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TO STUDY THE CHANGES OF Ca, Mg, Na IN FLY ASH AMENDED SOIL

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CERTIFICATE.

This dissertation entitled "To study the changes of Ca, Mg & Na in Fly ash amended soil", has been carried out at the School of Environmental Sciences, JNU, New Delhi. The work is original and has not been submitted in part or full for any other degree or diploma of any university.



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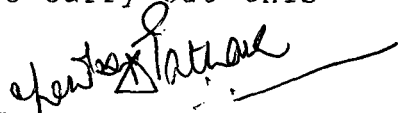
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INTRODUCTION

INTRODUCTION

Homo Sapiens may well pride himself on being the most evolved and so the most intelligent, of the living creatures. But rarely has he given evidence of his collective wisdom. At least it is not reflected in his actions which more often than not have lacked a sense of proportion or balance. On the contrary instances demonstrating his propensity of going to the extremes are too numerous. In the process he often takes neither a cosmic view nor one of immediate practical relevance.

That is why in his own inimitable, profligate style he went on merrily denuding this earth. He went on over exploiting the natural resources with a devil-may-care attitude. And when this resulted in a gross ecological imbalance threatening his very existence he went to the other extreme. Awakening suddenly to the need for protecting the environment, he again displayed only a myopic vision.

Today, coal is the most important fossil fuel for power generation throughout the world. It is agreed that the economy has to bear a social cost in terms of damage to environment for most

developmental activities. In the use of coal, the damage to environment is at two levels open cast mining seriously damages the environment around the mines. Not only is the topography of the area changed, dust and slime generated poses a serious health hazard.

On the top of that, use of low quality coal in power generation which is expected to predominate in the future, brings about the additional problem of ash disposal. This increasing trend towards its such use in power production and the great concern about the danger of polluting environment call the attention to the reduction of fumes and ashes escaped from the stacks.

Fly ash is the main residue of coal combustion. It is an inert material cleaned from flue gas and particulate materials, which either escapes to the atmosphere or is trapped by emission control devices (Electrostatic precipitators, scrubbers etc.). The average ash content of thermal grade coal is 28% with the percentage going up to as high as 42% for inferior grades.

The fly ash produced has to be either disposed

off or utilized. A certain quantity of fly ash is used in concrete and ceramics and as base materials in road beds (Buttermore et al., 1972). Successful reclamation of spoil areas with fly ash have been also reported (Adams et al., 1972; Capp., 1978): more over it has been added to soil to lessen high acidity or correct some deficiencies in plants (Furr., et. al; 1975). Since the utilization in constitutional materials consume only a certain quantity of the total production of fly ash, a great amount of it still has to be disposed off. The usual methods of ash disposal are:

- a. Dumping in a disposal area
- b. Placement and compaction in a controlled fill.
- c. Slurrying with water followed by pumping into a lagoon or impoundment. etc.

Besides above usefulness as construction material and others fly ashes have been suggested as amending and micro element enriching materials in agriculture (Capp and Engle, 1967; Martens et al., 1970; Martens, 1971; Phung et al. 1978). They have been used also to improve soil physical properties (Amos and wright, 1972; Chang et al., 1977, Giedrojc et al., 1980; Giedrojc and Hryniewicz. 1981.)

Analysis of flyash reported that a large number of essential nutrients, like P, K, Ca, etc. and toxic elements like heavy metals may be present and the unsatisfactory disposal of this material may present a problem. Presence of as much as 46 elements have been reported in coals used in electric power generation (Block and Dams, Env. Sc. Tech.9, 1975). They have reported the presence of a number of alkali and alkaline earth metals in coal and coal ash. Klein et al, Env Sc Tech., 9/10 (1975) 1976) have reported trace elements flow from a coal fired power plant and have given the rates of atmospheric discharge (g/min.) of alkali metals (Na, K, Rb and Cs) and alkaline earth metals (Mg, Ca and Ba).

The two thermal power stations, Badarpur and Indraprastha around Delhi, is the major supplier of electricity to Delhi. Huge amount of flyash is being produced there. Most of the flyash are being continuously dumped in nearby areas, of thermal power stations. But since last few years it is also being used in agriculture for amending soil with it. Out of fourteen essential elements, obtained from the soil by plants, six are used in relatively large quantities. They are N, P, K, Ca, Mg & S.

(Brady, 1974). Today we know almost all the constituent of fly ash, among which, certain can prove to be important nutrients for crops. But care must be taken to ensure that it doesn't contaminate the soil or ground water.

The present piece of work was undertaken to study the fly ash amendment effect on soil using fibre glass columns. A laboratory experiment under controlled conditions was set up to study the effect of fly ash amendment over accumulation and movement of Na, Ca and Mg in soil columns at certain intervals for a period of 2 months, with an objective of fly ash utilization in Agriculture. Here, it has been tried to simulate the exact field condition by maintaining the soil profile. The detailed result has been incorporated in this dissertation.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Fly ash is the main residue of coal combustion. It is an inert material, cleaned from flue gas and particulate materials which either escapes to the atmosphere or is trapped by emission control devices. Therefore, the increase in coal use for power production produces large amounts of fly ash, with consequent concern about the environment and human health. Chemically all naturally existing elements can be found in fly ash (Klein et al 1975; Kaokinen et al 1975). Thirty two elements were found at higher total concentrations in the fly ash than in the soil (Furr A Keith, 1976). Since coal residue also contain potentially hazardous substances, improper handling and disposal could cause undesirable environmental effects. On a global basis the annual production of fly ash is estimated to be 56×10^6 metric tonnes (Adriano et al 1980) and by 2000 A.D. it is expected to go up to 650 - 850 million metric tonnes.

Up to now fly ash has been used mainly for making cement, concrete mixing and ceramics but a great amount of it still has to be disposed off. Fly ash has been suggested also as an amending and

micro element enriching material in agriculture (Capp and Engle, 1967; Masters, 1971; Phung et al., 1968), and in land reclamation (Capp, 1978). It has been used also to improve soil physical properties (Amos and Wright, 1972; Chang et al., 1977; Giedrojć and Hryniewicz, 1981). In view of the increasing trend towards fly ash production, and its suggested agricultural use, great attention has to be paid to possible side effects.

FLYASH CHARACTERISTICS

The physical, mineralogical and chemical properties of fly ash depends on the coal's geological origin, combustion conditions, efficiency of particulate removal and degree of weathering before final disposal. A classification system for coal fly ash has been developed to provide the basis for a uniform nomenclature that can be used by investigators in different disciplines to describe samples of coal fly ash. This system is based on chemical composition, hydration pH and particle size distribution. Seven taxonomic groups are generated by the distribution of the Silicic ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$), Ferric ($\text{Fe}_2\text{O}_3 + \text{SO}_3$), and Calcic ($\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) components of the fly ashes. Prefixes and suffixes

denoting hydration pH, elevated trace and minor element concentrations and texture are added to the group names to further describe the sample. (W.R. Roy and R.A. Greffin, 1982) fly ash consists of many minute, glass like particles, which range in particle size from 0.01 to 100 μm (Davison et al; 1974). Spherical shaped particles constitute most of the fly ash especially in the finer fractions.

In 1986 certain physicochemical properties of fly ash collected from a coal fired power plant at Kanpur (26 26'N latitude and 86 22'E longitude). India were studied. Textural analysis reveals that a major fraction of fly ash mass (65%) is composed of silt-sized particles (0.02 to 0.002 mm). Sand sized particles (2.0 to 0.02 mm) represented 25%, while clay sized particles (<0.002mm) represented only 10%. The bulk density and optimum moisture content of freshly collected fly ash samples were measured, being 1.02 g cm^{-3} and 2.1% respectively. Water extracts from fly ash were alkaline and contained excessive amounts of soluble salts. Samples of each fraction of fly ash (sand, silt and clay) were analysed for concentrations of four macro elements (N,P,K and Ca) and four trace elements (B, Cu, Mn and Zn), Except for N, fly ash contained

higher concentrations of all elements than normally found in soil. (L.C. Mishra & K.N. Shukla; 1986).

Chemically almost all naturally existing elements have been found, in fly ash (Klein et al 1975; Kaokiness et al 1975) Presence of as much as 46 elements in coals used in electric power generation have been reported (Block and Dams, 1986). Following chemical composition of fly ash have been found:

NAME	FORMULA	PERCENTAGE
Silica	SiO_2	62
Alumina	Al_2O_3	26
Iron oxide	Fe_2O_3	6.3
Calcium oxide	CaO	1.13
Magnesium oxide	MgO	0.49
Sodium oxide	Na_2O	0.28
Potassium oxide	K_2O	1.28
Titanium dioxide	TiO_2	1.80
Phosphorous Pentaoxide	P_2O_5	0.40
Sulfur Trioxide	SO_3	0.30

Silica, Alumina and Iron oxide represent about 90% of the total. Because of the high temperature at which the fly ash is produced in a high efficiency

boiler, the ash consists of glassy particles (generally spherical) of complex silicates of these three elements.

Intermediate amount of Mg, K, Na and Ti; and lesser amounts of B, Zn, Mn, Cu and numerous other elements are also present in the fly ash (Rees and Sidrak 1956; Capp et al, 1970; Martens et al 1970; Planks et al 1975).

FLYASH IMPACT ON BIOSPHERE

The increasing trend of fly ash production with its unscientific disposal has created a threat to life-support system. Its potential towards ecological imbalance has been extensively reviewed by various workers of present day world. (Page et al 1979, Terman 1978, Turner and Strojjan 1978; Vagna et al 1975; Berry and Wallace 1974; A Wadage, 1986; C.J. Warren, 1984 etc.)

Fly ash effects on Biosphere is three fold i.e. on all the Life-support systems:

- i. Effects on Air
- ii. Effects on water

iii. Effects on soil

Being very light fly ash is readily carried by wind during transportation dumping and burying. The major air pollution of fly ash in the nearby areas of thermal power plant is due to either absence inefficiency of trapping devices. Since fly ash contains potentially toxic elements, there is a great possibility that nearby soils and water bodies which are not directly affected by run off or leaching could become contaminated due to deposition of air born particulates.

Fly ash effects on water bodies is two pronged; one on ground water via vertical leaching effects and the other on surface water due to lateral migration of leachates along with surface run off. The vertical leaching occurs due to improperly sited and designed waste disposal ponds and landfills with inadequately lined ponds. It provides a great opportunity for groundwater contamination, since the soil below the impoundments is always saturated and under a hydraulic head (Phillips et. al 1974). Water bodies adjacent to the disposal sites becomes contaminated through surface run off from the site. Effects of this contamination is first noticed in

the fish and other aquatic organisms. Concentration of trace elements in water considered more toxic to aquatic organism at lower levels than those considered harmful to terrestrial animals, humans and vegetation (Phillips et al, 1974). As, Cd, Cr, Hg, Ni and Pb can cause serious effects on certain aquatic species at concentrations as low as 0.01 mg/l. (Phillips et al 1974; Quality criteria for water EPA 1976).

Soil is a crucial life support system, since the bulk of all food production depends on it. Pollution effects on soil is different from air and water. Soil is having more buffering capacity. Pollutants remain for quite longer period over it. Fly ash movement from a thermal power plant vicinity to further distance either through aerial movement or through water move towards agricultural lands. In both conditions, it is the soil which gets affected (Wangen L.E. & Turner FB, 1980) soil microbial activity also gets altered due to fly ash. This change has been extensively studied. (Elliott et al., 1982; Parr et al, 1983; Townsend & Gillham, 1975, M.F. Arthur, T.C. Zwick, D.A. Tolle and P. ,Van Voris et al 1983 etc.).

**ALKALINIZATION OF SOIL THROUGH THERMAL POWER PLANT
FLY ASH FALLOUT:**

Fly ash fallout rates in the vicinity of a thermal power station of 540 MW capacity were measured in tonnes per square Kilometer per month for 6 months of the post-rainy period from October to March. The concentrations of the alkali metals (Li, Na, K, Rb and Cs) and alkaline earth metals (Be, Mg, Ca, Sr, and Ba) were determined by A.A.S. in a number of fly ash samples collected at selected sites in the vicinity of thermal power plant. These elements were also determined in soil samples collected from different depths to ascertain the leach profile and also in samples collected from contamination free areas.

A comparison of the analysis data for the soils collected from the contaminated and uncontaminated areas confirm that the soil horizon around the thermal power plant has received an input of alkali and alkaline earth metals from the dust fallout emitted by the thermal power plant. Element concentrations (P.Pm.) in the top 30 cm of the soil in the contaminated area were found as follows (the values in parenthesis are those in the uncontaminated soil).

: Li 80(2.5); Na 7100 (4800); K 21000 (13600); Rb 1.9(0.5); CS 1.1 (0.25); Be 1.3 (Nil) Ba 210 (150); Ca 31750 (29000); Mg 16500 (11500); and Sr 18.8(8.0). The alkalization of the soil around the thermal power plant as a result of flyash fallout is thus confirmed by the above data. Even at a depth of 90 cms, the concentrations of all these elements in the contaminated soil are much higher than those found in the top 30 cm. of uncontaminated soil.

The input of macroelements to the soil horizon as shown by their percent increase, is in the order: K>Na>Mg>Ca; for microelements the input is in the order: Cs>Rb>Li>Sr>Ba (in the case of Ba a trace presence of 1.3 PPM was observed compared with its absence in the uncontaminated soil. The higher concentrations of the elements in the Soil Samples from the contaminated area, up to a depth of 90 cm show that the surface deposition of the elements has penetrated into the soil to a considerable depth.

The retention concentration of individual elements in the 30-60 and 60-90 cm profiles compared with the concentration in the top 0-30 cm are (%): Li, 78.1, 50.1; Na, 89.4, 77.2; K, 85.7, 74.7; Rb, 76.8, 57.8; CS, 66.7, 47.6; Be, 56.7, 31.5; Ba,

83.8, 74.3; Ca, 91.3, 86.6; Mg, 90.2, 81.4, Sr, 82.9, 69.5. The leaching action of the elements has been found to be in the order:

K>Mg>Ca>Na>Ba>Sr>Li>Rb>Be>Cs.

(C.B. Patel; G.S. Pandey, The Sc of Total Env. 1986).

FLYASH APPLICATION IN AGRICULTURE

It has been a common practice in the past and even now a days to put bottom ash burned in home in gardens. It has been used in several areas in England to reclaim land for growth of forage and pasture crops (Barber, 1974). Several elements in coal fly ashes are important for plants from nutritional point of view. Plant deficiencies of B, Mo, P, K, Zn etc. can be corrected by its use (Martens et al 1970; Martens 1971; Doran and Martens, 1972;). Normally not more than 2.5% of fly ash application is preferred to correct trace element deficiency. Fly ash also helps agriculture by increasing water holding capacity of soil. In sandy soils this practice helps very much. These possible methods of flyash application in fields can solve our fly ash problems a lot, but side effects must be checked first. A number of scientists have studied these

practices for various crops in various conditions. The results has been found satisfactory.

PHYSICOCHEMICAL CHARACTERISTICS OF FLYASH AMENDED SOILS:

The physical and chemical properties fo coal ashes are dependent on the coals geological origin; combustion conditions efficiency of particulate removal and degree of weathering before final disposal. The physical properties related to the agronomic use of flyash amended soils were characterised by determining water holding capacity, bulk density, hydraulic conductivity, and modulus of rupture on laboratory compacted soil cores. Fly ash from a coal fired power generating plant was mixed with fuse California soils at ratio of 0, 2.5, 5.0, 10.0, 25.0 and 50.0% by volume. The moisture release characteristic of each mixture were also determined. Results indicated that a small amount of fly ash added to soils does appear to affect some measured physical properties of soils. At application rates >25% there was a consistent increase in water holding capacity (except a Domino loam soil) and a decrease in bulk density and modulus of rupture in all soils tested. The hydraulic

conductivity increased with small amounts of fly ash, but declined rapidly as fly ash volume increased. Although fly ash application increased the water holding capacity of soils, the amount of water available to the plant did not change significantly. At low application rates, fly ash amendment appeared useful in improving certain agronomic properties of soils. (A. C. Chang, L.J. Lund, A.L. Page and J.E. Warneke. J. Env. Qual. Vol. 6, No. 3, 1977)

Fly ash from a coal fired power station was incorporated with each of a fine (0.2-0.5mm) and 'coarse' (1.4-2.0mm) sand fraction to give mixtures containing 0, 10, 20, 30, 40, 50, 75 and 100% flyash by weight. The addition of 10% by weight of ash increased the available water capacity by factors of 7.2 (1.0-7.2% by wt.) and 13.5 (0.4-5.4% by wt.) for the 'fine' and coarse sands respectively. Subsequent additional 10% increments of ash increased the capacity by smaller amounts. The saturated hydraulic conductivity of the sands decreased markedly with ash addition. The changes in available water capacity and hydraulic conductivity were associated with an increase in capillary pores at the expense of non capillary Pores. (D.J. Campbell, W.E.Fox, R.L. Aitken and L.C. Bell Aust. J. Soil Res., 1983).

Coal residues, applied on cropland, are not practical sources of essential plant nutrients N, P and K. However, they can effectively serve as a supplementary supply of Ca, S, B, Mo and Se to soils. Fly ash could also be an effective amendment in neutralizing soil acidity. Many of the observed chemical and biological effects of fly ash applications to soil resulted from the increased activities of Ca^{2+} and OH^- . Most unweathered fly ashes, especially those coming from the subbituminous and lignite coals of the western U.S. are found to be high in these constituents and usually will cause high soil salinity. The accumulation of B, Mo, Se and soluble salts in fly ash amended soils appear to be the most serious constraints associated with land application of fly ash to soil. Fly ash amendment also affects soil microbial activity. These effects have been widely studied in recent years. Microbial respiration was reduced with increasing fly ash treatments in the sand soil, whereas in sandy loam, a significant depression was only recorded at the highest ash addition for both total and cumulative CO_2 evolved. Total CO_2 release was actually increased by 3% and 6% ash amendment on the sandy loam. A highly negative correlation

was found between respiration and ash treatment for the sandy soil ($r=-0.9904$, $P<0.005$) but not for the sandy loam. (M.H. Wong, W.C. Wong, *Env. Poll.* 40, 1986).

AMENDMENT EFFECTS ON CROPS:

Large number of scientists have studied amendment effects on various crops. Plants of two important crops of our India, wheat (cultivar N-4) and gram (cultivar H-355) were dusted with 2, 4 and 6 gm^{-2} day^{-1} of flyash for 45 days. Both crops showed an increase in the height of the plants, dry weight and Chlorophyll and Carotenoid content. The higher dusting rates affected the photosynthetic pigment contents (P.S. Dubey, K.Pawar, S.K. Shringi and L. Trivedi; *Agro Ecosystems*, 1982).

High levels of Cd, Pd and Se were found in Barley and Cabbage plants grown in the greenhouse on soil amended with refuse incinerator fly ash. (A Wadage, M. Hutton, *Plant & soil*, 1986)..

Fly ash contains a high percentage of S, Ca and Mg with small percentage of N, P & K. These constituents may prove good for reclaiming saline

soil due to its ameliorative property and help increase the yield of the crop. In an experiment at the Research farm of B.H.U. Varanasi for two consecutive Kharif Seasons of 1980 and 1981, fertility levels of N, P, K. (Low: 60, 40, 30 ; medium: 80, 40, 40, and High: 120, 80, 60 kg NPK/ha) and four levels of fly ash (control, 10, 20, & 30% of soil) making 12 treatment combinations, was laid out in a split plot design with three replications by keeping fertility levels in the main plots and fly ash in the sub plots. Up to 20% fly ash application yield increases, which may be due to its ameliorative effect on soil which enhances the availability of pH dependent nutrient by bringing down the soil pH. Beyond 20% yield decreases. It may be due to increased osmotic potential, as salt content increases, restricting the uptake of major nutrients. (N.B.Singh, Mahatim Singh, Fertiliser News, 1986). Experiments have been carried out also for some heavy metal contents .

LEACHINGS OF FLYASH AMENDED SOILS :

The exchangeable cations determine to a large extent the chemical and physical properties of soils. The most significant are those of exchangeable

hydrogen, sodiums and calciums.

A model based upon concepts of multispecies ion chromatography and mobile immobile water was developed to simulate the leaching of major soil cations during steady, continuous infiltration of electrolyte solutions into soil columns. This model assumes that a fraction of exchange sites is readily accessible to the mobile solution located in large intra-aggregate pores and that the remaining slowly accessible exchange sites are located in the immobile solution inside smaller pores within aggregates. Ion exchange is assumed to occur instantaneously for all the partitioned exchange sites. Diffusive transfer of ions between the mobile and immobile solution phases results in a time lag for cations leaching from the two compartments of exchange sites, as well as early breakthrough for ion concentration in effluent flowing from the soil column.

TH-2B03



The numerical model was verified by comparing calculated break through curves for 2 ion transport with those obtained with an analytical model and by simulating $Mg^{2+} \rightarrow Ca^{2+}$ exchange during steady flow of solutions through columns of three soils. Sensitivity analysis for mobile - immobile water

parameters showed the model to describe cation transport through aggregated porous media. (R.S. Mansell, S.A. Bloom, M.M. Selim & R.D. Rhue; Geoderma, 1986).

Column leaching experiment was designed to evaluate the relationship among leachate properties, weathering process and solid phase characteristics of an alkaline fly ash. Fly ash was weathered with 0.005 mol/L H_2SO_4 in a series of five leaching columns. Acidification of the ash leaching occurred in a stepwise fashion involving three buffer stages. Chemical dissolution and mobilization of elements was greatest in the first column and decreased to minimal dissolution and maximum accumulation of weathered products in ash of the fifth column. Results indicated that unreacted fly ash consists of spherical micron sized particles composed of mullite enclosed in a two phase glassy matrix. The external glass was enriched in Ca, Mg, Fe and Al. The interior glass matrix was composed primarily of Si and a major portion of the total Na and K. The ash also contained a highly reactive inorganic phase composed largely of submicron sized CaO fragments on the surface of ash particles. Initial dissolution characteristics were dictated by the reactions of

the CaO fragments and surface associated soluble salts. Leachate characteristics were largely controlled by dissolution of the external glassy matrix after the rapid dissolution of surface salts. Solid state migration and removal of Na from the interior glassy matrix was active under acidic leaching conditions (C.J. Warrer and M.J. Dudas; J. Ew Qual, 1984).

Total salts leached from column packed soil manure mixtures were significantly less than the total salt inputs. The loss of cations, calculated from the total soluble plus exchangeable cations in the control column and in the added manure minus these quantities after leaching, was greater for calcium (Ca) and potassium (K) than for Magnesium (Mg) and Sodium (Na) which was attributed to reversible K fixation and precipitation of Ca salts from solution. The measured decrease in cations exchange capacity (C.E.C) ranged from 54 to 84% of the total cation losses. Assuming that fixation of K releases an equivalent amount of other cations; than the total loss of cations minus the decrease in C.E.C. was used to estimate the precipitation losses of the cations presumably as sparingly soluble compounds, such as carbonate sulfate and phosphate.

Measured K fixation was greater in pulse irrigated than in continuously irrigated columns. S.A.R. values obtained in the effluent collected from soil manure mixtures were generally equal to or smaller than those measured in the manure free columns. (A Shaviv, W. A. Jury and P.F. Pratt; Soil Science, 1986).

As a flyash landfill in Southeastern Wisconsin, dry ash has been placed directly in contact with a shallow sand and gravel aquifer. Substantial modification of ground water quality has occurred primarily by Sulfates, calcium and Magnesium. However after eight years, the contamination has spread less than 200 meters from the site in a permeable aquifer. In addition, toxic metals contained in the ash have proven quite immobile in the ground water. Fortuitous location of the disposal site in alkaline sediment upflow from ground water discharge in a marsh appears to have limited the extent of contamination (Douglash S. Cherkaver; Ground water 1980).

MATERIALS AND METHODS

MATERIALS AND METHODS

Fibre glass columns were used in which soil was filled up to 70 cms maintaining the profile as it was in the field from where soil was collected. After mixing flyash (collected from Badarpur thermal power station) in upper 15 cm. layer of the columns except the control one, it was leached with double distilled water (2 litres/day in each column) for 60 days. Small quantities of soil were removed periodically and the important parameters were analysed.

SOIL: COLLECTION AND PREPARATION:

Soil was collected layerwise from uncultivated land around J.N.U. Nursery to a depth of about 75 cms. The each layer of soil samples were mixed thoroughly to ensure uniformity and then was air dried. Later they were powdered and sieved through a 2mm perforated sieve and were filled into the columns.

Before the addition of soil, the column was first prepared with a 4 cm layer of gravel at the bottom and a 4 cm layer of fine sand on top of it.

Then the sieved soil was carefully poured in and the columns were stabilized by passing double distilled water through it for two days.

FLY ASH COLLECTION

Fly ash was collected from Badarpur thermal power station, Delhi. It was mixed in the upper 15 cms layer of the columns except the control one. In rest of the two pairs of columns fly ash was mixed in 2.5% w/w. of total and 5% w/w of total respectively.

LEACHING AND SAMPLING:

The soil columns were leached with double distilled water. 2 litres of double distilled water were added daily in each column drop by drop for 60 days. Flow was maintained steady at 75 to 80 drops per minute for each column. Every day leachates were collected in small buckets placed in the base of the columns. The experiment commenced on 25.1.1988. The soil samples were drawn out for analysis on various intervals of 0, 5, 10, 20, 40 and 60 days. Samples were collected at three different depths of column: 10, 30 and 50 cms. Leachates were also

collected for analysis.

ANALYSIS

Samples were analysed for the following parameters:

1. pH
2. Electrical Conductivity
3. Organic Carbon
4. Available Calcium
5. Available Magnesium
6. Available Sodium
7. Total Calcium
8. Total Magnesium
9. Total Sodium

In addition to the soil samples collected periodically, ray flyash from Badarpur thermal power station and field soil (layerwise) were also analysed for above parameters.

pH: 3 gms. of soil samples or fly ash weight out and 30 ml of distilled water was added and stirred thoroughly. pH was then determined by digital pH meter. The pH of the leachates were also determined by the same instrument.

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

ORGANIC CARBON:

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 oxidising agent. Here the oxidising agent used is acidified potassium dichromate ;and the excess of dichromate is back titrated with Ferrous Ammonium Sulfate using Diphenylamine as an indicator.

Reagents:

- (a) Standard 1N Potassium dichromate: 12.257 gm of $K_2Cr_2O_7$ was dissolved in distilled water, and the solution diluted to 250 ml.

- (b) Ferrous Ammonium Sulfate: An N/2 solution was prepared by dissolving 98 gms of Ferrous Ammonium Sulfate in distilled water. 15 ml. of

concentrated H_2SO_4 was added and the volume made up to 500 ml. This was then standardized with 1N $K_2Cr_2O_7$ solution.

(c) Diphenylamine indicator: 0.5 gm of reagent grade Diphenylamine was dissolved in 20 ml water and 100 ml of concentration H_2SO_4 .

(d) 85% H_3PO_4 .

(e) Solid NaF

Procedure: 2 gms of soil sample or fly ash (raw) was taken in a 500 ml conical flask. Subsequently, 10 ml of 1N $K_2Cr_2O_7$ was pipetted into the soil and the two were mixed by swirling the flask. Then 20 ml of concentrated H_2SO_4 was added and mixed by gentle rotation for one minute 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 adding 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 Diphenylamine indicator were added.

Then this solution was back titrated with Ferrous

Ammonium Sulfate solution delivered from a burette. The colour 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 brilliant green giving one drop end point.

Calculation: % of organic carbon = $10(1-T/S) \times f$

where T = Sample Titration (ml ferrous solution)

S = Standardization blank titration (ml ferrous solution)

the factor f was derived as follows:

$$f = (1.0 \text{ N}) \times \frac{12}{4000} \times \frac{1}{0.77} \times \frac{100}{2} = 0.194$$

Here 2 is the sample wt. in gms.

$\frac{12}{4000}$ is the meq weight of carbon,

the 77% recovery factor was found by Walkley

So, % of organic carbon = $10(1 - T/S) \times 0.194$

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

Here 1.724 is the Van Bemmelen factor. Carbon to organic matter factor is based on the assumption that soil organic matter contains 58% carbon.

Organic carbon determination in leachate: 25 ml of leachate was taken in place of 2 gm. of soil samples and other reagents was mixed accordingly as discussed in case of soil. A blank with distilled water (25 ml) was also run in the same way. Here factor f will be

$$f = (1.0 N) \times \frac{12}{4000} \times \frac{1}{0.77} \times \frac{100}{25} = 0.0155$$

$$\% \text{ Organic Carbon} = 10 (1 - T/S) \times 0.0155$$

$$\& \% \text{ Organic Matter} = \% \text{ Organic Carbon} \times 1.724$$

CALCIUM (Available and Total):

Available and total calcium in the soil and calcium content in leachate were determined by the atomic absorption spectroscopic (A.A.S.) 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 wave length 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 method for calcium is the interference from other elements. Interferences are due to silicon, aluminium phosphate and sulfate which depress calcium sensitivity. So lanthanum or strontium is added to standards and samples to control chemical interference.

AVAILABLE CALCIUM

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

(c) Strontium Chloride: 3.0428 gm. of strontium chloride was dissolved in 500 ml distilled water.

Procedure: 4 gms of soil was taken in a conical flask and 100 cc of ammonium acetate was added. Extraction was done by shaking this solution in a mechanical shaker for one hour and filtering through No. 42 Whatman filter. The Calcium standards and samples were run through the A.A.S. at 422.7 nm.

Calculation: The concentration was determined by multiplying the reading of instrument with the degree of dilutions.

TOTAL CALCIUM

Soil sample was digested in HClO_4 and HNO_3 mixture and the digested solution was diluted to 100 times. Subsequently Ca concentration was determined as in the case available Calcium

Procedure: 0.5 gm soil was digested with 5 ml HClO_4 and 10 ml HNO_3 on a hot plate till colourless solution is left. It was filtered through No. 42 filter paper and made up to 50 ml. The calcium standards and samples were run through the A.A.S. at 422.7 nm.

Leachate Calcium: Leachates of different time intervals were filtered using No. 42 filter paper and after suitable dilution were run through A.A.S. at 422.7 nm.

Calculations: Instrument leachings were multiplied with degree of dilution.

MAGNESIUM (AVAILABLE AND TOTAL)

Available and Total magnesium both in the soil as well as leachate here determined by the atomic

absorption spectrophotometric (A.A.S.) method as suggested in Chemical Analysis of Ecological materials. (Allen, 1974).

Principle: In this method magnesium 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 wave length 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 magnesium in the solution.

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

AVAILABLE MAGNESIUM

Reagents:

(a) Extractant: Ammonium Acetate (pH 9). The same extractant used for Ca determination was used here.

(b) Magnesium Standards: A stock solution of 1000 P.Pm. magnesium was prepared by dissolving 1.0136 gm magnesium sulfate in water containing about 1 ml concentrated H_2SO_4 . This was then diluted to one 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: The procedure was the same as that for Ca analysis. The standards and samples were run through the A.A.S. at a wave length of 285.2 nm.

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

TOTAL MAGNESIUM

The procedure was the same as that for Ca

analysis. The standards and samples were run through the A.A.S. at a wave length of 285.2 nm.

Calculations: The concentration of magnesium was calculated by multiplying the instrument readings with the degree of dilution.

Leachate Mg: Leachates of different time intervals were filtered using No. 42 filter paper and after suitable dilution were run through A.A.S. at 285.2 nm.

Calculations: The instrument readings were multiplied with degree of dilution.

SODIUM (AVAILABLE AND TOTAL)

Available and total sodium in the soil and sodium content in leachate were determined by the flame photometric method as suggested in the chemical analysis of Ecological materials (Allen, 1974).

Principle: In this method sodium is extracted in the form of a solution and this solution is sprayed into the flame. When atoms of an element are heated in a flame some of the heat energy is absorbed by

few of the atoms which become excited. On reverting to the ground state the electrons lose this energy which is emitted as electro-magnetic radiation. For each element there are certain permitted shifts giving rise to a series of lines, each series being characteristic of the element. The intensity of anyone line is governed principally by flame temperature, other atomic species present and the number of atoms of the element in the flame at any one instant.

AVAILABLE SODIUM

(a) Extractant: Ammonium Acetate (pH 9) the same extractant used for Ca determination was used here.

(b) Sodium standard: 100 P.Pm. stock solution was prepared by dissolving 0.2542 gm dry NaCl in water and it was made up to one litre.

Suitable working standards were prepared using the same stock solution.

Procedure: The procedure was same as that for calcium analysis. The standards and samples were run through

the flame photometer.

Calculations: the concentration was determined by multiplying the reading of instrument with the degree of dilution.

TOTAL SODIUM

The procedure was the same as that for calcium analysis. The standards and samples were run through the digital flame photometer.

LEACHATE SODIUM

Leachates of different time interval were filtered with No. 42 filter paper and after suitable dilutions were run through flame photometer.

Calculations: Instrument readings were multiplied with degree of dilution.

EXPERIMENTAL RESULTS

Physico chemical properties of Experimental soil and fly ash

PARAMETERS	SOIL			FLY ASH
	0-15 cm	15-40 cm	40-90 cm	
pH	7.92	7.93	8.18	7.70
Water holding capacity (%)	26.23	28.07	30.4	66.95
Electrical conductivity (m mhos/cm)	0.11	0.12	0.12	0.11
Organic Carbon (%)	0.171	0.169	0.114	0.41
Available Calcium (ppm)	1440	1448	1456	1390
Total Calcium (ppm)	21470	21530	21560	1448
Available Magnesium (ppm)	250	197.5	230	132.5
Total Magnesium (ppm)	4170	4210	4720	990
Available Sodium (ppm)	60	58.75	65	62.5
Total Sodium (ppm)	187.5	202.5	177.5	85

Table 1. Periodic Changes in pH in the Soil Columns

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	7.92	7.83	7.82	7.72	7.73	7.78
	b (30 cm)	7.93	7.60	7.54	7.87	7.51	7.78
	c (50 cm)	8.18	7.78	7.75	7.88	7.98	7.62
Column amended with 2.5% Fly ash	a (10 cm)	8.29	8.11	8.11	8.07	8.09	7.81
	b (30 cm)	7.99	7.90	7.71	7.83	7.69	7.58
	c (50 cm)	8.23	8.15	7.97	8.01	7.84	7.57
Column amended with 5% Fly ash	a (10 cm)	7.95	7.88	7.79	7.76	7.81	7.58
	b (30 cm)	7.95	7.85	7.77	7.78	7.68	7.50
	c (50 cm)	8.16	8.07	7.80	7.76	7.81	7.53

pH of Fly Ash = 7.7

Table 2 Periodic. Changes in E.C (mmhos cm-1) in the Soil Columns

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	0.11	0.10	0.08	0.06	0.08	0.07
	b (30 cm)	0.12	0.08	0.10	0.10	0.06	0.06
	c (50 cm)	0.12	0.083	0.09	0.08	0.06	0.06
Column amended with 2.5% Fly Ash	a (10 cm)	0.12	0.08	0.07	0.06	0.05	0.04
	b (30 cm)	0.11	0.08	0.085	0.09	0.07	0.07
	c (50 cm)	0.115	0.08	0.10	0.04	0.06	0.05
Column amended with 5% Fly ash	a (10 cm)	0.12	0.10	0.095	0.085	0.07	0.06
	b (30 cm)	0.13	0.09	0.105	0.08	0.085	0.09
	c (50 cm)	0.11	0.10	0.085	0.087	0.09	0.08

E.C.(mmhos cm-1) of Fly ash = 0.11

Table 3. Period changes in Organic Carbon (%) in Soil Columns.

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	0.171	0.169	0.169	0.166	0.166	0.166
	b (30 cm)	0.169	0.166	0.169	0.166	0.166	0.166
	c (50 cm)	0.114	0.114	0.112	0.109	0.109	0.112
Column amended with 2.5% Fly ash	a (10 cm)	0.197	0.195	0.193	0.190	0.193	0.190
	b (30 cm)	0.171	0.169	0.169	0.171	0.166	0.166
	c (50 cm)	0.112	0.109	0.112	0.109	0.106	0.106
Column amended with 5% Fly ash.	a (10 cm)	0.224	0.223	0.221	0.217	0.217	0.216
	b (30 cm)	0.171	0.169	0.171	0.169	0.166	0.169
	c (50 cm)	0.113	0.112	0.109	0.112	0.109	0.109

Organic Carbon (%) of Fly Ash = 0.41

Table 4 Periodic changes in available Ca (p.p.m) in Soil Column

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	1440	1420	1403	1390	1340	1330
	b (30 cm)	1448	1442	1440	1401	1381	1383
	c (50 cm)	1456	1460	1459	1454	1390	1389
Column amended with 2.5% Fly ash	a (10 cm)	1435	1400	1385	1370	1345	1325
	b (30 cm)	1445	1445	1437	1397	1342	1333
	c (50 cm)	1452	1462	1465	1449	1372	1365
Column amended with 5% Fly ash	a (10 cm)	1425	1390	1380	1375	1320	1317
	b (30 cm)	1446	1441	1427	1385	1344	1345
	c (50 cm)	1454	1468	1471	1444	1362	1372

Available Ca (p.p.m) in Fly Ash = 1390

Table 5 Periodic changes in Total Ca (p.p.m) in Sopil Column

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	21470	21310	21260	21200	21150	21130
	b (30 cm)	21530	21400	21380	21360	21410	21420
	c (50 cm)	21560	21490	21480	21470	21570	21570
Column amended with 2.5% Fly ash.	a (10 cm)	19100	18960	18900	18830	18790	18780
	b (30 cm)	21520	21410	21370	21350	21420	21410
	c (50 cm)	21560	21480	21470	21490	21580	21570
Column amended with 5% Fly ash	a (10 cm)	16650	16510	16460	16410	16350	16330
	b (30 cm)	21540	21420	21380	21370	21430	21430
	c (50 cm)	21550	21470	21460	21480	21550	21560

Total Ca (p.p.m) in Fly ash = 1448

Table 6. Periodic changes in available Mg (p.p.m) in Soil Columns.

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	250	225	212.5	250	180	200
	b (30 cm)	197.5	265	185	225	217.5	177.5
	c (50 cm)	230	265	290	275	247.5	185
Column amended with 2.5% Fly ash	a (10 cm)	234	224	221	237.5	177.5	212.5
	b (30 cm)	201	253	203	210	217	193
	c (50 cm)	232	270	313	282	231	180
Column amended with 5% Fly ash	a (10 cm)	222	205	201	231	182	203
	b (30 cm)	198	237	198.5	226	210	182
	c (50 cm)	221	275	316	273	242	182

Available Mg (p.p.m) in Fly Ash = 132.5

Table 7. Period changes in Total Magnesiums (p.p.m) in Soil Columns.

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for control	a (10 cm)	4170	4040	4000	3915	3890	3880
	b (30 cm)	4210	4160	4125	4030	4010	4000
	c (50 cm)	4720	4590	4510	4390	4260	4230
Column amended with 2.5% Fly ash	a (10 cm)	3785	3660	3590	3485	3465	3445
	b (30 cm)	4195	4060	4020	3960	3945	3945
	c (50 cm)	4665	4565	4515	4350	4380	4300
Column amended with 5% Fly ash	a (30 cm)	3355	3230	3195	3045	3025	2985
	b (30 cm)	4185	4115	4080	3990	3970	3965
	c (50 cm)	4710	4580	4510	4370	4360	4335

Total Mg (p.p.m) in Fly Ash = 990

Table 8. Periodic changes in available Na (p.p.m) in Soil Columns.

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	60	52.5	50	55	50	42.5
	b (30 cm)	58.75	62.5	57.5	53	50	52.5
	c (50 cm)	65	75	65	68	62.5	55
Column amended with 2.5% Fly ash	a (10 cm)	62.5	53.75	48.5	54	48.75	45
	b (30 cm)	58	62	55	52.5	45	46.5
	c (50 cm)	65	72	65	67.5	60	55
Column amended with 5% Fly ash	a (10 cm)	63.5	57.5	55	57.5	58	46.25
	b (30 cm)	57.5	62.5	57.5	50	46	48.75
	c (50 cm)	66.25	71.25	67.5	68.75	64	60

Available Na (p.p.m) in Fly Ash = 62.5

Table 9. Periodic changes in Total Na (p.p.m)in Soil Column

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
Unamended Column for Control	a (10 cm)	187.5	170	162	150	144.5	140
	b (30 cm)	202.5	195	187.5	195	185	179
	c (50 cm)	177.5	175	177.5	180	180	177.5
Column amended with 2.5% Fly Ash	a (10 cm)	174	160	153	135	132.5	129
	b (30 cm)	198	186	188	189.5	184	170
	c (50 cm)	175.5	170	173	178.5	177	173
Column amended with 5% Fly ash	a (10 cm)	164	140	130	128	124	122
	b (30 cm)	200	193	188	194	191	182
	c (50 cm)	174	168	172	178.5	180	171

Total Na (p.p.m) in Fly ash = 85

Table 10. Periodic changes of Ca (p.p.m) in leachate

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
		-	-	-	-	-	-
Unamended Column for Control		-	368	320	194	84	28
		-	-	-	-	-	-

Column amended with 2.5% Fly Ash		-	402	332	196	94	34
		-	-	-	-	-	-

Column amended with 5% Fly ash		-	436	348	206	100	40
		-	-	-	-	-	-

Table 11. Periodic Changes of Mg (p.p.m.) in Leachate

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
		-	-	-	-	-	-
Unamended Column for Control	-	-	200	187	198.5	86.5	42
		-	-	-	-	-	-

Column amended with 2.5% Fly Ash	-	-	245	220	240	77	39.5
		-	-	-	-	-	-

Column amended with 5% Fly ash	-	-	285	247	279.5	74	39
		-	-	-	-	-	-

Table 12. Periodic Changes of Na (p.p.m.) in Leachate

Treatment Type	Time in days Depth in cms	0 Day	5 Days	10 Days	20 Days	40 Days	60 Days
		-	-	-	-	-	-
Unamended Column for Control		-	86	76	84	16	07
		-	-	-	-	-	-
		-	-	-	-	-	-
Column amended with 2.5% Fly Ash		-	88.5	79.5	83.5	13.5	08
		-	-	-	-	-	-
		-	-	-	-	-	-
Column amended with 5% Fly ash		-	100.5	79	83.5	13.5	11
		-	-	-	-	-	-

Table 13 : Periodic Changes in pH, E.C. & O.M. in leachate

Treatment Type	Time in days Depth in cms	5 days	10 days	20 days	40 days	60 days
Unamended Column for control	pH	8.00	8.06	8.22	8.10	7.80
	E.C. (mmhos/cm)	0.40	0.015	0.017	0.017	0.015
	O.M. ($\times 10^{-3}$)	6.7	1.3	1.3	1.3	0.6
Column amended with 2.5% Fly ash	pH	8.01	8.08	8.12	8.05	7.7
	E.C. (mmhos/cm)	0.038	0.016	0.015	0.12	0.010
	O.M. ($\times 10^{-3}$)	6.0	2.3	0.65	1.6	0.85
Column amended with 5% Fly ash	pH	7.97	7.97	8.09	7.95	7.6
	E.C. (mmhos/cm)	0.038	0.016	0.016	0.013	0.010
	O.M. ($\times 10^{-3}$)	4.7	2.7	0.6	3.0	0.1

Table 14 Correlations between various Parameters

No.	Variable Factors	Correlation Coefficient r
1.	pH X Av Ca	0.481
2.	pH X Av Mg	0.235
3.	pH X Av Na	0.341
4.	E.C. X AV Ca	0.782
5.	E.C. X AV Mg	0.310
6.	E.C. X AV Na	0.752
7.	T Ca X T Na	0.581
8.	T Ca X T Mg	0.961
9.	T Ca X O.C.	-0.984

RESULTS AND DISCUSSION

RESULT AND DISCUSSION

pH:

It is observed from the table 1 that pH decreases sharply in all the layers "a", "b" and "c" up to tenth day of experiment. After ten days the layer "a" follows a uniform pattern of decrease with a slight increase on fortieth day. In layers "b" and "c", substantial changes in either direction after tenth day is found. This difference between upper layer "a" and other lower layers may be due to the fact that layer "a" receives double distilled water whereas the lower layers "b" and "c" receives the leachate coming through upper layer which might be containing various types of soluble salts. This causes change in pH pattern to a great extent in lower layers. Various factors are responsible for pH changes in soil, viz. Base Saturation, Unsaturation, Buffering capacity of soil, Microbial activity in soil, Partial pressure of CO₂, Mineral and organic acids formation, etc. Mobile-immobile phase phenomenon (which is described in detail while discussing Calcium changes in this dissertation) may also

have contributed in above pattern of pH change.
(R.S. Mansell, S.A. Bloom et al; Geoderma, 1986).

E.C.

Electrical Conductivity values are related to the amount of soluble salts ;and other ions present in the media. Table 2 shows a substantially decreased pattern in all the three layers in first fifth day of experiment. Later on layer "a" shows slight gradual decrease in E.C. values throughout. Layers "b" and "c" does not show a uniform pattern of either increase or decrease after fifth day, although variation is less, throughout the experimental period. These patters has been attributed due to the leaching of soluble salts from all the layers. Slight non-uniformity in lower layers is largely due to the leached salts coming from upper layers.

Organic Carbon:

Organic carbon content decreases as we move down the layers. This is shown by the organic carbon content of layers "a", "b" and "c" which is

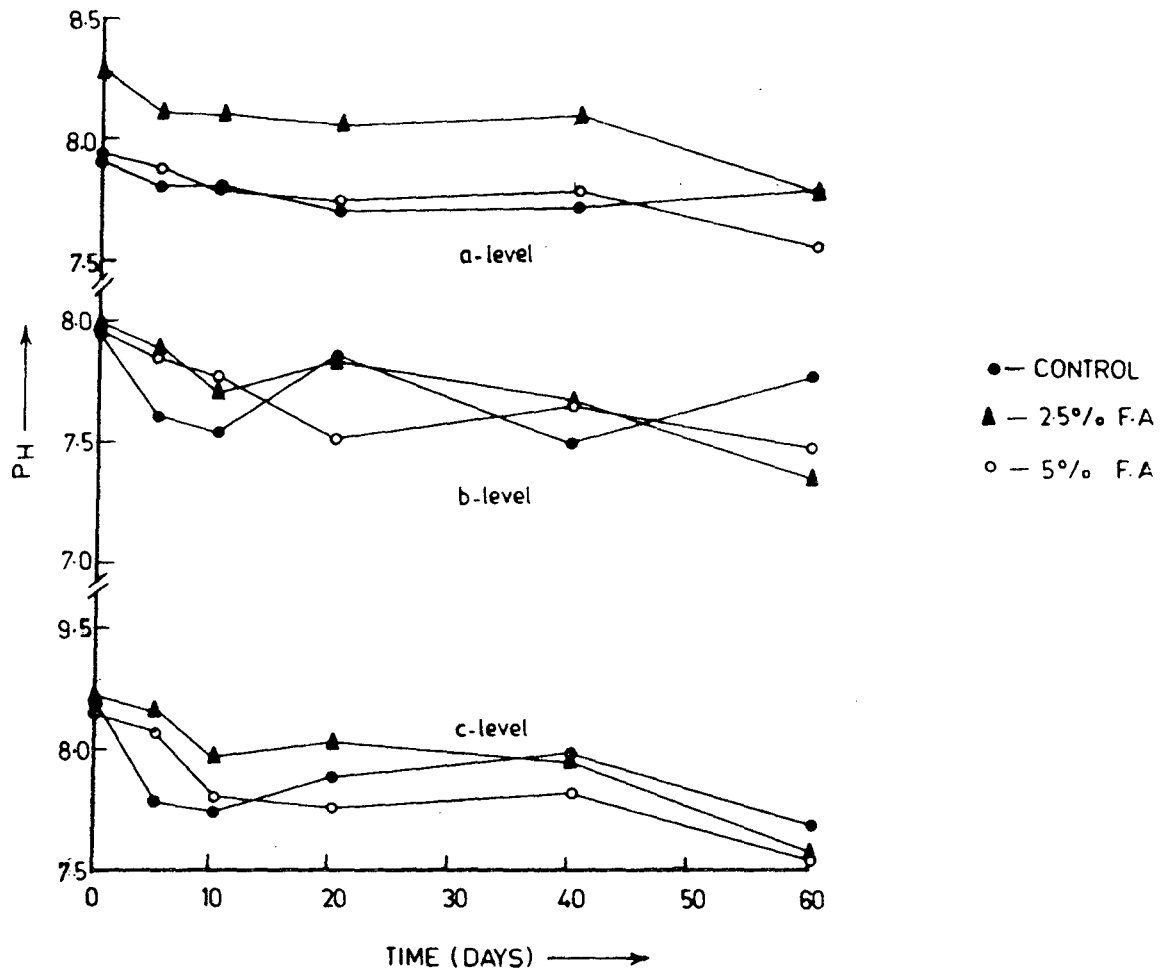


Fig. 1 : pH in different layers

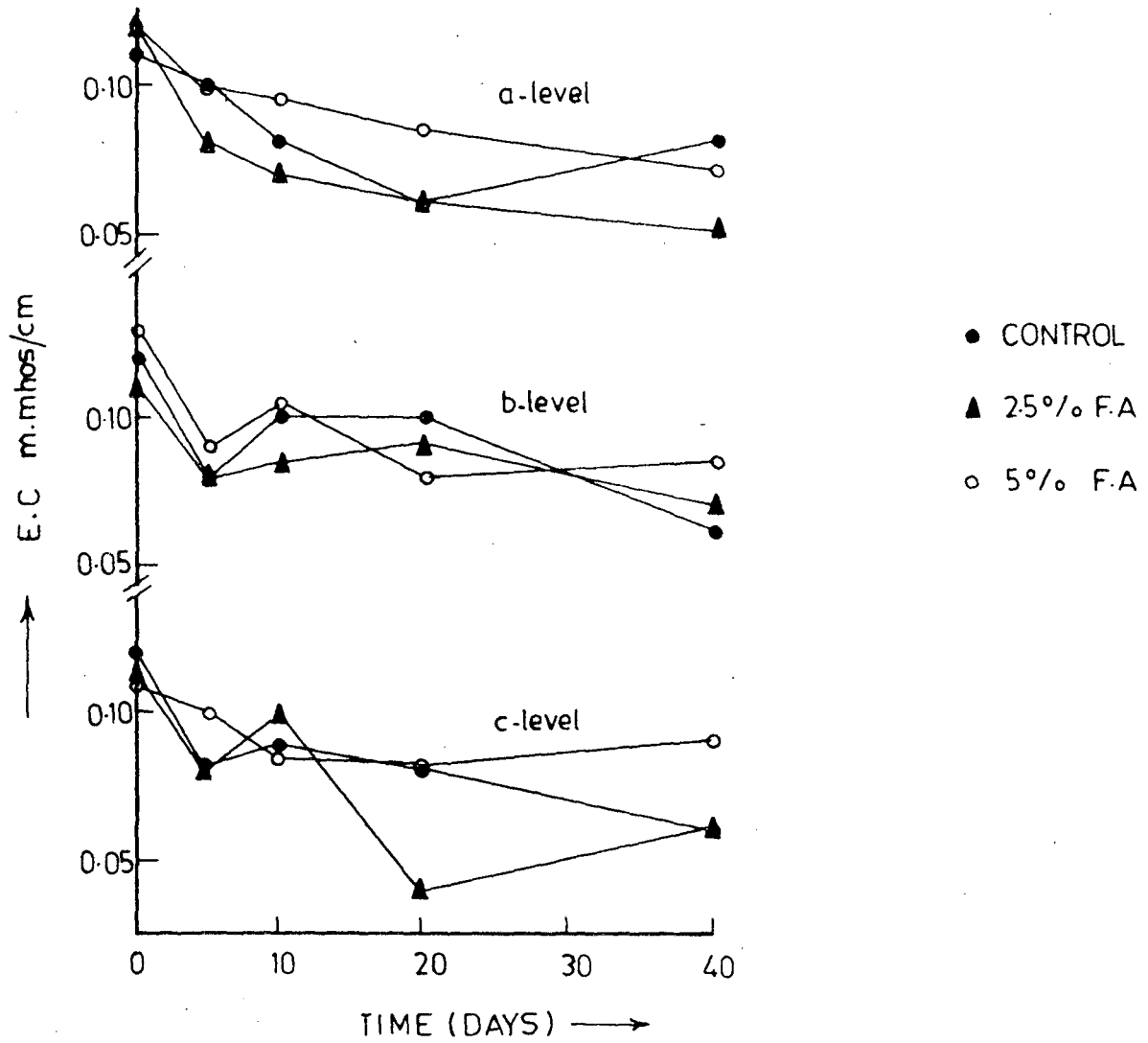


Fig. 2 : E.C. in different layers

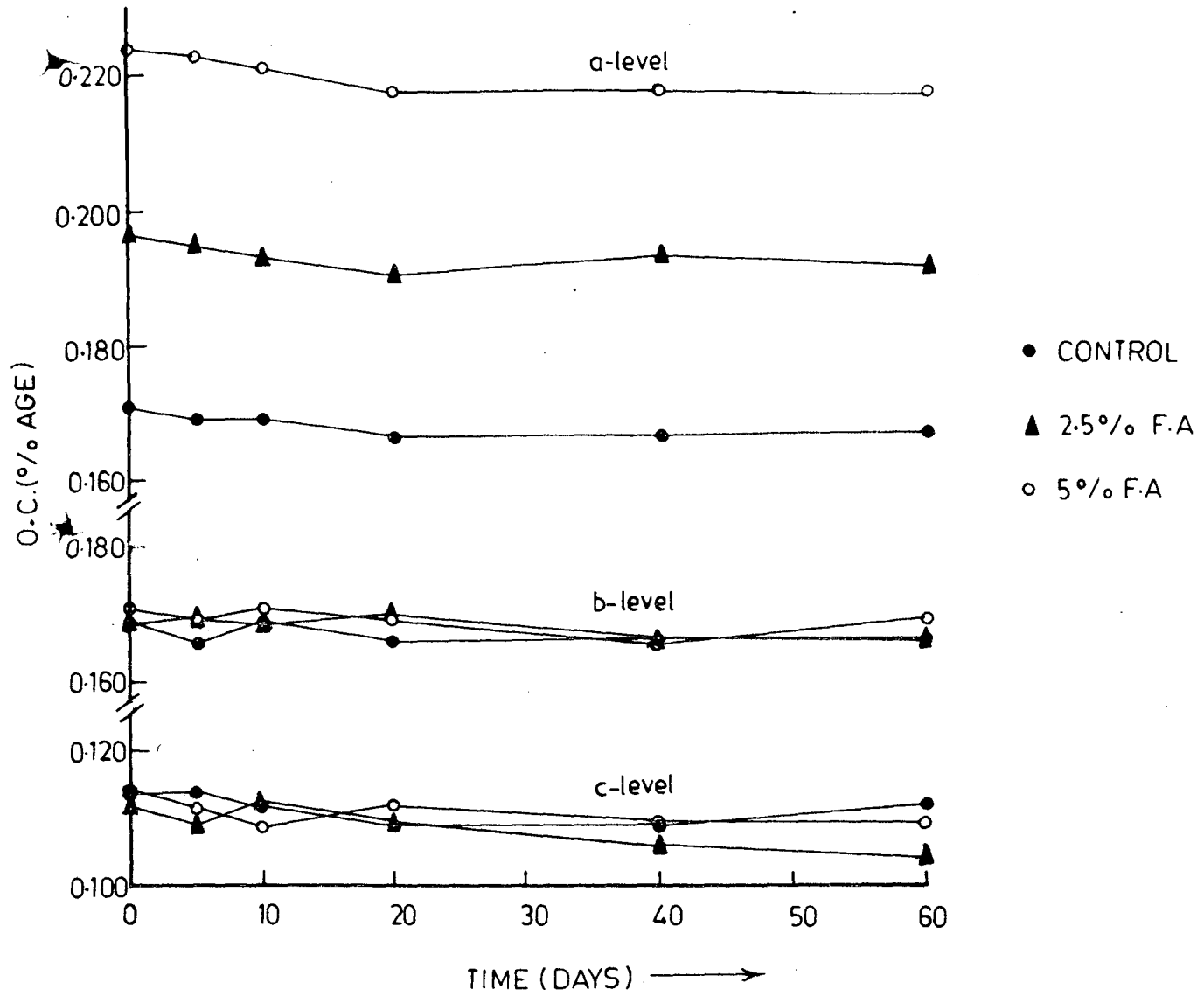


Fig. 3 : O.C. in different layers

0.171, 0.169 and 0.114 (in percentage) respectively. It is evident from table 3 and figure 3 that there is very very slight change in organic carbon content of soil throughout the experiment. Layer "a" of column containing 5% flyash shows more organic carbon content than the column containing 2.5% flyash which in turn have more organic carbon than control one. This pattern is in fact due to the more organic carbon content of flyash than that of the soil. The almost no change in organic carbon after leaching over period of experiment is largely due to the fact that it is negligibly soluble in double distilled water.

Calcium (Available):

It is observed from the Table 4 and figure 4 that calcium level change with time follows different path in the three layers. Fly ash contains substantial amount of available calcium. In layer "a" there is gradual decrease in available calcium concentration throughout the period. In first five days there is sharp decrease in all the three types of column. Calcium content in column amended with 5% fly

ash decreases more rapidly than the column amended with 2.5% fly ash which in turn more rapidly than control in first five days. The rate of decrease lessens on twentieth day of experiment which, again, follows usual path.

Layer "b" shows constancy of available calcium content up to tenth day which decreases sharply on twentieth day and later on slightly.

Layer "c" shows slight increase in calcium (available) content in first ten days. Subsequently it decreases till fortieth day which later on shows constancy.

Fly ash available calcium content is 1390 P.P.M. which is near to the soil available calcium content. This is manifested in graph for layer "a". The gradual decrease up to tenth day of experiment is mostly due to leachings. The decreased rate of decrease on twentieth day brings before us the possibility of some calcium release in available form during that period. This increase may be due to weathering effect added by time lag effect. Here the increase is not pronounced. This is probably due to the

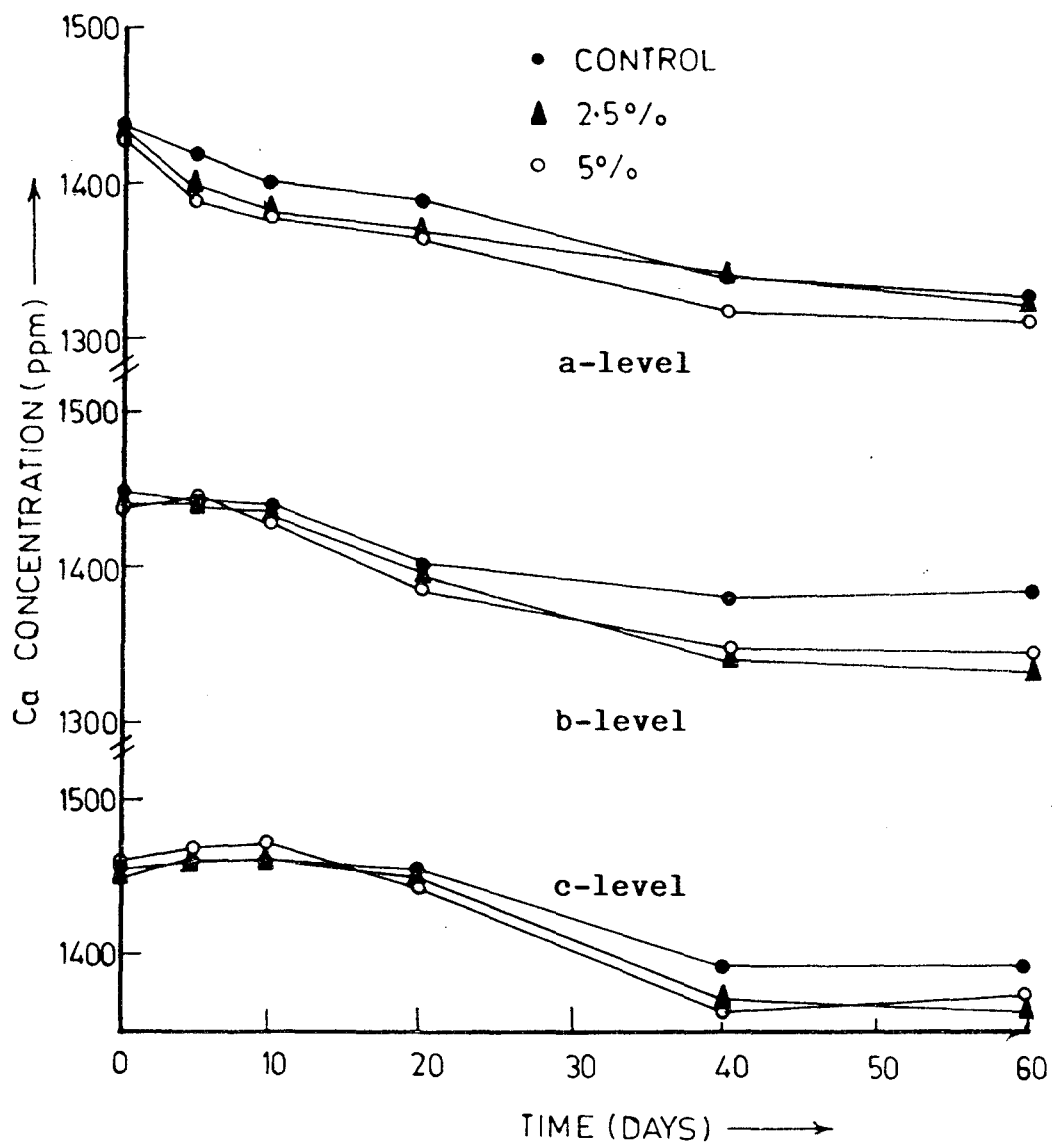


Fig. 4 : Available Ca in different layers

precipitation of calcium as phosphates which is very much probable in our case, as pH is high as well as phosphate content is considerable in soil and fly ash. The increased rate of decrease in treatment columns can be understood with the help of Glassy matrix structural concept of fly ash. The two new concepts: (i) Time lag effect (ii) Glassy matrix of fly ash which explains our change is as follows:-

Time lag effect due to Mobile-immobile phase in soil aggregates: A concept based upon multispecies ion chromatography and mobile-immobile water was developed to simulate the leaching of major soil cations during steady continuous infiltration of electrolyte solutions into soil columns. This model assumes that a fraction of exchange sites is readily accessible to the mobile solution located in large intra-aggregate pores and that the remaining slowly accessible exchange sites are located in the immobile solution inside smaller pores within aggregates. Ion exchange is assumed to occur instantaneously for all the partitioned exchange sites. Diffusive transfer of ions between the mobile and immobile solution phases results in

a time lag for cation leaching from the two compartments of exchange sites, as well as easy breakthrough for concentration in effluent flowing from soil column (R.S. Mansell et al; Geoderma, 1986).

Glassy Matrix in Flyash: Unreacted flyash consists of spherical micron-sized particles composed of mullite enclosed in a two phase glassy matrix. The external glass was enriched in Ca, Mg, Fe and Al. The interior glass matrix was composed primarily of Si and a major portion of the total Na and K. The ash also contained a highly reactive inorganic phase composed largely of submicron-sized CaO fragments on the surface of ash particles. Initial dissolution characteristics were dictated by the reactions of the CaO fragments and surface associated soluble salts. Leachate characteristics were largely controlled by dissolutions of the external glassy matrix after the rapid dissolutions of surface salts. Solid state migration and removal of Na from the interior glassy matrix was active under acidic conditions. (C.J. Warren and M.J. Dudas; J. Env. Qual. 1984)

Constancy of Ca level in layer "b" is probably due to accumulation of Ca from the upper layer. But after twenty days it shows gradual decrease due to leaching, which is also found in layer "c" but not supported by leachate Ca content. This brings a possibility of precipitation of Ca as phosphates ^{and microbial immobilisation} which then becomes unavailable. Available Ca contents increase up to tenth day of experiment in layer "c" is due to dominance of accumulation over leaching effects. Later on it decreases probably due to the same cause as in layer "b".

Calcium (Total):

It is evident from the Table 5 and figure 5 that different patterns of change are followed in different layers. Layer "a" shows gradual decrease in concentration over time. Layer "a" graphic lines are separated due to the fact that total Ca content in fly ash is very very less than the total Ca content of soil. In layer "b" there is gradual decrease in Ca concentration till twentieth day of experiment which increases on fortieth day and later on

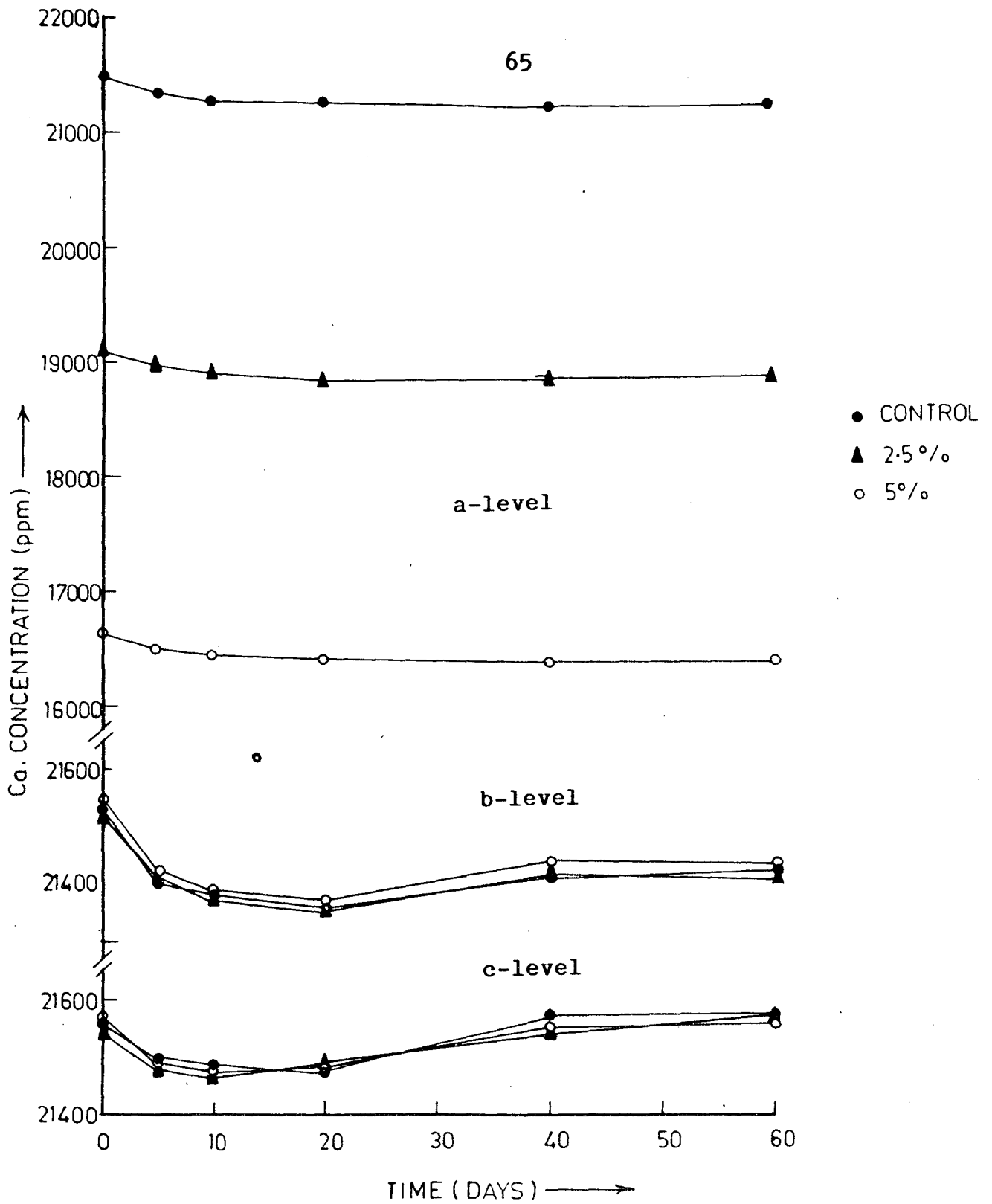


Fig. 5 : Total Ca in different layers

shows slight change. Layer "c" follows similar pattern like layer "b" but here unlike layer "b" there is slight increase on 20th day and later on more increase in Ca concentration than layer "b".

From the above pattern of all the layers it becomes clear that in layer "b" and "c" accumulation starts occurring from twentieth day of experiment till end. It is probably more due to precipitation of Ca as phosphates, which is supported by the pH and phosphate content of soil. In layer "a" leaching effect predominates. In layer "b" and "c" all leaching, accumulation, precipitation, weathering, etc. occurs but in early part of experiment leaching seems to predominate while later on accumulation and precipitations plays role predominantly.

Leachate Ca:

Ca content in leachate shows gradual decrease throughout the experiment. The overall leachate Ca concentration is less. Most of the Ca gets leached within ten days of experiment. This type of pattern shown by leachates periodic

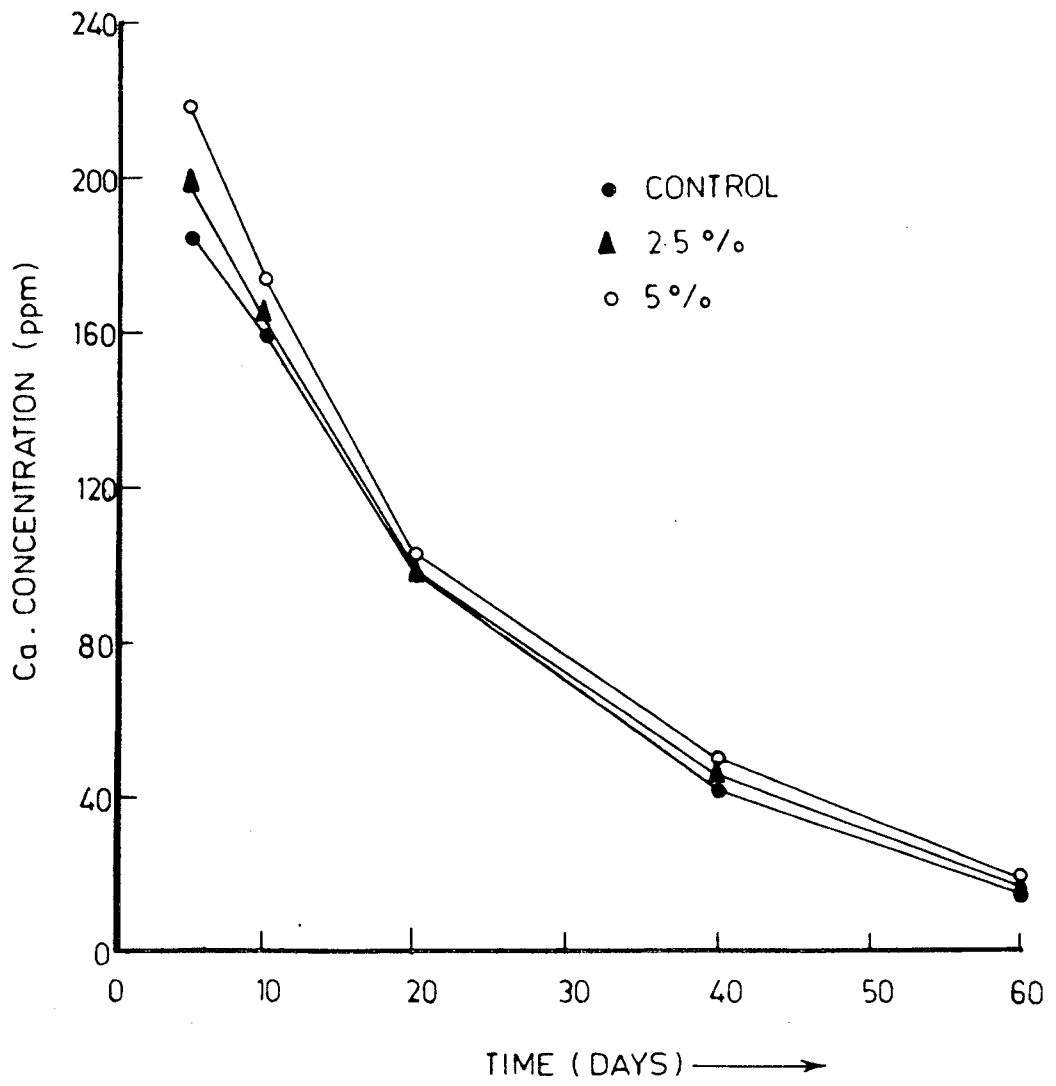


Fig. 6 : Ca in Leachate

concentrations follows the total and available Ca periodic concentration of soil. The Ca in leachates is largely due to the precipitation and accumulation of Ca in lower layers "b" and "c".

Magnesium (Available):

Table 6 and figure 7-9 says that Mg level change with time is not following similar pattern in all the three layers for the two types of fly ash amended soil columns and one control. In layer "a" initially there is more Mg (available) in control than the column containing 2.5% flyash which in turn contains more than the column with 5% flyash. There is gradual decrease in Mg level up to tenth day of experiment which increased sharply on twentieth day catching the initial level. This on further leaching comes down sharply on fortieth day which, again, shows increase on sixtieth day of experiment.

Layer "b" shows sharp increase in concentration on fifth day with sudden decrease on tenth day of experiment. Twentieth day analysis again shows increase in Mg level and later on up to

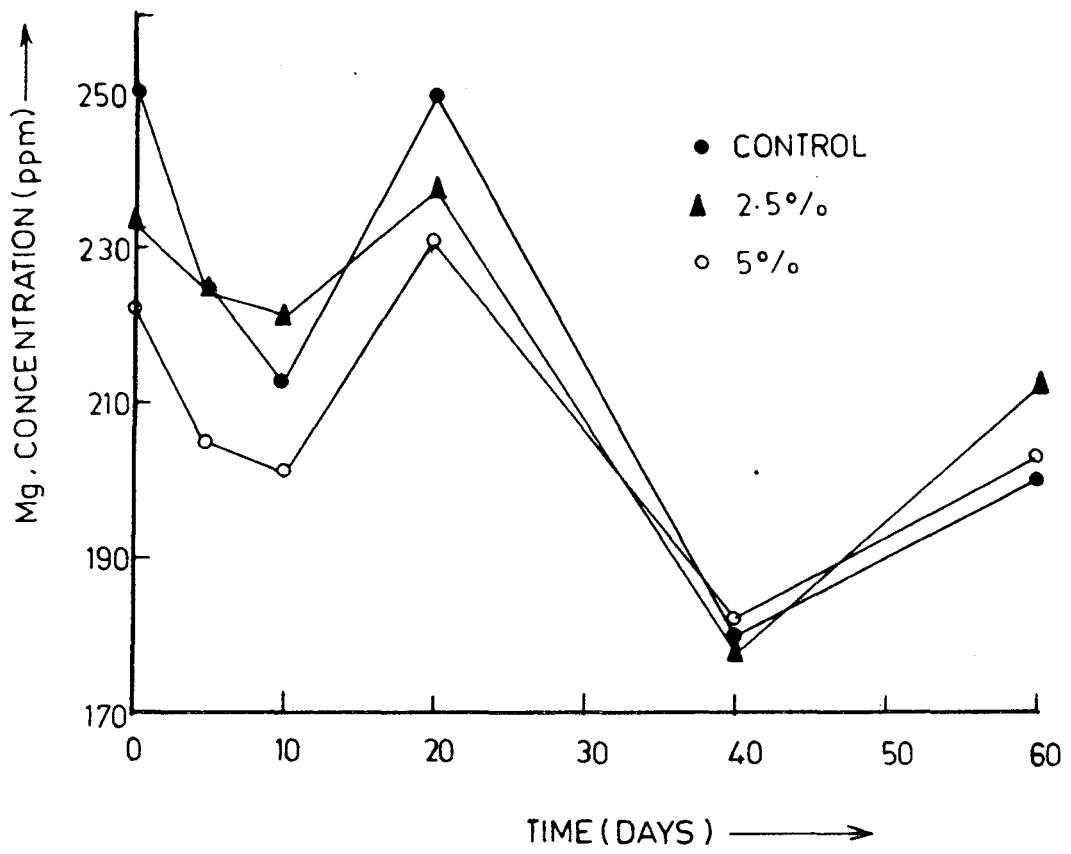


Fig. 7 : Available Mg in layer a

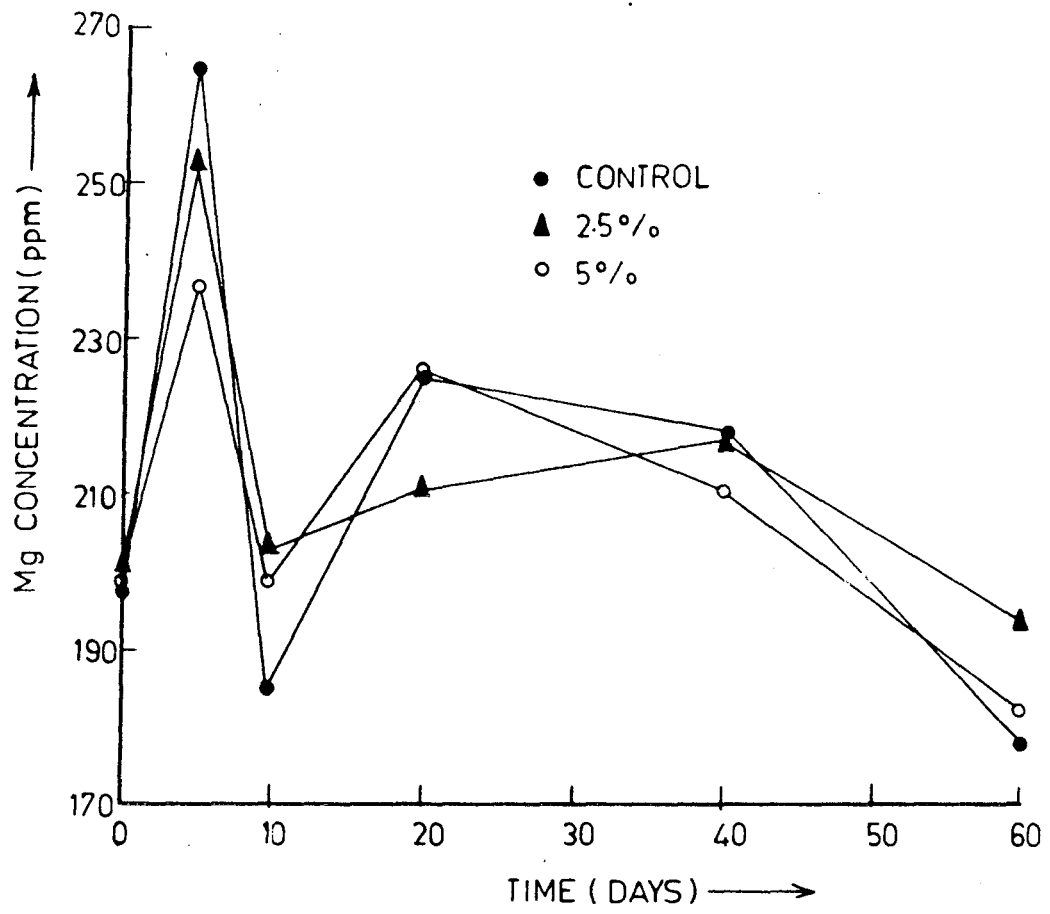


Fig. 8 : Available Mg in layer b

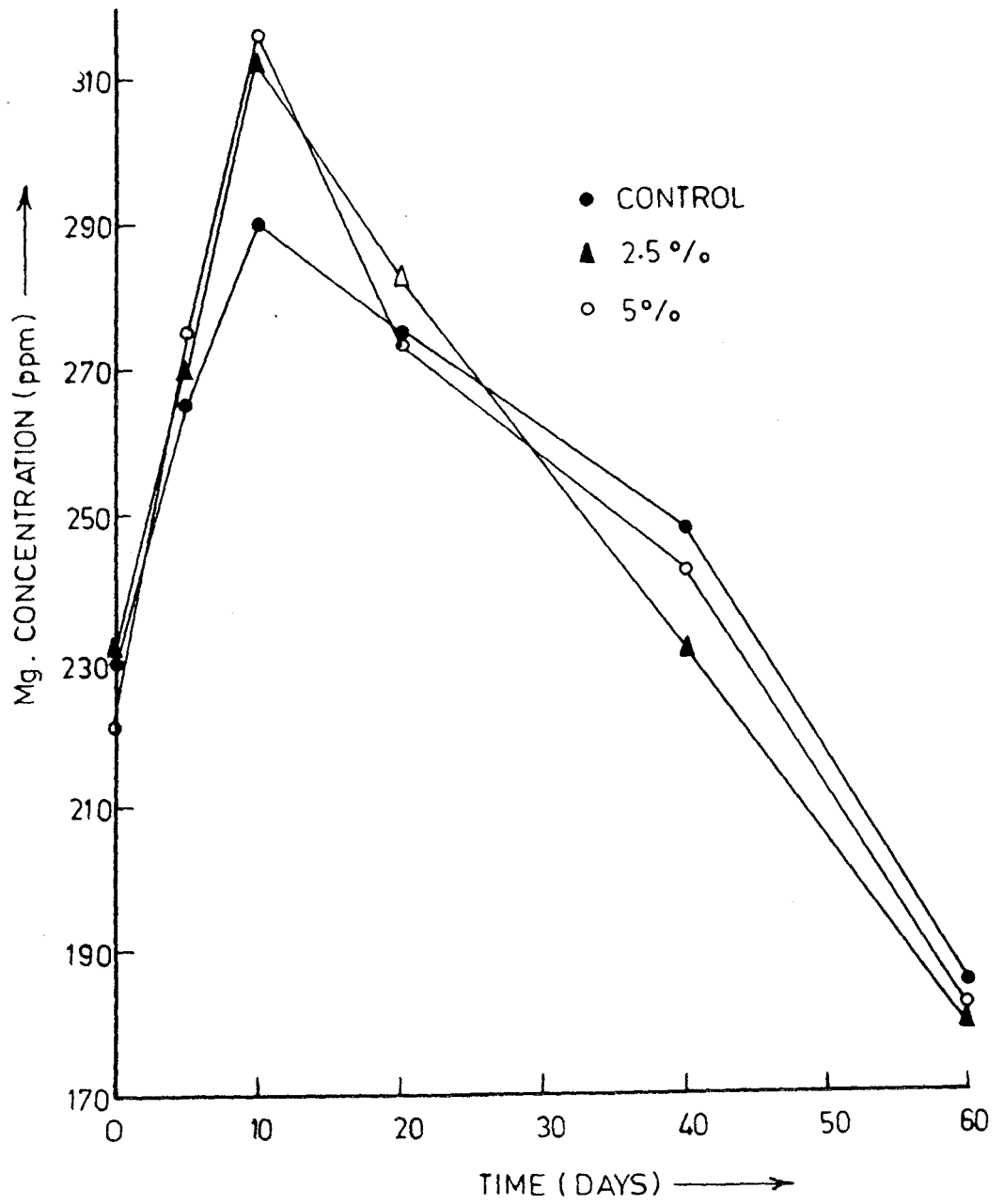


Fig. 9 : Available Mg in layer c

sixtieth day a gradual decreased pattern is observed.

Layer "c" level of Mg (available) goes on increasing till tenth day of experiment which thereafter decreases gradually till last day of the experiment.

Flyash contains Mg (available) in lesser amount (132.5 P.P.M.) than that of the soil (250, 234, 222 P.P.M. in layers "a", "b" and "c"). It is manifested from the graph of the layer "a" in figure . Sharp decrease up to tenth day in layer "a" is largely due to leaching effects. Subsequent sharp increase is probably due to time lag effect of Mobile-immobile phase (which is discussed in full details while discussing Ca changes). Weathering, Microbial activity, etc. may also have contributed. *Later on leaching predominates.*

Total salts leached from column packed soil manure mixtures were significantly less than the total salt inputs. The loss of cations, calculated from the total soluble plus exchangeable cations in the control column and in the added manure minus these quantities

after leaching, was greater for Ca and K than for Mg and Na which was attributed to reversible K fixation and precipitation of Ca salts from solutions (A. Shaviv, W.A. Jury and P.F. Pratt; Soil Science, 1986).

Layer "b" shows sharp increase in Mg level on fifth day as more leaching of Mg is possible and accumulation may have taken place from upper layer. By tenth day level comes down as near (or even lower in control) as initial one largely due to leaching. Time lag effect of soil aggregate, weathering, microbial activity etc. probably increases the magnesium level on twentieth day which leaches down with time showing gradual decrease till the end of experiment.

Increase in layer "c" concentration till tenth day of experiment to great extent is due to more accumulation of Mg. More accumulation occurs as this layer receives water coming through layer "a" and "b" both. Further sharp decrease till end is probably due to overriding effect of leaching over other effects.

Magnesium (Total):

All the layers show gradual decrease in total Mg concentration with increase of time. Up to twentieth day of experiment, decrease is sharp. The decrease is more sharp in layer "a" than in "b" and "c". The total Mg content in soil is substantial. These patterns are evident from figure .

Total magnesium amount in fly ash is 990 P.P.M. which is very very less as compared to the total Mg content of soil (4200 - 4500 P.P.M.). This has caused the separation of graphic lines of control, columns mixed with 2.5% fly ash and 5% fly ash in layer "a" as evident from figure 10-11. Layer "a" graph says more leaching of Mg from amended columns. This may be due to the glassy matrix structure of fly ash in which Mg is at the external matrix and thus its rate of leaching is faster (C.J. Warren, and M.J. Dudas. J. Em. Qual, 1984).

Layers "b" and "c" show slight gradual decrease as simultaneously accumulation and other processes like weathering, microbial effects

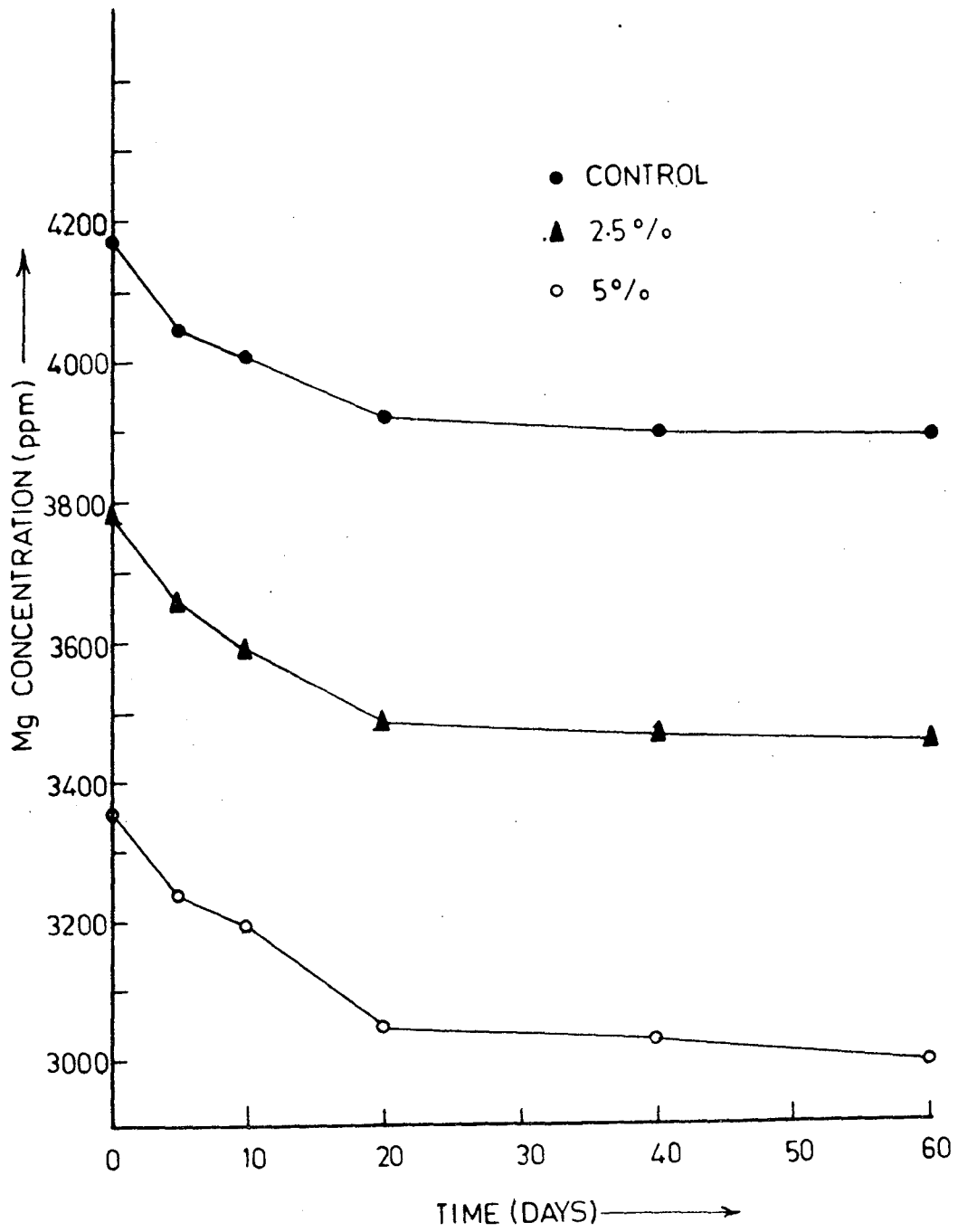


Fig. 10 : Total Mg in layer a

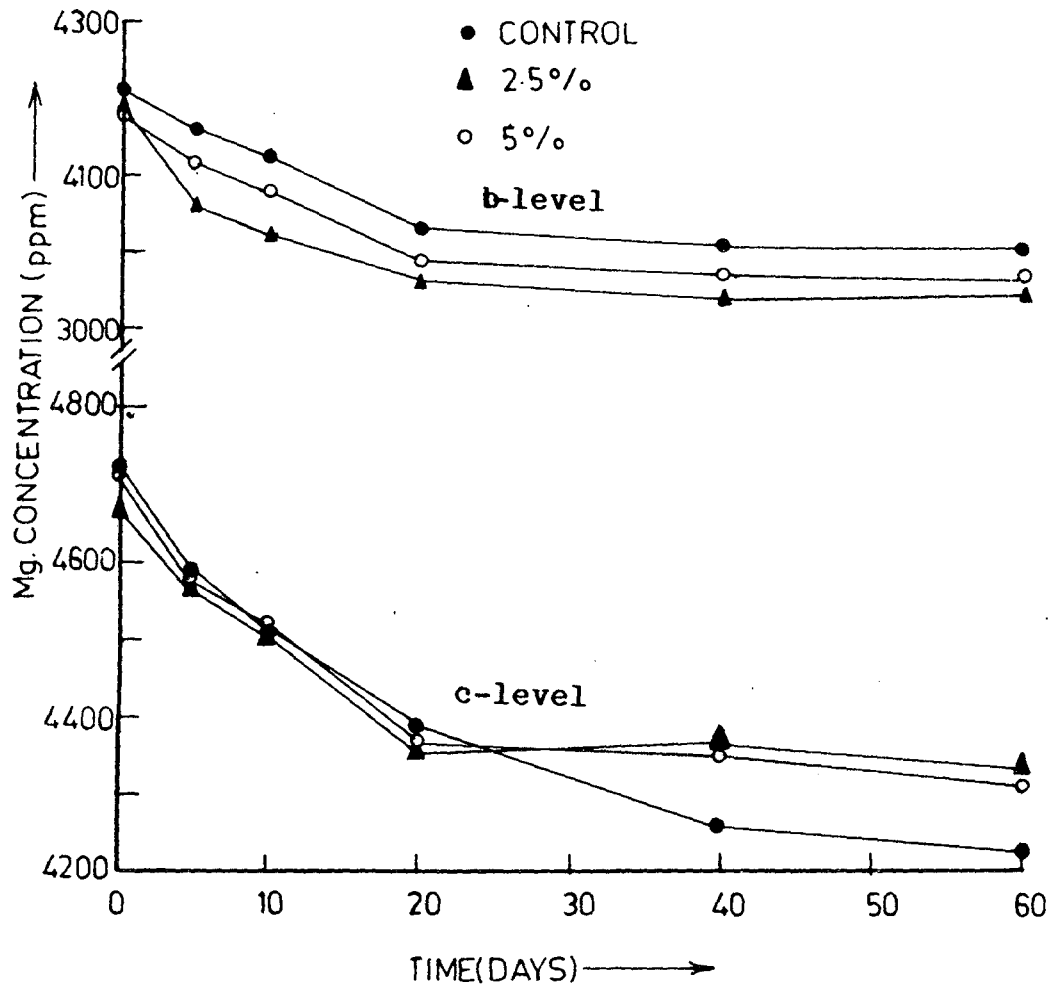


Fig. 11 : Total Mg in layer b & c

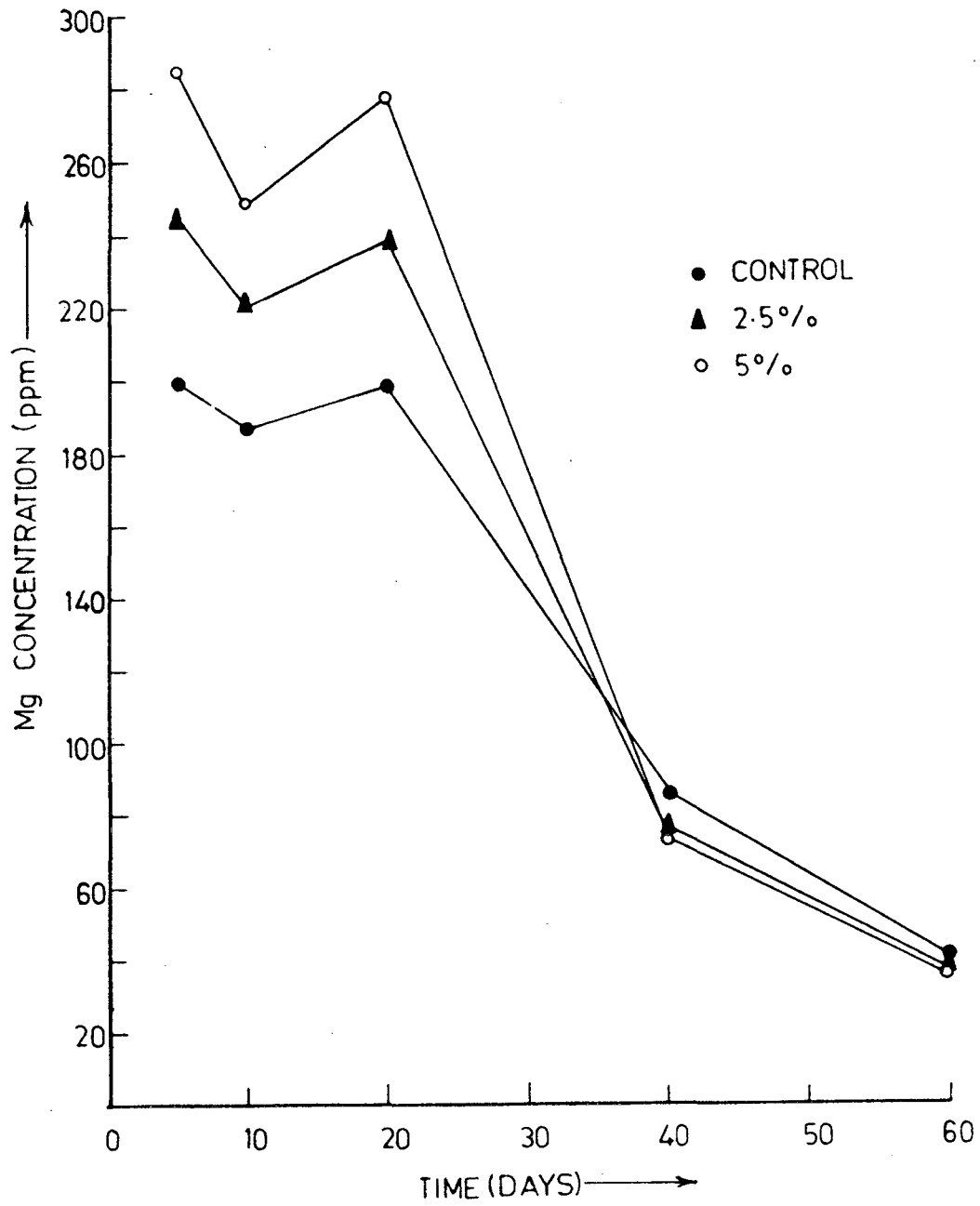


Fig. 12 : Mg in Leachate

etc. also goes on. The increase-decrease patterns as found in the available one are not found in the total's pattern. This is probably due to the fact that Mg (total) is very very large as compared to Mg (available) and changes are not that much substantial such that it can affect the pattern.

Magnesium (Leachate) :

Mg concentration in leachate has followed the pattern as shown in figure 12 says that leaching is maximum till 5th day of experiment which decreases on tenth day. It again increases up to the fifth day level on twentieth day which further shows sharp decrease on fortieth day. There is slight difference between fortieth and sixtieth day leachate concentration of Mg.

Sodium (Available)

It is observed from the Table 8 and figure 13 that the sodium (available) concentration in various layers follow different patterns. Pattern of layer "a" is different from layer "b" and "c". In layer "a" Na (available)

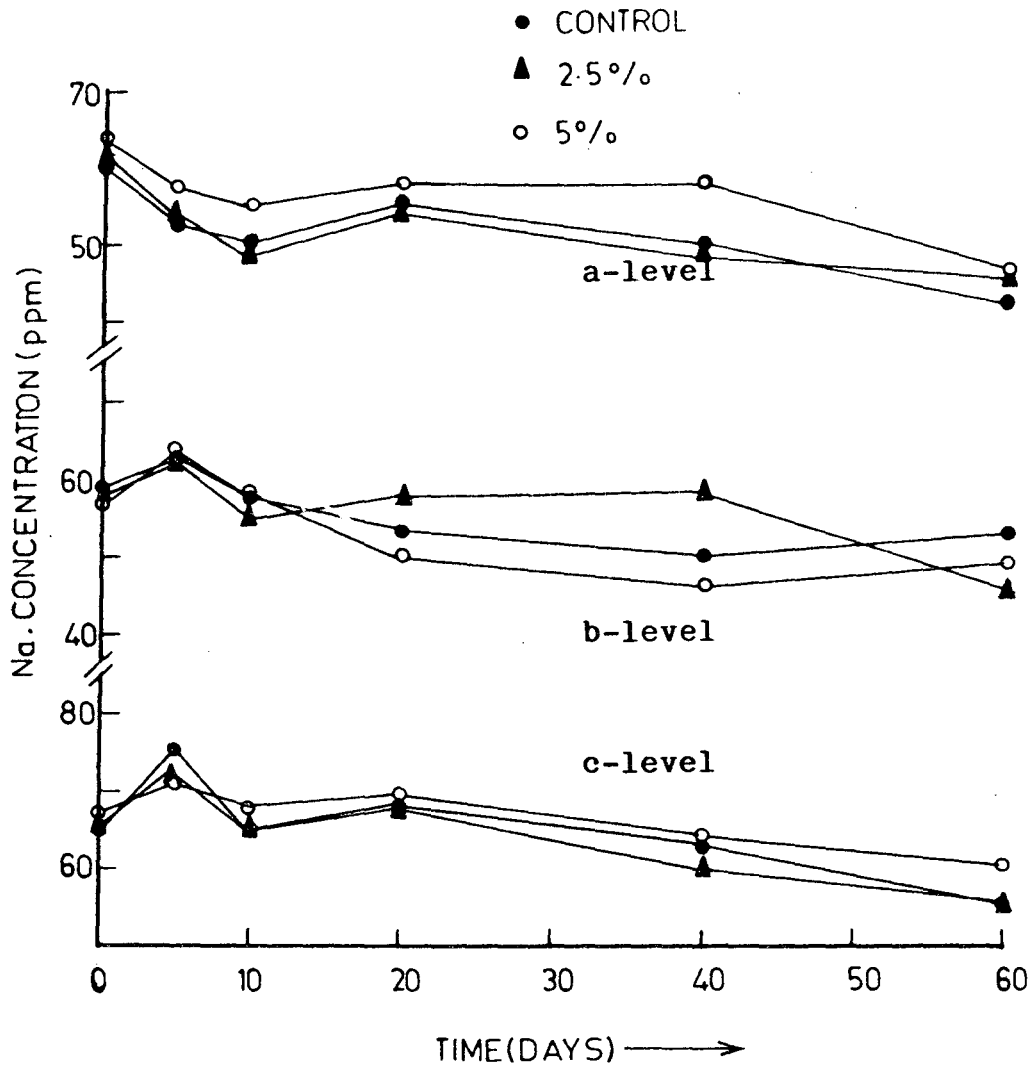


Fig. 13 : Available Na in various layers

concentration decreases gradually up to tenth day which increases on twentieth day of experiment. Subsequently it follows a gradual decrease. The overall difference comes about 18 P.P.M. One remarkable thing in layer "a" which is amended with 2.5% and 5% (w/w) fly ash in two treatment columns while leaving one without amendment as control, is that the initial sodium content is approximately similar in all the three. This is due to the fact that available sodium content in flyash is similar to that in the soil.

Layer "b" and "c" show similar patterns with the difference that over all points there is more concentration of sodium in layer "c" with a slightly increased trend on twentieth day. Over all difference in these layers comes about 10 P.P.M.

The above patterns of Na (available) concentration in different layers of soil over the two-month period in present experiment may be due to the difference of situations in which the three soil layers are, as one of the important causes. Sodium leaching is less

complex as compared to Mg and Ca. First layer receives double distilled water and only leaching effect takes place while in second and third (i.e. "b" and "c") layer accumulation of Na coming from upper layers is one of the phenomenon going on inside soil. The phenomenon overriding other will manifest in the patterns. *Soil characteristics of light texture type also contributes.*

One recent concept of "Time Lag Effect" due to mobile-immobile phase in soil aggregates can explain very well the increase in concentration on twentieth day in layer "a" and also such increase in layer "b" and "c". According to the above concept the Na from the intramolecular pores are readily accessible to mobile solutions and leaches down first. But the Na from slowly accessible exchange sites are located in the immobile solution. Its diffusive transfer to mobile solution phase creates a time lag due to which increased Na (available) concentration is manifested after a decrease. In fact a competition sets up among various effects, whichever predominates gets manifested in the pattern.

Sodium (Total)

After going through table 9 and figure 14 we see that there is decreasing trend throughout the experimental period in layer "a" while in layers "b" and "c" initial decrease is up to fifth and tenth day of experiment respectively. Thereafter the graphic lines for both lower layers make a slight arch with a slight decreasing trend towards the end of experiment. The initial concentration for all the three sets of experiments are same for layers "b" and "c". The overall change in Na concentration is 40 P.P.M. in layer "a" and 10 P.P.M. in layers "b" and "c".

The total sodium content in flyash is 85 P.P.M. Thus Na content of flyash is more in available form. Layer "a" shows sharp rate of decrease of Na concentration till twentieth day of experiment which thereafter slows down. The overall gradual decrease is due to leaching of sodium. Its rate is faster in first twenty days. Graph line shows greater gradient for column containing 5% flyash than column containing 2.5% which in turn has greater than

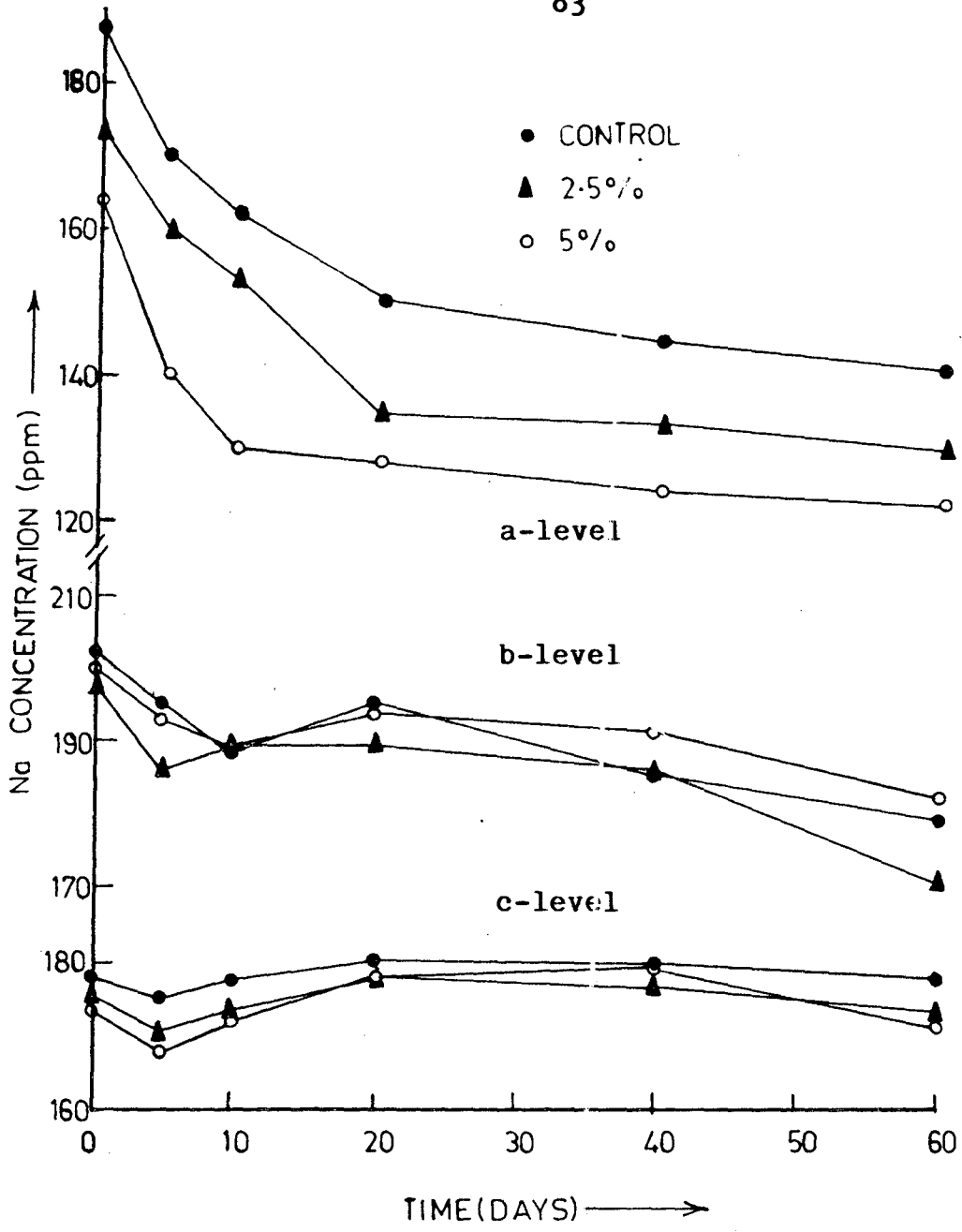


Fig. 14 : Total Na in various layers

control one. Here this trend projects that ions are getting leached from fly ash easily than from soil. This may be due to the structural difference of soil aggregates than fly ash particles.

In layer "b" we see a decrease in Na level up to tenth day. It says that more leaching than accumulation is taking place. Thereafter level goes up probably due to predominance of accumulation which slowly come down towards the end of experiment. The over all difference comes about meagre 10 P.P.M.

Layer "c" receives Na coming out with mobile solutions from both upper layers "a" and "b". Thus increased accumulation has taken place. So this layer shows decrease only for five days which increases subsequently till twentieth day. Thereafter same level is maintained till fortieth day of experiment and finally a slight decrease occurs towards the end of experiment. After fifth day of experiment, pattern of this layer is largely due to the predominance of accumulation which slightly slackens towards the end of experiment. The other factors like

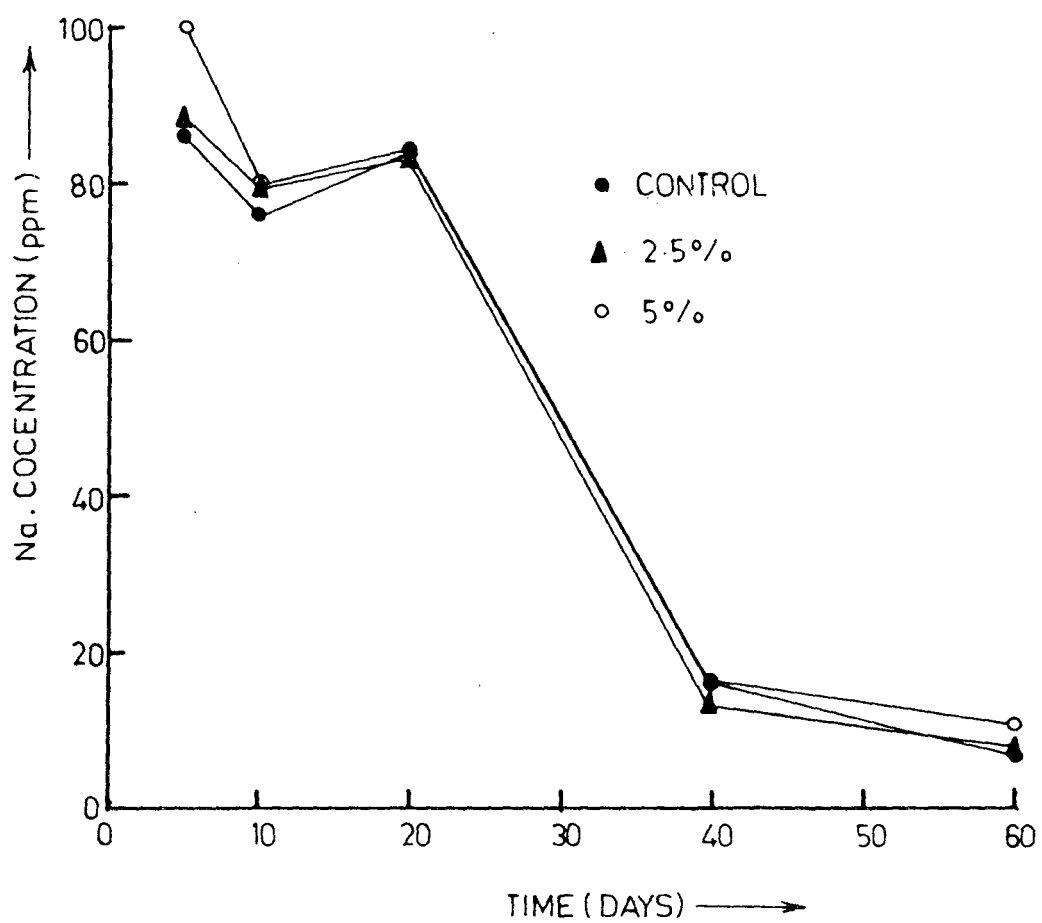


Fig. 15 : Na in Leachate

weathering, mineralization, microbial activity may also be contributing.

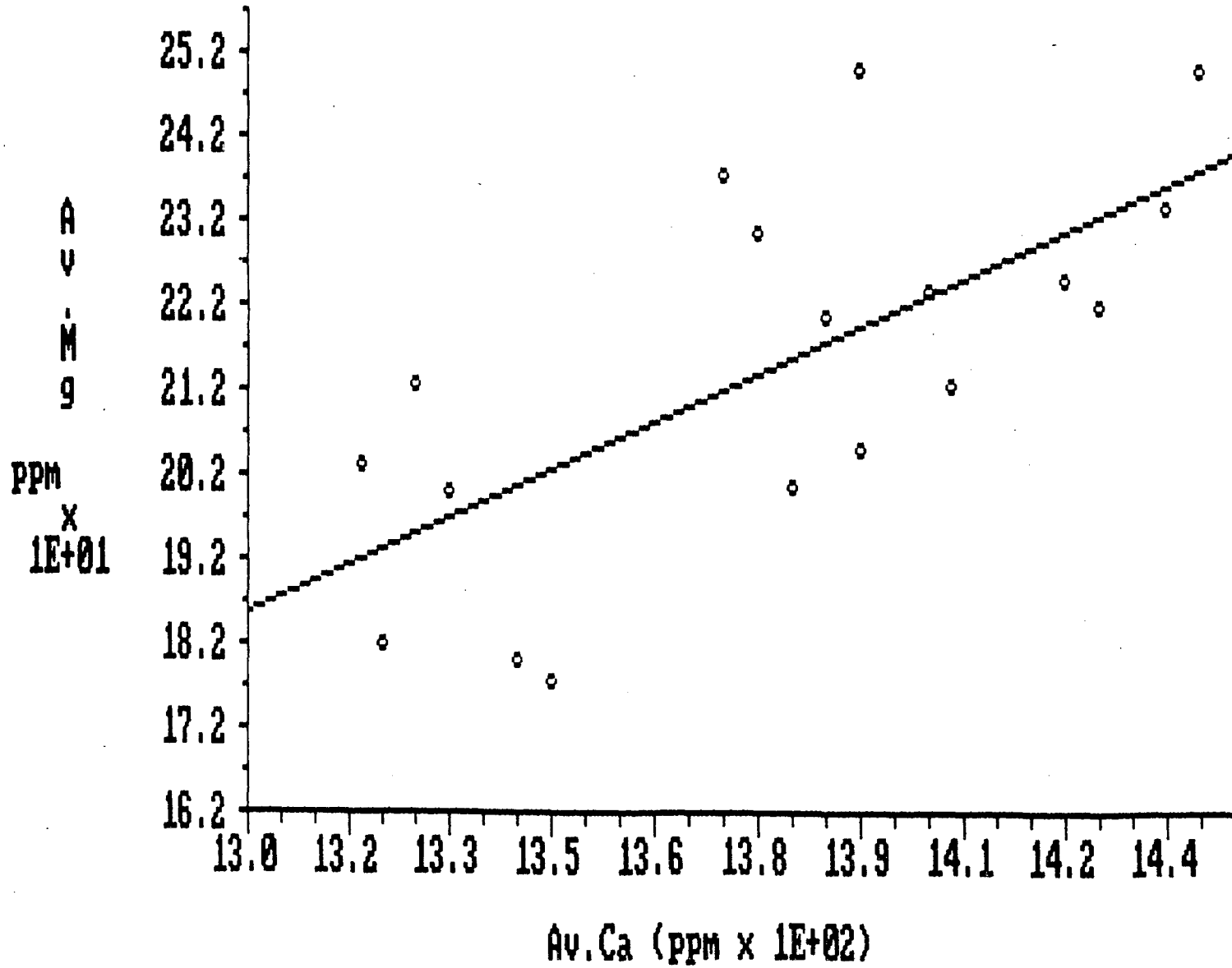
Sodium (Leachate)

By the observation of Table 12 and figure 15 it is apparent that leaching rate is maximum in first five days which decreases slightly on tenth day of experiment. On twentieth day Na level again shows an increase with a subsequent sharp decrease till fortieth day. After fortieth day and towards end of experiment very slight change is observed.

Correlation Co-efficient :

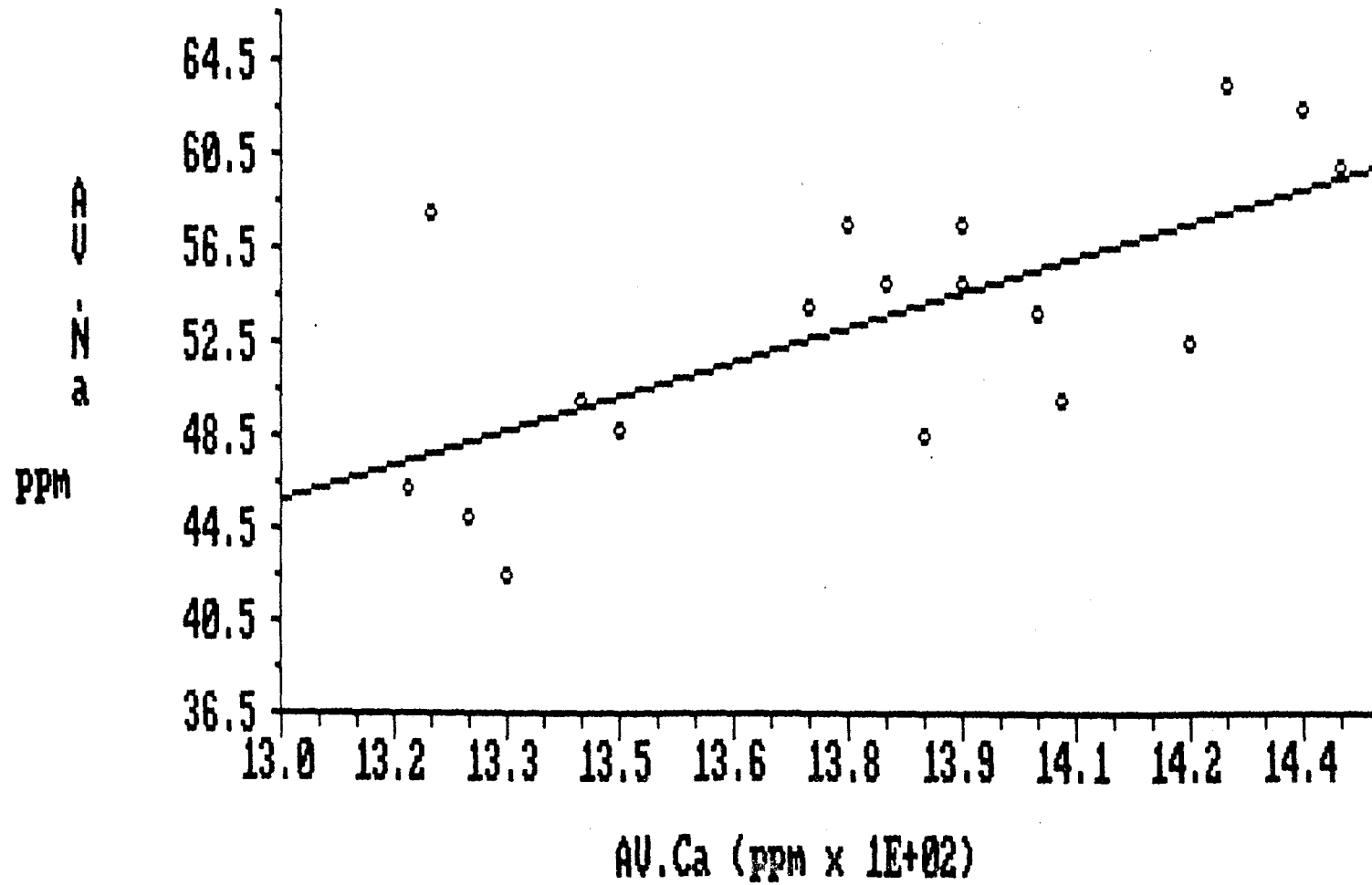
From correlation co-efficient data it is apparent that pH of soil is largely dependant on available Ca content whereas towards E.C. both Ca and Na contributes. Correlation co-efficient values are significant for T Ca vs. T Na, T Ca vs. T Mg and T Ca vs. O.C. correlations.

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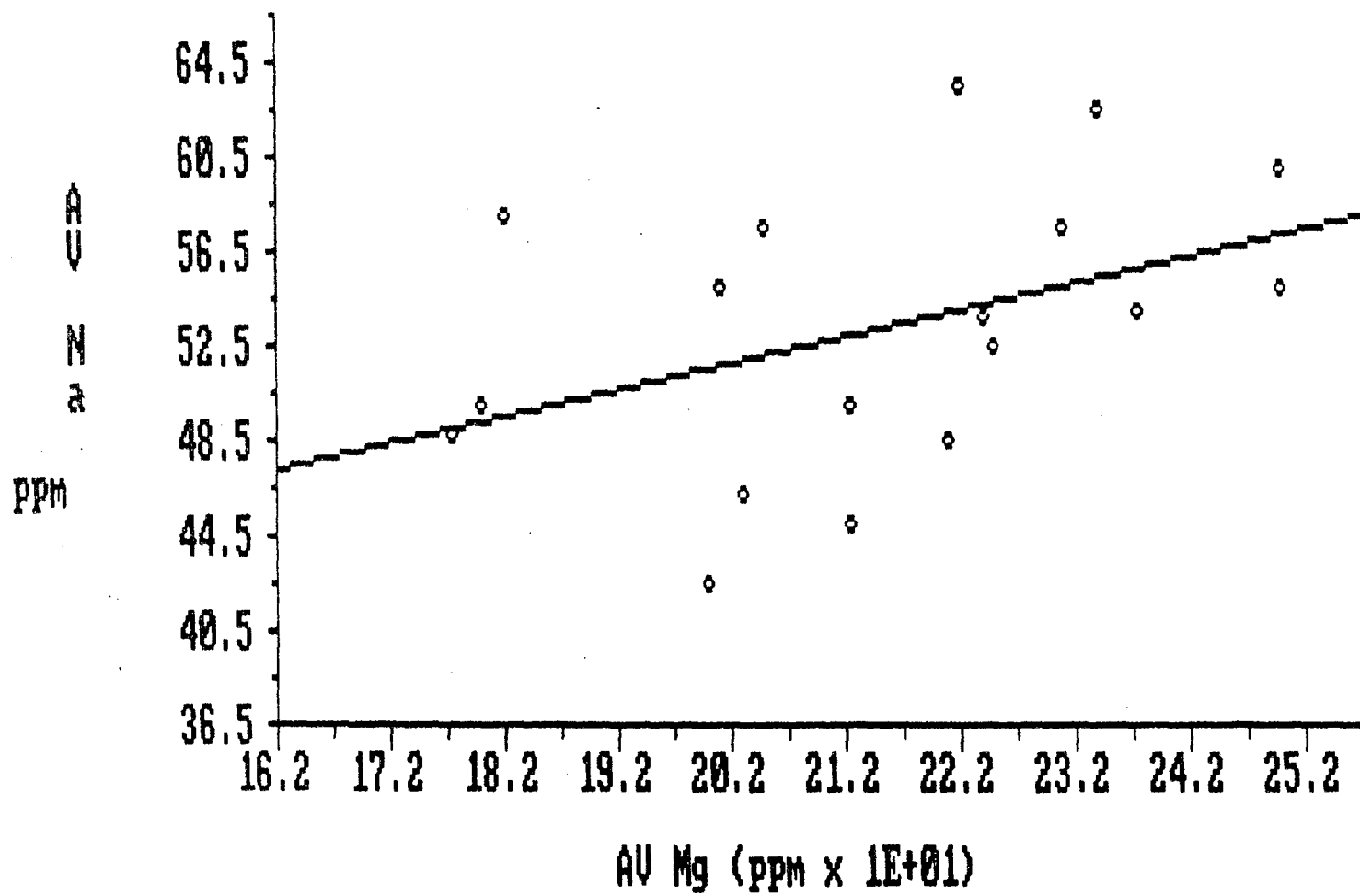
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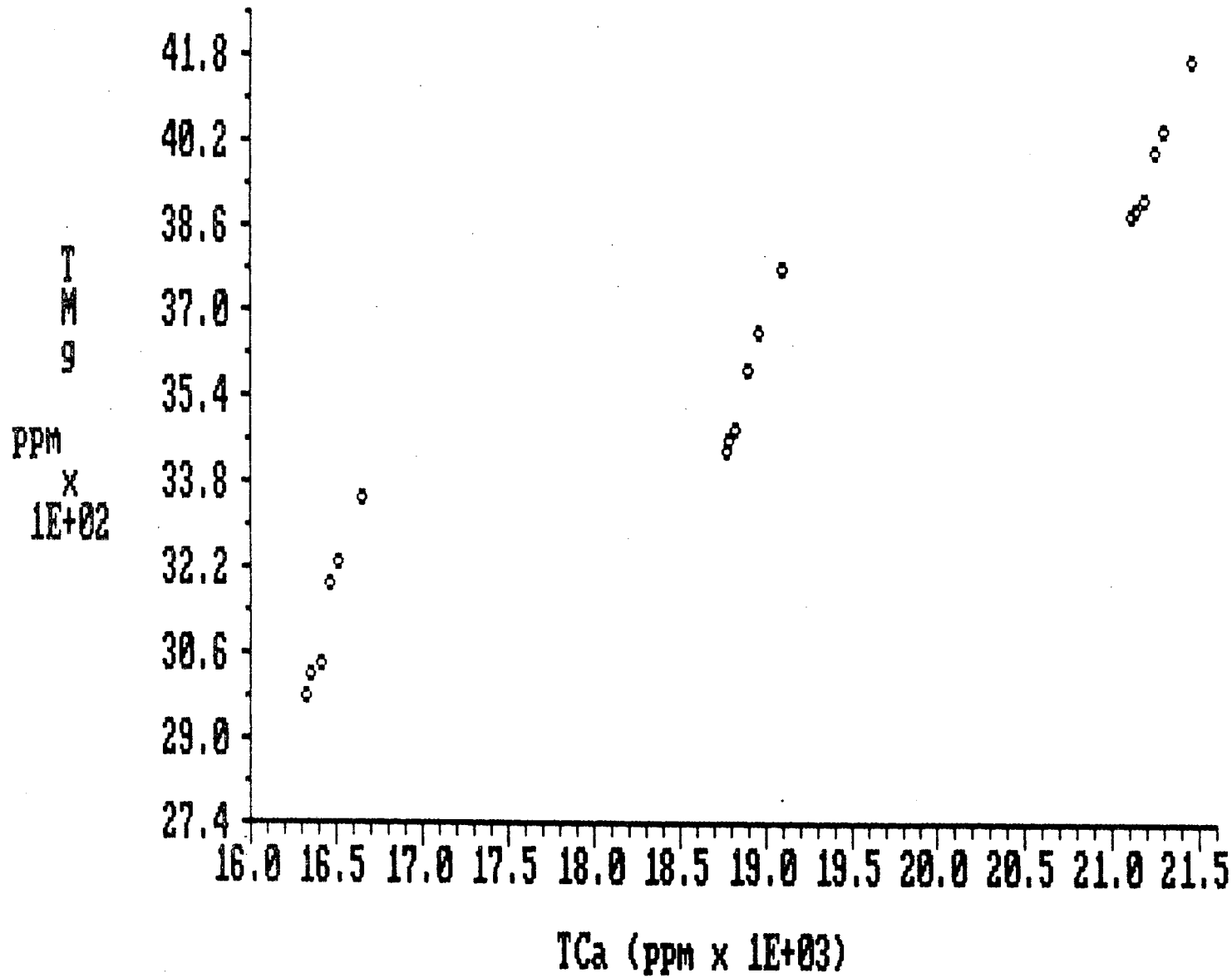
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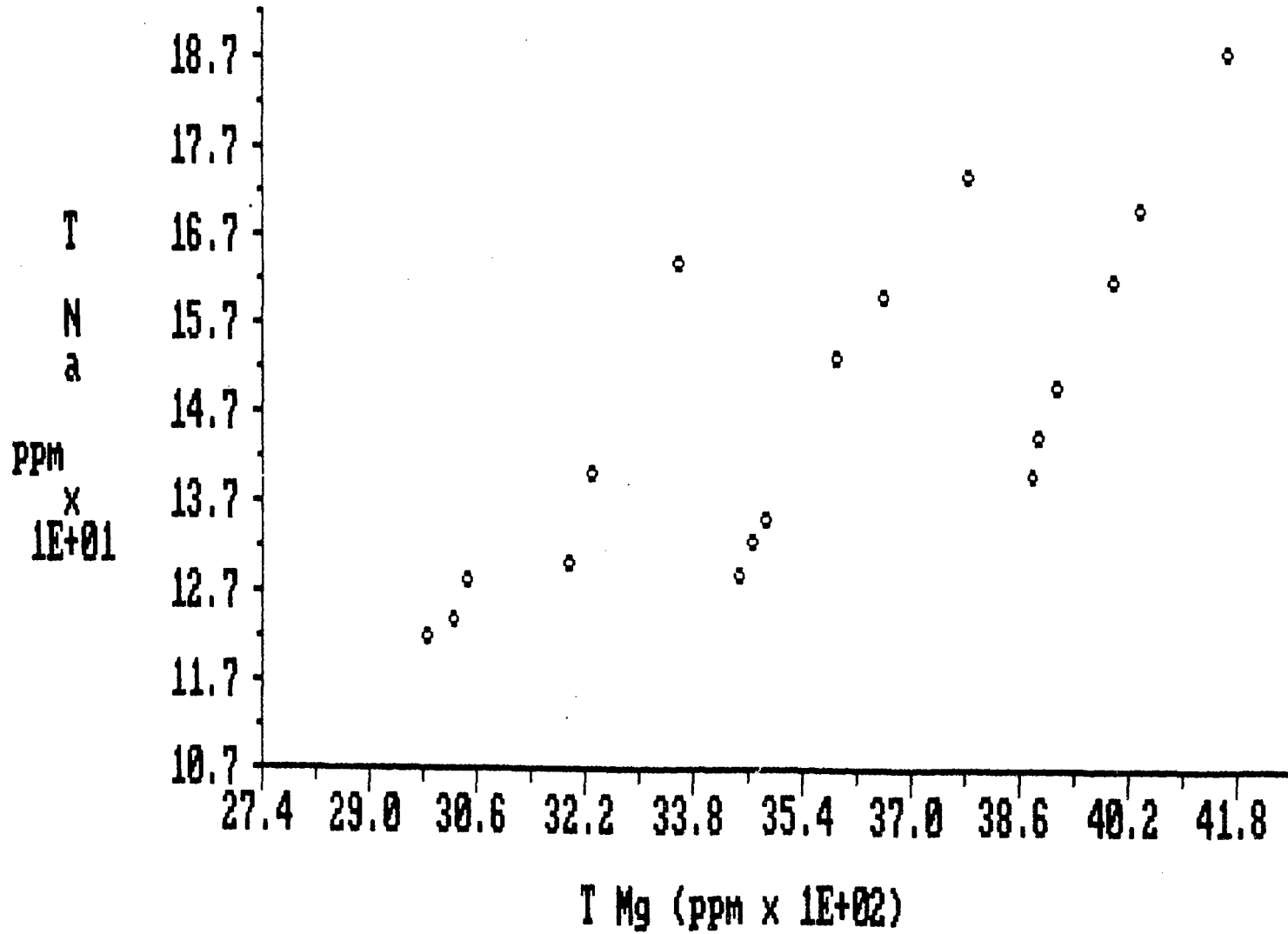
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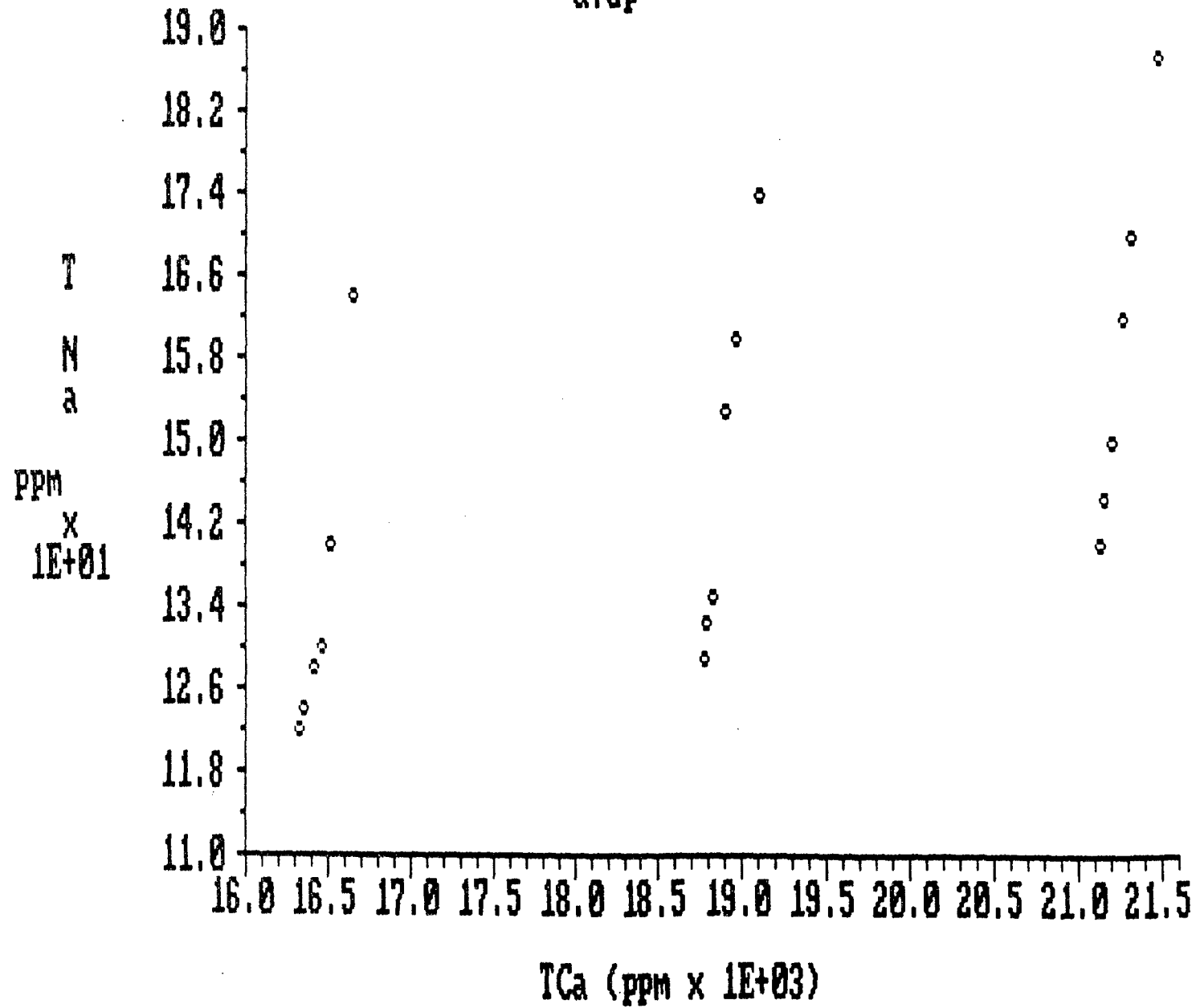


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SUMMARY AND CONCLUSION

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Delhi soil was filled in the fibre glass columns up to 70 cms maintaining the profile of soil as it is in the field. After mixing fly ash (collected from Badarpur thermal power station) in upper 15 cm layer of the columns, except the control one, it was leached with double distilled water (2 litre/day in each column) for 60 days to study the changes of Ca, Mg, Na and other soil parameters. The results obtained from the experiment are summarised here.

- i. pH and E.C. values has decreased periodically in our experiment whereas O.C. change is very very less.
- ii. There is evidence of Ca level decrease in upper layer due to leaching but in lower layers accumulation is also observed. This observation is supported by the less Ca content in leachate. pH being in basic range, Ca precipitation as phosphates is proposed. Fly ash content of Ca is largely in available form and available Ca content of fly ash is near to the available Ca content of soil.

iii. Different patterns of Mg level change in different layers is observed. Leaching effect predominates in upper layer where as accumulation contributes substantially in lower layers, which is manifested in the graphic patterns obtained. Fly ash contains over all less amount of Mg. There is correlation among leaching and accumulation phenomena in the three layers and the leachate concentration.

iv. The Na content in soil as well as fly ash is very less. Fly ash contains Na also in mostly available form. Na leaching predominates in upper layer where as ^{both} accumulation ^{and leaching} plays important role in lower layers. Leachate concentration corresponds the change pattern in the layers although Na in leachate is less.

We find that the total content of the all three Ca, Mg. and Na is very very less in fly ash as compared to soil. But the available Ca and Na is in a considerable amount as compared to soil which can even prove beneficial. The leachate content is

almost inconsiderable for ~~Ca & Mg~~. Periodic changes studied for above parameters in different soil layers indicate accumulation in lower layers but at the same time it is not substantial in leachates. In the case of calcium it is proposed that probably precipitations as phosphates ^{and microbial assimilation} has taken place which is supported by the pH and phosphate content of soil and fly ash. Mg and Na also show some accumulation.

Overall Ca content is more in our experimental soil and Na is less. This is probably due to the cause that more Ca makes soil more porous and mass flow of Na, being more soluble, predominates. Apart from that bivalency of Ca also plays role.

Important role of Ca in determining soil properties is also supported by the correlation coefficient values with pH and E.C. as tabled in table . The +ve correlation found between TCa and TNa is due to the fact that over the total experimental period both TCa and TNa follows same pattern of change due to leaching, accumulation, precipitation, immobilisation, etc. effects. -ve correlation has been found between Tca and organic carbon content of soil. TCa and TMg correlation

are also due to the above reason.

So when we integrate the whole results and think in terms of our experimental objective we came to the conclusion that as far as Ca, Mg and Na parameters are concerned, Badarpur thermal power plant fly ash with application rate of 2.5% and 5% of total ^{Soil} indicates the possibility of utilization of fly ash through land application for agricultural production although, it shows the possibility of underground contamination particularly when soil is of light texture one. But from the point of view of Environmental problem, we suggest that an extensive long term research project should be taken to assess the possibility of hazardous effects including groundwater contamination.

BIBLIOGRAPHY

BIBLIOGRAPHY

Allen, E. Stewart., Grimshaw, H. Max., Parkinson, A. John., & Quarmby Christopher. Chemical analysis of Ecological Materials. (1974) Oxford, Blackwell.

Arthur, M.F., Zwick, T.C., Tolle, D.A., and Voris, P. Van., (1983). Effects of fly ash on microbial CO₂ evolution from an agricultural soil. Soil Science. 210-216.

Adams, L.M., Capp, J.P. and Eisentrout E. Reclamation of Acidic Coal Mine Spoil with Fly Ash. Bureau of Mines Report of Investigations R1-7504(1971).

Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C. and Straughan I.R. Utilisation and disposal of flyash and other coal residues in terrestrial ecosystems: A Review. J.Env. Qual.9: 333-344(1980).

Brady, N.C., The nature and properties of soil (1974).

Bishwas and Mukherjee, Soil Science (1987).

Block C. and Dams. R. Inorganic composition of Belgian coal ashes. Environ. Sci. Technol. 9 (1975), 148.

Barber, G., in Ash utilization, proceedings of the third international Ash utilization symposium, sponsored by National Coal Association, Edison Electric Institute, American Public Power Association, National Ash Association and Bureau of Mines, Pittsburgh, Pa., Bureau of mines information circular 8640, (1974).

Chang A.C., Lund L.J., Page A. L. and Warneke J.E.: Physical properties of fly ash amended soils. J. Env. Qual. 6, 267 (1977).

Capp, J.P., and Engle, C.F. (1967). Fly ash in agriculture. Bur. Mines. Inf. Circ. No. 8348.

Cherkaner, D.S. (1980). The effect of fly ash disposal on a shallow ground water system. Ground water 18: 544-550.

Capp, J.P., and Spencer J.D. Fly ash utilization- A summary of Applications and Technolgy. Bureau of Mines Information Circular IC-8433 (1970).

Campbell, D.J., Fox, W.E., Atken, R.I. and Bell, L.C. (1983). Physical characteristics of sands

amended with fly ash. Aust. J. Soil Res. 21, 147-54.

Dudas. M.J., Long term leachability of selected elements from fly ash. Environ. Sci. Technol. 15: 840-843 (1981).

Doll, E.C., and Lucas, R.E. (1973). Testing soils for potassium, calcium and magnesium in soil testing and plant analysis. (Eds L.M. Walsh and J.D. Beaton) p.p. 133-51 (Soil Sci. Soc. Am: Madison, Wisc.)

Dudas M.J. (1981). Long-term leachability of selected elements from fly ash. Environ. Sci. Technol. 15: 840-843.

Dubey, P.S., Pawar K., Shringi, S.K. and Trivedi L. (1982). The effects of fly ash deposition on photosynthetic pigments and dry matter production of wheat and gram. Agro. Ecosystems, 8: 137-140.

Elseewi, A.A., A.L. Page, and S.R. Grimm. (1980). Chemical Characterization of fly ash aqueous systems. J. Env. Qual. 9:424-427.

Furr A.K., Parkinson, T.F., Hinrichs, R.A., Van Champan, D.R., Bache, C.A., Gutenmann, W.H., John.,

L.e., St., Jr. Pakkala, I.S. & Lisk, D.J. (1977). National survey of elements and radioactivity on fly ashes. Absorptions of elements by cabbage grown in fly ash soil mixtures. Environ. Sc. Technol., 11, 1194-1201.

Furr, A.K., William C. Kelly., Carl. A. Bache, Walter H. Gutenmann, and Donald J. Lisk., (1976). Multielement uptake by vegetables and millet grown in pots on fly ash amended soil. J. Agric. Food Chem. Vol.24, No. 4, 885-888.

Giedrojć, B., Fatyga, J., and Hryniewicz, Z. (1980). The effect of fertilization with ashes from black coal burned in electric power stations on the properties of sand soil and crops. Polish J. Soil Science. 13: 163.

Hodgson. L., Dyer. D and Brown D.A. Neutralisation and dissolution of high calcium fly ash. J. Env. Qual. 11: 97-98 (1982).

Hodgson, D.R. & Holliday, R. (1966). The agronomic properties of pulverised fuel ash. Chem. Ind., 20: 785-790.

Jones, L.H., and Lewis, A.V. (1960). Weathering of fly ash. *Nature* 185, 404-5. .

Jackson M.L., *Soil Chemical Analysis* (1973). Prentice hall of India Pvt.Ltd.

Kopsick, D.A., and Angino E.E. Effect of leachate solutions from fly ash and bottam ash on ground water quality. *J. Hydrol.* 54: 341-356.

Klein D.H., Andren A.W., Carter J.A., Emory J.F., Feldman C., Fulkerson W., Lyon. W.S., Ogle. J.C., Talmal.Y., Van Hook R.I. and Botton N. Pathways of thirty seven trace elements through coal fired power plant. *Environ. Sci. Technol.*, 9/10 (1975). 976.

Martens, D.C., (1971). Availability of plant nutrients in fly ash. *Compost science* 12 (16) 15. .

Mansell., R.S., Bloom. S.A., Selim, H.M. and Rhue, R.D. (1986) Multispecies Cation leching during continuous displacement of electrolyte solutions through soil columns. *Geoderma* 38: 61-75.

Mishra, L.C., & Shukla, K.N. (1986). Edaphic properties of fly ash from a coal fired power plant

at Kanpur, India. Environmental Pollution (Series B.) 11: 55-66.

Martens, D.C., et al (1975). Effect of soil application of fly ash on chemical composition and yield of corn (ZEA MAYS L) and on chemical composition of displaced Soil solutions. Plant and soil, 42: 465-476.

Phung. H.T., Lund L.J., Page A.L. and Bradford G.R., Trace elements of flyash and their release in water and treated soils J. Env. Qual. Vol. 8, No.2 (1979).

Patel C.B., Seth P.C., Pandey G.S., Fly ash fallout from a thermal power station in a post rainy season, J.Inst. Eng. (India), 65 (1985).

Phung, H.T., Lam, H.V., Page, A.L., and Lund, L.J. (1979). The practice of leaching boron and soluble salts from fly ash amended soils. Water, Air, Soil Pollut. 12, 247-54.

Page, A.L., Elseewi, A.A., and Straughan I.R. (1979). Physical and chemical properties of fly ash from coal fired power plants with reference to envrironmental impacts. Residue Rev. 71, 83-120.

Patel, C.B., & Pandey, G.S. (1986) Alkalinization of soil through thermal power plant fly ash fall out. The science of the total environment, 57: 67-72.

Rees, W.J. & Sidrak G.H. (1956). Plant nutrition on fly ash. Plant soil., 8, 141.

Roy, W.R., and Griffin., R.A. (1982). A proposed classification system for coal fly ash in Multidisciplinary Research. J. Env. Qual., Vol.11, No.4, 563-568.

Shaviv, A., Jury, W.A., and Pratt P.F. (1986). Exchange, Fixation, and precipitation of cations during leaching of soils amended with manure: 1. Column experiments soil science Vol. 141 No.3 : 237 - 243.

Taylor, E.M., Schuman G.E. (1988). "Fly Ash and lime amendment of acidic coal spoil to aid revegetation. J. Env. Qual. Vol. 17 No.1. 120.

William, R. Roy., Robert A., Griffin., Donald.R. Dickerson, and Rudolph M. Schuller (1984). Illinious

Basin Coal fly ash. 1. chemical characterisastion
and solubility. Environ. Sci. Technol., 18, 734-739.

Wong., M.H. & Wong, J.W.C. (1986). Effects of fly
ash on soil microbial activity. Environmental
Pollution (Series A) 40 127-144.

