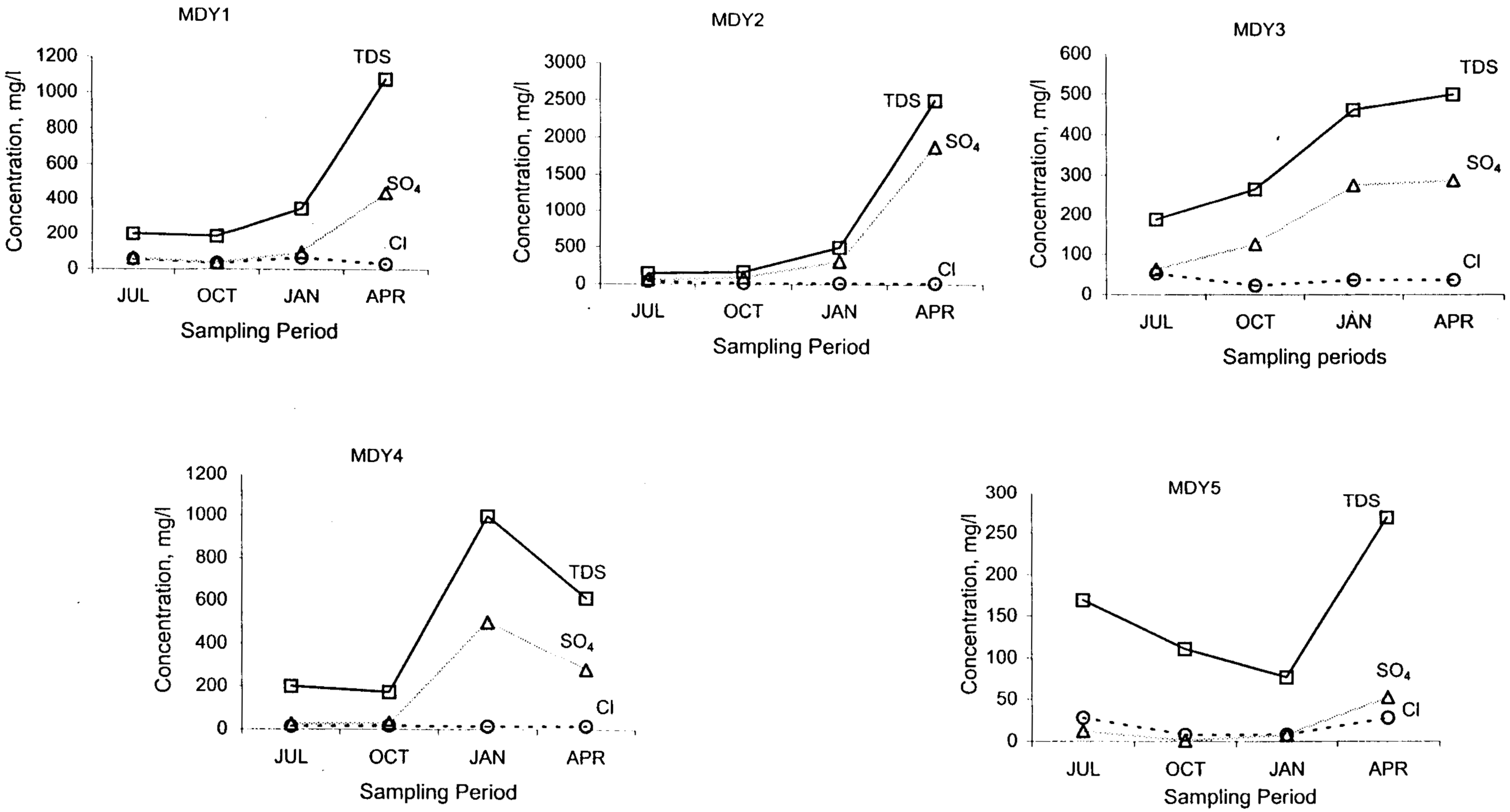


Fig. 16(a) Temporal variation in the concentration of selected contaminants in well waters (MDY 1-MDY 5)

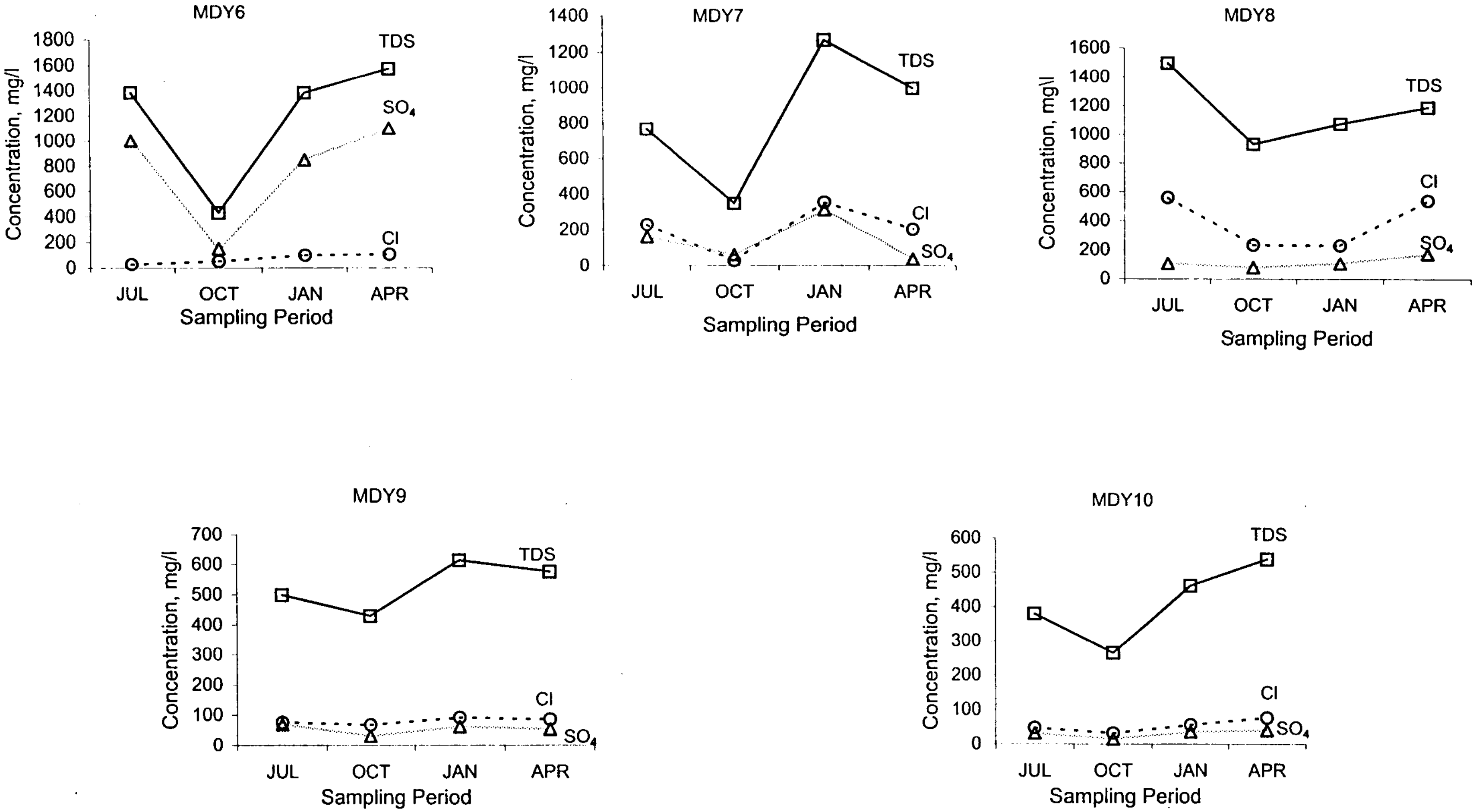


Fig. 16(b) Temporal variation in the concentration of selected contaminants in well waters (MDY 6-MDY 10)

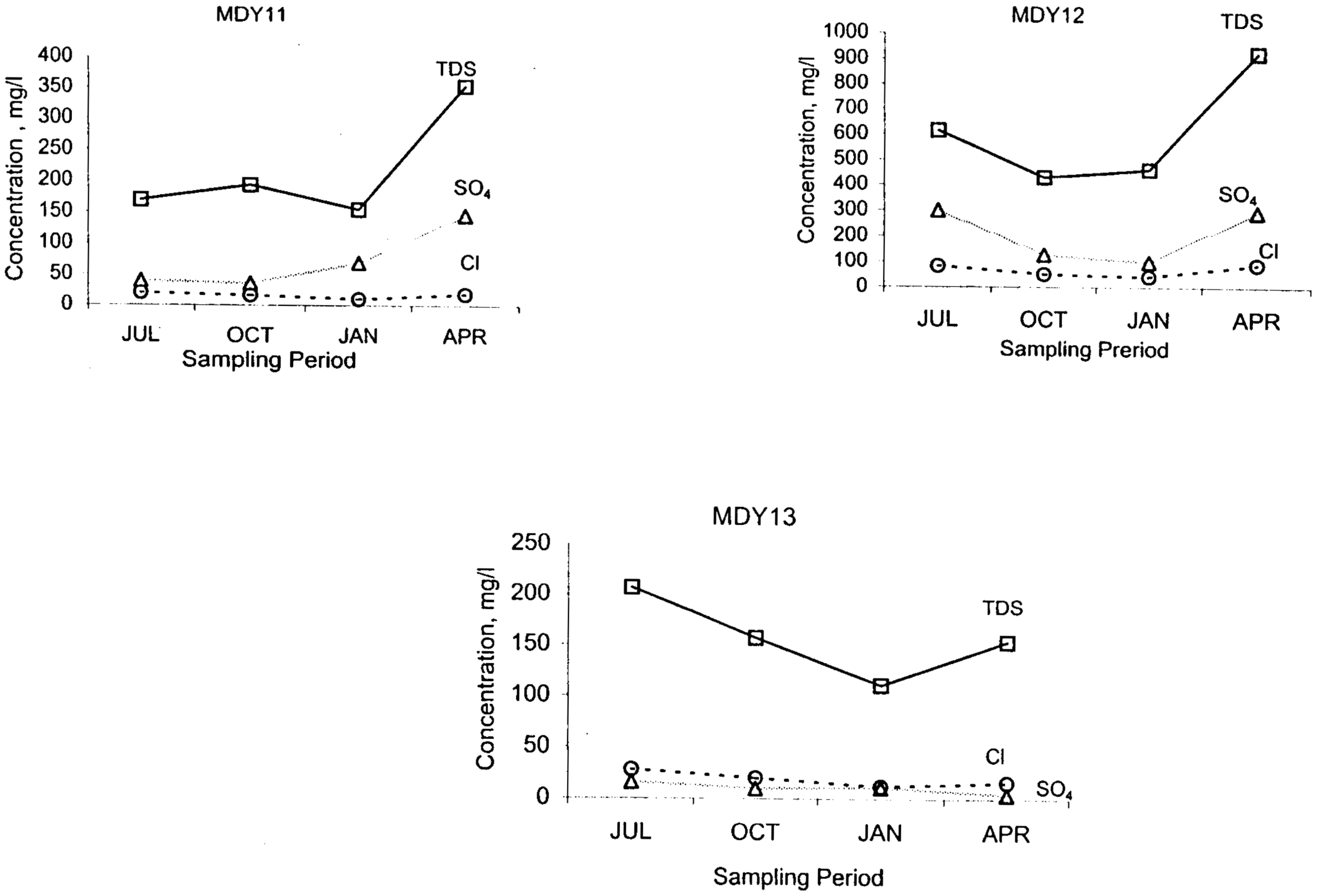


Fig. 16(c) Temporal variation in the concentration of selected contaminants in well waters (MDY 11-MDY 13)

It may be noted that all the wells do not follow similar pattern in temporal variations. In wells MDY1, MDY2 and MDY3, the level of dissolved solids and sulphate increases from July 96 to April 97 and reaches a maximum in April. The level of increase from January to April is steep in the case of Wells MDY1 and MDY2 whereas, it is gradual in MDY3. The first two wells are located very close to the mining boundary than the third well, which may be the possible reason for the above finding. Variations in chloride observed are not significant in these wells.

The water quality data indicate that the wells MDY8, MDY9 and MDY10 have higher levels of chloride than of sulphate in their waters during all the observations, and follow a similar trend. These three wells are located on the western part of the mine pits and may have the influence of sea water also. Among these three wells, MDY8 is observed to be more affected by sea water intrusion, as evident from its high level of chloride. In the case of wells, MDY4 and MDY7, it is found that they contain significantly high levels of sulphate during January than in April, contrary to the expected trend. The possible reasons for these variations could be that the well water is subjected to high fluctuations due to variations in the flow of effluents through the open drains, sea-water intrusion, surface run-off from precipitation, and uneven topography of the terrain.

Identification of sulphate source using isotopic data

Dissolved sulphates in rivers, lakes and other water resources are derived generally from either of the following sources :

1. Sulphate in rain water
2. Oxidation of pyrites and other forms of reduced sulphur
3. Leaching of sulphate minerals
4. Other natural sources such as geothermal water
5. Sulphates of agricultural and industrial origin such as fertilizers and industrial effluents (Robinson and Bottrell, 1995)

Sulphate present in water may be from only one source or from multiple sources. Environmental stable isotopic data provide authentic information on the actual source. In case of sulphate, its sulphur and oxygen carry variable isotope signatures ($^{34}S/^{32}S$, $^{18}O/^{16}O$), which can help to delineate the exact source of its origin.

Isotopically, the sources represent two groups: relatively heavy sulphate (^{34}S- enriched) from evaporite minerals, and relatively light sulphate (^{34}S-depleted) derived from reduced sulphur sources such as sulphide minerals or organic sulphur in soil. Trembaczowski and Halas

(1993) distinguished the major sources of river water sulphate in SE Poland using sulphur and oxygen isotopes and also noted marked seasonal variations in the isotopic compositions due to bacterial activity. Bottrell and Robinson (1993) investigated the isotopic composition of sulphate sources to the Xingwen Karst aquifer, Peoples Republic of China, and observed that rain and percolation sulphate have uniform $\delta^{34}S$, ranging from +0.4 to +1.6‰, mine drainage sulphate has $\delta^{34}S$ values from +2 to +3 ‰; and sulphate in shale drainage has $\delta^{34}S$ around +6‰.

In the present study, a set of five well water samples and a sample from the mine effluent were subjected to stable isotope, $^{34}S/^{32}S$ analyses and the results of isotopic composition and the sulphate level in these samples are presented in Table 27.

Table 27 $\delta^{34}S$ and sulphate of selected well water samples

Sl.No.	Sample Code	Concentration of sulphate, mg/l	$\delta^{34}S$‰
1.	MDY-1	437	+2.5
2.	MDY-2	1875	-1.5
3.	MDY-6	1100	+0.5
4.	MDY-7	38	+7.2
5.	MDY-8	173	+7.7
6.	Mine Effluent(ME)	2860	-2.8

A plot of sulphate concentration versus $\delta^{34}S$ for the above (Fig.17) indicates that wells with Nos. MDY.1, MDY2 and MDY6 have sulphate derived from clay mine effluents as evidenced by the $\delta^{34}S$ values of –1.5 to +2.5‰, which are close to the value for mine effluent. The remaining wells show values around +7‰, which are markedly different from the range of the earlier ones. These enhanced $\delta^{34}S$ values may be due to intrusion of sea water.

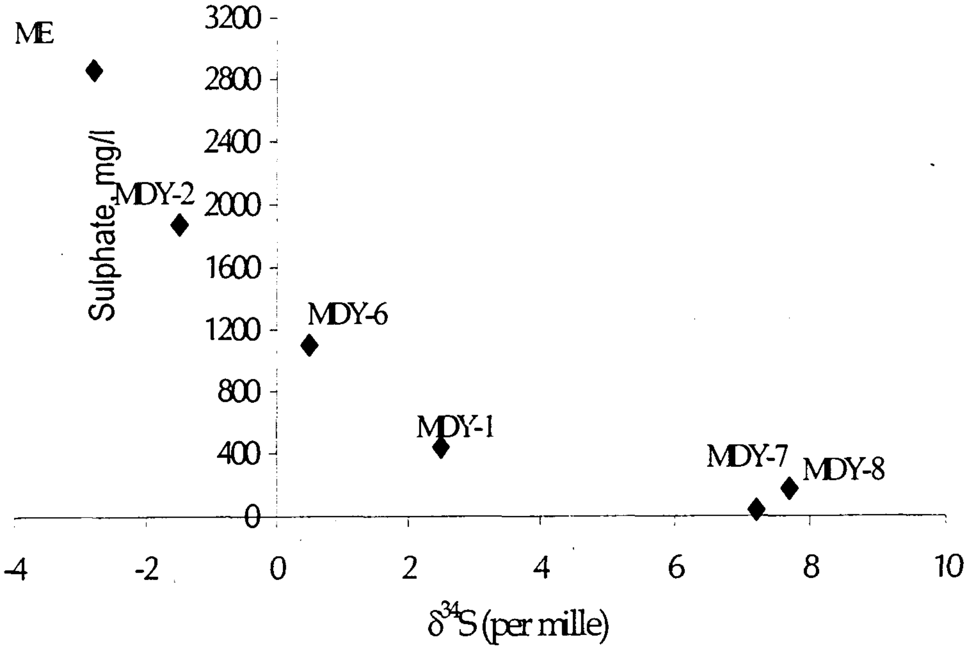


Fig. 17 $\delta^{34}S$ versus Sulphate

Treatment of mine effluent

An attempt was made to treat/neutralise the acidic mine effluent by conducting laboratory scale batch experiments. Mine effluent was simulated in the laboratory using ferrous sulphate and sulphuric acid to meet the quality requirement as observed in the clay mine effluent. The simulated effluent had pH between 2.3 and 2.5 and, iron content between 350 and 360 ppm. Quicklime (CaO) was used as the neutralising as well as precipitating agent for the batch experiments. One litre of simulated effluent was taken in glass jars and lime at different doses, varying from 1 to 5 g was added in different jars. The mixture was stirred for 1 minute using a magnetic stirrer at 1000-1500 rpm. The stirred mixture was kept for 5 minutes to allow the precipitate to settle and the supernatant solution was analysed for change in quality. Change with respect to pH and iron content was monitored (Table 28). The quantity of sludge formed during the treatment was also measured to assess the quantum of sludge that would be generated during the process of treatment.

Table 28 Results of the batch experiment on the treatment of mine effluent

Sl. No.	Lime dose g/l	pH	Iron mg/l	Wet Sludge ml	Dry Sludge g
1	1.00	2.60	275	0.3	0.10
2	2.00	2.85	195	1.0	0.18
3	3.00	3.65	165	2.9	0.42
4	3.50	5.70	1.9	14.5	0.46
5	3.75	6.60	1.72	16.5	0.53
6	4.00	10.10	1.7	20.5	0.64
7	5.00	11.50	1.71	23.5	0.75

Fig. 18(a) and 18(b) depicts the results of the treatment studies. The results indicate that around 3.75 kg of lime is required to neutralise one cubic metre of mine effluent. If the effluent quantity is known, its neutralisation and precipitation of iron could be achieved by dosing required amount of lime before it is discharged from the mining area. Calcium hydroxide formed by the hydrolysis of quicklime, while neutralising sulphuric acid, precipitates iron as $Fe(OH)_3$, as per the following equation :

$$5CaO + Fe_2(SO4)_3 + 2H_2SO_4 + H_2O \longrightarrow 5CaSO_4 + 2Fe(OH)_3\downarrow$$

Due to poor solubility of calcium sulphate, pollution due to sulphate also will be subdued.

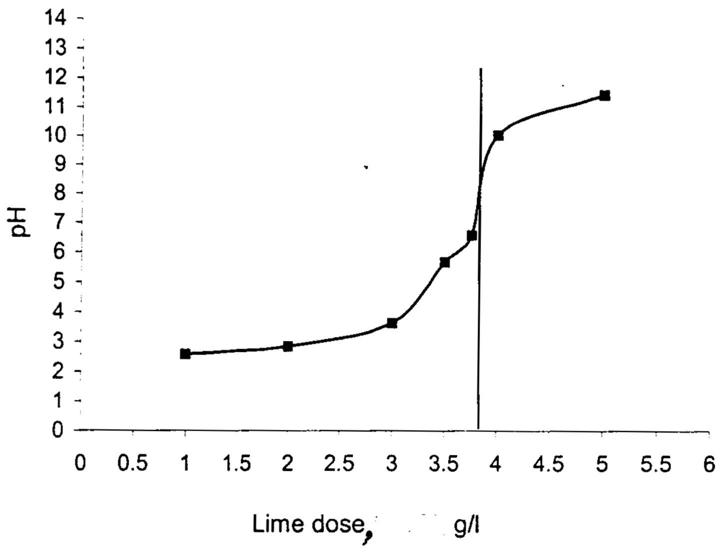


Fig.18(a) Neutralization of mine effluent with lime – Batch experiment

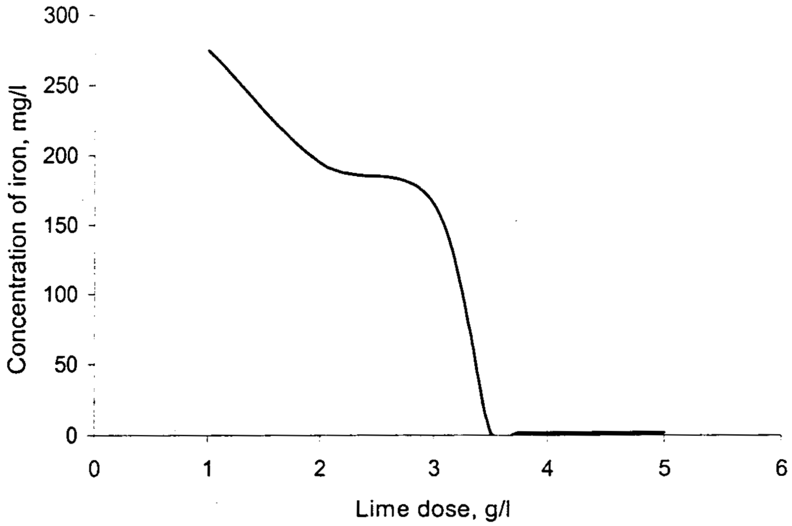


Fig.18(b) Decrease of iron-content at different doses of lime – Batch experiment

CONCLUSION

The investigation has been worthwhile, since it could bring out an apparently hidden source of pollution of groundwater. Sulphate, originating from the drainage of clay mine, has been identified as the major pollutant in the well water of Madayi, affecting over 61% of the observation wells. An economic and suitable method for treating the mine effluent has been worked out at laboratory scale. After necessary scaling up, the method can be used for treating the mine effluent effectively.

Sulphate in combination with magnesium or sodium in drinking water can cause a laxative effect. In fact, magnesium sulphate is the well known purgative, epsom salt. The adult laxative dose of either magnesium sulphate or sodium sulphate (glauber's salt), is of the order of 2 g (Irving, 1974). The desirable limit of sulphate in drinking water is 200 mg/l (BIS, 1991). Quantities beyond this desirable limit causes gastro-intestinal irritation when sulphate is present as magnesium or sodium salt (BIS, 1991).

PART IV

SUMMARY

SUMMARY

Groundwater is scarce and is the prime source of potable water for majority of the rural population in India. It is getting increasingly polluted by domestic, agricultural and industrial activities. There is no easy way to treat polluted groundwater, unlike surface water which may be treated if polluted. Hence, the precious groundwater in natural underground reservoirs, must be guarded against pollution, at any cost, for the use of posterity.

Literature revealed that researches on the actual source of pollution of groundwater are rare, and that reports are often based on surmises and circumstantial evidences. These aspects are brought out in Part I ("General Introduction") and Part II ("Review of Literature") of the Thesis. Further researches to pin down the actual source of pollution were thus called for.

Part III is devoted fully to the present investigation on the theme " Investigation on the Transport of Pollutants to Aquatic Environment with Special Reference to Groundwater". Two projects have been investigated. Since, `Materials, Instruments and Methods' used in these

projects are similar, details regarding these are given at the outset, to avoid any possible repetition.

In Chapter I of Part III, details of investigation on `Transport of Pollutants from the Sewage Stabilization Pond of Kozhikode Medical College' are furnished. This work was carried out during July 1993 to June 1995, using 23 observation wells in the area. Nitrate was found to be the major pollutant in the wells. The pond effluent was found rich in nitrate. Vertical movement of pollutants through soil was examined using a multilevel point sampler, and migration tendencies of a few ions were compared using a soil column. All circumstantial evidences pointed to the pond effluents as well as human and animal wastes of other origin in the study area as the source of well-water pollution. That, this is so was confirmed through isotopic technique based on $^{15}N/^{14}N$, designated as $\delta^{15}N$. First step measures for alleviating nitrate pollution have been suggested. Need for proper treatment of pond effluents was highlighted.

Results of investigation on the `Transport of Pollutants from Effluent Discharged by a Clay Mining Industry at Madayi in Kannur District' are presented in Chapter II. For this study, undertaken during July 1995 to April 1997, 13 observation wells in the vicinity of the mining area were put to use. Sulphate was found to be the major pollutant in most of the wells, some were also affected by acidity. Since, the mine effluents are characterized by low pH and high sulphate content, the source of well-water pollution became apparent. The ratio of SO_4/SO_4+Cl further strengthened the view. It was confirmed using isotopic technique based on $\delta^{34}S$.

An economical method employing lime was found effective in removing acidity and iron from the mine effluent. Due to poor solubility of calcium sulphate (the side product), extent of sulphate pollution also will be considerably lowered.

PART V

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APPENDIX - I

COMPUTATION OF DISPERSION COEFFICIENT, D_L

Hydrodynamic dispersion coefficient,

$$D_L = \frac{1}{8}\left[\frac{x - ut_{0.16}}{\sqrt{t_{0.16}}} - \frac{x - ut_{0.84}}{\sqrt{t_{0.84}}}\right]^2$$

where, $t_{0.16}$ and $t_{0.84}$ are the times required for $C/C_0 = 0.16$ and $C/C_0 = 0.84$ to reach a particular distance x in the column.

C_0 : initial concentration and C : concentration at time t.

Length of the soil in the column (x) = 60 cm

Diameter of the column (d) = 9.1 cm

Area of the column (A) = $\pi d^2/4 = 65$ cm^2

Rate of flow (Q) = 18 ml/min

Average linear velocity (V) = 18/65 = 0.277 cm/min (since Q=AV)

Effective porosity = 0.596

Average pore velocity (u) = Linear velocity/ Effective porosity

= 0.277/0.59 = 0.465 cm/min

From the Break through curve :

	$t_{0.16}$	$t_{0.84}$
Nitrate :	180 min	354 min
Chloride :	402 min	720 min

Hydrodynamic dispersion coefficient for Nitrate:

$$D_L = \frac{1}{8}\left[\frac{60-0.465\text{x}180}{\sqrt{180}} - \frac{60-0.465\text{x}354}{\sqrt{354}}\right]^2$$

$= 1.8\ \text{cm}^2/\text{min} =$ **108 cm^2/hr**

Hydrodynamic dispersion coefficient for Chloride:

$$D_L = \frac{1}{8}\left[\frac{60-0.465\text{x}402}{\sqrt{402}} - \frac{60-0.465\text{x}720}{\sqrt{720}}\right]^2$$

$= 1.9\ \text{cm}^2/\text{min} =$ **114 cm^2/hr**

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