"Accumulation and Movement of Some Heavy metals in Sewage Treated Delhi Soil"

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To

BHAIYA

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BHABHI

SCIENCE IS THE SEARCH FOR
TRUTH - IT IS NOT A GAME
IN WHICH ONE TRIES TO BEAT
HIS OPPONENT, TO DO HARM
TO OTHERS.

-PAULING

CERTIFICATE

This dissertation entitled "Accumulation and Movement of Some Heavy Metals in Sewage Treated Delhi Soil" has been carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted in part or full for any other degree or diploma of any University.

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ABBREVIATIONS

SYMBOL		
1.	PT	Primary Treated Sewage
2.	F. T.	Final Treated Sewage
3.	COD	Chemical Oxygen demand
4.	O. C.	Organic Carbon
5.	BOD	Biochemical Oxygen Dema
6.	E. C.	Electrical Conductivity
7.	CM	Centimeter
8.	Meq	Milli-equivalents
9.	Mgd	Million Gallons per day
10.	Mg/l	Milligrams/litre
11.	ppm	Parts per million

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INTRODUCTION

The population explosion, increased industrialization, agricultural development and recreational activities all lead to a corresponding increase in the volume of effluents and diversity of pollutants, discharged into the natural environment. So these activities disturb the prevailing normal environmental conditions (Hart and Stander, 1972).

One of the most pressing problems facing metropolitan areas today is disposal of large volumes of liquids and solid wastes, generated by urban and industrial activities. Now there is great need to conserve and reuse water resources. But there are so many problems associated with water pollution, resulting from discharging wastes into surface water There is air pollution problem from the incineration of the waste and the scarcity of suitable sites for land fill operations. These activities have prompted municipalties and other Governmental agencies to investigate alternative means of disposal operations. So this is currently receiving wide spread attention especially with the disposal of wastes onto Agricultu land (Page 1974).

Waste water or sewage is an outcome of man made activities; urban sewag consist of industrial as well as domestic sewage. Domestic sewage mainl contains organic load but it also is a source of heavy metals like Cu, Cd, Zn and Ni (Leeper, 1978). Previously disposal was a big problem and mainly these wastes were discharged into water bodies like rivers, lakes, ponds, oceans etc. But once when it was realized that these bodies are quite sensitive to discharge of waste water containing lot of pollutants and chemicals which are harmful for aquatic flora and fauna, interest in this field gained momentum. To solve this problem and minimize these harmfu effects, sewage treatment plants came into existence. Till date sewage treatment plants, were designed in such a way so that their main job is to remove mainly organic load from waste water and not the dissolved chemical (like heavy metals and other chemicals). When it was established that these treated and untreated sewage have lot of plant nutrients like Nitrogen, Phosphorus, Calcium and Potassium etc., people diverted this sewage after treatment for irrigation of their lands. This practice is going on for a long time. It is a fact that except developed and a few developing countries, most of other countries don't have treatment facilities and they are using simply raw sewage for irrigation purpose. When once this waste containing heavy metals is discharged on the land, either as to solve a disposal problem or for irrigation purposes, the heavy metals become part of soil system. Soil system is a very complex heterogenous system, which includes, air, water and solid phases. Once a chemical has been added to the surface of a soil, there will be tendency for it to move downward, depending on the amount of moisture and some other factors. An understanding of chemical movements or leaching in this type of system is of environmental concern, because of the possibility that the chemical will ultimately reach ground water and contaminate it.

This leaching or movement mechanism is controlled by principal factors like adsorption, absorption and ion exchange phenomena. These properties are responsible for the pattern of movement. Apart from these processes, certain other properties like soil chemical concentration, soil water content soil organic matter etc. also play an important role in deciding the fate of waste water constituents in soils (Spyridakis and Welch, 1976).

Environmental pollution and its effect on plant and animal life has brought tremendous awareness regarding waste disposal. The huge build up in the amount of waste material and concurrent decrease in disposal sites have led to a renewed interest in the study of the application of sewage to soil. In general, chemical constituents (like nitrogen and phosphorus) of waste waters, which behave as "pollutants" in surface water disposal system become nutrients for plant growth in a land recycling system. So the land recycling of waste is receiving increasing importance as a means of waste water reclamation and water pollution control.

Though land disposal of raw sewage and treated sewage effluents are not new, they attracted attention only recently. There are many sites where relatively large volumes of sewage effluents are used to irrigate agricultur lands.

Previously the main objective behind the application of treated municipal and industrial effluents and wet sludges to the land was considered simply as "disposal of waste". But now-a-days it is a valuable resource for any nation, because since it contains enormous quantity of plant nutrients. So it is necessary to use land treatment as one of the available alternatives in the waste management system. Currently land as a waste management system is getting an edge over the surface water discharge method, because discharging of any pollutants over lands has less environmental impact than discharging them in any water body.

The main objective or aim of discharging the sewage effluent on the land is:

(a) Recyling of potential sewage pollutants through the production of agriculture.
(b) Reclamation of waste water.
(c) Minimisation of environmental pollution.

Many researchers have stated that soil is a "living filter" (for e. g. see Lee, 1976). According to this concept vegetative cover is an integral part of the system. It also includes the microbial and physiological activities occuring within the soil system. This system is capable of renovating the sewage effluents by removal and utilization of nutrients applied. So this process of utilizing soil-plants complexes for waste water discharge is called the land treatment process.

Waste water application to soil-plant system can provide an efficient treatment only under very strict condition of control of both the quality and quantity of disposed effluent as well as land management devices. The benefits of application of municipal sewage and sludges on land are many and it is an established fact that crop production has been increased by the use of municipal sewage effluents. There are so many advantages of sewage disposal on land for irrigation and other purposes.

Despite these advantages one can not neglect the manifold problems associated with land application of waste water. Ground water contamination with nitrates, chlorides, phosphates and other hazardous chemicals including heavy metals like cadmium, zinc, copper, chromium, nickle etc. have listed to be potential chemical problems. The fate of pathogenic bacteria and viruses when water moves through the Soil is also of utmost concern (Lance, 1978). Hence critical analysis of environmental consequences of land disposal of sewage effluents becomes necessary to evaluate the success of this system.

Since it is recognised that sewage from industrial areas consist of many heavy metals and they will be phytotoxic if they accumulate in higher concentration, in root zone. These are also injurious to animals, since animals are the part of the ecosystem and food chain ends on living human beings. So these facts have drawn the interest of researchers in this field. It is well known fact that continuous irrigation makes the irrigated soil becoming "Sewage Sick".

In India, sewage utilization as a source of irrigation and nutrient suppl started as early as in 1896. Since than, sewage farming is practised, including the use of raw sewage, diluted sewage and some times partially treated sewage. It is reported that the number of sewage farms in country comes around 132, covering about 12000 hectares (Krishnamoorthy et. al., 1973). That area under sewage irrigation rose from 12,267 hectar in 1965-66 to nearly 40,000 hectares during 1978-79, indicates a trend of continuous expansion of sewage irrigation utilization programme in India (Gaur, 1978).

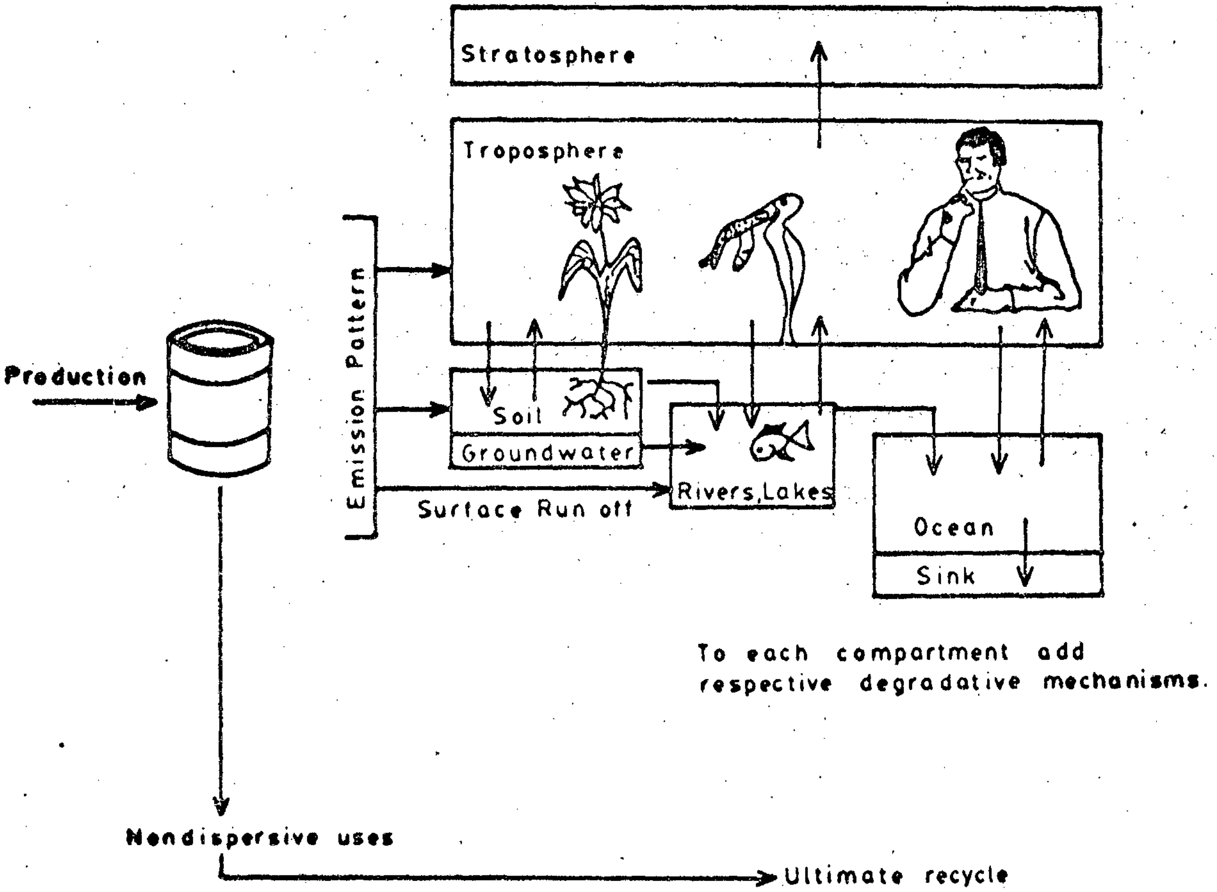
In Delhi around 140 MGD of domestic as well as industrial sewage is being treated at three different sewage treatment plants namely, Okhla, Keshopu and Coronation Pillar. Among them Okhla is the biggest one in India (Sekar and Bhattacharya 1979). Okhla sewage treatment plant is treating 90 MGD sewage. After Primary treatment, 45 MGD primary treated sewage is being discharged into Agra canal and 45 MGD for secondary treatment unit. After that the treated effluent is diverted for irrigating lands. In Delhi, as on 1979, a total area of about 2604 acres was under sewage irrigation and in the following period approximately additional 2932 acres were added up (Sekar, 1984).

So the main objective behind this study was to obtain:

(i) Information about changes in physical and chemical properties

(ii) Fate of certain metals like Cu, Cd, Zn and Ni in soil profile (column study) when subjected to short term application with sewag effluents.

There is very little information on the fate and mobility of heavy metals applied to soil through sewage effluents. Thus, the present study was conducted to know the fate of four heavy metals, when applied to soils in the form of raw and treated effluents.



To each compartment add respective degradative mechanisms.

Fig. 1. A schematic representation of the flow of the chemical product from production to the environment. (Source: Chemicals in the Environment - Distribution, Transport Fate and analysis by W. Brock Neely. (1980).

REVIEW

The present study is an attempt to study the fate of heavy metals like Cu, Zn, Ni and Cd in soil a system, when subjected to urban sewage or waste. The toxic action of heavy metals depends mainly on the available concentration of the metal concerned. Many of the metals function as micronutrients at lower concentration and the toxicity is expressed only at higher concentration (Luckey et. al., 1975). The precipitation, accumulation and migration of metals reaching the soil system are influenced by many physico-chemical and biological factors.

In this chapter, the migration and accumulation of different metals present in urban sewage, and their effects on the soil system and the influence of the different factors which govern the distribution are discussed briefly.

Introduction of metals to soil system leads to permanent changes in soil and therefore their addition to soil should be based upon their total concentration in soils (Leeper, 1978). Metals generally tend to accumulate in the top layers of the soil with various degree of "availability" (Banin et. al., 1981). In initial stage of sewage irrigation, they may be bound to th solid phase of the soil with high absorption energies and will not be readily available to plants. With prolonged use of sewage effluents for irrigation some metals are liable to build up to a toxic levels and cause damage to sensitive crop or plants. Sposito et. al., (1983) reported that the repeated application of sewage-sludge or effluent over a long period of time to an arid zone agricultural soil, tend to promote trace metal accumulation into solid organic or inorganic phases, which are readily extractable with comparatively mild reagents indicating the potentials of metals as toxicants in the soil environments. Patterson (1971) said that sewage irrigation can be phytotoxic in two ways, firstly continued and repeated application of domestic sewage or sludge over a longer time and secondly the use of sludges from industrial areas containing large quantities of toxic metals. Many industrial waste streams are highly acidic and can alter soil properties to which they are applied (Taylor, 1967).

An effect of such streams is the release of naturally occuring elements. This depends on the length of exposure of soil to the leaching solution.

In sewage effluents all the metals are associated with suspended solids and only after acidic digestion, metals can be detected in samples (Nennah et. al., 1983). Most of the heavy metals, which are associated with suspended solid in sewage end up in the sludge (Bouwer et. al., 1974) Bouwer and Chaney (1974) mention that organic matter in the final effluents may significantly contribute to the binding of metals through cation exchange and chelation reactions. The metal species present in crude sewage are in fairly unstable equilibrium between soluble and insoluble forms. It depends on the state of metals in which they are being discharged into sewage and the composition of sewage itself. Nature of sewage includes redox-potential, pH, hardness, presence of various anions such as phosphate and sulphate and the presence of organic matter capable of complexing, or absorbing the metal species (Coker and Matthews, 1983).

Trace elements applied to the soil, regardless of their form in which they are applied may follow the following fate (Page 1974).

(1) It may pass through the soil unchanged

(2) It may form insoluble or sparingly soluble inorganic and organic compounds.

(3) It may be sorbed by soil colloids as cations, anions or molecules.

(4) It may get volatilized from the surface or be taken up by plants.

Mechanism which controls soil solution concentration of heavy metals according to Spyridakis and Welch (1976) includes:-

1. absorption by silicate through surface sorption, surface complex formation, lattice penetration and ion exchange.

2. Surface sorption or surface precipitation of carbonates or/ silicates.

3. Metal fixation and absorption by organic matter.

4. Biological uptake and immobilization.

The sorption and desorption reactions are controlled by pH, Eh, concentration of competing metals and concentration of other ions capable of forming inorganic complexes and organic chelates. pH and Eh are the most significant factors because they are responsible for the retention of the applied metals in the top few centimeters of soils (Spyridakis and Welch 1976).

CHEMISTRY

Chemistry of metals in soil is very complex, and is not completely understood. The inadequacy of analytical techniques is one of the drawbac The reason is that the concentration of water soluble metals and ligands to be measured are often below the detection limits of the conventional analytical methods (Bhel et. al., 1983). Distribution of metals in different ionic forms is a field, little explored so far and information regarding the same is scarce. Metals may be present in the inorganic forms such as oxides, hydroxides and sulphides (Mosey et. al., 1971). It may also be present as loosely bound organic complexes such as with humic acid and polysaccharides (Holtzclaw et. al., 1978).

According to Page (1974) the large fraction of trace metals (Cu, Zn, Ni and Cd) is found in complex form with organic matter. A small fraction probably also exists in soil solution predominantly as divalent cations. In soil system solid phase and solution phase exist and play important role. These two phases in soil system include several types of binding of which one of them is electrostatic. This binding is influenced primarily by the valency of the ion and charge density of the solid phase (Spyridakis and Welch, 1976).

Metals come through sewage to soil and establish an equilibrium between the two phases.. Schlscha et. al., (1982) reported that whenever this chemical equilibrium in soil system is altered, the accumulated waste water oriented metals in organic complexes and inorganic precipitates become reactive. This is the main mechanism by which the metal present in the soil in immobile forms get mobilized and become available for plants. When sewage suspended matter or sludge is applied into soil, it is subjected to oxidation by microorganisms (Lagerwerff et. al., 1976). This oxidation reaction could possibly release heavy metals to the soil solution. In solution mostly cations of the trace metals are present. At the neutral pH (pH 7), the concentration of cations in soil solution is in the range of less than 0.05 ug/ml. In acidic soils (pH 5-6) metal concentration usually is high in solution phase. While in alkaline or calcarious soils (pH 7. 5 to 8. 5) metal concentration usually is lower. Although the factors which govern the solubilities of the cationic species in soil solution are not known, and on the basis of limiting values assumed that at pH 5-8. 5 the concentration of cations of trace elements do not exceed 0. 25 ug/ml.

Under reduced conditions, Cu, Zn, Ni and Cd could form sulphates which are quite insoluble . For anaerobic soils the solubilities of the metals are limited by sulphide precipitation. So when these trace elements are applied to soil, it is retained largely in the surface layer to the depth of mixing (tillage) regardless of their forms (Page 1974).

FACTORS WHICH CONTROL AVAILABILITY AND DISTRIBUTION OF METALS IN SOIL SYSTEM

Many researches have explored the factors affecting the pattern of distribution of various elements between the solid and solution phase of the soil and between the soil and plants. They suggested that soil pH, texture, chemical and minerological composition and organic matter affect this distribution.

Many materials present in the soil can also react with trace metals. Some of these materials are clay, organic matter, iron hydroxide, manganese oxides, carbonates, inorganic chemical compounds, organic acids, amino acids humic acid, fulvic acid. Biological systems also have significant role on altering the distribution of the metals in between the solid and solution phase (Keeney and Wildung, (1977); Lindsay (1972-1973) Chaney and Giordano (1977).

Important factors which influence the chemistry of heavy metals are described in detail in the following section:

Hydrogen Ion Concentration (pH)

pH of the system, to a great extent, influence the dynamics of heavy metals in a soil system. When pH of the system is increased, the mobility of metals is found to decrease (Hem 1972). The concentration of H^+ ion is the main factor which plays a significant role in this. An inverse relation of solubility of metals and plant availability has been observed by many workers in the field (for example Sinha et. al.,(1978) ; Mc Bride and Blariak (1979); Andersson and Nilsson (1976); Fillipovic et. al., 1961 and others). Higher solubility of metals at lower pH is attributed to the competition of H^+ with metals. In this competitive reaction H^+ gets preferentially adsorbed on the exchange sites and this results in higher mobility of metals while in case of higher pH metal oxides hydrate along with their hydroxides, and thus get precipated (Khan, 1982). The study conducted by Kisk and Hassan (1973) on Cu sorption by clay minerals resulted in similar findings, showing competition of H^+ ions and metal cations for binding sites, resulting in higher concentrations of Cu as free metal ions in the solution phase at lower pH. The H^+ ion concentration affects the precipitation of iron and aluminium oxides and the absorption and desorption of trace elements in and on these precipates. It also affects the direct precipitation of metallic oxides, hydroxides and carbonates. According to Nilson and Andersson (1974) hydrous ferrioxide binding with Cd was lowest at a pH value of 4.5 but increased to a maximum at a pH value of 5.8. Jenne (1979) states that oxides of Fe and Mn adsorbed heavy metals and subsequent movement of heavy metals in soil under leaching condition is dependent upon pH and oxidation-reduction reactions. Street et. al, (1978) observed reduced Cd solubility and plant uptake with increasing pH. The Author also noted that $CdCO_3$ appeared to control Cd solubility above pH 7.25. Martin and Focht (1977) stressed that pH and precipitation of iron and manganese oxide play important roles in immobilizing metals.

Emmerich et. al., (1982) report that pH reduction in soil layer could increase the solubilization of metals and induce movement in soil profile. Korte et., al., (1976) have also documented similar findings in aerobic conditions. In agricultural situation where sewage and sludge have been applied to the soils, and movements of metals measured (Boswell, 1975, Hineslaye- et. al., 1972) pH of the soil is found to be an important factor which influences the solubility of the metals and control mobility. Emmerich et. al. (1982) found that in sludge-soil layers Cu was almost entirely complexed with organic matter. They reported that the pH of the system decreased and there was a change in chemical species from complexed form to the free ionic form even with ample of organics to complex the Cu. It is also reported that there was no change in chemical form of Cd and Zn across the sludge-soil interfaces in almost all the columns. In contrast, the total solution metal concentration across the sludge-soil interfaces changed dramatically. The stabilization of chemical forms in the soils suggested that there was perhaps an equilibrium between free ionic organic and inorganic forms and this equilibrium was probably influenced by many factors with pH being one of the most important factors. Change of soil pH probably shifts metals from organically complexed form to free ionic form in solutions. The effect of pH on equilibrium seemes to be different for each metal. Since small percentage of Zn and Cd are in organic form the effect of pH on their chemical forms is less apparent. An alkaline pH induces a low solubility of heavy metals and probably plays a role in the retention of the metals in the soil surface layers (Hern 1972). Iskandar (1978) observed a decrease in soil pH with high application of waste water. He attributed this decrease in pH to nitrification and observed movement of applied metals to a depth of 15 to 30 cm. The increased mobility of the metals at lower pH leads to increased availability of metals to plants. Chang and Broadbent (1980) reported that any soil process which increases the acidity of the soil will have a pronounced influence on solubility, movement and plant uptake of trace metals. Tyler (1978) studied the leachability of Zn, Ni, Cd and Cu in two organic forest soils. He found that residence time for these metals decreased with decreasing pH of rain water applied. The amount of Cu, Zn, Ni and Cd metals retained was dependent upon pH of the soil sample, with retention dramatically increasing above pH 7. 0 to 7. 5 with the exception of Ni (Harter 1983).

SOIL ORGANIC MATTER

Interaction of soil organic matter (SOM) and soil colloids influence the distribution of metals. The particle interaction between these two are due to H-bonding. This interaction occurs only on the external surface and does not disturb the inner group of soil organic matter containing oxygen atoms. These oxygen atoms are available to react with metal ions without any steric hinderance. This clay-metal-SOM complexes, so formed, restrict the mobility of heavy metal in the presence of soil organic matter. However on the decomposition of soil organic matter, metals become free to move through the soil (Santillan et. al., (1975).

Trace metals, such as Cu, Ni, Zn and Cd and others, exhibit high affinities for soil organic matter. More or less stable and insoluble complexes between these elements and soil organic matter may form. It is known that gruops which bind with metal ions are mainly carboxylic, phenolic and amide functional groups in the organic matter. It is generally thought that trace elements in the solution phase exist as soluble organic complexes (Page 1974). Bondietti et. al., (1973) found that sesqioxide and humic acid in soils are responsible for Cd adsorption and limit their mobility. But there may be considerable increase in mobility of Cd in sandy soils which is low in organic content. Retention of heavy metals by both insoluble humic acid and soluble fluvic acid has been reported by Boyed et. al., (1981) and Saar and Weber (1980).

Haltzclaw et. al., (1965) and Sposito et. al., (1976) have reported the importance of organic matter in relative mobilities of Cd, Zn, Ni and Cu in the soil system. Cu was considered to be closely associated with humic acid fraction and strongly complexed. Cd, Zn and Ni were less strongly complexed and therefore were considered more mobile than Cu. Studies conducted by Leeper (1972) emphasized that metals are strongly held by colleids and by organic chelates. Among those metals which are present in sewage and sludge only Zn is relatively unchelated in the soil and therefore is more mobile. He suggested that only Zn and Cd are likely to remain active and get into the food chain. Wolverton et. al., (1983) found the positive correlation between organic carbon 0. 87 for Zn and 0. 55 for Cu. Nickle is highly mobile and this high mobility is governed by its high complexing nature due to which highly stable and soluble metal-soil organic matter (SOM) complexes are formed. This facilitates the translocation of metals as their complex through soil (Lund et. al., 1976), Khan et. al., (1982). The lowest Cd-SOM Complex mobility is due to its lover solubility constant (Desai and Ganguley (1979). The removal or solubilization generally follow the pattern of Irving- williams series : Zn > Cd > Ni > Cu. This series predicts that metal organic bond strengths are of the order Cu > Ni > Zn > Cd. This shows that greater the organic metal bond strength the less soluble, the complex is. According to this series Cd is the most soluble metal followed by Zn then Ni and Copper being the least soluble (Irving and Willams, (1948). Cu is typically adsorbed to sites containing Fe and Mn hydrous oxide and mobile under acid condition. Cu can also complex to soil organic matter at suitable pH levels. So Cu mobility is extremely limited by pH condition (Hodgson et. al., 1966, Boswell; 1975, Chang and Broadbent, 1980) indicated that organic source of metals are less mobile than inorganic salt sources. They found that inorganic Zn was more mobile in soils than inorganic Cu and reported translocation of 7.5 cm for Zn and 50 cm. for Cu. Similar conclusion were reached by Swindle and Jeckson (1965).

"ION EXCHANGE"

Mobility of elements in soil depends upon adsorption. Lagerwerff et. al., (1972) identified that adsorption of Cd to collidal material via Coulomb type forces as the major cause of its immobility in soils. When adsorption was related to soil organic matter content, the strength of absorption was found to depend on pH, increasing with increasing pH (Gerritse et. al., 1982). Shuman (1975) noted that Zn absorption increased in a soil containing clays and organic matter and related Zn adsorption to the cation exchange capacity of the soil. The low mobility of most metals in some soils was due to specific adsorption which followed the order of manganese oxide > organic matter > iron oxide > clay minerals.

A general trend of increase in mobility of metals in soil is observed with increase in the anionic concentrations. The significant anions were Cl^-, HCO_3^-, CO_3^{--}, PO_4^{---}, NO_3^- and SO_4^{--} etc. Donar (1978) has reported that increased Cl^- complexation with Ni (II), Cu (II) Cd (II) resulted in increased mobility. The extent of complexation is directly related to the concentration of Cl^- in solution. Hanhe and Kroontje (1973) investigated that both hydroxy and chloride complexes may contribute to the mobilization of Cd and Zn and noted that Cd and Zn hydrolize above pH 7 and 8 respectively.

TEMPERATURE

Micronutrients like metals come into the available form through a number of complicated soil chemical reactions. Temperature influences the availability of metal, mainly in two ways : (1) Influence of temperature on the biological system, : Slight increase in temperature leads increased microbiol activities which in turn results in hastened degradation of organic complexes and release the metals (Miller (1974) Alaxander (1977). (2) Physico-chemical reactions: Physico-chemical reactions lead to changes in the chemistry of metals in the soil, which release available form of metals (Lindsay, 1972).

SOIL MATRIX

The influence of soil texture on the mobility of metals is through its influence on organic matter and clay content of the soil. Organic matter, particularly humic acids, bind metal ions over a wide range of pH in soil; Clay minerals also bind metallic ions. Both of them differ in adsorption capacity in relation to pH (Coker and Matthews, 1983).

Banin et. al., (1981) studied distribution of metals in soil profile irrigated with sewage effluent. They found that even after 28 years of effluent irrigation, metal accumulation is continued to a thin top layer of the soil. The contents of all elements studied were highest in the upper most segment (3-10cm. of the soil profile) and then fell steeply with depth. In soil solutions neutral or anionic species of metal is more likely to move through a negatively charged soil matrix, than a positively charged species of the ion. Taylor and Griffin (1981) found that Cd moved downward to a considerable depth in their experiments where as Ni was more uniformly distributed over total soil depth than other metals. There is a possibility of chelation of Ni by organic matter in certain podzolic soils. It was reported that concentration of surface absorbed and/or precipitated Zn and Cu were apparently increased upto 0-24cm depth by application of effluents. Kirkham (1975) found movement of Cd, Cu, Ni and Zn to a 61 cm. in soil below a sludge holding lagoon that had been used for three years. Concentration of surface absorbed and/or precipitated Ni and Cd was higher throughout the profile of the effluent irrigated soil than where effluent irrigation had caused increased concentration of surface absorbed and/or precipitated heavy metals in the soil surface. (EPA, 1978). This is corroborated by the studies of Sidle and Sopper (1976) and Ketchum and Vaccaro (1977).

In soil system the behaviour of Ni is similar to Zn in mobility. Fuller (1977) and Cash and Paul (1979) reported that Ni is absorbed to the reactive surface of the hydrous oxide of Fe and Mn. In aerobic system Ni may be reduced and precipitated (Bohn et. al., 1979). According to Brown (1983) the depth of movement appeared to be independent of the soil characteristics despite the range of clay content and CEC. Study conducted by Hineslay et. al., (1982) indicated that the retainment of metals in the surface of soil varies with the metal concerned. Zinc and Nickle was found to remain in highest concentration (23-56%) while Cu (22-31%) and Cd (17-26%) remained lesser in the top 15 cm on the soil profile. Trace metals not retained in the surface 15 cm, are removed by plants or transported to the depth below 15 cm from surface. Similar result was obtained in the experiment conducted by Siddle and Kardos (1977). They found 10 times more retention of Zn then Cu in the surface layer. Carballaro and Mc Bridge (1978) reported Cu to be more strongly adsorbed than Cd on slit loam and therefore less mobile. Parker et. al. , (1978) monitored that more than 95% of Cd, Zn and Cu remained at 0 to 25 cm depth. Zn commonly occurs in three form (a) soluble divalent (b) chelated but easily extractable and (c) tightly bound in soluble precipitates. The soluble fraction is highly mobile in acid soils and may be easily leached (Gall, 1936). Chelation of Zn with organic components of the soil and adsorption of Zn on clay and Fe oxides are important mechanisms of Zn fixation (CAST 1976). The importance of the characteristics of a particular soil on distribution of metals is demonstrated by many workers (Fuller 1977, Doner, 1978).

Cu moved least readily through all soil columns. The least mobility of metals was observed in a mineral soil with relatively high pH, CEC and exchangeable base content. The order of mobility of metals in soils was Cu > Zn > Ni > Cd (Tyler and Mc Bridge, 1981). Emmerich et. al., (1982) found that free ionic Cd, Cu, Ni and Zn were approximately 55, 2, 65 and 70% respectively of the total metal present in soil solution from soil amended with sludge and incubated under laboratory condition for 25 months.

Zn movement in soil profile and factors that influence this mobility have been well documented by Berrow and Webber, (1972). They determined movement of surface applied Zn in several soils and concluded that mobility was related to soil pH, organic matter content, phosphate content and clay mineral concentration. Jurinak and Torne(. . . . . .) found that valency state affected Zn movement in soil, the greater mobility of negatively charged zincate ion (ZnO_2^{-2}) was attributed to less soil adsorption.

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MATERIAL AND METHOD

1. COLLECTION OF SEWAGE SAMPLES AND OTHER EFFLUENTS:

Grab samples of raw sewage, P. T. sewage and F. T. sewage effluent from Okhla treatment plant were collected at three different occasions and were analysed for their physico-chemical characteristics. The influent to this plant is mainly from domestic source, New Delhi Municipal Corporation area. Diagram of the treatment plant is given in figure 2.

Sampling and preservation:

Samples were collected from the respective points in the wide mouthed plastic bucket and transferred to clean polythylene containers. For metals analysis, the samples were preserved immediately at the spot with nitric acid.

The samples were brought to laboratory and analysed for their characteristics. Samples were stored in a cold room at temperature of 0-4^{o}C and time to time were taken for further studies.

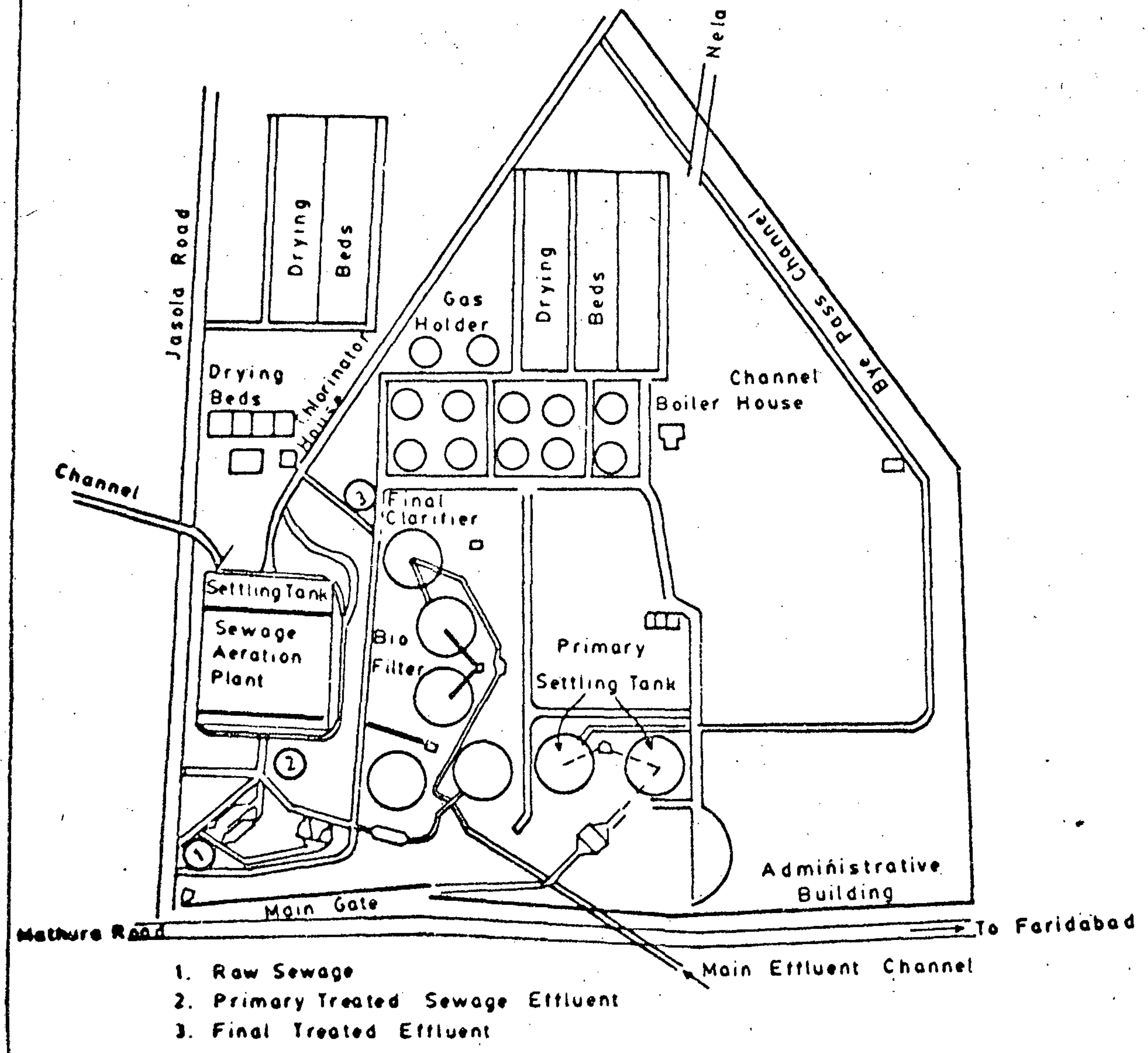
2. ANALYSIS OF RAW SEWAGE AND OTHER EFFLUENTS :

1. pH: pH of the raw sewage and other effluents were measured by dipping the electrodes into the effluent. Philips PR 9405-M pH meter used during this study.

2. Electrical Conductivity (E. C.):

Electrical Conductivity of samples were determined by using Systronics direct reading conductivity meter, which was previously standardized with 0. 1 KCl solution.

Fig.2. LAY OUT PLAN OF OKHLA SEWAGE TREATMENT PLANT



3. Chemical Oxygen Demand:

(i) COD is a measurement of the oxygen equivalent which is required to degrade and destroy the organic matter content of the sample.

(ii) To determine the COD of the samples method given by standard methods for examination of water and waste water 15th edition (1980) followed.

Principle :

Organic matter is oxidized by boiling mixture of chromic acid and sulphuric acid. After refluxing unreduced $K_2Cr_2O_7$ is titrated with ferrous Ammonium Sulphate (FAS), and amount of $K_2Cr_2O_7$ consumed is determined. In this matter the amount of oxidizable organic matter is calculated in terms of oxygen equivalent.

Chemicals:

(i)	Sulphuric Acid (H_2SO_4)	Analar	Glaxo	India
(ii)	Pot. Dichromate ($K_2Cr_2O_7$)	Analar	Glaxo	India
(iii)	Silver Sulphate (Ag_2SO_4)	LR	BDH	India
(iv)	Ferrous Amm. Sulphate ($Fe\ (NH_4)_2\ (SO_4)_2 \cdot 6H_2O$)	LR	Sarabhai	India
(v)	Mercuric Sulphate	LR	Sarabhai	India

Reagents:

(a) Standard potassium dichromate solution (0. 25N):

Dried 12. 259 gm Potassium dichromate dissolved in distilled water & diluted to 1000 cc.

(b) Silver Sulphate Sulphuric Acid Solution :

This solution was prepared by dissolving 10 gm of Ag_2SO_4 in 1000 ml. of Conc. H_2SO_4.

(c) Ferroin Indicator Solution:

0. 695 gm Ferrous Sulphate and 1. 485 gm of 1-10 phenanthroline were dissolved in 100 ml. of distilled water.

(d) Ferrous Ammonium Sulphate Solution: (0. 25 N)

98 gm of FAS dissolved in distilled water. In this 20 ml. of Conc. H_2SO_4 was added and than diluted to 1000 cc. This solution standardized against $K_2Cr_2O_7$ Solution.

To determine the COD, an assembly prepared which was consisting a hot plate, flat bottom 500 ml reflux flask with 24/29 size narrow neck mouth and condenser with 24/29 size ground glass joint. (See figure 2B).

Procedure :

20 ml. of the sample was taken in flat bottom flask and 0. 5 gm mercuric sulphate, 10 ml. of Potassium dichromate solution and 30 ml of Silver Sulphate - Sulphuric acid mixture were added.

After that flasks were attached to condensers and the contents were refluxed for 2 hours. The flasks were removed and added about 80 ml of distilled water. Cool the flask and excess of dichromate was titrated against FAS Solution using ferroin indicator to a raddish brown end point. A Blank with 20 ml of distilled water was also run simultaneously.

Calculation:

$$\text{COD (mg/l)} = \frac{(a - b) \times C \times 8000}{\text{Sample (ml)}}$$

Where:

a = Blank titre value

b = Sample titre value

c = Normality of Ferrous Ammonium Sulphate

4. Biochemical Oxygen Demand:

BOD is a test which measures the oxygen demand for the biochemical degradation of organic material. BOD determined as method given by "Standard Method" for the examination of water and waste waters (1980). BOD determination method consist in the measurement of dissolved oxygen on the very first day and after placing the sample, under specific condition for five days and differences of two reading make BOD determination.

Apparatus:

(i) Incubation bottles: 300 ml capacity with ground glass stoppers.

(ii) Incubator: Incubator which can be controlled at 20 ± 1°C.

Chemicals :

	Name	Grade	Source
(i)	Potassium dihydrogen phosphate (KH_2PO_4)	Analar	BDH India
(ii)	Sodium hydroxide (NaOH)	LR	Glaxo India
(iii)	Amm. Sulphate $(NH_4)_2SO_4$	Analar	BDH India
(iv)	Calcuim Chloride	GR	Sarabhai, India
(v)	Ferric Chloride	LR	Sarabhai, India

Reagents :

(a) Phosphate Buffer: Dissolved 42. 5 gm of KH_2PO_4 in 700 ml water and added 8. 8 gm NaOH. Solution pH was adjusted to 7. 2. In this solution 2 gm of $(NH_4)_2SO_4$ Added and volume made upto 1 liter.

(b) Magnesium Sulphate Solution : 25 gm of $MgSO_4 \cdot 7H_2O$ dissolved in one liter of water.

(c) Calcium Chloride Solution : 27. 5 gm of anhydrous $CaCl_2$ dissolved in one liter of distilled water.

(d) Ferric Chloride Solution: 0. 125 gm Ferric Chloride $FeCl_3 \cdot 6\,H_2O$ dissolved in one liter of distilled water.

(e) Dilution Water: 5 liter of distilled water aerated to overnight and added five ml of each, Phosphate buffer, magnesium sulphate, Calcium Chloride & Ferric Chloride.

Procedure:

A known volume of the sample was pipetted into the BOD Bottle and after that remaining portion filled with dilution water and stoppered immediately.

So there were no exchange of air bubbles. The dissolved oxygen in the original sample was determined by dissolve oxygen method. The blank dilution water and diluted sample were incubated for 5 days at 20°C. After 5 days, dissolve oxygen was determined in the incubated sample and blank.

$$\text{BOD (mg/liter)} = \frac{(a-b)}{\dfrac{\text{ml of sample}}{\text{ml of dilution water}}} - (b - c)$$

Where:

a- dissolved oxygen in incubated blank

b- dissolved oxygen in incubated sample

c- dissolved oxygen in original sample

(5) Dissolve Oxygen (D. O.): D. O. was determined by Iodometric titration method as given in "Standard Method" for the Examination of water and waste water (1980).

(a) Chemicals :

	Name	Grade	Source
(i)	Magnous Sulphate ($MnSO_4 \cdot 4H_2O$)	LR	Sarabhai Chemicals In
(ii)	Sodium Hydroxide ($NaOH$)	LR	BDH, Glaxo, India
(iii)	Sodium Iodide	LR	IDPL, India
(iv)	Sodium Azide (NaN_3)	LR	IDPL, India
(v)	Sulphuric Acid	Analar	Glaxo, India
(vi)	Starch	LR	BDH, India

(vii)	Sodium Thio Sulphate	LR	IDPL, India
(viii)	Potassium Iodate	Analar	Glaxo, India

(b) Solution :

(i) Magnous Sulphate Solution : 48 gm of $MnSO_4 . 4H_2O$ was dissolved in 100 ml of distilled water.

(ii) Alkali-Iodide Azide Solution: 50 gm of NaOH and 15 gm of KI were dissolved in 100 ml of distilled water to which 1 gm o Sodium Azide in 40 ml distilled water was added and mixed.

(iii) Starch Solution: 0.5 gm of soluble starch added to 10 ml. of boiling water.

(iv) Standard thio Sulphate Solution: (0.0125N) 3.15 gm $Na_2S_2O_3 . 5H_2O$ dissolved in one liter of distilled water.

Procedure :

300 ml capacity BOD bottle was filled with the effluent sample and D. O. fixed by the addition of 2 ml of $MnSO_4$ Solution and 2 ml of Alkali-Iodide-Azide reagent below the surface of the sample in the bottle. Stoppered the and mixed for a few times. Opened the bottle stopper, added 2 ml conc. H_2SO_4 and again stoppered and mixed thoroughly until the solution was complete. A 100 ml volume of the solution was measured out and titrated against 0.0125N $Na_2S_2O_3 . 5H_2O$ solution using starch Indicator.

Calculation:

$$\text{Dissolve oxygen content (mg/1)} = \frac{\text{Value of thio Sulphate required for 100 ml sample X 10}}{\text{Volume of thio Sulphate required for 10 ml of 0.0125N Potassium Iodate}}$$

6. Phosphate : It is determined by Vanadomolybdo phosphoric Acid Colorimetric Method : as given in "standard Method" 1980:

Principle : Under acidic condition Ammonium molybdate and dilute orthophosphate Solution reacts and form molybdophosphoric Acid. In the presence of Vanadium,yellow Vanado molybdophosphoric Acid. is formed. The intensity of the yellow colour is proportional to phosphate concentratic

Apparatus: Beckman spectrophotometer used in this test at 470 nm.

Chemicals:

(i)	Hydrochloric Acid	MERCK, India
(ii)	Ammonium Molybdate $(NH_4)_6 \cdot Mo_7O_{24}. 4H_2O$	IDPL, India
(iii)	Ammonium Metavanadate $(NH_4) VO_3$	Roanal, Budapest Hungary
(iv)	Phenophthlein	MERCK, India

Reagents:

(i) Vanadate: Molybdate Solution:

(A) 25 gm of Ammonium molybdate dissolved in 300 ml distilled water.

(B) 1. 25 gm Amm. metavanadate dissolved in 300 ml of water by heating. After cooling 330 ml of HCL was added. Mixed

(ii) Standard Phosphate Solution: 219. 5 gm of anhydrous KH_2PO_4 dissolved in 1 liter. 1. 00 ml = 50. 0 ug $\underline{PO_4\ P}$.

Procedure :

pH of the sample adjusted in acidic range and then took 35 ml of samples in 50 ml nessler tube. Added 10 ml of vanadate molybdate reagent and diluted to the mark with distilled water. Prepared simultaneously with 35 ml of distilled water. After 10 minutes, measured the Absorbance of sample at 470 nm.

Standard curve prepared by using suitable volume of standard phosphate solution.

7. Organic Carbon:

Organic Carbon content of the sample was determined by using Walkey-Black rapid titration method as described by Piper (1950).

Principle: When sample digested with chromic acid and sulphuric acid heat of dilution destroy the organic matter. Remaining dichromate measures by titration with standard ferrous ammonium sulphate solution.

Chemicals :

	Name	Grade	Source
(i)	Potassium dichromate ($K_2Cr_2O_7$)	Analar	Glaxo, India
(ii)	Sulphuric Acid	Analar	Glaxo, India
(iii)	Phosphoric Acid	--	MERCK, India
(iv)	Diphenyl amine	Analar	BDH, India
(v)	Ferrous Amm. Sulphate	LR	Sarabhai, India

Reagents :

(a) Potassium dichromate (1N): 49 gm of $K_2Cr_2O_7$ dissolved in 1 liter of distilled water.

(b) Ferrous Amm. Sulphate (N/2): 196 gm of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ dissolved in water, added 15 ml of sulphuric acid and made upto 1 liter.

Procedure : Suitable volume of sample (10 to 20 ml) was pipetted into 500 ml conical flask and was added with 10 ml of 1 N $K_2Cr_2O_7$ and 20 ml of conc. H_2SO_4.

The mixture was allowed to stand for 30 minutes and diluted to 200 ml. with water. 10 ml of phosphoric Acid followed by 3 drops of diphenyl indicator were added. The solution was back titrated against Ferrous Amm. Sulphate to a brilliant green end point. A Blank was also run in the same way.

$$\% \text{ of Organic Carbon} = \frac{\text{Blank Titre Value} - \text{titre Value} \times 0.003 \times 100}{2 \times \text{ml of Sample.}}$$

(8) Total Nitrogen :

Total Nitrogen was determined by Kjeldahl method.

Chemicals:

	Name	Grade	Source
(a)	Potassium Sulphate (K_2SO_4)	AR	IDPL, India
(b)	Sodium hydroxide (NaOH)	LR	BDH, India
(c)	Sulphuric Acid (H_2SO_4)	AR	Glaxo, India

...

(d)	Mercuric Oxide (HgO)	LR	BDH, India
(e)	Amm, Sulphate $(NH_4)_2 SO_4$	AR	BDH, India
(f)	Sod. thio Sulphate ($Na_2S_2O_3$. $5H_2O$)	LC	IDPL, India
(g)	Boric Acid (H_3BO_3)	AR	Glaxo, India
(h)	Copper Sulphate ($CuSO_4$)	AR	Glaxo, India

Reagents:

(i) Digestion Reagent: 134 gm of K_2SO_4 was dissolved in 650 ml NH_3 free distilled water and added 200 ml H_2SO_4. A solution containing 2 gm of HgO in 25 ml of Amm. sulphate was added to this and final volume made upto 1000 C. C. This reagent was stored at temp. above 14°C to prevent crystallization.

(ii) NaOH - $Na_2S_2O_3$ Solution: 500 gms of NaOH and 25 gm of $Na_2S_2O_3$. 5 H_2O were dissolved in Amm. free water and diluted to 1000 ml.

(iii) Indicator Boric Acid: 20 gm of boric acid was dissolved in distilled water . 10 ml of mixed indicator was added and diluted to 1000 ml.

(iv) Mixed Indicator: 0.2 gm methyl red was dissolved in 100 ml of 95% ethyl alchol and 0.1 gm methylene blue in 50 ml of 95% ethyl alchol and mixed.

(v) Standard $H_2 SO_4$: 0.01 N H_2SO_4 was prepared and standardize against Q1 N Na_2CO_3.

Procedure: Suitable volume of sample was digested with 50 ml digestion reagent in a kjeldahl flask. The sample was cooled, diluted around 150 ml and then added with NaOH-$Na_2S_2O_3$ reagent till pH rose just above 8.3 using phenolphthlein indicator . The mixture was distilled and about 100 ml of distillate was collected in 50 ml indicating boric acid. The concentration of NH_3 liberated was measured by titrating the distillate with 0.02 N H_2SO_4 to a pale lavendir end point.

$$\text{Total Kjeldahl Nitrogen (mg/l)} = \frac{A - B \times 280}{\text{ml of sample}}$$

Where A = ml of sample titre value

B = ml blank titre value

METAL ANALYSIS : Heavy metals were determined by Atomic Adsorpt-ion Spectrophotometry method as given in EPA "Methods for CHEMICAL ANALYSIS of WATER and WASTES (1983).

Digestion: Nitric acid-perchloric acid mixture (10:1) used for digestion purpose. Measured amount of sample taken into 500 ml. beaker and volume was reduced upto 10 ml over a hot plate (controlled temperature). 10 ml of digestion mixture was added to this reduced volume of sewage and refluxed on the hot plate, till sample became clear. After cooling sample was diluted upto 100 ml and then filtered. From the filterate specific metals were determined by atomic absorption spectrophotometer by using specific hollow cathode lamp and reported as total content. Instrumentation laboratory AA/AE spectrophotometer 457, used in this study. Wave length for corresponding elements and flame used were given below:-

Elements	Wave length	flame gases
Cu	324. 7	A-AC
Zn	214. 0	A-AC
Ni	232. 0	A-AC
Cd	228. 8	A-AC

III. COLLECTION, PREPARATION, ANALYSIS OF SOIL USED IN COLUMNS

Soil samples used in this study were collected from nursery inside the University campus. It was an 'undisturbed' soil, which had not received any type of effluent. Soil Samples were randomly collected from different spots in the same field at 0 to 15 Cm depth. All samples were then mixed thoroughly and brought to laboratory.

The mixed sample was air dried, powdered in a mortar and pestle and sieved through a 2 mm perforated sieve. A portion of soil sample was stored in polythene bags for further analysis. Remaining sieved soil was filled in eight PVC columns.

ANALYSIS:

(i) pH of SOIL: pH of Soil was determined by using pH meter (Philips) in 2:5 soil: water suspension (Piper-1950).

(ii) Electrical Conductivity: By using the above pH suspension, E. C. was determined with a systronix direct reading E. C. meter and reported as m. mhos/cm.

(iii) Available Nitrogen: Available nitrogen was determined with using Subbiah & Asija (1956) method.

Chemicals

	Name	Grade	Source
(i)	Pot. Permagnate ($KMnO_4$)	LR	BDH, India
(ii)	Sod. Hydroxide (NaOH)	LR	BDH, India
(iii)	Sulphuric Acid (H_2SO_4)	AR	Glaxo, India
(iv)	Boric Acid (H_3BO_3)	AR	Glaxo, India
(v)	Methyl Red.		BDH, India

Reagents :

(a) Potassium Permagnate Solution (0.32%): 3.2 gm of $KMnO_4$ dissolved in distilled water and final volume made upto 1000 ml.

(b) Sodium hydroxide Solution (2.5%): 25 gm of NaOH flaks dissolved in distilled water and volume made upto 1000 ml with distilled water.

(c) 0.002N H_2SO_4 Solution : 0.55 ml of H_2SO_4 (conc) diluted to 1000 ml.

(d) Indicator Boric Acid (4%): 40 gm of H_3BO_3 dissolved in distilled water and then added to 5 ml of mixed indicator, final volume made upto 1 liter. The boric acid Solution was adjusted by dilute acid from bluish colour to pink.

Procedure : 20 gm of sample soil weighed on filter paper, wrapped and put into the Kjeldhal distillation flask. Soil sample was moistened with distilled water. 100 ml of 0.32% $KMnO_4$ and 100 ml of 2.5% NaOH then added to this. Few pieces of porcelain also dropped inside the flask. Mouth of flask than fitted immediately . The end of receiving tube dipped in the 25 ml of Boric acid . NH_3 absorbed in Boric acid Solution and titrated against N/50 H_2SO_4 till blue colour change to pink. The volume of H_2SO_4 was estimated.

1 ml of 0. 02N H_2SO_4 = 0. 28 mg N

$$\text{PPm of Nitrogen} = \frac{\text{Titer Value x 0. 28 x 100}}{\text{Weight of Soil}}$$

IV. Organic Carbon: Walkey-Black Method as given by Chopra and Kanwar (1976)

Chemicals

	Name	Grade	Source
(i)	Pot. dichromate ($K_2Cr_2O_7$)	AR	Glaxo, India
(ii)	Sulphuric Acid	AR	Glaxo, India
(iii)	Phosphoric Acid	AR	Merck, India
(iv)	Ferrous Amm. Sulphate ($FeSO_4$ $(NH_4)_2SO_4 \cdot 6\ H_2O$)	LR	Sarabhai, India

Reagents

(i) Pot. dichromate (1 N): 49. 0 gm of $K_2Cr_2O_7$ dissolved in 1 liter of distilled water.

(ii) Ferrous Amm. Sulphate (N/2): 196 gm of (FAS) dissolved in distilled water, added 15 ml H_2SO_4 and made final volume 1 liter.

Procedure :

.5 gm of soil (0. 5 mm) was taken in a 500 ml conical flask . To it Added 10 ml of N $K_2Cr_2O_7$ Solution and 20 ml of (conc.) H_2SO_4. Shaked well and put it as such for 30 minutes in darkness. 200 ml of water, 10 ml of phosphoric acid and 1ml of diphenyl indicator solution were added and a bright violetcolor was developed. Titrate against N/2 FAS, to sharp green end point .

Calculation:

$$\% \text{ of organic matter in soil} = \frac{Z \times 100}{58} \quad \text{or} \quad Z \times 1.724$$

$$\text{Where } Z = \frac{(x-y) \times 0.003 \times 100}{2 \times W} = \% \text{ of orgc. C of Soil.}$$

x = Vol. of FAS required for reducing 10 ml of $K_2Cr_2O_7$ (Blank reading)

y = Vol. of FAS required for reducing the excess of dichromate

w = Weight of soil.

V. METAL ANALYSIS :

Method used for the analysis of total heavy metal content in soil as [illegible] given by Lund et al (1976).

In this method, heavy metals viz. Zn, Cd, Cu, Cr and Ni were dissolved in 4N HNO_3. It consisted of refluxing 1 gm of soil sample with 25 ml of 4N HNO_3 at 80°C for approximately 12 hours. After digestion the sample were filtered and concentration of heavy metals determined by Atomic

Absorption Spectrophotometer (described earlier page No. - 32 Heavy metals dissolved by 4N HNO_3 are refered to as total concentration.

IV SOIL COLUMNS PREPARATION :

For the purpose of studying accumulation and movement of heavy metals in soil columns, eight PVC Columns of the following specification were specially designed (See figure 2 B) and prepared at USIC, JNU.

Specifications:

(a) Material used - PVC
(b) Height of the Columns - 60 cm
(c) Inner diameter of the columns - 15.24 cm
(d) Bottom of the Columns - Iron screen fitted.

Columns were having side holes (both side) at the regular interval of 7.62 cm for easy sample collection at different depths. Iron stands were prepared to hang the columns vertically. (See Figure 2C).

V COLUMNS FILLING:

Gravels collected from Yamuna river side and washed thoroughly with tap water then it was washed with dilute HCl and again with distill water. It was used to fill the bottom of the each column about 5 cm height followed by acid and water washed fine sand upto 5 cm more. Air dried soil samples (sieved through 2 mm). was used to fill the remaining height of the column. The Soil column measured 46 cm. and weighted 11 kg.

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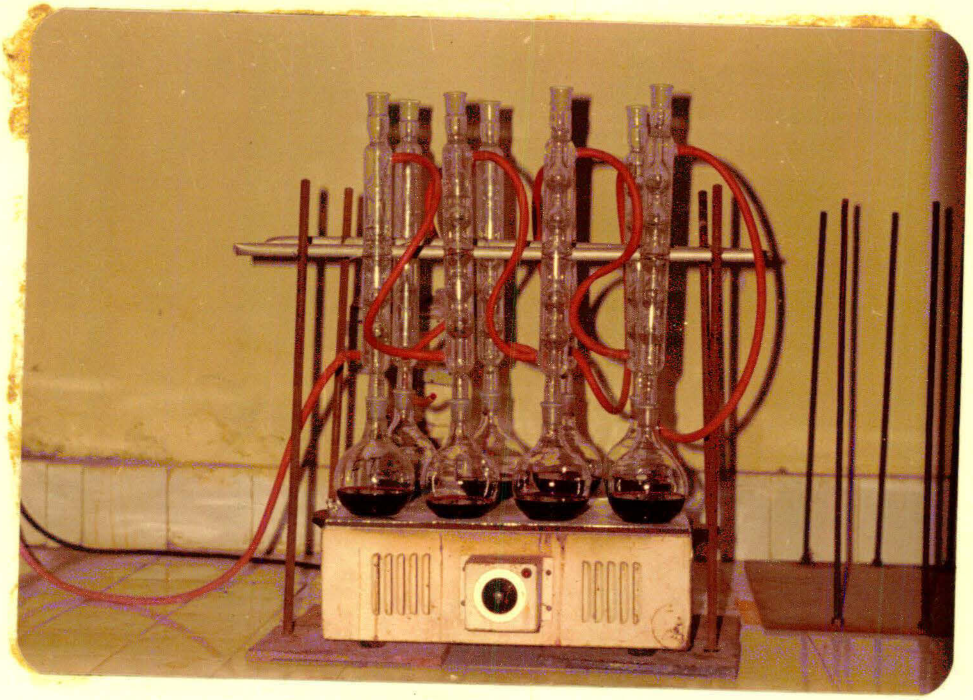

Fig 2(a) COD ASSEMBLY

Fig. 2(c) EXPERIMENTAL SET UP OF COLUMNS.

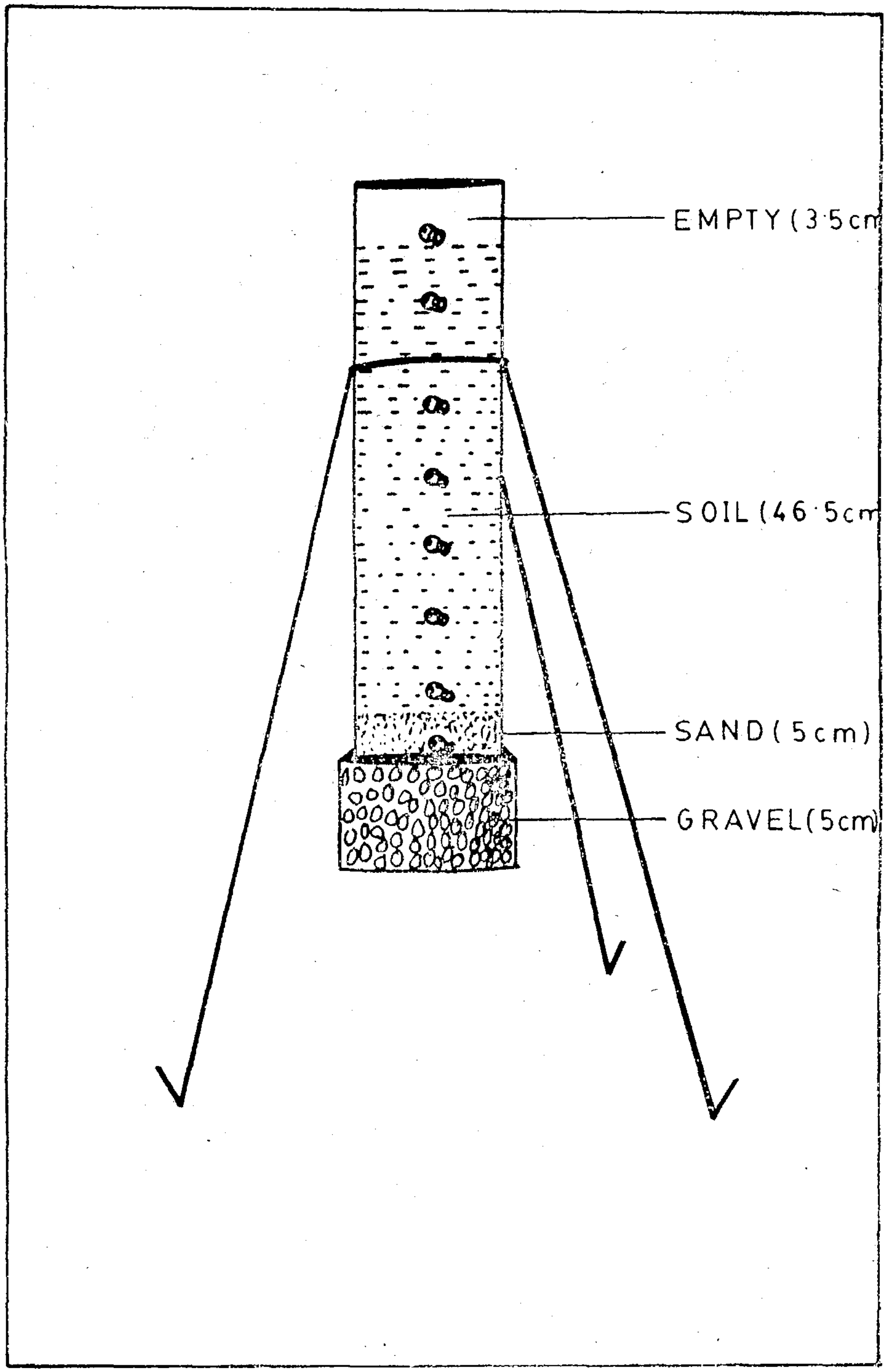

Fig. 2b. COLUMN.

VI RAW SEWAGE and EFFLUENTS STUDY USING COLUMNS:

Columns were arranged in two series to render duplicate columns per set of study. The soil sample in each column was first stabilized by passing tap water before using for present study. After stablizing the columns they were marked for respective samples as follows:

Columns 1 and 2 for raw sewage (ii) 3 and 4 for Primary treated (iii) 5 and 6 with final treated and (iv) 7 and 8 FOR Tap water control. Samples of sewage effluents and tap water were poured into columns continuously at a fixed rate of one liter/day. The process was continued for 50 days.

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"EXPERIMENTAL RESULTS"

(i) PROPERTIES OF SEWAGE EFFLUENTS :

The physico-chemical characteristics of raw sewage and other effluents were assessed at three different intervals during the months of December (1983), January and February (1984). Results are presented in table 2. The analysis of different physical and chemical characteristics of raw sewage and other effluents revealed that the composition of these are not constant, as the values of the individual physical and chemical characteristics of a particular effluent showed variations at different periods. The results shows that the properties of sewage effluents were altered considerably because of treatment at various stages.

PROPERTIES:

i. PH: The pH of raw sewage, primary treated sewage and final treated sewage did not show any significant variation among themselves. Their pH also not changed between different periods. pH of the final treated effluent showed a maximum value of 7.46. Raw sewage and primary treated sewage showed 7.43 and 7.42 pH value respectively the variation in pH during different treatment process is shown in Figure 3.

ii. ELECTRICAL CONDUCTIVITY :

Figure 3 shows that electrical conductivity of different effluents and raw sewage did not show any significant change among themselves. There were not much variation in EC of different effluents during different periods of sample collection. Raw sewage, primary treated sewage and final treated sewage were having E.C. 1.18, 1.27 and 1.26 m. mhos/cm respectively.

iii. CHEMICAL OXYGEN DEMAND : Raw sewage showed highest value for COD (296.5 mg/l). There are large variation in COD during different periods for a specific effluent. For primary treated and final treated effluents the COD value obtained were 195.6 and 74.3 mg/l respectively. During treatment process COD value were reduced considerably (figure 4.).

iv. BIOCHEMICAL OXYGEN DEMAND : BOD follows the similar trend of COD as figure 5 shows and recorded highest in case of Raw sewage (131.8 mg/l). The lowest BOD was obtained in the case of final treated effluent (15.15 mg/l). Primary treated sewage was having a BOD value of 87.0 mg/l.

v. ORGANIC CARBON : Results of organic carbon estimation indicated that raw sewage was having maximum level of organic carbon (0.016%). Other effluents like primary treated and final treated sewage were in the range of 0.007 and 0.003% respectively (Table 2).

vi. TOTAL NITROGEN : In the case of total nitrogen, there were large difference in values, obtained at various interval. In all the trend was a regular decrease, with highest value coming from raw sewage (35.84 mg/l) and lowest from final treated effluent (12.32 mg/l) with medium value (15.2 mg/l) in primary treated effluent (Table 2, Figure 6).

vii. PHOSPHATE : Raw sewage samples registered maximum value of 25.75 mg/l during different periods. 12.4 and 3.39 mg/l phosphate value were recorded for primary treated and final treated effluent respectively. A decreasing trend in the concentration was observed in the case phosphate (Fig. 6), similar to above parameters.

viii. TOTAL METAL CONTENT : Result presented in table 2 and Figure 7.

(a) Copper (Cu): There was a decreasing tend for raw sewage to final sewage. While raw sewage was having maximum value 0.627 ppm, final treated sewage recorded lowest value of 0.106 ppm and 0.242 ppm in primary treated sewage.

(b) Zinc (Zn): Highest concentration was seen for Raw sewage with 1.255 ppm, while Primary treated and final treated sewage showed values 1.103 and 0.709 ppm respectively.

(c) Nickle (Ni). The sewage sample were not having detectable level of Nickel (Detectable Limit of Ni 0.001 ppm)

(d) Cadmium (Cd) : Cadmium concentration was very less. For raw sewage its is 0.016 ppm, and while 0.005 and 0.002 ppm respectively for primary treated and final treated effluents.

(2) PROPERTIES OF EXPERIMENTAL SOIL :

Physico-chemical and Mechanical properties of experimental soil were studied as detailed in methodology and results are presented in Table 1. The experimental soil contained 68.4% Sand, 19.5% silt and 12.1% clay. Its water holding capacity was around 29.48%. pH and E.C . measured were 8.5 and 0.119 mmhos/cm. respectively. Cation exchange capacity was found to be 19.4 meq/100 gm.

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Soil was having 0.395% organic matter content. Available nitrogen and available phosphorus was in the range of 31.7 and 23.0 ppm respectively. Result indicated that Ni and Cd were below detectable limit and insignificant. In case of Cu and Zn values obtained were 3.235 and 5.055 ppm respectively.

(3) EFFECT OF THE RAW SEWAGE ON :

Soil Columns : The influence of raw sewage on pH, EC., organic carbon and heavy metals like Cu, Cd, Zn and Ni, in soil columns at a different deapth were analysed after treating the columns for 50 days and results are presented in Table 6(six) and in figures 8 to 13. Sample drawn from columns at various height (3.5, 11.0, 18.5, 27.0 & 42.0) and corresponding changes in pH EC and organic matter were determined. Metals were also analysed in samples to understand their distribution. Analysis has been done after the '50 days' treatment. In case of pH variation in soil columns, the upper layer (3.5 cm) pH was a bit lower and changed from 8.5 (mean value) of original soil to 7.67, while in other samples at lower depth were around equal to the soil matrix pH. Variation in electrical conductivity was clearly seen from the study. At 3.5 cm height it was around 0.81 m mhos/cm and at 11.0 cm it reduced to 0.28 mmhos/cm. while in remaining samples it was constant and found to be 0.24 mmhos/cm. Organic carbon was higher in top most layer and other samples were found around soil matrix concentration. Zn concentration were higher in the first two samples while other, shown similar concentration to that of soil matrix. The 3.5 cm height sample was having Zn around 8.12, and second one 6.89 while remaining sample were around 5.1 ppm. The similar trend was followed by Cu and was higher in

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upper two sample the values were 11. 11 and 5. 03 ppm. Remaining samples were having 3. 86, 3. 92, 3. 79 ppm respectively and was around experimental soil concentration. Concentration of Ni and Cd were well below the detectable limit.

(4) EFFECT OF PT SEWAGE : The experimental pattern with primary treated sewage was followed hereas in case of raw sewage for 50 days. Samples were collected from different depth and measured for different parameters so as to understand the accumulation and migration of metals in soil profile. The results are reported in table 7(Seven) figure 8 to 13. pH value was lower in top layer sample (3. 5 cm). While in other samples it was around 8. 4, which is the same as the pH of the original soil.

Highest Electrical Conductivity observed was 0. 77 mmhos/cm at 3. 5 cm depth. It decreased with depth of the soil column to 0. 31, 0. 29, 0. 28, and 0. 26 respectively. Organic carbon at various depth did not vary much and was around 0. 292, 0. 285, 0. 296, 0. 296 and 0. 255% respectively. Zn concentration was higher in upper two samples (6. 84 and 6. 11 ppm) while lower sample were shown (5. 27, 5. 10, 5. 09 ppm) around experimental soil concentration. Cu also followed the similar trend and reported highest at 3. 5 cm depth (6. 96 ppm) and decreased with depth. Ni and Cd values at different depth were insignificant and below detectable limit of analytical instrument used.

(5) EFFECT OF F. T. SEWAGE : The experimental pattern with final treated sewage was followed as in case of raw sewage. The results

followed the same pattern as described earlier and are reported in table 8(Eight) and figure 8 to 13.pH change varied from 8. 37 to 8. 7. Samples from the top leyer shown a value of 0. 845 m mhos/cm while for lower samples the values were around 0. 50 m mhos /cm variation in organic carbon was not much and were very close to one another. Zn was found to be 5. 99 ppm at 3. 5 cm depth and in the remaining samples the concentration did not show much variation (4. 98 - 5. 01 ppm). Distribution pattern of Cu was very much similar to Zn. 5. 03 ppm of Cu was present at 3. 5 cm depth. Remaining samples at different depth were 4. 10, 3. 61, 3. 86, 3. 67 ppm respectively and was very close to experimental soil level.

(6) VARIATION IN CONTROL SOIL COLUMN AFTER 50 DAYS

Two column treated with tap water in similar manner as the sewage treated ones. Results observed are reported in Table 9(Nine) and figure 8-13. These column served as control columns. In these columns, value obtained for pH follow at various depth the order of 8. 6, 8. 45, 8. 37, 8. 3, 8. 3 respectively. Electrical conductivity was higher (0. 44 m mohes/cm at 3. 5 cm depth and decreased slowly to reach constant value. Variation in organic carbon was not observed. Zn & Cu values were also very close to one another at various depth and their distribution did not change much. In upper layer samples Zn and Cu levels obtained 5. 11 and 4. 41 ppm. For Cd and Ni values the concentration was insignificant.

***

TABLE : 1

"PHYSICO-CHEMICAL, and MECHANICAL PROPERTIES OF EXPERIMENTAL SOIL "

	PROPERTIES		MEAN VALUE
1.	Particle Size analysis		
		% Sand	68. 4
		% Silt	19. 5
		% Clay	12. 1
2.	Water Holding Capacity (%)		29. 48
3.	PH		8. 5
4.	Electrical Conductivity (m mhos/cm)		0. 119
5.	Cation Exchange Capacity (meq/100 gms)		19. 4
6.	Organic Carbon (%)		0. 395
7.	Available Nitrogen (PPM)		31. 7
8.	Available Phosphorus (PPM)		23. 00
9.	Heavy Metal Content (PPM)		
		Cu	3. 235
		Zn	5. 055
		Ni	< 0. 001
		Cd	< 0. 001

TABLE : 2

"PHYSICO-CHEMICAL CHARACTERSTICS OF RAW SEWAGE AND OTHER EFFLUENTS "

	CHARACTERISTICS	RAW SEWAGE MEAN VALUE	PRIMARY TREATED MEAN VALUE	FINAL TREATED EFFLUENT MEAN VALUE
1.	PH	7.43	7.42	7.46
2.	E C (m mhos/cm)	1.18	1.27	1.26
3.	C. O. D. (mg/1)	296.2	195.6	74.3
4.	B. O. D. (mg/1)	131.8	87.0	15.15
5.	Organic Carbon (%)	0.016	0.007	0.003
6.	Total Nitrogen (mg/1)	35.84	15.22	12.32
7.	Phosphate (mg/1)	25.75	12.4	3.39
8.	Metal Content (PPM)			
	Cu	0.627	0.242	0.106
	Zn	1.255	1.103	0.709
	Ni	< 0.001	< 0.001	< 0.001
	Cd	0.016	0.005	0.002

TABLE : 3

" COMPARISON OF RAW SEWAGE AND EFFLUENTS CHARACTERISTICS WITH STANDARD PERMISSIBLE LIMITS* FOR WASTE WATER EFFLUENTS AND WATER TO BE IRRIGATED ON LAND".

	PARAMETER	SAMPLE ** RANGE	SCOFIELD (1935)	OKUN & PONGHISH (1975)	I S I (1977)
1.	Total Solids (mg/1)	-	-	800-1200	-
2.	PH	7.42 - 7.46	-	6.8 - 7.2	5.5 - 9.0
3.	Electrical Conductivity (m mhos/cm)	1.18 - 1.27	0.75 - 200	-	-
4.	B O D (mg/1)	15.15 - 131.8	-	-	500
5.	Chloride (mg/1)	-	-	70 - 200	600

* T. Sekar and A. K. Bhattacharyya (1982) "Effects of Sewage Effluents on Carbon mineralization and Nitrogen Mineralization of a Soil"
Water Treatment and Utilization, 2; 447-446.

** Experimental results

TABLE : 4

"IRRIGATION WATER QUALITY CRITERIA FOR TRACE ELEMENTS Cu, Zn, Ni and Cd. "

	ELEMENTS (mg/1)		EFFLUENT SAMPLE ***			FWPCA*	IRRIGATION	WATER
			RAW SEWAGE	PT. SEWAGE	FT. SEWAGE	ANY SOIL	CONTINUOUS USE NAS** COURSE TEXTURED SOIL	SHORT TERM FWPCA FINE TEXTURED SOIL
1.	Cadmium	(Cd)	0. 016	0. 005	0. 002	0. 005	0. 01	0. 05
2.	Copper	(Cu)	0. 627	0. 242	0. 106	0. 2	0. 2	5. 00
3.	Nickle	(Ni)	<0. 001	<0. 001	< 0. 001	0. 5	0. 2	2. 00
4.	Zinc	(Zn)	1. 225	1. 103	0. 709	5. 0	2. 0	10. 00

* Federal Water Pollution Control Administration (1968).

** National Academy of Science (1973).

Ref. Page A. L. (1974).

*** Experimental results.

TABLE : 5

"PH AND HEAVY METAL CONTENT OF SOURCE & TAP WATER. (BEFORE EXPERIMENT)"

	PH	Zn ppm	Cu ppm	Ni ppm	Cd ppm
Tap Water	7.4	0.56	0.38	< 0.001	< 0.001
Raw Sewage	7.05 - 7.85	1.215 - 1.296	0.609 - 646	< 0.001	0.018-0.015
Primary Treated Sewage	6.9 - 7.9	1.085 - 1.121	0.199 - 0.286	< 0.001	0.004 - 0.007
Final Treated Sewage	7.1 - 7.85	0.703 - 0.715	0.113 - 0.10	< 0.001	< 0.001 - 0.004
Experimental Soil	8.5	5.05	3.23	< 0.001	< 0.001

TABLE : 6

"VARIATION OF pH, EC, ORGANIC CARBON AND SELECTED METALS LIKE Cu, Zn, Ni & Cd IN SOIL COLUMNS WITH DEPTH WHEN SUBJECTED TO RAW SEWAGE APPLICATION FOR 50 DAYS.

S. No.	Depth (cm.)	pH	E C m. mhos cm.	Organic Carbon %	Zn ppm	Cu ppm	Ni ppm	Cd ppm
1.	3.5	7.67	0.81	0.477	8.12	11.11	0.102	0.023
2.	11.0	8.27	0.28	0.285	6.89	5.03	0.051	< 0.001
3.	18.5	8.42	0.245	0.255	5.18	3.86	< 0.001	< 0.001
4.	27.0	8.3	0.242	0.27	5.12	3.92	< 0.001	< 0.001
5.	42.0	8.37	0.24	0.225	5.19	3.79	< 0.001	< 0.001

Note: All values are average of duplicate columns.

TABLE : 7

"VARIATION OF PH, EC, ORGANIC CARBON AND SELECTED METALS LIKE Cu, Zn, Ni and Cd IN SOIL COLUMNS WITH DEPTH WHEN SUBJECTED TO PRIMARY TREATED SEWAGE EFFLUENT APPLICATION FOR 50 DAYS

Sr. No.	Depth (cm)	PH	EC m mhos/ cm	Organic Carbon %	Zn ppm	Cu ppm	Ni ppm	Cd ppm
1.	3.5	7.6	0.77	0.292	6.84	6.96	< 0.001	0.017
2.	11.0	8.1	0.31	0.285	6.11	4.82	< 0.001	0.008
3.	18.5	8.4	0.29	0.296	5.27	3.86	< 0.001	< 0.001
4.	27.0	8.4	0.282	0.296	5.10	3.67	< 0.001	0.002
5.	42.0	8.4	0.265	0.255	5.09	3.79	< 0.001	< 0.001

Note: All values are average of duplicate columns.

TABLE : 8

"VARIATION OF PH, EC, ORGANIC CARBON AND SELECTED METALS LIKE Cu, Zn, Ni & Cd IN SOIL COLUMNS WITH DEPTH WHEN SUBJECTED TO FINAL TREATED SEWAGE EFFLUENT APPLICATION FOR 50 DAYS".

Sr. No.	Depth (cm)	PH	EC m mhos/ cm	Organic Carbon %	Zn ppm	Cu ppm	Ni ppm	Cd ppm
1.	3.5	8.37	0.845	0.275	5.99	5.03	< 0.001	0.008
2.	11.0	8.42	0.56	0.285	5.01	4.10	< 0.001	< 0.001
3.	18.5	8.7	0.51	0.255	4.99	3.61	< 0.001	0.004
4.	27.0	8.6	0.505	0.262	4.95	3.86	< 0.001	< 0.001
5.	42.0	8.57	0.505	0.247	4.98	3.67	< 0.001	< 0.001

NOTE; All values are average of duplicate columns.

TABLE : 9

" VARIATION OF PH, EC, ORGANIC CARBON AND SELECTED METALS LIKE Cu, Zn, Ni and Cd IN SOIL COLUMNS WITH DEPTH WHEN SUBJECTED TO CONTROL TAP WATER APPLICATION FOR 50 DAYS "

Sr. No.	Depth (cm)	PH	EC m mhos/cm	Organic Carbon %	Zn ppm	Cu ppm	Ni ppm	Cd ppm
1.	3.5	8.6	0.44	0.222	5.11	4.41	< 0.001	0.004
2.	11.0	8.45	0.245	0.255	4.51	3.55	< 0.001	0.002
3.	18.5	8.37	0.27	0.284	4.95	3.30	< 0.001	< 0.001
4.	27.0	8.3	0.265	0.292	5.02	3.30	< 0.001	< 0.001
5.	42.0	8.3	0.235	0.270	4.90	3.79	< 0.001	< 0.001

Note: All values are average of Duplicate Columns.

TABLE : 10

"VARIATION OF ORGANIC CARBON(%)WITH DEPTH IN SOIL COLUMNS "

Sr. No.	Depth (cm)	Raw Sewage Treated Columns Mean Value	P. T. Sewage Treated Columns Mean Value	F. T. Sewage Treated Columns Mean Value	Tap water Treated Columns Mean Value
1.	3.5	0.470	0.29	0.275	0.22
2.	11.0	0.285	0.285	0.285	0.25
3.	18.5	0.255	0.296	0.25	0.28
4.	27.0	0.27	0.296	0.26	0.27
5.	42.0	0.22	0.255	0.247	0.27

TABLE : 11

" VARIATION OF E. C. WITH DEPTH IN SOIL COLUMNS "

Sr. No.	Depth (cm)	Raw Sewage Treated columns	P. T. Sewage Treated columns	F. T. Sewage Treated columns	Tap Water Treated columns
		Mean Value	Mean Value	Mean Value	Mean Value
1.	3.5	0.81	0.77	0.84	0.44
2.	11.0	0.28	0.31	0.56	0.24
3.	18.5	0.24	0.29	0.51	0.27
4.	27.0	0.24	0.28	0.50	0.26
5.	42.0	0.24	0.26	0.50	0.23

TABLE : 12

"VARIATION OF P^H WITH DEPTH IN SOIL COLUMNS"

Sr. No.	Depth (cm)	Raw Sewage Treated Columns	P. T. Sewage Treated Columns	F. T. Sewage Treated Columns	Tap Water Treated Columns
1.	3.5	7.6	7.6	8.37	8.6
2.	11.0	8.27	8.1	8.42	8.45
3.	18.5	8.42	8.4	8.7	8.37
4.	27.0	8.31	8.4	8.6	8.3
5.	42.0	8.37	8.47	8.57	8.3

67

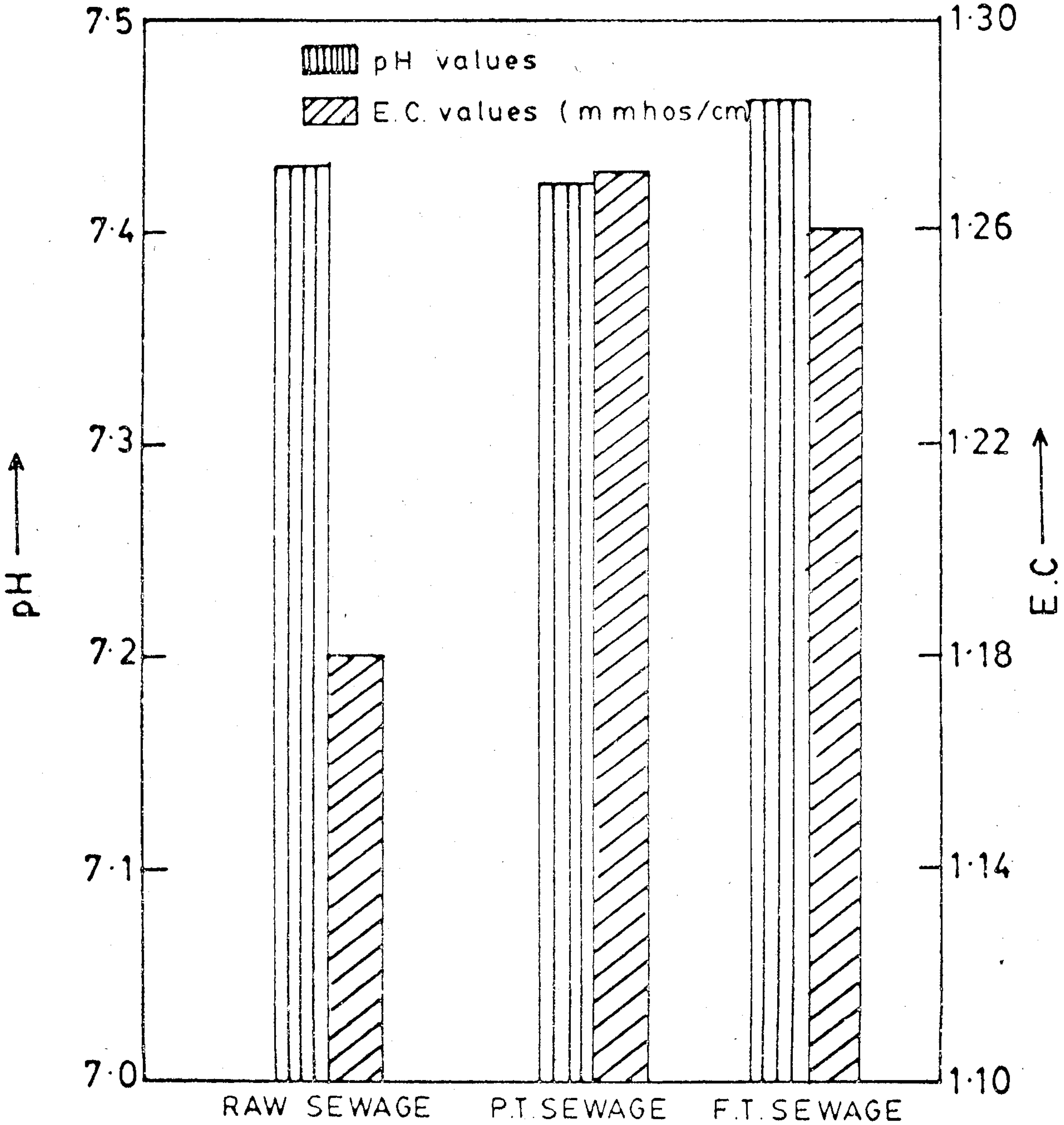

Fig.3. pH and E.C. values of different effluents.

68

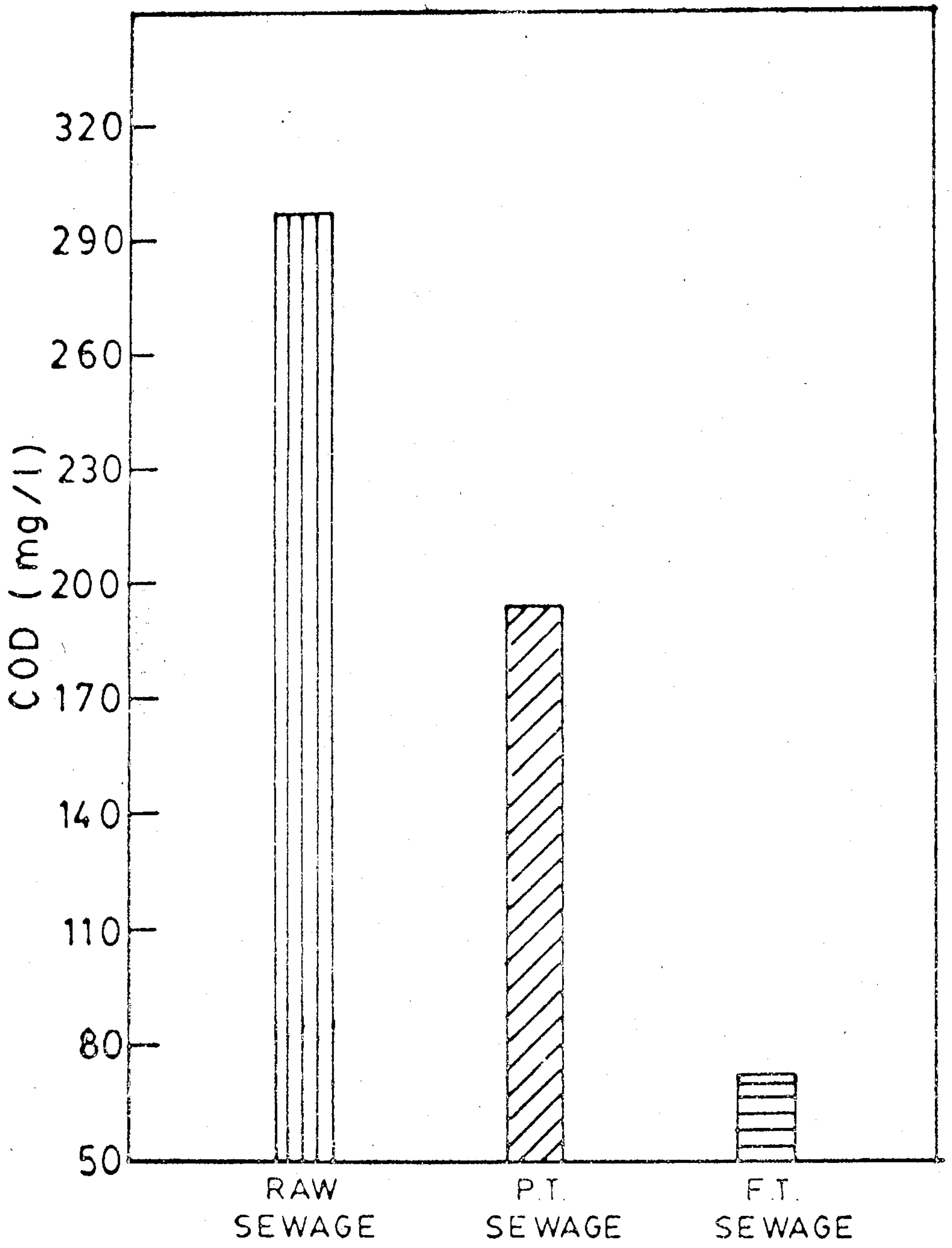

Fig. 4. COD values of different effluents.

59

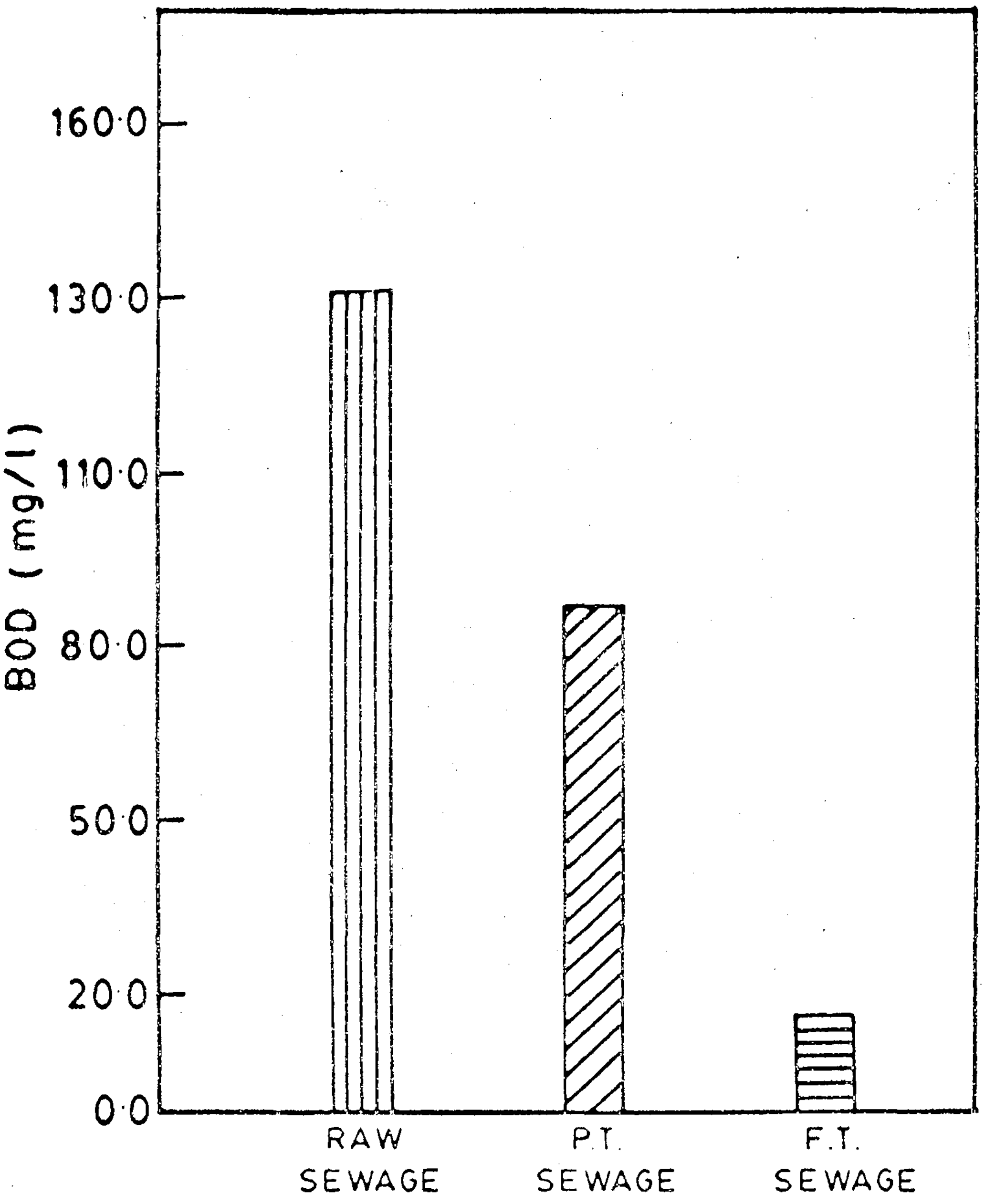

Fig. 5. BOD values of different effluents.

70

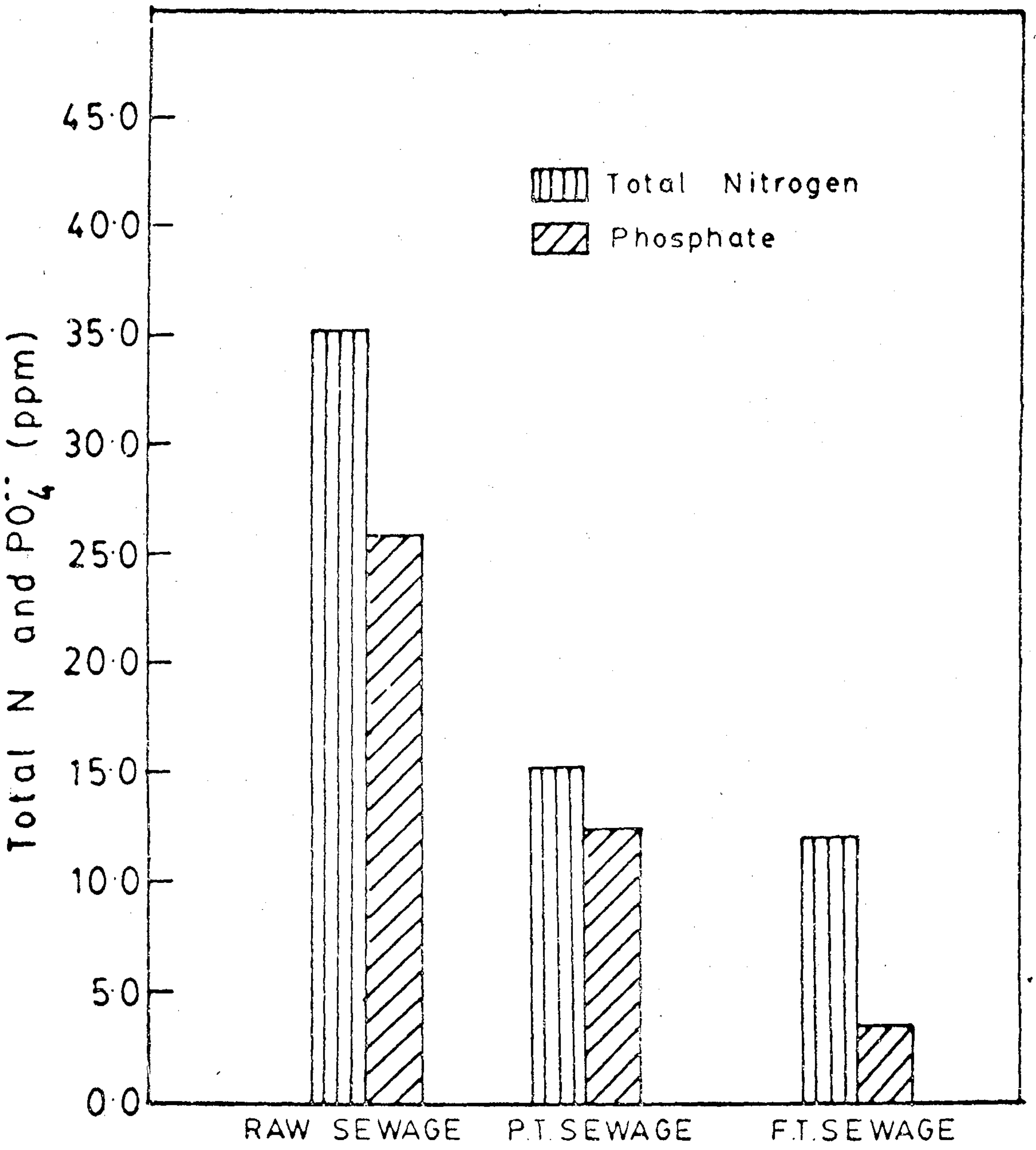

Fig. 6. Total Nitrogen and Phosphate in different effluents.

71

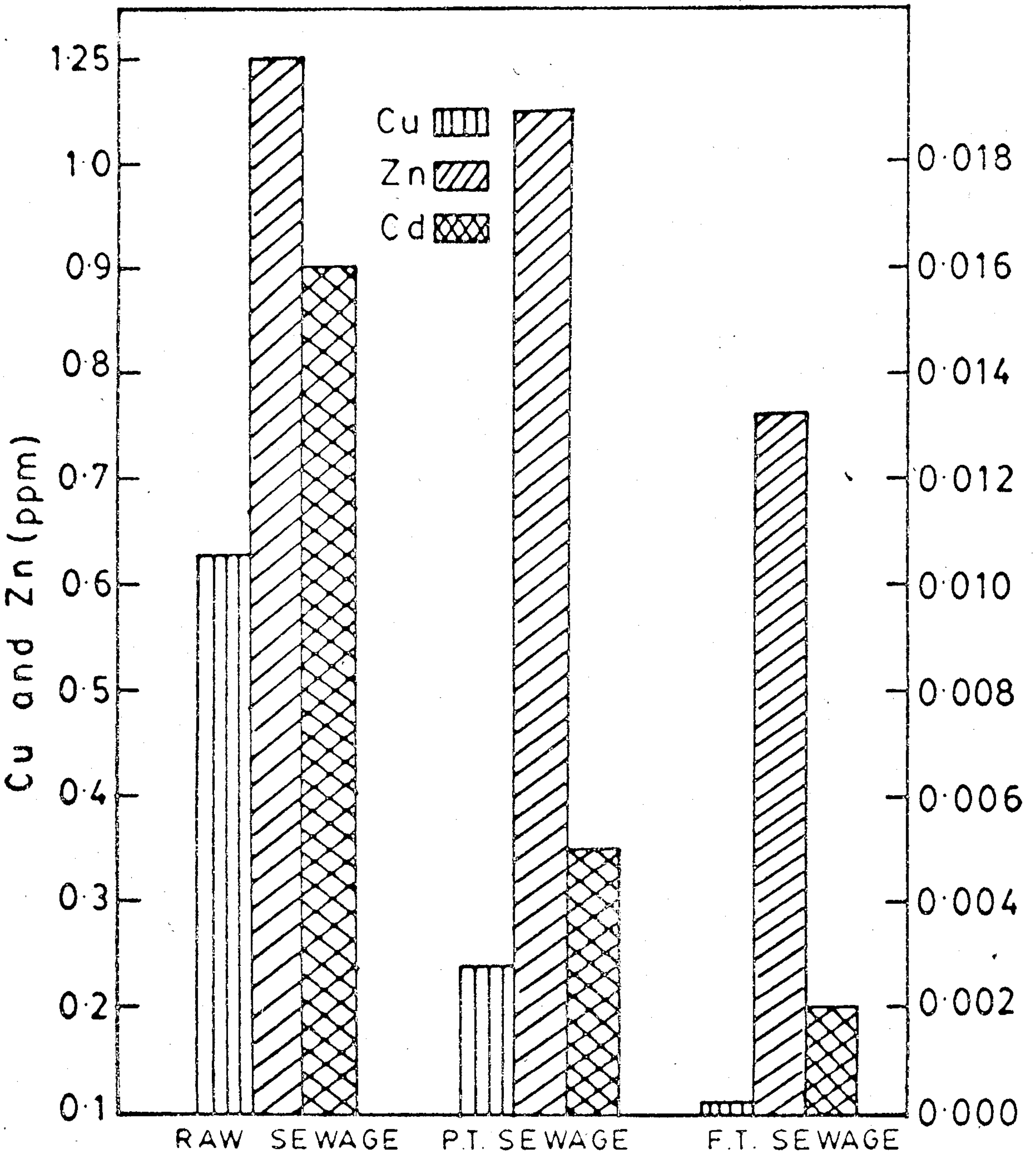

Fig. 7. Cu, Zn and Cd values in different effluents.

72

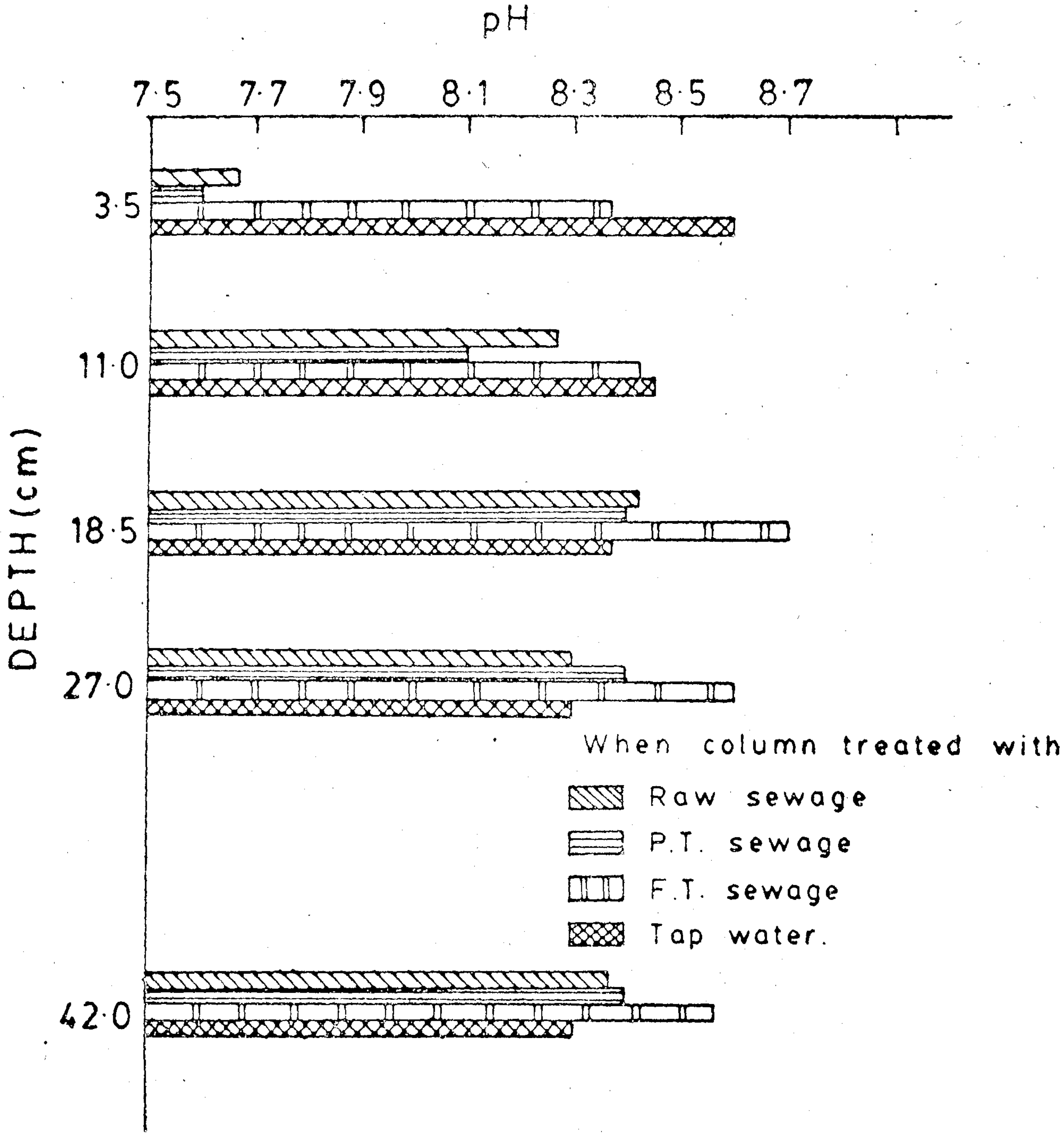

Fig. 8. Effect of different effluents on pH values at different depths of soil column

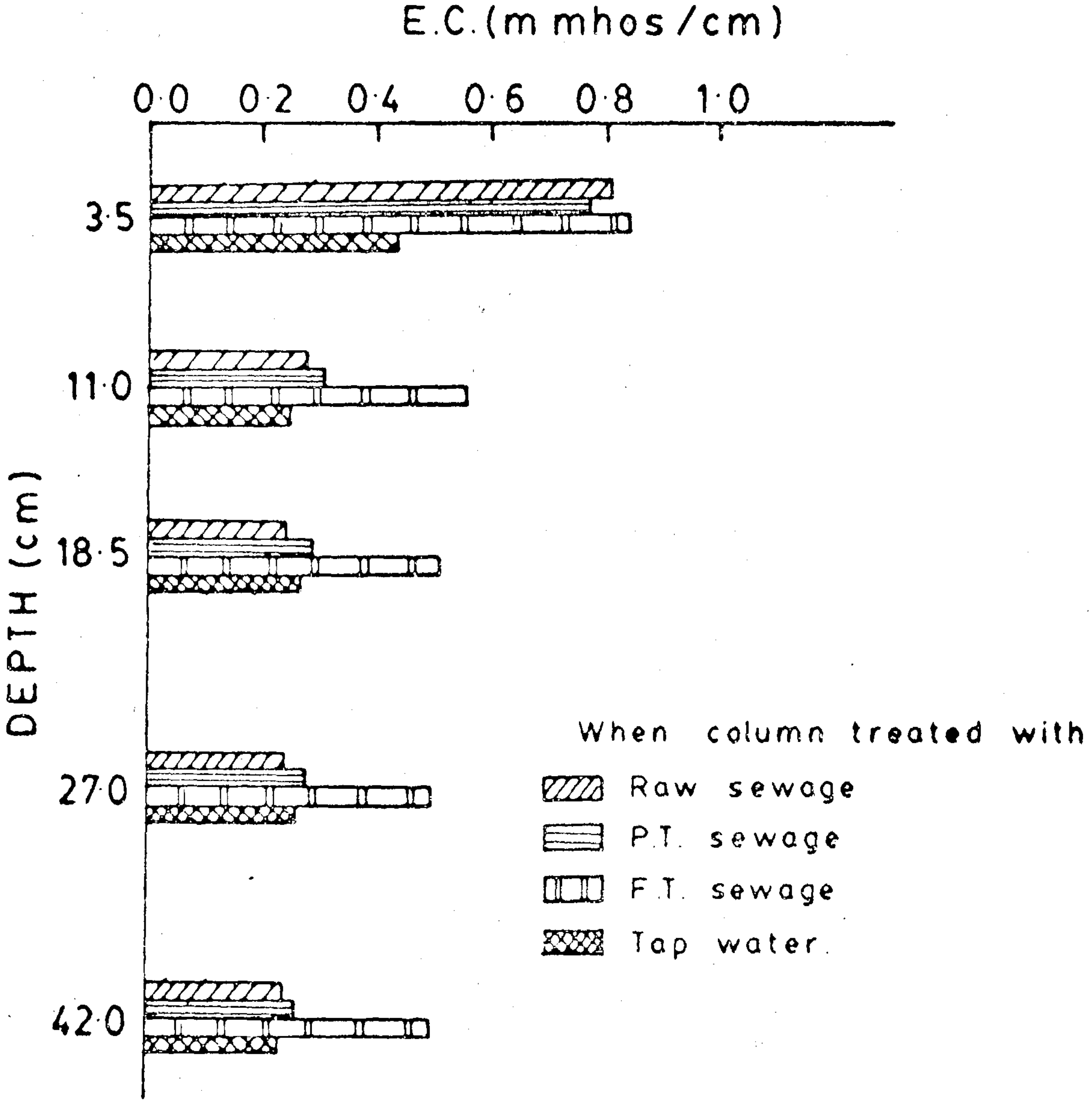

Fig.9. Effect of different effluents on E.C. values at different depths of soil column.

74

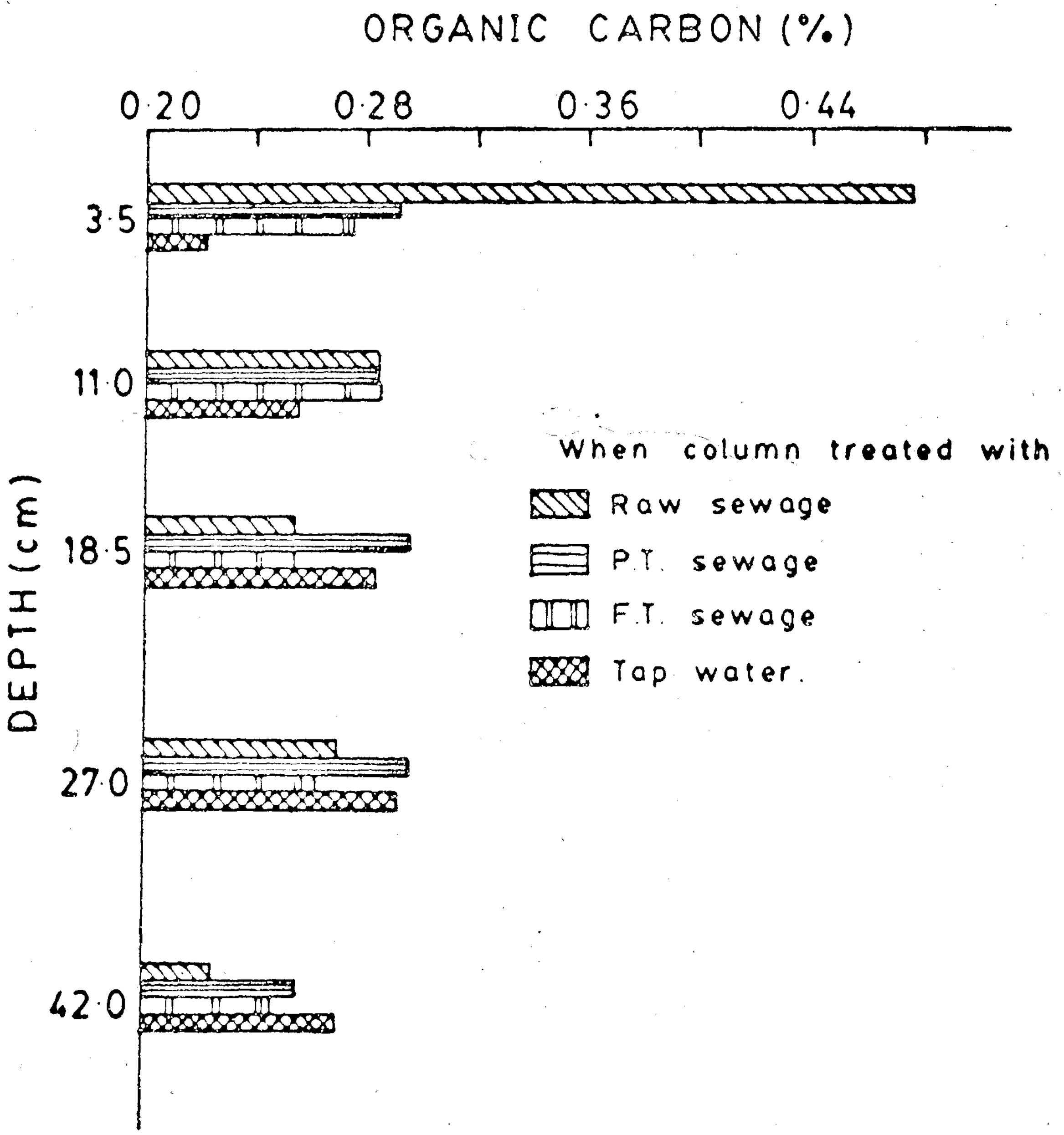

Fig.10. Effect of different effluents on organic carbon values at different depths of soil column.

75

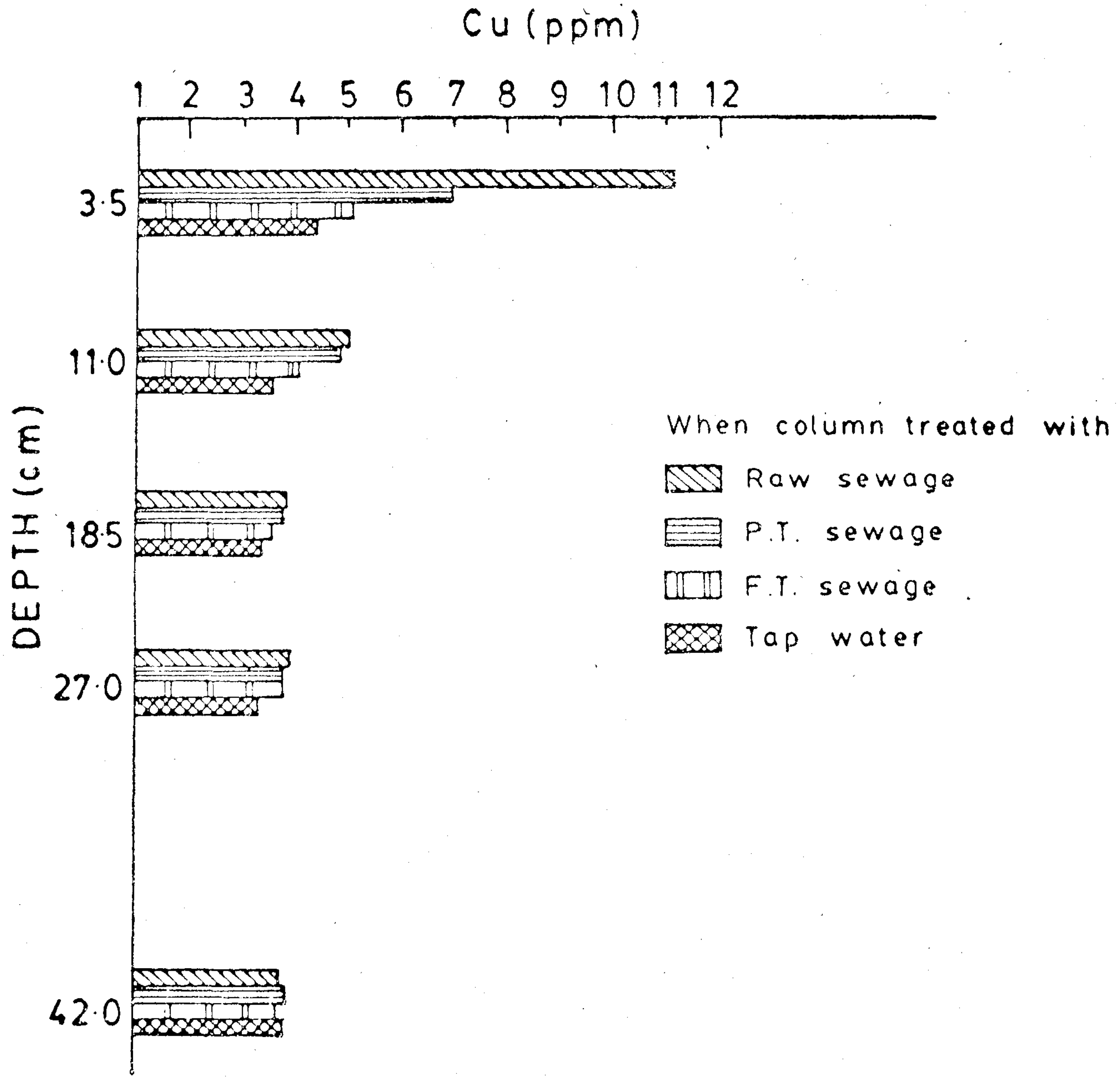

Fig. 11. Effect of different effluents on Cu values at different depths of soil column.

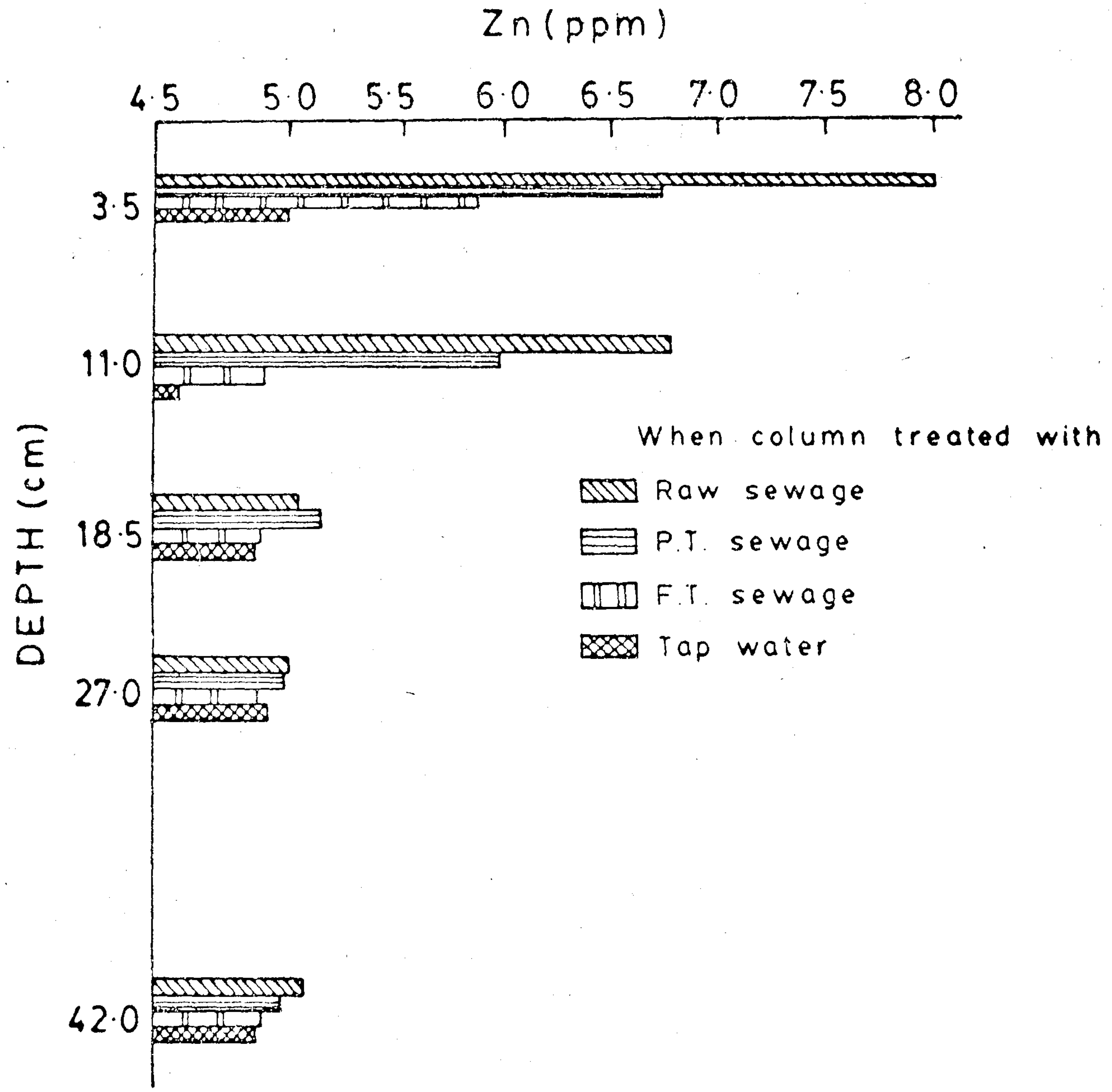

Fig. 12. Effect of different effluents on Zn values at different depths of soil column.

77

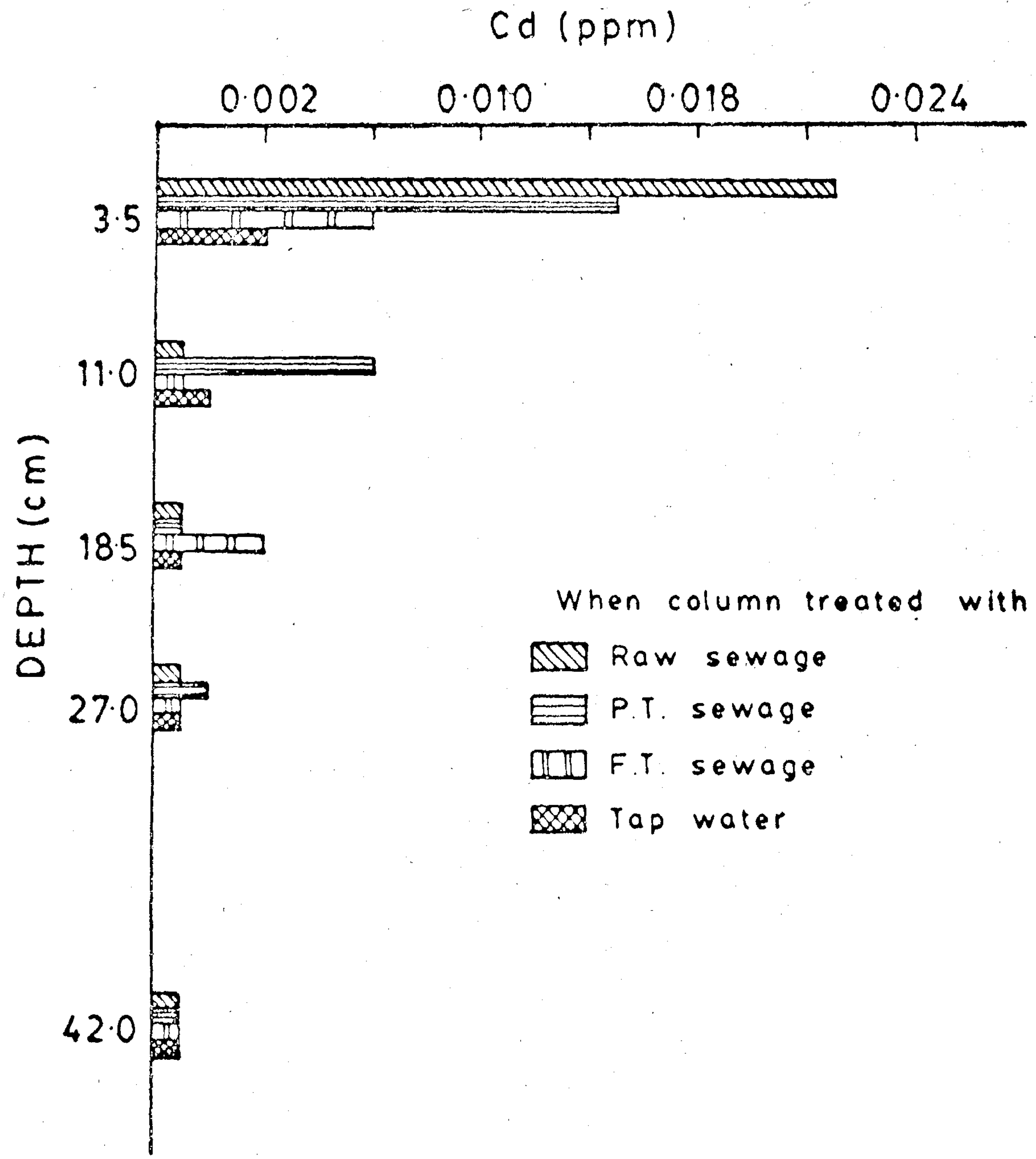

Fig. 13. Effect of different effluents on Cd values at different depths of soil column.

79

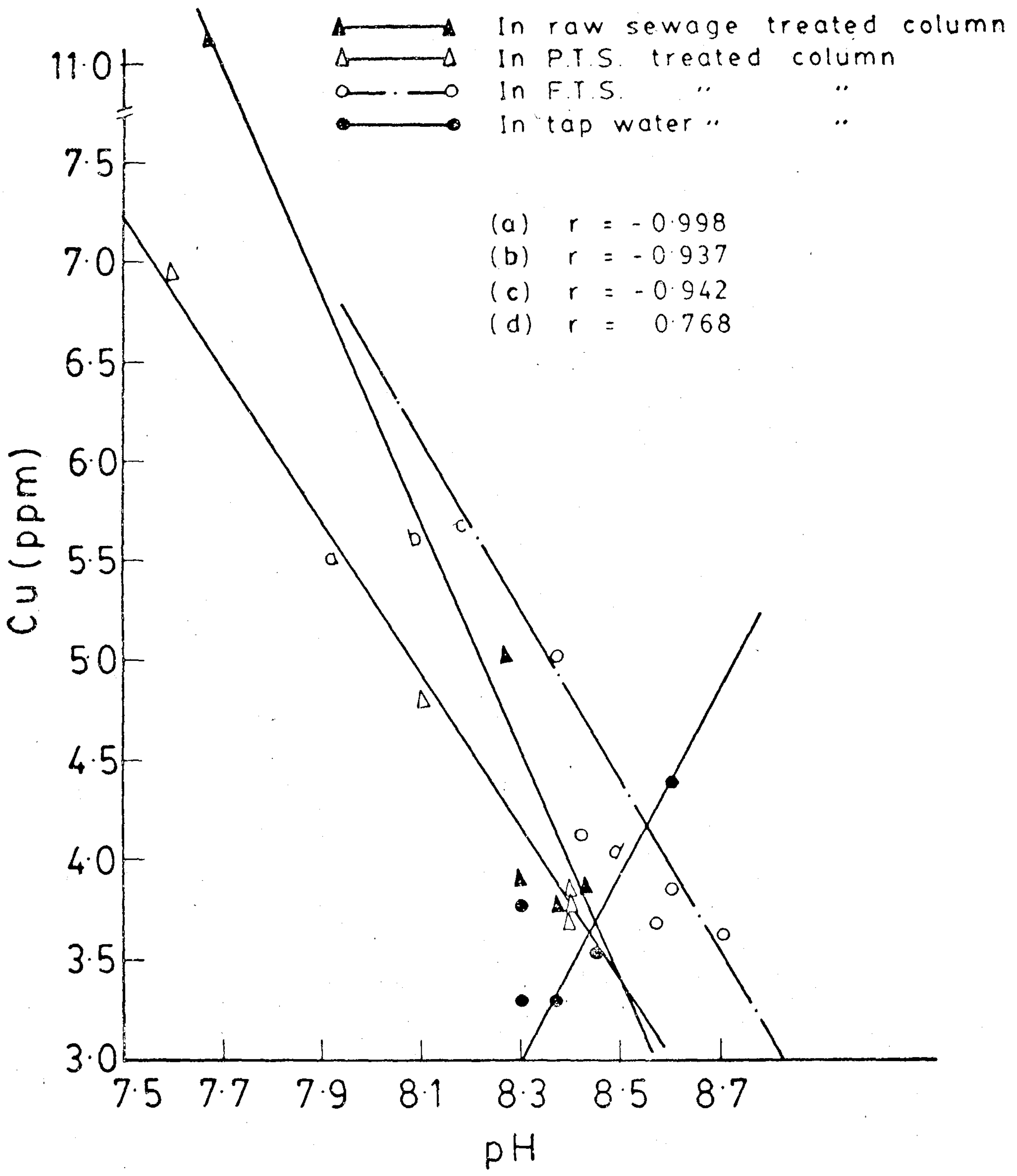

Fig.14. Relation between pH and Cu distribution in soil columns.

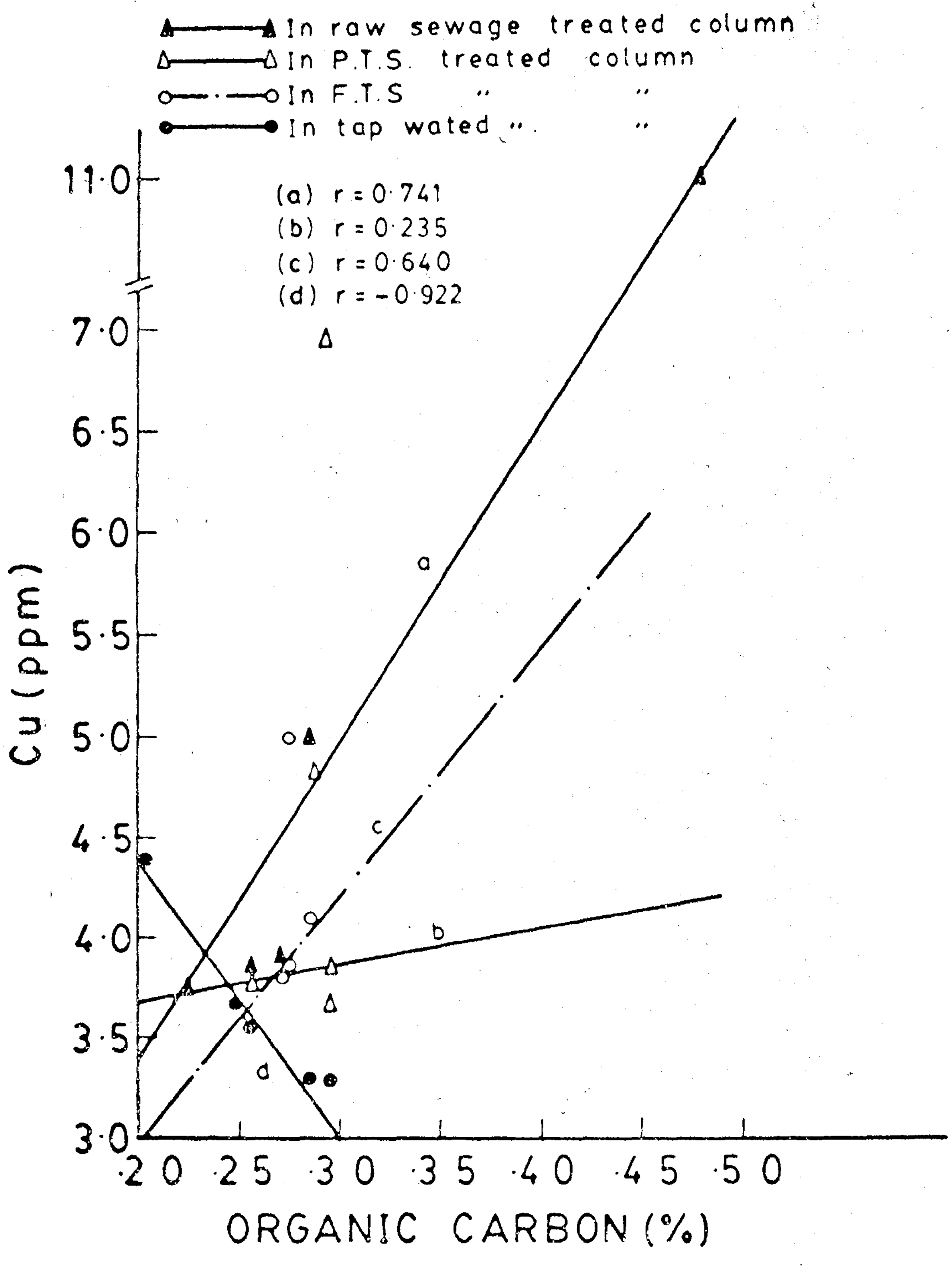

Fig.15. Relation between organic carbon and Cu distribution in soil columns.

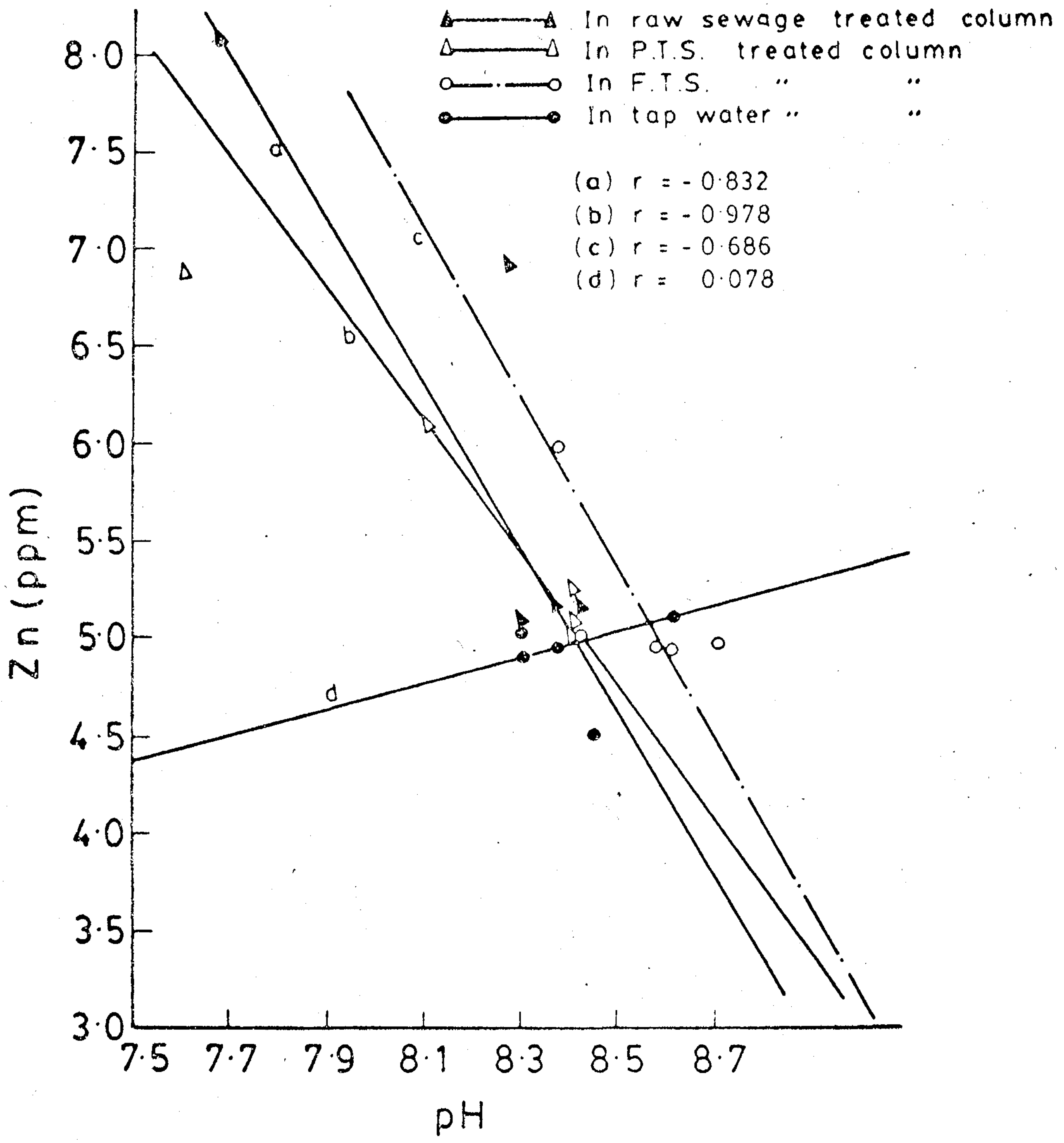

Fig.16. Relation between pH and Zn distribution in soil columns.

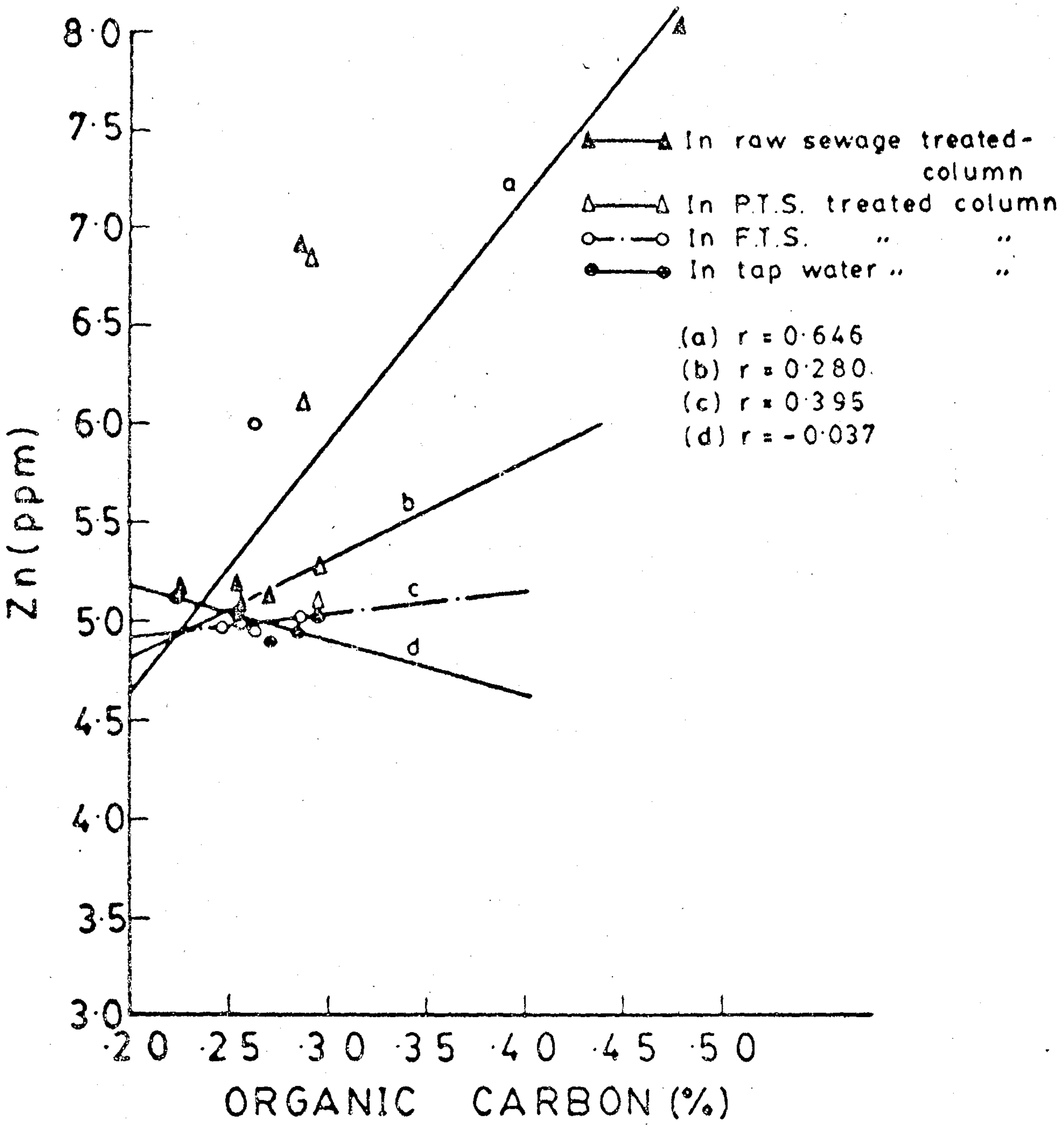

Fig.17. Relation between organic carbon and Zn in soil columns.

DISCUSSION

1. CHARACTERIZATION OF RAW SEWAGE AND SEWAGE EFFLUENTS:

In present study, raw sewage and other treated sewage effluents from Okhla treatment plant were assessed for their physico-chemical characteristics. If the reuse of sewage effluents is required, it is necessary to characterise sewage first, to avoid environmental detrimental effect. Parameter, has to be analized depending on the purpose. In fact, the selection of treatment site and quantity of waste water to be applied on to the land are to a larger extent, decided by the quality of sewage (Sekar 1980). The important parameters to be studied before the use of sewage for irrigation purpose has been well documented by Ellis (1978).

Results of the study are presented in both tabloid and figuroid form. It shows clearly that raw sewage and other treated effluents contain different plant nutrients, like Nitrogen, Phosphate (table 2. figure 6). Besides these, sewage effluents contain other inorganic salts, organic matter and heavy metals (Cu, Zn, Ni and Cd etc.). Present study has been carried out to assess the quality of different effluents because parts of these effluents have been used in irrigation. Though the main work has been carried out on the distribution pattern of metals in soil profile, treated with raw sewage primary treated sewage and final treated sewage. These results were compared with control column study, where soil columns treated with tap water. Different constituents of these effluents are discussed because they limit the use of these effluents (Mishra, 1965).

Characterization of Raw sewage, Primary treated sewage and Final treated sewage are based on the fact that many of the sewage farms in India especially that of Delhi, are using the effluents of all categories (like Raw sewage, P. T. sewage and Secondary treated effluents) for irrigation. The successful reuse of raw sewage and other treated sewage effluents in irrigation require good managements (Sekar 1980). Soil system has vast capacity to minimize the pollutant effect which causes due to excessive total solids organic carbon, COD, BOD etc., which are features of organic ladden wastes. It is a fact that during the treatment process, most of the organic matter get removed. It also reduce the nutrient value of these effluents. Sekar (1980) also have discussed about similar conclusion. Conventional treatment process modify the organic load of raw sewage but these treatment methods may not modify the mineral characteristics upto that extent. Tebutt (1965) and Raman et. al., (1973).

Raw sewage, Primary treated sewage and Final treated sewage were having pH value 7.43, 7.42 and 7.46 respectively. Values are quite close to one another except for only a slight increase observed in final treated effluents. That can be attributed to removal of or precipitation of some active H^+ ions during the secondary treatment process. Electrical conductivity values for the three effluents were 1.18, 1.27 and 1.26 m mhos/cm respectively. E. C. value in case of raw sewage is lower than other values and can be explained on the basis of ionic complexation and chelation with organic matter. It can be assumed that during primary treatment due to oxidation reaction some of the ions get freed and are responsible for increase in EC of other two effluents.

pH values found were well within the acceptable limit 5.5 to 9.0 fixed by ISI (1977). But was higher than the acceptable limit 6.8 to 7.2 fixed by Okun and Ponghis (1975).

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Electrical Conductivity values for all sewage sample were in the acceptable limits of 0.75 to 200 (m mhos/cm) (Scofield 1935).

COD and BOD values indicated that organic load reduced considerably during the treatment process. This is mainly due to the removal of organic materials as sludge. Some of the organic matter degrade during oxidation process. Organic carbon also followed the similar trend. BOD value obtained for Raw sewage, P. T. Sewage and Final Treated sewage were 131.8, 87.0 and 15.15 mg/l. This values come in the range of ISI (1977) set limit for irrigation purpose (Table 3).

Total nitrogen and phosphate followed the above trend and got reduced considerably during the treatment process as shown in figure 6. This decrease can be ascribed to the organic form of nitrogen which were removed with sludge during the process. Similar conclusion can be drawn in case of phosphate reduction.

HEAVY METALS: In Raw Sewage Cu and Zn was higher in concentration and were 0.627 and 1.225 ppm respectively. While in case of final treated effluent they decrease to the level of 0.106 and 0.709 ppm respectively (Table 2). This shows that Cu is removed to a greater extent then Zn., this can be explained on the basis of Cu-organic matter bond strength, which is higher for Cu than Zn. According to Irving and williams (1948) series metal organic matter bond strength is in order of Cu > Ni > Zn > Cd. Cd values followed the similar pattern but were too low and not significant. Similar results were found in the study carried by Nennah et. al., (1983). Bouwer et. al. (1974) described that most of the heavy metals, which are associated with suspended solid in sewage, end up in the sludge. Concentration of Ni was too low and was below the detectable

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limit. It is attributed that larger part of sewage is contributed by domestic source where any consumption source of Ni can not be expected.

Heavy metals values which have been observed in the different types of effluents have been compared with standard values fixed by various institutions. It was found that Ni in the sewage sample was insignificant. For any soil, limits fixed by Federal water pollution control administration (1968) show that Cd and Cu concentration is higher, than acceptable value in raw sewage. Value obtained for Cu, Cd was 0. 627 and 0. 016 ppm respectively, while fixed value were 0. 2 and 0. 005 ppm. Primary treated effluent and final treated effluent found within the limit. In case of Zn the concentration was 1. 255ppm which is below from permissive limit 5. 0 ppm.

When compared permissive limit to the limit fixed by National academy of Science (1973) for coarse textured soil, for the continuous use of effluents for irrigation. Cu was found to be higher than the limit while Zn and Cd were within the limit. The values obtained in all effluents for the metal was within the limit fixed by Federal Water Pollutions Control Administration for short term use of effluents for irrigation (Table 4).

pH, EC and Organic Carbon Variation in Soil Columns:

Samples were drawn from different depths (3. 5, 11, 18. 5, 27 and 42 cm) of column prepared for the study. It was found that the pH value at 3. 5 cm depth decrease to 7. 6 from 8. 5, where 8. 5 is the initial pH of the soil. While in remaining sample result were very close to one another and around experimental soil pH value. The decrease in PH at the upper layer can be attributed to the degradation of organic matter by microbial activity and formation of some organic acids like humic acid and fulvic acid. The pH values obtained in this case were lesser, than other soil columns treated with F. T. sewage. In the case of control Tap Water column, the trend was reverse. pH values decreases slowly with depth. While in Raw sewage treated columns values increased. Similar results were described by Iskandar and Legett (1976). Broadbent et. al. 1977 also reported the similar result and attributed the process to the release of H+ during nitrification of ammonium salt and organic nitrogen added through waste water. The above process of decrease found in soil columns treated with P. T. sewage can be demonstrated on the same basis as in case of soil columns treated with raw sewage. pH value of soil columns treated with F. T. sewage did not show any significant change and values obtained at various depth were close enough to one another and to that of untreated soil. Variation of pH with depth are shown in table 11 figure 8.

Variation in electrical conductivity in soil columns treated with sewage effluents are reported in table 11 and figure 9. Iskandar and Leggett (1976) noted slight reduction in specific conductance of the soil after waste water application and explained it as due to less soluble Salts, in the applied effluents than the soil solution. However in present study the effluents found to contain more soluble salts than the initial soil solution. Electrical conductivity of all the soil columns increased, even when columns were treated with tap water. E. C. was found higher at upper layer in all the columns and decreased to a constant value with depth. This increase in E. C. of soil treated with raw sewage P. T. Sewage, F. T. sewage and water can be demonstrated on the basis of presence of soluble salts in these effluents. These finding are well supported from research carried by Bole (1979) and Sekar (1980). In present study it was noted that when columns treated with raw sewage for stipulated times, conductivity observed at top layer was higher (0. 81 m mhos/cm). Rest of the values at different depth were low and around 0. 28, 0. 24, 0. 24, 0. 24 m mhos/cm respectively . with depth. The increase in electrical conductivity at top layer can be explained in following manner. It is possible that ions attached with organic matter may get released, when the pH of the layer shifted a bit towards acidic range. The same thing can be said about soil columns treated with P. T. sewage. Variation in organic carbon, in soil columns with depth are reported in table 10 and figure 10. Figure shows that organic matter content in top layer of soil columns treated with raw sewage registered maximum deposit and value obtained were around 0. 470% . This value decrease slowly as depth increase. In present study it was observed that though the all sewage effluents registered increase over tap water control, organic matter was decreased in all treatments from initial organic matter level, except in case of top layer of raw sewage treated columns. This reduction may be due to that the quantity decomposed during the experimental period may be greater than that organic matter, contributed by the sewage effluents. Similar results were obtained by Sekar (1980) in his study. However Beck et. al., (1977) and Quin and Woods (1978) reported that long term application of raw sewage and sewage effluents can increase the organic matter content especially of the top layer of soils.

DISTRIBUTION OF METALS IN SOIL COLUMNS TREATED WITH SEWAGE EFFLUENTS :

Samples taken from different depth were analysed for metal content and their distribution is reported in table 6, 7, 8 and 9 and in figure 11, 12, 13. In case soil columns treated with raw sewage, it was found that most of the added metals (Cu, Zn, Ni and Cd) were concentrated in top layer samples

(3.5 cm). Zn and Cu was highest and was present in concentration of 8.12 and 11.11 ppm respectively. While Ni and Cd was lowest (0.102 and 0.023 ppm). Zn found only in higher concentration (8.12 and 6.89 ppm) at 3.5 and 11.0 cm depth. At the lower depth it was around 5.18 ppm and very close to experimental soil matrix concentration. Cu followed the same trend and recorded 11.11 and 5.03 ppm in upper two samples. While at lower, concentration Cu reached to original soil value. Ni and Cd only were detected in upper layer samples. At lower depth their results were well below the detectable limit.

All these results shows that metals are deposited in the top layer mostly. This can be assigned to the presence high concentration of organic matter in the layer. Organic matter have the capability of chelate and form complexes with metals like Cu, Zn, Ni and Cd. Distribution of Zn and Cu followed the same pattern in the case of soil column treated with P. T. sewage as in case of columns treated with raw sewage. But there was difference in concentration in the top layer. In case of raw sewage treated columns concentration of Zn and Cu was found 8.12 and 11.11 ppm, while in this case it was 6.84 and 6.96 ppm respectively. This reduction in the concentration of these metals are due to the treatment process. Because it is established that in primary treatment most of the organic load gets removed as sludge. It has been reported that largest concentration of metals are associated with organic matter and form chelate complexes. Certain forms of these metals also remained adsorbed on to the surface of colloidal materials. Similar conclusions were reached at by Nennah et. al., (1983) Bouwer et. al., (1974), Bouwer and Chaney (1974) from their studies in soil system. Concentration of Ni and Cd was quite insignificant in this case also. It was observed that columns treated with Primary Treated Sewage, Cd concentration noted at 3.5 cm and at 11 cm depth were 0.017 and 0.008 ppm respectively.

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Distribution of metals were also observed in columns treated with F. T. Sewage and reported in table 8. Only Zn and Cu concentration in the top 3.5 cm layer were found above the experimental soil concentration, while remaining samples were almost similar to the untreated soil concentrations. This reduced concentration can also be explained on the basis reduction in organic load during primary and secondary treatment. The recorded concentration which are still higher in comparison to tap water control soil columns, which is expected. These soluble metals ions later get complexed in surface layer soil. The process of adsorption also play a critical role in this case. As in the case of other treatment the concentration Ni and Cd for P. T. Sewage treatment was insignificant or negligible. Ni and Cd were insignificant in soil without treatment.

In the controlled column experiment, metals concentration did not show any change in different layer. The top layer Zn and Cn were 5.11 and 4.41 ppm respectively, which is slightly higher than the original soil concentration and expected due to the addition of tap water.

The phenomenon of most metals being deposited on surface layer of soil due to pH and has important role in controlling the distribution of metals and alkaline condition restricts to a great extent the movement of metals in the soil profile. Studies conducted by Hem (1972), Sinha et. al., (1978), Boswell (1975), Hineslay et. al, (1972) Emmerich et. al., (1982).. Support for similar conclusions. It was noted that metals concentrations in soil columns treated with sewage effluent were consistently higher than those treated with normal tap water, and this differences are due to the relatively high concentration of metals present in sewage effluents.

Result of this study shows that there were no movement of metals down the column. Factors that inhibit the movement in this case could be possibly soil layer pH, the quantity of sewage applied or the time involved, for the movement to take place. This accumulation of heavy metals in the root zone can influence metal uptake by plants to a great extent. Negative correlation with pH were found in case of Cu distribution in all three cases (when columns treated with raw sewage, P. T. sewage and F. T. sewage. r-Values obtained (see figure 14) were (i) - 0. 937 (ii) -0. 998 and (iii) -942 respectively and are quite significant. While in case of control columns study this correlation obtained was positive and significant (r-0. 768). One of the main difference between the tap water treated soil, and sewage treated soils, is the higher content of organic matters in the latter (0. 016% R. S; 0. 007% P. T.).

The top layer concentration of Cu and Zn in both treatments are found to higher than the tap water treated ones. Significant difference in between this two treatment is also observed, the latter having lesser concentration of metals. Keeping in mind the reduction of organic matter in the sewage sample with sewage treatment programme, and the change in metal concentration in top layer, it appears reasonable to conclude that in the sewage treated soils organic matter, rather than clay minerals, hydrous oxides of iron and Aluminium etc. are important in keeping the metal in the top layer. Correlation of pH and Zn distribution also followed the same trend. Its r-values obtained was (i) r=-0. 832 (ii) -0. 978 and (iii)-0. 686 respectively for columns treated with raw sewage P. T. sewage and F. T. sewage, which are significant.

Unlike that of copper no significant correlation was obtained in the case of Zinc. Similar inverse relation has been reported by many other worker in the field (Sinha et. al. , (1978) McBride and Blariak (1979), Anderson and Nilsson (1976) Fillipovic et. al (1961) and others).

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By the application of sewage effluents, in case of columns, treated with raw sewage and P. T. sewage, pH of the top layer changed significantly from 8.5 (pH of experimental soil) to 7.6. This decrease can be due to degradation of organic matter by microbial activity in aerobic surface zone resulting in the formation of organic acids. During this organic matter degradation, some of the active ions also comes in solution phase.

Correlation between organic matter content and metals (Cu &Zn) distribution were also drawn (figure 15 and 17) positive correlation were found in all three cases and r-values were significant (i. e. r = 0.5 above). Negative Co-relation were observed in soil columns treated with tap water. Zinc also followed the similar pattern and significant in case of soil columns treated with raw sewage. These correlation can be justified on the basis of formation of organic matter - Cu and organic matter - Zn complexation and chelation. Wolverton et. al., (1983) reaches at the same conclusion from similar study. It can assumed on the basis of above study that organic matter play important role in retention of heavy metals in the surface zone.

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SUMMARY

This chapter summarises the results of the experiments conducted in connection with the present investigation. Investigations were carried out on laboratory set of soil columns, where columns were treated with raw sewage, P. T. sewage, F. T. sewage and tap water for 50 days. Physico-chemical changes were observed in soil columns after the stipulated time.

There was considerable reduction in pH. In case of soil treated with raw sewage, the upper layer sample showed the lowest pH (7. 67), while pH of experimental soil was (8. 5). Where as the reduction in pH values was not significant in the samples from a depth of 11 cm onward whose pH was 8. 27 to 8. 42. The soil columns treated with F. T. and tap water do not follow the similar trend as in case of soil columns treated with raw sewage and P. T. sewage.

Experimental soil showed an EC of 011 m mhos/cm. On application of sewage of all the three types, EC rose upto approx. 0. 8 m mhos/cm. Reduction in EC values was observed with increase in depth with the highest reduction being in the case of soil column treated with raw sewage whereas the lowest reduction was observed for F. T. sewage.

Accumulation of organic carbon was seen in the case of soil columns treated with raw sewage but organic content reduced with depth. Reduction in organic carbon content from that of experimental soil was seen in all the columns treated with different effluents except upper layer treated with raw sewage.

All the above observed changes may be due to the formation of organic acid compounds as well as other associated factors which might have reduced the pH of the soil. The release of active ions during these processes leads to an increase in E. C.

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Of the four metals analysed namely Cu, Zn, Ni and Cd, only Zn and Cu was present in significant amount. While Ni and Cd were present in lesser amount. In case of all the sewage effluents, highest concentration of metals was present in raw sewage. In raw sewage treated soil, the top layer showed maximum accumulation of these metals. A depth wise decrease of these metals was observed in all the treatments.

These results indicate that there is less threat of land pollution from the application of primary treated sewage and final treated sewage unlike the use of raw sewage from Okhla sewage Treatment Plant on Delhi soil for irrigation purpose. However, studies are necessary to arrive at a definite conclusion with regard to the application of waste water on SOIL-ECOSYSTEM.

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