Accumulation and Movement of Available Calcium and Magnesium in Sewage Treated Delhi Soil

Dissertation submitted to the Jawaharlal Nehru University in partial fulfilment of the requirements for the award of the degree of

MASTER OF PHILOSOPHY

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CERTIFICATE

This dissertation entitled "Accumulation and movement of Available Calcium and Magnesium in Sewage treated Delhi Soil" has been carried out at the School of Environmental Sciences. 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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ACKNOWLEDGEMENT

I am grateful to Dr. A.K. Bhattacharyya, Associate Professor, School of Environmental Sciences for suggesting me the topic of this study, his inspiring guidance and thoughful discussions at all the stages of work as well as preparation of this dissertation.

I thank the authorities of Delhi Water Supply and Sewage Disposal Undertaking for giving me the permission to collect the samples from Okhla Sewage Treatment Plant, New Delhi, for my research work. I am indebted to Mr. S.K. Sharma, Water Analyst and Mr. R.K. Vig, Chemist of the aforesaid sewage treatment plant for their active help and cooperation.

I express my sincere thanks to Prof. V. Asthana, Dean and Prof. (Mrs) Anjali Mookerjee (former Dean) for providing me with necessary facilities and kind help.

I am thankful to Prof. J.M. Dave for his keen interest and kind encouragement during this study.

My words of appreciations are due to my colleagues and friends Supriya, Mukesh, Mahapatra, Vaidyanathan, Sajid and others for their various timely help and cooperation. I sincerely thank Panigrahi and Aziz for their helpful discussions. I also wish to thank Mr. Ravinder Kumar and Mr. D. Sur for their excellent typing and cartographic work.

Finally I like to thank Jawaharlal Nehru University for providing me with the financial assistance in the form of J.R.F. to carry out this research work.

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• . INTRODUCTION

INTRODUCTION

Increasing urbanization and industrialization throughout the world are clearly exerting great pressure on limited natural resources. Like other resources, fresh water also is becoming scarce and costly. As natural sources of supply are running out and the importation of water is very expensive, the possibility of reusing wastewater may increase the potential resources and delay the process of reaching the critical point.

For several reasons, land treatment of wastewater has been acknowledged to be an environmentally and economically viable waste disposal method. Even when streams and rivers are available for the final disposal of sewage by dilution, the advanced and costly treatment generally necessary to render them suitable for discharge into such waters is often beyond the financial capacities of most communities. This has called for the development of an efficient and low cost treatment process and land has been looked upon not only as an appropriate location for the ultimate disposal of wastewater but also an opportunity to manage them with minimum environmental impacts.

Arid lands are not usually endowed with readily accessible, renewable water supplies. Therefore where increasing populations make demands on the available water resources, conventionally treated wastewater from urban centres become important for irrigating croplands. The wastewater from treatment plants is rich in plant nutrients especially Carbon, Nitrogen and Phosphorus. If discharged directly into a stream, these nutrients would stimulate growth of aquatic plants in the stream and cause a eutrophic condition. During the cycle of growth and decomposition of these aquatic plants, dissolved oxygen in the water sometimes would be periodically depleted to the point of concern for fish survival.

But the land system design seeks to take advantage of the nutrient value of the treated wastewater by spraying it on the soil and letting the crop cover use the nutrients. Due to this land treatment the following major processes occur.

1. The root system takes up the soluble nutrients.

- The soil particles mechanically strain suspended solids and adsorb bacteria, viruses, phosphorus and heavy metals.
- 3. Soil microorganisms consume dissolved organic and nitrogenous materials (Matchske, 1978).

The obvious arguments in favour of using organic wastes for crop production are that crops yields can be increased and long term soil productivity can be sustained. However, it is obvious that care must be taken to ensure that sewage applications do not contaminate the soil.

Contaminants of domestic sewage may be categorised as (1) Disease causing microorganisms, (2) Dissolved minerals, (3) Toxic chemicals (heavy metals, pesticide residues etc) and (4) Biodegradable organic matter.

Clearly, the irrigation of crops with wastewater is very attractive because it is treated to a level comparable with or better than secondary treatment, and the crops utilize the water as well as the nutrients it contains. On the other hand, among the negative consequences, toxic compounds or pathogenic organisms may be recycled and introduced to trophic food chains that include man. Other hazards are: soil and aquifer contamination, damage to crops, health risks to farm workers and people who live near the irrigation zone, as well as to cattle feeding on agricultural products irrigated with wastewater (Marquez, 1981).

In India sewage farming started in 1895. Since then it is being practised in different modes using raw sewage, dilute sewage and also partially treated sewage.

According to a recent survey by the Central Board for Prevention and Control of Water Pollution, sewage production in the country was 2400 million gallons per day (MGD). In the union territory of Delhi alone, the volume of sewage production is put at around 230 MGD. This sewage is treated at three existing sewage

treatment plants, namely, Okhla, Keshopur and Coronation Pillar, the major one among them being Okhla. The present capacity of Okhla wastewater treatment plant is 88 MGD and it can withstand an overload of 25%. As on 1980, a total area of about 2604 acres was under sewage irrigation and in the following period 2932 acres were added up.

Soils subjected to sewage application have to be studied not only for irrigational purposes but also from the standpoint of the changes in its nutrient status.

Of the fourteen essential elements, obtained from the soil by plants, six are used in relatively large quantities. They are Nitrogen, Phosphorus, Potassium, Calcium, Magnesium and Sulphur (Brady, 1974).

Not only are Calcium and Magnesium essential to the complex biochemistry of plant growth, but their presence in the soil in adequate amounts and in suitable proportions to one another and to other exchangeable cations such as Alumunium, Hydrogen and NH_4^+ is necessary if the soil is to be a suitable medium for plant root development (Tisdale and Nelson,1975).

A deficiency of Calcium manifests itself in the failure of the terminal buds of plants and apical tips of roots to develop as a result of which plant growth ceases. Magnesium is the only mineral constituent of chlorophyll and its importance is obvious

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for without chlorophyll the green plants would fail to carry out photosynthesis.

The present investigation was undertaken to assess the characteristics of raw sewage, primary and secondary treated effluents from Okhla sewage treatment plant in the light of their suitability for irrigation as well as to evaluate the potentiality of plant nutrient availability.

A laboratory experiment under controlled conditions was set up to study the effects of these effluents on the accumulation and movement of available Calcium and Magnesium in the soil columns at regular intervals for a period of 2 months. The detailed results of this experiment have been incorporated in this dissertation.

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REVIEW OF LITERATURE

REVIEW OF LITERATURE

Of the three locations for the ultimate disposal of wastes surface waters, atmosphere and land, the land represents not only an appropriate disposal medium for many wastes but also an opportunity to manage wastes with a minimum of adverse environmental effects.

Land application of wastewater offers great scope in reclaiming water resources and has proved to be a widely acclaimed practice for several decades, especially in the arid countries (D'Itri 1977). The first method of wastewater disposal adopted in modern times was that used to prevent the pollution of the River Thames near London in the mid 19th century; the method of choice was disposal by irrigation (Okun and Ponghis 1975).

In India it has been reported that one of the first sewage farms was established as early as 1896 at Ahmedabad (Vidyarthy and Mishra 1977). Wastewater reclamation and reuse in agriculture is common in China, India and Israel and to a limited extent in Europe and the USA.

Benefits of land application of wastewater

In arid regions, water shortage is a continuing problem, sometimes limiting agricultural and economic growth. In this context, subjecting municipal wastewater to varying degrees of treatment and reusing the reclaimed water in agricultural production becomes increasingly attractive.

Progressive attention has been given to waste disposal systems in which soils are employed according to the 'living filter' concept. The use of corn, hay, trees and soil to purify the effluent has been described as a 'living filter' (Loehr 1977).

Beek et al. (1977) conducted studies on a sewage farm that had been using raw sewage for the past 50 years. He found that intermittent flooding of the soil with sewage water resulted in a 98% decrease in BOD and phosphate removal of 96%. But the removal of nitrogenous compounds was less effective. Hill (1972) determined the wastewater renovation potential of diverse soils by applying 1 inch of effluent semi weekly for 2 years to undisturbed soil columns. Chemical analysis of the leachate showed that the acid soils removed virtually all the PO_4 , 85% Potassium, 75% Calcium and Magnesium but less than 10% Sodium. The alkaline soil on the other hand removed less than 50% Calcium.

The feasibility of wastewater effluent application in the irrigation of grassland and in sugar cane culture was studied in Oahu, Hawaii (Gordan 1975). It was found that when secondary effluent was applied to grass and sugar cane, the soil and vegetative cover was highly effective in removing phosphorus, potassium,

suspended solids, total organic carbon, boron, and viruses. Parizek et al. (1967) sprayed treated sewage on crop land and forested areas for seven years and showed that the soil and harvested crops together removed 50 to 100% of the applied phosphorus and nitrogen.

Liquid wastes if discharged into surface water bodies like streams, rivers and lakes would bring undesirable alterations of physical, chemical and biological characteristics of water and would thus result in the deterioration of water quality (Bouwer and Chaney, 1975; Lee 1976). Soil percolation is considered to be an effective means of removing heavy metals and other contaminants that can cause serious problems when emptied into streams and lakes (Loehr 1977).

Sewage can also be used as an insect pest inhibitor (Byers and Zeiders 1976). According to them treatment of reed canary grass with municipal sewage effluent caused a decrease in the population of cereal leaf beetle and fruit fly, two pests of this grass. They concluded that the use of reed canary grass would serve as a good receptor for sewage effluent.

The analysis of sewage for their potential use as fertilizer was studied (Sommers 1977, Doty et al. 1977). The metals like Zinc and Cadmium were seen to be of major concern because these when applied to soil in excessive amounts could reduce plant yield or impair the quality of food or fiber produced. But a detailed chemical

analysis and controlled application could produce good results. Dhua (1979) maintained that 2,92,000 million tons of sewage and sullage available per annum in India if suitably utilised can irrigate 0.1 million hectares of cultivable land. More recently Goduer and Hooli (1986) reported that the manure from sewage produced for one day in the whole of India would be enough for cultivating 0.2 million hectares of biennial or 0.1 million hectares of annual crop.

Effect of sewage on crops

One of the most important factors governing wastewater irrigation has been its effect on crop yield. A host of informative reports have appeared in the past few decades to illustrate the influences of sewage effluent on the yield of different crops. Many efficiently operated sewage farms showed tremendous increases in crop yield.

A report by Sopper and Kardos (1973) on the yield of sillage corn and reed canary grass due to sewage irrigation, showed that in a span of 7 years with an irrigation rate of 5 cm per week the results were quite encouraging. The annual yield increase ranged from 8 to 34% for corn grain, 5 to 30% for corn sillage, 85 to 191% for red clover and 79 to 139% for alfafa.

Studies were conducted on the effect of municipal wastewater on cotton yields (Day et al. 1981; Bielorai et al. 1984). The results showed that cotton irrigated with wastewater grew taller with more vegetative growth than did cotton irrigated with pump water. The yield of lint cotton was higher and there was no change in the quality. In addition, Bielorai (1984) found that drip irrigation of cotton increased irrigation and fertilization efficiency and minimised ecological damage.

In Germany, Tietjen (1977) reported the effects of sewage sprinkler irrigation on a variety of crops. He found that sugar beets and potatoes showed a remarkable increase in yield from sewage application in dry years when natural water supply was insufficient. Over a 10 year period the annual increase in yield due to sewage irrigation over the control fields ranged from 19 to 272% for potato, 1.3 to 122% for sugar beet and 29.5 to 88.8% for winter rye.

Day et al. (1963, 1979) conducted studies on the effect of sewage on yield and quality of grain and forage crops. He irrigated them with wastewater and with well water containing equivalent N, P and K as that of the wastewater. He found that wastewater produced equal or sometimes higher yields. Barley, oats and wheat efficiently utilised the fertilizer elements in sewage effluent for

grain production. They utilised the nitrogen in the sewage as efficiently as they used the nitrogen in commercial fertilizer to produce high protein grain (Day et al. 1962).

In Israel, cotton was irrigated with treated sewage. Effluent irrigation replaced N-fertilization resulting in a yield increase in cotton, despite a small decline in lint percentage (Feigin et al. 1978). By adjusting fertilizer application to effluent quality and available N in the soil before the cotton is sown, considerable amounts of N fertilizer was found to be saved and hazards of nitrate leaching below root zone was diminished. Lazlo Vermes (1977) observed that the average yearly yields of grain corn, sillage corn and lucerne irrigated with effluent surpassed the non-irrigated fields yields by 60 to 150%.

In India on the other hand, there are no detailed reports on the yield pattern of the crops irrigated with sewage. There are only reports naming the different crops that have been tried out in various sewage farms. Pillai et al. (1955) reported that legumes, vegetables, fruits and fodder crops were grown successfully in the Madurai sewage farm. He found that grasses were very responsive and guinea grass used as fodder yielded at the rate of about 100 tons per acre per annum.

Effluent Irrigation: Problems and its solutions

Effluents applied to the land by irrigation undergoes a variety of physical, chemical and biological reactions. Some contaminants become fixed in the soil, others are held on the exchange complex where plants can utilize them, while others may leach to the water table below (Hill, 1972).

Land wastewater application systems in the past have not paid proper attention to the potential problems associated with chemical contamination of ground water in the region of discharge (Lee, 1976). Ground water contamination with nitrates, chloride, phosphates and other hazardous chemicals including certain heavy metals like Cadmium, Mercury, Zinc and Copper have been listed to be the potential chemical problems.

When sewage effluent is used as a sole water source for irrigation, the nitrogen loading may exceed crop uptake, normal denitrification and other losses and this excess will move downwards as NO_3^{-} . Bramm (1975) found an increase in nitrate concentration of the ground water below sewage irrigated fields. According to King and Morris (1972) application of large quantities of sewage would increase the danger of ground water pollution by the leaching of NO_3^{-} N into the ground water below the pollution site. However, Sopper (1976) reported non significant increases

in nitrate nitrogen concentrations in the ground water of crop land and forest areas which had received sewage effluent for nearly 7 years.

Another significant problem of sewage irrigation is the heavy metal accumulation in soil due to long term application. The possibilities of contaminating the soil and subsequently the food chain with heavy metals in sewage must be considered before heavy or prolonged application can be safely used. The concentration of heavy metals in treated domestic sewage is quite low when there is no addition of heavy metal laden industrial effluent. It is evident from available reports that secondary treatment methods are highly efficient in removing organic characteristics and in modifying the mineral characteristics of raw sewage (Oliver and Cosgrove 1975; Raman et al. 1973).

According to Higgins (1984) no detectable heavy metal contamination of ground water occured as a result of sewage sludge application. He concluded that little, if any migration of heavy metals occured through the soil. But Rohde (1962) reported on heavy metal accumulation, especially Copper and Zinc in the soils of raw sewage farms.

In any event raw wastewater should not be used for irrigation because food crops may become contaminated with pathogens,

grease and other deleterious substances may clog the soil and prevent further use, offensive odours may create a nuisance and farm workers may be infected with pathogenic organisms (Okun and Ponghis, 1975). The use of sewage wastes in growing vegetables to be eaten raw can result in outbreaks of typhoid fever, cholera, dysentry and enteric fever (Burge and Marsh, 1978). They found that though even treated sewage contained pathogens, the majority of illness were caused by application of raw or inadequately treated sewage to crops which are consumed raw. Mutlak et al. (1980) reported that despite considerable reduction of pathogens due to detrimental environmental conditions, sufficient number of pathogens can survive to form a potential hazard from crops consumed in the uncooked form.

The pathogenic bacteria commonly found in sewage effluent include Salmonella, Shigella, Mycobacterium and Vibriocomma (Foster and Engelbrecht, 1973). But the bacteria are removed from the sewage during percolation through soil by straining, sedimentation and adsorption. In most instances the survival of pathogens is less than two to three months.

It is thus apparent that effluent is to be treated before land application. But due to the prohibitive costs involved in treatment of domestic waste, this affects the viability of land application as a practicable and cost effective technology (Morris and Jewell, 1977).

Effect of sewage on soil chemical properties

The ability to develop acceptable land disposal systems for wastes requires an understanding of the reactions and transformations that take place when wastes are applied to the soil. Soil is a composite medium, containing inert rock, gravel and sand, reactive clay minerals, organic matter, living and dead vegetative and animal matter plus a large variety of soil microorganisms. The capacity of a soil to handle complex organics varies with soil properties and climatic conditions. Improper drainage and aeration will result in anaerobic conditions and less soil assimilative capacity. Accumulation of various chemical constituents of the sewage can occur in soil treated with waste water. This accumulation depends on the loading rate, soil type to which application is done, and the crop systems raised.

Many things can happen to the waste materials applied to the soil. The important items include being used by a crop, becoming part of the soil, leaching through soil, being moved by erosion or surface run off, and leaving the soil plant system as a gas or water vapour (Loehr, 1977).

Day et al. (1972) studied soil that had been irrigated with waste water for 14 years. He found a significant increase in the concentration of soluble salts, nitrates and phosphates over the values obtained for well water irrigated soil. These

effects were seen to be more pronounced in the surface and subsurface layers.

Kelling et al. (1977) reported increased concentrations of organic N & inorganic N in sandy loam and silt loam soil treated with liquid sewage sludge. He found that upto 50% of the applied organic nitrogen was mineralized within 3 weeks of application.

According to Lance and Whistler (1972), short frequent cycles of flooding soil columns (2 days flooded, 5 days dry) with secondary sewage effluent caused no nettremoval of nitrogen but almost all of the ammonium and organic nitrogen was transformed to the nitrate form. Broadbent et al. (1977) examined the properties of soil after prolonged waste water application and compared the changes in chemical properties with soils from adjacent sites. They observed prominent increases in nitrate concentration throughout the 0-150 cm layers of the soil that received waste water.

Sopper (1976) analysed the soil in two areas that had received the highest application of effluent. From these results he concluded that the effects of effluent irrigation on exchangeable potassium, organic matter, pH and total nitrogen are small and inconsistent. However, significant changes in the concentrations

of Calcium, Magnesium, Sodium, Manganese, Boron and Phosphorus were observed and related to heavy application of sewage effluent.

Intermittent flocoing of soil with sewage water resulted in 96% decrease of the phosphate. In addition the sewage water raised the pH of the soil and increased the organic matter content, mainly of the top layers (Beek et al. 1977).

According to Loehr (1977) the BOD removal efficiency of the soil can be affected by the amount of vegetative cover and the infilteration capacity. Anything that adds surface area at the soil-air interphase will increase the biological decomposition capacity of the soil disposal system.

Quin and Wood (1978) recorded higher pH values and higher levels of organic carbon, total nitrogen and exchangeable calcium and sodium in O-15 cm layer of the soil in the Templeton effluent irrigation scheme, N. Zealand. Masand et al. (1978) found increases in the organic matter status of the soil layers from O-5 cm when 20 cm and 40 cm of sewage were applied to a column of sandy soil.

The effects of applying chlorinated secondary sewage on soil were evaluated by Klausner and Kardos (1975) on two aeration parameters-Oxygen diffusion rate and concentration of oxygen in

soil gas. Application of 5.1 cm of sewage effluent at weekly intervals did not degrade the soil's aeration status.

Oxygen is an important component of a soil system. If soil is organically overloaded, oxygen can become a limiting factor and the biological system may become anaerobic. Anaerobic conditions will predominate if excessive flooding or water logged conditions prevail. When the oxygen content is close to zero, the waste application rate is approaching the maximum for the local environmental conditions.

Effect on Calcium and Magnesium

De Jong (1978) leached sewage effluent through columns of the A, B and C horizons of a loamy sand and A horizon of a clay. The columns were 10 cm diameter and 20 cm length. In one treatment a head of effluent varying from 2 to 5 cm was always maintained on the columns (flood treatment) and in the other method ponding was minimized (trickle treatment). He found that neither temperature (7, 13 or 18° C) nor method of application (flood or trickle) affected the passage of sodium, calcium, magnesium and sulphate ions. But leaching with the sewage effluent increased the pH and the sum of exchangeable (Na + K + Ca + Mg) in the soil presumably due to displacement of adsorbed H and/or aluminium.

Hill (1972) applied sewage effluent semi-weekly for 2

years to some acid and alkaline soil. He found that all the acid soils removed greater than 85% K and 75% calcium and magnesium. But the calcareous soil containing abundant limestone particles removed less than 50% calcium and released three times the magnesium added in the effluent for 21 months. He concluded that this alkaline soil added unwanted hardness to the percolate by flushing available magnesium from weathered calcareous minerals. When irrigation water is applied to a calcareous soil, the native calcium carbonate often undergoes certain changes depending upon the activity of the ions in the soil solution (Yadav and Girdhar, 1981).

Silverman and Munoz (1980) conducted studies on the microbial mobilization of Calcium and Magnesium in soils amended with 0.5% glucose solution and incubated in air and anaerobically for 2 weeks under water logged conditions in the laboratory. Glucose was taken as a model of simple plant carbohydrates. Incubation in air resulted in a 2.4 to 29.4 fold increase in the Calcium content relative to control soils and a 0.7 to 41 fold increase in the Magnesium content of soil solutions. Under anaerobic incubation there was 2.7 to 15.3 fold increase in Calcium and 1.5 to 47 fold increase in Magnesium content of soil solutions. He concluded that Calcium and Magnesium could be mobilized in a variety of soils when glucose

is metabolized by indigenous microorganisms in water-logged soil and this could be responsible for the release of Calcium and Magnesium from exchange sites and other mineral reservoirs.

Sposito et al. (1978) reported that fulvic acid, the water soluble fraction of human compounds has been shown to interact with calcium to form calcium chelates.

Edwards and Bennet (1985) determined the effect of sewage sludge on movement of surface applied calcium with controlled leaching studies in the laboratory. Although high levels of calcium carbonate and sewage sludge were applied, no differences were detected in the calcium contents of the leachate. He therefore reported that the soil apparently served as a sink for the calcium. His studies indicated that significant Calcium translocation can also be achieved in a shorter term.

The complexation reaction of bivalent metal cations with organic acids that are expected to be found in soil solutions have become a subject of considerable interest in recent years. Sposito et al. (1978) investigated the reaction of Ca^{2+} , an important and ubiquito^{US} metal cation in soil solutions with fulvic acid extracted from sewage sludge. They reported that (i) a relatively strong ion pair is formed between Ca^{2+} and the most acidic functional groups in fulvic acid and (ii) a weaker ion pair is formed between Ca^{2+} and the more weakly acidic functional groups.

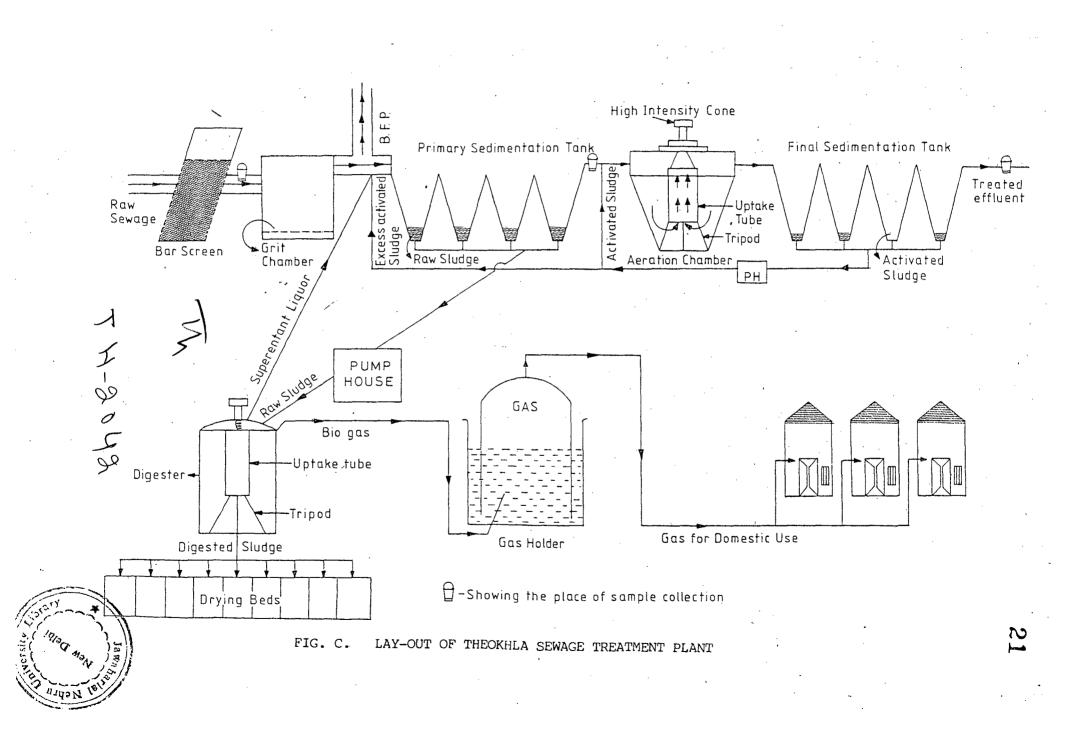
MATERIALS

ATERIALS AND METHODS



FIG. A. PHOTOGRAPH OF A SINGLE COLUMN





MATERIALS AND METHODS

Columns made of PVC were filled with soil and treated with municipal effluent for 60 days. All treatments were done in duplicates. Small quantities of soil were removed periodically and the important parameters were analysed.

Soil: Collection and Preparation

Soil was collected from uncultivated land around J.N.U. Nursery to a depth of about 15 cm. The soil samples were mixed thoroughly to ensure uniformity and then air dried. Later they were powdered and sieved through a 2mm perforated sieve and filled into the columns. Each column (as shown in Fig.A) was made to the following specifications:

Height = 60 cm

Inner diameter = 15 cm

Holes at intervals of = 7.5 cm

Thick wire mesh at the bottom

Before the addition of soil, the column was first prepared with a 5 cm layer of gravel at the bottom and a 5 cm layer of fine sand on top of it. Then the ^{sie}ved soil was carefully poured in and the columns were stabilized by passing tap water through it for two days.

Effluent collection

Effluent was collected from Okhla Sewage Treatment Plant, New Delhi. Three types of sewage namely Raw, Primary treated and Secondary

treated sewage were taken.

Treatment

Eight soil columns were treated with the effluent, two each for raw, primary treated sewage, secondary treated sewage and tap water as control. One litre of effluent for 24 hours was added by a continuous drip arrangement. The experiment commenced on 18.2.86. Effluents were collected from Okhla at intervals of 21 days on 18.2.86, 11.3.86.and 2.4.86. The soil samples were drawn out for analysis every 15 days on 4.3.86, 19.3.86, 3.4.86 and 18.4.86. Sampling was also done at four different depths of the column: surface layer, 15 cm, 30 cm and 45 cm.

Analysis

Both the soil and effluent samples were analysed for the following parameters:

1. pH.

2. Electrical conductivity

3. Organic carbon

4. Available nitrogen

5. Available calcium

6. Available magnesium

In addition to this, the effluent samples were analysed separately for:

1. Dissolved oxygen

- 2. Biochemical oxygen demand
- 3. Chemical oxygen demand

The original soil was also tested for cation exchange capacity and mechanical analysis.

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10 gm of soil weighed out and 50 ml of distilled water was added and stirred thoroughly. pH was then determined by Phillips pH meter. The pH of the water samples were also determined by the same instrument.

2. Electrical conductivity

The same 1:5 soil:water ratio was used to measure the electrical conductivity. A Systronics direct reading E.C. meter was used for both the soil and effluent samples.

3. <u>Organic carbon</u> (Walkley-Black method) Principle:

This method involves the oxidation of the organic matter by an oxidising agent added to the soil in excess, and the subsequent titration and determination of the excess oxidizing agent. Here the oxidising agent used is acidified potassium dichromate and the excess of dichromate is back titrated with ferrous ammonium sulphate using diphenyl amine as an indicator.

Reagents

a) Standard IN Potassium dichromate.

12.257 gm of $K_2 Cr_2 O_7$ was dissolved in distilled water, and the solution diluted to 250 ml.

b) Ferrous ammonium sulphate.

An N/2 solution was prepared by dissolving 98 gm of ferrous ammonium sulphate in distilled water. 15 ml of concentrated H_2SO_4 was added and the volume made upto 500 ml. This was then standardised with 1 N K₂Cr₂O₇ solution.

c) Diphenylamine indicator.

0.5 gm of reagent grade diphenylamine was dissolved in 20 ml water and 100 ml of conc. $\rm H_2SO_4.$

d) 85% H₃PO₄

e) Solid NaF

Procedure

A. Soil:

In the case of soil samples, 2 gm of the soil was placed in a 500 ml conical flask. Next exactly 10 ml of 1 N $K_2Cr_2O_7$ was pipetted into the soil and the two were mixed by swirling the flask. Then 20 ml of conc. H_2SO_4 was added and mixed by gentle rotation for 1 min. to ensure complete contact of the reagent with the soil. The mixture was allowed to stand for 20 to 30 minutes. A standardization blank (without soil) was run in the same way. The mixture was then diluted to 200 ml with water and 10 ml of 85% H_3PO_4 , 0.2 gm NaF and 1.5 ml diphenyl amine indicator were added.

Then this solution was back titrated with ferrous ammonium sulphate solution delivered from a burette. The col^{OUr} was dull green at the beginning, then shifted to a turbid blue as the titration proceeded. At the end point this colour sharply shifted to a brilliant green giving a 1 drop end point.

B. Effluent:

Here, 25 ml of the effluent sample was taken in a conical flask and 10 ml of 1 N $K_2 Cr_2 O_7$ solution and 20 ml of conc. $H_2 SO_4$ were added. After mixing the mixture was allowed to stand for 30 minutes and then diluted to 200 ml with distilled water. 10 ml of $H_3 PO_4$ was added and the solution was back titrated with ferrous ammonium sulphate using four drops of diphenylamine as indicator. The end point was a brilliant green. A blank with 25 ml distilled water was also run in the same way.

Calculation

\$ of organic carbon in soil = <u>a-b x 0.003 x n x 100</u>

% of organic matter in soil = % of organic carbon in soil x 1.724

where

a = volume of ferrous ammonium sulphate required for blank titration

b = volume of ferrous ammonium sulphate for soil samples

n = strength of ferrous amm. sulphate

w = weight of soil in gm

1.724 is the Van Bemmelen factor

Carbon to organic matter factor is based on the assumption that soil organic matter contains 58% carbon.

, s of organic carbon in $= a-b \times .003 \times n \times 100$ effluent sample v

where

a = blank titration value

b = sample titration value

n = strength of ferrous amm. sulphate

v = volume of effluent sample

4. Available Nitrogen

The available nitrogen in the soil was determined by the Subbiah and Asija (1956) method.

Principle

When soil is digested with alkaline permangnate solution, it releases ammonia both from the inorganic ammonium compounds and the organic nitrogen pool by a process of oxidation and hydrolysis. Reagents

a) Sodium hydroxide solution (2.5%)

25 gm of NaOH was dissolved in 1 litre of distilled water

b) Potassium permangnate (0.32%)

3.2 gm of ${\rm KMnO}_4$ was dissolved in 1 litre of distilled water c) Mixed indicator

0.1 g of methylene blue was dissolved in 50 ml of 95% ethanol and 0.2 gm of methyl red was dissolved in 100 ml of 95% ethanol and the two were mixed. 10 ml of this solution was added to 2% Boric acid solution to give the mixed indicator solution.

d) Boric acid solution (2%)

20 gm of boric acid was dissolved in 1 litre of distilled water

e) Standard sulphuric acid (0.02 N)

Procedure

A. Soils:

20 gm of the soil sample was taken in a kjeldahl flask along with 20 ml of distilled water. 100 ml of ${}^{\rm K}{\rm MnO}_4$ solution and 100 ml of 2.5% NaOH solution were then added. The contents of the flask were distilled and 75 ml of the distillate collected in 20 ml mixed indicator solution. The boric acid was then titrated against standard 0.02 N ${\rm H}_2{\rm SO}_4$ to a pale lavender end point.

B. Effluent:

The above procedure was followed for the effluent samples also, the only difference being that 50 ml of sewage was taken instead of the 20 gm of soil.

Calculation

 $1 \text{ ml of } 0.02 \text{ -N H}_2SO_4 = 0.28 \text{ mg of N}$ ppm of Nitrogen = (a-b) x 0.28 x 1000 x

where

5.

a = sample titration value

b = blank titration value

x = weight of soil in gm or volume of effluent

Available calcium

Available calcium in both the soil and effluent samples were determined by the atomic absorption spectrophotometric (AAS) method as suggested in Chemical Analysis of Ecological Materials (Allen, 1974).

Principle

In this method the calcium is extracted in the form of a solution and this solution is sprayed into a relatively cool flame in which the atoms tend to remain in the ground state. Radiation of a characteristic wavelength from a hollow cathode discharge lamp is passed through the flame and the decrease in intensity is measured using a detector system. This decrease is related to the concentration of calcium in the solution.

The biggest drawback in the application of flame methods for calcium is the interference from other elements. Interferences are due to silicon, aluminium, phosphate and sulphate which depress calcium sensitivity. So lanthanum or strontium is added to standards and samples to control chemical interference.

Reagents

a) Extractant: Ammonium Acetate (pH 9)

200 to 300 ml of distilled water was taken in a large aspirator. 575 ml of glacial acetic acid and 740 ml of 0.880 ammonia solution were added and mixed. This mixture was diluted to 10 litres and mixed thoroughly. The pH was checked and brought to 9.0 ± 1 by adjusting with drops of acetic acid or ammonia as necessary.

b) Calcium standards

A stock solution of 1000 ppm calcium was prepared by dissolving 0.2530 gm of dry calcium carbonate in 2.5 ml of 1N H^C1. The solution was gently boiled to drive off carbon dioxide, cooled and made up to 100 ml with distilled water. From this suitable working standards were prepared.

c) Strontium cnloride

3.0428 gm of strontium chloride was taken in a 500 ml volumetric flask and diluted to the mark with distilled water.

Procedure

A. Soil:

2 gm of soil was taken in a conical flask and 50 ml of ammonium acetate was added. Extraction was done by shaking this solution in a mechanical shaker for 1 hour and filtering through No.44 Whatman filter. 2 ml of this clear filterate was taken in a 50 ml volumetric flask and 2 ml of strontium chloride was added. This was then diluted to the mark with distilled water. The standards and samples were run through the AAS at a wavelength of 422.7 nm. B. Effluent

10 ml of filtered sewage was taken in a 100 ml volumetric flask and 4 ml of strontium chloride was added. The solution was made upto the mark with distilled water and run through the AAS. Calculation

The concentration was determined by multiplying the reading got from the instrument with the amount of dilution.

6. Available Magnesium

The available magnesium content also was determined by the same method of atomic absorption spectrophotometry. Here, again strontium was added to supress interference.

Reagents

a) Extractant: Ammonium Acetate M (pH 9)

The same extractant used for calcium determination was used here.

b) Magnesium standards

A stock solution of 1000 ppm magnesium was prepared by

dissolving 1.0136 g magnesium sulphate in water containing about 1 ml conc. H_2SO_4 . This was then diluted to 1 litre and mixed thoroughly. From this stock solution suitable working standards were prepared.

c) Strontium chloride

3.0428 gm of strontium chloride dissolved in 500 ml distilled water.

Procedure

1.

A. Soils:

The procedure was the same as that for calcium analysis. The magnesium standards and samples were run through the AAS at 285.2 nm.

B. Effluent:

l ml of filtered sewage was taken in a 100 ml volumetric flask along with 4 ml of strontium chloride and made upto the mark. This was then fed into the AAS along with the other magnesium samples. Calculation

The concentration of magnesium in the soil and effluents were calculated by multiplying the instrument readings with the degree of dilution.

ANALYSIS OF ONLY EFFLUENT SAMPLE

Dissolved Oxygen (DO)

The dissolved oxygen content of the effluent was determined

by iodometric method suggested in 'Standard Methods for the Examination of Water and Wastewater' (APHA, 1980).

Principle

This test is based on the addition of divalent manganese solution followed by strong alkali to the sample in a BOD glass stoppered bottle. DO present rapidly oxidises an equivalent amount of the dispersed divalent manganous hydroxide to a higher oxidation state (brownish-orange in colour). This brownish orange colour indicates the presence of oxygen. In the presence of iodine and subsequent acidification, higher manganese hydroxide reverts to divalent state and liberates iodine equivalent to the original DO content of the sample. The iodine liberated is titrated with a standard solution of sodium thiosulphate using starch as indicator. Reagents

a) Manganous sulphate

36.4 gm of $MnSO_4$. H₂O was dissolved in distilled water, filtered and diluted to 1 litre.

b) Standard sodium thiosulphate titrant

3.15 gm of $Na_2S_2O_3$. $5H_2O$ was dissolved in distilled water and diluted to 1 litre. This solution was then standardised against KIO₃ solution.

c) Alkalí-iodide azide reagent

50 gm of NaOH and 15 gm of KI were dissolved in distilled

water and diluted to 100 ml. 1 gm of sodium azide dissolved in40 ml of distilled water was added to this and mixed thoroughly.d) Standard potassium iodate

0.446 gm of potassium iodate previously dried at about 120[°]C was dissolved in distilled water and diluted to 1 litre. e) Starch indicator

5 gm of soluble starch was made into a smooth paste with cold water and poured into 1 litre of boiling water with constant stirring. After cooling the clear supernatant was used. Procedure

To the BOD bottles filled with effluent sample, 2 ml of manganous sulphate and 2 ml of alkali iodide azide reagent were added, dipping the pipette little below the surface. The bottle was then carefully stoppered to exclude air bubbles and mixed by inverting at least 15 times. When the precipitate formed had sett-led to the lower third of the bottle, the mixing was repeated to allow the precipitate to settle completely leaving a clear supernatant liquid. Then 2 ml of conc. H_2SO_4 was added immediately after removing the stopper. The stopper was replaced and the contents mixed by gentle inversion until all the precipitate dissolved, loo ml of the sample was taken in a conical flask and the liberated iodine immediately titrated with standard thiosulphate to a pale yellow straw colour. Then 2 ml of starch solution was added and the

titration continued till the disappearance of blue colour. Standardisation of $Na_2S_2O_3$ solution

10 ml of standard potassium iodate was pipetted into a conical flask containing 100 ml water. 2 ml of conc. H_2SO_4 and 2 gm of potassium iodide were added and the iodine liberated was immediately titrated against sodium thiosulphate solution using starch as indicator.

Calculation

Dissolved oxygen content $mg/l = \frac{a \times 10}{b}$

where

a = volume of thiosulphate required for 100 ml
 of sample

b = volume of thiosulphate required for 10 ml of 0.0125 N potassium iodate

2. Biochemical Oxygen Demand (BOD)

BOD is defined as the amount of oxygen required by micro organisms to stabilize biologically decomposable organic matter in a waste under aerobic conditions. The samples are filled in BOD bottles with adequate dilution and the DO is measured on the first day. The samples are then incubated at 20° C for 5 days and the DO again determined on the 5th day. The difference in DO values give the BOD.

Apparatus

- 1) Incubation bottles: 300 ml capacity with ground glass stoppers
- 2) Incubator: A BOD incubator which can maintain a temperature of $20 \pm 1^{\circ}C$.

Reagents

a) Dilution water

10 litres of distilled water aerated for 48 hours by bubbling compressed air to attain DO saturation. To this 10 ml each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride, were added.

b) Phosphate buffer solution

10.625 gm of potassium dihydrogen phosphate was dissolved in 175 ml of distilled water containing 2.2 gm of NaOH. The pH was adjusted to 7.2 and 0.5 gm of ammonium sulphate was added. The solution was then made upto 250 ml.

c) Calcium chloride solution

6.875 gm of anhydrous calcium chloride was dissolved in 250 ml of distilled water.

d) Magnesium sulphate solution

6.250 gm of magnesium sulphate (Mg SO $_4$, 7H $_2$ O) was dissolved in 250 ml of distilled water.

e) Ferric chloride solution

0.125 gm of Fe Cl₃, $6H_2O$ was dissolved in 1 litre of distilled water.

Procedure

15 ml, 30 ml and 60 ml of each of the raw, primary and secondary effluents were taken in a 1000 ml volumetric flask and made upto the mark with dilutor water. These solutions now represented 1.5%, 3% and 6% of the effluent samples. From each 1000 ml volumetric flask three BOD bottles were gradually filled taking care that no air bubbles were trapped. The neck of the bottle was tapped to remove air bubbles, if any, and immediately stoppered. One bottle was kept for the determination of initial (zero day) dissolved oxygen and the other two were incubated for 5 days at 20° C. The bottle incubated were water sealed and the DO determined' on the fifth day. Three blanks using dilution water only were prepared along the same lines and analysed.

Calculation

BOD mg/l =
$$(D_1 - D_2) - (B_1 - B_2) \times 100$$

% of sample

where

3.

 $D_1 = DO$ of diluted sample on zero day $D_2 = DO$ of diluted sample on 5th day $B_1 = DO$ of diluted blank on zero day $B_2 = DO$ of diluted blank on 5th day

Chemical Oxygen Demand (COD)

COD was determined by the method given in Standard Methods for the Examination of Water and Wastewater (APHA, 1980).

Principle

The chemical oxygen demand determines the amount of oxygen required for chemical oxidation of organic matter using a strong chemical oxidant, such as potassium dichromate under reflux conditions. A sample is refluxed with a known amount of potassium dichromate in sulphuric acid medium and the excess of dichromate is titrated against ferrous ammonium sulphate. The amount of dichromate consumed is proportional to the oxygen required to oxidise the oxidizable organic matter.

Apparatus

Reflux apparatus: flat bottomed 250-500 ml capacity flask with ground glass joint and a condenser. Hot plate: A large hot plate to hold a series of refluxing sets. Reagents

a) Ferrous ammonium sulphate (0.25 N)

24.5 gm of ferrous ammonium sulphate was taken in a 250 ml volumetric flask and dissolved in distilled water. 20 ml of conc. H_2SO_4 was added and the volume made upto the mark. This solution was then standardised using potassium dichromate solution.

b) S'tandard potassium dichromate (0.25 N)

3.0647 gm of previously dried $K_2 Cr_2 O_7$ was dissolved , in distilled water and diluted to 250 ml.

c) Ferroin indicator

0.695 gm of Feso_4 and 1.485 gm of 1, 10 phenanthroline

were dissolved in 100 ml distilled water.

d) Silver sulphate solution

2.5 gm of Ag_2SO_4 was dissolved in 250 ml of conc. H_2SO_4 . e) Mercuric sulphate crystals

Procedure

20 ml each of the three effluent samples were taken in 500 ml COD flasks. 0.5 gm of HgSO₄, 10 ml of standardised potassium dichromate and 30 ml of silver sulphate were added and mixed by slow swirling. The flask was connected to a condenser and refluxed on a hot plate for 2 hours. The flasks were removed, cooled and 80 ml of distilled water added. This was then 'titrated against ferrous ammonium sulphate using ferroin indicator till the colour changed from green to wine red. Two blanks with 20 ml distilled water were also run the same way.

Calculation

 $\frac{\text{COD mg}}{\text{mg}} = \frac{(a-b) \times c \times 8000}{\text{vol. of samples (ml)}}$

where

a = blank titre value

b = sample titre value

c = normality of ferrous ammonium sulphate

Mechanical analysis

Mechanical analysis of original soil was done by hydro-

meter method suggested by Piper (1966).

Cation exchange capacity

The cation exchange capacity of the original soil was determined by the neutral (N) ammonium acetate extraction method (Jackson, 1973).

Reagents

a) Ethyl alcohol (95%)

b) 1N Ammonium acetate (pH 7)

c) Potassium chloride 10%

pH was adjusted to 2.5.

d) Boric acid solution

contained mixed indicator (methyl red & methylene blue)

e) Sodium hydroxide solution (40%)

f) Standard sulphuric acid

Procedure

33 ml of ammonium acetate and 5 gm of soil were taken in a centrifuge tube and centrifuged for 10 minutes. The supernatent liquid was discarded and the procedure repeated two more times. Next the soil was centrifuged with ethyl alcohol and the decanted liquid rejected. The same process was repeated three times with 33 ml of KCl, but this time the decant liquid was collected separately each time and the volume made upto 100 ml with the KCl extract. This solution was then transferred to a Kjeldahl flask and diluted to 200 ml with distilled water. 25 ml of NaOH was added and the distilled ammonia was collected in 50 ml of boric acid-indicator solution. This was then back titrated with standard H_2SO_4 (0.01 N). A blank with equal amount of KCl solution was also run in the same way.

Calculation

CEC meq/100 g soil: $100/v \times a \times 100$

where

v = volume of extract distilled from the 100 ml a = ml of (N) H_2SO_4 required for titration w = weight of soil in gm

EXPERIMENTAL RESULTS

Table 1. Physical-Chemical Properties of Experimental Soil

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PAR	AMETERS	MEAN VALUE		
1.	Particle size analysis	% Sand 57.40		
		% Silt 30.43		
		% Clay 12.17		
2.	рн	8-45		
3.	Water holding capacity	34.5 %		
4.	Electrical conductivity	0.095 mmhos/cm		
5.	Organic carbon	0.2586 %		
6.	Available calcium	1442.3 ppm		
7.	Available nitrogen	56 ppm		
8.	Cation exchange capacity	8.2 meg/100 gm		
9.	Available magnesium	128.1 ppm		
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Parameters	Raw Sewage	Primary Treated Sewage	Secondary Treated Sewage
1. pH	7.50	7.58	7.74
 Electrical conductivity (mmhos/cm) 	1.05	1.05	1.20
3. COD (mg/1)	247.50	217.80	69.30
4. BOD (mg/l)	108.40	66.25	15.20
5. Organic carbon (%)	0.0126	0.0063	0.003
6. Available nitrogen (ppm)	26.80	22.40	17.36
7. Available calcium (ppm)	234	256	256
8. Available magnesium (ppm)	19.5	22.1	22.0

Table 2. Physico-Chemical Characteristics of Effluents Collected on 18.2.86

Data represent average of duplicate samples.

Table 3. Physico-Chemical Characteristics of Effluents Collected on 11.3.86.

Par	àmeters	Raw Sewage	Primary Treated Sewage	Secondary Treated Sewage
 1.	рН	7.50	7.66	7.94
2.	Electrical conductivity (mmhos/cm)	1.02	0.95	1.20
3.	COD (mg/l)	270	160	70
4.	BOD (mg/l)	112.90	61.10	20.29
5.	Organic carbon (%)	0.0168	0.0058	0.0036
6.	Available nitrogen (ppm)	28.56	22.96	15.68
7.	Available calcium (ppm)	236	255	254
8.	Available magnesium (ppm)	18.9	20.5	19.5

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Data represent average of duplicate samples.

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Table 4. Physico-Chemical Characteristics of Effluents Collected on 2.4.86.

Par	ameters	Raw Sewage	Primary Treated Sewage	Secondary Treated Sewage
1.	рН	7.40	7.20	7.60
2.	Electrical conductivity (mmhos/cm)	1.08	1.26	1.02
3.	COD (mg/l)	305	140	35
á .	BOD (mg/l)	140.50	55.30	14.90
5.	Organic carbon (%)	0.0144	0.007	0.0024
5.	Available nitrogen (ppm)	25.20	19.60	15.12
7.	Available calcium (ppm)	240	248	247
8.	Available magnesium (ppm)	19.9	22.0	21.9
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Data represent average of duplicate samples.

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Par	ameters	Raw Sewage	Primary Treated Sewage	Secondary Treated Sewage
 1.	рН	7.46	7.48	7.76
1.	pn	7.40	/ • 40	
2.	Electrical conductivity (mmhos/cm)	1.05	1.08	1.14
3.	COD mg/l	274.1	172.6	58.1
4.	BOD mg/l	120.6	60.8	16.79
5.	Organic carbon (%)	0.0146	0.0063	0.0036
6.	Available nitrogen (ppm)	26.85	21.65	16.05
7.	Available calcium (ppm)	236	253	252
8.	Available magnesium (ppm)	19.4	21.5	21.1
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Table 5. Average of the Physico-Chemical Characteristics of all three batches of Effluents

	Applicat	ion of Sewage	;	• •	1
•		•	• •		
Èffluent type	Depth in cm	15 days	30 days	45 days	60 days
RAW SEWAGE	Surface Layer	7.45	7.60	7.55	7.50
	15	7.90	8.20	8.15	8.20
	30	8.00	8.15	8.30	8,35
`	45	8.10	8.25	8.25	8.40
PRIMARY TREATED SEWAGE	Surface . Layer	7.65	7.75	7.60	7.65
SEWAGE	15	8.30	8.25	8.00	8.25
2	30	8.20	8.30	8.25	8.45 /
	45	8.20	8.30	8.30	8.45
SECONDARY TREATED SEWAGE	Surface Layer	8.20	8.00	8.15	8.35
SEWAGE	.15	8.10	8.20	8.30.	8.45
	30	8.25	8.30	8.40	8.40
	45	8.00	8.35	8.35	8.50
TAP WATER	Surface Layer	8.20	8.30	8.45	8.65
	15 [´]	8.35	8.30	8.45	8.50
٢	30	8,30	8.40	8.50	8.55
	45	8.40	8.50	8.60	8.55
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Table 6. Periodic Changes in pH in the Soil Columns under the Application of Sewage

pH in the original soil - 8.45 Data represent average of duplicate samples.

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Effluent type	Depth in cm	15 days	30 days	45 days	60 days
RAW SEWAGE	Surface Layer	0.110	0.270	0.450	0.60
	15	0.090	0.120	0.180	0.27
`	30	0.095	0.120	0.210	0.24
. · · *	45	0.085	0.150	0.180	0.24
PRIMARY TREATED SEWAGE	Surface Layer	0.112	0.240	0.420	0.63
SLWAGE	15	0.097	0.150	0.180	0.30
	30	0.090	0.180	0.210	0.27
•	45	0.095	0.120	0.210	0.30 ·
SECONDARY TREATED SEWAGE	Surface Layer	0.120	0.240	0.480	0.75
00.000	15 .	0.110	0.210	0.450	0.60 .
•	30	0.110	0.270	0.510	0.63
	45	0.120	0.240	0.480	0.57
TAP WATER	Surface Layer	0.075	0.120	0.240	0.30
	15	0.080	0.120	0.210	0.27
	30	0.075	0.125	0.210	0.24
	45	0.075	0.120	0.210	0.24

Periodic Changes of EC (mmhos/cm) in Soil under the Application of Sewage Table 7.

EC of original soil - 0.095 mmhos/cm Data represent average of duplicate samples.

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Effluent type	Depth in cm	15 days	30 days	45 days	60 days
RAW SEWAGE	Surface Layer	0.2821	0.5818	0.6206	0.6432
	15	0.2697	0.2650	0.2456	0.2830
	30	0.2586	0:2586	0.2650	0.2766
	45	0.2508	0.2508	0.2586	0.2573
PRIMARY TREATED SEWAGE	Surface Layer	0.2586	0.2844	0.2715	0.2830
DUNAGL	15	0.2350	0.2327	0.2327	0.2508
	30	0.2586	0.2508	0.2456	0.2447
	45	0.2350	0.2508	0.2508	0.2701
SECONDARY TREATED SEWAGE	Surface Layer	0.2586	0.2456	0.2586	0.2766
DDUAGE	15	9.2468	0.2327	0.2327	0.2508
	30	0.2350	0.2508	0.2586	0.2508
	45	0.2350	0.2327	0.2508	0.2573
TAP WATER	Surface Layer	0.2355	0.2456	0.2315	0.2315
	15	0.2350	0.2315	0.2350	0.2251
	30	0.2468	0.2350	0.2315	0.2315
	45	0.2350	0.2456	0.2350	0.2315

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Table 8. Periodic Changes of Organic Carbon (%) in Soil under the Application of Sewage

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Organic Carbon of original soil - 0.2586% Data represent average of duplicate samples.

Effluent	Depth	15 days ,	30 days	45 days	60 days
type	in cm		-		
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RAW SEWAGE	Surface Layer	117.6	184.8	176.4	173.6
•	15	65.8	72.8	61.6	72.8
	30	67.2	64.4	68.6	70.0
	45	63.0	61.6	63.0	64.4
PRIMARY TREATED SEWAGE	Surface Layer	75.6	84.0	77.0	78.4
SLINAGL	.15	64.4	65.8	67.2	68.6
	30	67.2	68.6	64.4	64.4
+ 	45	61.6	57.4	58.8 -	63.0
SECONDARY TREATED SEWAGE	Surface Layer	68.6	70.0	72.8	61.6
	15	67.2	61.6	61.6	54.6
	30	61.6	57.4	56.0	49.0
.'	45	61.6	54.6	50.4	50.4
TAP WATER	Surface Layer	53.2	50.4	49.0	44.8
-	15	50.4	51.8	50.4	46.2
	30	51.8	49.0	44.8	43.4
	45	50.4	47.6	42.0	43.4

Table 9. Periodic Changes in Available Nitrogen (ppm) of soil under the Application of Sewage

Available Nitrogen in original soil - 56 ppm Data represent average of duplicate_samples.

Effluent type	Depth in cm	15 days	30 days	45 days	60 days
RAW SEWAGE	Surface Layer	2022.5	1714.2	1905.3	1772.6
	15	2270.9	2062.7	2178.3	2084.1
	30	2278.3	2081.0	2186.1	2140.5
	45	2228.2	2125.8	2318.2	2127.0
PRIMARY IREATED	Surface Layer	1907.1	1838.2	2001.0	1838.0
SEWAGE	15	2201.5	2115.2	2230.9	2117.6
	30	2169.9	2081.5	2258.9	2193.1
-	45	2157.0	2172.1	2300.2	2155.3
SECONDARY TREATED	Surface Layer	1989.7	1846.3	2077.5	1882.0
SEWAGE	15	2181.6	2092.0	2322.7	2102.3
	. 30 .	2176.3	2153.2	2352.1	2160.7
	45	2193.6	2118.2	2320.9	2189.9
TAP WATER	Surface• Layer	1809.3	1792.0	1789.6	1766.7
	15	1793.6	1790.4	1785.8	1761.2
	30	1780.1	1781.8	1780.0	1765.5
	45	1776.7	1781.2	1773.9	1750.0

Table 10. Periodic Changes in Available Calcium (ppm) of Soil under the Application of Sewage

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Available Calcium in original soil - 1442.3 ppm Data represent average of duplicate samples. 2

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Effluent type	Depth in cm	15 days	30 days	45 days	60 days
RAW SEWAGE	Surface Layer	129.9	163.2 ′	172.8	213.7
	15	75.7	48.0	50.9	81.1
· · ·	30	63.1	30.9	59.2	60.2
•	45	58.7 .	31.6	35.8	50.6
PRIMARY FREATED SEWAGE	Surface Layer	99.2	133.8	131.9	174.8
	15	43.7	35.1	54.0	71.9
	30	41.2	32.9	38.7	60.0
	45	39.8	31.6	40.5	62.8
SECONDARY IREATED SEWAGE	Surface Layer	77.9	129.2	133.6	191.7
SEWAGE	15	38.6	37.7	40.1	88.6
	30	40.0	32.8	39.9	62.7
· .	45	32.1	32.6	38.0	51.3
TAP NATER	Surface Layer	61.5	63.9	69.3	71.3
	15	50.9	48.7	52.1	55.8
	30 .	40.5.	40.9	41.7	51.7
	45	39.1	38.6	43.8	50.9

Table 11. Periodic Changes in Available Magnesium (ppm) of soil under the Application of Sewage

Available Magnesium in original soil - 128.1 ppm Data represent average of duplicate samples. . •

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	Days	Corelation coefficient 'r'	Signif level	icance
Cax Mg	15	612	P.0	3
· .	30	983	P.0	01
	45	954	P.0	01
•	60	980	Р.0	01
CaxC	15	301	Р.3	•
	30	728	P.0	07
	45	696	P.0	1
	60	685	P.Ø.	1
CaxN	` 15	497	P .1	<u></u> .
	30 -	796	P.00	02
-	45	785	P.0	02
	60	708	P .0	1
СахрН	60	.859	P.0	01
Ca x EC	60	575	not si	gnifica

Table 12. Corelation coefficients between available Calcium and other soil parameters in sewage amended soil

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•	Days	Corelation coefficient 'r'	Significance level
	15	0.00	
MgxC	15	.828	.001
	30	.698	.01
	45	.719	.008
•	60	.665	.01
•			
Mg x N	15	.840	.001
	30	.759	.004
•	45	.792	.002
	60	.668	.01
Mg x pH	60	782	.003
	· · · · · · · · · · · · · · · · · · ·		
Mg x EC	60	.675	not significant
-			N

Table 13. Corelation coefficients between available Magnesium and other soil parameters in sewage amended soil

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RESULTS AND DISCUSSION

RESULTS AND DISCUSSIONS

It is observed from Table 6, at surface layers of the soil , the pH values have decreased by about one unit within 60 days. This may be due to the fact that since the surface layers are in direct contact with the atmosphere, they are subjected to aerial oxidation and microbial activity. As organic matter decomposes a substantial amount of organic and mineral acids are formed and this could result in the decrease of soil pH in the surface layer. The organic nitrogen added through the sewage effluents and the release of H^+ ions during nitrification of ammonium salts could have also contributed to the lowering of pH (Broadbent et al. 1977).

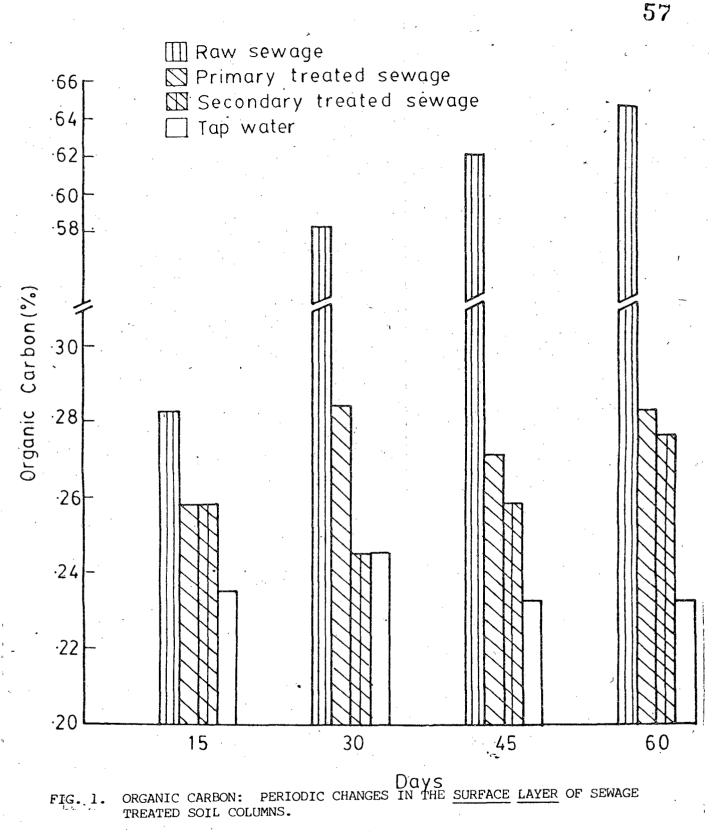
Electrical conductivity

pН

Electrical conductivity values increased in the sewage treated soil columns. Electrical conductivity values are related to the amount of soluble salts and other ions present in the medium. Accumulation of these ions in the soil from the effluents could have resulted in the increase of electrical conductivity. Bole (1979) reported that the electrical conductivity of the surface layer upto 90 cm of soil columns increased appreciably when treated with effluents. Electrical conductivity values in the surface layer of secondary treated soil columns were higher than the other two treatments, reaching a peak value of 0.75 mmhos/cm at the end of 60 days. At the same time the surface layer of raw and primary treated soil columns showed only 0.60 and 0.63 mmhos/cm respectively (Table 7). This could be due to increased organic matter accumulation on the surface layers of raw and primary sewage treated soil columns leading to ionic complexation and chelation of soluble ions with organic matter thus resulting in slightly lower electrical conductivity values in these layers.

Organic carbon

There was an increase of organic carbon content in the different layers of the effluent treated soil columns due to the presence of organic carbon in the effluents. Raw sewage contained more organic carbon (0146%) than either the primary-or secondary treated sewage (.0063 and .0036% respectively). Thus the values were higher in all layers of the raw sewage treated soil columns. Again, the sharp increase of organic carbon within 30 days in the surface layer of the column treated with raw sewage (Table 8) could be due to the higher organic content (0.0168%) in the second effluent sample compared to the first sample (0.0126%). Microbial mineralization of the organic matter accumulated on the surface layer of the raw sewage amended column might also contribute to the increased organic carbon of these layers (Beek et al. 1977; Quin and Woods, 1978). The peak value of organic carbon (0.6432) was found at the end of 60 days at



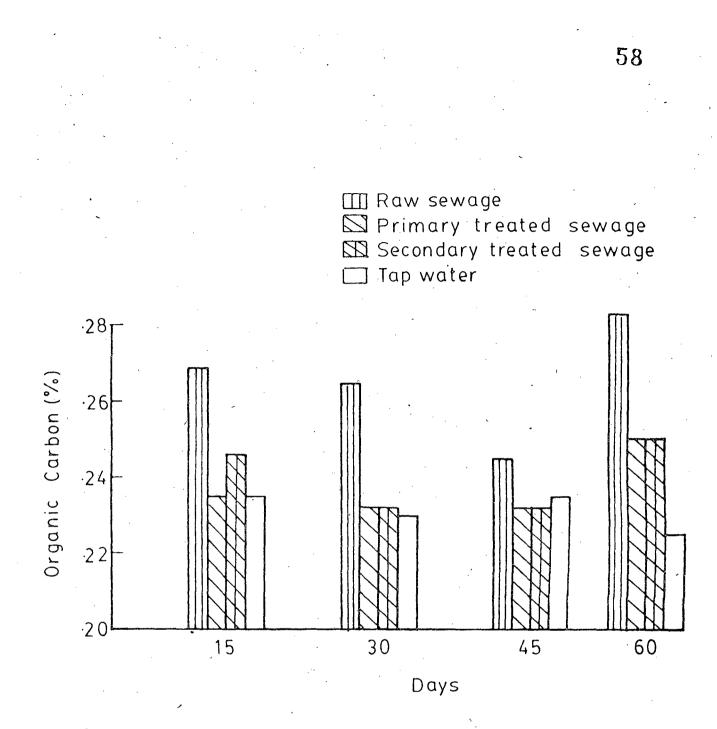


FIG. 2. ORGANIC CARBON: PERIODIC CHANGES AT 15 CM DEPTH IN THE SEWAGE TREATED SOIL COLUMNS.

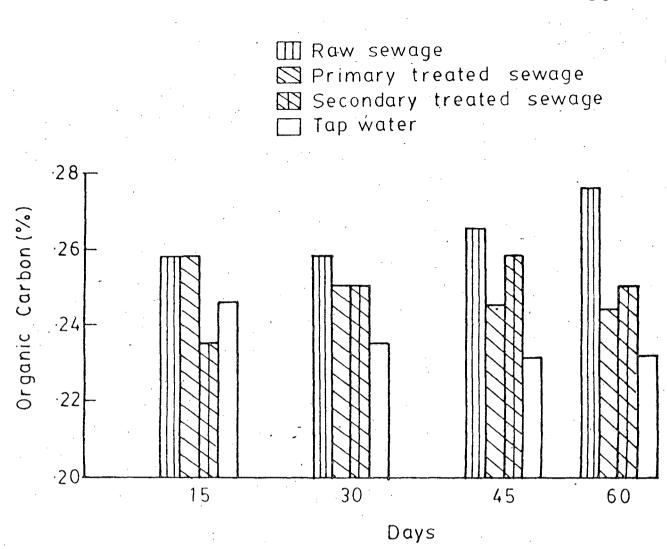
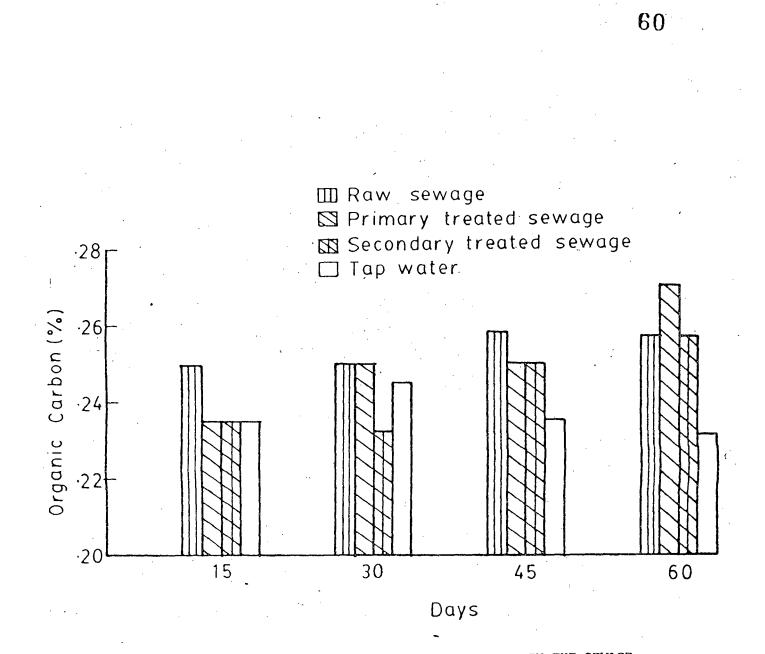
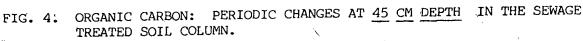


FIG. 3. ORGANIC CARBON: PERIODIC CHANGES AT <u>30 CM DEPTH</u> IN THE SEWAGE TREATED SOIL COLUMNS.







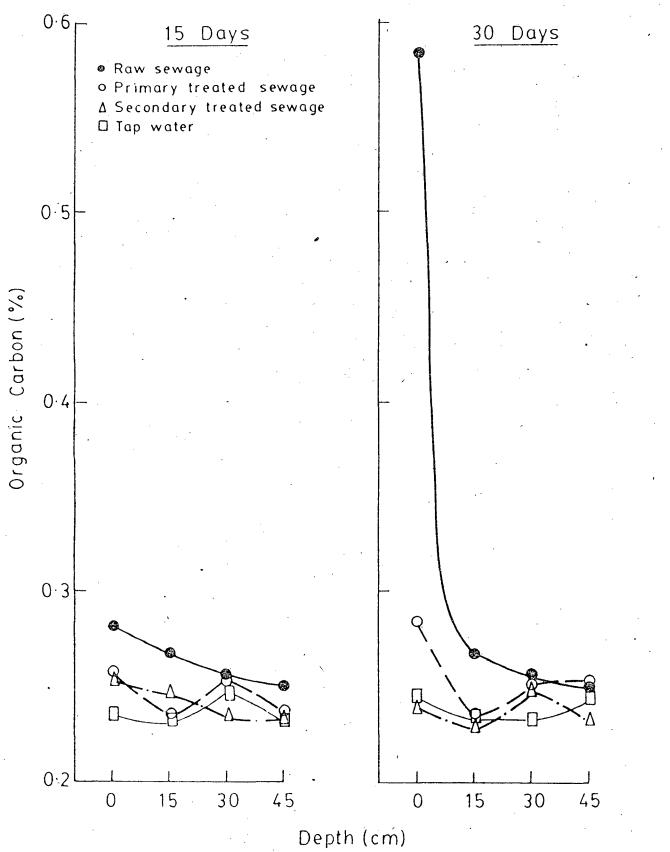


FIG. 5. ORGANIC CARBON: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (15 AND 30 DAYS).

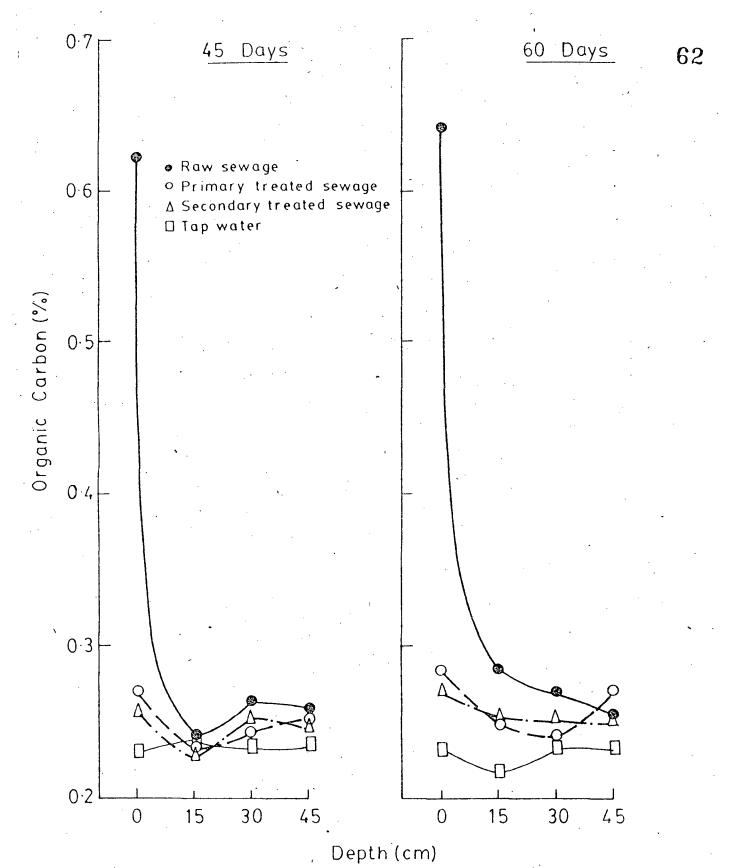


FIG. 6. ORGANIC CARBON: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (45 AND 60 DAYS).

the surface layer of the raw sewage treated column. The slight decrease in the final values of almost all the other layers showed that organic carbon contributed by the effluents might have been balanced by the quantity lost due to decomposition during the treatment.

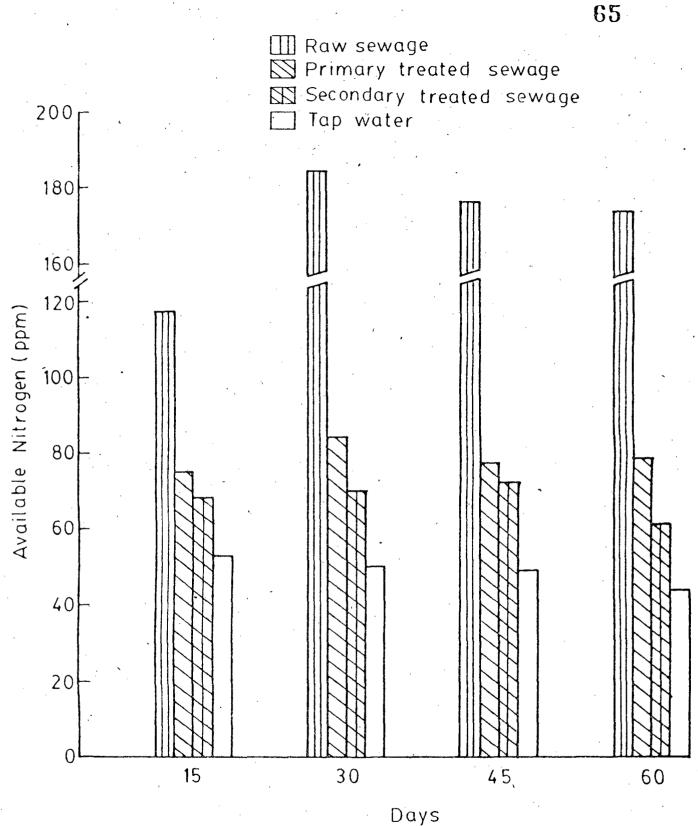
The tap water treatments showed a decrease in organic carbon throughout the experiment. This was because it did not receive any organic matter during the treatment. The loss could have been due to normal microbial decomposition processes (Sekar and Bhattacharyya, 1982).

Available nitrogen

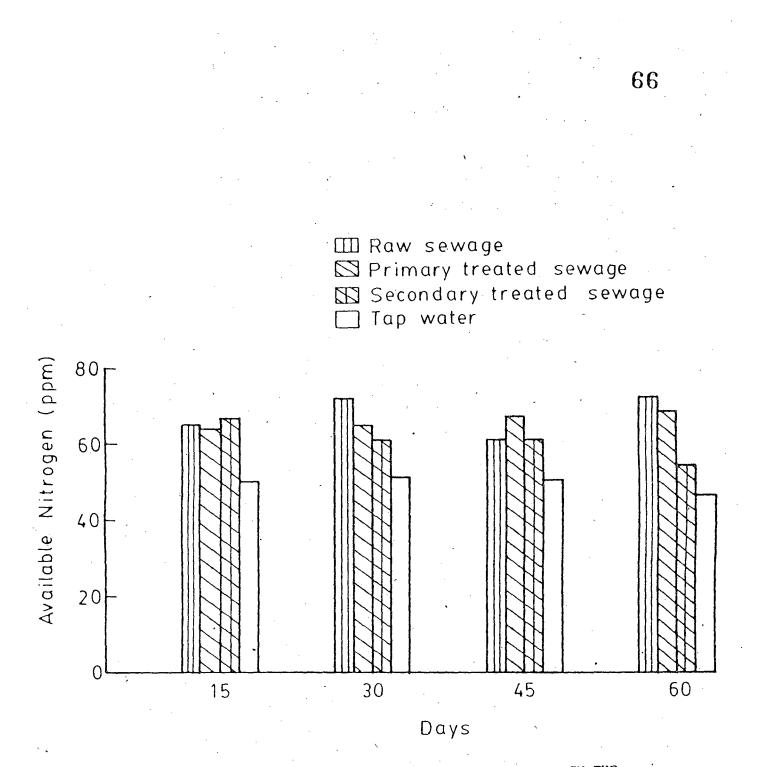
There was an increase in the available*nitrogen in the soil columns. The surface layers of all the effluent treated columns showed an evident increase in available nitrogen. This could be due to the mineralization of organic nitrogen from the organic matter accumulated at the surface layer. The surface layer of the soil column treated with raw sewage showed a significant increase within the 30 days period and was more than either of the other two treatments. This was probably due to the presence of more available nitrogen in the raw sewage 26.85 ppm (Table 5) than the primary or secondary treated sewage §21.65 ppm and 16.05 ppm respectively). The peak value of 184.8 ppm was obtained at the surface layer of the raw sewage treated column.

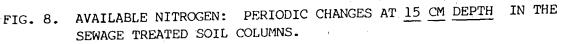
There was a slight decrease in available nitrogen towards the end, indicating that the rate of loss of nitrogen exceeded the amount entering the soil profile through effluents. This could be due to the activity of denitrifying bacteria. Gilbert et al. (1979) reported that nitrogen removal processes in sewage treated soil columns include (i) denitrification (ii)volatilization of NH_{A}^{+} (iii) adsorption of NH_{4}^{+} by clay fractions (iv) incorporation into microbial tissue and (v) adsorption of NH₃ by organic matter. Lance and Whisler (1972) intermittently flooded soil columns with secondary sewage effluent and conclu^{ded} that the nett nitrogen removal observed was probably due to a combination of several reactions dominated by denitrification. In addition microbial processes affecting nitrogen removal was more prominent in the surface 15 cm of the soil profile where carbon, nitrogen sources and environmental conditions necessary for denitrification were concentrated (Gilbert et al. 1979). All these factors might have contributed to the decrease in available nitrogen of the surface layer towards the end. Broadbent et al. (1977) reported that the optimum pH for nitrification was neutral to slightly alkaline, which was the pH range of the soil column under the present experiment.

These variations were similar to the results obtained by Sekar and Bhattacharyya (1982) while working on the effects of



PERIODIC CHANGES IN THE SURFACE LAYER OF AVAILABLE NITROGEN: PERIODIC SEWAGE TREATED SOIL COLUMNS . FIG. 7.





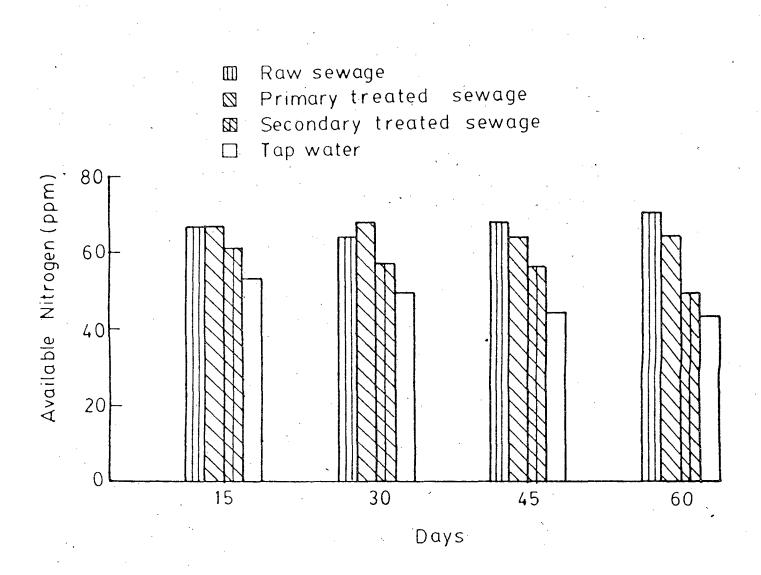
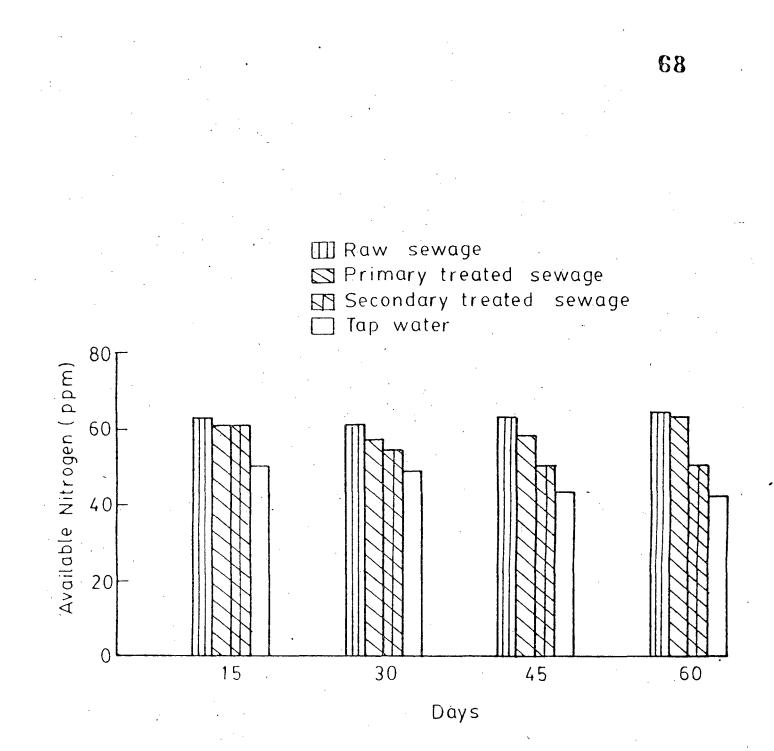
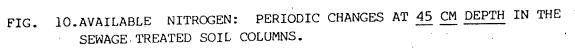


FIG. 9. AVAILABLE NITROGEN: PERIODIC CHANGES AT <u>30 CM DEPTH</u> IN THE SEWAGE TREATED SOIL COLUMNS.





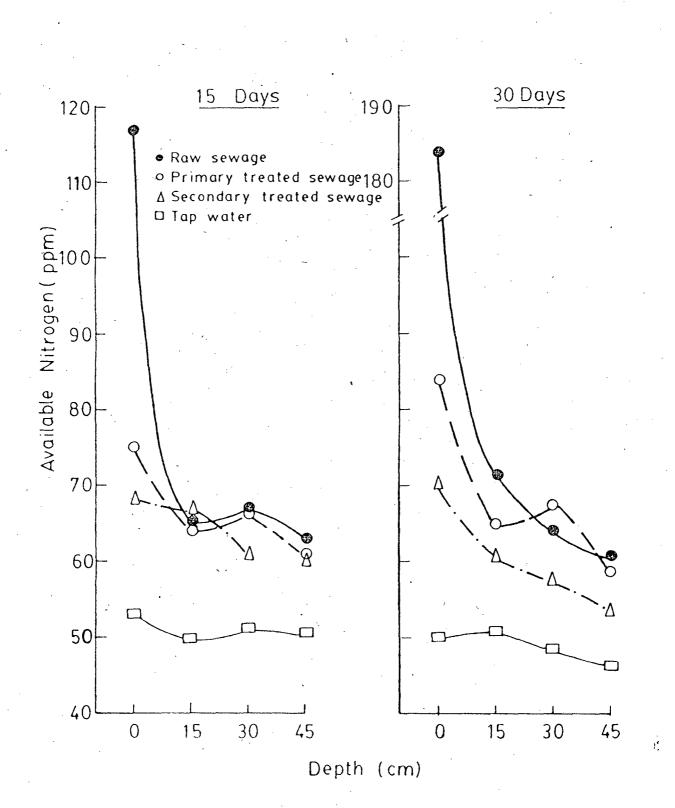


FIG. 11. AVAILABLE NITROGEN: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (15 AND 30 DAYS).

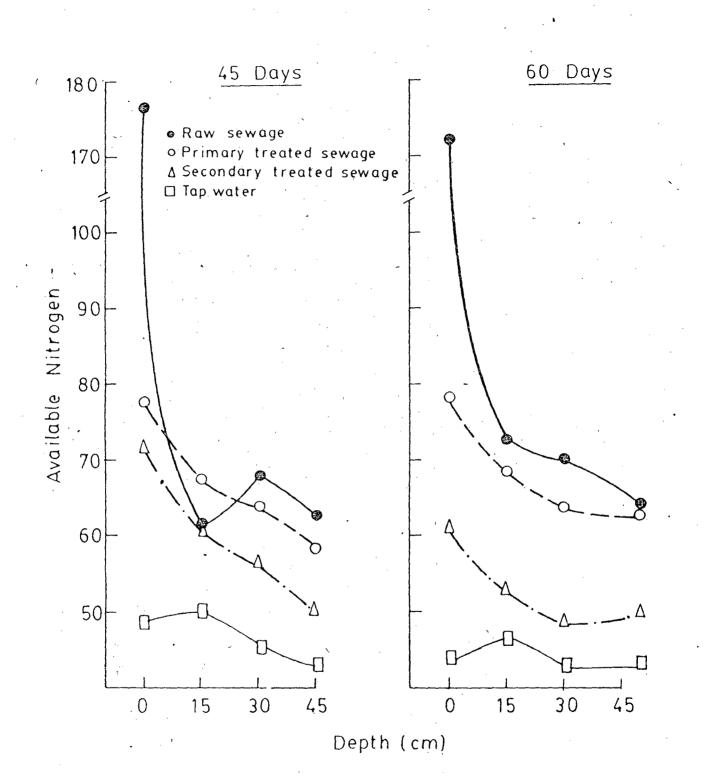


FIG. 12. AVAILABLE NITROGEN: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (45 AND 60 DAYS).

sewage on carbon and nitrogen mineralization of Delhi soil. The gradual decrease in the available nitrogen content of the tap water control treatments could be due to the loss of nitrogen at every stage. Available Calcium

The Calcium concentration in the sewage treated soil columns followed a cyclic pattern of increase and decrease. This trend is clearly illustrated in Fig. 13 to Fig. 16. At all depths (surface, 15 cm, 30 cm and 45 cm) the concentration decreased during the first 30 day interval followed by a trend of increase during the 30-45 days interval. Again after 45 days, the concentration showed a gradual decrease. At 45 days, the Calcium content was at the peak, and it was higher than the 15 days concentration - except probably in the case of the raw sewage treatments of the soil column. The highest concentration of Calcium observed in the soil sample during the whole period of the experiment was 2352.1 ppm in the case of a secondary treated sewage treatment after 45 days. But even the lowest concentration of Calcium (1714 ppm) found at the surface layer of the raw sewage treated column was significantly higher than the original soil concentration of 1442.3 ppm. Calcium concentration in tap water was approx. 33 ppm. During the first 15 days of tap water treatment, there was an appreciable increase in concentration. The highest concentration observed was 1809.3 ppm - at 15 days on the surface layer. Towards the end of the treatment, the Calcium concentrations of the

tap water treated columns showed a tendency to decrease.

This trend can be explained on the basis of (a) the affinity Calcium shows towards organic binding sites, (b) binding with clay colloids, and (c) microbial activity. Calcium forms a metal-organic complex with organic matter in the soil (Sposito et al. 1978; Nightingale & Smith 1967; Schnitzer & Skinner 1967). Metal organic ligation involves structural configurations in which the metal is bonded to organic matter by way of (i) carbon atoms yielding organo metallic compounds, (ii) carboxylic groups producing salts of organic acids or (iii) electron donating atoms, O, N, S, and P etc. forming coordination complexes (Rubin 1974; Rainbow 1985). Calcium readily chelates with the fulvic acid found in sewage (Sposito et al. 1978). Calcium also exhibits high ability to bind with anthropogenic organic chelates like EDTA, NTA etc. (Lerman and Childs 1973). Sewage contains very high organic content of a particulate as well as dissolved nature. Most of the available form of calcium gets binded with these materials and becomes unavailable for further binding processes. As a result the concentration of calcium in the soil materials goes down initially. Apart from this, there are exchangeable clay colloid sites where Ca⁺⁺ may be bound. At 30 days interval the raw sewage treated column showed the lowest concentration of 1714 ppm (Table 10), probably due to the presence of very high organic matter, especially of a particulate nature.

Raw sewage contained more organic matter (organic carbon = .0146%) than the primary or secondary treated sewage (organic carbon = 0.0063% and .0036% respectively) as shown in Table 5. This is indicated also by the low calcium concentration observed in the filtered raw sewage (236 ppm) as against 253 ppm of primary treated and 252 ppm of secondary treated sewage, for during filter-ation (done to facilitate analysis) the organic particulate matter is removed along with the attached calcium.

Simultaneously with the situation of calcium being bonded with clay colloids and organic matter by way of chelation, absorption, adsorption etc., the process of establishment and growth of a microbial population also sets in. This microbial growth and hence their decomposition is probably of a sigmoidal nature (Stotzky 1972). As a result of microbial activity in the soil, calcium is mobilized (Silverman & Munoz 1980). Carlson et al. (1971) reported increased levels of calcium and magnesium in the saturation extract of soil pastes that were allowed to stand for several days; they attributed these increases to microbial activity. Due to the microbial population initially being very low, the mobilization of calcium is not significant as compared to the process of binding with organic materials. This results in a nett decrease in calcium concentration at 30 days. As the micro organisms undergo rapid multiplication, the microbial activity rises. So the release of calcium from exchange sites and other reservoirs leads to an increase in the concentration of available calcium. This is indicated by the peak in calcium levels at 45 days. Cation exchange can also contribute to this increase (Brady 1974). A substantial amount of organic and mineral acids are formed as the organic matter decomposes. The hydrogen ions thus generated will tend to replace the calcium in the soil colloidal complex.

Calcium concentration rises with the increase in depth (Fig. 17 and Fig. 18). This is similar to the results reported by Tan et al. (1985) that the bottom section of sludge amended soil columns contained more calcium than the top sections. At all time periods (15, 30, 45 and 60 days) there is a sharp increase in the calcium concentration till the 15 cm depth. This is followed by a more or less stabilization in concentration with further increase in depth. In many cases the level of calcium at the 45 cm depth was slightly lower than that at 30 cm. For example, at the 15 day period (Fig. 17) the surface layer concentration of raw sewage treatment was 2022.5 ppm. This increased to 2278.3 ppm at the 30 cm layer.With further increase in depth, the calcium concentration was slightly lower - 2228.6 ppm at 45 cm layer.

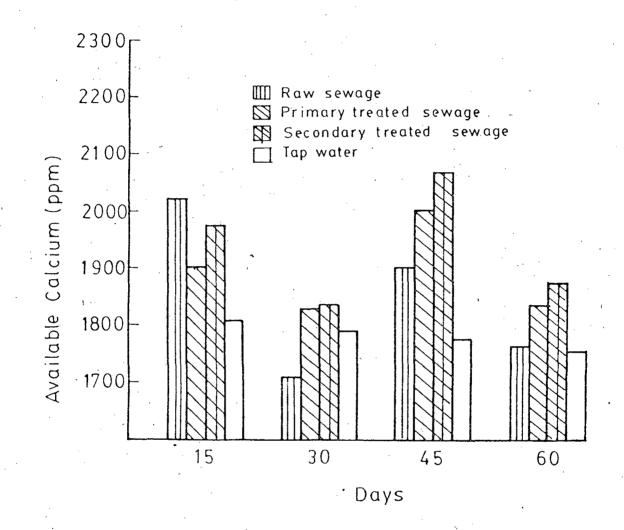


FIG. 13. AVAILABLE CALCIUM: PERIODIC CHANGES IN THE SURFACE LAYER OF SEWAGE TREATED SOIL COLUMNS.

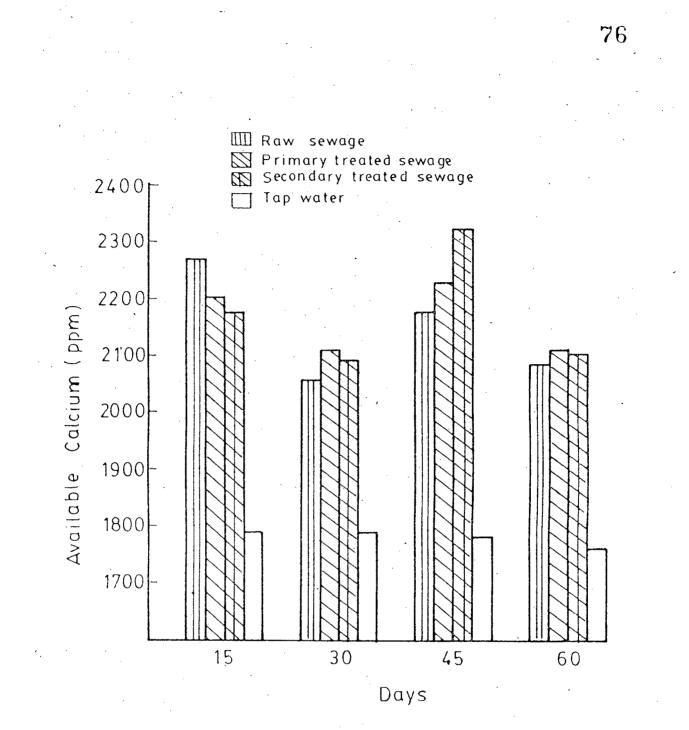


FIG. 14. AVAILABLE CALCIUM: PERIODIC CHANGES AT 15 CM DEPTH IN THE SEWAGE TREATED SOIL COLUMNS.

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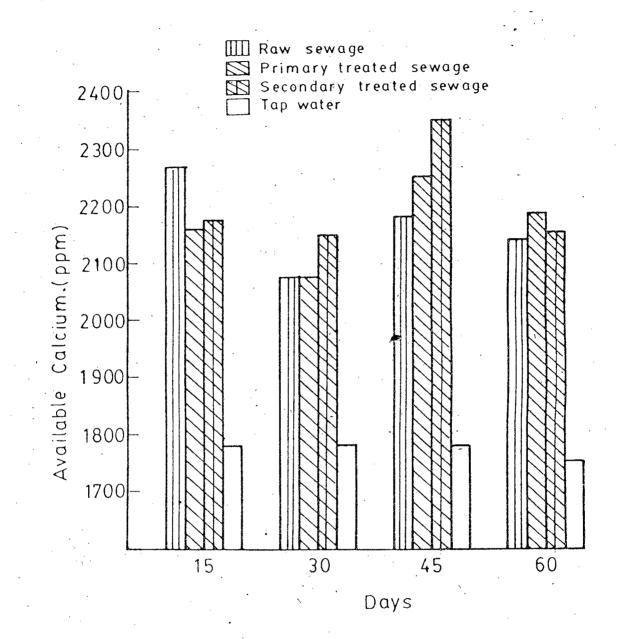
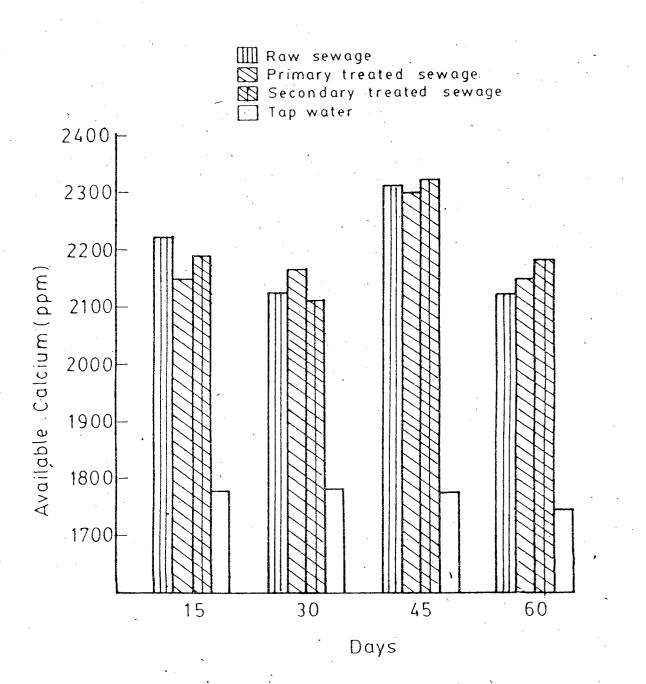
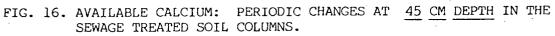


FIG.15. AVAILABLE CALCIUM: PERIODIC CHANGES AT <u>30 CM DEPTH</u> IN THE SEWAGE TREATED SOIL COLUMNS.





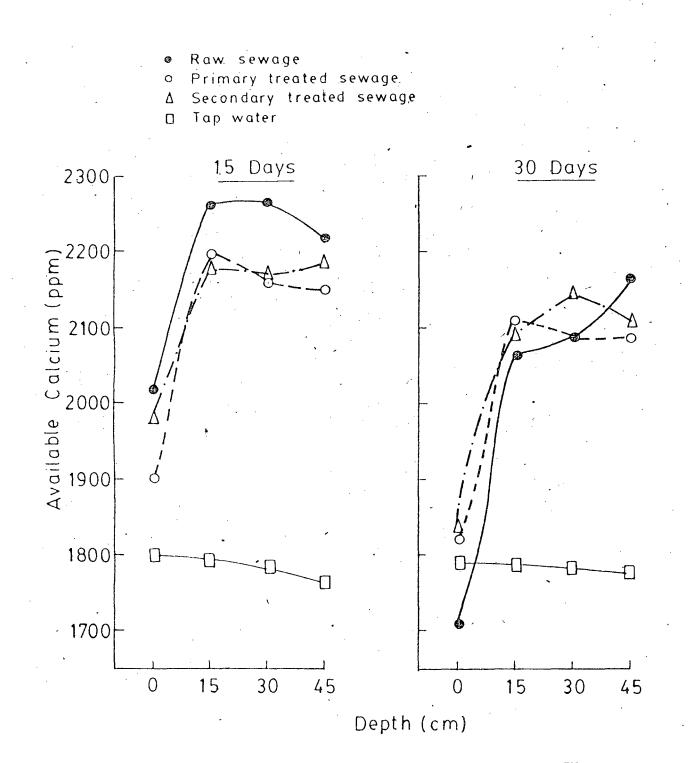


FIG. 17. AVAILABLE CALCIUM: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (15 AND 30 DAYS).

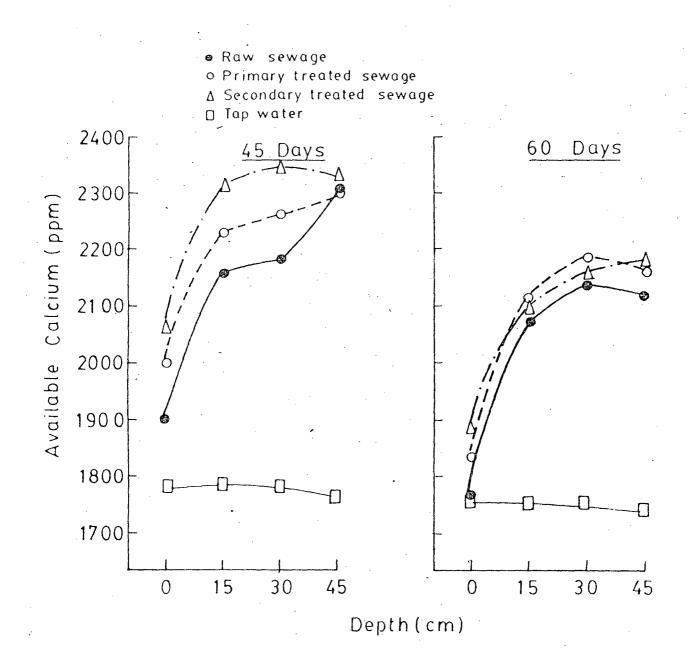


FIG. 18. AVAILABLE CALCIUM: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (45 AND 60 DAYS).

It has been reported that a significant fraction of calcium in aqueous medium is in a dissolved form (Rainbow, 1985). On application of sewage to the soil column, a significant fraction of the dissolved calcium is being carried down with the percolating water after saturating the surface layer. Simultaneously it is being scavenged off from the aqueous phase by the unsaturated soil matter. Thus as the water flows downwards the calcium concentration in the dissolved phase decreases, thus lessening the availability of calcium for further binding with the soil. This phenomenon could explain the trend of increase in calcium content with depth followed by a more or less tendency to stabilize.

Available magnesium

The magnesium concentration in the surface layers of the soil column increased on sewage treatment and reached a peak concentration at 60 days. The initial concentration of magnesium in the experimental soil was 128.1 ppm. After treatment, it reached a peak value of 213.7 ppm in the surface layer of the raw sewage treated columns (Table 11). However, this rate of increase in concentration was not uniform during the whole period of sewage treatment. During the interval of 30-45 days, the rate of increase in magnesium accumulation was considerably lesser than that during the period 15-30 days and 45-60 days (Fig. 19). In the surface layer

of primary treated soil columns the magnesium content increased from 99.2 ppm at 15 days to 174.8 ppm at the end of 60 days. In all the other layers (15, 30 and 45 cm in depth) there was at first a decrease and then an increase. For example, Mg concentration (75.7 ppm) at the 15 cm level of raw sewage amended column decreased to 48.0 ppm at the 30 days interval and then increased (81.1) towards the end of the experiment. Magnesium concentration in tap water was 3.9 ppm. Unlike the case of calcium, the Magnesium concentration showed a steep decrease from the initial soil concentration (128.1 ppm) for the first fifteen days. With increase in depth, the Magnesium concentration showed a significant decrease. This might be due to the leaching effect of the percolating water.

Magnesium shows an ability to form chelates with organic compounds (Rubin 1974). The ability of stabilized organic matter to form complexes is generally attributed to the so called humic and fulvic acids (Leland et al. 1973). Schnitzer (1969) reported the order and stability constants of metal-fulvic acid complexes for several divalent cations with fulvic acid. The stability constant for Magnesium was found to be less than that of Calcium (Schnitzer and Hanson 1970). Thus Magnesium gets less chelated than calcium. As the duration of sewage treatment continues, the

growth and activity of the microbial community also gets hastened thus enhancing the release of organic matter bound Magnesium. Silverman and Munoz (1980) found a 0.7 to 41 fold increase in the Magnesium content of soil solutions as a result of the action of microorganisms. Since the magnesium-organic complex is not as strongly bound as the calcium-organic complex, the microbial activity remains dominant causing a gradual increase in the soil Magnesium concentration.

In the case of Magnesium concentration at different depths (15, 30 and 45 cm) in a column, the trend of Magnesium accuulation was different (Fig. 23 and 24). The concentration showed a sharp fall until the 15 cm depth. For the next 15 cm the rate of decrease in magnesium concentration was lesser than the earlier 15 days. For example, at the 30 day interval in the raw sewage treated column, the surface layer concentration was 163.2 ppm while at the 15 cm depth the magnesium concentration was 48.0 ppm. This observed low level of Magnesium accumulation could be the result of the scavenging process of Magnesium for the sewage solution phase by the upper layers of the soil column. So as the percolating sewage comes down, it is being gradually deprived of its dissolved Magnesium. Magnesium also acts as a nutrient for microorganisms and is incorporated into its body

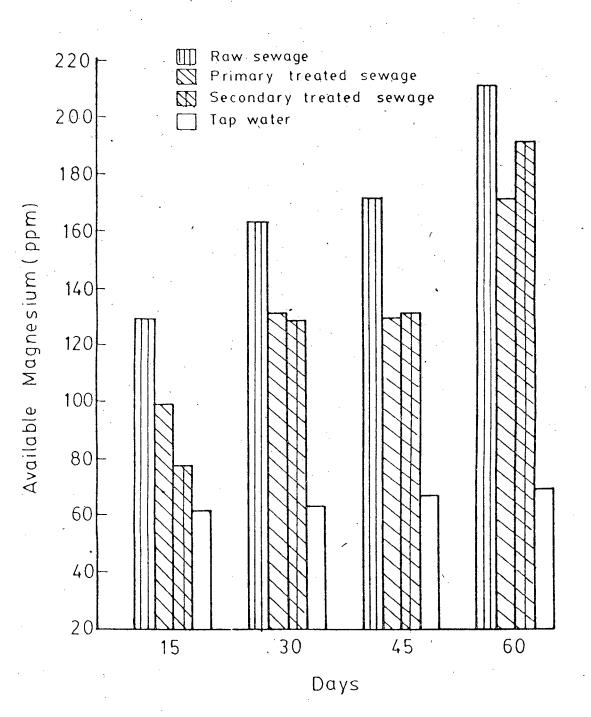


FIG. 19. AVAILABLE MAGNESIUM: PERIODIC CHANGES IN THE SURFACE LAYER OF SEWAGE TREATED SOIL COLUMNS.

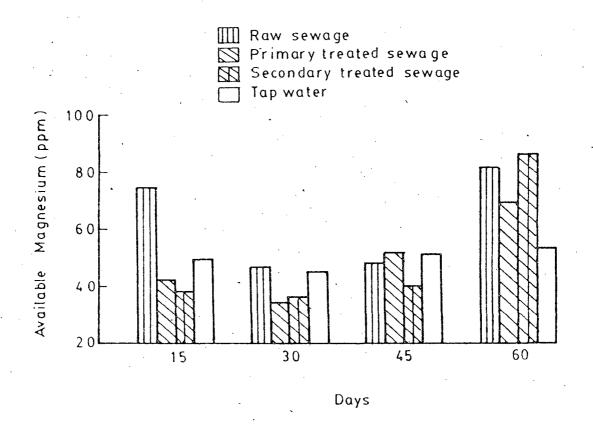


FIG. 20. AVAILABLE MAGNESIUM: PERIODIC CHANGES AT 15 CM DEPTH IN THE SEWAGE TREATED SOIL COLUMNS.

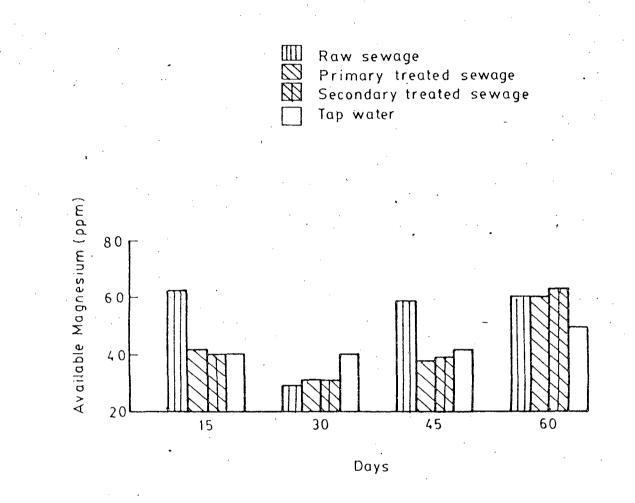


FIG. 21. AVAILABLE MAGNESIUM: PERIODIC CHANGES AT 30 CM DEPTH IN THE SEWAGE TREATED SOIL COLUMNS.

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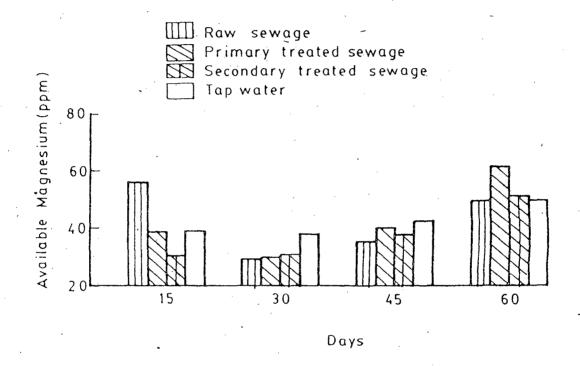


FIG. 22. AVAILABLE MAGNESIUM: PERIODIC CHANGES AT 45 CM DEPTH IN THE SEWAGE TREATED SOIL COLUMNS.

- Raw sewage
- o Primary treated sewage
- ∆ Secondary treated sewage

🛛 Tap water

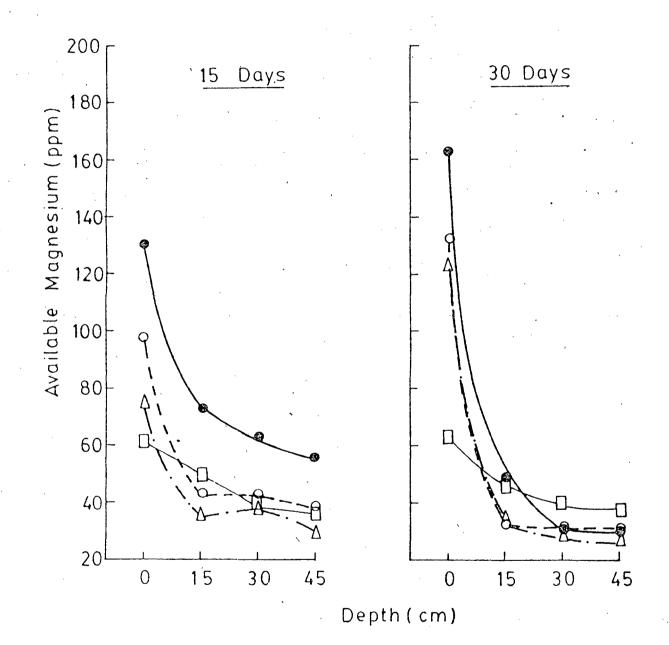


FIG. 23. AVAILABLE MAGNESIUM: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (15 DAYS AND 30 DAYS).

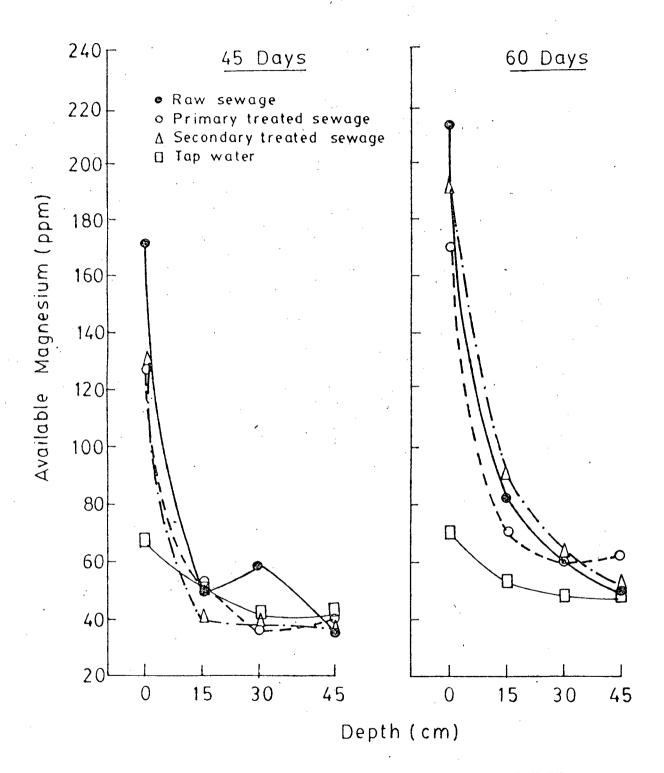


FIG.24. AVAILABLE MAGNESIUM: DISTRIBUTION AS A FUNCTION OF DEPTH IN SEWAGE TREATED SOIL COLUMNS (45 AND 60 DAYS).

tissues. Calcium-Magnesium competition for binding sites could contribute to this situation too. Another possible reason is the high level of leaching occuring during the passage of the percolating sewage through the soil column. For instance, Hill (1972) reported that when sewage effluent was applied to soil columns, in the case of alkaline soils, three times the Magnesium added in the effluent was leached out.

Corelation between Calcium, Magnesium and other soil parameters:

The constants of corelation analysis between calcium and magnesium of soil on one side and other soil parameters on the other have been presented in Table 12 and 13. In the present study it was found that Calcium and Magnesium showed highly negative corelation (Fig. 27 and Fig. 28). As the concentration, of calcium increased with depth that of Magnesium decreased. But the significance of corelation between these two factors varied with the duration of exposure.

The negative corelation observed between calcium and magnesium might be due to the result of calcium-magnesium competition for binding sites on the clay surface. The antagonistic behaviour of calcium with magnesium has been reported by different workers (Mandal and Sinha 1968; Kansal and Sekhon 1973, 1974; Ahlawat 1978 and Nad 1979).

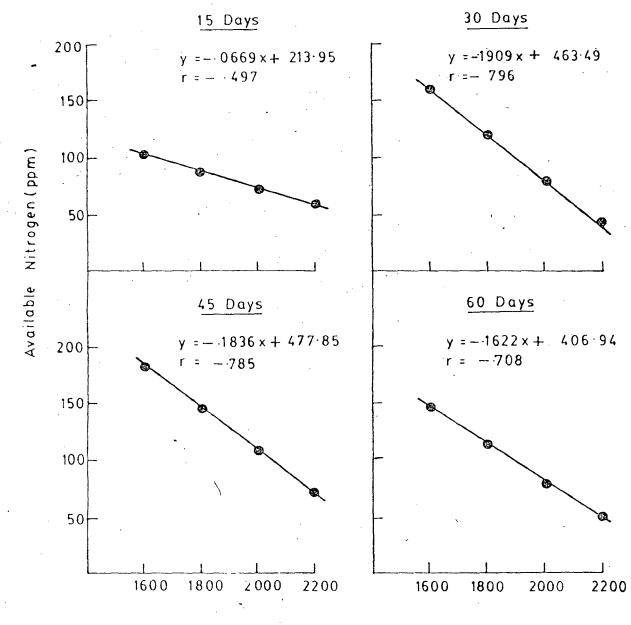
When corelation analysis was attempted between Ca & C and Ca & N it was found that they were negatively corelated. This indicates that organic matter mineralization releases large amounts of available calcium, thus increasing the calcium concentration.

In case of magnesium, the corelation with carbon and nitrogen was positive. It has been found that magnesium is mainly concentrated at the surface layers of the column, suggesting the release of magnesium due to decomposition of organic matter on the surface as well as the addition of fresh magnesium from the effluents.

Calcium and pH was found to be positively corelated whereas magnesium and pH were negatively corelated. This indicates that the formation of calcium salts during the sewage treatment has increased the soil pH. Similarly, due to the antagonistic behaviour of magnesium, its corelation with pH showed the opposite trend.

The corelation constants of calcium and magnesium with EC were found to be non-significant.

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Available Calcium (ppm)

FIG.25. RELATIONSHIP BETWEEN AVAILABLE CALCIUM AND AVAILABLE NITROGEN IN SEWAGE TREATED SOIL COLUMNS.

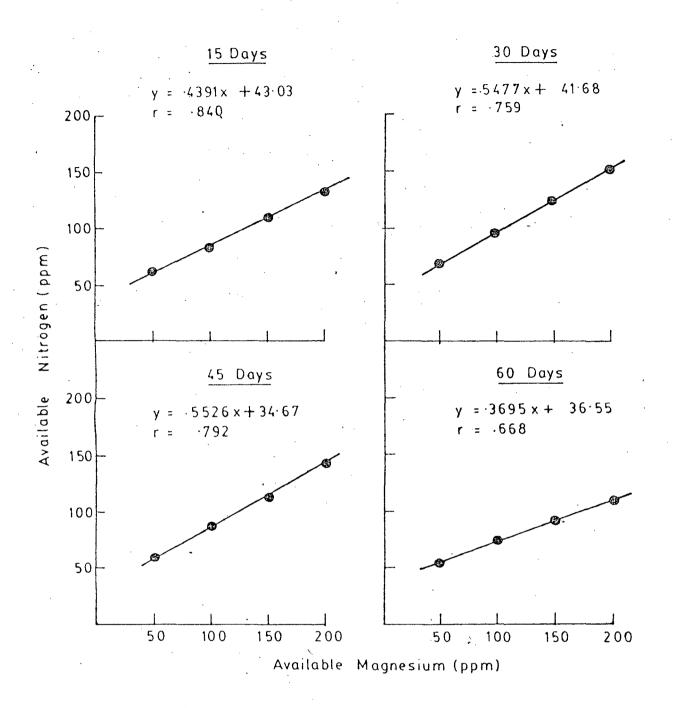
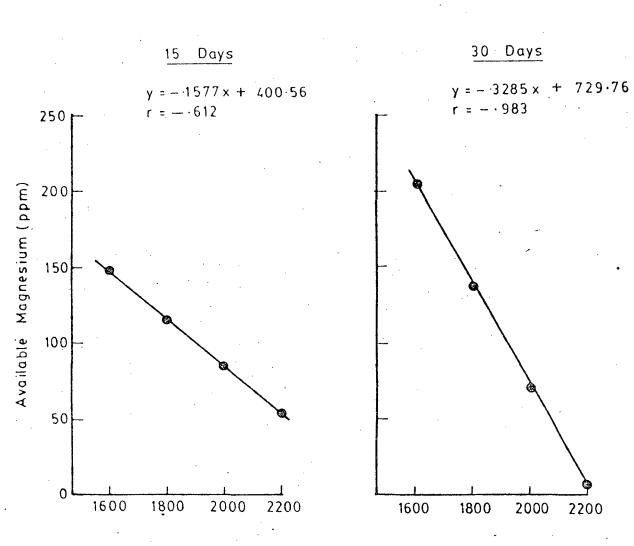


FIG. 26. RELATIONSHIP BETWEEN AVAILABLE MAGNESIUM AND AVAILABLE NITROGEN IN SEWAGE TREATED SOIL COLUMNS.



Available Calcium (ppm)

FIG. 27. RELATIONSHIP BETWEEN AVAILABLE CALCIUM AND AVAILABLE MAGENSIUM IN SEWAGE TREATED SOIL COLUMNS (15 AND 30 DAYS).

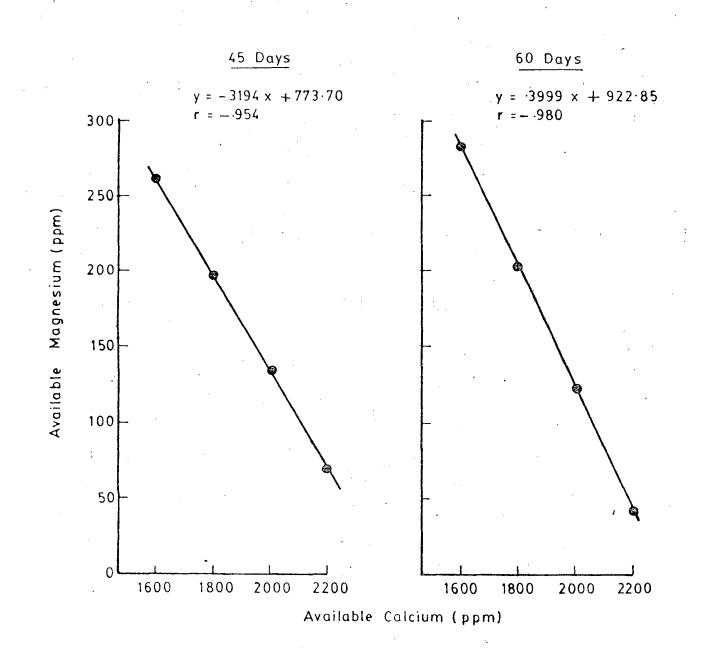


FIG. 28. RELATIONSHIP BETWEEN AVAILABLE CALCIUM AND AVAILABLE MAGNESIUM IN SEWAGE TREATED SOIL COLUMNS (45 AND 60 DAYS).

SUMMARY AND CONCLUSION

Summary and Conclusion

Soil from Delhi was filled in P.V.C. columns and treated with sewage effluent for a period of 2 months to study the accumulation and distribution of available calcium, magnesium and other soil parameters. The results obtained from the experiment are summarised here.

The pH values at the surface layer of the soil column showed a slight decrease. This could be due to (i) release of H^+ ions through nitrification and (ii) formation of organic and mineral acids. There was a significant increase in the electrical conductivity of the effluent treated soil. This was due to the accumulation of salts in the soil from the effluents.

In case of organic carbon a significant increase in concentration was observed especially in the surface layer of the column treated with raw sewage. This was due to (i) contribution from the effluent, (ii) accumulation and mineralization of the suspended and particulate organic matter. An appreciable increase in the available nitrogen content in the surface layers could be the result of (i) addition of fresh effluents, and (ii) mineralization of organic nitrogen. There was a slight increase in the concentration of available nitrogen in the lower layers of the soil column as compared to tap water controls.

The available calciumcontent of the soil treated with effluents showed a cyclic pattern of increase and decrease with the passage of time, especially at the surface layers. This trend could be explained

on the basis of (i) input of calcium from the effluent, (ii) chelation with organic matter, (iii) sorption on clay colloids and (iv) microbial activities. The soil was found to act as a sink for calcium because most of the applied calcium was accumulated in the soil as expected.

A significant increase in the available magnesium concentration was observed at the surface layers of the soil column treated with raw, primary and secondary treated sewage. In general, all the lower layers of the effluent treated columns showed a substantial decrease in magnesium concentration as compared to that of the surface layer. This indicates the antagonistic behaviour of calcium and magnesium.

It is now clear that Delhi soil has the ability to retain significant amounts of available calcium and magnesium, both of which are important plants nutrients. Delhi is characterised by an overall semi arid climate with an average rainfall of 62.5 cm. The soil is alluvial in origin and is a sandy loam. Loams possess the desirable qualities of both sand and clay but not their harmful properties and are thus most suitable for agriculture.

From the environmental point of view, at this stage, we can suggest that irrigation with secondary treated sewage is a practical and advantageous proposition for Delhi soil. But long term studies regarding the accumulation of toxic substances, heavy metals and pathogens are necessary before large scale utilisation of municipal wastewater for agriculture.

BIBLIOGRAPHY

- *Ahlawat, V.K. (1978) M.Sc. (thesis), Haryana Agricultural University, Hissar, Haryana.
- Allen, S.E. (1974) Chemical analysis of ecological materials. Blackwell Scientific Publications, London.
- APHA (1980) Standard Methods for the Examination of Water and Wastewater. 15th edn. American Public Health Association. Washington, DC, USA.
- Baker, D.E. (1971) A new approach to soil testing. Soil Science, 6: 381-391.
- Baumann, D.D. and Dworkin, D.M. (ed) (1978) Planning for water reuse. Maaraufa Press Inc. Chicago.
- Beek, J., DeHaan, F.A.M. and Van Riemsdyk, W.H. (1977) Phosphates in soil treated with sewage water: I General information on sewage farms, soil and treatment results. J. Environ. Qual., 6: 4-7.
- Bielorai, H., Vaisman, I. and Feigin, A. (1984) Drip irrigation of cotton with treated municipal effluents. I : Yield response. J. Environ. Qual., 13: 231-234.
- Bouwer, H. and Chaney, R.L. (1974) Land treatment of wastewater. Adv. Agron., 26: 133-176.
- Bole, J.B. (1979) Land applications of municipal sewage wastewater: changes in soil chemistry. Agron Abstract (Environ. Qual) 71st Annual meeting of Am. Soc. Agr. held at Fort Collins, Colarado, Aug. 5-10, 1979.
- Bower, C.A., Ogata, G. and Tucker, J.M.(1968) Sodium hazard of irrigation waters as influenced by leaching fraction and by precipitation or solution of calcium carbonate. Soil Science, 106: 29-34.
- Brady, N.C. (1974) The nature and properties of soils. 8th Edition. Macmillan Publishing Co. Inc., New York.
- Bramm, A. (1975) as quoted by C. Tretjen (1977) The agricultural reuse of municipal wastewater in Braunschweig, Germany. In: Wastewater Renovation and Reuse. (ed.) F.M. D'Itri. Marcel Dekker Inc., New York. pp. 69-88.

Broadbent, F.E., Pal, D. and Aref, F. (1977) Nitrification and denitrification in soils receiving municipal wastewater. In: Wastewater Renovation and Reuse. (ed) F.M. D'Itri, Marcel Dekker Inc., New York. pp. 321-48.

Burge, W.D. and Marsh, P.B. (1978) Infectious diseases of landspreading sewage wastes. J. Environ. Qual., 7: 1-9.

Byers, R.A. and Zeiders, K.E. (1976) Effect of spray irrigation with municipal sewage effluent on the Cereal leaf beetle and the fruit fly infesting reed canary grass. J. Environ. Qual., 5: 205-206.

Carlson, R.M., Overstreet, R. and Naylor, D.V. (1971) Effect of microbial activity on saturation extract composition. Hilgardia 40: 553-564.

Carpena, O. and Lax, A. (1972) Determination of exchangeable cations in calcareous soils. Soil Science, 113:194-99.

Day, A.O., Tucker, T.C. and Vavich, M.G. (1962) Effect of city sewage effluent on the yield and quality of grain from barley, oats and wheat. Agron. J., 54: 133-138.

Day, A.D., Stroehcein, J.L. and Tucker, T.C. (1972) Effect of treatment plant effluent on soil properties. J. Water Pollut. Cont. Fed., 44: 372-75.

Day, A.D., McFadyen, J.A., Tucker, T.C. and Cluff, C.B. (1979) Commercial production of wheat grain irrigated with municipal wastewater and pumpwater. J. Environ. Qual., 8:403-406.

Day, A.D., McFadyen, J.A., Tucker, T.C. and Cluff, C.B. (1981) Effects of municipal wastewater on yield and quality of cotton. J. Environ. Qual., 10: 47-49.

DeJong, E. (1978) Movement of sewage effluent through soil columns: The Major Ions (Na, Ca, Mg, Cl and SO₄). J. Environ. Qual., 7: 133-136. Dhua, S.P. (1979) Organic manures for higher harvests. Sci. Today, 8(2): 14-19.

D'Itri, F.M. (1977) Wastewater Renovation and Reuse. Proc. of International Conference on the Renovation of Wastewater through Aquatic and terrestrial Systems. Marcel Dekker Inc., New York. p. 705.

- Doty, W.T., Baker, D.E. and Shipp, R.F. (1977) Chemical monitoring of sewage sludge in Pennsylvania. J. Environ. Qual., 6: 421-426.
- Dugan, G.L. (1975) Land disposal of wastewater in Hawaii. J. Water Pollut. Contr. Fed. 47: 206-7.

Eaton, F.M., McLean, G.W., Predell, G.S. and Doner, H.E. (1968) Significance of silica in the loss of magnesium from irrigation waters. Soil Science, 105: 260-272.

Fegin, A., Bielorai, H., Dag, Y., Kipnis, T. and Giskin, M. (1978) The nitrogen factor in the management of effluent irrigated soils. Soil Science, 125: 248-254.

Foster, D.H. and Engelbrecht, R.S. (1973) In: Recycling treated municipal wastewater and sludge through forest and cropland (eds) W.E. Sopper and L.T. Kardes, Pennsylvania State Univ. Press, Pennsylvania, pp. 247-270.

Gerba, C.P. (1975) Fate of wastewater bacteria and viruses in soil. J. Irrigation and Drainage Div., 101: 157.

Gouder, B.Y.M. and Hooli, M.A. (1986) Sewage also serves. Science Reporter, 23(8): 528-531.

Higgins, A.J. (1984) Land application of sewage sludge with regard to cropping systems and pollution potential. J. Environ. Qual., 13: 441-448.

Hill, D.E. (1972) Wastewater renovation in Connecticut soils. J. Environ. Qual., 1: 163-166.

Jackson, M.L. (1973) Soil chemical analysis. Prentice Hall of India Private Ltd., New Delhi. Jurinak, J.J. and Griffin, R.K. (1972) Nitrate ion adsorption by calcium carbonate. Soil Science, 113: 130-135.

Kansal, B.D. and Sekhon, G.S. (1973) Agrochimica 18: 94.

Kansal, B.D. and Sekhon, G.S. (1974) Agrochimica 18: 518.

- Kelling, K.A., Walsh, L.M., Keeney, D.R., Ryan, J.A. and Peterson, A.E. (1977) A field study of the agricultural uses of liquid sewage sludge. II Effect of soil N and P. J. Environ. Qual. 6: 345-352.
- Klausner, S.D. and Kardos, L.T. (1975) Oxygen relationships in a soil treated with sewage effluent. J. Environ. Qual. 4: 174-178.
- King, L.D. and Morris, H.D. (1972) Land disposal of sewage sludge. III: Effect on soil nitrate. J. Environ. Qual., 1: 442-446.
- Lance, J.C. and Whistler, F.D. (1972) Nitrogen balance in soil columns intermittently flooded with secondary sewage effluent. J. Environ. Qual., 1: 180-186.
- Lee, G.F. (1976) Potential problems of land application of doemstic wastewaters. In: Land treatment and disposal of municipal and industrial wastewater (eds) R.L. Sanks and T. Asano. Ann Arbor Sci. Publ. Inc., Ann Arbor, Mich. pp. 179-192.
- Leland, H.V., Shukla, S.S. and Shinp N.F. (1973) Factors affecting distribution of lead and other trace elements in sediments of southern Lake, Michigan. In: Trace Metals and Metal organic interactions in Natural Wasters (ed) Singer, P.C. Ann Arbor Sci. Publ. Ann Arbor, Michigan, pp. 89-130.
- Lerman, A. and Childs, C.W. (1973) Metal organic complexes in natural waters: control and distribution by thermodynamic, kinetic and physical factors. In: Trace Metals and Metal organic interactions in Natural Waters (ed) Singer, P.C. Ann Arbor Sci. Publi., Ann Arbor Michigan, pp. 201-236.

Loehr, R.C. (1977) Land disposal of wastes.In: Pollution Control for agriculture. Academic Press Inc., New York, pp.259-288. *Loehr, R.C. (1977) Land as a waste management alternative: Proc. of the 1976 Cornell Agricultural Waste Management Conference held on April 28-30, 1976. Ann Arbor Science Publ. Inc., Ann Arbor, Mich., p. 811.

- Lombin, G. and Fayemi, A.A.A. (1976) Magnesium status and availability in soils of western Nigeria. Soil Science, 122: 91-99.
- Lombin, G. and Fayemi, A.A.A. (1976) Evaluation of various soil tests for available magnesium in western Nigeria. Soil Science, 122: 59-64.

Mandel, S.C. and Sinha, M.K. (1968) J. Indian Soc. Soil. Sc. 16: 37.

- Martin, J.P. and Page, A.L. (1969) Influence of exchangeable calcium and magnesium and of percentage base saturation on growth of citrus plants. Soil Science, 107: 39-46.
- Marquez , H.M. (1981) Land treatment: a viable solution for the management of wastewater in the metropolitan area of the valley of Mexico. In: Municipal Wastewater in Agriculture (ed.) F.M. D'Itri, Academic Press Inc., New York, pp. 163-194.
- Masand, S.S., Chaudry, T.N., Kapur, O.C. and Sharma, S.K. (1978) Modification of sandy soil by application of sewage suspension. Indian J. Agri. Res., 12: 5-9.
- Matchske, D.E. (1978) Opportunities and constraints in the reuse of wastewater. In: Planning for Water Reuse. (ed) D.D. Baumann and D.M. Dworkin. Maaroufa Press Inc., Chicago, pp. 139-157.
- Morris, C.E. and Jewell, W.J. (1977) Regulations and guidelines for land application of wastes: A fifty state overview. In: Land as a Waste Management Alternative. (ed) R.C. Loehr. Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan, pp. 9-28.
- Mostafa, M.A.E. and Ulrich, A. (1976) Interaction of calcium and magnesium in nutrition of intact sugarbeets. Soil Science, 121: 16-20.

Mutlak, S.M., Hamdi, Y.A., Nour, M.A., Bakal, N., Al Gazzály, M. and Ayar, N. (1980) Sewage farming in Iraq: A potential hazard for pollution. J. Environ. Qual., 9: 677-680.

*Nad, B.K. (1979) Ph.D. (thesis), I.A.R.I., New Delhi.

Nakayama, F.S. (1968) Calcium activity, complex and ion pair in saturated CaCO₃ solution. Soil Science, 106: 429-434.

Nightingale, H.I. and Smith, R.L. (1967) Evidence for the presence of calcium organic complexes in sodic soils. Soil Science, 103: 261-264.

Okun, D.A. and Ponghis, G. (1975) Community wastewater collection and disposal. World Health Organization, Geneva, pp. 211-220.

Oliver, B.G. and Cosgrove, E.S. (1975) Metal concentrations in the sewage effluents and sludges of some southern Ontario wastewater treatment plants. Environ. Letters, 9: 75-90.

Paliwal, K.V. and Gandhi, A.P. (1976) Effect of salinity, SAR, Calcium: Magnesium ratio in irrigation water and soil texture on the predictability of exchangeable sodium percentage. Soil Science, 122: 85-90.

Pasricha, N.S. and Ponnamperuma, F.N. (1977) Na⁺ - (Ca²⁺ + Mg²⁺ - (Ca²⁺ + Mg²⁺) Exchange equilibria under submerged soil conditions. Soil Science, 123: 220-223.

Pillai, S.C., Rajgopalan, R. and Subramanian, V. (1955) Sewage farming and sewage grown crops in relation to health. Bull. of the Natl. Inst. of Sciences of India, No. 10: 160-179.

Piper, C.S. (1966) Soil and Plant Analysis. Univ. Adelaide, Australia.

Quin, B.F. and Woods, P.H. (1978) Surface irrigation of pasture with treated sewage effluent. I: Nutrient status of soil and pasture. N.Z.J. Agri. Res., 21: 419-426.

Rainbow, P.S. (1985) The biology of metals in the Sea. Inter. J. Environ. Studies. 25: 195-211. Raman, A., Sundaramoorthy, S. and Varadarajan, A.V. (1973) A study on the treatment of sewage for industrial uses. In: Proc. Symp. Environ. Pollution, held at CPHERI, Nagpur on Jan.17-19, 1973, pp. 159-63.

Rhoades, J.D. (1972) Quality of water for irrigation. Soil Science, 113: 277-284.

- Ritchey, K.D., Silva, J.E. and Costa, U.F. (1982) Calcium deficiency in clayey B. Horizons of Savanna Oxisols. 'Soil Science, 133: 378-382.
- Rohde, G. (1962) as quoted by H. Bouwer and R.L. Chaney (1974) Land treatment of wastewater. Adv. Agron. 26: 133-156.
- Rubin, A.J. (1974) Aqueous environmental chemistry of metals. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan.
- Schnitzer, M. (1969) Relation between Fulvic acid, a soil Humic compound and inorganic soil constituents Soil. Sc. Am. Proc. 33: 75-81.
- Schnitzer, M. and Hanson, E.H. (1970) Organo metallic interactions in soil 8: An evaluation of the methods for the determination of stability constants of Metal-Fulvic acid complexes Soil Science 109: 333-339.
- Schnitzer, M. and Skinner, S. (1967) Organo metallic interactions in soil. Soil Science 103: 247-252.
- Sekar, T. and Bhattacharyya, A.K. (1982) Effect of sewage effluents on carbon and nitrogen mineralization of a soil. In Waste Treatment and Utilization, Vol. 2, Pergammon Press Oxford, pp. 447-460.
- Silverman, M.P. and Munoz, E.F. (1980) Microbial mobilization of calcium and magnesium in waterlogged soils. J. Environ. Qual., 9: 9-12.
- Sommers, L.E. (1977) Chemical composition of sewage sludges and analysis of their potential use as fertilizer. J. Environ. Qual., 6: 225-231.

- t

- *Sopper, W.E. and Kardos, L.T. (1973) Vegetation responses to irrigation with municiple wastewater. In: Recycling Treated Municipal Wastewater and Sludge through Forest and Cropland. Pennsylvania State University, The University Press, pp. 271-294.
- Sopper, W.E. (1976) Use of soil vegetation biosystem for wastewater recycling. In: Land treatment and disposal of Municipal and Industrial Wastewater. (ed) R.L. Sanks and T. Asano, Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan, pp. 17-43.
- Sposito, G., Holtzclaw, K.M. and Madore, C.S. (1978) Calcium ion complexation by fulvic acid extracted from sewage sludge soil mixture. Soil Sci. Soc. Am. J., 42: 600-606.
- *Stotzky, G. (1972) Activity, ecology and population dynamics of micro-organisms in soil. Crit. Rev. Microbial. 2: 59-137.
- Subbiah, B.V. and Asija, G.L. (1956) A rapid procedure for estimation of available nitrogen in soils. Curr. Sci., 25: 259-260.
- Tan, K.H., Edwards, J.H. and Bennett, O.L. (1985) Effect of sewage sludge on mobilization of surface applied calcium in Greenville soil. Soil Science, 139: 262-269.
- Tietjen, C. (1977) The agricultural reuse of municipal wastewater in Brannschweig, Germany. In: Wastewater Renovation and Reuse. (ed) F.M. D'Itri, Marcel Dekker Inc., New York, pp. 69-88.
- Tisdale, S. and Nelson, W. (1975) Soil fertility and fertilizers. Macmillan Publishing Co. Inc., New York.
- Touchton, J.T., King, L.D., Bell, H. and Morris, H.D. (1976) Residual effects of liquid sewage sludge on coastal Bermudagrass and soil chemical properties. J. Environ. Qual., 5: 161-164.
- Vidyarthy, G.S. and Misra, R.V. (1977) Country reports India. In: Organic Recycling in Asia. FAO Soils Bulletin No.36, pp.36-74.
- Yadav, J.S.P. and Giridhar, I.K. (1981) Effects of different Magnesium: Calcium ratios and sodium adsorption ratio values of leaching water on the properties of calcareous versus non-calcareous soils. Soil Science, 131: 194-198.

* Original not seen.