TN -53

MOVEMENT OF POLLUTANTS IN SUBSURFACE ENVIRONMENT

NATIONAL INSTITUTE OF HYDROLOGY
JAL VIGYAN BHAWAN
ROORKEE - 247667 (U.P)
INDIA

PREFACE

The subsurface is the medium through which pollutants move from the soil surface to groundwater. Polluting substances are subjected to complex physical, chemical and biological transformations while moving through the subsurface material, and their displacement depends on the transport properties of the water air porous medium system. Pollution caused by human activities, agriculture, mining and industry has brought about a growing interest in the role of subsurface material in the ground water pollution.

The National Institute of Hydrology established the Man's Influence Division in 1986 with the major objectives of studying the erosion and sedimentation in a watershed, forest influences on hydrological region, environmental impact assessment of water resources projects, and water quality model studies. Therefore studies are done in this division on effects of changes in the hydrological cycle on social, environmental and ecological aspects related to water resources. In view of the aggrevation of ground water pollution problems in the country, it was envisaged to study the present status of knowledge about subsurface movement of pollutants.

The report has been prepared after extensive literature survey available on ground water pollution. The report includes, the activities generating pollutants, type of pollutants and behaviour of pollutants besides the mathematical models which describe the movement of pollutants in the subsurface environment.

The report has been prepared by Sri Sudhir Kumar, Scientist in Man' s influence Division. He was supported by Scientific staff namely Sri Yatvir Singh, Sri Rakesh Goyal, Sri Zafar Abbas, and Sri T.R. Sapra. The report has been typed by Sri S.P. Singh Sri Avdhesh Sharma , and Sh. Y.P.S. Verma.

CONTENTS

LIST OF FIGURES

List of Tables

1.0 INTRODUCTION

1.1 General

The use, development and management of water resources is one of the most important factor affecting the socio-economic structure of community. Among all water resources, ground water is regarded as the best resources, for any type of use. If ground water is to continue to play an important role in the development of the water resources potential, then it will have to be protected from the increasing threat of surface contamination. The growth of population and of industrial and agricultural activities, coupled with the resulting increased requirement for energy development, has began to produce quantities of waste that are grater than that which the environment can easily absorb. This production of waste often poses a threat to groundwater quality and has already resulted in many incidents of ground water contamination. Moreover, the pressure to reduce surface water and air pollution are in part responsible for ground water pollution.

Degradation of groundwater quality can take place over large areas from intensively farmed fields, or it can be caused by point sources such as septic tanks, garbage disposal sites, cementaries, mine spoils, oil spills or other accidental entry of pollutants into the underground environment. A third possibility is contamination by line sources of poor quality water, like seepage from polluted streams.

The mechanism of ground water pollution is quite different from that of surface water and is more complicated. Surface water pollution is rapid and becomes evident in comparatively short time from perceptible changes in colour, taste, odour and at times by dead equatic life. The process of ground water pollution is comparatively much slower and the time lag between pollution discharge at land surface and its reception in ground water may be several years or decades.

Moreover, the wide range of contamination sources is one of the many factors contributing to the complexity of the problem.

1.0 Need for Pollutant movement studies

Source activities releasing contaminants into the subsurface, which involve the greatest potential for significant pollution of ground water may be conveniently grouped under four major categories (Dunlap, 1985).

1. Waste disposal activities that utilize the sub-Surface as a pollutant receptor, such as hazardous waste landfills, industrial waste ponds and lagoons, waste water land treatment operations, and disposal wells.

2. Industrial and commercial operations involving the handling of large quantities of chemical substances which may be accidentally released into the subsurface is significant amounts as the result of leaks and spills occuring during transport,

storage, and utilization activities.

3. Agricultural operations involving intentional application of chemicals to the land.

4. Water reclamation activities entailing either direct or indirect artificial recharge of ground water with contaminated water.

Since these source activities primarily responsible for release of pollution into the subsurface cannot be eliminated completely, the goal of ground water protection efforts must necessarily be the control or management of these sources to ensure that released pollutants will be sufficiently attenuated within the subsurface to prevent significant impairment of ground water quality at points of withdrawal or discharge. This goal can be effectively achieved only if control and management options are based on definite knowledge of the transport and fate of pollutants in the subsurface environment. Such knowledge is required for:

(i) establishment of criteria for design, location and operation of new potential sources of pollution, such as new hazardous waste disposal sites and facilities for land treatment of wastewater, in order that these critiera will permit maximum practible use of the subsurface as a pollutant receptor while assuring minimal entry of pollutants into ground water and movement of any pollutants which do enter groundwater to points of withdrawal or discharge.

(ii) assessing the probable impact on ground water quality of existing sources, such as hazardous waste dumps and spill sites, in order to determine a level of remedial action that is both cost effective and sufficient to prevent serious degradation of ground water quality at points of withdrawal or discharge, and

(iii) development of improved methods for removing pollutants from and renovating already polluted aquifer.

Source control and management options not based on knowledge of pollutant transport are almost certain to result in either under control, with excessive pollution of ground water, or over control, resulting in uneconomical under ütilization of the subsurface as a pollutant receptor.

2.0 ACTIVITIES GENERATING POLLUTANTS AND THE TYPE OF POLLUTANTS

There are many human activities that contribute pollutants to the subsurface. The major activities which contribute significantly to pollution problem are (i) Agriculture, (ii) Household, commercial and industrial activities, and (iii) Mining. These activities of pollutant generation and the type of pollutants generated are described in brief here.

2.1 Agriculture

While certain solid and liquid agricultural wastes occur in concentrated forms, low-level ground water pollution in rural areas occur as a result of the wide spread leaching of excess nutrients applied to both arable and pastoral land as inorganic and organic fertilizers (Atkins, 1976). Major contaminant is nitrate, derived both from fertilizers and as a result of the transformation of organically bound nitrogen in the soil to inorganic forms by bacteria (mineralization) following the ploughing of land (Smith and Young, 1975). The quantity of nitrate released for leaching by ploughing may be large and can exceed the total annual quantities of nitrogen normally applied as fertilizer. (Krutler and Janes, 1975; Young et.al.,1976). Increased sulphate and chloride concentrations derived from the use of ammonium sulphate and potassium chloride fertilizer may also occur in drainage water from farm land. The residues of pesticides and herbicides may be leached from the soil and the examples of ground water contamination have been reported (La Fleur et.al.,1973 ; Snagaroff, 1977). Contamination of ground water may also take place by (i) faecal bacteria from free ranging livestock (ii) farmland slurries and (iii) silage effluents (Table 1). Extremely high BOD values of silage effluents, together with the organic contaminants resulting from the fermentation could lead to intense ground water contamination including the onset of anoxic conditions. Fig.1 shows the various agricultural activities contributing to ground water pollution.

2.2 Household, Commercial and Industrial Activities

These activities produce both solid as well as liquid wastes. The characteristics of the waste produced by solid and liquid wastes are summarized in Table 2 and Table 3 respectively.

2.2.1 Solid waste

Household solid waste is generally rich in biodegradable organic material which produces carbondioxide and methane gases. The leachate from this type of waste contains high concentrations of volatile fatty acids. With time the organic carbon component of leachate changes to carbohydrates. Other major constituents of household solid waste are sulphate and chloride, which reach the peak value within a year or two of waste disposal and

Table 1 : Pollutants resulting from agricultural activities

Source	Potential characteristics of Leachate/effluent	Rate of effluent production or rate of solid-waste production
Arable crops, fertilisers, Pesticides, etc.	Increased nitrate, ammonia, sulphate, chloride and Phosphate from fertilizers, Faecal bacterial contamination from organic fertilizers. Organochlorine compounds from pesticides	Rate of leachate production dependent on local climatic/irrigation regime, Applications 10 to 10^3 kg/ha/yr. Partial uptake of fertilizer components by crops
Livestock, feaces and urine	Cattle: Suspended solids 90 000 mg/ BOD 10 000 mg/l Total N 4 000 mg/l Faecal coliforms 2×10^5/g	- 15 m^3/yr/animal
	Pigs: Suspended solids 100 000 mg/l BOD Total N 5 000 mg/l Faecal coliforms 3×10^6/g Faecal streptococci 8×10^7/g Heavy metals, variable	- 3 m^3/yr/animal
	Sheep: Similar S.S.,BOD, N to cattle Faecal coliforms $1\text{-}2 \times 10^7$/g Faecal streptococci 4×10^7/g	- 2 m^3/yr/animal
	Poultry: Suspended Solids 36 000 mg/l BOD 36 000 mg/l Total N 17 000 mg/l Faecal coliforms 10^5-10^7/g Faecal streptococci 10^6-10^7/g	- 50 m^3/yr/10^3 birds
Intensive units livestock yards	Effluent formed by washing down, diluting faeces and urine 3 to 10 times. Suspended solids, BOD,Nreduced Chloride 200-400 mg/l	Cattle units 10^3-10^5 m^3/yr Pig units 10^3-10^4 m^3/yr

Washings/drainage from farm buildings and yards	High Suspended solids, high organic content, high BOD Mineral oil from machinery. Faecal bacteria	Variable quality - 10^3 m^3/yr washing wastes/head of livstock
Silage	High Suspended solids, BOD 1 - 6 x 10^4 mg/l Organic components - carbohydrates phenols	0.3 m^3/yr/tonne 10^2 - 10^3 m^3/yr/livestock

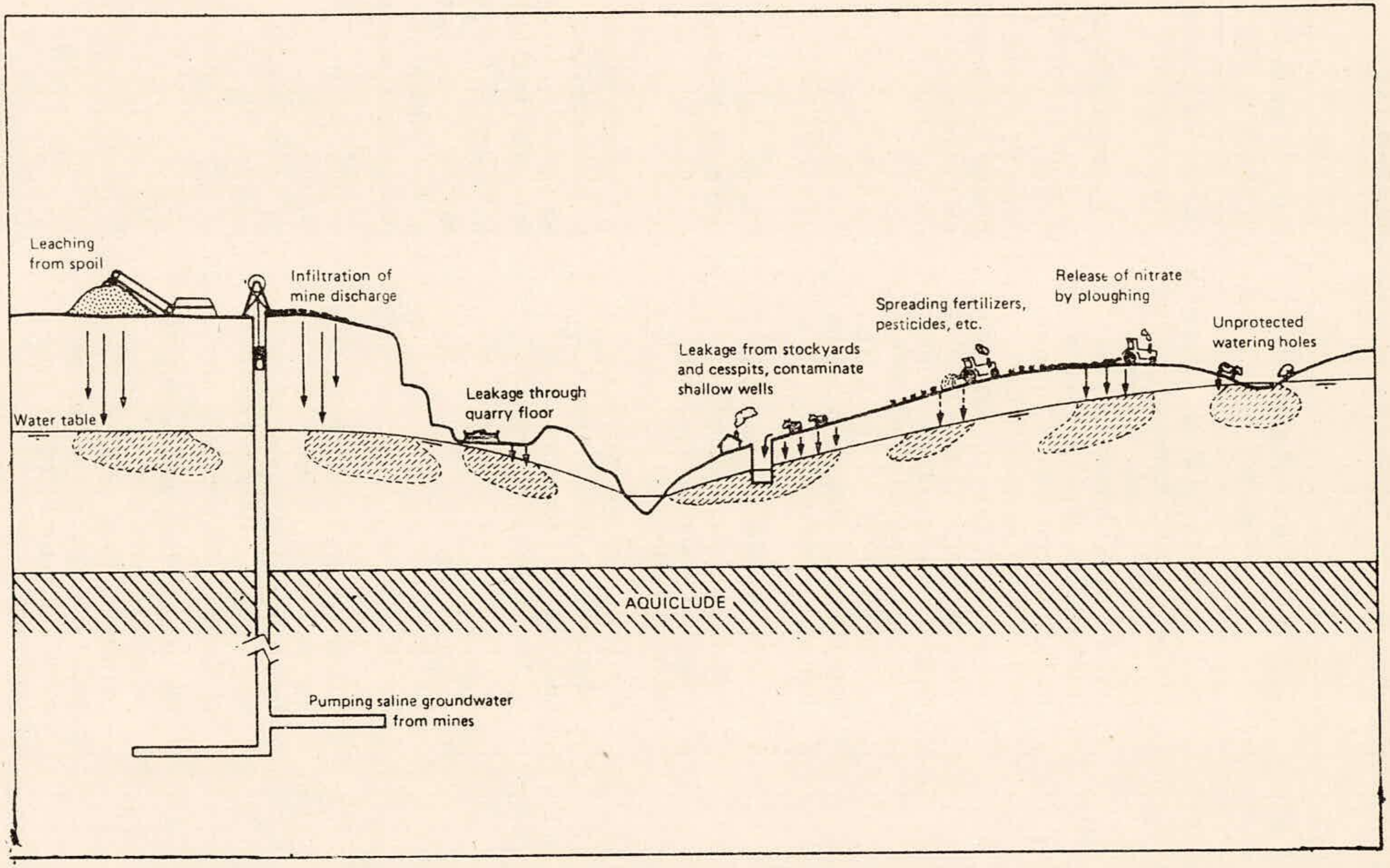

Fig. 1: Sources of contamination from agriculture and mineral exploration

Table 2 : Household, commercial and industrial solid wastes

Source	Potential characteristics of leachate	Rate of solid-Waste production
Household wastes	High sulphate, chioride, ammonia BOD, TOC and suspended solids from fresh wastes. Bacterial impurities. In humid climates leachate composition changes with time, initial TOC manly voltile fatty acids (acetic) butyric, Propeionic). Subsequently changing to high molecular weight organics humid substances, carbohydrates). Period of change 5- to 10 years after deposition of wastes in humid, temperate regions.	0.2 to 0.4 tonnes/yr/person Characteristic landfill size 10^4 to 10^8 m^3 Rate of leachate production dependent on climate
Commercial wastes	Similar to domestic wastes may also include phenols mineral oil and hydrocarbon solvent wastes	Co-disposal with domestic wastes
Industrial wastes	Variable. May contain toxic substances - heavy metals, oils, phenols, solvents, pesticide/nerbicide residues	0.3 tonnes/yr/person in industrialized societies' industrial landfills 10^4 - 10^6 m^3 May be co-deposited with domestic commericial wastes
Power generation (Thermal)	Pulverised fuel ash. Up to 2% by weight soluble constituents, solphate. May contain concentrations of Germanium and Selenium Ply ash and flue gas scrubber sludges. Finely particulates, containing disseminated heavy metals. Sludges of low on unless neutralised by lime additions	10^4 - 10^5 tonnes/year

Table 3 : Household, Commercial and Industrial Liquid Wastes

Source	Potential Characteristics of leachate/effluent	Rate of leachate or effluent production
	(a) Sewage	
Raw sewage (Human faeces and urine)	suspended solids - 6×10^4 mg/l BOD -5×10^4 mg/l Total N - 1×10^4 mg/l Faecal coliforms-1×10^7/gram Faecal streptococci - 1×10^6/gram	0.4-0.6 m^3/yr/person (0.3-0.5 kg/yr/person)
Septic tanks	Suspended solids 100-300 mg/l BOD 50-400 mg/l TOC 100-300 mg/l Total solids 300-600 mg/l Ammonia 20- 40 mg/l Chloride 100-200 mg/l High faecal coliforms and streptococci trace organisms, grease	40-60m^3/yr/person (Assuming connection to waterflush toilet system)
Sewage,primary treatment	Suspended solids 25-150 mg/l BOD 30-250 mg/l Grease removed	
Sewage, Secondary, treatment	Suspended solids 14- 45 mg/l BOD 10 - 50mg/l Ammonia nitrified2.0 mg N/l Nitrate 30- 40 mg/l Chloride 100-200 mg/l Coliforms 1000-4000 mg/l	$10^4 - 10^8$ m^3/yr
Sewage, tertiary	Suspended solids 0 BOD 0 - 10 mg/l	
Sewage, quanternary treatment	Virus and bacteria free	
Sewage sludge, digested	Solids 4 - 7 mg/l Organic matter 2 - 4 mg/l Heavy metals if mixed with storm water discharges, High Al, P, K, N (as NH_3) Leachate - Ammonia 10-25 mg/l Potassium 1-10 mg/l Sodium 1 - 50 mg/l Zinc 1000-4000 mg/l	$10^4 - 10^5$ m^3/yr

	(b) Storm Water drains	
Street drainage	High suspended solids (1000 mg/l) Hydrocarbons, minerals et. from roads, service areas etc. High chlorides or urea from de-icing. Wide variety of compounds from accidental spillages. Bacterial contamination high, but order or magnitude lower than sewage	Variable rates. May be treated at sewage works, mixed with foul water drainage.
	(c) Industrial	
Flood and drink manufacturing	High BOD, suspended solids often high, colloidel and dissolved organic substances. Odours	$10^3 - 10^7$ m^3/yr
Textile and Clothing	High suspended solids, High BOD, Alkaline effluent	$10^4 - 10^6$ m^3/yr
Tanneries	High BOD, total solids, hardness, chlorides, sulphaides, chromium	$10^3 - 10^6$ m^3/yr
Chemicals		
-Acids	Low pH	$10^5 - 10^9$ m^3/yr
-Letergents	High BOD, saponified soap residues	
-Explosives	Low pH, high organic acids, alcohols, oils	
-Insecticides herbicides	High TOC, toxic benzene derivatives, Low pH	
-Synthetic resins and fibres	High BOD	
Petroleum and petrochemical		
-refining	High BOD, chloride, phenols sulphur compounds	$10^6 - 10^8$ m^3/yr
-process	High BOD, suspended solids, chloride, variable pH	
Foundries	Low pH, High suspended solids phenols, oil	$10^7 - 10^9$ m^3/yr
Plating and metal finishing	Low pH, High content of toxic heavy metals, sometimes as sludges	$10^7 - 10^9$ m^3/yr
Engineering works	High suspended solids, soluble cutting oils, trace heavy metals, variable BOD, pH	$10^4 - 10^7$ m^3/yr

Thermal power	Increased water temperature, slight increase in dissolved solids by evaporation of cooling wastes	$10^3 - 10^4$ m^3/yr/ megawatt
	(d) Miscellaneous Sources	
Deep Well injection	Various concentrated liquid, wastes often toxic, Brines Acid and & alkaline wastes, Organic Wastes	$10^4 - 10^6$ m^3/yr.
Accidental spillages	Various liquid in transit, hydrocarbones, petrochemicals, acids, alkalies, soluvents, Liquids may enter surface drains or soak aways	Generally 10 m^3 per incident
Leakage from storage tanks and pipelines	Aqueous solutions, hydrocarbones, petrochemicals, sewage	$10 - 10^3$ m^3 per incident

then decrease irregularly over a long period of time. Cellulose, in the form of waste paper, retards the movement of halogenated hydro carbons by adsorption followed by degradation.

Commercial wastes are often of a similar composition to, and are codisposed with domestic wastes but may contain quantities of oils, phenols and hydrocarbon sollvents which may leache from the landfill. Lechates from domestic and commercial wastes may be serious ground water contaminants by virtue of their dissolved constitutents and high biological oxygen demand (BOD), which produce extensive and persistent anoxic conditions in both the unsaturated and saturated zones of aquifers on which the wastes are deposited.

The composition of the industrial waste varies with the source, ranging from cynide wastes from metallurgic al operations, through sulphite-rich paper and pulp manufacturing waste, mercury-rich materials from electrical industry, to solid residues from the petro-chemical industries such as PCBs, pesticide or herbicide residues and phenol-rich tar wastes. In many cases toxic substances are present which, if solubilized may present major threat to ground water quality.

The coal ash from power stations is generally considered to be relatively inert, containing only about 2 percent of soluble material, principally as sulphate, but in addition traces of metals such as germanium and selanium. However, fly ash presents a more serious problem since its high surface area; volume ratio renders it generally more reactive. Dreesen et.al.(1977) noted that the most important pollutants which may be extracted from fly ash are Mo, F, Se, B and As. Sludges formed by the aqueous scrubbing of flue gases typically contain cynide and heavy metals and are of low pH unless naturalized by lime addition. The leachate from such sludges is generally rich in B, Cd, Mo, Hg, Se and Pb.

Shallow ground water can also be polluted by the organic residues and pathogens due to burial of corpses.

2.2.2 Liquid wastes

The principal ground water contaminants in human sewage are the result or the high BOD, suspended solids, faecal bacteria, chloride and ammonia in raw sewage. Reduction of BOD, suspended solids and bacteria and viruses may be achieved by biological and physical treatment, but the anions persist in the final effluent. Discharge of treated effluents onto the outcrop of water table aquifer s may lead to the development of plumes of contamination defined by increased chloride concentration within the saturated zone (Edworthy et.al.1978).

The water in storm-water drains contain high concentration of suspended solids composed of particulate matter of vegetable, animal and mineral origin washed from paved surfaces. High concentrations of dissolved road de-icing agents such as sodium chloride and urea may be present reasonally, while immiscible layers or emulsions of hydrocarbons and other organic compounds, such as tetraethyl lead, occur as the result of exhaust emissions from vehicles and accidental spills. Bacterial contamination is commonly high but may vary rapidly over short-time periods as the result of intense flushing during heavy rain storms.

The industrial processing of the raw products of agriculture, i.e. food and fibre, produce potentially contaminating effluents generally high in BOD and suspended solids. Effluents from textile processing characteristically alkaline while tennery waste water contain high concentrations of dissolved chlorides, sulphides and chromium. Food and drink process wastes commonly give rise to taste and odour problems.

The effluents resulting from the refining and processing of petroleum and petrochemicals have a high potential for pollution, due to their high BOD leadings and toxic sulphur compounds and phenols waste waters from metallurgical processing and finishing facilities are characteristically acidic with high suspended solids, which in the case of planting and finishing waste may include significant quantities of toxic heavy metals, phenols and oils.

Similarly liquid wastes are produced by thermal power plants, coal distitation plants etc.

The widc variety of liquids stored in tanks and transported by road rail or in pipelines represent, in the event of accidents-spills or leakage, potential threats to ground water, particularly shallow water table aquifers. The magnitude of such incidents may range from leakage of a few cubic meters of oil from a domestic tank, which in itself could jeopardise adjacent, shallow domestic water supply wells, to several thousand cubic meters loss from undetected leaks in pipelines (Venlocke et.al.,1975).

2.3 Mining Activity

The waste products of querrying for building stone, lime for cement and agricultural use, filters (gypsum, barytes, etc.) and road stone are generally inert. These wastes import few additional chemical characteristics to water percolating through them, with the possible exception of increasing the suspended solids load if crushed material is present.

The principal solid mining wastes that have a potential to pollute ground water come from coal and metal ore exploitation. (Table 4) In the former case, the waste rock generally consists of pyrite rich (FeS_2) shales and sendstones. Weathering of these shales and sandstones causes oxidation of the disseminated sulphides leading to the formation of sulphate ions, a lowering of the pH, and the mobilization of iron & manganese. This produces a leachate high in sulphate, iron and dissolved and suspended solids and low in pH. Similarly leachate form disseminated sulphide ores may produce leachate rich in above mentisoned pollutants along with high dissolved and particulate metal concentrations (Fig. 2).

Drainage waters from collieries characteristically

Table 4 : Pollutants resulting from miniming activities

Source	Potential Characteristics of leachate/effluent	Rate of effluent production or rate of solid-waste production
	(a) Mining, solid wastes	
Coal-min drainage	High total dissolved solids, suspended solids. Iron, Often acid. May contain high chlorides from connate water	10^5 - 10^7 m^3/year
Colliery wastes	Leachate similar to mine drainage waters	10^5 - 10^7 tonnes/yr. of wastes per collery. Quantity of leachate dependent on climate
Metal's	High total suspended solids. Possibly low pH. High sulphates from oxidation of sulphides. Dissolved and particulars metals. Washing and mineral dressing waters may contain organic flocculants	10^5 - 10^7 tonnes/yr wastes per mine Quantity of leachate dependent on climate
	(b) Mining, liquid wastes	
Oil and gas well brines	High total solids (10^3-10^5 mg/l) High $CA^{2+}$and Mg^{2+}(10^2-10^5 mg/l) High Na^+ and K^+ (- 10^4 mg/l) High Cl^-(10^4-10^5 mg/l) High SO_4^{2-}(10-10^3mg/l) Oil, up to 10^3 mg/l Possibly high temperature	10^3-10^4 m^3/day per well
Saline intrusions, due to overpuming close to coastlines and estuaries	Na^+ 10^3-10^4 mg/l Mg^{2+} 10^2-10^3 mg/l Ca^{2+} 10^2 mg/l K^+ 10^4-10^2 mg/l Cl^- 10^3-10^4 mg/l SO_4^{2-} 10^2-10^3 mg/l Alkalinity (as $CaCO_3$) 10^2 mg/l	Landward movement rate of saline wedge varies with pumping regimes and aquifer type. Example: 4 km in 40 yrs (1925-65)along estuary of R.Thames, UK.

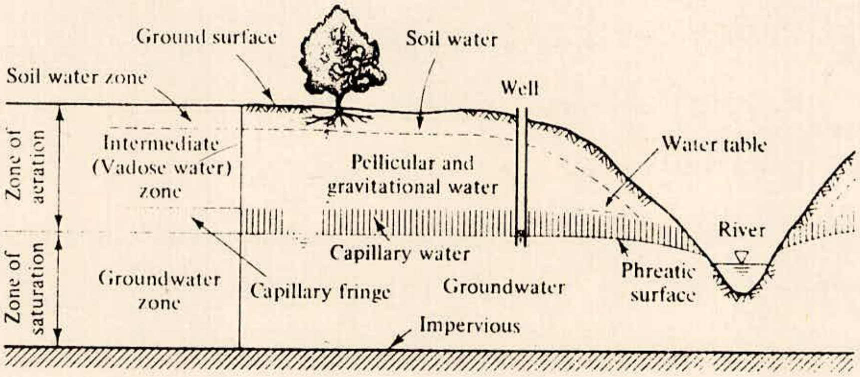

Fig. 2 : Subsurface moisture zones

possess both high suspended and dissolved solids, particularly iron and sulphate ions resulting from the oxidation of ferrous sulphides in the host rock. Chloride concentration may also be high because of connate water trapped within the sedimentary rock. Headworth and Wilkinson (1977) have described an example from England where 13 Km^2 of chalk aquifer has been contaminated as a result of the discharge of mine drainage water since 1907.

Drainage water from metal ore mines contain lower concentrations of chloride and sulphate, but higher concentration of dissolved heavy metals. Organic flocculents are often present in waste water from the screening and dressing of ores on site.

Concentrated brines, often containing traces of hydro-carbons, and at high temperature, are frequently associated with oil and gas reserves. Duriang the inital phases of development of such resources the hydro-carbon/water systems are often under artasian conditions and contamination of overlying aquifer system may occur as the result of either allowing the liquids to spill out on the surface and percolate down into shalalow aquifers, or by upward leakage around incompletely qruted production well causings.

Graound water contamination may occur indirectly as a result of ground water development. High rates of pumping close to the coast or estuaries may lead to the land ward migration of saline water underlying the fresh ground water wedge with the result that coastal boreholes may be come contaminated with salt water (IHP, 1978).

3.0 TYPE OF SUBSURFACE POLLUTANTS

The pollutants generated by various human activities (as described in previous chapter) can be grouped into three major groups i.e.

i) Inorganic pollutants

ii) Organic pollutants

iii) Biological pollutants

3.1 Inorganic Pollutants

Major inorganic pollutants are heavy metals, nitrate, phosphorous, cynide, carbonate, chloride, sulphate, fluoride etc. Inorganic pollutants are generally soluble in water.

Contaminated ground water generally shows increased levels of chloride, sulphate and sodium ions. Elevated nitrate levels upto 50-100 mg/L are not exceptional in contaminated ground waters (Csaki and Endredi, 1981, Zoeteman et al.1981). Levels of metals in contaminated soil and ground water can also reach very high values near dumps of specific waste material and under conditions of low pH and low redox potential.

Presence of certain elements or compounds in water supplies poses possible health risks to human beings and animals. Precise toxicological limits have been determined for relatively few potential contaminants. In many cases the effect on individuals varies according to their state of health, age, diet, body weight and other factors.

A summary of possible health effects of selected inorganic contaminants is given in Table 5.

3.2 Organic Pollutants

Organic pollutants include mineral oils (e.g. fuels, heating oils, motor oils and cutting oils), pesticides (e.g. herbicides, insecticides, fungacides, nematocides), chlorinated hydrocarbons and aromatic hydrocarbons. Organic pollutants are generally partially soluble in water, solubility of some of the pesticides is shown in table 6.

Like chlorides and related inorganic ions, some organic contaminants are often easily transported through the soil. Compounds like chlorinated hydrocarbons and aromatic hydrocarbons are found most frequently near contaminated sites (Giger and Schaffner, 1981; Zoteman et al., 1981). Due to their high water solubility and resistance to biological or chemical degradation, these volatile chemicals remain in ground water for many years. Retardation of these chemicals during ground water movement is related to the carbon content of the solid phase and the octanol-water partition coefficient of the chemical.

Beside these compounds a large group of more polar, halogenated substances can be present in ground water e.g. bis(-2-chloroisopropyl) ether and trifluoromethyl aniline (Zoeteman et al.1980). In contaminated anaerobic ground waters organic sulphides have been found, such as diprophyldisulfide, and chlorinated dialkyl sulfides, which are supposed

Table 5: Health and other risks associated with the presence of selected inorganic contaminants in ground water

Contaminant	Toxicity to humans (assuming 80 Kg body weight)	Other effects
Arsenic	Fatal dose in 130 mg cumulative	Possibly carcinogenic at lower values
Barium	Fatal dose in 600 mg cumulative	
Boron	Fatal dose 5-20 g	Nausea and intestinal cramp at lower concentrations
Calcium		Possibly contributes to gallstone formation at high concentration Non cumulative
Cadmium	Fatal dose in 9 g	Cumulative in liver, Kidney and pancreas
Chloride		Emetic at high levels,. High concentrations undesirable for heart diseases.
Copper		Large concentrations (2 mg/day) act as intestinal irritant leading to vomiting Non cumulative
Cynide	Fatal dose - 50 mg	
Iron		Taste and colour objectionable above 0.1 mg/L.
Lead	Cumulative poison	
Magnesium		Objectionable taste, possibly related to encephalitis-like disease at high concentration.

Table 6 : Solubility of pesticides in soil water

Pesticide	Solubility (mg/L or ppm)
Chloroamben	700
2,4 - D	620 (Acid)
Propham	32-250
Bromacil	815
monuron	230
Sima zine	5
Puopa zine	-
Dichlobenil	-
Atra zine	70
Chloropropham	89
Prometone	-
Ametryn	185
Diuron	42
Prometryne	48
Chloroxuron	4
Paraquat	Very soluble
DDT	0.01

to be reaction products of alkylbromides and hydrogen sulfide.

Organic compounds are generally carciogenic and mutagenic Toxicity of some organic pollutants is given in Table 7.

3.3 Biological Pollutants

Pollution of ground water by biological pollutants is mainly due to presence of pathogenic bacteria and virus.

Bacteria are unicellural micro-organic with rigid bodies, similar in size to fine silt or coarse clay particles (0.5 to 10 μ m), whose mobility in ground water flow system may be limited by infiltration in the rock pores.

Viruses are smaller microbes than bacteria, being from 20 to 200 nm (10^{-3}m) in size. Biologically they are parasites which are incapable of reproduction outside a host organism. Due to their small size viruses are capable of passing through an ultramicro-scopic filter. The most important pathogenic bacteria and viruses which ought possibly be transported to the subsurface water are (Gerba and Keswich, 1981),

Bacteria: Salmonella sp., shigell sp., yersinia enterocolitic, y.pseudotuberculosis, leptospira sp., francisellatubarensis, dyspepsiacoli, vibrio sp., legionell sp. and ETEC

Viruses: hepatitis virus, polio virus, coxsackie virus, adenovirus, rotavirus, and Norwalk-like virus

The presence of these bacteria and viruses can cause health risks, such as:

Table 7 : Toxicity of organic pollutants

Contaminant	Toxicity to mammals	human health criteria (Majetic and Clark 1980)
Bis (2-ethyl-hexyl)pthalete	-teratogenic and cytotoxi to mammals	10 mg/L
Dioutyl phthalate	- teratogenic to mammals	160 mg/L
Diethyl phthalate	- terotogenic, mutagenic and carcinogenic to mammals	60 mg/L
Dicnlorabenzena	- affects the central nervour system adversely	1-100 mg/L
	- caises b;ppd dosprder. - disrupts normal enzyme activity in the livers and kidneys of rats	0.230 mg/L
	- affects skin and respiratory system of of human	
	- carcinogemic to mammals	
Nephthalena	- causes development of cataracts - teratogenic to human	0.46 mg/L
Toluene	- may be teratogenic	17.4 mg/L
Tetrachloro athylene	-affects the central nervour system -teratogenic, mutagenic and carcinogenic to mammals	8 m/L
Lindane	- carcinogenic	0.02 g/L

s) Typhoid/paratyphoid (Entric fewer), (b) cholera,

c) Bacteria dysentary, (d) Amoebic dysentary,

e) Gastroentritis, (f) Leptospiral jaundice (Weil's diseases),

g) Poliomyetitis, and (h) Epidemic infective hepatitis.

Apart from these three groups, radioactive pollutants are also of great concern. Six radionuclides are of special hydrogeological concern due to their toxicity, environmental mobility and relatively long half life (Table 8).

Five of the six radionuclides -^{3}H (Tritium), ^{90}Sr, ^{129}I, ^{137}Cs and ^{239}Pu are created in the process of nuclear power generation and may enter ground water flow systems either by intentional release or accidental escape from radioactive waste management facilities or also from nuclear weapon testing.

Table 8 : Nuclear and Health Physics data for selected Radionuclides

Radionuclides	Half life (Years)	Major Radiation	Critical Organ	Biological half-life	MPC(1) (Ci/ml)
^{3}H	12.26	β	Total body	12 days	3×10^{-3}
^{90}Sr	28.1	β	Bone	50 Years	3×10^{-6}
^{129}I	1.7×10^{7}	βγ	Thyroid	138 days	6×10^{-8}
^{137}Cs	30.2	ργ	Total body	70 days	2×10^{-3}
^{226}Ra	1600	αγ	Bone	45 days	3×10^{-8}
239	24,400	αγ	Bone	200 years	5×10^{-6}

(1) Maximum permissible concentration for water consumet by members of general public without readily apparent ill effects.

4.0 SUBSURFACE ENVIRONMENT AND POLLUTANTS

4.1 Subsurface Environment

Subsurface environment here means the conditions in which water occurs beneath the ground surface i.e. the occurrence of water with respect to subsurface material.

The subsurface occurrence of ground water may be divided into zones of saturation and aeration. In the zone of saturation all interstics are filled with water under hydrostatic pressure. The zone of aeration also known as unsaturated zone, consists of interstices occupied partially by water and partially by air. Over most of the landmasses of the earth a single zone of aeratin overlies a single zone of saturation and extends upwards to the ground surface, as shown in Fig.2. The zone of saturation is bound at the top by either a limiting surface of saturation or overlying impermeable strata such as clay beds or bedrock. Water occuring in the zone of saturation is commonly referred to simply as ground water.

As far as pollutants are concerned the unsaturated zone acts as the buffer between human activity and the ground water source. As such, it serves two functions: as reactor and as storage reservoir. Unlike from a storeroom, it is almost impossible to retrieve a pollutant from the unsaturated zone. A pollutant which enters the top soil is transferred by the water movement through big reactor, and if it is not decomposed, or become consumed by vegetation

, or attached to the soil material, it will finally reach the aquifer and contaminate the ground water. Thus unsaturated zone can be considered as a pollutant filled time bomb, which ticks slowly, but will eventually explode.

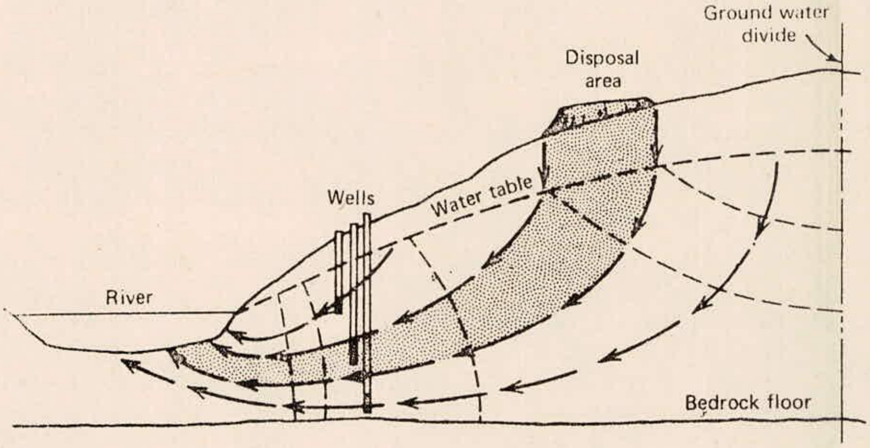

Fig. 3 : Flow of contaminants in a water table aquifer (humid region)

Once dissolved contaminants reach the water table, they enter the groundwater flow system the direction of which depends upon the hydraulic gradient, Fig.3. All pore spaces between soil particles below the water table are saturated. The relative unavailability of dissolved oxygen in the saturated zone limits the potential for oxidation of pollutants. Varying levels of attenuation may still take place, depending on the geologic conditions.

To assess the amount of pollutants reaching the ground water system (saturated zone), it becomes important to know the behaviour of various pollutants in the subsurface environment.

4.2 Behaviour of pollutants in Subsurface Environment

4.2.1 Inorganic pollutants

The most important inorganic pollutants in subsurface are nitrates and heavy metals.

Nitrate:

The use of a small area for waste disposal can produce severe NO_3 leaching problem in localized area, but by far the most extensive problem of NO_3 in the unsaturated zone is generated by vast areas of agricultural land under intensive crop production.

The N cycle has been presented in many different forms and degrees of detail involving transformation in soils, waters, air, plants and animals. However, the simplified biological N cycle presented by the Panel of Nitrates (1978) illustrates the behaviour of N in the soil (Fig.4). Organic N, the reservoir of N in soil, mineralizes by ammonification and then by nitrification. The conversion of NO_2^- to NO_3^- is usually much faster than conversion of NH_4^+ to NO_2^- so that NO_2^- exists in very small concentration and NO_3^- is the final stable product of the mineralization process in well aerated soils. Any of the mineral forms (NH_4^+, NO_2^-, and NO_3^-) can be assimilated by plants and micro organisms and return to the soil as organic N. The dentrification fixation reaction represent a loss to the atmosphere and a return to the soil system.

As a first approximation, NO_3^- in the soil system, including the unsaturated zone beneath the soil root zone, moves with and at the same rates as the movement of the

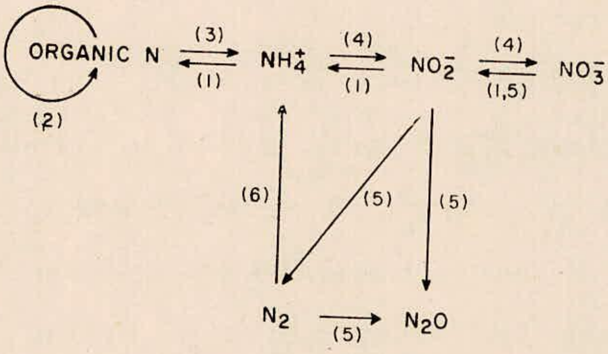

Fig. 4 : Simplified biological N cycle showing major reactions. The numbers in parentheses indicate processes: (1) conversion to organic forms, i.e., assimilation: (2) transformations within the organic pool: (3) ammonification: (4) nitrification: (5) denitrification: (6) fixation (Panel on Nitrates 1978).

percolating water. However, the relative rate of the flux of NO_3^- with respect to that of water is dependent on the chemical property of the soil material. The relative $N\bar{O}_3$ flux in positively charged soils that absorb NO_3^- is less than unity, where as in negatively charged soil materials that repel NO_3^-, it is greater than unity. In neutral soils, the relative flux is near unity (Prett & Jury, 1985).

A number of investigators have found that acid kaolinitic and amorphous soils absorb NO_3^- and that adsorption is greatest in volcanic ash derived soils having largely allophanic minerals (Rich and Thomas 1960, Thomas 1960, Singn and Kanehiro 1969, Kinjo and Prett, 1971, Schalscha et al.1974). Kinjo and Pratt (1971) and Leon and Pratt (1974) found that 3 or 4 pore volumes of effluent were required to move peak concentrations of NO_3^- to the bottom of columns of allophenic subsoil materials and that about 6 or 7 pore volumes were required to remove essentially all the NO_3^-.

On the other extreme, the flux of NO_3^- in soils that contain dominantly smectite clays (montamorillonites and micaceous minerals) is faster than that for water because of anion exclusion from a fraction of the soil water (Berg and Thomas 1969, Dyer 1965, Thomas and Swaboda 1970, Smith 1972, Bresler 1973a, Bresler and Laufer 1974, Appelt et al.1975, Tullock et al.1975). Tullock et al.(1975) correlated the relative rate of flux of Cl^- and water through laboratory columns with the cation-exchange-capacity (CEC) of soils.

From all comparative studies, the movement of Cl^- and NO_3^- behave identically in such studies so that data for Cl^- can be used to predict the behaviour of NO_3^-. Relative flux for NO_3^- and/or Cl^- in such column studies range from 1.0 to 2.0 for soils containing smectite clays, indicating that the effects of exclusion volume can be demonstrated in laboratory columns. However the practical effects of both positive and negative adsorption on the movement of NO_3^- in field situations have not been demonstrated.

Heavy metals

Heavy metals show poor geochemical mobility in unsaturated zone resulting from low solubilities, from adsorption and ion exchange effects on minerals or organic materials e.g. clay or humic substances, from precipitation and coprecipitation, and from the fixation in biological material or in newly formed mineral substances.

The solubility of the heavy metals is generally controlled by the most abundant anions in natural water i.e. hydroxide, hydrogen carbonate, carbonate, sulfate, chloride, nitrate and sulfide. Solubility of some of the heavy metals is listed in Table 9. Complexation by inorganic or organic complex forming substances may change the solubility in pore solutions of the unsaturated zone, e.g. fulvic acids, tartaric acid, citric acid, and salicilic acid tend to increase solubility whereas humic acids chelates to low solubility. The change in Eh, pH, temperature or the composition of pore solution causes the precipitation of some compounds. In the precipitate some foreign ions are commonly trapped in or substituted within the structure

Table 9 : Solubility products of different heavy metals

		(at 25°C)
$BaSO_4$	$(Ba^{2+})\ (SO_4^{2-})$	1.08×10^{-10}
$CuCO_3$	$(CU^{2+})\ (CO_3^{2-})$	1.37×10^{-10}
$FeCO_3$	$(Fe^{2+})\ (CO_3^{2-})$	2.11×10^{-11}
$RaSO_4$	$(Ra^{2+})\ (SO_4^{2-})$	4.25×10^{-11}(20°C)
$ZnCO_3$	$(Zn^{2+})\ (CO_3^{2-})$	6×10^{-11}
$PbCO_3$	$(Pb^{2+})\ (CO_3^{2-})$	1.5×10^{-13}
$Ni\ (OH)_2$	$(Ni^{2+})\ (OH^-)^2$	1.6×10^{-14}
$CdCO_3$	$(Cd^{2+})\ (CO_3^{2-})$	2.5×10^{14}
$Fe(OH)_2$	$(Fe^{2+})\ (OH^-)^2$	1.65×10^{15}
$Mn\ (OH)_2$	$(Mn^{2-})\ (OH^-)^2$	7.1×10^{-15}
Hf_2CO_3	$(Hg^+)^2\ (CO_3^{2-})$	9×10^{-17}
HgCl	$(Hg^+)\ (Cl^-)$	2×10^{18}
Nis	$(Ni^{2+})\ (SS^{2-})$	2×10^{-21}
Zns.β	$(Zn^{2+})\ (S^{2-})$	1.1×10^{-24}
Pbs	$(Pb^{2+})\ (S^{2-})$	3.4×10^{-28} (18°C)
CdS	$(Cd^{2+})\ (S^{2-})$	3.6×10^{-29}
$Fe(OH)_3$	$(Fe^{3+})\ (OH^-)^3$	4×10^{-38}
Cu_2S	$(Cu^+)^2\ (S^{2-})$	2×10^{-47} (18°C)

of the newly formed substances. This process (called coprecipitation) is very effective in removing trace elements e.g. Cu, Pb, Zn, W and V, when Fe $(OH)_3$ and $Mn(OH)_2$ are precipitated. Radium is coprecipitated when barite is formed.

Clay minerals, zeolites, hydroxides of iron and manganese, humic substances, plant roots, microbial slimes, and microorganisms adsorbs the heavy metals, because these substances have surface with small unbalanced electrical changes which attract ions from water.

The hydrogeological implications of the complexing of the transition metal ions (e.g. Fe, Mn, Co, Zn, Pb, Cu, Ni, Cr) by inorganic or oroganic ligands alter their adsorption or precipitation from solution. The adsorption of radioactive cobalt and zinc is significantly decreased in the presence of dissolved oroganic carbon (DOC) compounds, which are found in all natural waters. This decrease is due to the formation of organo-cobalt and organo-zinc complexes, whose sorption behaviour may differ from that of the hydrated metal ions and whose increased solubility in solution reduces the effectiveness of precipitation (Jacson et al.1980).

4.2.2 Organic pollutants

Organic pollutants which come in contact with organic and inorganic solid phase of the unsaturated zone may move and interact with it, a process which leads to changes in the properties of the pollutants or of the unsaturated zone. The physico chemical processes in the unsaturated zone involved consist of adsorption, formation of bonded residues, and surface conversion of the contaminants.

The main groups in organic pollutant are pesticides and aromatic compound. The interaction of these compounds in unsaturated zone is discussed briefly.

i) Pesticides

These organic compounds are quite varied in their structure and thus also in chemical properties. There are also extreme variations in their rates of decomposition in soils and sediments. The mobility of a pesticide in soils depends upon adsorption by minerals or organic matter. Adsorption retards the movement depending upon the residence time of the molecule on the absorbing surface.

The herbicides diquat and paraquat are removed by way of adsorption of organic cations by ion exchange. Scott and Weber (1967) showed that paraquat is rendered unavailable to plant roots when it is adsorbed by montmorillonite. Similarly, Weber and Coble (1968) showed that diquat become unavailable for microbial degradation when it is adsorbed on smectite, but is degradable when it is on the external surfaces of kaolinite.

Many pesticides (e.g. triazines) are organic bases that have the potential for being adsorbed through protonation at mineral surfaces. Weber (1970) has discussed the chemistry of these chemicals and their reactions with and adsorption by colloids in soils and sediments.

Other kinds of pesticides form complexes with exchange cations on minerals but through less energetic bonds e.g. ethyl dipropyl thiolcarbamate (EPTC)(Mortland and Meggitt, 1966). These complexes are stable against atmospheric moisture, but when placed in water, they are displaced from the mineral surface. Therefore EPTC is likely to stay in the solution phase and move with the water.

Some pesticides have very little affinity for mineral surfaces and have very low solubility. Since mineral surfaces are generally hydrophilic, such species are not attracted. An example is DDT, which has very low solubility. Work by Shi (1970) strongly suggests that certain fractions of soil organic matter are the main sites of DDT adsorption and that the mineral fraction adsorbs very little of the compound. Thus DDT is expected to move through the unsaturated zone alongwith the suspended oroganic solids (Vinten et al.1983).

The pesticides in unsaturated zone may also degrade with time. The degradation may be chemical reaction (Konard et al.1969, Armstrom and Konard 1974, Yaron and Saltzman 1978, Saltzman and Mingelgrin 1984) or biological activity (Andus 1960, Helling et al.1971, Kaufman 1974).

ii) Aromatic compounds

The reaction of this group of chemicals with soil matrix is extremely varied. Their properties depend upon the structure and in particular the functional group they possess. For example, analine is a base and may be adsorbed in its cationic form by mineral surfaces.

The halogenated aromatic molecules are generally characterised by low solubilities in water and relatively little adsorption on mineral surfaces from water solution. Organic matter in soils and sediments act as much more effective absorbent for these materials (Filinow, et al.1976) So these compounds (PCB's or PBB's) move in percolating water as extremely small particulates and also in solution but in very low concentrations not more than a few parts per bilion. Chlorobenzenes are not adsorbed on mineral surfaces as long as the surfaces are hydrophilic but can be adsorbed if the surfaces become hydrophobic, or conversely , organophilic (McBride et al.1977). Similar is the case with benzene.

Though benzene has no functional group in its structure, yet its electron cloud is capable of interacting with some electron accepting transition metal ion such as Cu(II), Ag(I), Fe(III), and VO(II) when they occupy exchange sites on some clay mineral surfaces (Pinnavaia et al.,1974). By this interaction either coordination complexes or radical cations of benzene are formed which can be adsorbed on clay mineral surfaces. A number of alkylbenzenes and other aromatic molecules such as toluene, anisole, napthalene and anthracene undergo similar ractions.

4.2.3 Biological pollutants

The unsaturated zone, especially its upper few meters, is a large microbiological reactor. It is infested with microorganisms and many biochemical as well as chemical, physical, and physiochemical reactions take place in this zone.

Microorganisms tend to become concentrated at solid surfaces of particles rather than to be uniformly dispersed. Such interactions with clays or organic matter may have important consequences for their survival. Bacteria clay agglomerates give some protection to the organism and also provide some nutrition via the exchangeable cations. The nature of the physical chemical attachment of microorganisms to sand, silt, and clays has been studied by Stotzky (1966a, 1966b, Lammers (1967), and Boyd et al.(1969).

Adsorption of viruses by particulate matter, including minerals, is an important phenomenon in soils and sediments. For example Serg (1973) showed that poliovirus can be strongly adsorbed on silt particles and that very little of it can be subsequently eluted.

5.0 MOVEMENT OF POLLUTANTS IN SUBSURFACE ENVIRONMENT

The modelling of pollutants transport in the subsurface environment deals with the formulation of a conceptual frame work and subsequent quantitative relationships, which permit one to determine the distribution of pollutants in space and time. Models are needed to understand the influence of various mechanisms involved in the transport process on one hand and in order to predict the pollutants transfer on the other hand.

In the following sections the transport models for various type of pollutants have been discussed. Inorganic pollutants are generally highly soluble in water, hence behave as solute. Inorganic pollutants are partially soluble. Insoluble portion of the organic pollutants behave as immiscible fluid and hence ceate the problem of multiphase flow system.

All these types of transport models are discussed below:

5.1 Solute Transport in Subsurface Environment

5.1.1 Saturated zone

Solute transport in generally viewed as the net effect of two processes, advection and dispersion. Advective transport is attributed to the average motion of the fluid. In processes involving displacement of miscible fluid in one dimension, with advection the only transporting mechanism, a sharp front would be maintained between the initial and displacing fluids, and this front would move at a velocity equal to the average linear pore-water velocity. The advective solute flux is given by

$$\bar{J}a = \bar{q}c \qquad \ldots (1)$$

Where $\bar{J}a$ is the mass of solute crossing a unit area of porus medium oriented normal to the flow direction per unit time $[Ml^{-2}T^{-1}]$, $\bar{q}$ is the specific discharge or Darcy flux $[LT^{-1}]$, and C is the solute concentration (mass of solute per unit volume of solution) $[ML^{-3}]$.

Dispersion causes mixing at the interface between two fluids of different composition, and, as defined by Fried (1975) "....is the occurrence and evolution of a transition zone between two domains of the fluid phase with different composition". Bear (1972) further described dispersion as being nonsteady and irreversible. The effects of advection and dispersion are shown in Fig.5, for one dimensional displacement of miscible fluids.

Dispersion is the result of the thermal kinematic energy of the molecules, which, in the presence of a concentration gradient, results in a net flux of solute toward the low-concentration zone. By modifying Fick's first law to account for the presence of the solid phase, the diffusion flux in porous medium becomes

$$\bar{J}_d = -\eta D_d \,\text{grad}\, C, \qquad \ldots (2)$$

Where $\bar{J}_d$ is the diffusive solute flux (mass of solute per unit area of porous medium per unit time due to diffusion) $[ML^{-2}T^{-1}]$, D_d is the coefficient of molecular diffusion

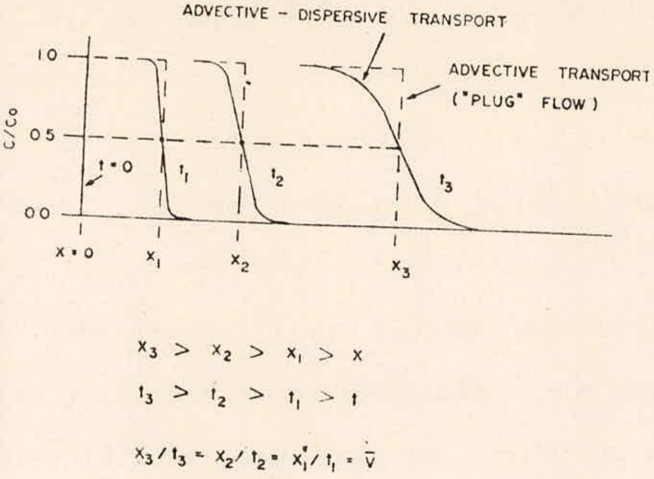

Figure 5 : Schematic representation of the advective and dispersive solute transport processes.

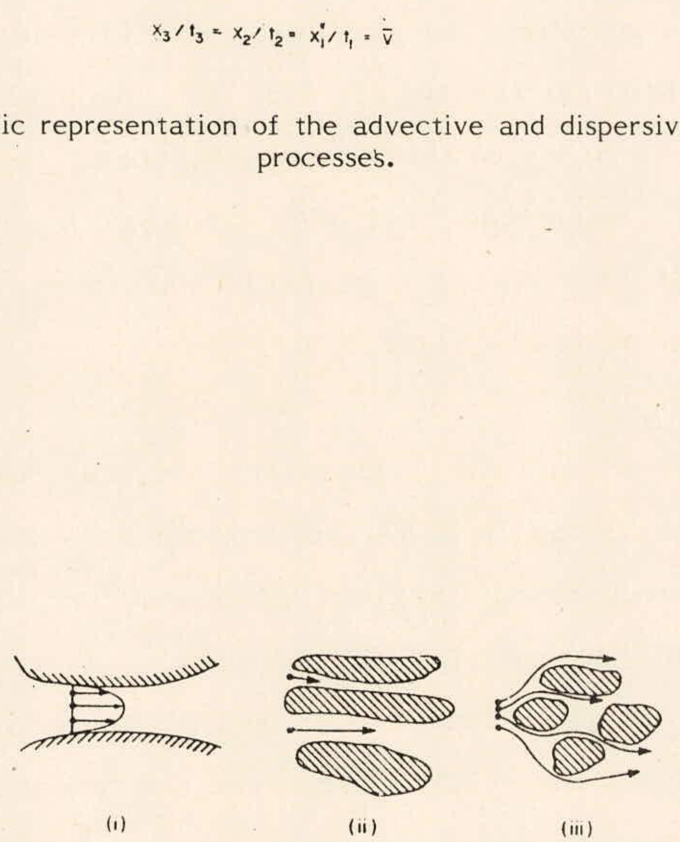

Figure 6 : Microscropic components of mechanical mixing

in the porous medium (effective diffusion coefficient)(L^2T^{-1}], is the porosity of the medium, and C is the solute concentration. The porosity term is introduced because the cross sectional area available for diffusion is reduced by the presence of the solid phase.

As a consequence of the tortuous diffusion pathway within the porous medium and the presence of the solution-solid interface, the effective diffusion coefficient is generally less than the diffusion coefficient in free solution, D_o. From a review of data on unconsolidated granular media obtained by several investigators, Perkins and Johnston (1963) suggested that the value of D_o/D_d is approximately 0.707. This is in reasonable agreement with the expression given by Bear (1972).

$$D_d = D_o \qquad . . . (3)$$

Where is the tortuosity of the granular medium, with a value close to 0.67, as suggested by Bear.

The mechanical mixing component of the dispersion process is the result of velocity variations within the porous medium. For homogeneous media, there are three microscopic mechanisms that give rise to velosity variations. These mechanisms include, (i) the velocity distribution associated with the flow of viscous fluid through a pore, (ii) variations in velocity as a result of different pore geometries, and (iii) fluctuations in the stream lines with respect to the mean flow direction (Fig.6). The mechanical mixing component of dispersion is analogous to diffusion in that spreading of the solute is the result of velocity variations across a concentration gradient. Consequently, on the macroscopic scale, the mechanical mixing component of the solute flux is commonly represented by an equation analogos to equation (2).

$$\bar{J}_m = -\eta D_m \text{ grad } C, \qquad \ldots (4)$$

Where D_m is the coefficient of hydrodynamic mechanical dispersion. Adding equations (2) and (4) gives the dispersive flux ($\bar{J}$) of the solute as

$$\bar{J} = -\eta D \text{ grad } C, \qquad \ldots (5)$$

Where D is the dispersion coefficient, defined as

$$D = D_d + D_m \qquad \ldots (6)$$

Recognising the advective and dispersive flux component, and applying the principle of conservation of mass gives

$$\frac{\partial(\eta c)}{\partial t} = \text{div } (\eta D \text{ grad } C - \bar{q}C) \ldots \qquad (7)$$

The specific discharge $\bar{q}$ in equation(7) is generally replaced by the average solution velocity according to the relation.

$$\bar{v} = (\bar{q}/\eta)^{w} \qquad \ldots (8)$$

Where $\bar{v}$ is the average solution velocity LT^{-1} and w is an empirical exponent. The work of Ellis and others (1968), as well as many other one dimensional miscible displacement experiments, indicates that the value of the exponent is very nearly 1 in granular materials and varies between 1 and 2 in other materials.

Substituting equation (8) into equation(7) and assuming the porosity to be constant and the fluid incompressible, gives

$$\frac{\partial c}{\partial t} = \text{div } \text{[illegible] grad } C) - \bar{V} \text{ grad } C \qquad \ldots (9).$$

This is frequently referred to as the advective-dispersion equations of simply the dispersion equation for solute transport. A rigorous development of equation(9) shows the tortuosity and dispersion coefficient to be second rank tensors)Bear, 1972).

Although equation (9) is in a more general form than is commonly applied to problems of contaminent migration, it is nevertheless subjected to several assumptions and limitations:

1. The contaminents are soluble in water.
2. The fluid properties (density and vescosity) are independent of solute concentration.
3. The fluid is incompressible
4. The coefficients of molecular diffusion and mechanical mixing are additive
5. Equation (8) is applicable
6. The solute is non reactive

A large number of laboratory experiments have been conducted to determine the validity of the advection-dispersion model. The majority of these have been one-dimensional miscible-displacement experiments in which the concentration history of the column effluent was compared to the concentrations predicted by the model. Under these conditions, and assuming the medium to be homogeneous, equation (9) reduces to

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - \bar{v} \frac{\partial c}{\partial x} \qquad \ldots (10)$$

Where x is the direction of flow and D_L is the component of the dispersion tensor in the direction of flow (longitudinal dispersion coefficient).

Solution of eq.(10) for a finit column (Brenner, 1962) result in almost straight lines when C/Co is plotted against log of pore volume (l_n ρV) on probability paper (Passioure and Rose, 1971). Other commonly used solutions of equation (10) are those of Ogata and Banks (1961), for a semi infinite medium, and of Danckwerts (1963), in which dispersion is treated as diffusion about a moving plane. These solutions are good approximations of the Brenner solution, and also the break through curve is symmetrical and passes through the point $C/C_o = 0.5$ and PV = 1.0, provided values of $\bar{V}L/D$ are large (Rose 1973).

In comparing predicted and measured breakthrough curves for non-reactive tracers, experimental variability undoubtedly contributes to the observed differences, nevertheless by considering a large amount of experimental data, Scheideggar (1963) concluded that consistant discripancies do occur. These discrepancies have been attributed to the presence of dead and pores (Baker 1977; Fatt et al.1966; Coats and Smith, 1964; Deans 1963) and to solution solid interface processes not accounted for in the spatial averaging process (Fried, 1975). Fried further explained that discrepancies between measured and predicted results seldom exceed 2 to 3% and concluded that, for practical purposes, the model is a good representation of dispersion process.

Although the conclusion of Fried appears to be appropriate for coarse grained geologic materials, a number of situations have been identified for which the advection-dispersion equation is not an adequate model (Gillham and Cherry, 1982). In fine grained materials where an anion was used as the tracer, the earlier appearance of the break through curve has been attributed to anion exclusion (Appelt et al.1975, Thomas and Swoboda, 1970, Kemper and Rollins, 1966). In aggregated media, an extreme tailing of the break through curve has been attributed to diffusion into or out of the aggregates (weeks et al.1976, Passioura, 1971, Parrioura and Rose 1971, Philip 1968), and similar effects observed for partially saturated media have been attributed to diffusion into relatively immobile zones of water (Bigger and Nielsen 1960, Orlob and Radha Krishna 1958). Typical deviations from the model are shown in Figure 7.

Numerous analytical solutions to eq.(9) are described in literature (Ogata and Banks, 1961, Brenner 1962, Biggar and Nielsen 1976, and Ogata 1970), most of which represent one dimensional cases for steady flow in homogeneous semi finite or finite porous media. Solutions for homogeneous media with uniform steady flow and three dimensional dispersion are described by Baetsle (1967, 1969) for contaminents entering the systems at point sources, and by Codell and Schreiber (1979) for point source, line source, and planar source inputs. Lenda and Zuber (1970) have presented various analytical solutions, including one for a cuboid source in a uniform, homogeneous flow field. The most comprehensive set of analytical solutions to the advection dispersion equation was prepared by Cleary (1978) who developed solu-

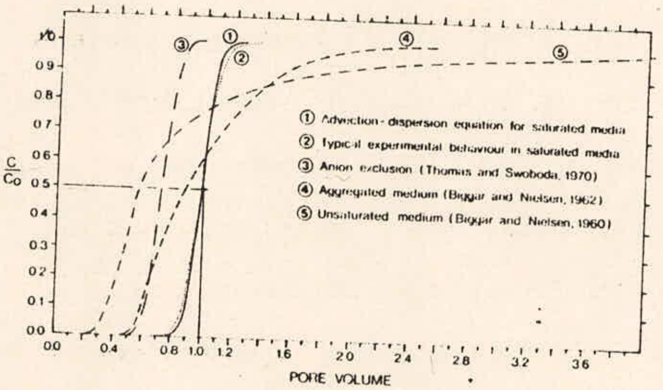

Figure 7 : Typical deviations from the break-through curve in saturated porous media predicted by the advective-dispersion solute transport model.

tions to cases covering a variety of contaminent input conditions including time dependent inputs of finite volume and concentration.

5.1.1.1 Transport concept for hydrogeologic systems

The good agreement between laboratory measurements and simulations based on the advection dispersion equation has led in recent years, to the direct application of the advection dispersion model to numerous problems of contaminent migration in various field situations. The extension of the model to field problems is problematic because geologic deposits are normally very heterogeneous at the macrosiopic scale. In contrast, the porous media used in laboratory experiments are relatively homogeneous or include only simple heterogenities. In this section the nature of the transport processes in the context of the conditions that exist or appear to exist in field situations and the role of advection, mechanical dispersion and molecular diffusion will be considered.

Molecular diffusion

Solute migration studies have generally been concerned with aquifer and the impact of contaminents on ground water supply. As a result, hydrogeologists have generally assumed advection to be the primary transport process, whereas laboratory experiments have provided considerable information on the nature of the dispersion process, such as the effect of velocity on the dispersion coefficient. Much of the available data was compiled by Perkins and Johnston

(1963) and later by Rose (1973). Fig.8a is a graph of dimensionless dispersion coefficients D_i/D_o versus peclet number Pe, defined as Vd/D_o, whereas d is a characteristic length of the medium, generally taken to be the mean grain diameter. The figure also includes a graph of the emperical equation of Perkins and Johnston (1963)

$$\frac{Di}{Do} = \frac{Dd}{Do} + 1.75\,\frac{\bar{v}d}{Do} \qquad \ldots (11)$$

The physical interpretation of the figure suggests that at low velocities (low Pe) the dispersion process is predominentaly the result of molecular diffusion, whereas at high velocities mechanical mixing process predominates. At intermediate values of pe, both diffusion and mechanical mixing play a significant role in the dispersion process.

For steady flow in the x-direction and dispersion in the x- and y-directions, and assuming the medium to be homogeneous and isotropic, equation (9) becomes

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} + D_T\,\frac{\partial^2 c}{\partial x^2} - \bar{v}\,\frac{\partial c}{\partial x} \qquad \ldots (12)$$

Where L_T is the dispersion coefficient in the y-direction, normal to the direction of flow. Figure 8b is a graph of the emperical relationship between D_f and P_e derived by Perkins and Johnston (1963)

$$\frac{DT}{Do} = \frac{Dd}{Do} + 0.055\,\frac{\bar{v}d}{Do} \qquad \ldots (13)$$

Thus the longitudinal and transverse dispersion coefficients appear to be related to the paclet number in a similar manner; however, diffusion controls the transverse dispersion to peclet numbers of approximately 1.0, but

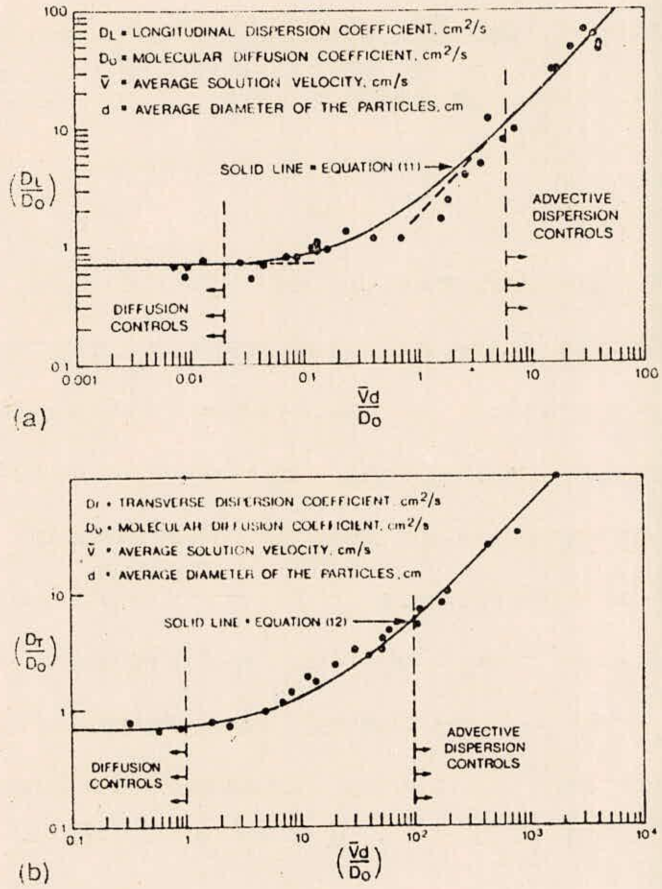

Figure 8 : Graphs of the dimensionless dispersion coefficient versus Peclet number, $\overline{V}_d/D_0$. (a) D_L/D_0 vs P_e. (b) D_T/D_0 vs P_e (after Perkins and Johnston, (1963).

controls longitudinal dispersion to paclet number of only 10^{-2}. Similarly, mechanical mixing appears to dominate the transverse and longitudinal dispersion coefficients at peclet number in excess of 100 and 1.0, respectively. So, it can be concluded from fig.6 that mechanical mixing dominates the dispersion coefficient only at high Peclet numbers, whereas at low peclet numbers the dispersion coefficient is approximately equal to the effective diffusion coefficient. Gillham and Cherry (1982) solved eq.10 for an infinite path and a step function solute input to calculate profiles of solute concentration versus distance for specified values of $t > t_o$, keeping the range of velocity such that the peclet number (assuming d=0.02 cm) was always in the range where the dispersion process is dominated by molecular diffusion and thus D was set equal to the effective diffusion coefficient (D_d). The set of results shown in fig.8 indicates that low values of ground water velocity have little influence on the advance of the solute front.

A further comparison of the effect of the graphs in relative to advection is represented by the graphs in Fig.9, which shows the rate of advance of the solute front, versus the rate of advance that would occur by advection alone. In the development of Fig.9, the rate of front advance has been calculated using $C/C_o = 0.5$ and 0.01 points on the fronts.

For analysis of contaminant migration in heterogeneous hydrogeologic systems with complex flow patterns

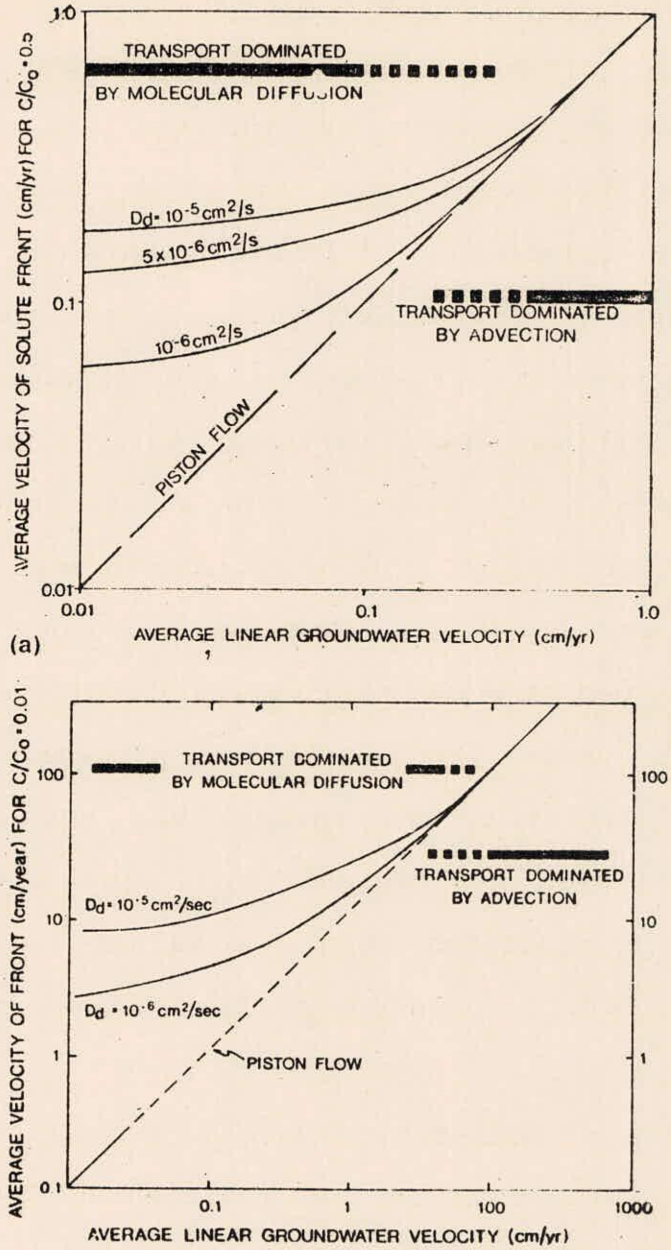

Figure 9 : Comparision of the average linear ground-water velocity and rate of solute front advance along a flow path with advection and molecular diffusion. (a) The front is defined by C/C_o - 0.5. (b) The front is defined by C/C_O = 0.01.

and time dependent boundary conditions typical of many field situations, numerical solution, procedures have been developed. Those include finite-difference methods, finite-element methods and the methods of characteristics. These methods have been described by Marino (1976), Bachmet et al.(1977), Pinder and Gray (1977) and Anderson (1979). Case histories in which numerical models based on the advection dispersion equation are used in the analysis of contaminated ground water systems are summarized by Konikov(1977).

Advective-Dispersive Transport

Although diffusive transport is probably the predominant transport mechanism in unfractured, fine grained materials and thus of particular importance in the long term environmental assessment of waste management areas, a wide range of ground water contamination problems occurs in hydrogeologic regims where the transport process is controlled by advection. These regimes are of particular importance because, as a result of their relatively high ground water velocities, they provide the most rapid avenue for contaminant migration from the subsurface to the biosphere. Furthermore, because ground water supplies in unconsolidated deposits are invariably associated with coarse textured materials, it is particularly important to understand mechanism of contaminant transport in these materials.

The preponderance of quantitative information concerning the advection dispersion process comes from laboratory experiments performed on small homogeneous samples of geologic or artificial porous materials. This information leads to the simplest conceptual model of solute migration in natural hydrogeologic environments the concept of "homogeneous medium". Applying this concept to contaminants injected continuously as a plane source in a one dimensional flow field would result in a contaminant from moving in the direction of flow at a velocity V. The concentration distribution at the front, after a sufficient travel distance from the source, would be Gaussian. Similarly, an instantaneous injection of a contaminent would result in the center of mass of the slug moving at velocity V, with the dimensions of the slug increasing with travel distance. The concentration distributions would have a Gaussion form both in the direction of flow and in the transverse directions. In applying this concept to field conditions and assuming that the macroscopic scale of description of the medium applies, the actual shape of the concentration profiles is presumed to be determined by dispersion coefficients or dispersivity values comparable to those obtained from laboratory experiments. These concepts are shown schematically in Figures 10a and 10b. Examples of this approach are given by Baetsle (1967, 1969).

Although this concept is appealing in its simplicity, the bulk of the field evidence, together with the results of some laboratory experiments, indicates that the concept of a homogeneous medium is inappropriate for

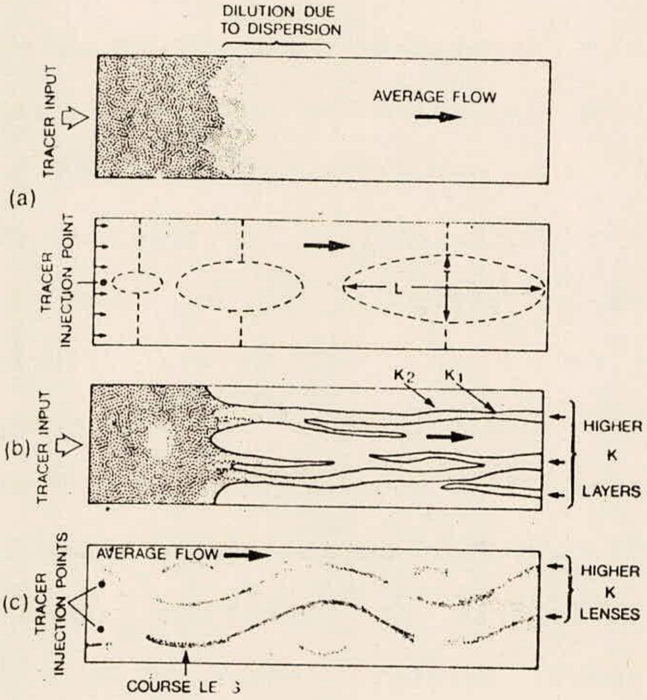

Fig. 10 : Dispersion in granular materials. (a) Simple dilution front and spread of a slug injection in homogenous materials. (b) Fingering of tracer front caused by heterogeneities (after de Josselin de Jong, 1958). (c) Spreading caused by high permeability lenses (after Skibitzke and Robertson, 1963).

natural hydrogeologic systems. In particular, the observed degree of spreading of a contaminent is generally much greater than would be predicted on the basis of laboratory dispersivity values. This increased spreading is usually attributed to the heterogeneous nature of field environments. An example of the effect of heterogeneities as perceived by the Joseelin do Jong (1959) is shown in fugure 10c. The solute is shown to move most rapidly through a network of high permeability "Fingers" situated in a matrix of lower permeability materials. The effect of heterogeneities as presented by de Josselin de Jong is supported by the results of several studies using two dimensional laboratory 'models. Notable examples are the work of Skibitzke and Robertson (1963), Theis (1967) and Hillier (1975). On the basis of results like those in Figure 10c, Skibitzke and Robertson observed that the presence of small, discrete lenses of high hydraulic conductivity within a sandstone matrix of lower hydraulic conductivity caused much stronger dispersion than when the lenses were not present.

At the laboratory scale of investigation used in the above studies, the distribution of the solute was controlled primarily by the complex velocity field resulting from the heterogeneous nature of the medium. Consequently, Gilhum and Cherry (1982) refer to this mechanism of solute migration as "heterogeneous advection". Heller (1972) suggested that if there are a large number of heterogeneities, if the heterogeneities are randomly distributed, and if the length of the flow path is large with respect to the scale of the heteorogeneities, Gaussian concentration distributions will be observed. Similar arguments were presented by de Josselin de Jong (1958). Thus the phenomenological aspects of heterogeneous advection process would be similar to those predicted by the advection dispersion equation. This has led to the commonly held view that heteorogeneities cause dispersion. It would be noted, however, that Gaussian concentration distributions would be observed only if water simples were collected over some representative number of heterogeneities, in which case the concentration could not be considered macroscopic. For the advection dispersion model to rest on a deterministic foundation, the equations would have to be redeveloped with parameters defined at a larger scale.

When contaminants enter the ground water zone in heterogeneous granular deposits, it is reasonable to expect that they move in complex patterns according to the heterogeneous advection model. As the contaminants are transported, primarily by advection in the more permeable heterogeneities, diffusion causes them to migrate from these heterogeneities into the adjacent heterogeneities of lesser permeability. The net effect is to reduce the concentrations and contaminent flux in the permeable zones and increase the concentrations in the less permeable zones. As time goes on, the diffusion tends to generate increasing uniformity of concentration distribution in the plume and a concentration front that would exhibit increasing speed and a gradual decrease in concentration toward the position of farthest advance. Dispersion at the macroscopic scale and at larger scales within the complex flow system is therefore accomplished primarily by molecular diffusion, which aquires its driving force from transient local concentration gradients imposed on the macroscopic system by preferential advective transport in the more permeable layers of lenses. Figure 11 is a schematic representation of the operation of these processes in a simple heteorogeneous system. Dispersion, as it is envisioned in the advection diffusion concept for heterogeneous systems, is an irreversible process similar to processes of dispersion at the macroscopic scale.

The advection diffusion representation of the contaminant migration process in heterogeneous unconsolidated deposits is not unlike that proposed for miscible displacement of fluids of different viscosity. In laboratory experiments involving two fluid of different viscosity in homogeneous granular media, Slobod and Thomas (1963) showed that at higher displacement velocities, a distinct fingering of the two fluids was observed whereas at lower velocities the extent of fingering was greatly reduced. The relative lack of fingering at low velocities was attributed to diffusion from the fingers into the zone of the porous medium between the fingers.

In the advection diffusion concept of contaminent migration, time and travel distance are necessary to cause plume regularity. In addition, the extent to which the

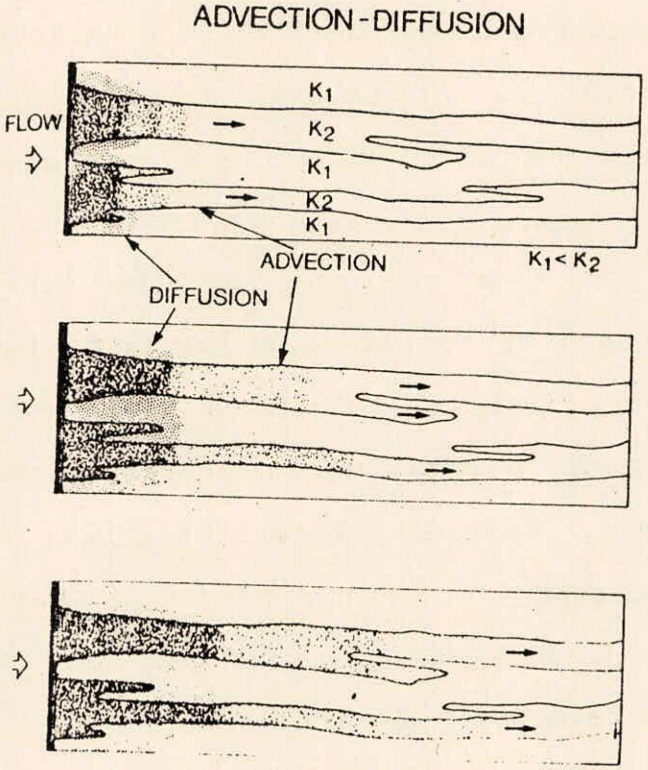

Fig. 11: Schematic diagram demonstrating the advection-dilusion transport mechanism.

plume is regularized would depend upon the thickness and permeability contrast between adjacent layers of the medium. In this context, a field experiment reported on by Sudicky and Cherry (1979) and by Sudicky and others (1980) is of interest. A slug of chloride tracer was injected into a shallow heterogeneous aquifer and allowed to migrate under the influence of natural ground water flow. Early in the text, the slug split into two distinct segment, presumably because of small but significant differences in permeability from one side of the test area to the other. Then each of the split segments of the slug rapidly evolved to a classical. Gaussian form in spite of the fact that each segment was migrating through materials with numerous distinct heterogeneities. The advection diffusion concept of solute migration may have further consequences with regard to the in situ measurement of transport parameters. As represented in the advection dispersion equation, dispersivity is a characteristic property of the geologic materials through which values must be specified so that the equation can be applied in a predictive manner.

5 1.1.2 Transport of Reactive Contaminants

Till this point, the discussion was focused exclusively on the migration of dissolved consti uents do not undergo chemical or biochemical reactions along flow paths. Many solutes of environmental concern, however, are subject to the effects of chemical reactions within the ground water system. The chemical processes that can affect the migration of contaminants in ground water include oxidation reduction (redox processes), precipitation fodissolution, ionpairing and complexing, and radio active decay.

The one dimensional form of the advection dispersion equation for homogeneous media (equation 9), modified to account for the effect of chemical reaction, can be written

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x2} - \bar{v} \frac{\partial c}{\partial x} - G \qquad \ldots (14)$$

where q is a source sink term that represents the rate at which the dissolved species is removed from solution (mass of solute per unit volume of solution per unit time)($ML^{-3}T^{-1}$). The reaction term G includes all specific chemical or biochemical processes involved in the alteration of the contaminant concentration in the solution of the contaminant concentration in the solution phase.

Migration with sorption

Sorption is the process of mass transfer between the liquid and solid phases that is most commonly incorporated into the advection dispersion equation. The reaction term in case of sorption can be expressed in the form:

$$G = \frac{\rho}{n} \frac{\partial q}{\partial t} \qquad \ldots (15)$$

where q is the concentration of the solute in the solid phase (MM^{-1}) and ρ is the dry bulk density of the porous medium (ML^{-3}). If it is assumed that the chemical processes occur rapidly relative to the flow rate and therefore that local chemical equilibrium is achieved, and it is further assumed that under isothermal conditions the concentration of the contaminants in solution is a function only of the concentration in the solid phase, it follows that

$$\frac{\partial u}{\partial t} = \frac{\partial q}{\partial c} \cdot \frac{\partial c}{\partial t} \qquad \ldots (16)$$

Substitution of equation (15) and (16) into equation (9) yields

$$\frac{\partial c}{\partial t} \left(1 + \frac{\rho \partial q}{\eta \partial c} \right) = D \frac{\partial^2 c}{\partial_x^2} - \bar{v} \frac{\partial c}{\partial x} \qquad \ldots (17)$$

various mathematical relations between q and c have been described by Golubev and Garibyants (1971) and Smith (1970). The most common isotherm (graph of c versus q) reported for ground water is the Freundlich isotherm, given by

$$q = Kc^{\alpha} \qquad \ldots (18)$$

Where K and a are empirical coefficients. For low concentrations a 1 and K=K. So eq.17 becomes

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial_x^2} - \bar{v} \frac{\partial c}{\partial x} \qquad \ldots (19)$$

where $D^{*} = D/R$, V = V/R and R is the retardation factor (the relative velocity of the reactive constituent), defined as

$$R = \frac{\bar{v}}{V'} = 1 + \frac{\rho}{\eta} kd \qquad \ldots (20)$$

The retardation equations was first incorporated into the advection dispersion equation by Vermeulen and Niester (1953), and this approach to represent the transport of adsorbed contaminants in ground water was first represented by Higgins (1959) and Nelson (1959).

The validity of applying eq.19 to simple hydrogeologic systems can be appraised by comparing simulated results with the results of laboratory experiments. Reynolde (1978) carried out the experiments with a column of fine sand of glacial origin in which strontium was used as the reactive tracer and $C\bar{l}$ and ^3H as the non reactive tracers. To compare his experimental results with the results of column experiments reported on by other investigators for various reactive constituents (like Sr^{2+}, Cs^{+}, Mg^{2+}, Atrazine, Lindane) with linear isotherms, Raynolds (1978) assembed a group of normalized break through curves. This curves were found to fit within the domain shown in Fig.12. Considering the variety of reactive species used as tracers and the range of experimental conditions, the similarity of the break through curves which is represented by the narrowness of the evelope curve, is remarkable.

For calcium migration through laboratory columns, James and Rubin (1978) reported asymmetrical break through curves at high transport velocities, but for low velocities they obtained symmetrical curves. The experiments that yielded symmetrical curves were conducted at velocities at which the dispersion process would be expected (on the basis of fig.8) to be dominated by molecular diffusion.

At the present time there is no generally accepted

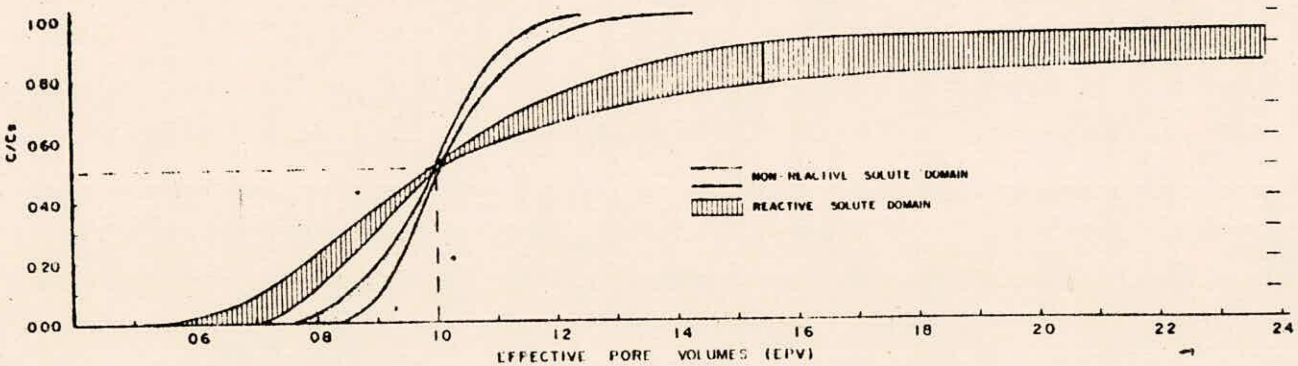

Fig. 12 : Normalized column breakthrough curves for reactive and nonreactive solutes (after Regnolds, 1978).

mechanistic explanation for the pronounced asymmetry of break through curves obtained from column experiments conducted at Peclet numbers above the diffusion-controlled range.

Migration with Precipitation and Dissolution

The primary mechanism of transfer between the liquid and solid phases for some ground water contaminants are precipation and dissolution. An analysis of the partioning between liquid and solid phases for the constituents can be carried out using computational models based on mass balance, charge balance, and mass action relations. Some computerised chemical models based on these relations for equilibrium calculations of aqueous systems have been developed (Truesdell and Jones 1974, Kharaka and Barnes 1973, Plummer and others 1975, Parkhurst and others 1978 etc.,) but these are not transport models as these models do not include velocity or dispersive terms. Grove and Wood (1972) included the activity coefficient effect and incorporated reactions for complexing of cations and anions, for precipitation and dissolution of gypsum, and for cation exchange (Na^+, Mg^{2+}, Ca^{2+}). They obtained good agreement between model simulations and laboratory and field experiments, and they concluded that the task of adding, or delating chemical reactions to described equilibrium processes involving other minerals or complexes would not be difficult.

Migration with Redox Processes

The contaminant migration in ground water is also influenced by oxidation reduction (redox processes). Almost all redox reactions of importance in ground water systems are mediated by bacteria e.g. oxidation of organic matter to CO_2, biomass and water, or conversion of NO_3 to N_2 through the process of denitrification.

Doner and Mclaren (1976) developed an expression to describe $N\bar{O}_3$ loss due to steady state denitrification.

$$G = \frac{d\,[No_3^-]}{dt} = \frac{(\nu + \beta)\ \bar{m}\ [No_3^-]\ M}{K_m + [No_3^-]} \qquad \ldots (21)$$

where NO_3^- is the concentration of NO_3^- in solution, ν is M utilized per unit biomass per unit time for maintenance of the bacterial population, β is N utilized per unit biomass in wasted bacterial metabolism, $\bar{m}$ is a steady state constant, K_m is a saturation constant, and M is the mass of organic matter available to the bacteria that mediate the reaction. Doner and Mclaren have successfully used equation 21 as the reaction term for simulation of NO_3 distribution in laboratory soil colums, but the necessity of obtaining values for the many parameters in the reaction term may render it impractical for analysis of field scale problem.

5.1.2 Unsaturated Zone

Convection (i.e. advection) with water is the chief mechanism for transport of solutes in the unsaturated zone (Raats, 1984). The fate of parcels of water in rather homogeneous boundary conditions can be determined on the basis of the traditional theory of mass balance and theory of momentum balance. It yields good estimates of patterns of penetration and of distributions of travel times of solutes.

Unfortunately, in practice, numerous factors may complicate the flow patterns, generally leading to more erratic patterns of penetration and wider distributions of travel times. Among these factors are (1) spatial variability of the physical properties and the boundary conditions; (2) coarse structures due to aggregates, cracks, and channels; and (3) secondary flows due to density gradients in the liquid phase and to instability of watting front.

5.1.2.1 Convective transport in structured media

In order to account for the structures of a soil, a substance may be considered to be divided between a mobile phase and a stagnant phase. The mobile phase may correspond to a network of large pores; such as the pores between aggregates. The stagnant phase may correspond to a network of the small pores, such as the pores in aggregates. Important features in the model are the ratio of the capacities of the two pore systems to store the substance and the finite response time associated with the exchange of the substance between the two pore systems. Another important factor is the mechanism of transport of the substance in the mobile phase.

For any constitutents , the combined balance of mass for the mobile and stagnant phases can be expressed as:

$$\frac{\partial \rho m}{\partial t} = -\nabla J - \frac{\partial \rho s}{\partial t} \qquad \ldots (22)$$

where ρ_m is the bulk mass density in the mobile phase, F is tne flux in the mobile phase, and ρ_s is the bulk mass density in the stagnant phase. The bulk mass density ρ_m in the mobile phase is assumed to be given by (Raats, 1984).

$$\rho_m = (Q_m + K)\, c, \qquad \ldots (23)$$

where c is the concentration in the mobile phase, Q_m is the volume fraction of the mobile phase, and the constant K describes instantaneous storage capacity in addition to the volume fraction Q_m. The flux J is assumed to be the sum of a convective component $Q_m V_m c$ and a diffuse component - D C

$$J = -Q_m V_m C - D \Delta c \qquad \ldots (24)$$

where V_m is the velocity of the mobile phase and D is the dispersion coefficient.

The mechanism of exchange between the mobile phase and its stagnant phase is assumed to be Fickian diffusion. If the mobile phase is assumed to be a well stirred fluid and the stagnant phase is assumed to occur is spheres of radius R, the the time rate of change of the bulk mass density s in the stagnant phase is assumed to be related to the time rate change of the concentration c by

$$\frac{\partial \rho s}{\partial t} = (Q_m + k)\nu \int_o^{t'} \frac{\partial c}{\partial t} \sum_{n=1}^{\alpha} 6 \exp\{-\eta^2 \pi^2 (t^2 - T')\}\, dT' \qquad \ldots (25)$$

where ν is the ratio of the bulk densities in the mobile and stagnant phases at equilibrium, $t^1 = (D/R^2)t$ is dimensionless current time, and $= (D/R^2)$ denotes instants in the past. The combination $\eta^2 \; \pi^2 \; R^2/D$ denotes a descrete spectrum of relaxation times. The sum $\sum_{n=1}^{\alpha} 6$ $\exp [-n^2 \pi^2 (t-\,.\,)]$ describes the memory of the stagnant phase for changes of concentration at the boundary between the mobile and stagnant phases.

If equation 23-25 are introduced in equation 22, a linear partial integro-differential equation results. For slow motion, this equation can be converted to either one of two alternative partial differential equations in which all derivative with respect to time occur. The resulting equations are

$$(Q_m+K)\frac{\partial c}{\partial t} + Q_m \; V_m \; \Delta C - D\bar{v}^2 C - Q_m(K)_r\{ 1-\frac{1}{15} \; \frac{R^2}{D} \; \frac{\partial}{\partial t} +$$

$$\frac{6}{945} \; \frac{(R^2)}{D}^{2} \; \frac{\partial^2}{\partial t^2} \; \cdots\cdots \; \frac{\partial c}{\partial t} \qquad \ldots (26)$$

and

$$1+\frac{1}{15} \; \frac{R^2}{D} \; \frac{\partial}{\partial t} - (\frac{R}{D}^2) \; \frac{\partial^2}{\partial t^2} + \cdots\cdots \; X \; (Q_m+K) \frac{\partial c}{\partial t} +$$

$$Q_m \; V_m \; \Delta c - DD^2 c = -(Q_{m+K}\}_r \; \frac{\partial c}{\partial t}$$

Neglecting all but the first terms of the infinite series in braces correspond to assuming instantaneous equilibrium between the mobile and stagnant phases. Retaining the second term of the infinite series in equation -26 introduces second order derivative. It represents the simplest possible model of the retardation of uptake and release of solute by the stagnant phase. Retaining the second term in the infinite series in eqn.27 introduces at once three new terms, which correspond to assuming an equivalent film resistance between the mobile and stagnant phase.

5.1.2.2 Secondary flows induced by density variation

In pollution problems one is often dealing with movement of fluid masses embedded in other fluids in porous media. Duyvenbooden and kooper (1981) described density currents underneath a waste disposal site near the North sea coast. The density of the percolate was about 1.01 kg dm^{-2}. Just above the fresh saline water interface at a depth of approximately 40 m, increased concentrations of HCO_3, NH_3, and Fe were found (w.r.t non polluted ground water with density 1.003 kg dm^{-3}) resulting in a density of 1.005 kg dm. Density currents have also been of concern in connection with placement of fertilizers (Raats, 1969).

Locally the influence of the change of the desnity and/or the viscosity can be read at once from darcy's law. The different between the actual flux J and the flux Jo of a reference liquid with the same distribution of the pressure is given by

$$J - Jo\, K \frac{\mu - \mu_0}{\mu}\, Jo + \frac{dk}{\mu}\, (\nu - \nu_0)\, g \qquad \ldots (28)$$

Where is the viscosity, K the intrinsic permeability, ν the density, and g the gravitational force per unit in Fig.13, the three surfaces for which $C = 0.9$, $C=0.5$, and $C=0.1$ respectively, at a fixed t, for a field for which solute at $C=1$ has been applied on the surface $Z=0$ at =t = 0. In Fig.13a, these are horizontal planes corresponding to an ideal homogeneous field and to uniform conditions, whereas in fig.13b, they are the irregular surfaces which one should expect in an actual heterogeneous field.

A complete, description of the concentration distribution in a heterogeneous field is achieved if we can determine $c(x,y,z,t\ )$ and particularly $Z_{0.1}(x,y,t)$, $Z_f(x,y,t)$ and $Z_o(x,t,y)$. This is a formidable task, which faces two obstacles at least, first the necessary detailed data on the distribution of soil properties and on boundary conditions in space are not available and secondly even if the data are available, the computational problem, is exceedingly complex. The traditional approach of transport modelling is to regard the field as an equivalent homogeneous unit and to attempt to predict the average distribution $C(z,t)$. This approach raises a few basic questions of relevance in applications like (Dagan and Brester, 1984); (1) is to possible to define a homogeneous field of effective properties such that the concentration distribution in it is identical to the average concentration $C(z,t)$ in the actual heterogeneous field, (2) if the answer is positive, how can we determine the effective properties? (3) What is the level of confidence in results as a function of the degree of variability and amount

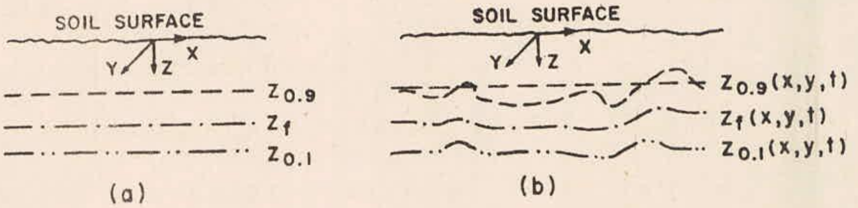

Fig. 13,a,b. : Surfaces of equal concentration at time t after beginning of solute transport : a ideal homogeneous field. b heterogeneous field mass; while the subscript o denotes the reference liquid.

Equation 28 is a key element in an analysis of density currents induced by a line source of salt (Raats, 1969) and also in an analysis of the movement of fluid mases embedded in other fluids in porous media (Yih, 1963, Raats 1981 a).

In a uniform ambient velocity field, the movement of embedded masses of fluid, both in the form of culinders with elliptical cross section and in the form of ellipsoids, is analogous to the movement of solid bodies in an ideal fluid (Yih 1963). It can be shown that the velocity of such embedded masses can be written in the concise form (Raats 1981 a);

$$V = AVo + k\,(\quad - \quad_{o})g$$

where V_o is the velocity of the ambient fluid and A and B are matrices which depend on the viscosities and the shape, but not the size, of the embedded fluid mass.

5.1.2.3 Spatial variability of the physical properties and the boundary conditions

The variation in the plane may occur in the rate of application of water on the soil surface as it happens for irrigation systems and even for rainfall.

If the field is regarded as a collection of homogeneous vertical columns of varying properties in the horizontal x,y planes, the concentration profile for each column is similar to that of a laboratory one, but C depends on x, y as well, because of heterogenity (Degan andBrasler, 1984). This point is illustrated schematically of data? (4) what can we say about the variation of C around its mean $\bar{C}$? and (5) are accurate and intricate models of transport in a column are needed in order to describe the average concentration in the field?

The answer to (1) question is generally negative (Bresler and Dagan 1981 1983 a,b) and therefore there is no answer to (2) , Answers to questions (3) and (4) can be obtained only if we take into account the heterogeneity (Dagan and Bresler, 1984). Paradoxically at first glance, the answer to question (5) is that fairly accurate description of the average behaviour of the solute transport in the field can be achieved by using simple flow models, precisely as is the case for the macroscopic laws of flow in a porous medium, which can be derived with the aid of relatively simple models of the pores.

Dagan and Bresler have developed a stochastic model based on two components (1) models of flow and transport in a homogeneous vertical column and (ii) the second order statistical structure of soil properties and boundary conditions. It has been shown that fairly accurate results for average concentration can be obtained by using crude models of flow and the computational gains may offset the additional complexity related to heterogeneity.

Recently Bresler and Dagan have solved the problem of transient water flow (an infiltration and redistribution cycle) and of solute transport, both being affected by the variability of saturated hydraulic conductivity.

(Dagan and Bresler 1983 and Bresler and Dagan 1983 a,b) fig.14 represents the average concentration profils of two different type of soil at two different times and stimulated by three different methods (curve I): by assuming that flow takes place in a deterministic uniform field of an assumed effective saturated conductivity; (2) by assuming steady gravitational flow in the heterogeneous field and (3) by simulation infiltration (unsteady) in the heterogeneous field.

Similarly, the curves II represent the concentration variance computed by methods (2) and (3) above.

Fig.14 shows that there is considerable difference between the average concentration profile computed for an equivalent uniform field and for the actual heterogeneous field in the case of Ponoche soil (Fig.14 a,b) and a significant, though lesser one; for the Bet Dagar field (fig.14 c,d). Furthermore, the steady flow mode performs similarly to the unsteady one for the more heterogeneous Bet-Dagan soil.

Finally, the concentration variance σc^2(Fig.14II) is zero at the soil surface, because of the assumption that C=1 is given deterministically and is also zero at large depth where C=0. Its maximum is reached close to the depth for which C=0.5 and can reach the maximal theoretical value $\sigma c^2 = 0.25$

The above discussion shows that there is a significant impact of soil spatial variability upon solute distribution.

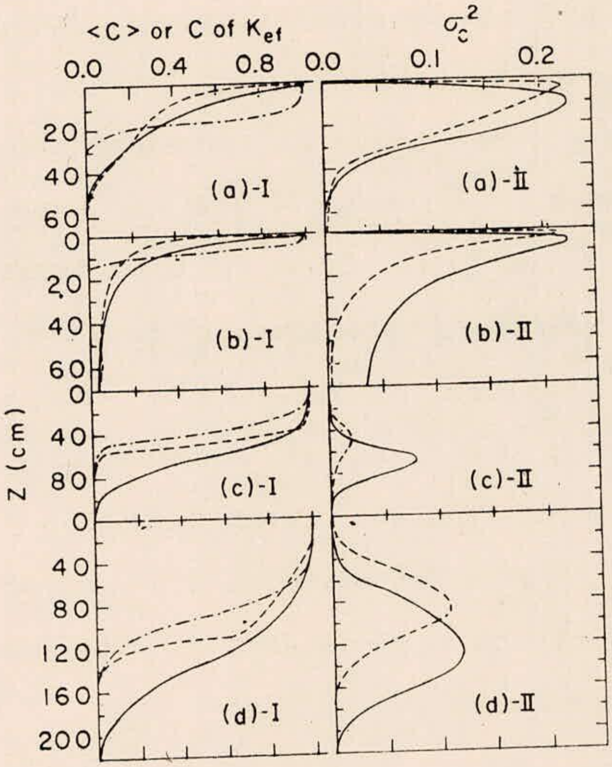

Fig. 14, a-d, : Average concentration C as a function of depth after infiltration (deterministic for uniform soil of effective conductivity, dashed-dotted line; for steady gravitational flow in heterogeneous soil, dashed lines: for unsteady infiltration solid line). II Concentration variance σ_e^2 as function of time (symbols as in 1). a Panoche soil, water rate of application Y = 0.5 cm/h, infiltration time t^i = 24 h: (b) Panoche soil, Y = 65 cm/h. t = 6h; (c) Bet-Dagan soil, Y = 0.5cm/h t_i = 24 h; d Bet-Dagan soil, Y = 6.5 cm/h. t^1 = 6h.

5.2 Biological Pollutants

The transport of bacteria and viruses is controlled mainly by the following factors:

a. the persistance of bacteria and viruses under the biological and chemical conditions in the unsaturated zone;

b. the physical and physiochemical processes which control the transport of bacteria and viruses.

5.2.1 Persistance of bacteria and viruses

Two groups of micro organisms must be differentiated when the subsurface survival of bacteria and viruses is considered (Pekdege 1984).

1. Allochthoric pathogenic microorganisms (parasitic bacteria and enteroxine producing bacteria), which enter the unsaturated zone due to contamination, and
2. Autochthonic soil and ground water microorganism.

The autochthonic microbial soil and ground water microorganisms flourish under favourable ecological conditions, developing high population densities ($\gg 100 ml^{-1}$) (Hirsch and Rades Rohkohl 1983). The allochthonic bacteria are usually eliminated in the subsurfa environment, but under oligotropic conditions they may survive without a substantial decrease, in the first few weeks. After this period, the elimination of bacteria and viruses may be approximately described by an exponential decay function eq.30 (Barge 1967, Merkli 1975)

$$C_{(t)} = C_o \, e^{-\lambda (t-t_o)} \qquad \ldots(30)$$

$t > t_o$ and $t_o < 20$ days

C_o., C_t = initial concentration and concentration at time t

λ = elimination constant = $\frac{\ln 2}{\tau_{1/2}}$

t = time

$\tau_{1/2}$ = half life time

The persistance of bacteria and viruses in the soil depends on the biological activity of the top soil. Cholerae sp. can survive only a few days in a biologically active top soil, but in sterile soils it may survive upto 6 months. Survival times for Salmonella sp. range upto 3 months, for streptocorcus faecalis upto 2 months, and for coliform bacteria upto 7 months (Althaus et al.1982).

Bacteria and viruses can survive even longer (> 6 months) in the deeper parts of the unsaturated zone under oligotrophic conditions. This means that under certain econological conditions, bacteria and viruses may survive a long period in the unsaturated zone until they are transported into the ground water.

5.2.2 Filtration Process

The removal of micro organisms from subsurface water is a complex process. It includes the time depending mechanism described earlier and the filtration mechanism, which depends on the length of the transport path. The filtration efficiency, which is defined as the ratio of the final concentration C_X to the initial concentration

C_o can be described by a factor f (Iwasaki 1937).

$$C_x = C_o \cdot e^{-\lambda_f x} \qquad \ldots(31)$$

The microorganisms transport may be limited by the pore size of the subsurface material as compared to the size of the microorganisms. However, mechanical filtration is not very effective in sandy and gravelly soil due to the small diameters of bacteria (0.2-5 µm) and viruses (0.25-0.02 µm) compared with the diameter of the pores, which (e.g. in uniform sands) are generally larger than 40µm. In natural sediments with heterogenic grain size distribution, only a small fraction of the pore diameters can interfere with bacteria transport (>10%) (Pekdegar, 1984)

The particle accumulation on a solid substance surface is mainly due to sedimentation, flow processes, diffusion, and interception (fig.15, Yao et.al.1971). Yao et al.give the following equations for filtration efficiency

$$l_n \frac{C}{C_o} = \frac{3}{2} \cdot (1-n) \cdot \alpha \cdot \eta \left(\frac{L}{d}\right) \qquad \ldots(32)$$

$$\eta = \eta_D + \eta_I + \eta_G \qquad \ldots(33)$$

$$\eta_D = 4.04\, P_e^{-2/3} = 0.9 \left(\frac{kT}{\mu d_p d v_f}\right)^{2/3} \qquad \ldots(34)$$

$$\eta_I = \frac{3}{2} \left(\frac{d_p}{d}\right)^2$$

$$\eta_G = \frac{(\rho_p - \rho) g}{18\ \mu v_f} , d_p^2$$

with

C_o, C = influent and effluent concentration

n = porosity

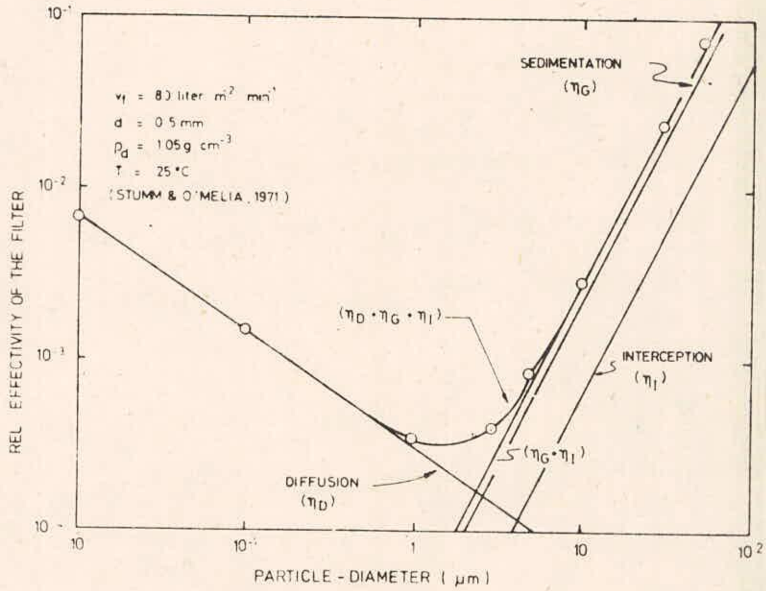

Fig. 15 : Filtration parameters in porous media (Yao et. al. 1971)

α = stabilization coefficient

η = single collector efficiency

d = grain size of filter material (m)

d_p = diameter of suspended particles(m)

L = bed depth (m)

η_D, η_I, η_G = single collector efficiencies for diffusion, interception sedimentation

ρ_e = Peclet·number = V_a/D_d

K= Boltzmann constant $(1.38054 \times 10^{-23})$J/K

T = absolute temperature (K)

μ = water viscosity (N, sm^{-2})

V_f = filter velocity ($m\ S^{-1}$)

ρ, ρ = density of suspended particles and water (kg m^{-3})

g= gravity constant (0.80665) $m\ s^{-2}$

Very important for the filtration efficiency is the duration of the contaminating process and the initial concentration of contaminants. During a continuous contamination process by organic substances and micro-organisms, the contaminated plume becomes smaller with time because elimination and filtration mechanism are favoured. At very high initial concentrations, floculation and aggregation can occur at the source of contamination so that only a limited transport into the aquifer can take place.

5.2.3 Transportation

A contaminated point source disperses as it travels through the unsaturated zone and enters the ground water so that the concentration in the contaminated plume decreases with time and with the transport distance. This process can be described by the general transport equation, Bear (1972) Eq.35.

$$\frac{\partial c}{\partial t} = \text{div}\left(\frac{D}{Rd} \cdot \text{grad } C - \frac{\nu_w}{R_d} \text{grad} \quad C\right) - \lambda c \qquad \ldots(35)$$

where

D = coefficient of hydrodynamic dispersion $D' + D_d + D_e$

D' = coefficient of hydromechanic dispersion

D_d = diffusion coefficient

D_e = coefficient of the active mobility of bacteria.

grad C = concentration gradient

V = average ground water velocity

R_d = retardation factor

ν_w = elimination constant

The dispersion equation in this form includes a term for the active mobility of bacteria, which decreases with decreasing temperature. Maeda et al.(1976) give for Escherichia Coli velocities of 1-0.1 md^{-1} at 20-10°C.

The lateral dispersion of bacteria is greater than that of conservative tracers, e.g. E.Coli has broader lateral dispersion as compared with the conservative tracers, Bromine-82 and fluoresceine (Seiler and Alexander 1983). On the other hand, the longitudinal distribution pattern of E.Coli is affected by filtration process.

The bacteria are transported mainly in the large pores, which causes after long travelling distances the formation of a narrow break through curve (Fig.16) (Havemeister et al.1983, Seiler and Alexander 1982).

The velocity of seepage water in the unsaturated zone is generally slow (Mathers et al.1979). Even in humid climates, the seepage velocity is rarely faster than 1 my^{-1} (Moser and Rauert, 1980), in the arid climates the velocity is slower due to lower annual ground water recharge. Only after heavy rainfalls or due to sewage reclaimation by land treatment, the seepage velocity in coarse soils may be much higher (upto few meters/ day). The ground water velocities are generally much higher than seepage velocity, if the level of water table changes, the bacteria may also be immobilized in the capillary fringe less known (Pekdeger 1985).

The continuous adsorption/desorption causes retardation of microorganisms with respect to water transport. The retardation is described by the retardation factor R_d (eq.36).

$$R_d = \frac{\nu_w}{\nu_m} \qquad \ldots(36)$$

where

ν_w= mean water velocity, and

ν_m= mean transport velocity of microorganism

The retardation factors can be obtained by laboratory and field tests (Mathers and Pekdeger 1981). In laboratory and field experiments, retardation factors between 1 and 2 were found for the indicator bacteria

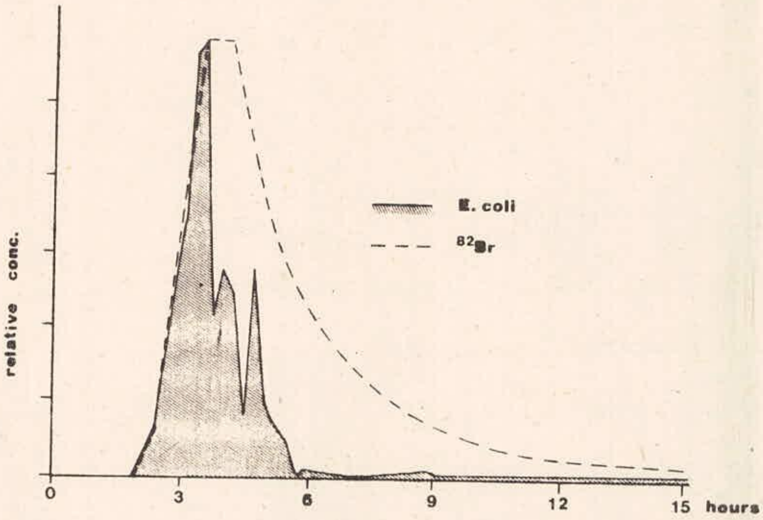

Fig. 16 : Breakthrough curves of E. coli and ^{82} Br in coarse gravel in a flow distance of 20 m (Seiler and Alexander 1983)

E.Coli and the tracer bacteria Serratia marcescens (Havemeister and Riemer 1983), Havemeister et al.1983, Jung and Schrider 1983, Schroter 1983, if the scale of the experiments were large enough (> few meters). In small scale experiments, the used formatism yields an apparantly higher retardation factor because a certain portion of the bacteria is held back by the filtration mechanisms, which are reversible over short distances. Most of the patnogenic viruses, especially the polio viruses, have high retardation factors which range upto to 500. These bacteria can be remobilized even after a few months, when the water table rises after heavy recharge (Fig.17).

A high dilution is expected when the bacteria and viruses pass slowly through the unsaturated zone in a vertical reaction and enter the generally faster flowing ground water in approximately a lateral direction (Anynymous, 1978).

The transport velocity of microorganisms may differ from the seepage velocity, since microorganisms are subjected to adsorption on soil particles (Fig.18). The equilibrium between the concentrations of the suspended (C_s) and adsorbed (Ca) microorganisms can be described by the Freundlich isotherm (Berg 1967, Merkli 1975) eq.

$$C_a = K\ C_s^n \qquad \ldots(37)$$

The empiric constants K and n are assumed to be specific for the investigated soil, rocks, and microorganisms. The adsoption of bacteria and viruses takes

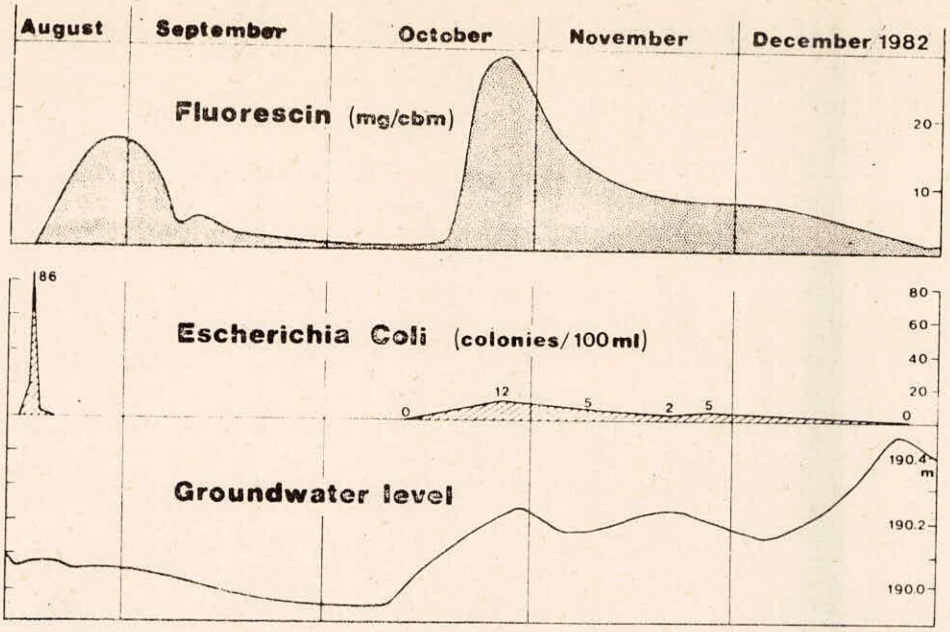

Fig. 17 . Effect of groundwater level fluctuations on bacteria transport (Kaess et. al. 1983).

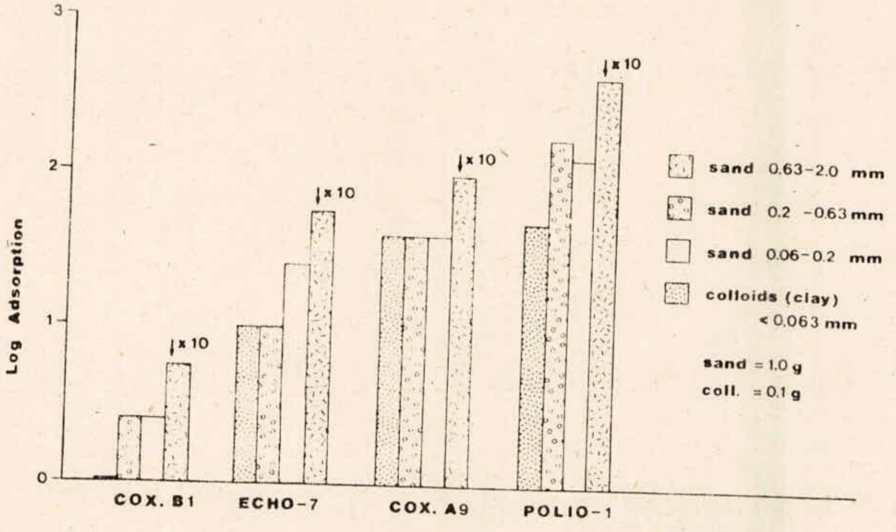

Fig. 18: Absorption of viruses on solid substance (Di ær et al. 1983)

place quite rapidly (24h **and** 2h, respectively; Althous et al.1982), whereas desorption velocity is

Model calculations based on adsorption coefficients and elimination coefficients show that unsaturated can provide a very effective protection against virus contamination. However, according to other observations, the viruses can be desorbed when the chemistry of water changes (Fig.19 Duboise et al.1976).

5.3 Organic pollutants

The organic contaminants which survive the adsorption degradation or other reactions move in the unsaturated zone, and can reach the saturated zone. The migration can be in the form of miscible fluid (dissolved in water) or immiscible fluid(insolube in water). Miscible organic material behave as the inorganic solute transport in the unsaturated zone, where as the immiscible fluids follow the principle of multiphase flow. In this section, the behaviour of immiscible organic contaminants will be dealt with in detail.

The principle of the two simultaneous flow of two fluids immiscible with one another in a porous media is shown in the well known diagram (Fig.20) of relative permeability for a wetting and on wetting fluid (wyckoff and Betset 1936). Water is usually the wetting fluids and mineral oils or chlorohydro benzene, for example, are the non wetting fluids. Since for each fluid flowing, only a part of the pore space and thus only a part of th

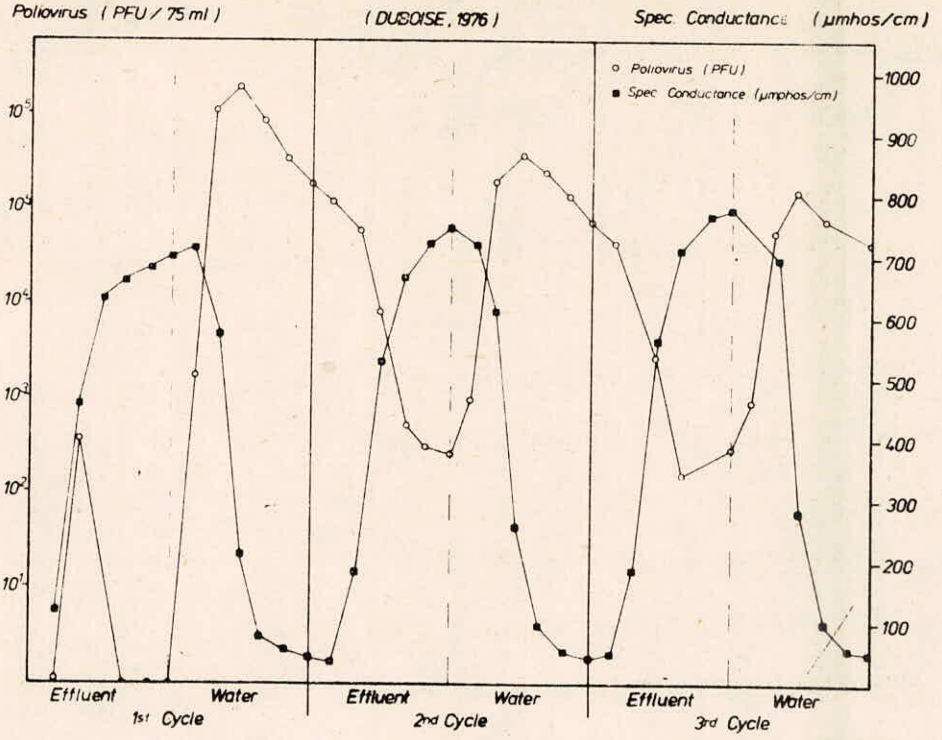

Fig. 19 : Transport of viruses in sewage effluent and destilled water (Duboise et. al. 1976).

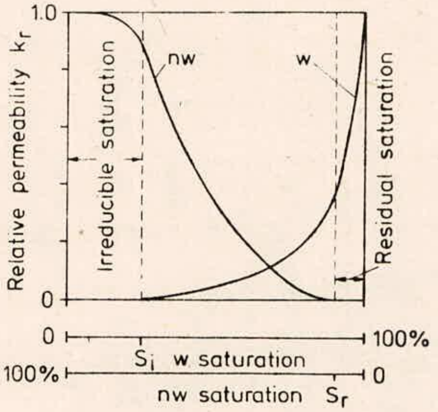

Fig. 20 : Relative permeabilities for a wetting (w) and a nonwetting fluid (nw) as a function of the degree of saturation.

cross section A under consideration is available, the discharge of each fluid must be lower, corresponding to their proportion of the cross sectional area A. The discharge of the two phases can described by the modification of the Darcy law, and can be written as

$$Qw = - \frac{K_r w \cdot K\rho w}{w} \; .A. \; \frac{d\,h\,w}{dx} \qquad ...(38)$$

and

$$Q_n w = - \frac{K_{rnw} K_{nw}}{\mu_{nw}} \; .A \; \frac{dh_{nw}}{d_x} \qquad ...(39)$$

where K represents the permeability, ρ the density, μ the dynamic viscosity, h the fluid potential, K_{rw} the relative permeability for water in the presence of a non wetting fluid and K_{rnw} relative permeability for non wetting fluid in presence of water. Subscripts w & nw represents the water and non wetting fluids respectively.

The relative permeability according to Eq.(38) and (39) depend on the degree of saturation (S) expressed as the proportion of pore space of each of the two phases (Fig.20). It is clear from the figure that the fluids must reach a minimum saturation degree before it can flow at all in the medium in question. Thus, water can not flow until the degree of saturation Sn is reached. Since it is in a state of irreducible saturation. The non wetting fluids can not flow until the degree of saturation Sn is reached, since these substances are in a state of residual saturation and under normal pressure conditions not mobilizable. The effect of residual saturation is the real reason why a particular quantity of a fluid immiscible with water in a porous medium can only spread out a specific distance and only occupy a certain volume of the medium.

The miscibility or immiscibility with water is the dicisive determining parameter for the migration process. Fluide miscible with water are fully displaced by water, while immiscible fluids are held back in residual saturation in the pore space and can be further transported by water only according to their solubility.

The density ρ is the next most important parameter to the extent that the difference in density between fluid and water determines the level in which the migration chiefly takes place relative to the aquifer: in the region of the ground water table ($P < 1$) or in the region of the impervious bedrock ($P > 1$). Even small density of differences of a few tens of grams per kilogram ground water can be decisive (Schwille 1984).

The viscosity on the other hand determines the velocity of the flow processes thus, the conductivity of the porous medium for the fluid concerned.

The surface tension is responsible for capillary effects as well as for the spreading of fluids on free water surfaces. It is without significance in the first phase of spreading, in which the effect of gravity prevails, but gains increasing importance towards the end of the spreading phase.

Mineral oil products (oil) and aliphatic chlorohydro carbons (CHC' s) are sufficiently representative for by far the largest proportion of organic substances immiscible with water which are potentially harmful to ground water, as far as migration behaviour is concerned (Schwille, 1981).

Whether infiltrating oil or CHC's reach the groundwater table or not, depends upon the spilled volume, the infiltration process (e.g. quasi-point or areal source, infiltration rate) and upon the retention capacity of the porous medium. The retention capacity for oil and CHC in the unsaturated zone lies in general by 3-5 1 m^{-3} in highly permeable media and at the most 30-50 lm^{-3} in media of low permeability (Schwille, 1984). The heterogeneity of the unsaturated zone (e.,g.,alteration of different permeable layers) and the degree of water saturation of the individual layers (e.g. so called perched capillary fringes at the boundary of less permeable to more permeable layers) results in a lateral component of the percolation process and consequqntly a broadening of the oil/CHC-body with increasing depth (Fig.21). The heterogeneity of the unsaturated zone thus results in general in a considerable reduction of the penetration depth in comparison with that of a homogeneous medium. The retention capacity of the unsaturated zone can therefore only be estimated satisfactorily with a good knowledge of its structure and

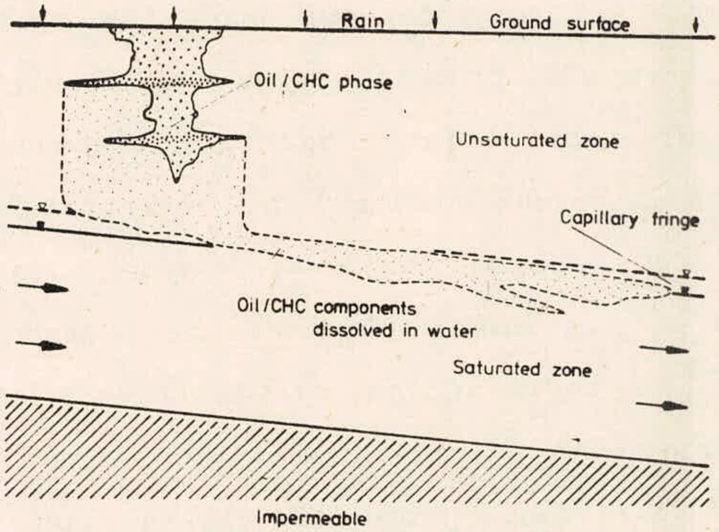

Fig. 21: Oil/Chlorohydrocarbon migration pattern (unsaturated zone)

moisture content. Oil and CHC's behave similarly as a phase in unsaturated zone, disregarding different percolation velocities as a result of different viscosities.

In principle, the given oil migration pattern (Fig.22) is applicable to crude oil, too. The flow characteristics of crude oils are very complicated, however, dissimilar (depending on their origin). At temperatures at which all crude oil components are dissolved within one another, crude oil is a true Newtonian fluid. When the oil is cooled, substances (Paraffins and others) crystallize out and ,form agglomerates. In this way, the flow behaviour of the oil is considerably altered. This microcrystalline precipitate can lead to stoppages in fine pored media, which can bring the flow of oil to a stop even though the viscosity of the oil itself would allow flow. For crude oils, therefore, the viscosity may be considered only as a first criterion for the velocity of the flow process.

The spreading of CHC's in ground water (saturated zone) is presented schematically in Fig.23. When the fluid has reached the surface of the saturated zone, the flow is slowed down since ground water must be displaced for the further downward movement of the plume, but the laterally effective component is clearly not of such decisive importance. The heterogeneity that

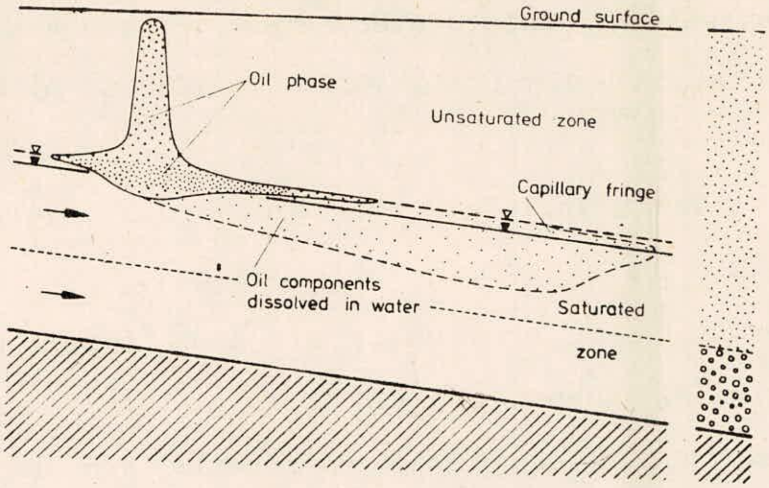

Fig. 22 : Oil migration pattern (saturated zone)

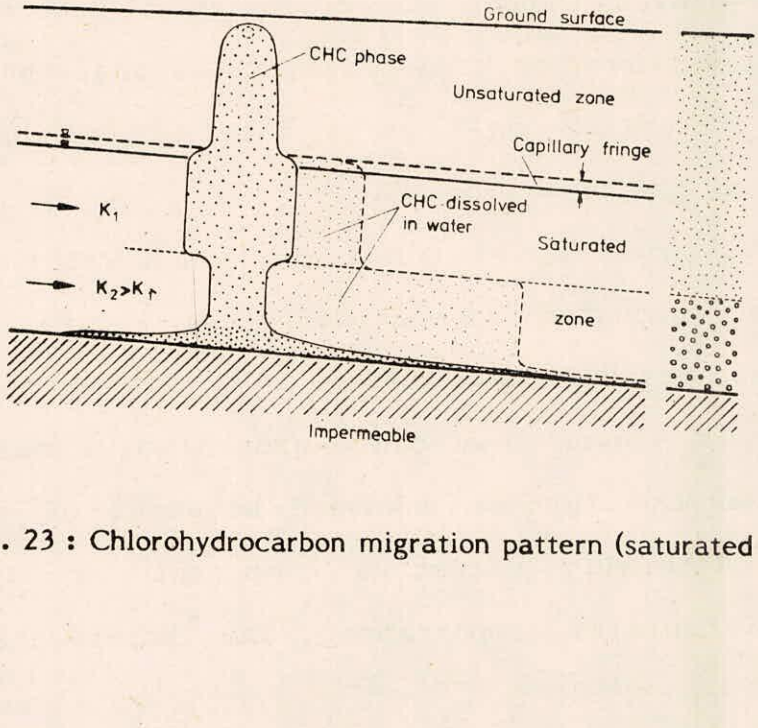

Fig. 23 : Chlorohydrocarbon migration pattern (saturated zone)

usually present in aoquifers results in a lateral spreeding on layers (as indicated in Fig.21). If the retention capacity of this zone is exeeded (this is governed by the residual saturation in the same manner as percolation in the unsaturated zone), when the fluid sinks right to the impervious bedrock and spreads out under formation of a more or less flat mound. The spreading out takes place under the pressure head in the mound and follows the relief of the bedrock as slavisnlyesas the oil over the ground water table.

In nature, however, the bedrock are in no way ideal planes as in Fig.23 but have as a rule a more or less undulating relief. The CHC' s keep strictly to the deepest parts of the relief, following the local depth contours, whose course in comparision with the ground water table is usually unknown or not sufficiently known. When the bedrock is formed of layers of comparatively low hydraulic conductivity then an estimate of the form is practically impossible.

6.0 CONCLUSIONS

Although the need for definitive information pertaining to the transport and fate of pollutants in the subsurface is immediate and pressing, the present state of knowledge on this topic is relatively primitive, reflecting the long prevailing lack of concern for ground water quality. Until the mid-1970s, information concerning subsurface behaviour of pollutants was garnered mainly from field monitoring studies conducted in response to observed and usually highly visible cases of ground water pollution. Since these cases were relatively few in number and dealt primarily with inorganic chemicals and bacteria, this information was very limited. More recently, increased interest in ground water, coupled with the availability of more effective analytical methodologies for organic pollutants and viruses, has resulted in rapid expansion of the body of information available from field monitoring studies of ground water quality. These data provide many useful, although limited, insights regarding the transport and fate of various pollutants in the subsurface. For example, the widespread detection of chlorinated ethanes and ethenes in ground water in areas where these substances have been released into the soil profile indicates strongly that they are highly mobile and persistent in the subsurface and, hence, should not be released in appreciable quantities into this environment. For the most part, however, monitoring data are pollutant and site specific and provide little rational basis for extrapolation of this information to other pollutants in different subsurface environmental situations.

Considering the large number and variety of pollutants that may be released to the subsurface and the wide range of environmental situations (geological, hydrological, chemical, and biological) they may encounter, it is apparent that a highly systematic approach must be followed in developing a capability for predicting subsurface transport and fate sufficient to meet the goals of ground water pollution control. Accordingly, the major thrust of transport and fate research should now to be directed towards the definition and quantitation of the processes governing the behaviour of pollutants in subsurface environments, coupled with the development of mathematical models that integrate process descriptions with pollutant properties and environmental (site) characteristics to yield quantitative estimates of subsurface transport and fate. The ultimate objective of this research should be to provide methodologies that will permit accurate prediction of the effect specific pollutants released into the subsurface from a particular source activity will have on the quality of ground water at points of withdrawal of discharge. Such research is specially difficult and costly because of the remoteness and relative inaccessibility of the environmental compartments with which it is concerned. It is interdisciplinary in nature and requires the input of a wide range of scientific and technical capabilities.

From the discussion in the report, following conclusions can be drawn

1. Various type of source activities i.e. agriculture, household, commercial, industrial and mining activities, produce large amounts of waste, which may be solid or liquid. The pollutants from these wastes may leach down to the ground water and deteriorate its quality.
2. Some pollutants are toxic for human beings. Heavy metal pesticides may prove fatal if present in high concentrations. Some organic pollutants may be mutagenic, teratogenic or may also be carinogenic.
3. Unsaturated zone acts as a buffer between the human activities and the ground water system. Physiochemical processes operating in the unsaturated zone contribute to the removal of nitrogen, phosphorous, heavy metals and microbes. The clay minerals and organic material exercise the major control.
4. The extensive work research carried out over the past two decades on the behaviour of mineral oil products under ground has provided a great deal of knowledge on immscible liquids (with water) which on the basis of theoretical consideration one may transfer to the organic chemicals.
5. The biological active layer at the boundary of water and for filteration of pathogenic bacteria

and viruses due to high content of sorptive small particles and microbial slimes.

6. In many investigations of contaminant occurrence and migration in ground water, reactive contaminants rather than unreactive ones are the focus of concern. The problem of predicting contaminant migration in these situations is compounded by combined interactions involving advection, dispersion, diffusion and chemical reactions such as adsorption, precipitation, coprocipitation, oxidation, reduction and complexing. In models that include the effects of advection, dispersion and reaction the reaction term rarely describes more than the effects of reversible linear sorption represented by linear isotherms.

7. The physical processes contributing to migration of pollutants through granular geologic materials are advection, mechanical mixing, and molecular diffusion. Mathematical expressions for these processes, when combined with the continuity equation, give the advection-dispersion equation. Solution of these equations, subject to the appropriate initial and boundary conditions, provide predictions of the spatial and temporal distribution of the pollutants.

8. In ground water regimes with low velocities, as in silty or clayey deposits, advection and mechanical dispersion commonly have little or no influence

relative to molecular diffusion. Although diffusion controlled hydrogeologic systems appear to be wide spread in nature, there have been few studies of the diffusion process in hydrogeologic systems of the factors that control the magnitude of the diffusion coefficient.

9. Modelling of flow and transport in spatially variable fields has been developed only recently. Many problems are still to be addressed e.g. (a) impact of adsorption and its spatial variability upon solute transport, (b) the feed back mechanism of change of soil properties due to presence of solute (c) the effect of root zone upon water and solute distribution and (d) the influence of spatial variability of depths larger than the few meters of the upper layer and particularly in the zone adjacent to a water table.

Although much research on contaminant migration in ground water has been conducted during the past two decades, this field of endeavour is still in its infancy. Many definitive laboratory and field tests remain to be done. it is these tests that will provide much of the framework for development of practical and reliable methods for assessing the impact of man s activity on the quality of the ground water enviro ent

REFERENCES

1. Althus, H., Jung K.D.,Mathess, G.,pekdeger, A., 1982, lebensdauer von Bakterian viren in Grund wasserleitern.Umweltubnesamt materialien 1/82, p.190, schmidt variag.

2. Anderson, M.P., 1979, Using modelsto simulate the movement of contaminants through groundwater flow systems; CRC Critical Reviews in Environmental Control, V.9, p.97-156.

3. Anonymous, 1978, Jahreshbericht des institute fur Radiohydrometrie der gsf. Neuherberg, Munchen.

4. Applet, H., Holtzclaw, K., and pratt,p.F.,1975, Effect of anion exclusion on the movement of chloride through soils: soil· sciences society of America proceedings, V.39, p.264-267.

5. Armstrong, D.E., Konrad, J.G.,1974, Nonbiological degradation of pesticides In: Guenziwd(ed) pesticides in soil and water. Soil Sci sec Am madison, wisc, p.123-131.

6. Atkins, S.F.,1976, Nitrogen leaching from fertilizers: lysimeter trails: Published results from Europe and USA. Imperial Chemical Industries Ltd. Agricultural Division Report, P.76.

7. Audus, L.J.,1969, Microbiological breakdown of herbicides in soil. In:Woodford EK, Sager GR(eds) Herbicides and the soil. Blackwell, Oxford, P.1-8.

8. Bachmat, Y., and others, 1978, Utilization of numerical groundwater models for water resource management: U.S.Environmental protection Agency, EPA-600/8-78-012.

9. Baetsle, L.H., 1967, Computational methods for the prediction of underground movement of radionuclides: Journal of nuclear safety, V.8, P. 576-588.

10. Baetsle, L.H.,1969, Migration of radionuclides in porous media, in duhamel, A.M.F., ed., progress in nuclear energy, series 12: Health physics, V.2, pt.I.

11. Baker, L.E.,1977, Effects of dispersion and dead-end pore volume in miscible flooding: Society of petroleum Engineering JOurnal, V.17, P.219-227.

12. Bear, J., 1972, Dynamics of fluids inporous media. Am Elsevier, Environ sci New York, P.764.

13. Bear, J., and verruijt, A., 1987, Modelling Groundwater Flow and Pollution-theory and application of transport in porous media. Reidel publishing company, Netherlands. pp.414.

14. Berg, G.(ed), 1967, Transmission of viruses by the water route. Wmiley-Interscience, New York.

15. Berg, G.,1973, Removal of viruses from sewage, effluents, and water, Bull.WHO 49, P.451-460.

16. Biggar, J.W., and Nielsen, D.R., 1960, Diffusion effects in miscible displacement occurring in saturated and unsaturated porous materials: Journal of Geophysical research, V.65, P.2887-2895.

17. Biggar, J.W., and Nielsen, D.R., 1976, spatial variability of the leaching characteristics of a field soil. Water Resources Research, V.12, P.78-84.

18. Boyd, J.W., Yoshid, T., Vereen, L.E., Cada, R.L., and Norrison, S.M., 1969, Bacterial response to the soil environment. Sanitary Engineering papers. Colorado State University, Pt.Collins, No.5, P.1-22.

19. Brenner, H., 1962, The diffusion model of longitudinal mixing in beds of finite length: Numerical values: Chemical Engineering Science, V.17, P.229-243.

20. Bresler, E., Dagan, G.,1981, Convectiv and porescal dispersive solute transport in unsaturated heterogeneous fields. Water Resources 17, P.1683-1693.

21. Bresler, E.Dagan, G.,1983a, Unsaturated flow in spatially variable fields. II.Application of water flow models to various fields.

22. Bresler, E.Dagan, G.,1983b, Unsaturated flow in spatially variable fields. III. Solute transport models and their application to two fields. Water resour. Res.19, P.429-435.

23. Creary, R.W.,1978, Analytical models for ground water pollution and hydrology: Princeton University, Water Resources Program. Report No.78-WR-15.

24. Coats, K.H. and Smith, B.D.,1964, Dead end pore volume and dispersion in porous media. Society of Petroleum Engineering Journal, V.4, P.73-84.

25. Dagan, G., Bresler, E.1983, Unsaturated flow in spatially variable fields. I.Derivation of models of infiltration and redistribution. Water Resources Res.19, p.413-420.

26. Deans, M.A.,1963, A Mathematical model for dispersion in the direction of flow in porous media: Society of Petroleum Engineering Journal, V.3, p.49-52.

27. Doner, H.E. and McLaren, A..,1976, Soil nitrogen transformation: A modelling study on Nriagu, J.ed. Environmental biochemistry (Vol.1): Ann Aroor, Michigan, Ann Arbor science Publishers, Inc., p.245-258.

28. Doner, H.E. and Mortland, M.M.1969b, Benzene complaxes with Cu(II) montmorilonite, science 166, p.1406-1407.

29. Dreasen, D.R.,Gladney, E.S.Owens, J.W.Perkins, B.L.Wienks, C.L.Wangen, L.E.,1977. Comparisons of levels of trace elements extracted from fly ash and levels found in effluents from a coal-fired power plant. Environ. Sci. Tech.Vol.11, p.1017-1019.

30. Doyvenboden, W., Van Kooper, W.F.1981, Effects on ground water quality of a waste disposal site in Noordwijk.

31. Ellis, R.R.Devi, L. and Wieranga, W.A.1965, The Investigation of water flow through porous mediums by means of radiotracers: Water Resources Research V.4, p.413-416.

32. Fatt, I., Maleki, M., and Upadhyay, R.N., 1966, Detection and estimation of Dead-end pore volume in reservoir rock by convential laboratory tests: Society of Petroleum Engg. Journal, V. 6, p. 206-212.

33. Fenn, D.B.Mortland, M.M. and Pinnavaia, T.J. 1973, The chemisorption of anisols in Cu-montmorillonita, Clays and Clay Minerals 21, p.313-322.

34. Fillinow, A.B.Jacobs, L.W. and Mortland, M.M.1976 Fate of polybrominated biphenyis (PBE's) in soils: Retention of hexabromobiphanyl in four Michigan soils. J.Agri.Food Chem.24p.1201-1204.

35. Fried, J.J.1975, Groundwater Pollution: New York, Elsevier, p.33c.

36. Gerba, C.P.Keswick, B.A.,1981, Survival and transport of entaric bacteria and viruses in ground water, study Environ. Sci.17, p.511-515.

37. Gillhem, R.W., Cherry, J.A.andnd Anderson, G., 1981, Hydrogeological studies of a sandy unconfined acuifer at an abandoned landfill.

38. Gillham, R.W. and Cherry J.A.1982, Contaminant migration in saturated unconsolidated geologic deposits, in Narsimhan, T.N.1982, Recent trends in hydrogeology, Special paper 189, Geological Society of America, pp.31-62.

39. Golubev, V.S. and Garibyants, A.A.1971, Heterogeneous processes of geochemical migration (special research report):New York Consultants Bureau (trans. from Russian), p.15c.

40. Havemeistar, G.Riemer, R, 1983, Transport von Bakterian und Viran in verschiedenen porosen median, Forum mikroorganismen und viran in groundwasserleitern", Proc. DVGW Wasserfachl Aussprachetag Munchen 83, March 1-4.

41. Helling, C.W.Kearney, P.C.Alexander, M.1971, Behaviour of pasticides in soils, Advan Agron 23, p.147-240.

42. Higgins, G.H.1959, Evaluation of the groundwater contamination hazard from underground nuclear explosions: Journal of Geophysical Research V. 64, p.1509-1519.

43. Hirsch, P.Rades-Rokkohl, E.1983, Die Zusammensetzung der naturlichen Grundwasser-Mikroflore and Untarsuchungen urber inhre wechselbeziehungen mit Fakalbakterian, Forum, Mikroorganismen und viren in grundwasserleitern. Proc. DVG Wasserfachl Aussprachetag Munchen 83, March 1-4 (in press).

44. Iwasaki, T, 1973, Some notes on sand filtration J.AWWA 29, p.1591-1602.

45. James, R.V. and Rubin, J.1978 Applicability of the local equilibrium assumption to transport through soils of solutes affected by ion exchange, in Proceedings, American Chemical Society, 176th ACS National meeting, p.225-235.

46. Jung, K.D., Schroter, J.1983, Lebensdawar and transport in typischen grundwasserliatern: Halterner Sands, Forum, Mikroorganismen und viran in grundwassarlaitern P(roc DVGW Wasserfachl Aussprachetag Munchen 83, March 1-4 (in press).

47. Jung, K.D.,Schroter, J.1983, Lebensdawar and transport in typischen grundwasseriaitern: Halterner Sands, Forum, Mikroorganismen und viran in grundwassarlaitern, P(roc DVGW Wasserfachl Aussprachetag Munchen 83, March 1-4 (in press).

48. Kaufman, B.D.Plimmer J.R.Kaarney P.C.Blacks, J.Guardia, F.S.1968, Chemical versus microbial decomposition of amitrole in soil, Weed Sci.16, p.266-272.

49. Kautman, D.D.1974, Degradation of pesticides by soil microorganisms, In: Guenzi WD(ed) Pesticides in soil and water. Soil Sci Soc.Am Medison, Wisc, P.133-202.

50. Kemper, W.P.and Rollins, J.B.1966, Osmotic efficiency coefficients across compacted clays: Soil Science Society of America Proceedings V.30, p.529-534.

51. Kharaka, Y.K. and Barens, I.1973, :Solution mineral equilibrium computations: Springfield, Virginie, National Technical Information Service Technical Report PB214-899, P.92.

53. Konikow, L.F.1977, Applications of solute-transport models to groundwater quality problems, in papers and proceedings of the Water Research Centre Conference: Berkshire, University of reading, Sept.6-8, 1976, p.625-643.

54. Konrac, J.G.Chesters, G., Armstrong, D.E.1969, Soil degradation of malathion, a phosphorodithioata, Soil Sci Soc. Am Proc. 33, p.259-262.

55. Kreitler, C.W., and Jones, D.C., 1975, Natural soil nitrate: the cause of Nittrate of ground water in kunnels county, Texas, Ground water, Vol.13, P.53-61.

56. Lammers, W.T., 1978, Separation of suspended and colloidal particles from natural water. Environ. Sci.Technol.1, p.52-57.

57. Maeda, J.Mimae, Y.F.Osawa, P.,1976, Effect of temperature on mobility and chemotoxis of Escherichia coli. Bacteriol 127, p.1039-1046.

58. Marino, M.A.1976, Numerical simulation of contaminant transport in subsurface systems: in Saleen, Z.A. ed.Advances in ground water hydrology: American Water Resources Association, p.113-129.

59. Mathess, G.Pekdgar, A.1981, Concepts of a survival and transport model of pathogenic bacteria and viruses in ground water water. Sci.Total Environ 21, p.149-159.

60. Mathess, G.,Pekdeger, A.Rast, H., Rauart, W.Schulz, H.D.1979, Tritium tracing in hydrogeochemical studies using model lysimeters, Isot Hydrol 1978, 2, p.769-785 IAE, Vienna.

61. McBridge, M.B., Pinnavaia, T.J. and Mortland, M.M.1977, Adsorption of aromatic molecules by clays in acqueous suspension. In: I.H.suffet (ed), Fate of pollutants in the Air and Water Environments, Part 1, Vol8, Wiley, New York, E.145-154.

62. Merkli, B.1975, Untarsuchungen uber machanisman and Kinatik der elimination von sakterien und viran im Groundwasser. Natruwiss Liss ETH, Zurich.

63. Mortland, M.M. and Halloran, L.J.1976, Polymerization of aromatic molecules on smectite. Soil Sci.Soc.Am.Proc.40, P.367-370.

64. Mortland, M.M. and Meggitt, w.F.1966, Interaction of ethyl-N, N-di-n-propyl-throlcarbamate (EPTC) with montmorillionite, J.Agric, Food Chem.14, p.126-129.

65. Nelson, J.L.1961, Recent studies at hanford on soil and mineral reactions in waste disposal, in proceedings, symposium on groundwater disposal of radioactive wastes, Berkeley, California, Aug.25-27, 1959: Berkeley, Sanitary Engineering Laboratory, University of California.

66. Ogata, A.,1970, Theory of dispersion of granular medium:J.S.Geological Survey Professional Paper 411-I, p.36.

67. Ogata, A. and Banks, R.S.1961, A solution of the differential equation of longitudinal dispersion in porous media: U.S. Geological Survey Professional Paper 411-A, p.7.

68. Orlop, G.T. and Rathakrishna, G.N.1958, The affects of entrapped gases on the hydraulic characteristics of porous media: American Geophysical Union Transactions, V.39, p.648-659.

69. Parkhurst, D.L. Plummer, L.N. and Thorstanson, D.C.1978, Chemical models in groundwater systems: Geological Society of America Abstracts with Programs, V.3, p.468.

70. Passicurs, J.B.,1971, Hydrodynamic dispersion in aggregated media 1. Theory: Soil Science, V.3, p.339-344.

71. Passiours, J.B. and Rose, D.A.1971, Hydrodynamic dispersion in aggregated media.2.Effect of velocity and aggregate size: Soil Science, V.3, p.345-351.

72. Parkins, T.K. and Johnston, O.C.1963, A review of diffusion and dispersion in porous media: Society of Petroleum Engineering Journal, V.3, p.70-84.

73. Pinnavais, T.J., Hall, P.L., Cady, S.and Mortland, M.M.1974, Aromatic radical cation formation on the intracrystal surfaces of transition metal layer lattics silicates. J.Phys. Chem.78, p.994-999.

74. Philip, J.R.P.1968, The Theory of absorption in aggregated media: Australian journal of Soil research, V.6, p.1-19.

75. Philip, J.R.1975a, Stability analysis of infiltration, Soil Sci Soc. Am. Proc.39, p.1042-1049.

76. Philip, J.R. 1975b, The growth of disturbance in unstable infiltration flows. Soil Sci Soc. Am Proc.39, p.1049-1053.

77. Pinder, G.P., Gray, W.G.1977, Sinite element simulation in surfaces and subsurface hydrology: New York, Academic Press, P.295.

78. Plummer, L.N.Parkhurst, D.L. and Kosiur, D.R. 1975, MLA 2: A computer program for modelling chemical reactions in natural waters: U.S.Geological survey Water Resources Investigation Report 75-61, p.73.

79. Raats, P.A.C.,1969, Steady gravitational convection induced by a line sour of salt in a soil. Soil Sci. Soc.Am Proc. 33, p.483-487.

80. Raats, P.A.C.1973 Unstable wetting fronts in uniform and nonuniform soil, Soil Sci.Soc.Am Proc.37, p.681-685.

81. Raats, P.S.C.1976, Analytical solutions of a simplified flow equation, Trans.Am Soc Agric. Eng.19,p.683-689.

82. Raats, P.A.C.1981a, Movement of fluid masses embedded in other fluids in porous media. EOS Trans.Am Geophysical Union 62, p.807.

83. Raats, P.A.C.1982, Convective transport of ideal tracers in unsaturated soil IN;NUREG/CP-0030, Proc. symp unsaturated flow and transport modelling. US Nucl Regulet Comm Washington, p.249-265.

84. Raats, P.A.C.1983, Implications of some analytical solutions for drainage of soil water. Agric water Manage, 6, p.161-175.

85. Reynolds, W.D.1978, Column studies of strontium and cesium transport through a granular geologic porous medium CMS Theses): Waterloo, Ontario, University of Waterloo, p.149.

86. Rose, D.A.1973, Some aspects of the ydrodynamic dispersion of solutes in porous materials: Journal of Soil Science, V.24, p.284-295.

87. Rose, D.A.,1963, The physics of flow through porous media: Toronto, University of Toronto Press.

88. Schroter, B., 1983, Der Einflub von Textur-und Struktureiganschaftten poroser median suf die dispersivit. Ph.D.Thesies, Univ. Kiel.

89. Scott, D.C. and Weber, J.B.1967, Herbicide phytotoxicity as influenced by adsorption. Soil Sci.104, p.151-158.

90. Seiler, K.P., Alexander, I.,1983, Lebensdauer and transport von bakterian in typischen grundwasserleitarn. Proc. DVGW Wasserfachl Aussprachetag Munchan 82, March 1-4 (in press).

91. Shin, Y.O.,1970, Adsorption of DDT by soils and biological materials, Ph.D.Thesis, Michigan State University, E.Lansing, MI.

92. Smith, S.J., and Young, L.B.,1975, Distribution of nitrogen forms in virgin and cultivated soils. Soil Science, Vol.120, p.354-360.

93. Smith, J.M.,1970, Chemical Engineering Kinetics: New York: McGraw Hill.

94. Snegaroff, J.1977, Apercu sur is pollution des souterraines par les pesticides, Colloque BRGM Protection des eaux souterraines captees pour 1 alimentation humins, Orieans, France.

95. Stotzky, G.,1966a, Influence of clay minerals on microorganisms.II. Effect of various clay aspecies, homoionic clays and other particles on bacterie. Con.J.Microbiol 12, p.831-848.

96. Stotzky, G.,1966b, Influence of clay minerals on microorganisms, III. Effect of particle size, cation exchange capacity and surface areas on bacteria. Can.J.Microbiol 12, p.1235-1246.

97. Thomas, G.W. and Swoboda, A.R.1970, Anion exclusion effects on chloride movement in soils: soil science, v.110, p.163-166.

98. Truesdell, A.H.and Jones, B.F.1974, KATE , a computar program for calculating chemical equilibria of natural waters: U.S.Geological survey, Journal of Research, v.z.p.233-274.

99. UNESCO, 1980, Aquifer contamination and protectio, IHP Project 8.3 France, pp.440.

100. Vanloocks, E, De Borger, R.Voets, J.P. and Verstraete, W.,1975, Soil and groundwater contamination by oil spills: problems and remedies. Intern.J.Environ.Studies.Vol.8, p.99-111.

101. Vinten, A.J.A.Mingelren, U.,Yaron, B.1983, The effect of suspended solids in waste water on soil hydraulic conductivity. II. Vertical distribution of suspended solids. Soil Sci Soc Amj 47:408-412.

102. Warq, C.H.,Giger, W. and McCarty, P.L.(ed), 1985, Ground water quality. John Wiely and Sons, Inc., N.Y.pp.547.

103. Weber, J.B.,1970 Mechanisms of adsorption of s-triazines by clay collcids and factors affecting plant availability. Residue Rev.132, p.93-130.

104. Weber, J.B. and Coble, H.L.1968, Microbial decomposition of diquat adsorbed on montmorillonita and Kaolinite clay J.Agric.Food Cham.16, p.475-478.

105. Weeks, O.L.Stewart, G.L. and Weeks, M.E.,1976, Measurement of non-exchanging pores during misible displacement in soils: Soil science, V.122, p.139-144.

106. White, I., Colombera, P.M.Philip, J.R.1976, Experimental study of wetting front instability induced by sudden change of pressure gradient. Soil Sci. Soc.Amj.40, p.824-829.

107. Wyckoff, R.D.Botset, H.G.1936, The flow of gas liquid mixtures through unconsolidated sands. Physics 7, p.325-345.

108. Yao, K.M.Habibian, M.T.C Melia C.R.1971, Water and Wastewater filtration: concepts and applications vol.5, Dep.Environ Sci Techn. Univ. N.Carolina, Chapel Hill, p.1905-1112.

109. Yaron, B.,Saltzman, S.,1978, Soil parathion surface interactions. Residus rev.69, p.1-35.

110. Yaron, B, Dagan, G. and Goldshmid, J.1984, Pollutants in porous media-the unsaturated zone between soil surface and groundwater. Springer verlag, Germany, pp.296.

111. Yih, C.S.1963, Velocity of a fluid mass embedded in anaother fluid flowing in a porous medium. Phys Fluids 6, p.1403-1407.

112. Young, C.P.Oakes, D.B. and Wilkinson, W.B.1976, Prediction of future nitrate concentration in ground water. Ground Water, Vol.14, p.426-438.

113. Zaborsky, O.,1974 Immbolized Enzymnas.CRC Prass, Clevaland, OH.

DIRECTOR - SATISH CHANDRA

STUDY GROUP - SUDHIR KUMAR

DOCUMENTATION STAFF - AVDHESH KUMAR
Y.P.S. VERMA