

THE RENOVATION OF DOMESTIC EFFLUENT  
THROUGH A FOREST SOIL

by

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## ABSTRACT

An investigation of the trend over time of the concentration of selected soil leachate constituents contained in domestic effluent applied to a ferro-humic podzol forest soil was undertaken. From July 15, 1976 to November 12, 1976, 2 cm of domestic effluent, selectively supplemented with commercial fertilizer, was sprayed twice weekly to a 900 m<sup>2</sup> plot situated on a mountain slope. Ten porous plate tension lysimeters installed at various depths and locations in the forest soil continuously extracted the resulting soil leachate. The soil leachate samples collected twice per week over the duration of the study, as well as the applied effluent samples, were analysed for chloride, nitrate and total Kjeldahl nitrogen and total and orthophosphorus.

Based on the concentrations of nitrate nitrogen, total Kjeldahl nitrogen, and total phosphate in the applied effluent as well as the average volume of effluent applied over the total irrigation plot, 48.4 kg/ha (43.2 lb/acre) nitrate nitrogen, 93.7 kg/ha (83.6 lb/acre) total Kjeldahl nitrogen, and 43.5 kg/ha (38.6 lb/acre) of total phosphate were applied to the plot during the project period.

The chloride ion gradually increased in concentration over the duration of the study until it eventually equalled the value of the chloride in the domestic effluent. This

gradual increase was a possible result of the retention of the initial amounts of applied chloride on the anion exchange sites in the soil, which when satisfied, allowed subsequent amounts of applied chloride to move through the soil with the applied effluent.

No ortho or total phosphorus was detected in the soil leachate samples collected over the duration of the study. While recognizing the possibility of microbiological immobilization of a portion of the applied phosphorus, the most likely retention mechanism was the adsorption of the phosphorus by the amorphous iron and aluminum compounds in the soil.

Nitrate and total Kjeldahl nitrogen were detected in low concentrations in the soil leachate samples only in the time interval following the application of domestic effluent containing greatly increased effluent concentrations of nitrate and total Kjeldahl nitrogen. The increased concentrations resulted from the addition of commercial fertilizers to the treatment lagoon. Such trends suggest microbiological immobilization was playing a role in the removal of the nitrogen compounds. The retention of ammonia, the major component of total Kjeldahl nitrogen, on the cation exchange sites and the retention of nitrate nitrogen on the anion exchange sites would also be occurring.

In order to investigate the magnitude of the reaction between phosphorus and the iron and aluminum compounds in



the podzol soil, batch scale laboratory tests were undertaken. The time-phosphorus adsorption results indicate that the phosphorus reacts very quickly with the amorphous iron and aluminum compounds in the soil on the plot. The Langmuir and Freundlich isotherms were calculated as was the phosphorus adsorption maximum based on the Langmuir isotherm. The calculated phosphorus adsorption would probably give a conservative estimate of the phosphorus removal potential since the isotherm is based only on the initial and not the long term phosphorus adsorption reactions.

Despite the fact that the soil water content was continually above the soil water content at the field capacity, no phosphorus and very little nitrogen was detected in the soil leachate samples. Such results suggest that a phosphorus or nitrogen balance may be a useful irrigation operating criterion rather than the commonly accepted water balance criterion. In such a situation the phosphorus or nitrogen requirements over the growing season of the crop would be evaluated and met by the application of domestic effluent.

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## 1.0 INTRODUCTION

The application of domestic effluent to land has received a great deal of consideration as an alternative method of treating domestic wastewater. The incentive to consider the recycling of domestic effluent has been generated by an increasing awareness of the problems associated with the discharge of effluent to bodies of water. The trend towards the increasing concentration of people in urban centers and the accompanying increase in the wastewater volume discharged to surface bodies of water has led to a general deterioration of surface water quality. If the manifestation of this decline of water quality was not a depletion of the dissolved oxygen in the watercourse and the associated chemical, physical, and biological implications of such a situation, it was a rapid acceleration of the eutrophication process. Eutrophication, a general term used to describe a complex sequence of changes in the aquatic environment caused by the presence of sufficient plant nutrients in water, is occurring in many water courses over a much reduced time span due to the addition of nutrients from man's activities. Whereas the natural eutrophication process in a waterbody may occur over thousands of years, the continual discharge of waste effluent has been reducing this time span to decades. The Okanagan Basin, Kamloops Lake and some parts of Kootenay Lake are testimony to the accelerated eutrophication process in some British Columbia waters. The

rapid increase in the natural process was attributed to the introduction of the nutrient compounds of nitrogen and phosphorus to the water. The land application of domestic effluent is viewed as a means of improving water quality by diverting nutrients from water to agricultural or forested land where ideally they would be utilized in the production of food and fibre crops.

A more fundamental view of the land application of domestic effluent is the attainment of the goal of "returning to the soil that which came from it". The plant nutrient compounds contained in the waste water are utilised to grow food from which the nutrients originally stemmed, resulting in the recycling of these nutrients. The reuse concept not only involves a reuse of the water component of the wastewater, but also the macro and micronutrients contained in the wastewater. The adsorption by the soil and the utilization of such plant nutrients by plants could convert an ecological liability to an agricultural asset.

Although the volume and method of applying effluent to the land may differ with time and location, the practice of recycling domestic effluent to the land is not a new concept. Land application of effluent dates back at least four centuries with some of the systems presently in use beginning operation over one hundred years ago. Historically, the rationale for land treatment emphasized disposal of the wastewater whereas the current rationale is based on reuse of the nutrient

material and/or treatment of the wastewater. Prior to the mid 19th century, the inhabitants of urban centers would temporarily store their wastes in vaults and privies. At periodic intervals the accumulated material would be transported to the surrounding countryside for disposal. A recognition of the relationship between the accumulating wastes and disease necessitated the development of storm drains which facilitated the rapid movement and handling of the wastes. The introduction of the centralized collection system and a recognition of the fertilizer value contained in the wastewater encouraged the emphasis on reuse and treatment of the wastewater. One of the earliest attempts at reuse rather than the disposal concept was the sewage farm at Bunzlau, Germany that began operation in 1550 (Pound and Crites, 1975). The late 1800's witnessed a proliferation of projects to apply domestic effluent on a managed agricultural basis by such cities as Berlin, Germany starting in 1869, Melbourne, Australia starting in 1893, Mexico City beginning in 1902 and Paris commencing in 1923. The land application of domestic effluent in the United States also dates to the turn of the century.

While the application of wastewater to land is prevalent in many parts of the world today, the methods employed may vary in such details as the degree of pretreatment, the quantity and quality of wastewaters applied, the manner of storage and application of the effluent, the type of vegetation grown, or the soil type being used. The Environmental Protection Agency in

the United States published an extensive field survey of 100 facilities where domestic or industrial effluents were applied to the land and discussed these operations in detail (Sullivan, Cohn and Baxter, 1973). For instance, at the Melbourne and Metropolitan Board of Works Sewage Farm in Weribee, Australia, 372,000 m<sup>3</sup>/day to 968,000 m<sup>3</sup>/day (80 Imgpd to 208 Imgpd) of domestic sewage is applied to 4,200 ha (10,400 acres) of crop land. Of that amount, 80% is subjected to primary treatment while 20% of the effluent volume is applied untreated. A grass crop is grown which sustains up to 15,000 head of cattle and 40,000 to 50,000 head of sheep during the spring and summer. In Mexico City, 47,000 ha (112,000 acres) of land are currently being irrigated with 2,166,000 m<sup>3</sup>/day to 17,328,000 m<sup>3</sup>/day (456 Imgpd to 3,648 Imgpd) of effluent. Plans call for an additional 40,000 ha (95,100 acres) of land to be eventually developed for the same purpose. The basically untreated effluent is applied to land used to grow vegetables including tomatoes, corn, chiles, and other truck garden crops as well as alfalfa and wheat. In India, land application of raw domestic sewage accounts for most of the treatment of 40% of the 2,083,000 m<sup>3</sup>/day (440 Imgpd) of wastewater produced by sewerred communities. Such treatment is carried out on 132 farms encompassing a total land area of 12,506 ha (30,902 acres). The crops produced on such sites include fodder grasses, cereals, beans, oilseed plants, cotton, sugar cane and various vegetable crops. On the sites irrigated with untreated domestic wastewater an

effort is made to restrict ground cover to non-edible crops. According to the survey, no facilities of the size and extent of those in Melbourne, Mexico City or India exist in the United States. The review found that the over 500 effluent irrigation projects currently in operation in the United States are much smaller in land area and handle a smaller volume of wastewater. Generally, the wastewater is treated to a secondary level prior to application to the land. In most cases a grazing crop is grown, harvested and then fed to animals. According to an Environmental Protection Service survey of facilities in Canada (Neurohr, 1975) there are 10 - 15 spray irrigation projects in operation with a small number in the planning stages. Using a sprinkler mode of operation, the city of Vernon, B.C. applies  $18,600 \text{ m}^3/\text{day}$  (4.0 lmgpd) of domestic effluent to agricultural land during the growing season. The effluent is subjected to secondary treatment prior to land application and the operation includes a facility that allows for up to seven months of effluent storage so that effluent irrigation is undertaken only during the growing season. A forage crop for animal consumption is grown on the land. Similar effluent irrigation projects are being planned for Salmon Arm, Cranbrook and 100 Mile House. While the details of the land application of sewage may vary, the essential purpose remains the same, the effective disposal of wastewater while securing the highest level of related benefits.

The most fundamental objective when applying domestic



wastewater to the land is for the resulting groundwater to contain smaller amounts of certain impurities in comparison to the amounts contained in the applied effluent. This renovation ability is derived primarily from the physical, chemical, and biological processes occurring within the soils that result in some degree of change in the levels of the constituents contained in the wastewater. Leeper (1972) classified the effluent-soil interactions into four main types. In the first case the material contained in the effluent may pass through the soil unchanged. A good example is the chloride ion which is so mobile in many soils that it is often used as a tracer in ground water percolation studies. Secondly, some of the applied material may be volatilized and released to the atmosphere. The nitrogen and carbon compounds are particularly susceptible to this type of reaction. Carbon compounds may be subjected to aerobic microbiological degradation with a subsequent release of carbon dioxide. Ammonia volatilization and denitrification of nitrates to nitrogen gas and nitrous oxide will occur readily under certain environmental conditions. Thirdly, constituents of the applied effluent may be removed from the soil solution by plants or micro-organisms. The plant uptake of nutrients contained in the effluent and the subsequent harvest of these plants is the most desirable interaction. The assimilation of sewage constituents by micro-organisms results in the incorporation of those materials into the soil organic matter. The fourth interaction between the applied

effluent and the soil constituents is the immobilization of specific constituents contained in the effluent. Several temporary or permanent constituent removal mechanisms are recognized: the ions contained in the effluent may displace ions attached to organic and inorganic colloids by ion exchange; they may undergo chelation into organic colloids; they may be absorbed into soil constituents or they may form amorphous or stoichiometric minerals. The distribution of the applied constituents contained in the wastewater among the four main effluent-soil interactions, as identified by Leeper (1972) is dependent on physical, chemical, and biological interactions which take place in the soil. These interactions are influenced by many factors related to the characteristics of the specific land treatment site and the characteristics of the effluent.

Of particular interest is the distribution of constituents contained in domestic water applied to a forest soil. Most forest soils, unlike grass or cropland, are covered with an organic layer of varying depth, composed of the products of the formation and decomposing activities of microflora. As plant or animal remains fall upon the soil, they are subjected to decomposition. A variety of organic complexes are formed which, with time, bear no trace of the original material. The native organic fraction in the soil originates from two sources: the original plant and animal debris entering the soil and the micro-organisms within the soil body. The latter work upon

the former and synthesize microbial protoplasm and new compounds which become part of the organic fraction (Allison, 1966; Alexander, 1965). While the organic layer exists in a dynamic state of continual decomposition, in general it has a relatively high organic carbon to nitrogen ratio (C:N) and a high organic carbon to organic phosphorus ratio (C:P). The addition of applied effluent to a soil with high C:N and C:P ratios will result in the biological immobilization of the readily available forms of nitrogen and phosphorus by the soil micro-organisms (Allison, 1966; Alexander, 1965; Webber and Lyshon, 1975).

The presence of iron and aluminum compounds in a low pH mineral forest soil (B horizon) also have a significant influence on the passage of phosphorus compounds contained in the applied effluent. The movement through the soil of the phosphorus compounds contained in the sewage is restricted by the chemical reaction that occurs between phosphorus and the aluminum and iron compounds (Hemwall, 1957; Kardos and Hook, 1976; Beek et al, 1977; John, 1974; Enfield and Bledsoe, 1975).

A major research project on the application of domestic effluent to a forest soil was undertaken at Pennsylvania State University (Pennypacker, Sopper and Kardos, 1967; Kardos and Sopper, 1974). From 1963 to 1969, 2.5 cm to 5 cm (.98 in to 1.9 in) of effluent per week was applied at .64 cm/hr (.025 in/hr) to forest soil plots containing stands of Hardwood and Red Pine trees. The soil texture varied from a silt loam to silty clay loam. Soil leachate samples, collected from deep

wells and from shallow tension lysimeters, were analysed for various constituents and compared with the constituents contained in the applied effluent. Phosphorus concentrations were reduced 97% to 99% at the 60 cm (23.6 in) depth on the Hardwood plot and the concentration in the deep wells ranged from .05 to .07 mg/l P on the same plots. This range of phosphorus concentration was similar to that found in the soil leachate samples collected from the deep wells on the control plots. The phosphorus removal was 93% to 97% in the soil leachate samples collected at the 60 cm (23.6 in) level on the Red Pine plots while in the soil leachate samples from the deep wells on the same plot the phosphorus concentration ranged from .03 mg/l to .06 mg/l P. Again, this range in phosphorus concentration values was similar to those found in the soil leachate samples collected from the deep wells on the control plots. The removal efficiency of ammonia nitrogen found in the soil leachate samples collected at the 15 cm (5.9 in) depth in the soil on both plots was 90% to 99%. Nitrate nitrogen removal was initially very high but increasing concentrations were detected with time. Research indicated that the nitrate-N removal efficiencies of up to 85% were achieved in the first year but after six years of irrigation with domestic effluent the nitrate-N removal efficiency was in the range of 27% to 70%. It was also noticed that an effluent application rate of 2.5 cm/week (.98 in/week) did not result in a mean annual concentration of greater than 10 mg/l at the

60 cm (23.6 in) depth in the soil while at a domestic effluent application rate of 5 cm/week (1.96 in/week), the nitrate-N concentration level at the depth of 60 cm (23.6 in) in the forest soil was greater than 10 mg/l  $\text{NO}_3\text{-N}$ . The figure of 10 mg/l was used for discussion because it is the upper limit for the nitrate-N concentration allowed in drinking water. While the major concern in the study was the renovation of phosphorus and nitrogen in the applied effluent, the fate of other dissolved minerals such as Mg, Ca, Cl, Mn, Na, and B were also studied. Research indicated that the application of the effluent not only accelerated tree growth but the nitrogen and phosphorus contents of the harvested crop were increased over the crops harvested on the control plots. Absolute amounts of phosphorus removed in one year ranged from 11.2 to 68 kg/ha (10 to 59 lb/acre) while that of nitrogen ranged from 40 to 400 kg/ha (36 to 356 lb/acre). The principal soil chemical change was a buildup of phosphorus in the top 30 cm (11.8 in) of the soil profile. There was no indication of adverse long term buildup of heavy metals in the soil. The chemical, biological, and physical properties of the soil as well as the operational procedures were the main factors that determined the resulting renovation of the effluent with respect to specific constituents in the applied domestic effluent.

## 1.1 RESEARCH OBJECTIVES

The general objectives of the research reported herein

was to observe the renovation of selected constituents of domestic sewage as the effluent passed through a coastal forest soil. Through a permanent set irrigation network, treated domestic effluent was sprayed on a second growth forest situated on a mountainous slope. Ground water samples were extracted through the use of porous plate tension lysimeters located at various depths in the soil profile. The analyses involved a determination of the chloride concentrations as well as the concentrations of the nutrient compounds nitrogen and phosphorus in the soil leachate and the applied effluent samples. While it is recognized that long term research into the renovation of domestic effluent through a forest floor would be a more accurate reflection of the possible effects of implementation of a full scale program, time limitations dictated a substantially shorter study. The research program involved twice per week applications of 2 cm (.80 in) of domestic effluent as well as twice weekly sampling of the resulting soil leachate beginning July 15, 1976, and ending November 12, 1976. Batch scale laboratory experiments involving soil samples collected from around the lysimeter installation areas and secondary treated sewage were undertaken to determine the theoretical phosphorus removal capacity of the soil at the test site. The phosphorus removal results from the batch scale tests were also used to confirm the phosphate concentration changes observed between the applied effluent samples and the soil leachate samples collected by the lysimeters.

The specific aims of the study were:

- 1) To review the soil physical, chemical, and biological properties which may influence the passage of chloride, total and ortho phosphate and total Kjeldahl and nitrate nitrogen through a forest soil.
- 2) To review the formation and composition of the particular soil found at the irrigation site. The intention will be to suggest that a similar effluent spraying program on a soil with different soil characteristics than those found at the site of this research may result in different renovation trends with time.
- 3) To observe and explain the short term trends (over four months) in the chemical composition of the soil leachate resulting from the application of domestic effluent to a forest plot. In particular, the trend in the concentration levels of ortho and total phosphorus, total Kjeldahl and nitrate nitrogen and chloride were monitored during the test period.
- 4) To evaluate the maximum potential of the forest soil to absorb phosphorus contained in domestic effluent. This will give an indication of the theoretical maximum amount of phosphorus the soil at the test site can immobilize if this were the only phosphorus removal mechanism available.

## 2.0 THEORY AND LITERATURE REVIEW

The application of domestic effluent to land results in physical, chemical, and biological interactions between the constituents in the applied effluent and various components of the soil system. These interactions result in the alteration of the type and the concentration of the constituents originally contained in the domestic effluent as well as altering the chemical and biological composition of the soil system. To ensure a desired concentration level of specific constituents with time in the resulting groundwater flow, as well as to prevent the accumulation of materials in quantities toxic to specific plants, these various effluent-soil interactions must be understood. A general understanding of the magnitude, the limit, and the interrelationships of these various interactions may suggest the degree and the extent to which a particular soil may be safely used as a site for the renovation of effluent. An appreciation for the magnitude of a particular effluent-soil interaction is ultimately an attempt to quantify the extent to which certain reactions will continue to occur with repeated applications of effluent. For example, the potential for the continual immobilization of phosphorus by the various iron and aluminum compounds in the soil depends on the species and the amounts of iron and aluminum compounds found in the soil. A general understanding of the limits of these interactions is important if an attempt is to be made to maintain an environment suitable for long term effluent application.



For example, the immobilization reaction between the phosphorus in the applied effluent and the various compounds of iron and aluminum takes place under aerobic conditions, with anaerobic conditions potentially causing resolubilization and subsequent mobilization of phosphorus. If the intention is to remove the phosphorus compounds, the formation of anaerobic conditions in the soil environment would probably defeat this purpose. Lastly, the interrelationship of these various interactions is important in so far as the result of a particular soil-effluent reaction may influence other soil constituents. For example, ammonia may replace another cation on the cation exchange sites, the result being the immobilization of the ammonia ion and the liberation of the previously immobilized cation. To understand the effluent-soil relationships is to recognize the natural role of soil as a dynamic medium for the decomposition of organic matter and the return of mineral elements to the nutrient cycle.

## 2.1 SECONDARY MINERALS AND ORGANIC MATTER

According to Lawton (1955), secondary minerals and organic matter constitute the most active portion of the soil with respect to chemical and physical properties. In particular the soil colloidal fraction, consisting of that portion of the soil fraction which lies in the particle diameter range .5 microns to 1.0 millimicrons, is recognized as determining the physical and chemical behavior of soils. This fraction of the

soil contains both mineral and organic matter existing as mineral-organic complexes or as separate phases.

### 2.1.1 Soil Organic Matter

According to Fraser (1955) the soil organic matter consists of plant residues in various stages of decomposition, the products of decomposition and biological or chemical synthesis, and lastly living micro-organisms or their decomposing and decomposed remains. Schnitzer and Khan (1972) divided the bulk of the organic matter in the soil into two groups termed: 1) non-humic substances and 2) humic substances.

According to Schnitzer and Khan (1972), non-humic substances include those compounds that still exhibit recognizable chemical characteristics of the original material. Such compounds include amino acids, proteins, fats, resins, waxes, and other low molecular weight organic substances found in the soil. The non-humic portions of the soil organic matter are readily broken down by micro-organisms when by themselves but may show resistance to degradation particularly if in combination with other organic compounds.

The humic substances form the major portion of the soil organic matter. Felbeck (1965) defined the humic substances as

"Those materials produced in the soils that are either yellow or brown to black coloured, acidic, polydispersed substances of relatively high molecular weight."

The humic fraction of the organic matter in the soil is further

subdivided into three classes of compounds according to their differential solubilities in alkali and acid solutions. The three different humic fractions are: 1) humic acid, 2) fulvic acid, and 3) humin. Research indicates that structurally the three humic sub groups have similar functional groups and have approximate equal molecular weights, with the chemical reactions in specific acid and alkali solutions forming the basis of division between each group.

The humic acid, as defined by Stevenson (1972) is,

"The material which is extracted from soil by alkaline solution and which is precipitated upon acidification".

According to Haworth (1971) 50 to 55% of the total humic molecule has been identified as being composed of amino acids (10%), hexosamines (3% to 10%), polycyclic aromatics (10%) and oxygen functional groups (26%). The oxygen functional groups include -COOH (11.2%), phenolic groups (7.2%), alcoholic OH (3.9%), carbonyl (1.5%) and methoxyl (1%). While the specific molecular structures are unknown, the remaining 45 - 50% of the total humic molecule unaccounted for seems to consist of easily oxidized unsaturated heterocyclic compounds.

The fulvic acid portion of the humic fraction of organic matter is

"Alkali-soluble material which remains in solution".

(Stevenson, 1972)

Felbeck (1965) suggested that the fulvic acid fraction of the soil organic matter has a lower molecular weight but is con-

sidered to possess the same "structural units" as humic acid. The difference in solubilities between fulvic acid and humic acid is attributed to the fact that fulvic acid has a higher oxygen content per unit weight. It seems to have less aromatic compounds and more aliphatic chains than does humic acid.

Humin is defined as the

"Alkali-insoluble fraction"

(Stevenson, 1972)

based on the solubility characteristics in an alkali solution. The humin component of the organic matter has similar chemical and structural properties to humic acid but its insolubility in the acid and alkaline solutions is attributed to its strong bond to the inorganic constituents in the soil. It also has the highest molecular weight.

According to Wada et al (1974) most soil organic constituents are present in an amorphous state (lacking order).

## 2.1.2 Secondary Minerals

### 2.1.2.1 Crystalline and Amorphous Clay Particles

The secondary minerals are the products formed as the result of the decomposition or alteration of the primary minerals. The fraction of secondary minerals with particle size range less than 2 microns is termed a clay, with fine or colloidal clay being those particles of effective diameter less than .2 microns. The lower size limit of the colloidal clay is comparable with molecular dimensions.

Recognizing the existence of mineralogic differences within the term clay, Mitchell et al (1964) suggested that a soil clay be regarded as consisting of weathered products of primary minerals which can be classified as crystalline clay minerals and amorphous materials. Brindley, as reported by Wada et al (1974), defined the amorphous state as one which lacks order as compared to the crystalline state which has order. The term crystalline refers to those substances which are well organized to yield X-ray diffraction patterns while those materials that do not yield X-ray diffraction patterns are noncrystalline or amorphous. Brindley, however, recommended that the term crystalline refer to long range order and the term noncrystalline refer to short range order when research indicated that some materials were amorphous to X-rays but yielded a diffraction pattern when subjected to an electron beam. In this terminology, long term order exhibits unit cell repetition generally in three directions but possibly in two or even one direction. Short term non-repetitive order is present in amorphous substances.

## 2.1.2.2 Crystalline Clay Minerals

### 2.1.2.2.1 Layered Silicates

Grimm (1968) identified two structural units that are involved in the structural lattice of most crystalline clay minerals. One unit consists of two sheets of closely packed oxygen atoms or hydroxyl groups in which Al, Fe, or Mg atoms

are embedded in octahedran coordination. The Al, Fe, or Mg atoms are equidistant from the six oxygen or hydroxyls. The second unit consists of a silica tetrahedron with a silica atom equidistant from four oxygen or hydroxyls. The silica tetrahedron groups are arranged to form a hexagonal network with the bases of the tetrahedrons in one plane and the tips of the tetrahedrons arranged in one direction. The resulting structure can be considered to consist of a perforated plane of oxygen atoms at the base of the tetrahedron structure: a plane of silicon atoms with each atom in the cavity created by the junction of the three oxygen atoms that are in the base of the tetrahedron and a plane of hydroxyl groups at the tip of the tetrahedral structure directly above the silicon atom. Combinations of these two basis structural units, with modifications, give rise to the structure of the clay minerals that have been identified in the collodial clay fraction of soil.

Rich and Thomas (1960) classified the layered silicates composed of the two basic units as two-layered or three-layered clay minerals and inter-stratified or inter-gradient clay minerals respectively.

Two common two-layered clay minerals are kaolinite and halloysite (Grimm, 1968). The kaolinite clay structure is composed of a single silica tetrahedral sheet and a single alimina octahedral sheet combined in a unit so the tips of the silica tetrahedrons and one of the layers of the octahedral form a common layer. The minerals of the kaolinite group consist of

unit sheets arranged in the above manner and stacked one above another. It has been suggested (Rich and Thomas, 1960) that halloysite consists of kaolinite layers separated from each other either by single molecules of water or numerous water molecules of definite configuration.

The three-layer clay minerals consist of an octahedral layer and two tetrahedral layers, one on each side of the octahedral layer. Such clay minerals include illite, vermiculite, and montmorillonite. Two thirds of the octahedral positions of the dioctahedral minerals are normally filled, the normal cation occupying this position being  $\text{Al}^{3+}$ . Divalent cations may be substituted for  $\text{Al}^{3+}$  and monovalent cations may occupy the vacant octahedral cation positions.  $\text{Si}^{4+}$  occupies the cation position in the tetrahedral layer but  $\text{Si}^{4+}$  may be replaced by partial substitution with  $\text{Al}^{3+}$ . Substitution of  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$  in the tetrahedral layer for  $\text{Si}^{4+}$  results in a negative charge on the clay crystal which is balanced by adsorption of cations to the surface of the particle.

The third group of crystalline clay minerals composed of the two basic units are the interstratified and intergradient clay minerals. This subgroup is included because of the recognition that individual layers of different clay minerals often are interstratified in a random or irregular fashion. Research indicates that incomplete hydroxyl - Al groups may exist in the interlayer space of expanded three layer minerals. The hydrated  $\text{Al}^{3+}$  ions in solution as a result of

weathering may be sorbed by the clay as exchangeable cations and then may polymerize and hydrolyze in the space between layers of the clay mineral.

#### 2.1.2.2.2. Oxides and Hydroxides of Aluminum, Iron, and Silicon

Within the category of crystalline clay minerals are included the oxides and hydroxides of iron, aluminum, and silicon (Rich and Thomas, 1960).

The most common iron oxides are hematite ( $\text{Fe}_2\text{O}_3$ ), which gives the bright red colour in soils, and goethite ( $\text{FeOOH}$  or  $\text{Fe}_2\text{O}_3\text{H}_2\text{O}$ ), which gives the soils a brown to dark reddish brown colour. According to Landa and Gast (1973) the hematite structure is composed of ferric ions arranged interstitially between oxygen layers in octahedral groupings. Goethite consists of essentially the same octahedral configuration with the edges of the octahedra shared to yield layers that are two octahedra wide. The iron oxides and their hydrates may occur as primary and secondary minerals or as discrete particles in the crystalline form.

The crystalline mineral gibbsite ( $\text{Al}(\text{OH})_3$  or  $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ ) is the most abundant form of free alumina in the soil. The basic structure of gibbsite consists of paired sheets of hydroxyl ions held together dioctahedrally by aluminum ions. The series of paired sheets are held together by hydrogen bonding between adjacent hydroxyls, arranged directly above and below one another. Often associated with gibbsite is the hydroxy



aluminum oxide, boehmite ( $\text{AlOOH}$ ). In the boehmite structure the aluminum ions are octahedrally coordinated by oxygen and hydroxyl ions.

The silicon oxides consist of a silicon tetrahedron in which a  $\text{Si}^{4+}$  ion lies equidistant from four oxygen ions ( $\text{SiO}_4^{4-}$ ). The excess negative charge of the tetrahedral unit is decreased by an oxygen ion being shared by two adjacent tetrahedra. The sharing in this way of three basal oxygen ions allows the formation of a tetrahedral sheet.

#### 2.1.2.3 Amorphous Clay Materials

As defined earlier, the term amorphous clay material refers to those materials that do not yield X-ray diffraction patterns and do not exhibit long term order or unit cell repetition in three directions. Generally they have only short range, non-repetitive order or long term order in only one direction. The amorphous clay minerals, usually the finest particles in the clay soil fraction, have a large specific surface area and a high chemical reactivity. When present in large amounts the amorphous clay materials have a marked effect on the physical and chemical nature of the soil. By their very definition, the amorphous system and the materials that make up the system can be described only in general terms. As opposed to the crystalline clay phase, the amorphous clay materials lack homogeneity and therefore lack the unique reactions that would distinguish certain phases of the material.

In general, the principal forms of amorphous clay materials are the oxides and hydroxides of iron, aluminum, and silicon, and the silicates of aluminum and iron all in combination with water and organic matter. (Rich and Thomas, 1960; Wada and Harward, 1974; Mitchell, et al, 1964; Wiklander, 1964; Bin Mohamed Ali, 1975). The principal forms of the amorphous clay materials may occur as discrete particles, as coatings on clay particles, or on the cation exchange sites of clay particles and organic matter (Grimm, 1968).

Wada and Harward (1974) found little research information on the composition and structure of the amorphous oxides and hydroxides of aluminum, iron, and silicon but Greenland (1971) suggested that organic compounds (humic and fulvic acids) were usually present. If the form of these compounds was in doubt the basis of the formation of these compounds was not.

Visentin (1974) suggested that the  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions in soil solutions are coordinated with a combination of six  $\text{H}_2\text{O}$  molecules or  $\text{OH}^-$  ions, with the hydrated ions tending to polymerize into a six membered ring unit or multiples of this unit. The reason for the formation of a six member ring unit lies with the fact that at a pH greater than three to four, the hydroxyl ion will occupy some, if not all, of the six coordination positions available around the ion instead of water molecules. Each hydroxyl attachment will neutralize half a position charge contributed by the  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  ion (if all

coordination sites are occupied by  $\text{OH}^-$ ), leaving another half charge on the  $\text{OH}^-$  unsatisfied. If this hydroxyl is shared equally between two metal ions, in a bridge formation, the charge will be neutralized. The result is the formation of the basic unit consisting of six hydrated aluminum or iron ions or multiples of these six membered units. This explanation is in agreement with research results reported by Hsu and Bates (1964), Hem (1968) and Hsu (1965). If the number of basic units joining together is allowed to increase, eventually the crystalline compounds of aluminum, iron and silicon are formed. However, research (Schwertman, 1966; Ng Kee Kwong and Haung, 1975) indicates that organic compounds may interfere with the formation of these crystalline compounds.

Schwertman (1966) noted that the X-ray analysis of soils and sediments indicated large quantities of non-crystalline forms of hydrous ferric oxide. He found this surprising in view of the fact that tests indicated freshly prepared ferric hydroxide will crystalize to crystalline goethite or hematite within a few months at room temperature. Laboratory work revealed that a strong adsorption of organic anions by the ferric hydroxide disturbed or prevented crystallization from occurring.

The inhibition or delay in the formation of crystalline aluminum hydroxide in the presence of citric acid was reported by Ng Kee Kwong and Haung (1975). The crystallization of aluminum hydroxide was hindered by citric acid because the coordination of the carboxylate groups with aluminum hampered

the hydrolysis of the terminal groups of hydrated aluminum ions.

Schwertmann, Fischer and Papendorf (1968) reported observing delays in the crystallization of iron oxides, and a shift in the nature of the products formed in the presence of citric acid. They found that the sorption of organics was responsible for the stability of non-crystalline or amorphous iron oxides in the soil.

Chen and Schnitzer (1976) were able to obtain scanning electron photographs of humic acid and fulvic acid and their metal complexes with  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$ .

In the soil complex the non-crystalline iron hydroxides may be expected to occur in situations where the iron ion is freshly formed as well as where the iron ions are stabilized by adsorption onto organic matter (Greenland, 1971). Such a situation is exemplified by the podzol B horizon. Greenland (1971) also suggested non-crystalline aluminum hydroxides have a widespread occurrence in slightly acid to acid soils such as the podzol soil.

Wada and Harward (1974) identified a portion of the amorphous clay material as being composed of silicates and aluminosilicates in amorphous aggregations with the sesquioxides. Visentin (1974) suggested such arrangements consisted of either iron-aluminosilicate or aluminosilicate cores surrounded by polyhydroxy Fe and Al phases. The core phase would have Fe and Al in a four-fold coordination in partial substitution for tetrahedral silicon. Cloos et al (1969) presented

a structural model with the composition varying between  $0 < \text{Al}/(\text{Al} + \text{Si}) < 1$ . In this model, a central core consisting of a tetrahedral network in which silicon is partially substituted by aluminum, carries a net negative charge. This negative charge is balanced by more or less polymerized cations forming a coating around the core. Organic matter may or may not be associated with these materials.

In summary, it is clear that there are different classes of amorphous clay constituents in soil. By their very nature the amorphous compounds are difficult to detect and frequently their presence is determined by implication. The amorphous components in a soil system have a common characteristic due to structural randomness but react differently in soil because of differences in chemical composition and structure.

The importance of distinguishing between crystalline and amorphous sesquioxides in soils was expanded upon by Mitchell, Farmer and McHardy (1964). They suggest that amorphous iron oxides will absorb 109 times as much phosphate as crystalline iron oxide while amorphous alumina can absorb 137 times as much phosphate as crystalline alumina. Thus the very fact that a soil contains amorphous sesquioxides has important ramifications on the use of that soil for the recycling of domestic effluent.

### 2.1.3 Soil Formation

#### 2.1.3.1 General Principles

The type and extent of the organic and mineral clay constituents that are part of a soil are the result of the lengthy process of soil genesis. The ultimate character of a soil and the type of interrelationships between the soil and the applied effluent depends on the stage of the development and the variables that shaped that development.

According to Simonson (1959) the modern concept of soil genesis consists of two overlapping steps:

- 1) The accumulation of the parent material
- 2) The differentiation of the horizons in the profile.

It is not to imply that there are two distinct stages of soil development - the fact is that the two processes overlap and merge. Of major importance in determining the effluent-soil interrelationships is the extent of the differentiation of horizons in a soil profile. This process of horizon differentiation in soils is due to four kinds of changes: 1) additions, 2) removals, 3) transformations, and 4) transfers in the soil system.

These four changes have a great bearing on the components that make up a soil system. As an example Simonson (1959) suggested that there may be additions, removals, transfers, and transformation of organic matter, soluble salts, carbonates, sesquioxides or silicate clay minerals. Organic matter added to the soil will undergo transformations due to microbial de-

gradation and the resulting product may be eventually transferred through the soil horizons. Similarly, the transformation of primary minerals may lead to the formation of silicate clay minerals, sesquioxide minerals or amorphous compounds which may be transferred to the lower soil horizons. In the genesis of soils, transformations of one substance into another substance occurs in all horizons with the resulting product possibly being transferred to another horizon. The nature of the soil then, is the result of the balance among individual processes acting in combination. A shift in this balance of the various combinations accounts for the development of soil differences. In other words, additions, removals, transfers, and transformations of the same parent materials in most soils result in horizon differentiation. The discrepancies between soil types occur because the relative emphasis of each process is not uniform between soil locations. In fact, the relative importance of each process in a horizon may change with time. The nature of a soil then is the result of the balance among the individual processes acting in combination in the soil. A shift in this balance of the various combinations accounts for the development of soil differences.

#### 2.1.3.2 Podzol Formation

The term podzolization refers to a particular combination of the four major soil genesis processes that results in the formation of the great soil group, the podzol. Of parti-

cular concern in the formation of a podzol soil is the alteration of parent material and the subsequent release of the iron and aluminum compounds. These metal cations, in combination with the organic matter present, form the amorphous sesquioxide particles that have the potential to uniquely influence the removal of specific constituents contained in applied domestic effluent.

Stobbe and Wright (1959) wrote that:

"The terms 'podzolization process' and 'podzolization' are often used as general terms for the overall reaction and processes which have resulted in the formation of podzols. More recently these terms have been associated by some workers more specifically with reactions which are involved in the movement and accumulation of sesquioxides and organic matter, features which are closely associated with the morphology of podzols."

In the conclusion of their paper, Stobbe and Wright (1959) summarize the prevailing view on the genesis of podzol soils. According to soil scientists, the decomposition of organic material and the subsequent release and movement of organic acids through the parent material brings about the chemical degrading of the same parent material. The significant reaction products of the decomposition of the parent material by organic acids are the aluminum and iron which are released to the soil solution. In a discussion of the possible forms of aluminum and iron, Schefferfield and Ulrich, as reported by Wright and Schnitzer (1963), suggested that the ferric ions in solution in equilibrium with  $\text{Fe}(\text{OH})_3$  are  $\text{Fe}(\text{H}_2\text{O}^{+3})_6$  below pH 2.5,  $\text{Fe}(\text{OH})^{+2} \cdot (\text{H}_2\text{O})_5$  above pH 3.0 and  $\text{Fe}(\text{OH})_2^{+1} \cdot (\text{H}_2\text{O})_4$  above

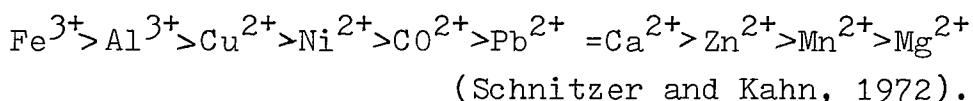


pH 7.5. Aluminum ions in solution in equilibrium with  $\text{Al}(\text{OH})_3$  are  $\text{Al}(\text{H}_2\text{O})_6^{+3}$  below pH 4 and  $\text{Al}(\text{OH})^{+2} \cdot (\text{H}_2\text{O})_5$  along with  $\text{Al}(\text{OH})_2^{+1} \cdot (\text{H}_2\text{O})_4$  and possibly  $\text{Al}(\text{OH})^{-1}_4 \cdot (\text{H}_2\text{O})_2$  above pH 4.5. The formation of the polymeric hydroxyaluminum compound and ferric hydroxy dimers is also recognized by Martin and Reeve (1960). Wright and Schnitzer (1963) conclude that in a podzol, the ferric ion can migrate as  $\text{Fe}(\text{H}_2\text{O})^{+3}_6$ ,  $\text{Fe}(\text{OH})^{+2} \cdot (\text{H}_2\text{O})_5$ ,  $\text{Fe}(\text{OH})_2^{+1} \cdot (\text{H}_2\text{O})_4$  and as a ferric hydroxide dimer; but since these ions have low solubilities under field conditions, reactions between the cation and the organic matter is a prerequisite prior to significant migration of iron and aluminum.

Mortensen (1963) suggested that the soil organic matter forms complexes with metals by ion exchange, surface adsorption, chelation reactions and complex coagulation and peptization reactions. The nature of the ligands in polymeric components of the soil organic matter usually involve carboxyl, hydroxyl, and amide groups which occur on polymers of lignin, polysaccharides, tannins, and proteins or on low molecular weight compounds such as amino acids. The ligands on polymers are restricted by the size of the polymer and usually serve as sites for ionic exchange rather than in a ligand exchange involving the metal cation. The single ligand groups will bind with the metal ion.

Wright and Schnitzer (1963) concluded that fulvic acid is the dominant fraction of organic matter involved in podzol-

ization. The functional groups such as carboxyl, hydroxyl, and carbonyl groups compose up to 60% of fulvic acid. These groups combine with the polyvalent cations to form water soluble complexes, some of which involve two or more ligand groups resulting in a metal chelate formation. In another paper, Schnitzer (1968) reiterated that fulvic acid was a major humic compound affecting most soil reactions. The major reaction leading to a metal-organic complex is the reaction between the metal ion ( $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ ) and the hydroxyl portion of the carboxyl and phenolic groups. The more stable compounds were formed by the reactions involving the organic compounds and trivalent cations ( $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ), rather than the divalent metal ions. At low pH the stability of metal-fulvic acid complexes are:



In a podzol the sesquioxides are found mainly in the soil B horizon. Ponomareva (1969) concluded that the mobility of the complex compounds with hydrated sesquioxides depended on both the ratio of the reagents and the degree of dilution of the solutions. He found that decreasing the  $\text{R}_2\text{O}_3$ :FA ratio (where FA is fulvic acid and R is the metal cation Fe or Al) and decreasing the  $\text{R}_2\text{O}_3$  concentrations, caused an increase in the mobility of the complex. For a  $\text{Fe}_2\text{O}_3$ :FA ratio of 20:1 and a  $\text{Al}_2\text{O}_3$ :FA ratio of 3:1, complete precipitation occurs. He also concluded that the Fe complex is 20 times more mobile than

the Al complex. Thus conditions that ensure the mobility of the sesquioxide-fulvic acid combination occur when fulvic acid is in a larger concentration than  $R_2O_3$  and when the solutions are dilute. These are the conditions in an eluviated horizon. Conversely, precipitation of the metal-organic complex occurs when the sesquioxides are predominant and the solutions are not dilute such as in the illuviated horizon.

The degree of podzolization depends on soil temperature, the relative supply and concentration of organic matter, the type of parent material and the resistance to chemical degradation to release  $Fe^{3+}$  and  $Al^{3+}$ , the oxidation-reduction conditions, the changes in soil moisture as determined by rainfall characteristics and the reactions in the various horizons.

#### 2.1.4 Description of a Podzol Soil

The genesis of a soil by the process of podzolization leads to the formation of a podzol soil with distinct soil characteristics. The podzol is one great soil group or a group of soils having a wide distribution. Occurring in regions of cool humid climate with an annual rainfall ranging between 50 cm (19.7 in) and 75 cm (29.5 in) and a mean annual temperature of 40 C, the podzol great soil group covers the largest portion of the habitable area on the earth's surface. Generally developed on well drained, acid, coarse textured parent material, the podzol exhibits an extraordinary profile development.

The L horizon is composed of readily identifiable, freshly

deposited organic matter that is deposited over a layer of partially decayed organic matter, the F layer. Also part of the LFH horizon and underlying these two forest floor horizons is the H layer, a raw humus layer which is the site for the formation of acid decomposition products of organic matter.

The Ah horizon is a mineral horizon. It contains an accumulation of organic matter at or near the surface, with the dominant feature being the absence of clay, hydrous oxides of iron and aluminum or both. In the lower portion of the A horizon, termed the  $A_e$  horizon or eluviated layer, a lighter colour develops due to the leaching of iron and aluminum compounds during the podzolization process. Also the lower portion of the  $A_e$  horizon is lower in organic matter content.

The A horizon is underlain by a darker coloured B horizon, or illuviated layer, with the major reaction products deposited and accumulated in this horizon being the amorphous sesquioxides and organic matter. The accumulated materials in the B horizon may be predominantly organic, predominantly sesquioxidic or predominantly organic covering a predominantly sesquioxidic horizon (lower B horizon). The consistence in the B horizon may vary from loose and friable to cemented and hard. The soil must allow unimpeded drainage of the moderate to high rainfall in order to facilitate percolation of the soil solution containing the eluviation products formed in the upper horizons. The unrestricted drainage and the moderate to high rainfall is reflected in the absence of carbonates and other

salts.

The C horizon is the unaltered parent material. It is the material from which the A and B horizons developed. It is relatively unaffected by the soil forming processes.

## 2.2 ION EXCHANGE

### 2.2.1 Cation Exchange

Most soils exhibit the physical chemical property of adsorbing cations to negatively charged clay particles and soil organic matter. The process, termed cation exchange, is a reversible process in which cations are exchanged between the liquid soil solution phase and the solid clay or organic matter phases. In the cation exchange process a cation attached to a clay or organic matter particle is replaced by another cation found in the soil solution, with the former cation subsequently being released to the soil solution. The exchange is stoichiometric in nature.

The total number of exchange sites per unit mass of soil is referred to as the cation exchange capacity (CEC). This capacity is generally reported in milliequivalents per gram of soil (meq/g) or milliequivalents per 100 grams of soil (meq/100 g) (Grimm, 1968).

#### 2.2.1.1 Source of Cation Exchange Phenomena

##### 2.2.1.1.1 Clay Minerals

Research indicates that the clay surface contains a net

negative charge while the edge of the clay material contains a positive charge (Grimm, 1968; Wayman, 1967; Wiklander, 1964; Rich and Thomas, 1960). Three mechanisms are believed to be responsible for the charge phenomena on the clay particle; isomorphous substitution, broken bonds and lattice defects.

Isomorphous substitution of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and the substitution of the divalent magnesium or the divalent or trivalent iron cation for trivalent aluminum in the octahedral sheet results in unbalanced charges on the clay particle. In the former case the larger diameter aluminum ion will replace the tetravalent silicon atom in the silica sheet and force the four oxygen atoms in the tetrahedron arrangement further apart. The substitution will decrease the positive charge by one and increase the negative charge by one. This negative charge must be balanced by an extra cation becoming attached to the clay particle. Similarly, the large diameter divalent magnesium and ferrous ions and the trivalent ferric ion will create strains within the octahedral units when they replace the trivalent aluminum cation. The substitution of the divalent ions for the trivalent ions will increase the negative charge which must be balanced at the planar clay surface by the addition of cations.

Broken bonds occur along the crystalline edges of the clay particles in either the tetrahedral or octahedral layers. In the octahedral layer the bonding between the aluminum and oxygen is  $Al - O - Al - O$ . If the breaking of the bond occurs

between the oxygen and aluminum atoms then the site becomes negative due to the exposed oxygen atom. In the tetrahedral arrangement the bonding between the silicon and oxygen atom is usually Si - O - Si - O. If the breakage occurs in the oxygen-silicon bond then the site similarly assumes a negative charge.

Lattice defects generally occur in the inter-layer between the tetrahedral and octahedral layers. If the defects were due to a deficit of aluminum ions then a negative charge would arise.

The net negative charge on the surface of the clay minerals and the balancing cations attracted to the clay surface form an electrical double layer. The inner layer is the negatively charged layer associated with the net negative charge on the particle. The layer is surrounded by the diffuse double layer composed of exchangeable cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ , and  $\text{Al}^{3+}$ . The diffuse double layer (Gouy Layer) involves a high concentration of counter ions at the particle surface, with the concentration tending to diffuse away toward the solution where the concentration is lower. In other words, the concentration of cations decreases with the distance from the clay particle until at some point in the solution, the concentration of cations and anions are equal. The Gouy concept of the diffuse double layer has been modified by Helmholtz and Stern (van Olphen, 1962).

Stewart and Webber (1976) list a range of CEC values for

the different size fractions found in the soil. For soil particles greater than .02 mm in diameter (sand) the CEC is 0, while for the particle diameter between .02 and .002 mm in diameter (silt) the CEC ranges from 3 to 7 meq/100 g. For soil particles less than .002 mm in diameter (clay) the CEC ranges from 22 to 63 meq/100 g. The general rule is that the soils rich in clay have higher adsorptive capabilities than those that contain small amounts of clay.

#### 2.2.1.1.2 Organic Matter

The more active portion of the soil, on a weight basis, in the ion exchange process, is the organic matter fraction (Alexander, 1961). The major portion of the soil organic matter is composed of the humus substances of unspecified chemical description (Schnitzer and Kahn, 1972; Felbeck, 1965; Stevenson, 1972). The ion exchange capacity of these organic compounds is based on their high content of oxygen-containing functional groups, including  $\text{-COOH}$ ,  $\text{C=O}$ , phenolic  $\text{-OH}$ , enolic  $\text{-OH}$ , and aliphatic  $\text{-OH}$  structures of various types. Stevenson lists the CEC range of values for fulvic acid as 890 - 1400 meq/100 g while the CEC range of values for humic acid is reported to be 485 to 870 meq/100 g. The fulvic acids, of lower molecular weight, have lower carbon content but higher oxygen content because of a greater number of the functional  $\text{-COOH}$  groups when compared to the humic acids. The result is a higher CEC for the fulvic acids than the humic acids. Stewart and

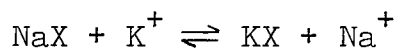


Webber (1976) give the CEC of soil organic matter as between 200 to 400 meq/100 g.

#### 2.2.1.2 Replacability of Cations

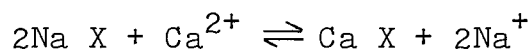
According to Wayman (1967) and Wiklander (1964), cation exchange is a redistribution of ions between the bulk solution and those surrounding a charged particle. For instance the cation exchange may be represented as follows:

- a) for ions of the same valence



where X is the exchange site

- b) for heterovalent ions



Grimm (1968) was of the opinion that all attempts to develop a theory of cation exchange that would permit the quantitative expression of exchange data in the soil by mathematical relationships have failed. The reason lies with the large number of variations on the nature of the clay mineral and the organic matter, nature of the ion, concentration of the ion, concentration of the exchange sites, etc. While the cation exchange reactions are highly complex and poorly understood, the literature contains some generalizations about the exchange process (Grimm, 1968; Wiklander, 1965; Wayman, 1967):

- a) The cation exchange is rapid, reaching equilibrium in a few minutes. (Wiklander)
- b) An increase in temperature will increase the reaction rate slightly (Wiklander) but it may reduce

the CEC and change the replaceability of cations. (Grimm)

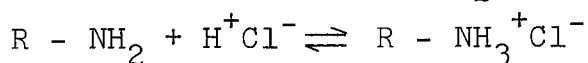
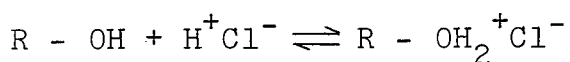
- c) The CEC is a stoichiometric reaction and the laws of mass action hold. In general, increased concentration of the replacing cation causes greater exchange by that cation but this is not the sole factor that explains the phenomenon. (Grimm)
- d) All things being equal, the higher the valence of the ion the greater is its replacing power and the more difficult it is to replace. In dilute solution the ionic replacement follow the series monovalent < <divalent < trivalent or  $\text{Na}^+ < \text{K}^+ < \text{NH}_4^+ < \text{H}^+ < \text{Mg}^{++} < \text{Ca}^{++} < \text{Al}^{+++}$  (Wayman)
- e) For ions of the same valence, the replacing power tends to increase as the size of ion increases. The adsorption of ions would be as follows:  
 $\text{Li} < \text{Na}^+ < \text{K}^+ = \text{NH}_4^+ < \text{Rb} < \text{Cs}^+$  (Monovalent)  
 $\text{Mg}^{++} < \text{Ca}^{++} < \text{Sr}^{++}$  (Divalent)  
 (Grimm)
- f) Maximum adsorption occurs at a high ratio of charge to ionic size (Wayman)
- g) The CEC is pH dependent with the CEC increasing with increasing pH (Black)

### 2.2.2 Anion Exchange

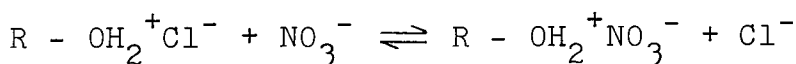
While the anion exchange capacity may be insignificant in most soils, the retention of anions is high in a soil with low pH and a substantial content of amorphous iron and aluminum compounds (Wiklander, 1964; Tisdale and Nelson, 1975; Grimm, 1968; Rich and Thomas, 1960; Wada and Harward, 1974). Such soils occur in the podzol great soil group.

The anion exchange sites in a podzol fall into two general categories. The first category includes the functional groups

on the organic matter present in the soil, while the second category is comprised of the amorphous aluminosilicates and hydrous iron and aluminum oxides (Wada and Harward, 1974). At a low pH the basic groups are activated by increased acceptance of protons. For instance the following examples of anion exchange reactions are given by Wiklander (1964).

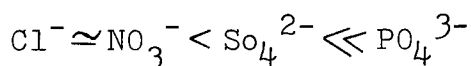


The anions ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $H_2PO_4^-$ ) then function as counter ions and are exchangeable with other anions in a manner similar to cation exchange.



The distribution of exchangeable anions and the factors that affect this distribution seem to be similar to that for cations as explained earlier (Wiklander, 1964).

In general the lower the soil pH, the greater is the anion adsorption. The bonding strength is in the order:



### 2.3 FATE OF CHLORIDE IN EFFLUENT APPLIED TO FOREST SOIL

In most soils the chloride ion is very mobile, frequently being employed as a tracer of the movement of soil water (Wetselaar, 1962; Smith, 1972). The fact that most soils usually have a small anion exchange capacity and the fact that there is no microbiological assimilation usually explains the mobility of the chloride ion.

In previous soil water quality studies during the application of domestic effluent to land, chloride was found to move through the soil unchanged. (Baars, 1964; Stone and Garber, 1952; Greenberg and McGauhey, 1955). These results were not substantiated by results obtained in water quality studies that involved the application of domestic effluent to forest land at Pennsylvania State University (1974). Substantial quantities of chlorides were removed in harvested crops and, as well, significant amounts were adsorbed by the soil.

Tullock, Coleman and Pratt (1975), carried out chloride movement studies with a  $\text{Ca}(\text{NO}_3)_2$  solution and 17 soil columns containing 17 different soils. They found that the chloride ion moved 2% to 25% faster than the soil water in 16 of the 17 soil columns. The one exception was a column of soil that contained an appreciable amount of free iron oxides (2.40%). These particular soil constituents demonstrated a significant positive charge or anion exchange capacity under acidic conditions that existed in the soil. This anion exchange capacity had to be satisfied before chloride could move freely through the soil column. Wiklander (1964), also observed a high anion exchange capacity in soils containing substantial quantities of amorphous sesquioxides.

## 2.4 FATE OF PHOSPHORUS APPLIED TO A FOREST SOIL

Phosphorus, nitrogen and potassium are the three major mineral nutrients required by plants and micro-organisms. The

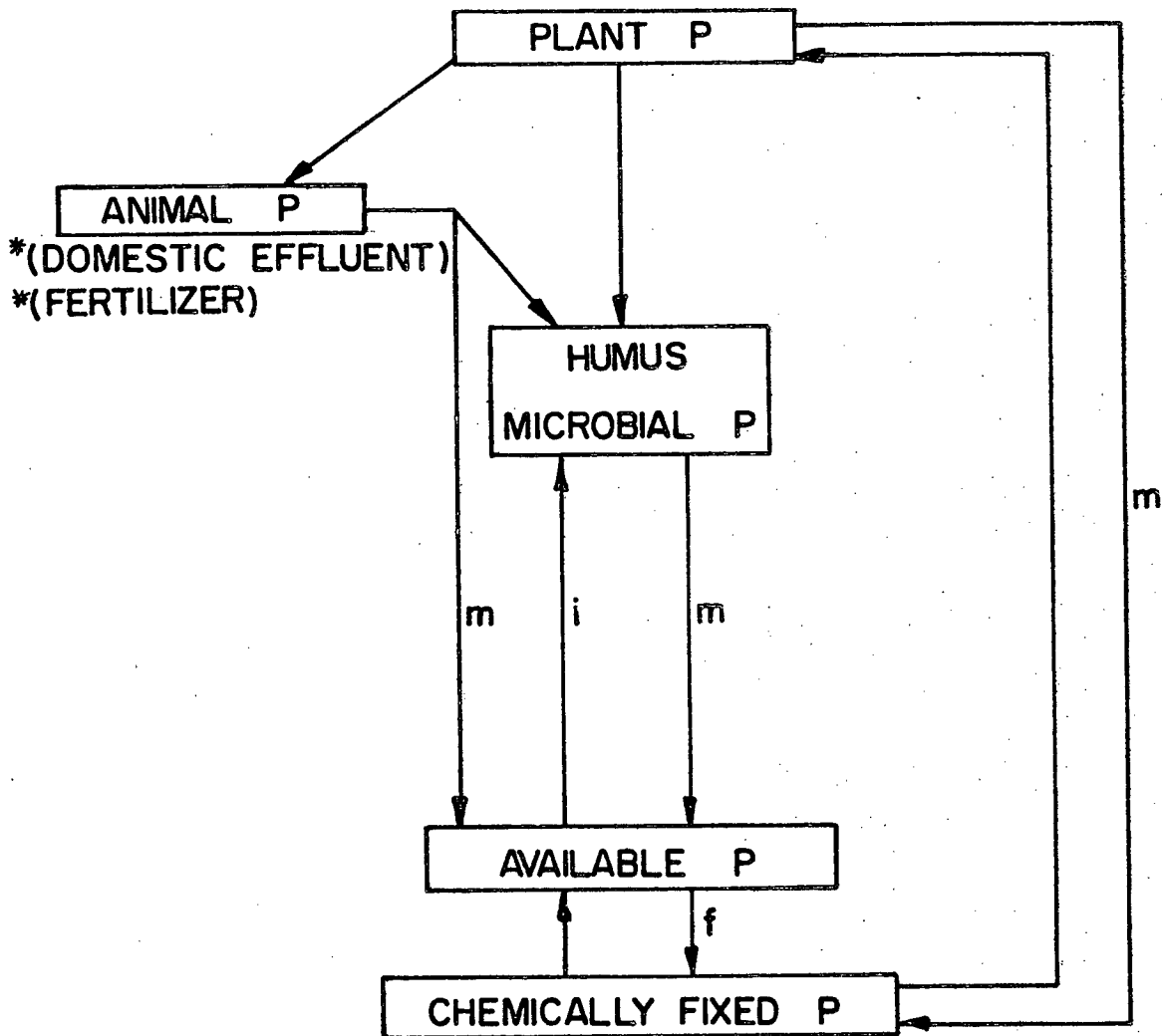
function of phosphorus in plants is the accumulation and release of energy during cellular metabolism. One of the principal goals in applying domestic effluent to the land is the assimilation of the phosphorus by a crop that can eventually be harvested. According to Alexander (1961), however, the phosphorus compounds also may be assimilated by micro-organisms or fixed chemically by inorganic constituents in the soil.

The phosphorus cycle as visualized by Alexander (1961) is presented in Fig 1. The inorganic phosphate ion may be assimilated into cell protoplasm of micro-organisms and/or a portion may be fixed by chemical reactions with portions of the soil matrix.

#### 2.4.1 Microbiological Assimilation of Phosphorus

Microbial growth requires the presence of available forms of phosphorus. Since this element is essential for cell synthesis, the development of microflora is governed by the quantity of utilizable phosphorus compounds in the environment. In environments where phosphorus is limiting, its addition will therefore stimulate microbiological activities and result in an increase in the immobilization rate. Research indicates that if the organic carbon : organic P (C:P) ratio in soil is greater than approximately 300:1, the microbiological immobilization of added phosphorus will occur, while if the C:P ratio is less than 200:1 mineralization of organic phosphates will occur (Alexander, 1961; Stevenson, 1964).

FIGURE I  
PHOSPHORUS CYCLE IN SOIL (AFTER ALEXANDER, 1961)



m = MINERLIZATION - CONVERSION OF ORGANIC P  
TO THE INORGANIC STATE

i = IMMOBILIZATION - CONVERSION OF INORGANIC P  
TO CELL PROTOPLAIM

f = FIXATION

\* AUTHORS ADDITIONS TO DIAGRAM

As a consequence, the organic layer (LFH horizon) in a podzol soil has the capacity to microbiologically immobilize a portion of the added phosphorus in the domestic sewage. Such proof is indirect. Stevenson (1964) suggested that mineralization and immobilization of nitrogen and phosphorus occur at an equal rate when the ratio of organic carbon : organic nitrogen : organic phosphorus (C:N:P) is 100:10:1. If the ratio is smaller the mineralization process will dominate. If the ratio is larger (i.e. more carbon) the immobilization reaction will dominate. A British Columbia Department of Agriculture survey of the lower Fraser Valley (Luttmerding and Sprout, 1968), reported that a soil sample similar to the soil subjected to irrigation had C:N ratios of 37.7:1 and 33.9:1 in the L horizon and the HF horizon respectively. While no organic phosphorus determination was undertaken, the C:N ratios suggest that if effluent were added to the soil, the nitrogen and phosphorus contained in the applied effluent would be immobilized by microbiological action.

#### 2.4.2 Chemical Fixation of Phosphorus

The fixation of inorganic phosphorus in a mineral acid soil is due primarily to the formation of iron and aluminum compounds of the form  $(M(H_2O)_3(OH)_2H_2PO_4)$ , where the symbol M represents iron or aluminum (Hemwall, 1957; Bache, 1964; Hsu, 1965; Kittrick and Jackson, 1954).

The sources of iron and aluminum are the oxides and

hydroxides of these metals in the amorphous or crystalline form, metal ions, or the iron and aluminum contained in the crystalline clay minerals (Hsu, 1965; Jacobs, 1964; Hsu and Rennie, 1962; Ballard and Fiskell, 1974; Harter, 1969; Muljadi et al, 1966; Chen et al, 1973a). While it is clear that the mechanism of phosphate removal involves the formation of new iron or aluminum phosphate phases (Kittrick and Jackson, 1954; Hemwall, 1957; Hsu, 1965; van Riemsdijk et al, 1977), there is confusion over the actual removal mechanism.

Kittrick and Jackson (1956) proposed the Unified Theory of phosphorus fixation in the soil. The Unified Theory proposes the formation and growth of separate phase phosphate precipitates of varying composition depending on the original Fe and Al compounds. The mechanism is one of chemical precipitation.

According to Kittrick and Jackson (1956) phosphorus fixation in soil has been attributed to either isomorphous substitution of P for Si in the tetrahedral structure of a silicate mineral or to adsorption. The authors dismiss the former mechanism completely. They suggest that the substitution of P for Si in the tetrahedral structure of the soil silicate minerals has been disproven experimentally, while the  $\text{PO}_4$  species is too large to replace  $\text{OH}^-$  in the crystal structure. Adsorption, or the process of concentrating ions from the soil solution at a solid phase either by chemical or physical forces, is only satisfactory in explaining the initial



reaction between phosphorus and the soil minerals. The authors reached this conclusion after observing, under the electron microscope, the growth of a new crystalline phosphate phase upon exposure of phosphorus to aluminum and iron oxides, a phenomenon that could not be explained by an adsorption mechanism. The explanation for the fixation of phosphorus therefore seems to lie with chemical precipitation or the removal of phosphate ions from solution and their chemical bonding to the solid phase. The solid phase formed may be as monolayer additions on the surface of a solid phase of the same kind (crystal growth) or addition to a second solid phase (chemisorption). The solid phase may also be in the form of a new particle. Electron microscope observations of the reaction between phosphates and the minerals indicate the formation of separate phase phosphate crystals with the new species formed being dependent on the temperature at which the experiment was conducted. They also observed that the fixation of phosphorus occurred in two stages. The slow reaction involves the fixation of phosphorus by iron and aluminum released during the weathering of soil minerals. The initial rapid reaction of phosphate is attributable to the more readily available forms of aluminum and iron such as amorphous iron oxides and aluminum hydroxides (Kittrick and Jackson, 1955). The decomposition of iron- and aluminum-bearing minerals in the presence of phosphate indicated to the authors that the chemical precipitation mechanism for phosphate fixation is controlled by

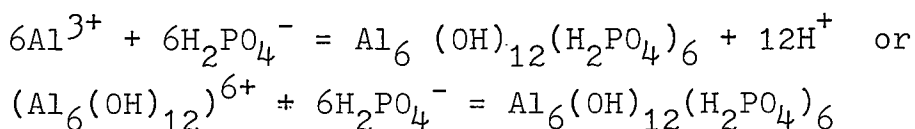
solubility product principles.

Bache (1964) acknowledged and expanded on the work of Kittrick and Jackson. In a paper on phosphate fixation by aluminum and iron, he found that P uptake occurs in three stages involving two sorption sites in addition to precipitation of phosphate. According to Bache, adsorption reaction involves the removal of a component in solution (such as phosphate) by its concentration in a solid phase (oxides or hydroxides of aluminum or iron). Two sorption reactions are identified: the usually irreversible chemisorption involving a large decrease in energy; or physical sorption which is usually reversible and involves a small decrease in energy. Precipitation on the other hand is the removal of two or more components from a solution by their mutual combination into a new solid phase. According to Bache, a high energy chemisorption of small amounts of phosphate over a wide pH range by the hydrous oxides of Fe and Al occurs. In the presence of larger amounts of phosphate,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions are precipitated as insoluble phosphates. Finally, if the activities of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are reduced to low values increasing amounts of phosphate are sorbed at low energy either by physical sorption or by replacing phosphate ions which may diffuse into the solid precipitate lattice.

Hsu (1965) elaborated on the discussion of the mechanism of phosphate fixation by proposing a molecular model that reiterated the observations and conclusions of Kittrick and

Jackson (1956). The author noted that it has been suggested that there are no special adsorptive forces, with the forces binding a molecule or ion to the surface or another phase exactly the same as those occurring between bound atoms in molecules or between molecules in compounds. It follows that adsorption is a special case of precipitation in which Fe and Al remain as constituents in the original phase and phosphate fixation occurs because of an attraction between phosphate and iron or aluminum. Precipitation occurs when the aluminum or iron is completely removed from the lattice and re-precipitates with phosphate to form a new phase. Adsorption occurs when phosphate can break only part of the Al and Fe linkage while leaving the iron and aluminum intact in the lattice.

Whether precipitation or adsorption occurs is dependent on the aluminum and/or iron present in the soil. At a low pH ( $\text{pH} < 4$ ) the hydrated aluminum ion is thought to be stable as a single ion because the individual positively charged units repel one another. With an increase in pH, the positive charges diminish on the individual ions allowing the formation of the basic six-sided polymer with Fe or Al at the six corners. In this case the reaction between Al and/or Fe and phosphate may be a typical precipitation reaction summarized by the following diagram and two equations.



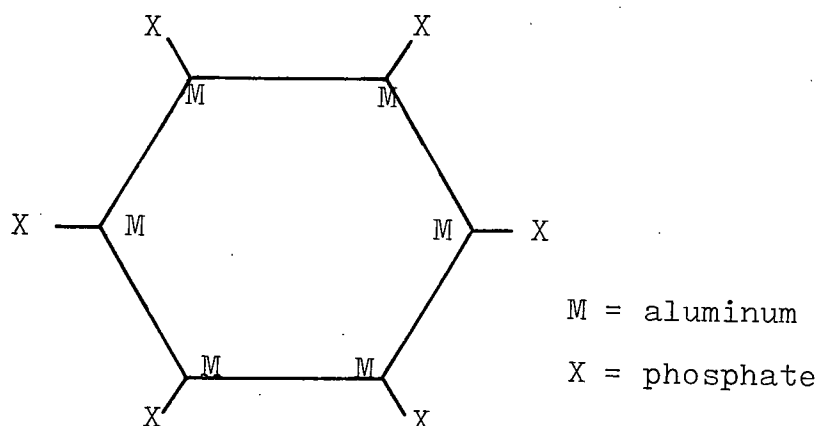


Fig 2 Phosphate precipitated as  $\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{PO}_4)_6$  or  $\text{Al}(\text{OH})_2 \cdot \text{H}_2\text{PO}_4$

Above pH=5 the activity of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  is limited according to Hsu and Bates (1964). The basic six-sided units will join together to form multi-unit polymeric structures which may be crystalline or amorphous in nature as explained earlier. The phosphate fixation will involve an adsorption process in which the phosphate molecule will be adsorbed at the surface of the oxide and hydrous oxides of Fe or Al. In this case, the Al or Fe does not leave the lattice of the amorphous compound. In most soils, because of the effect of pH, the surface reactive aluminum hydroxides and iron oxides dominate the phosphate fixation. This is especially true in a podzol soil where the formation of crystalline iron oxides and aluminum hydroxides is interrupted by the presence of organic acids. In the podzol

soil the iron oxides and aluminum hydroxides are in the amorphous form.

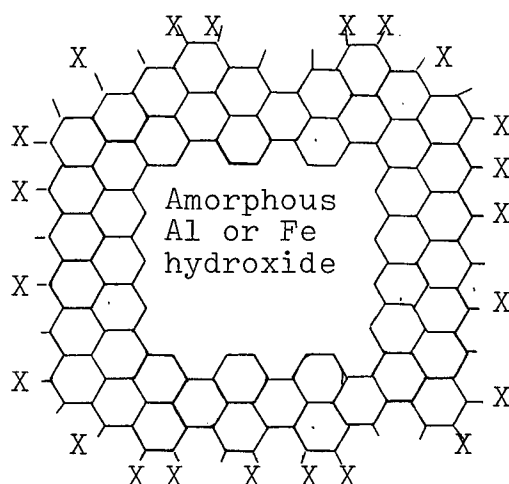


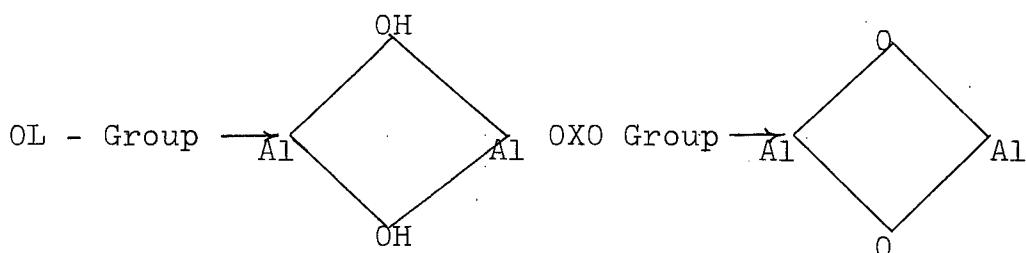
Fig 3 Phosphate Adsorbed by Amorphous Aluminum Hydroxide

According to Maljadi et al (1966a), the amorphous aluminum oxide, pseudo boehmite, has a greater capacity to adsorb phosphate than does the crystalline aluminum oxide gibbsite. The crystalline clay mineral kaolinite was found to have the smallest adsorbing potential. This is in agreement with Harter (1969) whose regression analysis of phosphorus adsorption as a function of five soil characteristics indicated that crystalline hydrous oxides and interlayer aluminum provide few adsorption sites for phosphate. Ballard and Fiskell (1974) and Chen et al (1973a) also reached similar conclusions.

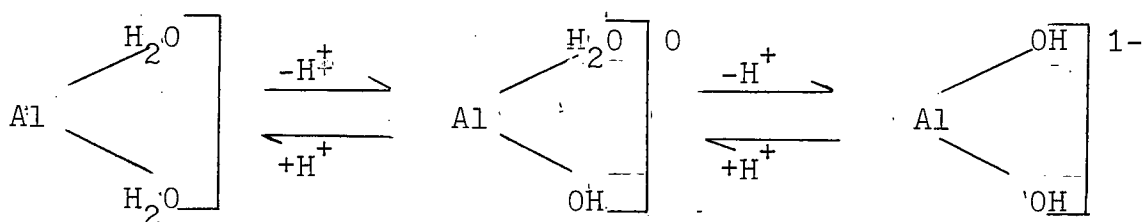
Research by a number of authors has focused on the identification of the phosphate reactive sites on the amorphous iron oxides and aluminum hydroxides as well as the crystalline clay minerals. Hingston et al (1972) investigated the interactions between various anions and the oxide surface of goethite (FeO-OH) and as gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). Solutions containing orthophosphate, pyrophosphate, tripolyphosphate, arsenate, silicate, selenite, sulphate, molybdate, and fluoride were shaken with known quantities of the adsorbent. The results indicate that the adsorption of the anions by the minerals involved the formation of a coordination complex at the oxide surface. The authors suggested that the terminal metal atoms (Fe or Al) on the surface of an oxide complete their coordination shell with OH groups and water molecules. According to coordination theory, the central atom or ion of the complex (Al or Fe) binds the coordinating groups or ligands (OH or  $\text{H}_2\text{O}$ ) to form a coordination sphere. The adsorption mechanism involves an exchange of the  $\text{OH}^-$  or the  $\text{H}_2\text{O}$  ligands for the  $\text{PO}_4^-$  ion. The  $\text{OH}^-$  ion or  $\text{H}_2\text{O}$  molecule are released to the soil solution. The authors observed that the displacement of a hydroxo group would be preceded by its conversion to an aquo group, the proton being supplied by the conjugate acid.

Rajan et al (1974) investigated the fixation of phosphate contained in a  $\text{K}_2\text{PO}_4$  solution by hydrous alumina oxide. The hydrous alumina oxide contained bayerite ( $\text{Al}(\text{OH})_3$ ) and pseudoboehmite ( $\text{AlOOH}$ ). Hydrous aluminum oxide has a structure

in which aluminum atoms are linked by OH groups (termed OL groups) and O groups (termed OXO groups).

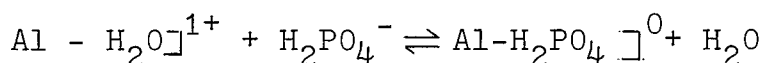


The coordinate positions on the surface aluminum atom of the polymeric complex are occupied by hydroxo or aquo groups. The relative proportion of the hydroxo and aquo groups are determined by the solution pH which in turn dictates the surface charge.

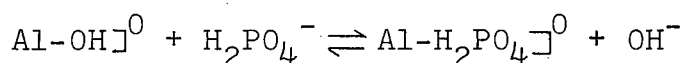


The results of the research confirmed that the adsorption of phosphate can occur by ligand exchange with the aquo, hydroxo or OL groups on the particle surface. At acid pH values the reactivity of these groups to ligand exchange is in the order

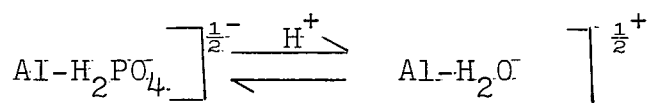
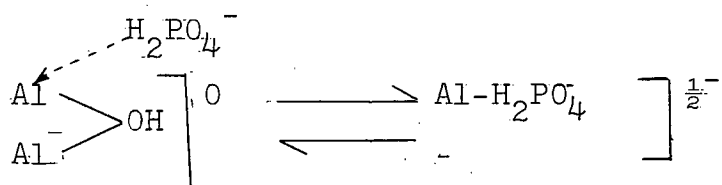
of aquo  $\approx$  hydroxo  $>$  OL. In such a situation, at low phosphate concentration, the more reactive aquo groups would be exchanged with phosphate resulting in the addition of a negative charge to the hydrous aluminum oxide surface but with no release of  $\text{OH}^-$  ions.



With increasing phosphate solution concentration the hydroxo groups would be replaced with phosphate ions. The effect would be an increase in  $\text{OH}^-$  ions in the solution but no change in the surface charge.



At higher phosphate concentrations the less reactive OL groups would become the major adsorption sites due to the breaking of OL bridge.



The breaking of OL groups and the formation of new adsorption sites seems to depend on the solution concentration and surface



coverage of phosphate. Finally, for the OXO groups to adsorb phosphate they must first be converted to OL groups through the very slow process of deoxolation.

#### 2.4.2.1 Reaction Kinetics of the Chemical Fixation of Phosphorus

The kinetics of the reaction of phosphates with aluminum and iron compounds has received a great deal of attention (Kittrick and Jackson, 1955; Olsen and Watanabe, 1957; Hsu, 1964; Chen et al 1973b; Kuo and Lotse, 1974; van Riemsdijk et al, 1977).

Kittrick and Jackson (1955) noted that the reaction of  $K_2PO_4$  with various soils was completed with a few minutes. A higher initial solution phosphorus concentration increased the rate of reaction between phosphorus and the soils for the first hour but thereafter the solution phosphate concentration had little effect on the reaction rate.

Hemwall (1957) demonstrated a rapid fixation of phosphate by kaolinite and montmorillite during the first four hours of an experiment with a much slower phosphorus fixation occurring over the next thirty days.

Chen et al (1973a), investigating the kinetic data for phosphate reaction with  $Al_2O_3$  and kaolinite, concluded the phosphate removal was very rapid for the first two hours. For the period 2 to 24 hours the reaction rate decreased but was still relatively fast. After one day the reaction rate slowed appreciably and could be described by a first order differential

equation of the form:

$$\frac{-d(P)}{dt} = K_{OBS} (P) \quad (t > 24 \text{ hours})$$

Where P is the total soluble phosphate  
 t is the reaction time  
 $K_{OBS}$  is the observed specific reaction rate constant

In a companion paper, Chen et al (1973b) suggested that adsorption equilibrium is established in a few hours whereas the effects over a longer time span are most likely due to leaching of Al followed by nucleation and growth of a new crystal phase. The authors felt that the nucleation and growth phase was the rate-determining step.

Hsu (1964) recognized two phosphate fixing reactions operating at different rates. The one operating at the rapid rate was due to surface adsorption of phosphate on the amorphous aluminum hydroxides and iron oxides already in the soil. Rennie and McKercher (1959), investigating the adsorption of phosphorus by Saskatchewan soils, found this reaction to be complete in a few hours. The second slower reaction is due to other similar amorphous hydroxide and oxide adsorption sites developed during the experiment. This reaction involves the fixation of phosphorus over a time span stretching many months. After laboratory work with aluminum systems, Hsu and Rennie (1962) concluded that the slow phosphate reactions occur when the activity product of aluminum, phosphate and hydroxyl ions exceed the solubility product of aluminum phosphate. The solid phase aluminum phosphate is precipitated in the process induc-

ing further decomposition of aluminum hydroxide. This decomposition process continues until the activity products of aluminum, phosphate and hydroxyl ions in solution are equal to the solubility product of both aluminum phosphate and aluminum hydroxide. The authors suggest that if the amount of phosphate is high enough, eventually all the aluminum hydroxide will be transformed to aluminum phosphate. The process may never occur if the phosphate concentration is at, or is reduced to, a low enough level by the rapid adsorption process. That a new crystal phase is formed has been documented by electron micrographs (Kittrick and Jackson, 1954; Chen et al 1973; van Riemsdijk et al, 1977). Chen et al (1973a) caution that the growth of the new crystal is more complicated than a simple stoichiometric reaction to form  $\text{AlPO}_4 \cdot n\text{H}_2\text{O}$ .

In general, several points concerning the reaction kinetics involved in the fixation of phosphate by the iron and aluminum compounds seem to be consistent throughout the literature: the initial rapid reaction occurs within 30 minutes to 1 hour; the slower phosphate fixation process occurs over several months and can be modelled mathematically by a first order differential equation; high initial phosphate concentrations increase the rate of phosphate fixation but after 1 to 2 hours the phosphate concentration had little influence on the reaction rate; temperature affects the slow reaction but does not influence phosphate fixation during the fast reaction; and phosphate fixation may be hindered when typical complexing

agents are in solution.

#### 2.4.2.2 Phosphorus Adsorption Isotherms

Phosphate adsorption data on soils are usually described by the Freundlich or Langmuir adsorption isotherms (Olsen and Watanabe, 1957; Hsu and Rennie, 1962; Muljadi et al, 1966a; Hingston et al, 1972; Chen et al, 1973a; Kuo and Lotse, 1974; Rennie and McKercher, 1959).

The Langmuir isotherm was originally applied to adsorption of gases on a plane surface with the mathematical derivation containing assumptions pertinent to that situation. The assumptions were firstly that there were discrete points for potential adsorption on the adsorbing material and secondly that each of these discrete points could independently hold one adsorbed molecule. In the application of the Langmuir adsorption to a phosphate - soil situation several problems arise. Firstly, the isotherm is assumed to be an equilibrium isotherm. As was discussed earlier, the equilibrium between phosphate and the soil is not instantaneous and in fact the phosphorous fixation process may occur over many years (van Riemsdijk et al, 1977). Secondly, the Langmuir isotherm does not recognize that the long term phosphate fixation involves the decomposition of soil minerals exposing new phosphate adsorption sites. The slow reaction continues by the gradual increase in crystal size of precipitated iron and aluminum phosphates, with the metal ions being contributed by the grad-

ual breakdown of clay minerals and hydrous oxides. Thirdly, the possibility of internal adsorption when dealing with porous bodies is not recognized in the Langmuir equation. Fourthly, the different regions of the adsorbing surface have different affinities for the phosphate (Rajan et al, 1974; Muljadi et al, 1966a). At an apparent phosphorus saturation of the soil surface, only a small percentage of the total area is covered. Chen et al (1973a) found that the experimental values are higher than predicted by the Langmuir isotherm at the lowest concentration ranges. They suggest that a small minority of the total sites have a higher affinity for phosphate than the majority of the sites. Olsen and Watanabe (1957), while recognizing these limitations, noted that it seemed plausible to suggest that the extent of the initial adsorption reaction between phosphate and aluminum and/or iron can generally be represented by the Langmuir isotherm.

The Langmuir equation written in its linear form is:

$$\frac{C}{(X/M)} = \frac{1}{Kb} + \frac{C}{b}$$

Where C = Equilibrium concentration

X/M = Amount of adsorbate per unit weight of adsorbent

K = constant relating the bonding energy of the adsorbent for the adsorbate

b = Adsorption maximum or the amount adsorbed when all the sites are occupied.

The Freundlich adsorption equation is an empirical formulation that relates the amount of adsorbate to the final concentration of the solution from which the adsorption occurs.

Based on thermodynamic considerations, the relationship uses empirical methods to determine the change in surface tension with changes in concentration. According to the Freundlich relationship, the amount of phosphorus adsorbed increases with increasing equilibrium concentration, the relationship being linear when plotted on logarithmic paper. As with the Langmuir isotherm, the Freundlich isotherm is based on an equilibrium situation but as was noted earlier, equilibrium is far from instantaneous. The linear form of the Freundlich isotherm is:

$$\text{LOG } (X/M) = \text{LOG } K + (1/n) \text{ LOG } C$$

Where  $X/M$  = amount of adsorbate per unit weight of adsorbent

$C$  = equilibrium concentration

$K$  &  $n$  are temperature dependent constants

Olsen and Watanabe (1957), in a comparison of the two isotherms suggested that the Langmuir equation was more applicable to small amounts of adsorbed phosphate while the Freundlich isotherm was applicable to a wider range of phosphate concentrations. Also, the Langmuir isotherm enables the calculation of an adsorption maximum value that is closely related to the surface area of the soil. Hsu and Rennie (1962) found that both isotherms seemed to be followed during the adsorption of phosphate by soil.

Muljadi et al (1966a) investigated the mechanism of phosphate adsorption by two potassium kaolinites and two

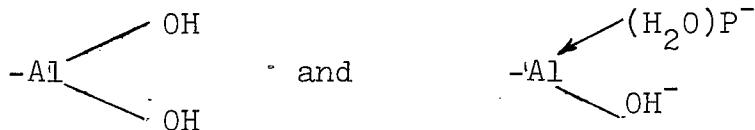
aluminum oxides at various pH values and at concentrations of phosphate ranging from  $10^{-4}$  to  $10^{-2}$  M. The experimental results indicate that the adsorption isotherm can be divided into three distinct regions according to phosphate concentration. The three regions are related to the affinity of phosphate for three energetically different reactive sites. The authors describe the regions as follows:

Region I - at low phosphate equilibrium concentration ( $< 1 \times 10^{-4}$  M) the adsorption isotherm rises steeply and remains close to the Y-axis. This region represents sites with high affinity for phosphates.

Region II - the second region begins approximately at an equilibrium concentration of  $10^{-4}$  M when the isotherm becomes convex to the Y-axis.

Region III - The third part of the isotherm is linear and occurs at medium to high equilibrium concentrations ( $10^{-3}$  M to  $10^{-1}$  M)

The authors proposed that the three distinct regions arise due to three energetically different types of reactive sites. The sites for adsorption in regions I and II are:



Region III is thought to involve the occlusion or adsorption of phosphate into the less ordered areas of the clay surface. Rajan et al (1974) found that the adsorption of phosphates by

iron and aluminum resulted in the same pattern when plotted according to the isotherms. As explained earlier, their explanations of such results are based on the displacements of aquo, hydroxo, and OL groups by the phosphate rather than with the explanation offered by Muljadi et al (1966a).

When the P sorption rate is equal to the P desorption rate in soils, the system is in equilibrium and the equilibrium relationship is described by the Freundlich or Langmuir isotherms. While the two isotherms are used in phosphate adsorption studies in soil, it must be recognized that equilibrium in the true sense of the word is not achieved in the soil in the face of repeated applications of effluent containing phosphorus compounds. According to Novak and Adriano (1975) the isotherms may describe the adsorption of phosphate only for the initial rapid adsorption reaction which is essentially complete within the first hour of the introduction of phosphorus to the soil. The long term fixation of phosphorus involves a release of iron and aluminum from clay lattices and the reaction of these ions with phosphate to form new crystal phases. This cannot be described by the isotherms. Rajan et al (1974) also noted that the Langmuir adsorption maximum probably estimates the adsorption due to the replacement of aquo and hydroxo groups alone. As a consequence the calculation of a theoretical Langmuir adsorption maximum will not indicate, other than in a general way, the phosphorus adsorption maximum to expect in the soil.



## 2.5 FATE OF NITROGEN IN EFFLUENT APPLIED TO A FOREST SOIL

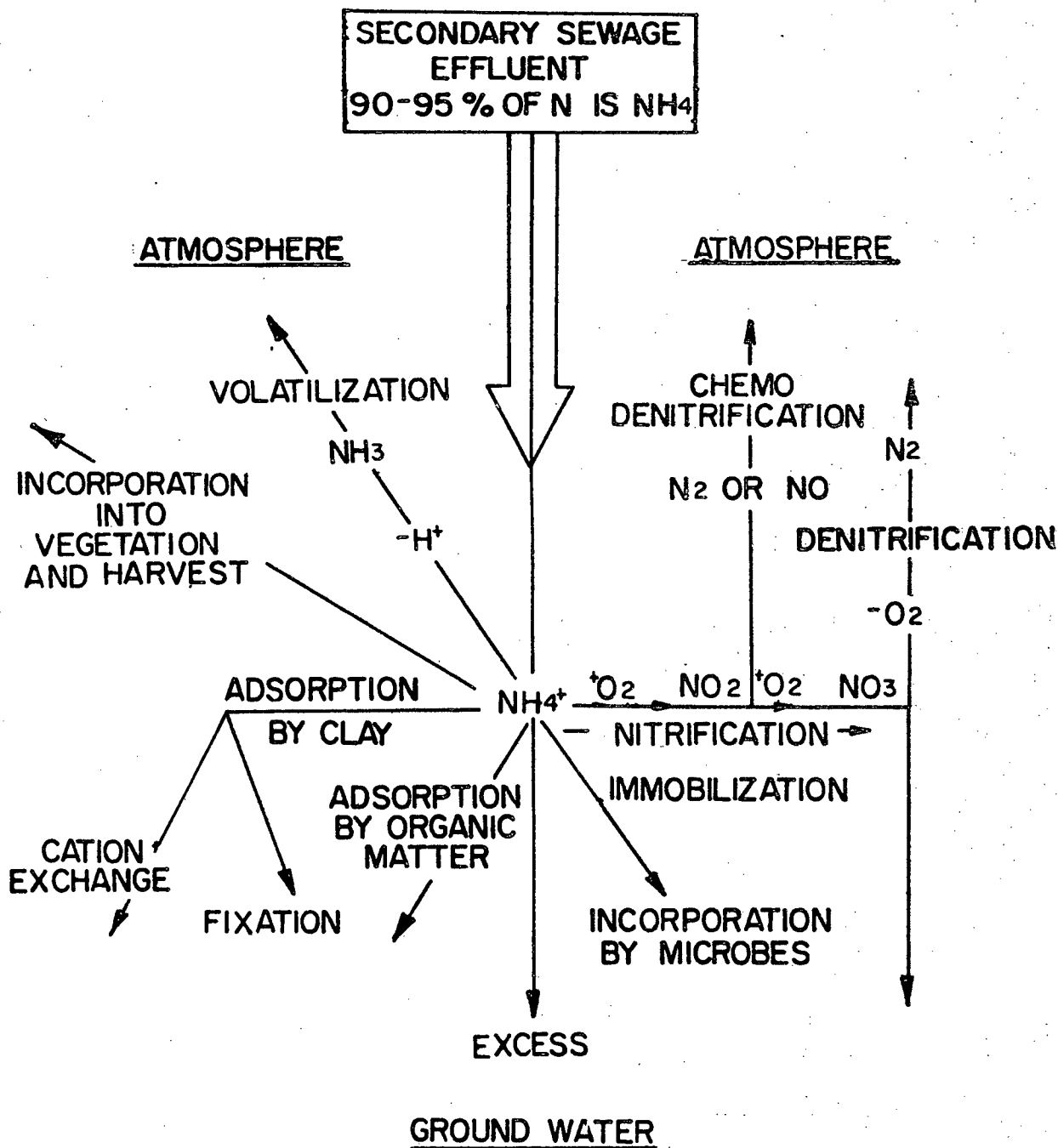
Nitrogen is the nutrient which plants require in the greatest quantity. The element serves as the keystone of proteinaceous matter in living tissue. As with the case of phosphorus, the principal goal in applying domestic effluent to the land is to have the nitrogen compounds assimilated by a crop that can eventually be harvested. Lance (1975) discussed the fate of nitrogen contained in sewage effluent applied to soil. He suggested the following reactions responsible for nitrogen removal. They are:

- (i) Volatilization of  $\text{NH}_3$
- (ii) Chemo Denitrification
- (iii) Biological Denitrification of  $\text{NO}_2^-$  and  $\text{NO}_3^-$
- (iv) Adsorption by organic matter
- (v) Adsorption by clay involving CEC or fixation
- (vi) Incorporation by micro-organisms
- (vii) Leaching of  $\text{NO}_2^-$  or  $\text{NO}_3^-$
- (viii) Erosion and surface runoff

These mechanisms are depicted on Fig 4.

Other authors have discussed the fate of nitrogen in domestic sewage applied to the soil (Walsh, Sumner and Corey, 1976; Miller, 1974; Oldham, 1975; Webber and Lyshon, 1975). No reference to the fate of nitrogen compounds contained in sewage applied to a podzol soil was found in the literature. In an attempt to explain the results of this research, reference is frequently made to the fate of urea fertilizer applied to forested podzol soil.

FIGURE 4  
REACTIONS RESPONSIBLE FOR NITROGEN REMOVAL



### 2.5.1 Nitrogen Immobilization

Immobilization is the microbiological conversion of inorganic nitrogen ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{NH}_4^+$ ) to organically bound nitrogen. Nitrogen mineralization is the conversion of organic nitrogen to the inorganic state (Alexander, 1961). While the two processes are occurring simultaneously in the soil, the nitrogen transformations may be greater for one process than the other at a given time. Stevenson (1964) suggested that both the mineralization and immobilization of nitrogen in soils are markedly affected by the organic carbon : organic nitrogen (C:N) ratio of the organic residues in the soil. The active decomposition of organic matter requires an active microbiological population which requires nitrogen for its growth processes. If the amount of nitrogen immobilized is to exceed the amount of nitrogen that is mineralized the added nitrogen must not be in amounts surplus to the microbial requirements. As a general rule, the critical ratio falls between a C:N ratio of 20 and 25:1 with wider ratios favoring immobilization and closer ratios favoring mineralization. Stevenson (1964) cautioned that while the C:N ratios are a prime soil factor in the mineralization or immobilization of nitrogen, the degree of resistance of these substances to biological decomposition is also important. The more available the organic material to decomposition, the greater the proliferation of the microorganisms and the greater the immobilization of added nitrogen. Also, the immobilization of added nitrogen is dependent on such

environmental factors as moisture, pH, aeration, temperature, and the inorganic nutrient supply of the soil.

Working with forest soils, Overrein (1967) found the immobilization of urea ( $\text{CO}(\text{NH}_2)_2$ ) to be extensive in the litter layer and also in the humus layer under certain conditions. The immobilization of urea was very temperature-dependent with the amounts of urea-N immobilized during a 90-day period being about 25%, 40%, and 65% of the total added at temperatures of  $4^\circ$ ,  $12^\circ$ , and  $20^\circ\text{C}$  respectively.

Salonius(1972) found that urea fertilization increased pH, microbial activity and immobilization of exchangeable ammonium nitrogen in soils.

Broadbent and Tyler (1962), working with two soils in a greenhouse, found that in an organic soil the added ammonia was immobilized by microbiological action while nitrate nitrogen was immobilized to a considerable extent when it was the nitrogen form present in the largest concentration.

While no literature results on the immobilization of nitrate and ammonium nitrogen contained in effluent applied to a podzol forest soil could be found, Miller (1974) wrote that the addition of effluent to a forest soil probably will increase the microbial population dramatically. Presumably the nitrate nitrogen and ammonium nitrogen in the effluent could be readily available as nitrogen sources (Lance, 1975). Walsh et al (1976), in a discussion on the immobilization of nitrogen contained in domestic sewage applied to a soil,

suggested that immobilization undoubtedly reduces the leaching of  $\text{NO}_3^-$ -N.

#### 2.5.2 Nitrogen Adsorption by Mineral and Organic Matter

The adsorption of nitrate nitrogen contained in domestic effluent applied to a soil column in the laboratory was found to be pH dependent (Preul and Schroeffler, 1968). At a pH of 6.3, significant adsorption of  $\text{NO}_3^-$ -N occurred while at a pH of 7.0 no significant adsorption occurred. This agrees with Wiklander (1964) who wrote that at a low pH,  $\text{NO}_3^-$ -N (and other anions) could be directly absorbed by the organic and inorganic constituents in the soil. This anion adsorption capacity would increase at low pH especially in the presence of amorphous sesquioxide clay materials.

The adsorption of ammonia and ammonium contained in domestic sewage applied to an agricultural situation was discussed by Preul and Schroeffler (1968), Bouwer and Chaney (1974), and Lance (1975). Preul and Schroeffler (1968) applied artificial domestic effluent made with laboratory chemicals to a series of soil columns packed with three different textured soils. The intention was to monitor the movement of nitrogen through the columns. They found that adsorption, along with biological action, was one of the main factors which controlled the movement of nitrogen through the soil especially if nitrogen was present as ammonium. Under well-aerated conditions, the ammonium was converted to the more mobile nitrate ion, while

under limited oxygen conditions adsorption of ammonium occurred with only minor biological interference.

More pertinent to the experimental conditions under which this research was conducted is the experimental work on the adsorption of ammonia and ammonium in the urea form in a forest soil. (Sohn and Peech, 1958; Young, 1964; Heilman, 1974; Young and Cattani, 1962; Chin and Kroontje, 1962).

Young (1964) investigated the retention and fixation of  $\text{NH}_3$  and  $\text{NH}_4^+$  by 76 soil horizon samples from 20 Pacific Northwest (PNW) soils during the application of aqua and anhydrous  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  under different degassing and fixing conditions. The major portion of the retained  $\text{NH}_3$  was associated with the organic fraction while the mineral fraction also retained ammonia. A portion of the retained ammonia was lost over the following months. A correlation of  $\text{NH}_3$  retention to CEC was also determined in some P.N.W. soils. For surface horizons of 19 P.N.W. soils the author found that  $\text{NH}_3$  retention (PPM) could be expressed by the equation  $338 + 92.1 * \text{CEC (meq/100 g)}$ . The author cautioned that there is limited specific data about what part various contributing soil fractions and sorption or retention mechanisms may actually play in these reactions under differing soil conditions.

Chin and Kroontje (1962), working with urea and a number of soils concluded that physically adsorbed urea may be easily desorbed by dilution while the chemisorbed urea existed primarily in the form of a relatively stable organic matter-urea

complex which may slowly be desorbed by dilution. Organic matter increased the retention of ammonia while wet soils had a lower capacity for urea adsorption than dry soils.

Mortland (1958) wrote that ammonia is chemically sorbed in greatest quantities by clay minerals under acid conditions or by organic matter under alkaline conditions. He concluded by stating that a combination of these two soil constituents will provide for chemical sorption of ammonia over a wide range of pH.

### 2.5.3 Nitrogen Volatilization

Nitrogen may be lost by the volatilization of ammonia either during or after application to the forest soil.

Nitrogen in waste water is predominantly in the organic and ammonium form (Bouwer and Chaney, 1974). If it is applied through a sprinkler system in this form, there will be no volatilization of nitrogen. If the pH of the effluent were to increase above pH 7 to pH 8, a portion of the ammonium ( $\text{NH}_4^+$ ) would be converted to ammonia gas ( $\text{NH}_3$ ). Staley (1971) found that there was a 0 - 21% volatilization loss of ammonia when swine effluent was applied to agricultural land. The original ammonia nitrogen concentration in the swine effluent being applied to the soil by sprinkler irrigation was 1540 mg/l ammonia nitrogen. These results may not be indicative of the volatilization losses of ammonia that would occur if domestic effluent was being applied to agricultural land.

No information on the conversion of ammonium to ammonia and the resulting volatilization of ammonia on the forest floor could be found in the literature. It is clear that urea applied to a forest floor is converted to ammonia in proportion to the rate of urea application as long as urease concentration is adequate in the soil. Volatile ammonia losses tend to increase exponentially with an increase in the rate of urea application (Overrein and Moe, 1967). This may or may not be indicative of the situation when effluent is applied to a forest floor.

#### 2.5.4 Chemo- and Bio-Denitrification

Denitrification is the reduction of  $\text{NO}_2^-$ -N or  $\text{NO}_3^-$ -N to gaseous forms of nitrogen (molecular nitrogen or oxides of nitrogen) (Allison, 1966). The microbiological reduction of nitrates and nitrites is brought about by a number of facultative anaerobic soil heterotrophs. In the absence of oxygen, these organisms use hydrogen as a terminal electron acceptor but may use  $\text{NO}_3^-$  and  $\text{NO}_2^-$  as substitutes. Chemo-denitrification involves the chemical or nonenzymatic reactions resulting in the decomposition of  $\text{NO}_2^-$ -N.

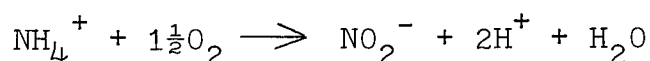
Denitrification in acid forest soils is limited due to the unfavorable pH environment for the anaerobic organisms (Overrein, 1967). Also, a well-drained porous soil will allow for the infiltration of oxygen thus preventing anaerobic conditions from developing. Allison (1966) suggested that denitrification may occur in small micropores of the soil aggregates



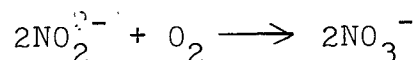
where oxygen may be deficient but such a nitrogen loss is insignificant compared to the total nitrogen loss in the soil.

### 2.5.5 Nitrification of Ammonia

Nitrification is the biological formation of nitrate ( $\text{NO}_3^-$ ) or nitrite ( $\text{NO}_2^-$ ) from compounds containing reduced nitrogen (Alexander, 1961). It involves two distinct steps and two distinct micro-organisms. The first step involves a conversion of ammonium to nitrite by the nitrosomonas bacteria family.



The second step is the conversion of nitrite to nitrate by the nitrobacter family of bacteria.



Lance (1975) reviewed some factors that affect nitrification of sewage in soil. The optimum temperature for nitrification is between  $30^\circ\text{C}$  and  $35^\circ\text{C}$  but it may proceed slowly at  $2^\circ\text{C}$  and will stop at the freezing point of water. The nitrification process requires 4.56 mg of oxygen for every milligram of nitrogen oxidized and is limited in conditions where the pH is less than 5. Freezing will reduce the nitrifiers with 2 to 3 weeks required to build the population to the pre-freezing level.

Otchere-Boateng (1976) reviewed the literature concerned with nitrification of ammonia in an environment similar to that which existed in this experiment. In several experiments with

urea application to Douglas Fir forest soils, no nitrification was detected at temperatures of  $5.5^{\circ}$ ,  $11^{\circ}$ , and  $22^{\circ}\text{C}$ . The conclusion was that the acid forest soil was not a conducive environment for the nitrifying organisms to proliferate. On the other hand, Bourgeois (1969) found considerable nitrification in the soil solution in an acid forest soil. Otchere-Boateng (1976) suggested that the biological productivity of the site, as well as the tree species, may explain why nitrification may or may not occur in Pacific Northwest soils at certain locations. Heilman (1974), working with urea applied to Pacific Northwest soils, found that at low temperatures ( $2.5^{\circ}$  and  $5^{\circ}\text{C}$ ) nitrification was restricted while at temperatures greater than  $5^{\circ}\text{C}$ , nitrification increased rapidly.

### 3.0 MATERIALS AND METHODS

#### 3.1 EXPERIMENTAL PROCEDURE

##### 3.1.1 Study Area

The study was conducted at the University of British Columbia Research Forest, located on the south fringe of the Coastal Mountains approximately 55 Kilometers east of Vancouver, British Columbia. Krajina (1969) placed the area in the Coastal Western Hemlock (CWHa) Biogeoclimatic Zone. The climate is Marine Humid with the annual precipitation ranging between 178 cm (70 in) and 280 cm (110 in). Of that yearly amount, 1% to 15% is in the form of snow with most of the precipitation occurring from the fall season to the spring season. The average daily temperature is above 10°C for four to six months of the year while it is less than 0°C for zero to three months of the year. The dominant tree specie in this geoclimatic zone is the Western Hemlock and to a lesser extent the Western Red Cedar.

According to Armstrong (1957) the area was subjected to four glaciations in the past; Seymour, Semiamu and Vashon were major events while the Sumas glaciers were restricted to the valleys. In general, granitic or associated rock types occur near the surface and usually are overlain with till and outwash.

##### 3.1.2 Experimental Site

The experimental site is located adjacent to Loon Lake

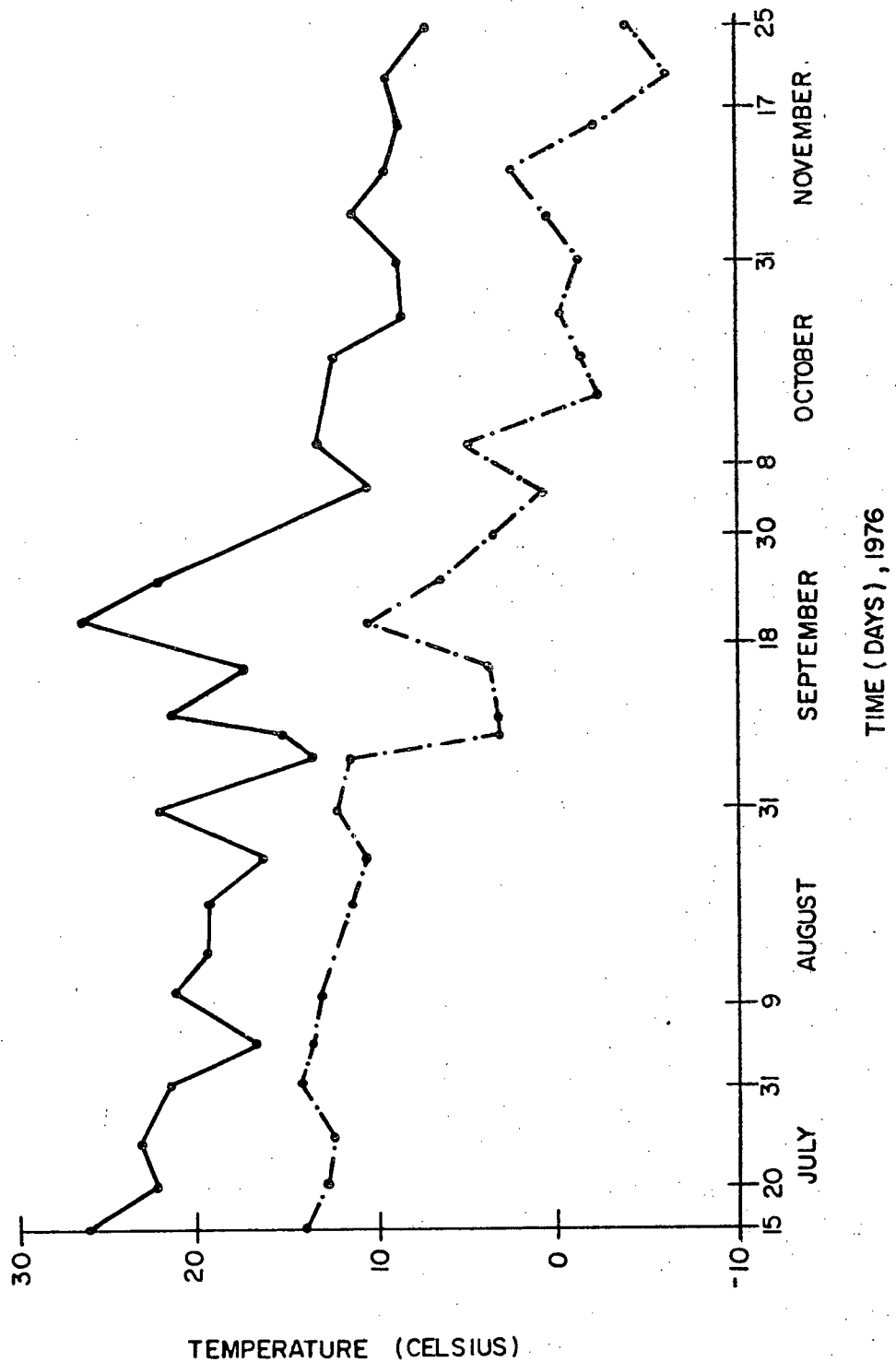
and Loon Lake Forestry Camp at an elevation of 354 m (1160 ft) above sea level. The 30 m by 30 m (100 ft by 100 ft) experimental plot is located on a west-facing  $25^{\circ}$  to  $30^{\circ}$  mountain slope covered with a 15 year old stand of Western Hemlock, Western Red Cedar and Douglas Fir trees. The area had been logged and slash-burned in 1958.

In an attempt to limit the introduction of ground seepage water from outside the perimeter of the plot, in particular from the upper reaches of the mountain slope, a ditch around the perimeter of the plot was constructed to the depth of the impermeable C horizon. The western lower edge of the plot borders on a logging road.

The maximum and minimum temperatures recorded during the irrigation period at the Department of Transport weather station at Loon Lake are given in Fig 5. The temperatures are plotted for every fifth day of the study.

The soil description (see Appendix A), carried out by G. Singleton of the Department of Soil Science at the University of British Columbia, shows the soil to be a ferro-humic podzol, closely resembling the description given for the Cardinal series in "Soil Survey of Mission Area" by Luttmerding and Sprout (1968) for the British Columbia Department of Agriculture (BCDA). (Since the area that the plot is situated on was logged 15 years earlier, resulting in disturbance of the soil surface, the soil classification was performed on an unlogged, undisturbed site approximately 30 m (262 ft) from the experi-

FIGURE 5  
MAXIMUM AND MINIMUM TEMPERATURES  
(D.O.T. STATION LOON LAKE)



mental plot). A summary of the results of the chemical analysis of a representative Cardinal silt loam soil sample collected by Luttmerding and Sprout (1968) is presented in Table 1. The values presented therein are typical estimates of selected chemical properties for the type of soil found at the experimental site.

A permeable organic layer ranging from 1 cm (.4 in) to 10 cm (3.9 in) in depth generally was present at the surface of the irrigation site. In particular, the deepest organic layer was found in the concave areas of the plot. The B Horizon on the plot has developed from ablation till overlying a dense and compacted till. The texture of the B horizon was gravelly sandy loam. As a result of the presence of live roots, as well as channels formed during the decay of the roots of trees subjected to logging, the soil was very porous and permeable. The mountain-side plot was covered with varying amounts of decaying slash, resulting from the logging of the plot.

A soil sample from the vicinity of each porous plate tension lysimeter (see section 3.1.4) was taken during the installation of the lysimeters. Each of the ten soil samples was oven dried at  $40^{\circ}\text{C}$  and then subjected to mechanical rolling in order to break up the soil aggregates resulting from the dehydration of the soil samples. Each soil sample was separated by mechanical sieving into that portion greater than 2 mm in diameter and that portion less than 2 mm in diameter.

The particle size distribution (texture) and the water

Table 1: Chemical Analyses of Selected Upland Soil Profiles  
(Luttmerding and Sprout (1968))

Cardinal Silt Loam - Orthic Humic Podzol

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Texture</u>	<u>pH</u> <u>(H<sub>2</sub>O)</u>	<u>pH</u> <u>(0.01 M</u> <u>CaCl<sub>2</sub>)</u>	<u>Organic</u> <u>Matter</u> <u>%</u>	<u>Total</u> <u>N</u> <u>%</u>
L	3.81- 2.54	pt	3.9	3.5	80.4	1.24
HF	2.54- 0.0	mu	3.8	3.0	80.6	1.38
Ae	0.0 - 1.90	l	4.2	3.5	5.2	0.17
Bhf	1.90- 7.62	sil	5.4	4.7	14.2	0.39
Bfh1	7.62-20.3	sil	5.5	4.9	9.1	0.24
Bfh2	20.3 -38.1	sil	5.5	5.0	8.2	0.21
Bfgj	38.1 -61.0	sil	5.5	5.1	5.4	0.13
BC	61.0 -78.7	l	5.5	5.0	5.4	0.16
IICg1	78.7 -99.1	fsl	5.6	5.3	2.1	0.05
IICg2	99.1+	fsl	6.0	5.7	-	-

Exchangeable Cations and Exchange Capacity -  
milli-equivalents/100 grams

<u>C-N</u> <u>Ratio</u>	<u>Pl</u> <u>p.p.m.</u>	<u>Ca</u>	<u>Mg</u>	<u>K</u>	<u>Na</u>	<u>Cation</u> <u>Exchange</u> <u>Capacity</u>	<u>Base</u> <u>Satu-</u> <u>ration</u> <u>%</u>
37.7	-	11.42	2.56	2.50	0.34	139.4	12.1
33.9	-	5.30	2.05	0.65	0.82	132.5	6.6
22.0	12.5	0.94	0.16	0.06	0.06	15.7	7.8
21.5	30.8	0.35	0.10	0.09	0.07	50.5	1.2
22.2	52.5	0.13	0.04	0.04	0.03	36.1	0.7
22.8	49.8	0.17	0.05	0.03	0.03	33.4	0.8
24.8	66.5	0.10	0.02	0.02	0.03	25.3	0.7
19.5	26.3	-	-	-	-	-	-
22.7	32.5	-	-	-	-	-	-
-	29.5	-	-	-	-	-	-

Table 1 (Continued): Exchangeable Cations and Exchange Capacity  
- milli-equivalents/100 grams

<u>Horizon</u>	<u>Depth</u> <u>(cm)</u>	<u>Texture</u>	<u>Fe</u> <u>%</u>	<u>Al</u> <u>%</u>	<u>Available</u> <u>S</u> <u>p.p.m.</u>	<u>Available and</u> <u>Organically</u> <u>Complexed</u>	
						<u>Cu</u> <u>p.p.m.</u>	<u>Zn</u> <u>p.p.m.</u>
L	3.81-2.54	pt	-	-	-	-	-
HF	2.54-0.0	mu	-	-	-	-	-
Ae	0.0-1.90	l	0.36	0.48	12.5	-	-
Bhf	1.90-7.62	sil	1.34	4.26	30.8	-	-
Bfh1	7.62-20.3	sil	1.33	4.20	52.5	-	-
Bfh2	20.3-38.1	sil	1.62	4.08	49.8	-	-
Bfhgj	38.1-61.0	sil	1.11	3.56	66.5	-	-
BC	61.0-78.7	l	0.83	2.92	26.3	-	-
IICg1	78.7-99.1	fsl	0.71	1.98	32.5	-	-
IICg2		fsl	0.50	0.98	29.5	-	-



retention properties were determined for the less than 2 mm fraction of each of the ten soil samples. The particle size distribution was evaluated by the Hydrometer Method as described by Day (1965). One alteration in the test procedure was made; according to Lameris (1964) the chemical Calgon previously used in the Hydrometer Test is not an effective particle dispersing agent since phosphate no longer is included in the product. A .02 N Sodium pyrophosphate  $\text{NNa}_4\text{P}_2\text{O}_7$  solution (with regard to  $\text{Na}^+$ ) adjusted to pH 9.5 was therefore used as a dispersing agent in the Hydrometer Test. Using the United States Department of Agriculture (USDA) system, each soil sample was grouped in a textural home. The soil water content at .33, .9, 3.0, and 15.0 bars tension was determined by using low and high pressure porous plate extractors. The results of the particle size analysis are presented in Table 2 while the soil water retention curves are presented in Figs 6, 7, and 8.

### 3.1.3 Description of the Domestic Sewage Treatment Lagoons

The effluent applied to the forested plot was treated wastewater from the Loon Lake Forestry Camp. Located on the shores of Loon Lake in the University of British Columbia Research Forest, the forestry camp is used mainly for educational and research purposes by the university and public school communities.

The wastewater treatment facility consists of two adjacent earthen lagoons located about 300 m (984 ft) south

Table 2: Physical Properties of Soil Samples From  
the Vicinity of the Lysimeters

Sampling Location	Texture	Particle Size Analysis (% of Total)			
		Clay	<2 mm		>2 mm
			Silt	Sand	
A1	GSL	0.61	28.72	31.78	38.89
A2	GSL	2.76	19.32	33.13	44.79
A3	GSL	2.81	26.60	40.69	29.84
B4	GSL		Did not analyse		
B5	GSL	4.36	12.29	23.00	60.35
B6	GSL		Did not analyse		
B7	GSL	4.19	24.57	31.16	40.07
C8	GSL		Did not analyse		
C9	GSL	1.10	23.14	30.85	44.91
C10	GSL	3.49	22.45	23.94	50.12
Average Value		2.76	22.44	30.65	44.14

GSL = Gravelly sandy loam

FIGURE 6  
WATER RETENTION CURVES (LYSIMETER LOCATION A)

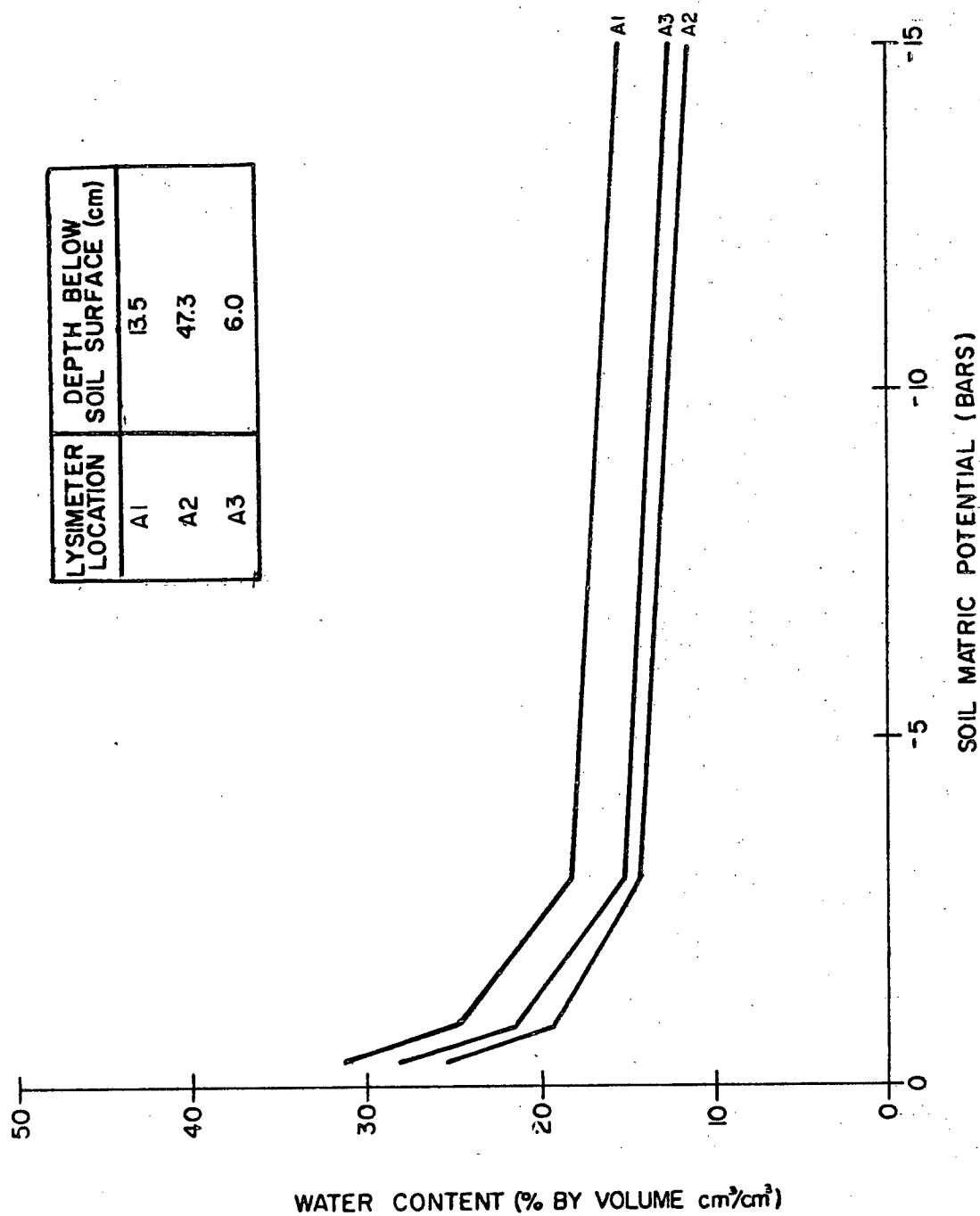


FIGURE 7  
WATER RETENTION CURVES (LYSIMETER LOCATION B)

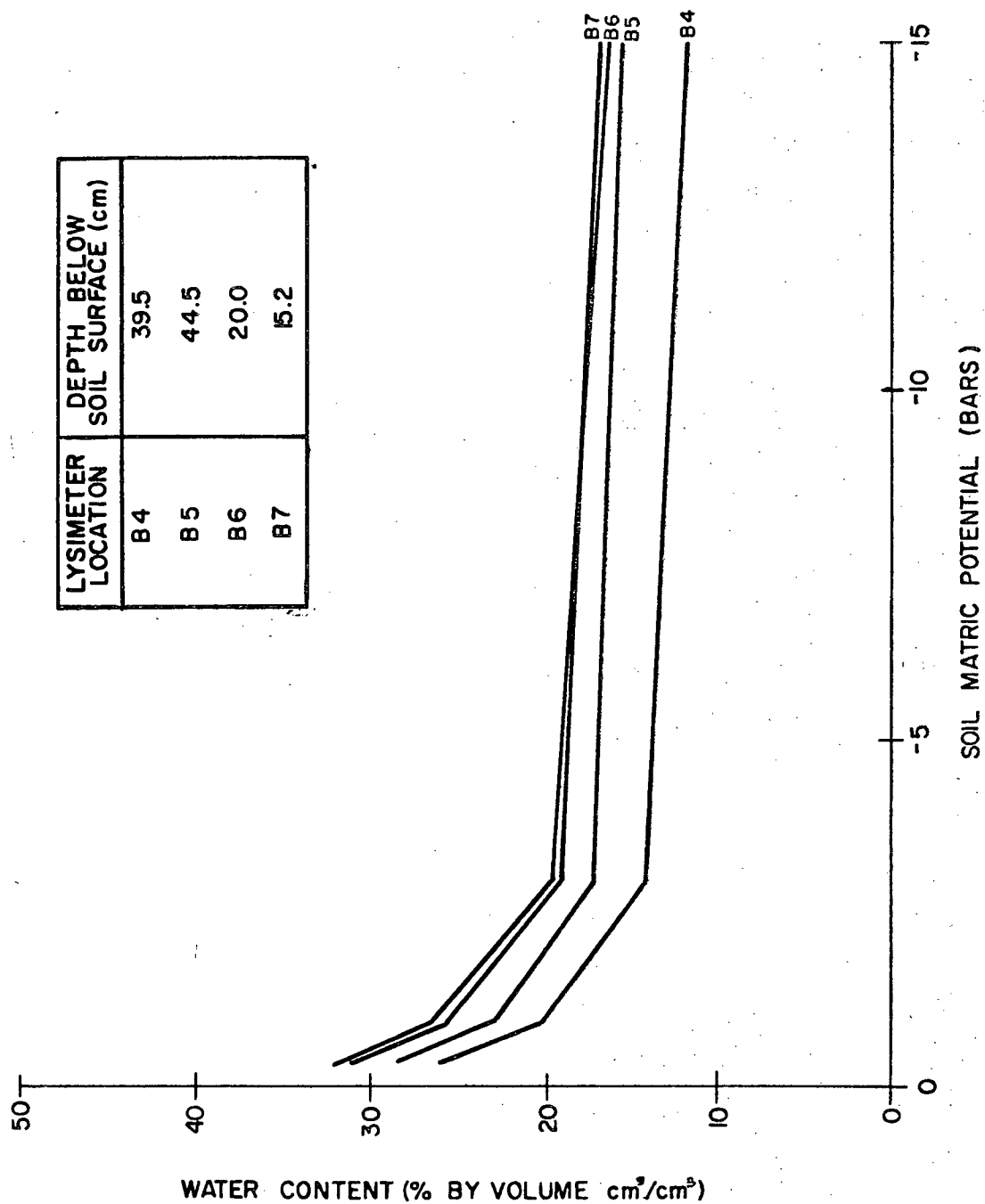
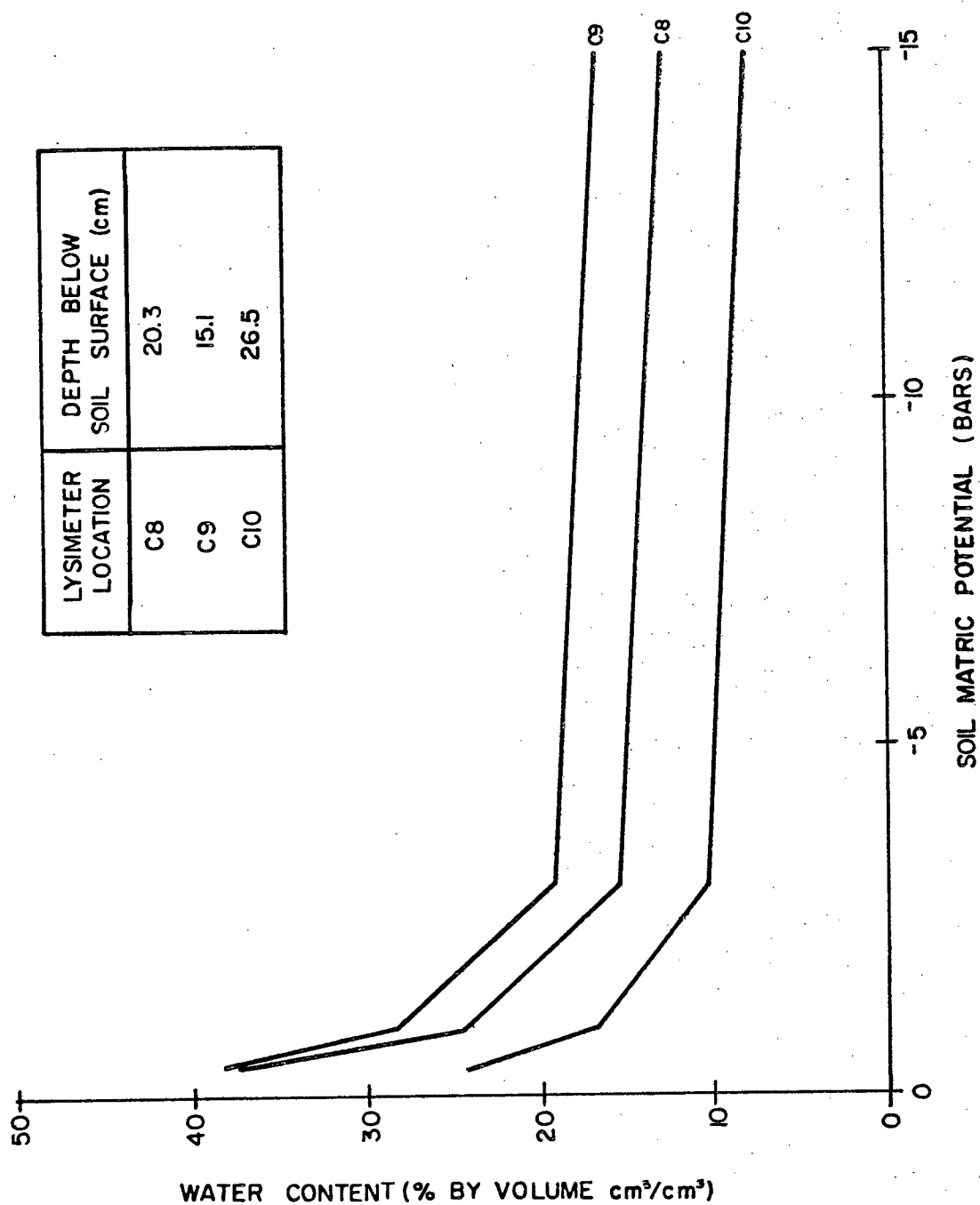


FIGURE 8  
WATER RETENTION CURVES (LYSIMETER LOCATION C)



of the forestry camp, with the bases of the ponds being about 5 m (16 ft) above lake level. Built into a mountain slope, the one side and the ends of the two lagoons were formed by the mountain slope while the second side of the lagoons and the earthen divide between the lagoons were constructed of material taken from the area excavated for the lagoons. This material was compacted during construction in an attempt to minimize, if not prevent, seepage of effluent to Loon Lake.

The construction of the lagoons partially into the slope of the mountainside interrupted the natural movement of groundwater flowing from the upper slopes to the valley bottom. To minimize the flow of groundwater into the lagoons and the subsequent dilution of the effluent, a tile line was installed at the level of the impermeable soil horizon around the three sides of the lagoons formed by the mountain slope. The tile line drained the groundwater to a ditch that passed the water to Loon Lake.

#### 3.1.3.1 The Effluent Treatment Process

Due to the camp use patterns, the resident population fluctuated over the term of the actual irrigation of the effluent. In general, no more than five to ten people per day were using the facilities during July, August and the first half of September while the population varied between twenty-five and seventy-five persons per day during the weekdays for the duration of the project. The fluctuating resident popu-

lation in the camp caused a large variation in the wastewater flow to be treated in the lagoon treatment facilities resulting in a variable effluent detention time in the lagoons.

The effluent treatment process involved aeration of the sewage followed by settling. The first lagoon, of  $144 \text{ m}^3$  capacity ( $5085 \text{ ft}^3$ ), served as an aeration basin. Three rows of perforated piping were located across the lagoon at a depth of 3 m (9.8 ft) below the free surface and served to distribute the air to the aeration basin. A pipe, approximately 7 m (23 ft) in length, through the earthen berm separating the two lagoons transferred effluent from the aeration basin to the larger settling lagoon.

The second lagoon, with a volume of  $1200 \text{ m}^3$  ( $42,378 \text{ ft}^3$ ) served as a settling basin. This lagoon had an overflow outlet that allowed the discharge of the treated effluent (treated meaning a B.O.D. reduction) to a small creek, which drains Loon Lake. The treated effluent used for irrigation on the mountain slope was drawn through a floating intake positioned 1 m (3.3 ft) below the free water surface and situated in the center of the lagoon area.

The quality of the effluent drawn from the settling pond and applied to the mountainside plot was extremely variable with regard to the constituents that formed the basis of the research. From the outset of the irrigation of the effluent, the concentration of the monitored constituents in the settling lagoon gradually decreased until they fell much below average

values documented for domestic treatment plants. The reason for such a decrease in the concentration values of the selected constituents was the infiltration of ground water into the lagoons. Not only did the concentration of the constituents decrease substantially after a rainfall event, but the elevation level of the liquid in the settling pond increased despite the fact that no wastewater was originating from the forestry camp. The dilution effect was especially severe during the term of the research because of the abnormally high amount of precipitation that fell on the area. To counteract this decrease in the concentration of the selected constituents and in an attempt to provide an effluent for irrigation that achieved the constituent concentration levels found in a normal domestic plant effluent, selected commercial fertilizers were added to the effluent in the settling basin.

### 3.1.3.2 Addition of Commercial Fertilizers to the Treatment Lagoons

In order to increase the concentration of nitrate nitrogen and total Kjeldahl nitrogen, two 22.7 kg (50 lb) bags of prilled ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) (34 - 0 - Terico Brand) were added to the settling lagoon on August 20, 1976 and two more bags were added on September 28, 1976. The manufacturer guaranteed that 17% of the total weight of each bag would be nitrate nitrogen while 17% of the total weight of each bag would be ammonia nitrogen. Two 22.7 kg (50 lb) bags of ammonium phosphate



( $\text{NH}_4\text{H}_2\text{PO}_4$ ) (11 - 55 - 0 Green Valley Fertilizer) were added on August 20, 1976, and two more bags were added on September 28, 1976. The minimum guaranteed analysis was 11% of the total weight would be total nitrogen while 55% of the total weight would be phosphoric acid. This would supplement the total Kjeldahl nitrogen (T.K.N.) and the phosphate found in the lagoons. To increase the chloride concentration in the effluent, ten 22.7 kg (50 lb) bags of muriate of potash or potassium chloride ( $\text{KCl}$ ) (0 - 0 - 60 Green Valley Fertilizer) were added on August 20, 1976 and ten more bags were added on September 28, 1976. The manufacturer guaranteed that 60% of the fertilizer would be soluble potash.

#### 3.1.4 Irrigation Equipment

The effluent was transported and irrigated through a permanent set pipe network. A permanently installed 5 hp pump located next to the treatment lagoon pumped the effluent from the settling basin to the irrigation site approximately 500 m (1640 ft) to the west. The volume of effluent being pumped was measured by a Trident Meters Limited volume measuring device set downstream from the pump in the 5.08 cm (2 in) diameter mainline. At the irrigation site eight sprinkler irrigation heads were used to apply the effluent to the forested plot. The sprinklers were located so that the effluent intensity was as uniform as possible over the plot being irrigated. The sprinkler heads were approximated 3.7 m (12.1 ft) above the soil

surface and generally were about 50 to 100 cm (19.7 to 39.4 in) above the tree tops except in two cases where the sprinkler heads were lower than the top of the trees in the vicinity. The effluent was applied at a rate of .40 cm/hr (.16 in/hr) over the whole plot.

The irrigation distribution network, the pipe mainline running from the sewage lagoons to the mountainside slope, the pump and the associated equipment were installed in 1972 by Dr. J. de Vries, with the costs of the equipment being borne by the U.B.C. Research Forest. The equipment was installed to facilitate research of the type reported in this thesis, in addition to research on the hydrology of mountain slopes undertaken by Dr. J. deVries and Graduate Students of the Department of Soil Science in the Faculty of Agricultural Sciences, U.B.C.

#### 3.1.4.1 Lysimeter Installation

Ten porous plate tension lysimeters were utilized to obtain soil leachate samples on a continuous basis during the irrigation period. Each plate consisted of an alundum disc of approximate radius 7.2 cm (2.8 in) and 2 cm (.8 in) thickness mounted on supports extending across an acrylic plastic plate assembly. The supports created a chamber between the bottom of the alundum disc and the acrylic plate which allowed the free movement of collected leachate to an acrylic tube. The tube permitted the leachate to pass to plastic tubing and ultimately to the collection bottle. The acrylic plate also was attached

to a frame that extended around the perimeter of the alundum disc to ensure that there was no air leakage. A more detailed description of the design, constructions and limitations of porous plate tension lysimeters has been reported by Cole (1958) and Bourgeois (1969). The lysimeters were washed with .001 N HCl and rinsed with distilled water prior to installation.

Within the mountainside plot three locations, labelled A, B, and C were chosen for the installation of the porous plate lysimeters. A pit was excavated down to the impermeable till on the down-slope edge of each of the three study areas. A conscious decision to dig on the down-slope side of each study area was made in order to ensure minimum disruption of the natural ground flow pattern through the study area. At each location a series of horizontal tunnels were excavated approximately to the length of an arm's reach and to a diameter that would allow the passage of the lysimeter to the installation point. The tunnel locations were also chosen so that the natural groundwater flow pattern to any lysimeter would not be disrupted by the placement of a lysimeter plate or tunnel above any other lysimeter. The lysimeter locations at each of the three sites were spread out as far as possible. Ideally, the lysimeters were placed just below the organic layer and on top of the C horizon. Practically, the success in following the latter guideline was not wholly accomplished due to minimum tunnel diameter required to allow the lysimeters to be put in position. Since it was impossible to dig into the C horizon, the tunnel had to

be excavated into the B horizon to a small depth thus preventing the lysimeter placement at the top of the C horizon or conversely at the bottom of the B horizon.

Three lysimeters were located at location A and labelled A1, A2, and A3, while four lysimeters were placed at location B and labelled B4, B5, B6, and B7, and three lysimeters were located at station C and labelled C8, C9, and C10. Table 3 summarized the depth to the top of each lysimeter as measured from the forest soil surface.

Great care was taken when installing the lysimeter plates in order to ensure maximum hydraulic contact between the soil and the porous alundum plate. First a location at the top of the horizontal tunnel was levelled to provide a flat site for the alundum plate to contact the soil matrix. Care was taken to remove protrusions such as rocks, roots, or soil aggregates as well as to fill in minor depressions with soil material taken from the immediate vicinity of the lysimeter. To provide an even greater potential for maximum hydraulic contact between the soil matrix and the alundum plate, a slurry of inert silicon carbide was applied to the alundum plate face. A negative pressure was applied to the tension lysimeter to semi-consolidate the silicon carbide slurry that would move to fill the spaces in the prepared soil face when the assembly was placed in position. The intention was to provide a continuous silicon carbide presence between the small soil depressions and the alundum plate thereby maximizing hydraulic contact and hence maximizing

Table 3: Depths of Lysimeters Below the Soil Surface

Lysimeter Location	Depth Below Soil Surface (cm)	Depth Below Soil Surface (in)
A1	13.5	5.3
A2	47.3	18.6
A3	6.0	2.4
B4	39.5	15.5
B5	44.5	17.5
B6	20.0	7.9
B7	15.2	6.0
C8	20.3	8.0
C9	15.1	5.9
C10	26.5	10.4

the ease of movement of soil leachate to the tension lysimeter.

The plate was then placed against the prepared soil face and rotated slightly back and forth in an attempt to force the silicon carbide into the soil face. The outlet from the tension lysimeter was facing out of the tunnel and positioned at the lowest point on the base of the lysimeter plate. In each case, a specially prepared vertical screw jack was used to force and permanently support the lysimeter plate against the tunnel roof. Each screw jack consisted of a 19.05 mm (.75 in) threaded rod screwed through a 10 cm by 10 cm (3.9 in by 3.9 in) plastic base plate. The soil material removed during the excavation of the tunnel was used to backfill the tunnel. The material was tamped into place to ensure a good degree of soil compaction and a minimum soil hydraulic disruption.

Three plywood boxes with plastic covered plywood lids were constructed and placed in each of the excavated pits. The spaces between the outer edge of the boxes and the edge of the pits were backfilled in order to minimize evaporation losses as well as to maintain the integrity of the lysimeter placement areas. The installed lysimeters were individually connected to the collecting bottles using Tygon plastic tubing (Tygon R 3603, 4.76 mm (.1875 in) inside diameter, and 7.94 mm (.3125 in) outside diameter). Each collecting bottle at the lysimeter locations was individually connected to a manifold common to each group of lysimeters at the three locations. In order to isolate the collection bottles for soil leachate sampling, a

valve was installed in the tubing that connected the lysimeter to each collecting bottle and a valve was installed in the tubing in the tubing that ran from each collecting bottle to the manifold. This arrangement allowed the leachate in each bottle to be collected without depleting the vacuum source or reducing the negative pressure in the lysimeters.

A mainline plastic tube connected the three manifolds to a Cartesian Manostat. It was recognized that vacuum leaks in the tubing, in the receiving bottles and in the lysimeters were inevitable. In order to maintain a constant vacuum in the lysimeters, a vacuum source had to be provided that could replenish the vacuum losses in the lysimeter system. The Cartesian Manostat was used to regulate and maintain the required tension (about 50 mm (1.97 in) of mercury) in the system by controlling the negative pressure release in the 100 pound propane cylinder used as a vacuum source. The propane cylinder was periodically evacuated with a pump to a vacuum of about 508 mm (20 in) of mercury.

### 3.1.5 Rainfall and Effluent Measurement Gauges

The amount of rain and effluent that reached the forest floor was determined through the use of sixteen rainfall gauges. Each collector consisted of a plastic cylinder approximately 6.5 cm (2.6 in) high, and either 9.55 cm (3.76 in) or 10.35 cm (4.07 in) in diameter, attached to the wide end of a plastic funnel. These acrylic cylinders with bevelled top edges were

mounted on each funnel to minimize splashing losses. Each funnel was placed in the neck of a 1 liter ( $61.02 \text{ in}^3$ ) plastic bottle, which for the purposes of stability, was in turn clamped to a metal post inserted in the ground. The volume of effluent or rain in the gauges was measured with a graduated cylinder.

Thirteen of the gauges were placed randomly on the plot while one gauge was placed at each of the lysimeter locations A, B, and C. The gauges at lysimeter locations A, B, and C were located in such positions that the collected effluent samples approximated the volume of effluent that was falling on the soil surface overlying the lysimeter plates.

The amount of effluent that was collected in the rain gauges during an irrigation event was measured immediately after the termination of that event. The amount of rain that fell between the end of one irrigation event and the commencement of the next irrigation event was measured immediately prior to the start of the latest irrigation event. The duration of rainfall that fell during the interval between the cessation and the commencement of irrigation several days later was determined prior to the start of irrigation by means of a tilting bucket gauge connected to an event recorder. The tilting bucket employed had a 20 cm (7.87 in) diameter receiver and a bucket capacity of .5 mm (.02 in) of rainfall. While the 16 rain gauges were used to determine the magnitude of the rainfall that had occurred between effluent spraying dates, the tilting bucket was used to determine the time and duration over which such an event occurred.



### 3.1.6 Soil Water Content Measurements

The fluctuation of the soil water content in response to natural rainfall and to the application of domestic effluent was monitored through the use of a Troxler Neutron Moisture Probe. A steel access tube was located at lysimeter locations B approximately 100 cm (40 in) from the four lysimeter plates. The water content of the soil was measured at depths of 15, 30, 50, and 70 cm (5.9, 11.8, 19.7, and 27.6 in) below the soil surface immediately before and immediately after the application of domestic effluent. The water content measurements were terminated on September 21, 1976 due to a malfunctioning portable Scaler Rate Meter.

## 3.2 ANALYTICAL METHODS AND MATERIALS

### 3.2.1 Effluent Irrigation Schedule

The forested plot was irrigated with effluent twice per week during the period June 15, 1976 to November 12, 1976. An effluent volume of eighteen cubic meters (3962 imperial gallons), as measured by the volume meter, was applied over the  $900 \text{ m}^2$  ( $10,000 \text{ ft}^2$ ) plot on each irrigation session. This schedule resulted in the application of an effluent depth of 2 cm (.79 in) per irrigation. Since the pump delivered .40 cm (.16 in) of effluent per hour, each of the 31 irrigation sessions required 5 hours.

There were two exceptions to this arrangement. No irrigation was undertaken on September 24 as the pump was being used

to deliver lake water to an adjacent plot. On July 15, 1976 and on July 29, 1976 less than 2 cm (.79 in) of effluent was applied to the plot. This was in keeping with the original intention of applying 2 cm (.79 in) of effluent per irrigation session minus the amount of rain that fell in the interval between the end of the last irrigation event and the next irrigation session. Abnormally high amounts of rainfall during the first week of August would have further delayed the application of effluent in the planned amounts if the original schedule was followed. It was then decided to alter the original irrigation schedule to one that involved the spraying of 4 cm (1.60 in) of effluent per week regardless of the amount of precipitation that fell on the forested plot.

### 3.2.2 Collection, Storage and Analysis of Soil Leachate

#### Collected by the Ten Lysimeters

The ten lysimeters were connected to the main vacuum source on July 7, 1976. The soil leachate collected over the next several days was used to flush out the lysimeters, the tubing and the receiving bottles, with the leachate being discarded.

With the commencement of the irrigation program to apply 2 cm (.79 in) of domestic sewage twice per week to the forested plot, a program to sample the resulting soil leachate collected by the lysimeters was begun. Prior to the commencement of irrigation on any one of the 31 irrigation days, the leachate samples resulting from the previous irrigation session and any rain that

fell in the time interval between irrigation events were collected from all the receiving bottles. The soil leachate samples collected on each of the 31 irrigation days had been gathered continuously by the lysimeters during the time span from the start of spraying on any of the 31 irrigation days through to just prior to the commencement of irrigation on the next irrigation date. Up to 2 liters of soil leachate in each of the ten receiving bottles were retained for analysis of the selected water constituents. Any excess sample was discarded from the receiving bottles.

Two samples of sewage effluent being applied to the mountain slope were collected during each irrigation event. The collection of such samples was facilitated by the insertion of a tap in the irrigation pipe mainline at the irrigation site.

The ten soil leachate samples and the two applied effluent samples were placed in ice-filled coolers until they could be stored in a laboratory refrigerator (temperature at  $4^{\circ}\text{C}$ ) later the same day. No preservatives were added to the samples. Over the next three days the samples were analysed for nitrate-nitrogen, total Kjeldahl nitrogen (TKN), total phosphate, ortho phosphate and chloride.

The sewage and soil leachate samples were analyzed according to the procedures outlined in Standard Methods for the Examination of Water and Wastewater (14th edition 1976). The nitrate nitrogen concentration in the samples was determined by the Ultraviolet Spectrophotometric Method employing the

Bausch and Lomb Spectronic 600 Spectrophotometer. The concentration of ammonia and organic nitrogen was determined by the total Kjeldahl nitrogen method. The determination of the total phosphate concentration in the samples involved the Persulphate Digestion Method to convert all the phosphate present to orthophosphate. These samples were subjected to the Stannous Chloride Colour Development Method to determine the ortho phosphate present in the digested samples. The intensity of the blue colour was measured photometrically by a Bausch and Lomb Spectronic 88 Spectrophotometer. The determination of the concentration of ortho phosphate in the applied sewage and soil leachate samples involved the Stannous Chloride Method as outlined for the determination of the total phosphate concentration. The chloride ion concentration in the samples was determined by the Mercuric Nitrate Method.

### 3.2.3 Phosphorus Removal Isotherms

#### 3.2.3.1 Time-Adsorption Study

Typical time-adsorption curves for phosphorus indicate an initial fast reaction followed by a secondary reaction which occurs at a slower rate, often described by a first order reaction equation. In order to establish the contact time required to reach equilibrium between the soil and the phosphorus in the sewage effluent, three time adsorption experiments were undertaken in the laboratory. The contact time was then used to indicate an equilibrium condition in the development of the

phosphorus adsorption isotherms.

The soil samples used in the development of the time-adsorption curves and the adsorption isotherms were the same samples collected from the immediate vicinity of the ten lysimeters during their installation. Subsamples of these collected samples had also been evaluated for water retention properties and particle size distribution. In preparation for the determination of the time adsorption curves and the phosphorus adsorption isotherms, the ten soil fractions of greater than 2 mm in diameter were consolidated into one large sample as were the ten soil fractions of less than 2 mm in diameter. The purpose of consolidating the individual samples was to obtain time adsorption curves and phosphate adsorption isotherms representative of the entire plot.

Three different time-phosphorus adsorption experiments were undertaken in the laboratory with only the total soil weight added to the domestic effluent being varied between experiments. The effluent was obtained from the secondary sewage treatment plant at Maple Ridge, British Columbia. In the first experiment a total of 60 g of soil was added to a flask containing 2 l of effluent while in the second study 100 g of soil was added to a flask containing 2 l of effluent. In the third time-phosphorus adsorption study, 200 g of soil was added to 2 l of effluent. A range of total weights was used to determine if a variation in total soil weight or the number of phosphorus adsorption sites would influence the contact time to reach

equilibrium between the phosphorus in the effluent and the soil. Of the 60 g of total soil weight used in the first time-phosphorus adsorption experiment, 45 g or 75% of the soil weight was less than 2 mm in diameter. In the second time-adsorption experiment, 70% of the 100 g total soil weight used was less than 2 mm in diameter while 175 g or 87% by weight of the 200 g of total soil weight used in the third time-adsorption experiment was less than 2 mm in diameter.

Each of the three soil samples were placed in beakers containing 2 liters of effluent. Each soil-effluent solution was subjected to stirring with a magnetic stirring bar. At various times ranging from one minute to 140 minutes after the commencement of stirring, samples were removed from the beakers. Each sample was immediately subjected to centrifuging at 2500 R.P.M. for 30 minutes to reduce the suspended material interference that might occur during the phosphate analysis. The removal of the suspended material also averted the re-entry of phosphorus from the solid phase to the liquid phase during the phosphorus concentration analysis. At the completion of the centrifuging, the centrate was analyzed for total and ortho phosphate as previously described. The resulting data indicated that a one and one half hour stirring time would permit the completion of the initial phosphorus removal step (for a more detailed description see section 4.5.1.1).

### 3.2.3.2 Phosphorus Removal Isotherms

Total and orthophosphorus adsorption removal isotherm data were generated in a series of laboratory batch scale experiments. Since both the initial ortho and total phosphorus concentrations were fixed values in the domestic sewage samples, the soil sample weights in the adsorption experiments had to be varied. Also for the phosphorus removal isotherms the percentage of the total soil weight that was less than 2 mm in diameter was approximately equal to the average percentage value of the total soil weight of particles less than 2 mm in diameter averaged over the ten individual samples. From Table 2 it can be seen that over the soil samples collected from around the ten lysimeter locations, an average of 56% of the total soil weight was less than 2 mm in diameter. As a consequence, approximately 60% of the total weight of each soil sample used in the adsorption experiments was less than 2 mm in diameter. One, three, five and one hundred grams of soil were added to beakers containing 1 l of effluent while four, five, six, seven, eight, ten, fifteen, twenty, and twenty-five grams total soil weight were added to beakers containing .5 l of domestic effluent.

The effluent-soil combinations were subjected to magnetic stirring for one and one half hours. At the end of this time the filtrate in each beaker was subjected to centrifuging followed by the analysis for ortho and total phosphate in the same manner and method as in the time-adsorption study.

#### 4.0 RESULTS AND DISCUSSION

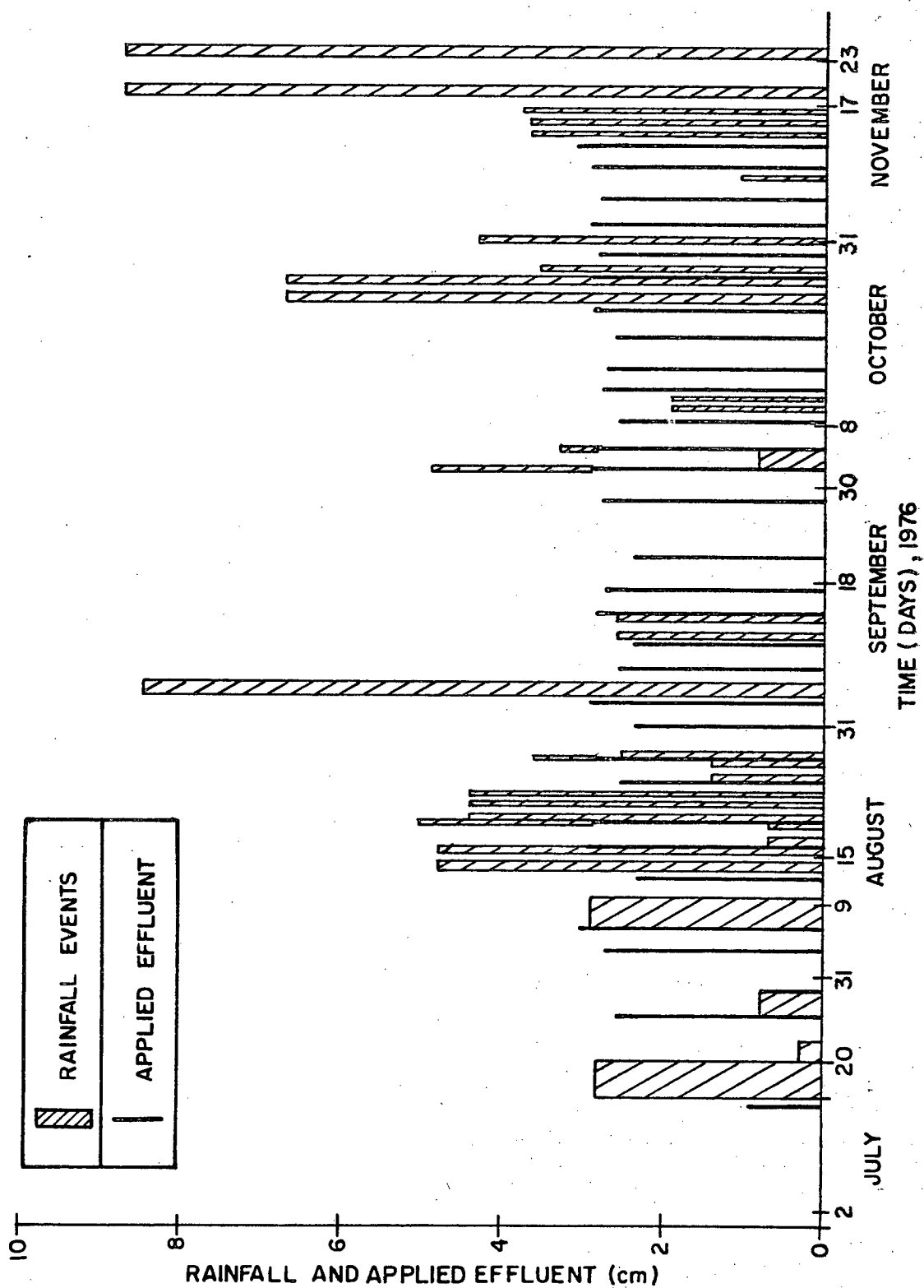
##### 4.1 Rainfall and Effluent Volume Measurements

The amount of effluent and rainfall that reached the forest floor was not uniform over the 900 m<sup>2</sup> plot. Not only did the tree branches alter the passage of effluent and rain to the forest floor, but each of the eight sprinkler heads also set up unique spraying patterns for the section of the plot that they individually covered. Wind, according to McKay (1970), will alter the rainfall or effluent pattern significantly as will evaporation between irrigation events held on two different days. The result was a varying amount of rain or effluent collected in each of the sixteen rain gauges over the same irrigation or rainfall event and between different irrigation events.

The rainfall and applied effluent amounts that fell on the plot during the experimental period are present in Fig 9. The amount of effluent for each of the 31 irrigation events, measured immediately after the cessation of each irrigation event, is an average value of the amount of effluent collected in each of the 16 rain gauges. A problem arose when the 5 hours required to apply 2 cm (.79 in) of effluent occurred during the period of a rainfall event. The rain gauges would be collecting not only the applied effluent but also the falling rain. In order to adjust the applied effluent volume for such occasions, the average effluent values over the 16 rain gauges for non-rain or negligible rainfall-irrigation days were averaged. Of the 31 days on which this irrigation of effluent was undertaken,



**FIGURE 9**  
**PRECIPITATION AND APPLIED EFFLUENT DATA**  
 (AVERAGE VALUES FROM 16 RAIN GAUGES SITUATED THOUGHOUT PLOT)



24 days had no rain or negligible amounts of rain. The amount of applied effluent as a result of averaging the effluent values recorded on those 24 days was 2.81 cm (1.11 in). On the 7 days that rain occurred simultaneously with the irrigation of effluent, the average amount of effluent collected over the 16 rain gauges had 2.81 cm (1.11 in) subtracted from it. The difference was assumed to be the amount of rain that fell during the irrigation period. The total average amount of effluent that was applied during the course of the project was 80.14 cm (31.55 in).

Prior to the commencement of irrigation, the amount of rain that fell in the time interval between the cessation of the last irrigation and the beginning of the current irrigation was measured. An average rainfall depth was calculated by averaging the measured rainfall depth in each of the sixteen gauges. Since the rain did not fall over the complete time period between irrigation events, the start and duration of each storm was determined from the tilting bucket data recorded on the event recorder. The average depth of rainfall over the 16 rain gauges, in conjunction with the start and duration of the same rainfall events from the operation of the tilting bucket is shown in Fig 9.

The uneven distribution of applied effluent over the forested plot resulted in a range of effluent depths measured in the 16 rain gauges, not only over each irrigation period, but over the term of the experiment. Of particular concern was the amount of effluent that reached the forest floor over-

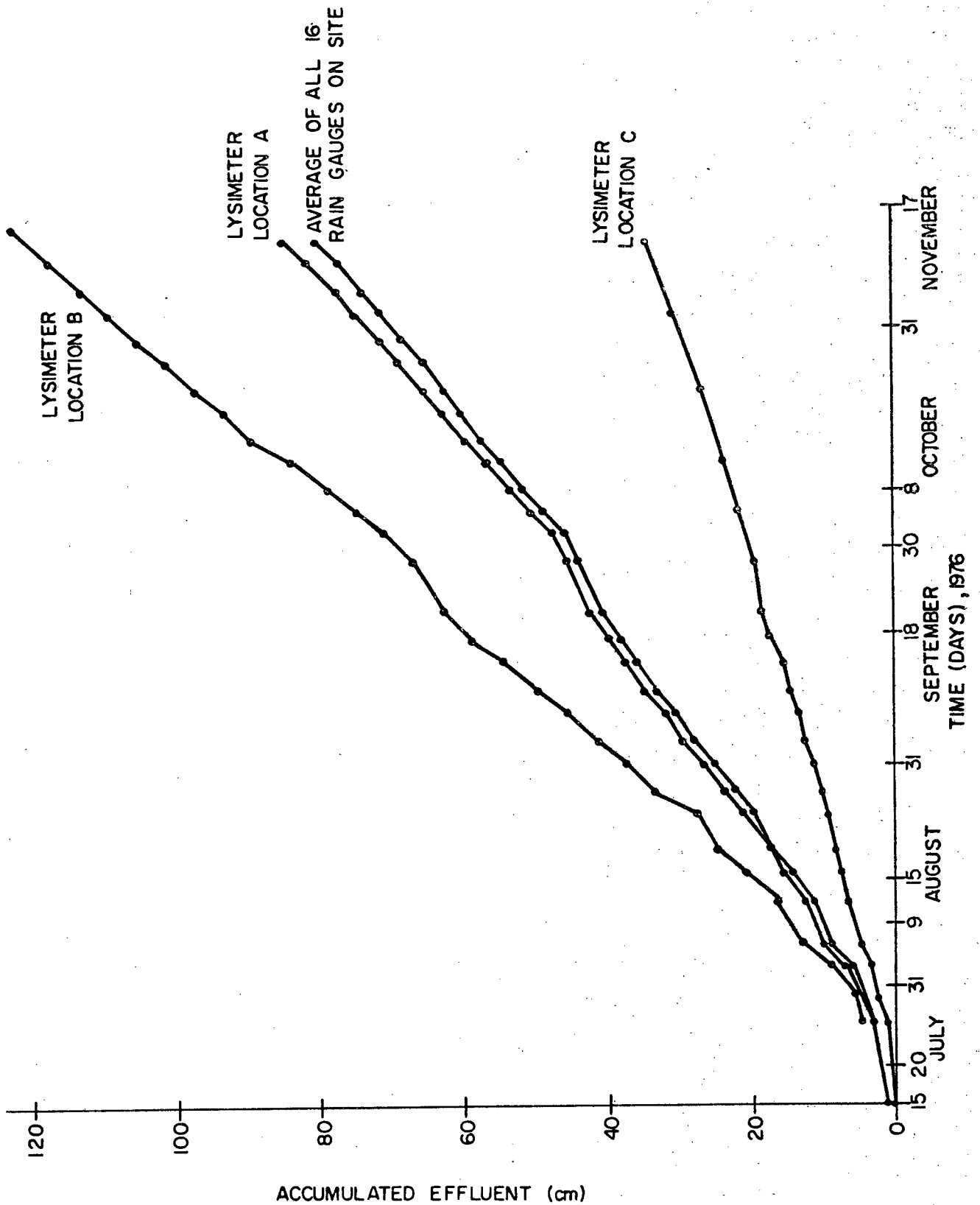
lying the lysimeters. The amount would influence the soil leachate characteristics collected by the lysimeters at each of these locations.

The mass curves of accumulated effluent depths over the term of the experiment as measured by the rain gauges at lysimeter locations A, B, and C are presented in Fig 10. Also presented in the same figure is the mass curve for applied effluent as determined by averaging the effluent depths measured in the 16 rain gauges.

From Fig 10, it is clear that lysimeter location B received the greatest amount of effluent over the irrigation period while lysimeter location C received the smallest amount. Lysimeter location B received a total of 122.50 cm (48.23 in) while lysimeter location A received a total of 84.41 cm (33.23 in) and lysimeter location C received a total of 34.25 cm (13.48 in) over the period of study. In the same period the average amount of effluent applied to the total plot as measured over the 16 rain gauges was 80.14 cm (31.55 in).

Based on the concentrations of nitrate nitrogen, total Kjeldahl nitrogen and total phosphate in the applied effluent as well as the average volume of effluent applied over the total irrigation plot, 48.4 kg/ha (43.2 lb/acre) nitrate nitrogen, 93.7 kg/ha (83.6 lb/acre) total Kjeldahl nitrogen and 43.5 kg/ha (38.6 lb/acre) of total phosphate were applied to the plot during the project period.

FIGURE 10  
APPLIED EFFLUENT MASS CURVES



#### 4.2 Water Content Measurements

The water content readings in the soil at depths of 15, 30, 50, and 70 cm (5.9, 11.8, 19.7, and 27.6 in) at lysimeter location B are summarized in Appendix C. The readings were taken just prior to and after the termination of the applications of domestic effluent on the irrigation days that occurred between July 19, 1976 and September 17, 1976.

The water content values at the soil field capacity (.33 bar) for the soil samples collected from the tension lysimeters at location B are given in Fig 7. For the soil sample collected from the vicinity of lysimeter location B4, the water content at field capacity is  $.260 \text{ cm}^3/\text{cm}^3$ . Similarly, for soil samples collected near lysimeter locations B5, B6, and B7, the water content at the field capacity is .286, .321, and  $.316 \text{ cm}^3/\text{cm}^3$  respectively.

Field capacity has been defined by Baver, Gardner and Gardner (1972) as

"The water content of a soil profile, usually the rooting zone, which has been thoroughly wetted by irrigation or rainfall and after subsequent rate of drainage out of the profile has become negligibly small."

It was commonly assumed that the application of a certain quantity of water to the soil will fill any soil water deficit to field capacity. When irrigating, it is almost universal practice to calculate the amount of irrigation water to be applied to the soil at any particular time on the basis of the deficit to field capacity of the soil layer to be wetted. The

development of the theory and more precise experimental techniques in the study of unsaturated flow has demonstrated the limitations of the concept of field capacity (Baver, Gardner and Gardner, 1972; Hillel, 1971; Kirkham and Powers, 1972).

In spite of demonstrated shortcomings, the water content at the so called field capacity is still considered to be the water content to be achieved when irrigation is undertaken to correct a soil water deficit condition. The usual procedure is to allow the water content to deplete to a value that is a percentage of the water content difference between the soil water content at  $-1/3$  bar and the water content at  $-15$  bars, where the  $-1/3$  bar water content is the laboratory estimate of the field capacity and the  $-15$  bars water content is the laboratory estimate of the so called wilting point. (the difference in the water contents at these two points is termed the available water storage capacity (AWSC)). When this water content deficit is reached, the soil is irrigated until the water content reaches a value equal to the water content value associated with  $-1/3$  bar matrix potential or the field capacity (Irrigation Design Manual, British Columbia Department of Agriculture, 1975).

A consideration of the field capacity for the soil samples taken from near the lysimeters at location B and the measured soil water content values indicate that at all times during the application of effluent the soil water content was above the so-called field capacity of the soil. Thus, according to

a water balance criterion, the forest soil was overloaded with water. In such a situation the application of domestic effluent would normally not be considered if the commonly accepted irrigation guidelines had been followed. This should be considered in any discussion of the constituent concentration results from the soil leachate collected over the test period.

#### 4.3 Chloride Concentrations in the Soil Leachate

For the period August 16, 1976 to November 23, 1976, during which chloride determinations were undertaken, all the soil leachate samples collected in the ten lysimeters contained chloride. Due to low chloride concentrations in the effluent from the forestry camp, the chloride determinations of the soil leachate and the applied lagoon effluent were not begun until August 16, 1976, four days before the commercial fertilizer, muriate of potash (KCl), was added to the treatment lagoons. The addition of the fertilizer was intended to increase the chloride concentration so it could be used as a tracer of the movement of the applied effluent through the forest soil.

The concentration of chloride in the applied effluent, as well as in the soil leachate samples collected at lysimeter locations A, B, and C, for the period August 6, 1976 to November 23, 1976, are shown in Figs 11, 12, and 13 respectively. The chloride concentrations in the applied effluent for a particular irrigation event are plotted on the same day on which the soil leachate resulting from that particular irrigation

FIGURE II  
CHLORIDE CONCENTRATION - LYSIMETER LOCATION A

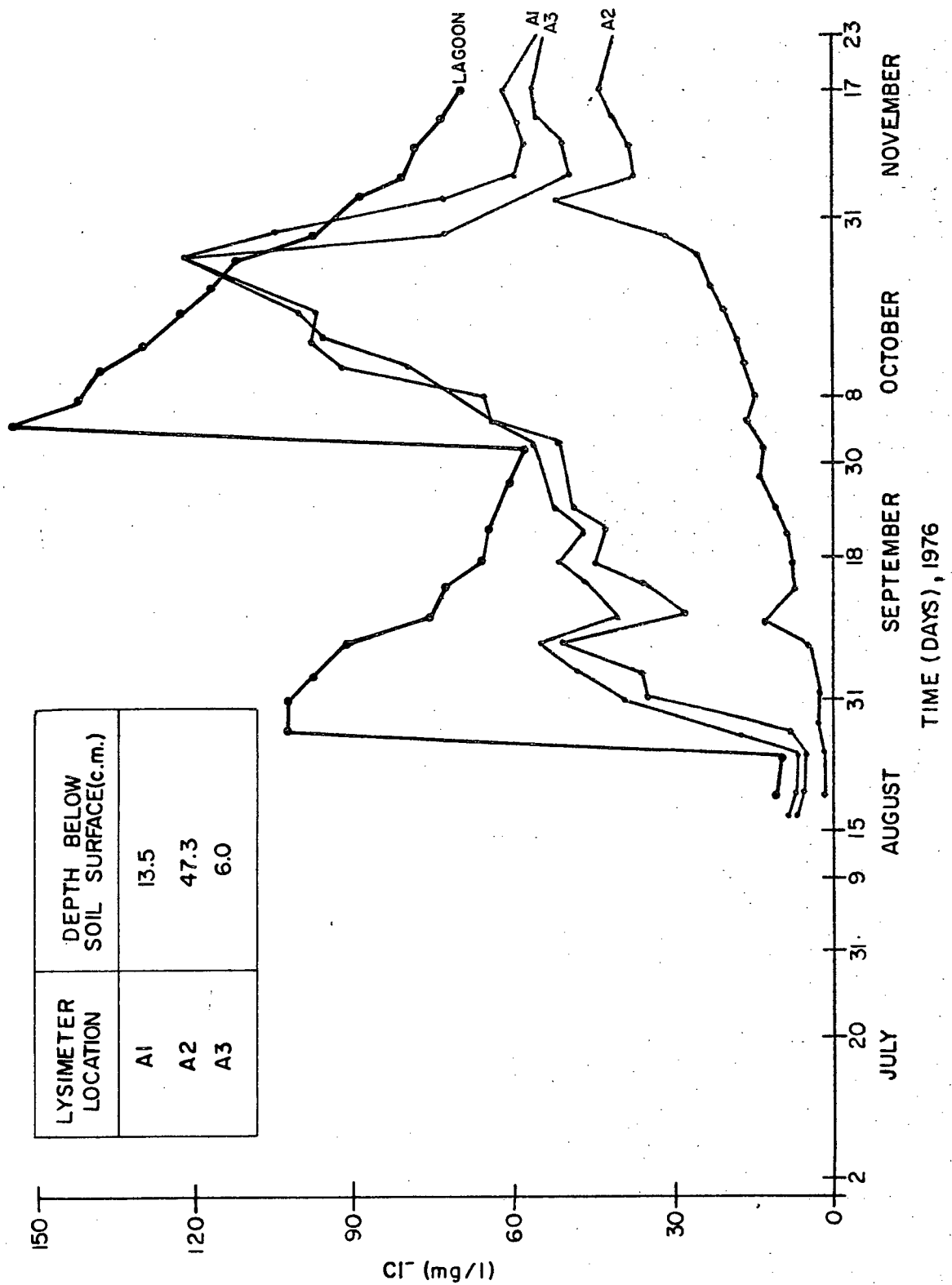




FIGURE 12  
CHLORIDE CONCENTRATION - LYSIMETER LOCATION B

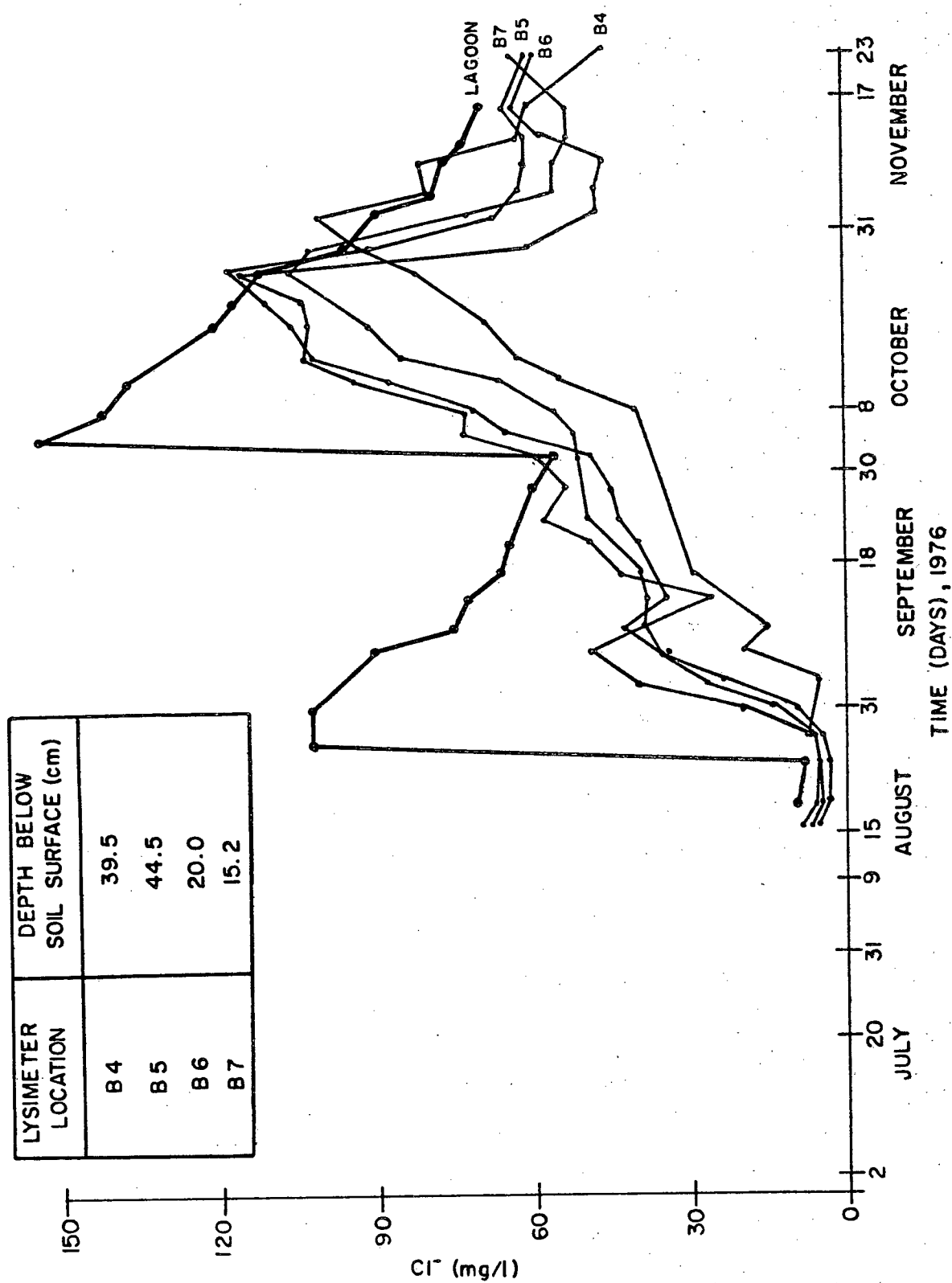
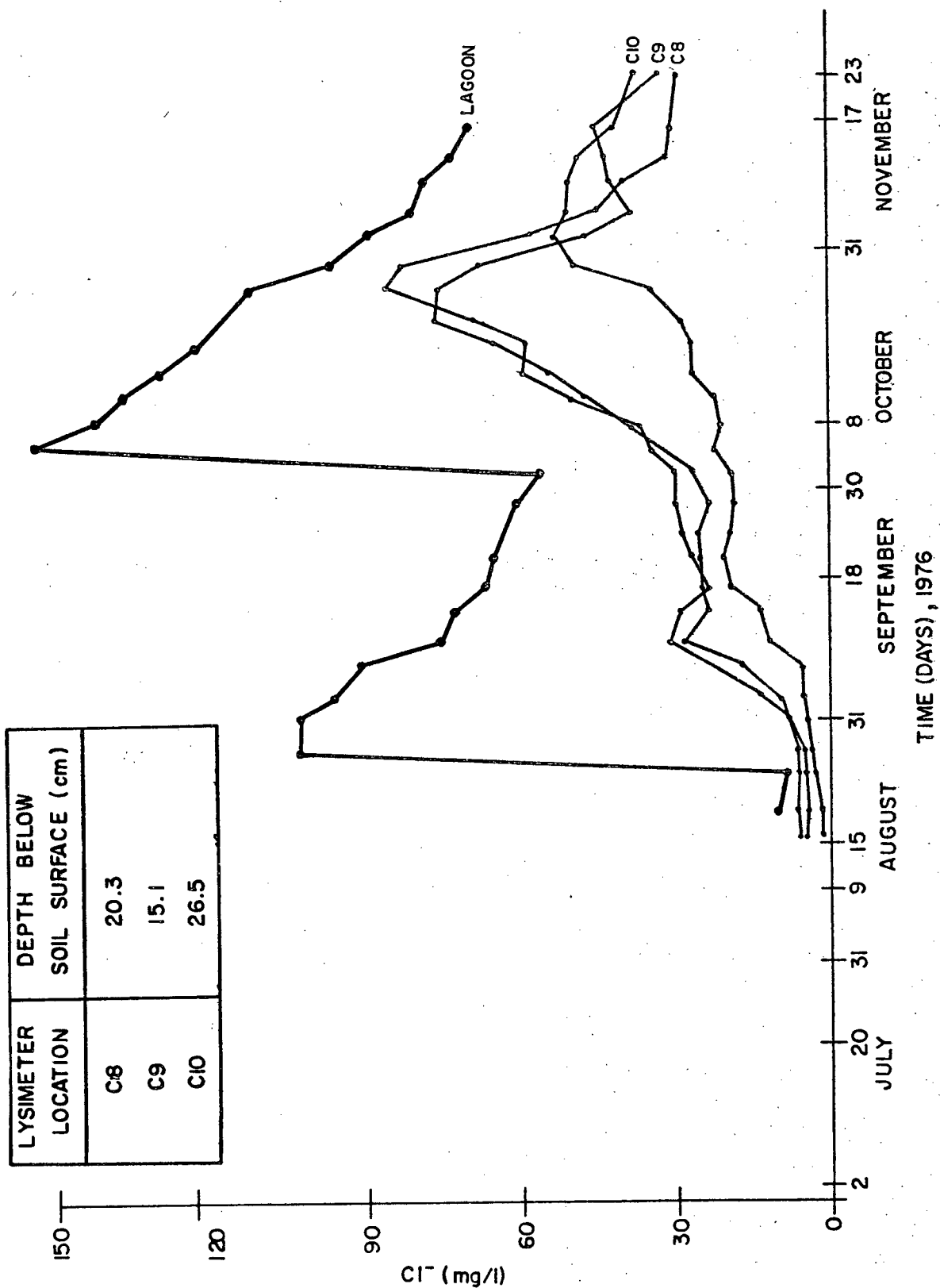


FIGURE 13  
CHLORIDE CONCENTRATION - LYSIMETER LOCATION C



event was collected. For example, on each diagram the lagoon chloride concentration shows a dramatic increase after August 24, 1976 and October 2, 1976 due to the addition of the muriate of potash (KCl) on August 20, 1976 and September 28, 1976 respectively. The effluent that contained the KCl addition was first applied on August 24, 1976 and October 2, 1976 but the soil leachate resulting from these irrigation events was not collected until August 27, 1976 and October 5, 1976. As a consequence, the increased lagoon chloride concentration applied to the forested area was plotted on the days on which the resultant soil leachate samples were collected, namely August 27, 1976 and October 5, 1976. This procedure was followed for the nitrogen and phosphorus applied effluent concentrations over the duration of the experiment.

The chloride concentrations in the applied effluent were never a constant value during the time period they were being tested for. It can be observed in Figs 11, 12, and 13 that the chloride concentration in the effluent was increased to 102 mg/l chloride with the addition of KCl. The continual introduction of groundwater and rainfall to the effluent lagoons gradually decreased the chloride concentration to a value of 56 mg/l chloride over a period of five weeks. At that point a further addition of KCl increased the chloride level in the lagoon to a concentration of 154 mg/l chloride. Subsequent groundwater dilution and rainfall decreased the chloride concentration to a value of 74 mg/l chloride over a five week period.

The chloride concentrations of the soil leachate samples collected by the lysimeters at location A are shown in Fig 11. In general, there was a steady increase of the chloride concentration in the soil leachate collected by the lysimeters A1, A2, and A3.

The response to the increased chloride concentration in the applied effluent was more pronounced in the soil leachate collected near the soil surface. The leachate samples collected by lysimeters A1 (13.5 cm (5.3 in) below the soil surface) and A3 (6.0 cm (2.4 in) below the soil surface) showed a rapid increase in the chloride concentration in response to the application of the effluent containing the high chloride concentration. This trend continued, with the two lysimeters collecting leachate samples that contained steadily increasing chloride concentrations. The exception to this trend was a decrease in the soil leachate chloride concentration in the soil leachate samples collected in lysimeters A1 and A3 over the period September 7, 1976 to September 10, 1976. This was a delayed response to the 8.4 cm (3.30 in) of rain that fell over the 42 hour period from 0600 hours September 4, 1976 to 2400 hours September 5, 1976. The chloride concentration in the applied effluent also influenced the chloride concentration values in the soil leachate. The increase in the chloride concentration of the soil leachate collected by the lysimeters A1 and A3 was small in the period September 24, 1976 to October 30, 1976 in comparison to the increase during the period October 2, 1976

to October 14, 1976. In the former time span, the chloride in the leachate collected by the lysimeters A1 and A3 was almost the same as chloride concentration in the applied effluent, while in the latter case the concentration in the lagoon was almost double that found in leachate collected by the same two lysimeters.

The peak chloride concentration in the soil leachate samples collected by lysimeters A1 and A3 was reached on October 26, 1976. The subsequent decrease in the chloride concentration was due to a combination of the two factors discussed above. On October 22, 1976, the chloride concentrations in the soil leachate samples collected by lysimeters A1 and A3 were just below the concentration in the applied effluent. On October 26, 1976, the concentration in the applied effluent was less than that in the resulting soil leachate collected by lysimeters A1 and A3. The next application of effluent on October 26, 1976 resulted in a sharp decrease in the chloride content of the soil leachate collected between October 26 and October 29, 1976. The concentration in the soil leachate collected by lysimeter A3 over the period, dropped from 120 mg/l to 72 mg/l while the chloride concentration in the soil leachate collected by A1 dropped from 120 mg/l to 100 mg/l. Not only did the decreasing chloride concentration in the applied effluent cause a decrease in the concentration in the soil leachate, but the resulting dilution by the rainfall also contributed to the decrease. Over the period 0600 hours October 24, 1976 to

1000 hours October 25, 1976, 6.7 cm (2.6 in) of rain fell on the plot while 3.5 cm (1.4 in) of rain fell between 2100 hours October 27, 1976 to 1000 hours October 28, 1976 and 4.3 cm (1.7 in) of rain fell between 1800 hours October 30, 1976 and 1100 hours October 31, 1976 on the forested plot. It was not until the period November 5, 1976 to November 16, 1976 that the chloride concentration in the soil leachate collected by the lysimeters A1 and A3 began to increase again. No rain fell during this period and the applied effluent chloride concentration was greater than that found in the soil leachate. The last irrigation of effluent took place on November 12, 1976. Soil leachate from lysimeters A1 and A3 was collected on November 16, 1976 and November 23, 1976. With no effluent being applied on November 16, 1976, the subsequent drop in the chloride concentration in the soil leachate collected between November 16, 1976 and November 23, 1976 was due to the dilution effects of the rainfall over the same period. From 1800 hours November 15, 1976 to 0900 hours November 17, 1976, 8.7 cm (3.4 in) of rainfall was recorded by the rain gauges on the plot.

The soil leachate collected by the deep lysimeter A2 exhibited the same trend in the chloride concentration over the period August 6, 1976 to November 23, 1976 as that found in the soil leachate collected by lysimeters A1 and A3. The difference between the concentration in the soil leachate collected on similar days in the two situations was one of magnitude. The chloride concentration in the soil leachate

collected by lysimeter A2 was consistently much lower in value when compared to that in the leachate collected by lysimeters A1 and A3. Also the response to the effects of dilution on the chloride levels in the leachate collected by lysimeter A2 was less pronounced, and was on a more time delayed basis than the fluctuations in the soil leachate samples collected by the shallow lysimeter.

A consideration of the chloride concentration in the soil leachate samples collected by the lysimeters at location B (Fig 12) and C (Fig 13), over the period of study indicates the same trend as noted above for the soil leachate collected at lysimeter location A. In general, the chloride concentrations in the soil leachate samples collected at these locations increased at a steady rate in response to the high chloride concentration in the applied effluent. The exception, as noted with the chloride in the soil leachate collected at lysimeter location A, was the concentration decrease in the soil leachate samples collected over the period October 7, 1976 to October 10, 1976, for the shallow lysimeters, and over the period October 10 to October 14, 1976 for the deep lysimeters. The decrease was caused by the dilution of the soil leachate by rain. In general, the chloride concentrations in the leachate collected in the shallow lysimeters at location B and C were of higher magnitude than those in the leachate collected from the deep lysimeters at the same locations. The dilution effects on the chloride concentrations in the soil leachate collected

by the deep lysimeters at lysimeter locations B and C were on a delayed basis, with the resulting chloride concentration decrease being much lower in magnitude.

A gradual rather than a sudden increase in the chloride concentrations in the soil leachate samples collected by the ten lysimeters with time was probably due to the anion sorption properties of soil on the irrigated plot. According to several authors (Wiklander, 1964; Grimm, 1968; and Tisdale and Nelson, 1966) the chloride ion is very mobile in most soils. Smith (1972) indicated that the chloride ions can move through the soil faster than the associated soil water because of anion exclusion (anions are excluded both from the vicinity of the negatively charged soil particles where the soil water is relatively mobile and from the narrow pores where soil water velocities are low). Thus, it could be expected that the chloride concentration in the soil leachate collected by the lysimeters would rapidly attain a level of the chloride in the applied effluent. But as discussed earlier, this was not observed even in the soil leachate samples collected by the shallow lysimeters A2, A3, B6, B7, C8, and C9 which were all less than 20 cm (7.9 in) below the soil surface. The retardation at shallow depths of the movement of the chloride ion was most likely due to the retention of chloride on the anion exchange sites of the organic matter while the positively charged amorphous iron and aluminum surfaces probably impeded the passage of the chloride ion at deeper depths in the soil horizon.



The chloride ion in the applied effluent was initially removed by the positively charged portions of the organic matter found in the LFH horizon of the soil profile. As these reactive sites were occupied, less chloride in the applied effluent was being removed from the soil solution and the soil leachate chloride concentration in this area gradually increased in magnitude. This phenomenon was reflected in the trend that saw the chloride concentrations gradually increase with time in the soil leachate samples collected by the shallow lysimeters. The chloride contained in the soil leachate that moved deeper in the soil horizon was capable of being retained by the positively charged amorphous aluminum and iron compounds. As these reactive sites were satisfied the chloride concentration in the soil leachate collected by the deep lysimeters A2, B4 and C10 increased in magnitude. The increase in the chloride concentration in the soil leachate collected from the deep lysimeters was delayed in comparison with the increase that occurred in the shallow lysimeters because the deeper the leachate moved into the soil profile, the greater the number of anion exchange sites the chloride would have to satisfy.

In a comparison of the trends in the chloride concentrations of the soil leachate samples collected by the lysimeters at locations A, B, and C over the test period, several anomalies are evident. While the trends in the chloride concentrations between soil leachate samples collected by the lysimeters were similar over time, the magnitudes of the chloride concentrations

on similar days were different. For instance, the concentrations in the soil leachate collected by the shallow lysimeters at locations A, B, and C were markedly variable. From Figs 11 and 12 it is evident that the shallow lysimeters at location A and location B collected soil leachate samples that contained chloride concentrations of approximately equal magnitude on the same days. Soil leachate samples collected by the shallow lysimeters at location C, however, were much lower in chloride concentrations (Fig 13). These differences were probably caused by the fact that lysimeter location C received only 34.2 cm (13.4 in) of effluent while lysimeter locations A and B received 84.4 cm (33.2 in) and 122.5 cm (48.2 in) of effluent respectively. Since the chloride concentration in the effluent applied to all three lysimeter locations were equal on similar days, it follows that on a mass basis, the lysimeter locations A and B received a higher amount of chloride than lysimeter location C. As a result, the anion exchange reactive sites were probably occupied in a shorter period of time in the former case than in the latter case.

A consideration of the chloride concentration over time in the soil leachate collected by lysimeter B5 (Fig 12) reveals a second anomaly. Despite the fact that lysimeter B5 was positioned 44.5 cm (17.5 in) below the surface, the chloride concentration in the soil leachate samples are very similar in magnitude to those found in the soil leachate samples collected in the shallow lysimeters B6 and B7 over the same period. The

existence of channels left behind by decayed roots that may have transmitted the applied effluent to the lysimeter and thus partially bypassed the soil matrix, has been suggested by Chamberlin (1972), and confirmed by de Vries and Chow (1973) and Nagpal and de Vries (1976).

The intention when monitoring the leachate collected by the lysimeters was to employ the chloride anion as tracer to indicate the presence of the applied effluent in the soil leachate. The results suggest that the chloride anion, rather than being completely mobile and moving with the soil leachate, in fact is adsorbed by the positive charges existing on the organic matter and the amorphous iron and aluminum particles in the podzol soil. Once those exchange sites were occupied with the chloride ion, subsequent applications of domestic effluent resulted in a gradual increase in the chloride concentration in the soil leachate collected by the lysimeters. Over the term of the experiment, the soil leachate collected closer to the soil surface contained the chloride ion in higher concentrations than the soil leachate collected deeper in the soil horizon. If the application of domestic effluent had been continued over a longer period of time there probably would have been little differences in the chloride concentrations in the soil leachate collected at the two general locations. The chloride concentration in the soil leachate was also influenced by rainfall. Rainfall acted as a dilutant, resulting in a decrease in the soil leachate chloride concentration. This was observed almost

immediately in the lysimeters close to the soil surface but was detected on a delayed basis in the deep lysimeters.

If the anion adsorption capabilities of the soil and the subsequent influence on the passage through the soil of the chloride ion are recognized, then it is clear that a major portion of the soil leachate resulted from the application of effluent. While this observation may seem obvious, it was felt that it must be confirmed. The reason for such a confirmation, as will be expanded upon later, is the fact that no total or ortho phosphate, and only small concentrations of TKN and nitrate nitrogen were detected in the soil leachate. In the absence of proof to the contrary, it could be suspected that the soil leachate collected by all the lysimeters may have been ground water flow originating from beyond the experimental plot perimeter.

#### 4.4 NITROGEN CONCENTRATIONS IN THE SOIL LEACHATE

The average amount of total Kjeldahl nitrogen (TKN) and nitrate nitrogen applied to the forested plot, along with the specific amounts of TKN and nitrate nitrogen applied to lysimeter locations A, B, and C during the study are presented in Tables 4 and 5. The values presented are a summation of the amounts of TKN and nitrate nitrogen applied on the individual irrigation days. The average amount of TKN and nitrate nitrogen applied on any individual irrigation day was calculated by using the average effluent depth measured over the 16 rain gauges

Table 4: Amount of Nitrate-N Applied to Forested Plot

Amount of Nitrate-N applied from July 15, 1976 to November 12, 1976	kg/ha	lb/acre
Over whole plot (average value)	48.4	43.2
At lysimeter location A	52.1	46.5
At lysimeter location B	72.9	65.1
At lysimeter location C	20.2	18.0

Table 5: Amount of TKN Applied to Forested Plot

Amount of TKN applied from July 15, 1976 to November 12, 1976	kg/ha	lb/acre
Over whole plot (average value)	93.7	83.6
At lysimeter location A	100.6	89.8
At lysimeter location B	141.4	126.2
At lysimeter location C	39.0	34.9

in conjunction with the TKN and nitrate nitrogen concentration in the effluent applied on that particular day. The amount of TKN and nitrate nitrogen applied to the lysimeter locations A, B, and C on any individual irrigation day was calculated by using the effluent depth as measured by the rain gauges at the individual lysimeter locations in conjunction with the TKN and nitrate nitrogen concentrations measured in the effluent on that particular day. The differences in the mass of TKN and nitrate nitrogen applied between lysimeter locations is due to the non-uniform application of effluent as discussed earlier.

#### 4.4.1 Total Kjeldahl Nitrogen

Figures 14 and 15 present time plots of TKN concentrations in the soil leachate collected by the lysimeters at location A and at locations B and C respectively. The concentrations of TKN in the applied effluent over the same period are shown in both figures also.

The TKN concentrations in the soil leachate samples collected by lysimeters B4, B7, C9, and C10 could not be determined due to inadequate sample volumes obtained with the lysimeters in question. The 500 ml of leachate required for the analysis of TKN at the low concentrations found in the soil leachate samples was consistently available only from the lysimeters A1, A2, A3, B5, B6, and C8.

As was the procedure with the chloride ion, the TKN concentrations in the applied effluent were plotted on the

FIGURE 14  
TOTAL KJELDAHL NITROGEN-LYSIMETER LOCATION A

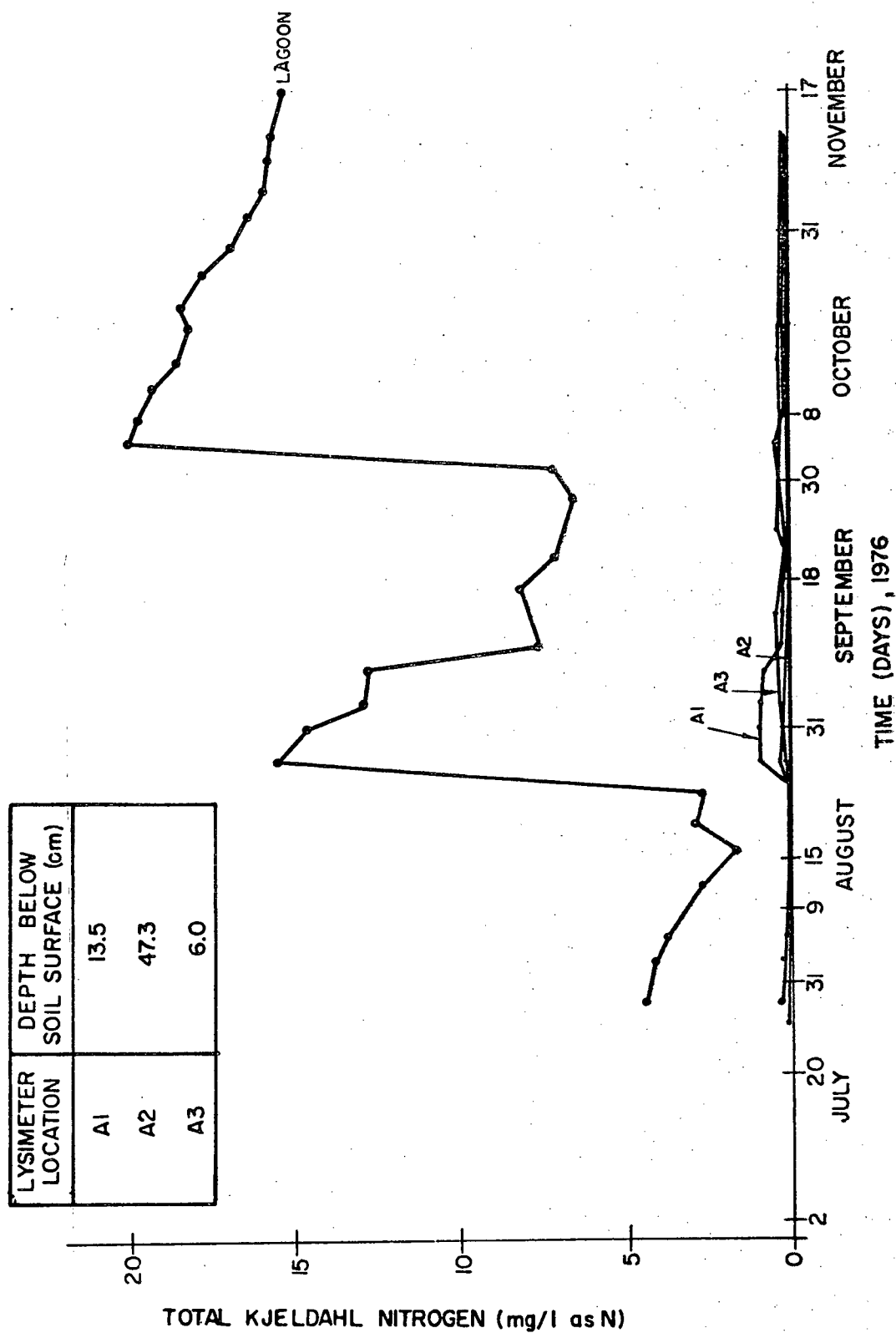
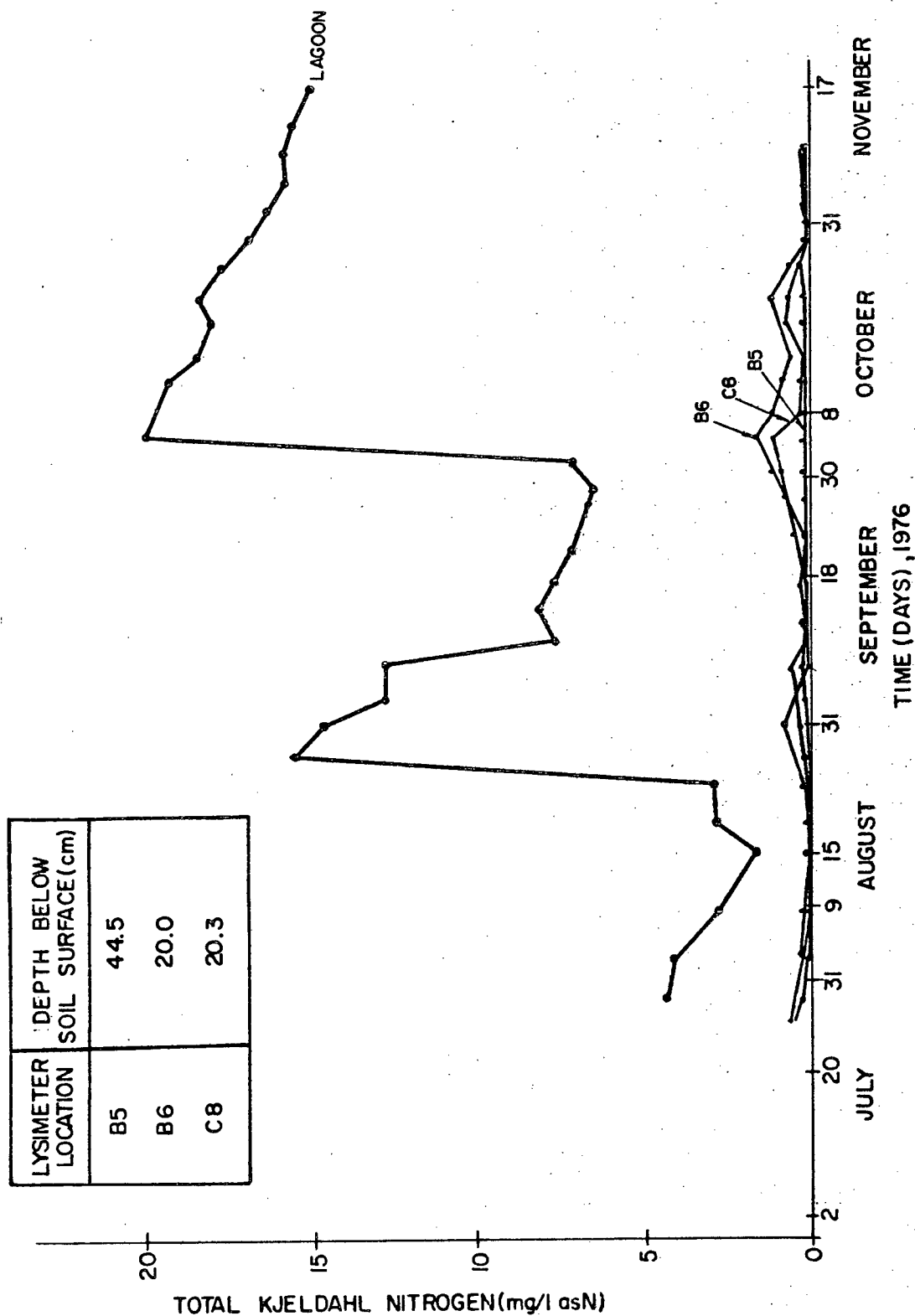


FIGURE 15  
TOTAL KJELDAHL NITROGEN-LYSIMETER LOCATION B & C





same days on which the soil leachate samples resulting from that particular irrigation event were collected.

The TKN concentration in the effluent applied on the 31 irrigation days was not constant as can be seen in Figures 14 and 15. It gradually declined in value between July 15, 1976 and August 20, 1976. The addition of the commercial fertilizer on August 20, 1976 increased the TKN value to 15.5 mg/l as N. Most of this TKN was in the ammonium form since the commercial fertilizer added was ammonium phosphate and ammonium nitrate. Seepage of ground water and the addition of rain water to the lagoon decreased the TKN concentration to 7.19 mg/l by September 28, 1976. A further addition of fertilizer on September 28, 1976 increased the TKN value up to 19.9 mg/l with further dilution decreasing the TKN concentration to 15.1 mg/l in the effluent lagoons by November 12, 1976.

From a consideration of the TKN concentrations found in the soil leachate collected by the lysimeters over the irrigation period (Figs 14 and 15), it is evident that very little of the TKN contained in the applied effluent moved with the effluent through the soil. The increase in the TKN in the soil leachate samples collected by the six lysimeters was in two stages, with the concentration decreasing to less than .15 mg/l in the period between the two general increases. The increases in soil leachate TKN were first detected immediately after the first application of the effluent containing the

fertilizer additions. Effluent containing the added fertilizer was first sprayed on the plot on August 24, 1976. The soil solution resulting from this application was continuously gathered in the lysimeters during the interval August 24, 1976 to August 27, 1976, when it was collected for analysis. The analyses of the soil leachate samples from all the lysimeters indicated large increases in TKN concentration, although the numerical values were still low. The measured TKN concentration subsequently decreased to the low levels that existed prior to August 27, 1976. Fertilizer was again added to the settling lagoon on September 28, 1976, with the first application of the amended lagoon effluent occurring on October 2, 1976. The TKN concentrations in the soil leachate samples collected in the lysimeters from October 2, 1976 to October 5, 1976 again increased in magnitude only to decrease over the following weeks, returning to the pre-August 27, 1976 TKN concentration levels.

To explain the observed TKN concentration trends in the soil leachate samples it is necessary to account for the ammonium ion, since the bulk of the TKN concentration in the domestic effluent applied to the forest soil was in the ammonium form resulting from the addition of ammonium phosphate and ammonium nitrate to the lagoon.

The most probable explanation for the observed TKN concentration phenomenon lies with the immobilization of the applied ammonium ion by the micro-organisms in the LFH horizon of the

forest floor. According to Alexander (1961), for a soil C:N ratio greater than 20:1, a portion of any added nitrogen would be subject to immobilization as a result of micro-organism cellular activity. In the analysis of a soil sample from the same soil series as that found on the irrigated forested plot, the C:N ratio of the L soil horizon was 37.7:1 while the C:N ratio of the HF soil horizon was 33.9:1 (see Table 1) (Lutmerding and Sprout, 1968). Prior to the application of the effluent supplemented with fertilizer, the soil micro-organism population was assuredly at a level that could assimilate a portion of the added ammonium. The same micro-organism population could not completely assimilate the increased nitrogen load when the effluent containing the commercial fertilizer was added to the forested plot. As a result the TKN level in the soil leachate collected by the lysimeters increased as a portion of the applied ammonium moved through the soil with the sewage effluent. The micro-organism population multiplied in response to the increase in the readily available ammonium and within a short period of time was able to assimilate an increased amount of the ammonium nitrogen. This resulted in a decrease in the soil leachate TKN concentrations.

As can be seen from Figures 14 and 15, the TKN concentration level in the applied effluent slowly decreased with time over the period August 17, 1976 to October 5, 1976. The decreasing TKN levels would reduce the amount of nitrogen available for micro-organism activity and as a consequence the

population would decrease. A sudden increase in the level of nitrogen applied to the plot when the effluent was supplemented with fertilizer on October 2, 1976 would cause the same phenomenon to occur in the organic layer of the soil as outlined above.

While it seems clear that the TKN concentration patterns in the soil leachate samples are related to micro-organism activity in the organic horizon of the forest floor, the experimental data gives no indication of the amount of applied ammonium that was immobilized. Black (1968) suggested that a portion of the applied ammonium is readily available for plant uptake by the plant roots. The thriving flora and fauna on the plot would have taken up a portion of the applied nitrogen. Also a portion of the ammonium may have been retained on the cation exchange sites existing in the soil, especially in the organic horizon. Young (1964) found that the retention of  $\text{NH}_3/\text{NH}_4^+$  in the organic horizons of 19 Pacific Northwest soils was related to the CEC by the following linear relationship:

$$\text{NH}_3 \text{ retention (ppm)} = 338 + 92.1 * (\text{CEC (meq/100 g)}).$$

From Table 1, the CEC of the L horizon and the HF horizon of a soil in the same series as the soil found on the experimental plot were 139.4 and 132.5 meq/100 g respectively. Based on Young's formula, a large proportion of the applied TKN was probably retained on the cation exchange sites in the soil, especially in the organic horizon. As was pointed out earlier, some researchers have indicated that the nitrification of a

portion of the applied ammonium may have occurred during the irrigation period inspite of the low soil pH. The experimental results do not give an indication as to whether this did or did not happen during the experimental period although the trend in the TKN concentration assumed to be due to microbiological immobilization may in fact have been partially due to nitrification.

#### 4.4.2 Nitrate Nitrogen

The nitrate nitrogen concentrations in the soil leachate samples collected over the period July 9, 1976 to November 23, 1976 by lysimeters A1, A2, and A3 are shown on Fig 16. Those collected over the same period by lysimeters B4, B5, B6, and B7 are shown in Fig 17 and lysimeters C8, C9, and C10 in Fig 18. The nitrate nitrogen concentrations in the applied effluent for the period July 15, 1976 to November 12, 1976 are shown in all three figures.

The nitrate nitrogen concentrations in the applied effluent were plotted on those days on which the resulting soil leachate samples were collected for analysis as was the procedure with the plotting of the applied effluent concentrations for TKN and chloride.

A consideration of the nitrate nitrogen concentrations in the soil leachate samples collected by the ten lysimeters over the period of study (Figs 16, 17, and 18) reveals a general pattern similar to that displayed by the TKN concentra-

FIGURE 16  
NITRATE NITROGEN CONCENTRATION - LYSIMETER LOCATION A

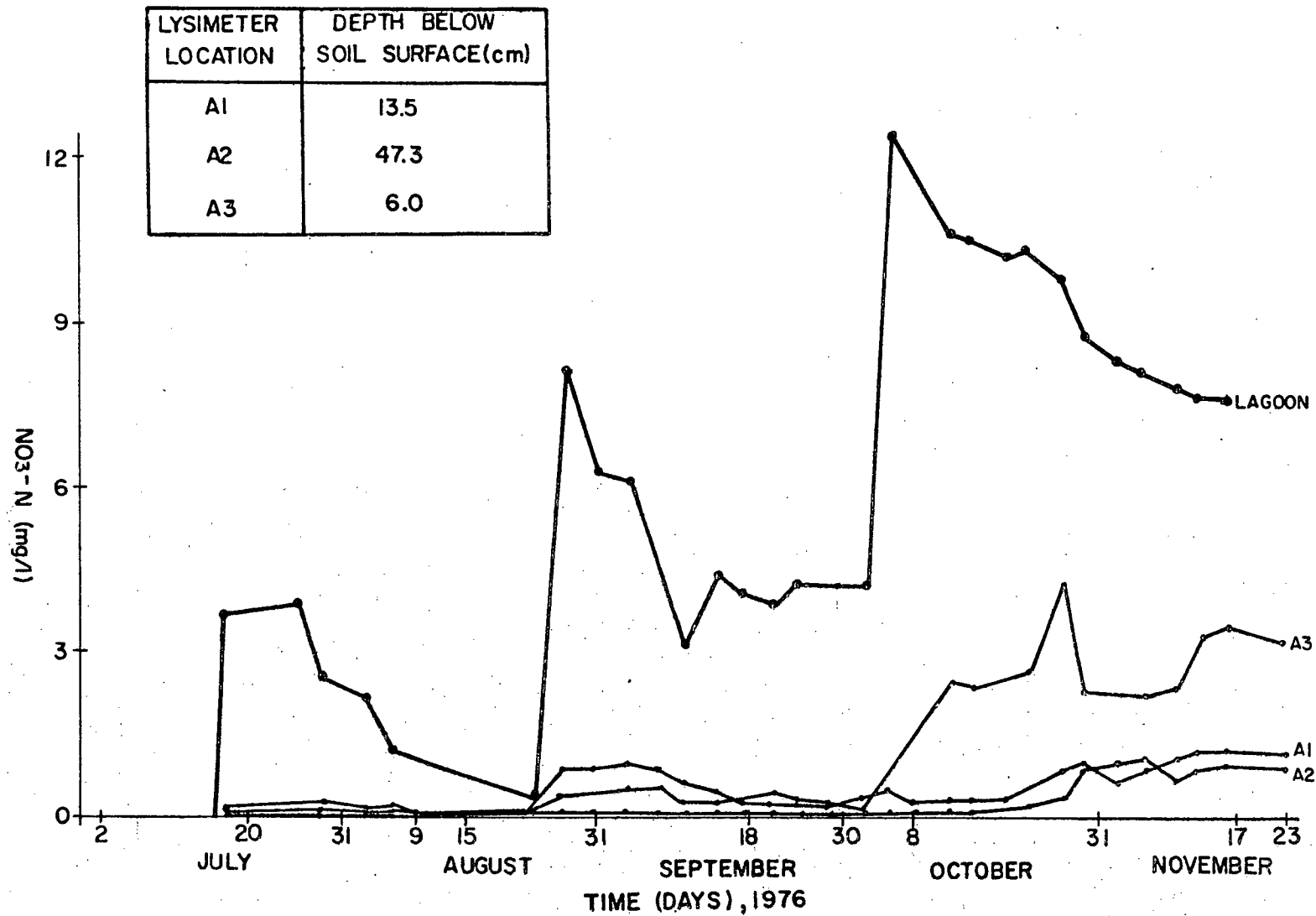


FIGURE 17  
NITRATE NITROGEN CONCENTRATION- LYSIMETER LOCATION B

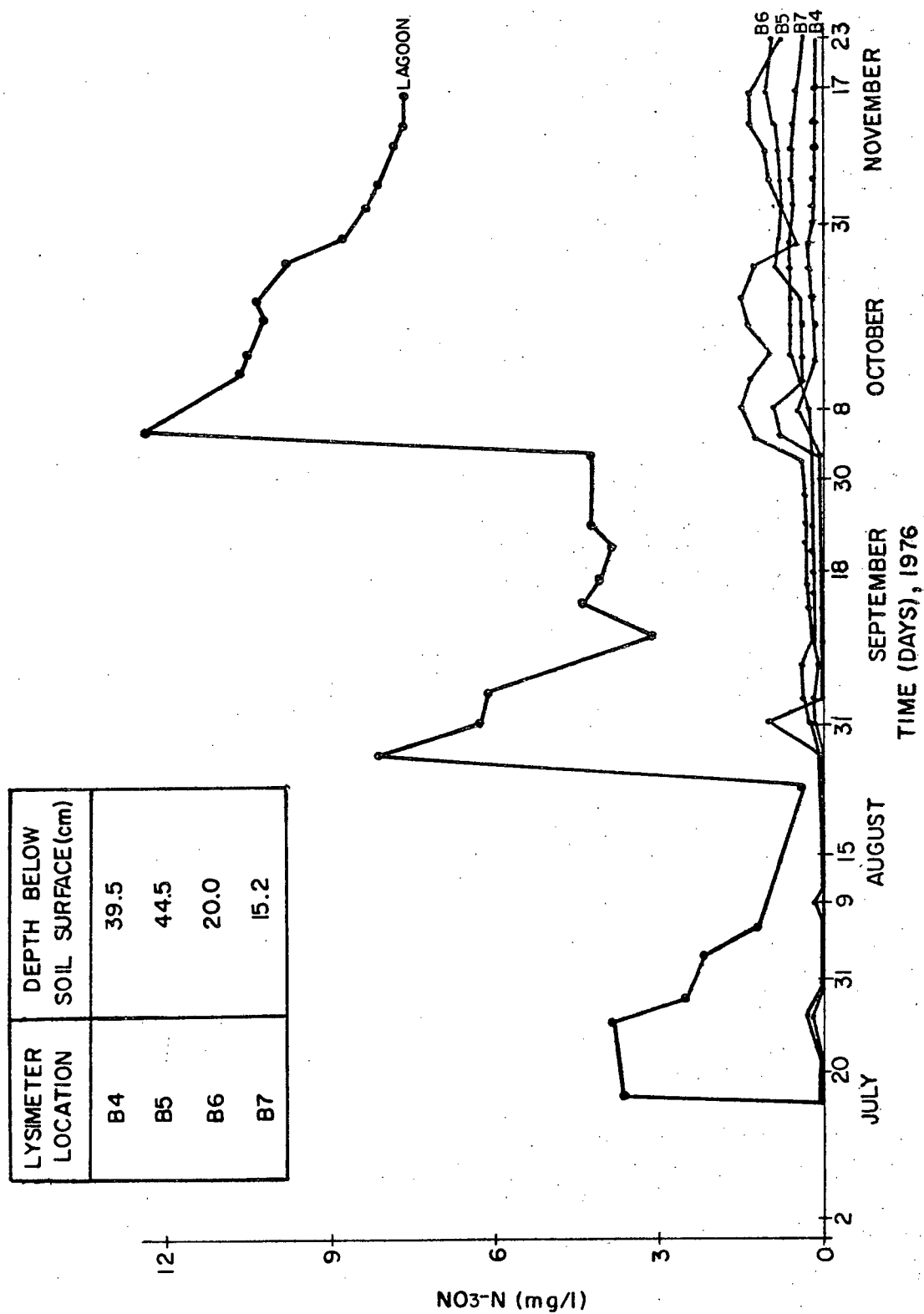
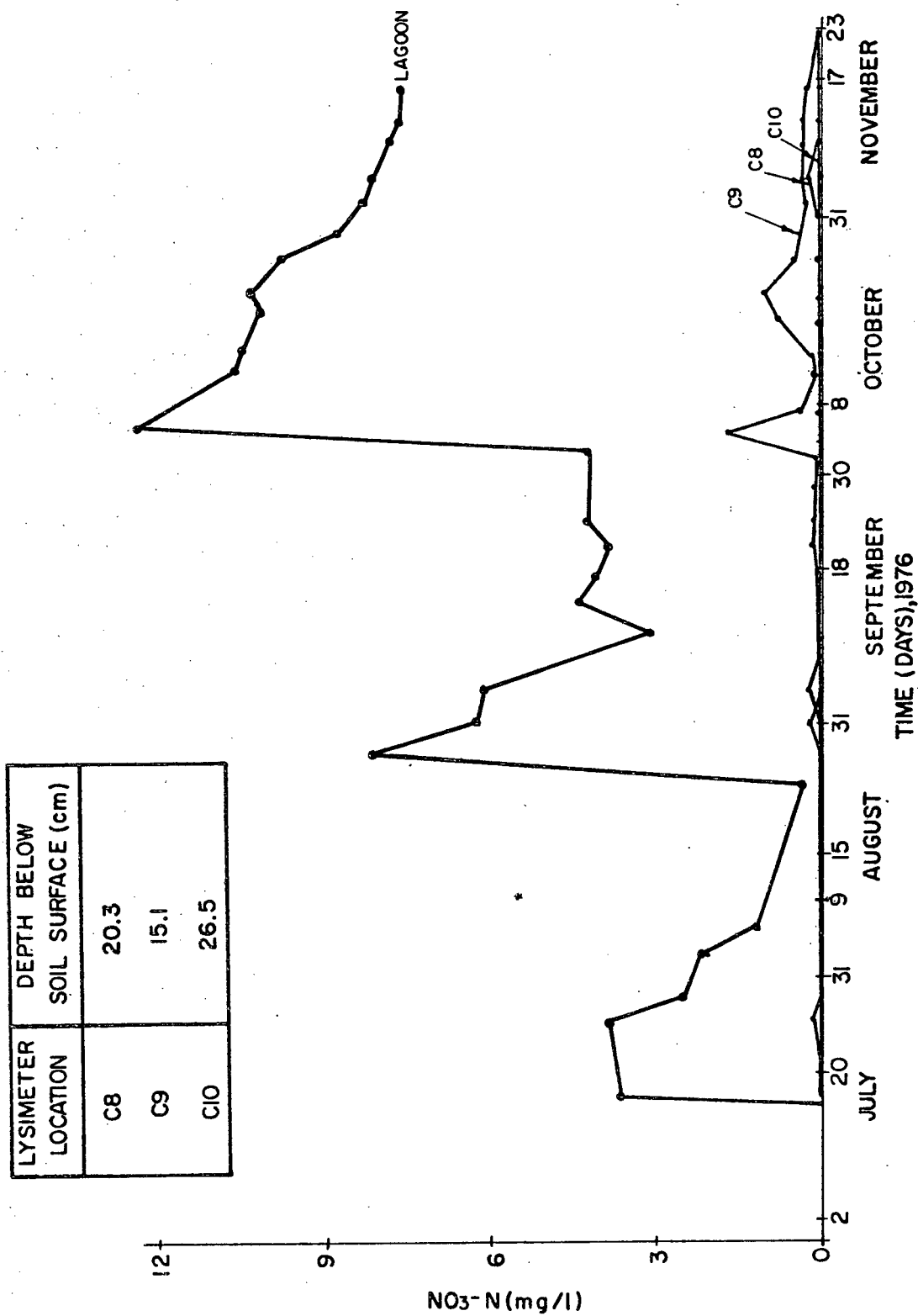


FIGURE 18  
NITRATE NITROGEN CONCENTRATION - LYSIMETER LOCATION C





tions. The nitrate nitrogen concentrations in the leachate samples were generally less than .05 mg/l until August 27, 1976. In response to the first application of effluent supplemented with fertilizer, the nitrate nitrogen concentrations increased in almost all of the soil leachate samples collected between August 24, 1976 and August 27, 1976. At lysimeter location A, the nitrate nitrogen concentration in the soil leachate collected by the lysimeters A1 and A3 increased to .85 mg/l while in the deep lysimeter A2 (47.3 cm (18.6 in) below the soil surface) it remained at 0.0 mg/l. The leachate samples collected by the lysimeters at location B over the period August 24, 1976 to August 27, 1976 showed a definite increase in the nitrate nitrogen concentration (Fig 17). The exception was the deep lysimeter B4 (39.5 cm (15.5 in) below the forest floor) where the nitrate nitrogen in the collected soil leachate sample remained unchanged at 0.0 mg/l. Over the same period of time, the nitrate nitrogen in the leachate samples collected by the lysimeters at location C (Fig 18) increased slightly in value except for the leachate collected by the deep lysimeter C10 (26.5 cm (10.4 in) below the forest floor) which remained at 0.0 mg/l. In a pattern similar to that observed with the TKN in the soil leachate samples, the nitrate nitrogen concentrations progressively decreased in magnitude over the following weeks. The nitrate nitrogen in the leachate samples collected during the period October 2, 1976 to October 5, 1976 then reversed this trend and again increased

in concentration. This increasing concentration in the nitrate nitrogen level in the samples was in response to the application of the effluent supplemented with the fertilizer on September 28, 1976. Beginning with the soil leachate samples collected with the lysimeters over the period October 2, 1976 to October 5, 1976, the nitrate nitrogen concentration in the soil leachate began to increase at a steady rate until the last irrigation day November 12, 1976. The early trend that saw an increasing nitrate nitrogen concentration in the samples collected after the application of the fertilizer supplemented effluent was similar to that displayed by the TKN concentrations over the same period. The fact that the nitrate nitrogen concentrations continued to increase with time until the last irrigation day was opposite to the phenomenon displayed by the TKN concentrations in the soil leachate collected over the same period. In the latter case the concentrations of TKN in the soil leachate returned to values less than .15 mg/l as N and remained at this level until the last irrigation day.

As an example, the trend in the nitrate nitrogen concentrations in the samples collected after October 2, 1976 by the lysimeters at location A (Fig 16) can be studied. The leachate samples collected by the shallow lysimeter A3 (6.0 cm (2.4 in) below the soil surface) increased to a peak value of 4.14 mg/l  $\text{NO}_3^-$ -N over the period October 2, 1976 to October 26, 1976. The dilution caused by the 6.7 cm (2.6 in) of rain

that fell over the period 0400 hours October 25, 1976 to 1000 hours October 26, 1976 and the 4.2 cm (1.7 in) of rain that fell over the period 1900 hours October 30, 1976 to 1000 hours October 31, 1976 caused the nitrate nitrogen level to fall to .95 mg/l  $\text{NO}_3^-$ -N. Subsequent applications of effluent increased the nitrate nitrogen level to a concentration of 3.4 mg/l  $\text{NO}_3^-$ -N by November 16, 1976. A similar trend was displayed by the nitrate nitrogen in the soil leachate collected by lysimeter A1. The only difference between the two situations was the fact that the nitrate nitrogen concentration levels in the leachate collected by lysimeter A1 were lower than those collected by lysimeter A3. The nitrate nitrogen levels in the leachate collected by the deep lysimeter A2 were similar in magnitude to those determined in the leachate collected by the lysimeter A1 over the period October 2, 1976 to October 23, 1976. The nitrate nitrogen in the leachate collected by A2 reached the same levels as the leachate samples collected by lysimeter A1 but on a delayed basis. From a consideration of Fig 16, it can be seen that the nitrate nitrogen in soil leachate collected in lysimeter A1 over the period October 22, 1976 to October 29, 1976 gradually reached a value of .90 mg/l  $\text{NO}_3^-$ -N while the same level was achieved in the leachate from lysimeter A2 over the period October 22, 1976 to November 2, 1976.

Leachate collected from the four lysimeters at location B showed similar responses to that collected at location A

except for deep lysimeter B5. The response of this lysimeter was similar to the shallow ones, thus indicating as discussed previously, that a channel left in the soil by a decayed root was probably permitting applied effluent to bypass a portion of the soil matrix as it passed through the various soil horizons.

The magnitude of the nitrate nitrogen increases in the leachate collected with the lysimeters at location C over the period October 2, 1976 to November 16, 1976 were not as pronounced as those which occurred at locations A and B. In fact, the nitrate nitrogen concentration trend in the soil leachate collected by lysimeter C9 was the only trend similar to the ones observed for the soil leachate samples collected by the lysimeters at locations A and B. The reason lies with the fact that location C received a total of only 20.2 kg/ha (18.0 lb/acre) of nitrate nitrogen over the period July 15, 1976 to November 12, 1976, whereas 72.9 kg/ha (6.5 lb/acre) of nitrate nitrogen fell on location B and 52.1 kg/ha (65.1 lb/acre) fell on location A. Since locations A and B were subjected to higher volumes of effluent and corresponding greater amounts of nitrate nitrogen than that received by location C, any subsequent soil leachate collected at locations A and B should contain higher concentrations of nitrate nitrogen.

The trends in the nitrate-N concentrations in the soil leachate samples were a direct reflection of microbiological immobilization in the soil horizon. As was discussed with

the results of the TKN concentrations over time, the micro-organism population would reach a population level sufficient to immobilize a specific amount of  $\text{NO}_3^-$ -N contained in the applied effluent. No  $\text{NO}_3^-$ -N would therefore move with the applied effluent through the soil as long as steady state conditions were maintained. In the time frame following the application of an increased concentration of nitrate nitrogen to the plot, a time lag in the increase in the micro-organism population capable of immobilizing the  $\text{NO}_3^-$ -N allowed for some nitrate-N to move with the liquid through the soil.

While the previous discussion was concerned with the trends in the nitrate nitrogen concentration on the soil leachate over the term of this experiment, it is probable that if the effluent application was to continue over a long term time period such trends would change. In the absence of denitrification, the applied nitrate nitrogen would allow the microbiological population to reach a level that could immobilize the nitrogen. Eventually the rate of release of nitrogen by mineralization would probably approximate the rate of input from the applied effluent with a corresponding increase in the nitrate nitrogen soil leachate concentration.

The continual increase in the nitrate nitrogen concentration after approximately September 30, 1976 may have been due to the decreased microbiological activity in response to cooler soil temperatures. Beginning at this time, the minimum daily air temperature was usually less than  $0^\circ\text{C}$  while the

maximum daily temperature was consistently less than  $10^{\circ}\text{C}$  (see Figure 5). The cooler temperatures reduced the microbial activity and curtailed the level of nitrate-N immobilization.

Alternatively the continual increase in the nitrate nitrogen concentration may have been the first indication of a nitrate nitrogen break through in the soil. The continual application of nitrate nitrogen in the effluent along with any formed by the nitrification of ammonium may have gradually satisfied the CEC in the soil over the course of the experiment. The gradual retention of nitrate nitrogen on the anion exchange sites would allow subsequent amounts of applied or formed nitrate nitrogen to move with the soil leachate, a phenomenon demonstrated by the chloride ion over the term of the experiment. The fact that TKN did not increase in concentration in the soil leachate samples after September 30, 1976 in a manner similar to that of nitrate nitrogen concentration indicates that in fact microbiological immobilization was not curtailed as suggested above but in fact the increasing nitrate concentration in the soil leachate was a reflection of a nitrate nitrogen break through.

According to Wiklander (1964),  $\text{NO}_3^-$ -N and  $\text{Cl}^-$  have an equal affinity for the anion exchange sites. The chloride concentrations in the soil leachate samples took up to five weeks to achieve the applied chloride concentrations. The chloride anion could not begin to move with the soil leachate through the soil until a portion of the applied chloride had

satisfied the anion exchange sites in the soil. Due to the high chloride concentration levels contained in the applied effluent, the chloride anion would dominate the anion exchange sites (mass action effect) but a portion of the nitrate nitrogen would also be retained. Not until a portion of the anion exchange sites had been occupied by the nitrate ion would nitrate nitrogen move with the soil leachate through the soil.

From a consideration of the trends of the nitrate nitrogen and TKN concentrations in the soil leachate with time it is clear that a nitrogen balance may be a suitable design and operating criterion to be used to recycle domestic effluent to a soil similar to the type found at the research site. Despite the fact that the soil water content was continually above field capacity, no nitrogen was found in the soil leachate samples except as noted above. If irrigation on such a site were undertaken only during the growing season, a nitrogen balance criterion may be a more suitable design basis than a water balance criterion for effluent application.

#### 4.5 PHOSPHORUS CONCENTRATIONS IN THE SOIL LEACHATE

The total and average amount of phosphorus applied to various parts of the 900 m<sup>2</sup> forested plot from July 15, 1976 to November 12, 1976, are given in Table 6.

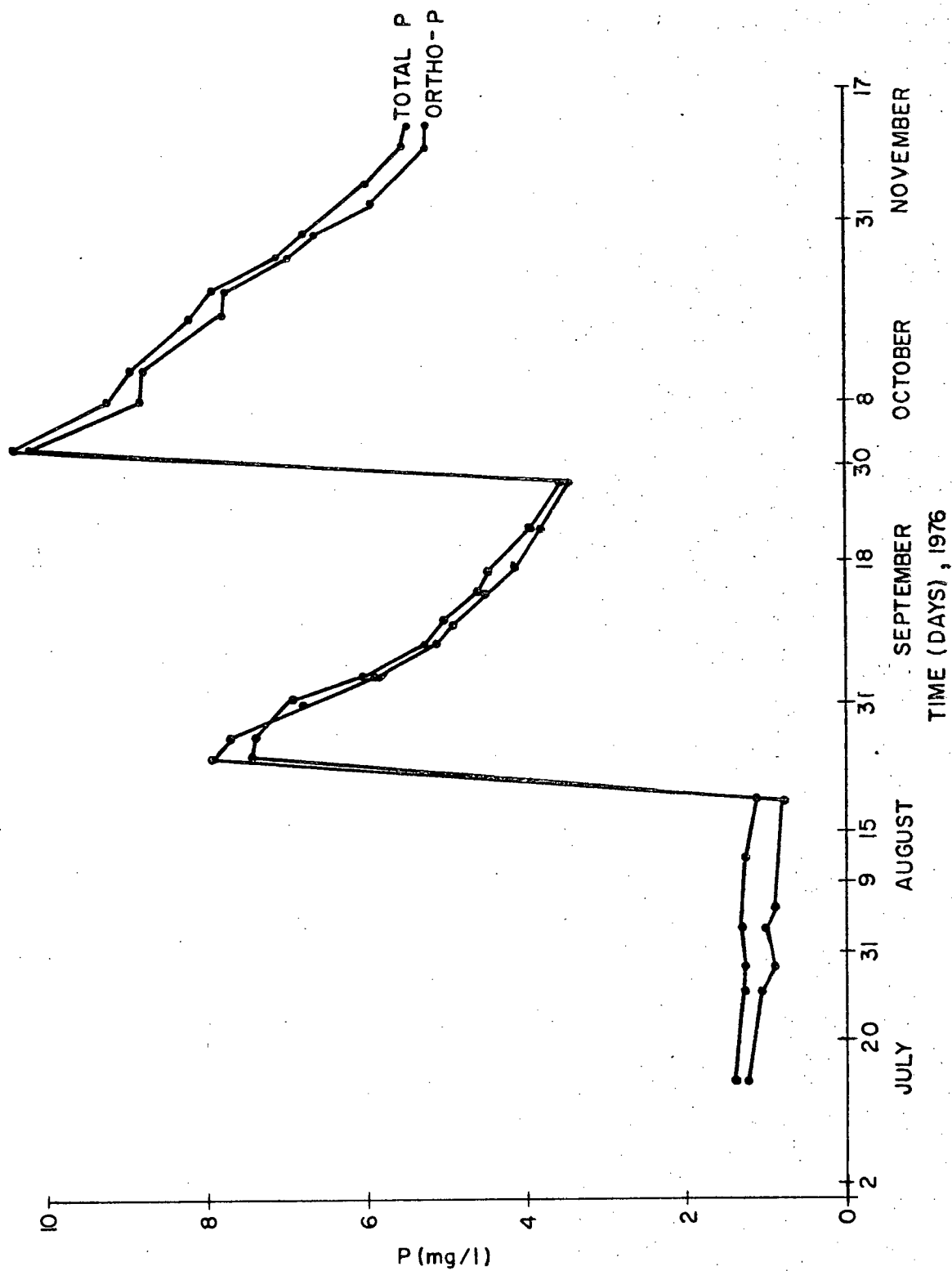
The concentrations of total and orthophosphate contained in the applied effluent are shown in Fig 19. Nearly

Table 6: Amount of Total-P Applied to Forested Plot

Amount of total phosphorus applied from July 15, 1976 to November 12, 1976	kg/ha	lb/acre
Over whole plot (average value)	43.5	38.6
At lysimeter location A	46.7	41.7
At lysimeter location B	66.2	59.1
At lysimeter location C	18.2	16.2



FIGURE 19  
TOTAL AND ORTHO PHOSPHORUS CONCENTRATION  
IN APPLIED EFFLUENT



all the total phosphate in the applied effluent was composed of orthophosphate. During the period of time between August 19, 1976 to November 12, 1976 the phosphorus in the applied effluent originating from the forestry camp was supplemented with commercial fertilizer as described earlier. In the days following the addition of the phosphate fertilizer, the total and orthophosphate concentrations gradually decreased in value due to the dilution effects of ground water and rainfall entering the second lagoon.

The sampling of the leachate during the period from July 15, 1976 to November 12, 1976 indicated no measurable total or orthophosphate in the soil leachate. Despite the fact that 66.2 kg/ha (59.1 lb/acre) of total phosphate was applied to lysimeter location B over the experimental period, no phosphate was detected in the soil leachate samples collected by even the shallowest soil lysimeters B6 and B7.

No results of similar experiments on a similar soil (ferro humic podzol) were found in the literature. Kohr (1973), applying domestic effluent to undisturbed soil cores situated in the laboratory, found the phosphorus concentration in the soil leachate samples collected at a soil depth of 45 cm (17.7 in) to be zero, except on several sampling days over the 9 month experimental period when phosphorus was detected in low concentrations. Such detections were of an isolated nature. The applied phosphorus concentrations were between 4.0 and 8.7 mg/l with a total of 30.2 kg P/ha (27 lb P/acre) being applied

to one soil column and 59.4 kg P/ha (53 lb P/acre) being applied to the second soil column. John (1974) added domestic effluent from the Kelowna sewage treatment plant to three columns containing disturbed oven dry soil samples from three locations in British Columbia. The Milner soil (orthic concretionary brown brunisol) containing high amounts of Al and Fe removed 99% of the applied phosphorus contained in the effluent over 22 complete leachings in a 77 day period.

The literature contains many references to the phosphorus concentrations in the soil leachate resulting from the application of domestic effluent on a full scale operation. Kardos and Hook (1976) found that over 9 years of the irrigation of domestic effluent to both an agricultural and a forestry situation, the sites had less than 3% phosphorus leaching losses. Beek et al (1977b), investigating the movement and accumulation of phosphorus at a sewage farm near Tilburg, The Netherlands, found that over a 50 year period 96% of the phosphorus in the applied domestic effluent had been removed from the soil leachate and had accumulated in the top 50 cm (19.7 in) of the soil profile. A study on the sewage farm at Melbourne, Australia (Johnson et al, 1974) reported that 91% of the P is being removed from the raw sewage during the passage of the effluent through the soil. Some parts of the farm have received sewage for the last 73 years.

The absence of phosphorus in the soil leachate samples collected by the lysimeters in this present study is probably

due to three causes. In the first case, immobilization of applied phosphorus by the micro-organisms present in the LFH horizon is likely. The high carbon content in the LFH horizon in combination with a large pool of readily available nitrogen and phosphorus compounds contained in the applied effluent would encourage a proliferation of the micro-organism population. Secondly, Harter (1969) found that a regression analysis of phosphorus adsorption as a function of five soil characteristics indicated that organic matter was important in the initial bonding of phosphorus by soils. He proposed that phosphorus is initially bonded to anion exchange sites on organic matter and subsequently transformed to less soluble iron and aluminum phosphates or incorporated into organic matter. It seems likely that the immobilization of the applied phosphorus in the organic layer is due to the micro-organism fixation and organic matter retention.

The third and most significant mechanism of applied phosphorus retention in the low pH podzol soil takes place with the amorphous aluminum and iron compounds present (Kittrick and Jackson, 1955; Chen et al, 1973a; Hsu and Rennie, 1962). Luttmerding and Sprout (1968), in a chemical analysis of a soil in the same soil series as that which was identified on the forested plot, found that the aluminum content ranged from .48% to 4.26% of the soil weight in the B horizon while iron ranged from .36% to 1.62% of the soil weight. In a study of the phosphorus retention capacities of forest soils, Ballard

and Fiskell (1974) found that such retention was attributed to amorphous aluminum and iron compounds and that on a unit weight basis, amorphous Fe is more active in P retention than is amorphous Al. Because of smaller total quantities of active Fe in the tested soils, Ballard and Fiskell (1974) suggested that active Fe contributes less to overall retention capacity than does active Al.

#### 4.5.1 Phosphorus Adsorption Isotherms

##### 4.5.1.1 Time-Phosphorus Adsorption Relationships

The results of the orthophosphate and the total phosphate time-adsorption studies are shown in Figures 20 and 21 respectively. In both Figures, the residual phosphate concentration of the treatment plant effluent is shown as a function of the reaction time with the soil samples. The time-adsorption response for a range of soil weights is also shown in both figures.

The rate of the phosphorus reaction with all the soil combinations was initially high, diminishing the effluent ortho and total phosphate concentrations to low but measurable values in a matter of minutes. The rate of phosphorus depletion was initially dependent on the weight of soil but after 120 minutes of elapsed experimental time, the amount of phosphate fixed in each of the soil-effluent solutions was relatively similar.

It can be seen in Fig 20 that the initial orthophosphate

FIGURE 20  
CONTACT TIME -EQUILIBRIUM CONCENTRATION  
FOR ORTHO-PHOSPHATE

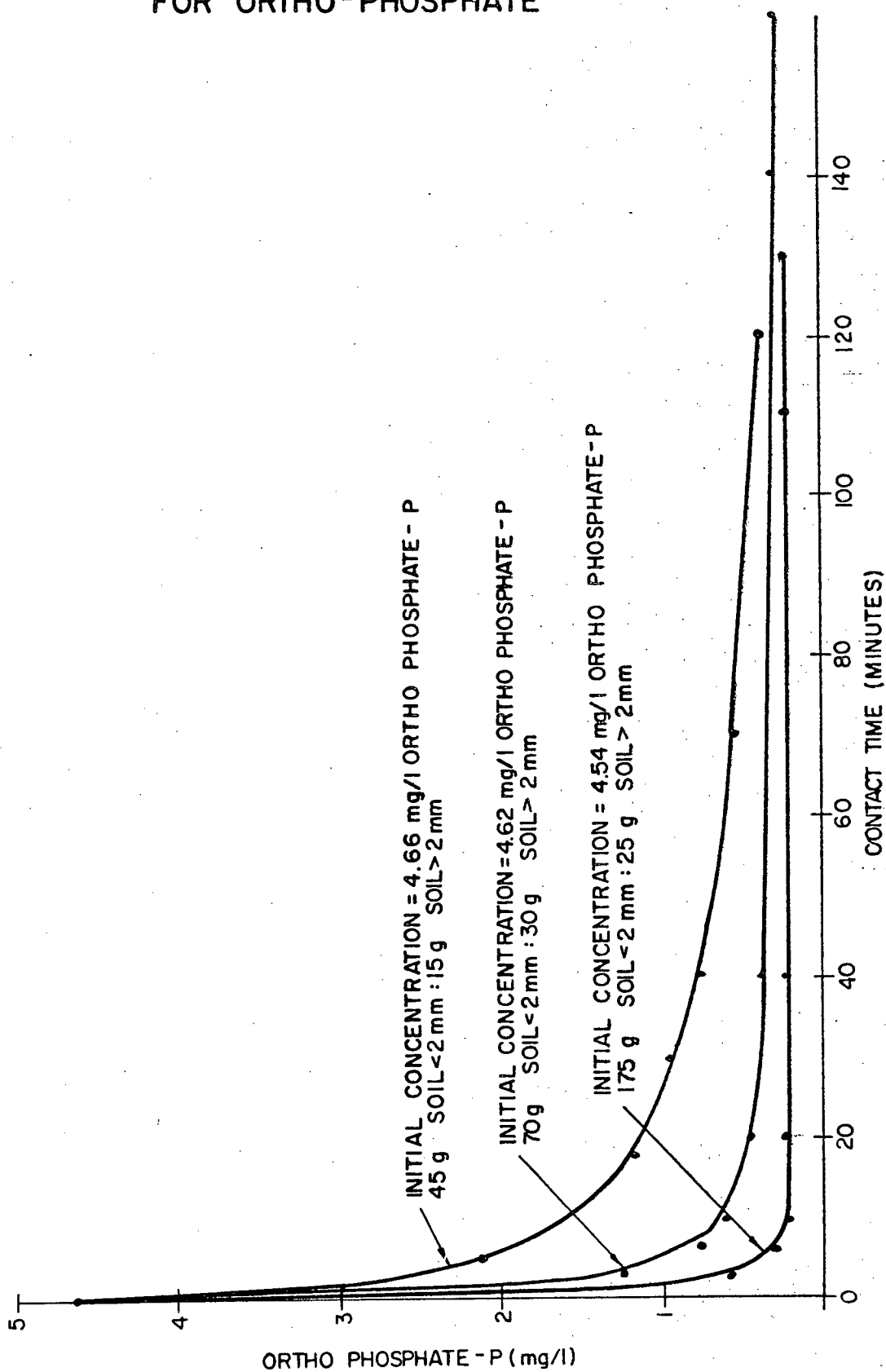
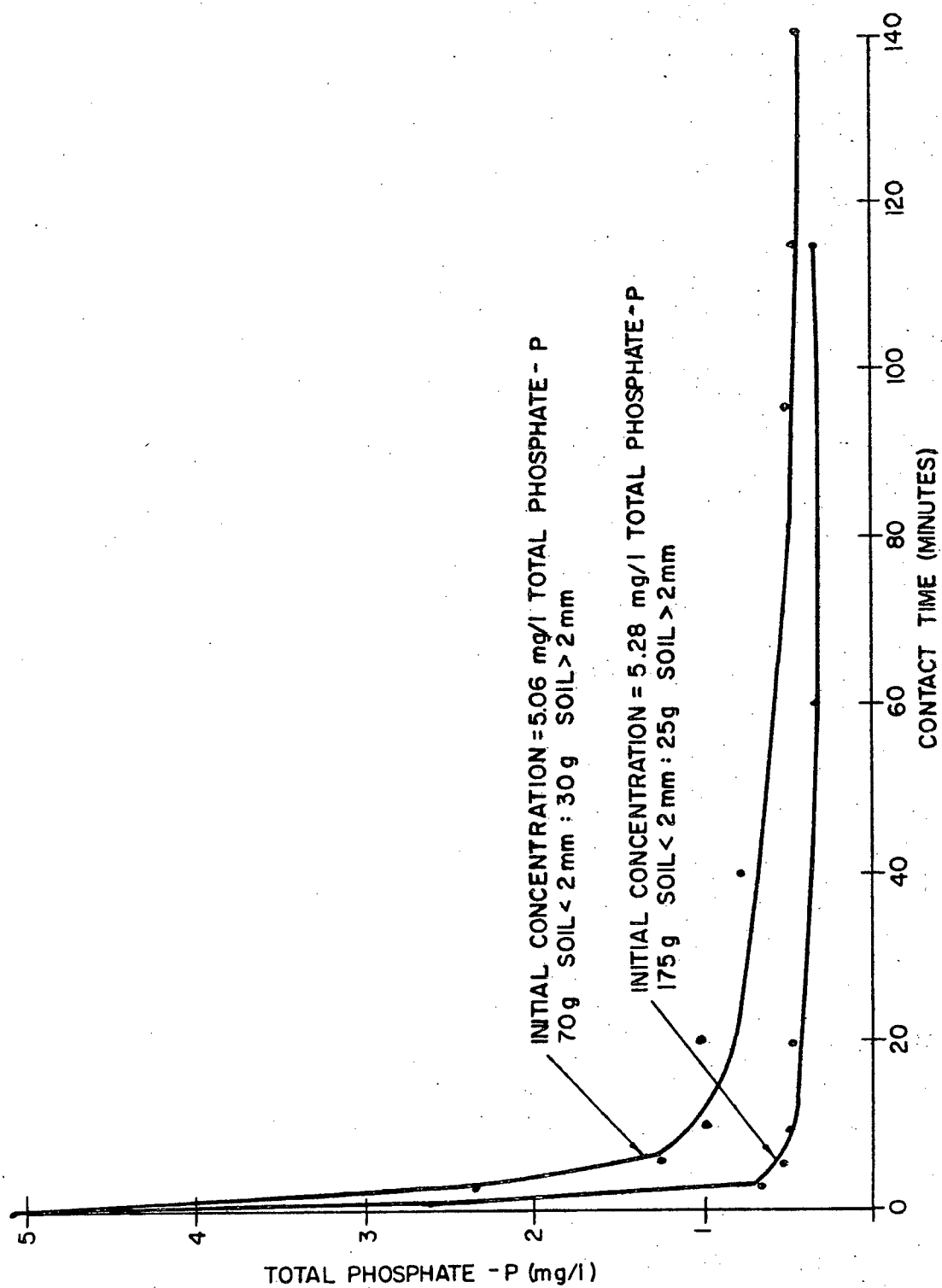


FIGURE 21  
CONTACT TIME-EQUILIBRIUM CONCENTRATION  
FOR TOTAL PHOSPHATE



concentration in the three test beakers was approximately 4.6 mg/l P. After 120 minutes of time had elapsed from the commencement of the experiments, the orthophosphate concentration in each flask was about 0.25 mg/l P or 5% of the initial orthophosphate concentration. After 1.5 minutes of reaction time the orthophosphate concentration in the suspension containing 200 g of soil was reduced to 10% of the initial effluent orthophosphorus concentration; it took 10 minutes and 70 minutes to reach the same levels in the suspension containing 100 g and 60 g of soil respectively. After 120 minutes of reaction time had elapsed, a further reduction in orthophosphate concentration values in the three experiments was small.

A consideration of Fig 21 indicates that the two time-adsorption studies involving a determination of total phosphate residual gave the same trend as for those time-adsorption experiments involving the determination of the orthophosphate residual as outlined previously.

The results of the time-adsorption studies undertaken to establish a time period to reach equilibrium between the phosphorus in the sewage effluent and the consolidated soil samples were similar to those found in the literature. Chen et al (1973b) found the phosphate removal to be very rapid in the first two hours of a time-adsorption study involving an aqueous phosphate solution reacting with alumina and kaolinite. For the period between 2 hours and 24 hours the reaction rate decreased, obeying a first order rate law over the next 60 days.



Rennie and McKercher (1959), using four Saskatchewan soils and a  $\text{KH}_2\text{PO}_4$  solution, were able to demonstrate that a one hour stirring time would permit completion of the adsorption reaction. Novak and Adriano (1975) were able to show that the phosphate adsorption was very rapid in the first 3 hours of the reaction between  $\text{KH}_2\text{PO}_4$  and some soil samples. There was a noticeable decrease in reaction rate occurring in the time period between 3 hours and 24 hours. Van Riemsdijk et al (1975) and Kuo and Lotse (1974) obtained similar results.

Chen et al (1973b) divided the phosphate removal kinetics into a rapid step which is complete within 24 hours and a slower step which may continue for months afterwards. The initial rapid phosphate removal was attributed to adsorption while the slower mechanism of phosphate removal involves the lattice dissolution to release ions of Fe and Al which react with phosphate. The result is the growth of a new aluminum phosphate or iron phosphate phase.

On the bases of experimental work and literature data, a ninety minute reaction time was chosen for the determination of the Langmuir and Freundlich isotherms. Although such a time base would not result in true equilibrium it would result in a relatively steady state after the completion of the rapid short term phosphorus concentration changes due to adsorption. This would be consistent with the observations of Novak and Adriano (1975) who cautioned that the adsorption isotherms only describe the initial adsorption reaction and not the long term

precipitation phenomenon. Some authors have used a twenty-four hour reaction time in the determination of adsorption isotherms (Chen et al, 1973b; Olsen and Watanabe, 1957; Muljadi et al, 1966; Zarnett, 1976) while others have employed eighteen hours (Hsu and Rennie, 1962), six hours (Rennie and McKercher, 1959), three hours (Rajan et al, 1974) and one hour (Harter and Foster, 1976). In most cases the longer reaction time was chosen in order to achieve a higher degree of agreement between duplicate determinations of the phosphorus adsorption isotherm.

#### 4.5.1.2 Langmuir and Freundlich Isotherm

The phosphorus adsorption data, plotted according to the Langmuir isotherm, are shown in Fig 22 for the adsorption of orthophosphate and total phosphate. On Table 7 the equation of the lines of best fit and the respective correlation coefficients by the method of least squares fit are given for the adsorption data. The data show that satisfactory agreement with the Langmuir isotherm exists as a straight line relationship of statistical significance was obtained for the adsorption by the soil of the total and orthophosphate contained in the domestic effluent.

The statistical correlation coefficients are not as close to 1.0 as some values reported in the literature. For example, Rajan et al (1974), working with laboratory prepared hydrous alumina oxide and a  $\text{KH}_2\text{PO}_4$  solution, obtained data

Table 7: Langmuir Adsorption Isotherm Equation of Line of Best Fit for Ortho and Total Phosphorus Determinations

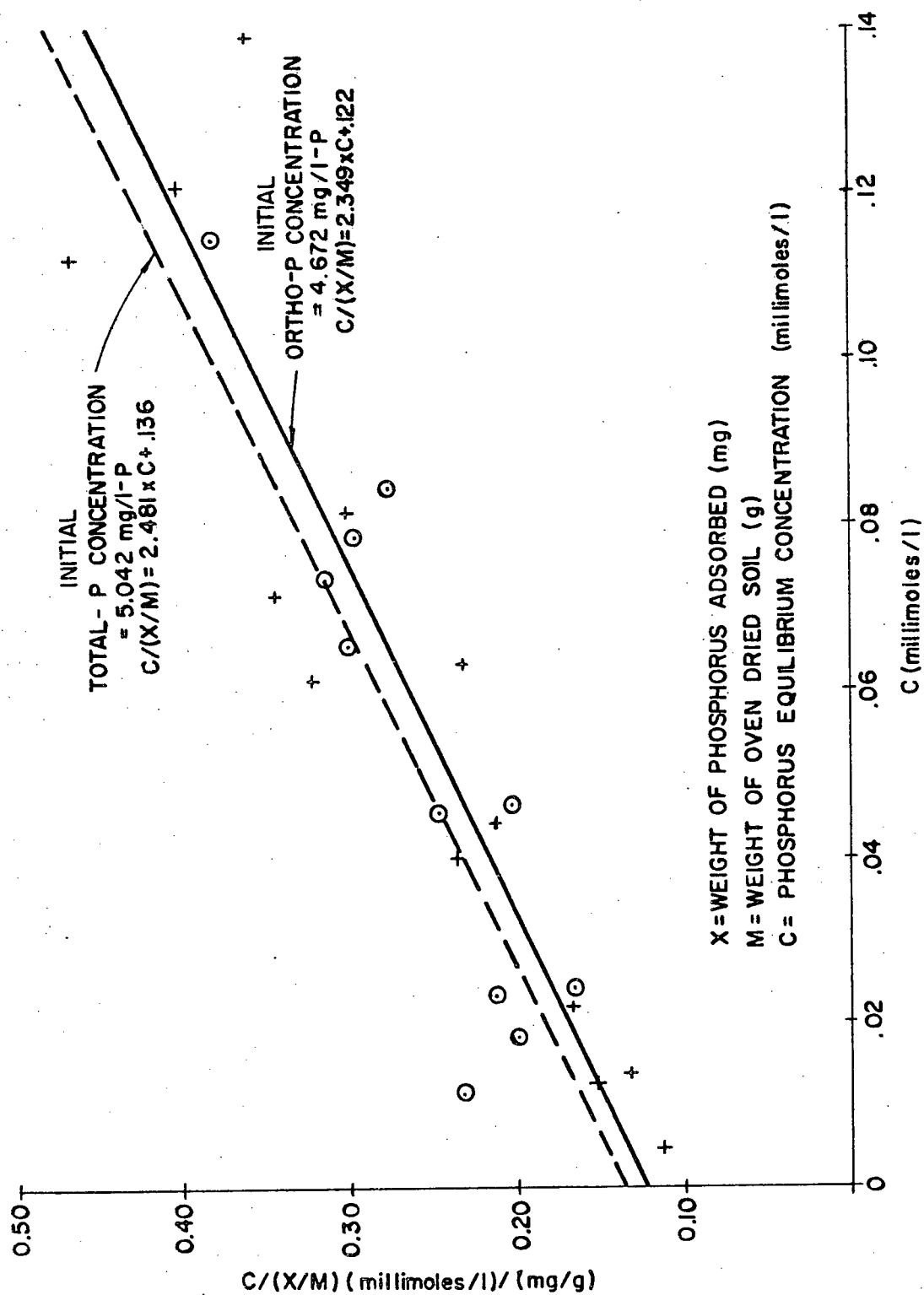
	Equation of line of best fit	Correlation Coefficient
Ortho-P	$C/(X/M) = 2.349 * C + .122$	.916
Total-P	$C/(X/M) = 2.481 * C + .136$	.901

Where C is Phosphorus equilibrium concentration  
(Millimoles/l)

(X/M) is Phosphorus adsorbed/g of soil  
(mg P/g of soil)

FIGURE 22  
PHOSPHORUS ADSORPTION ISOTHERM  
(PLOTTED ACCORDING TO LANGMUIR EQUATION)

SOIL WEIGHT = 1.0 g TO 100.0 g  
SOIL TEXTURE = 60% < 2 mm & 40% > 2 mm



that give correlation coefficients of .9999 and .9993 when plotted according to the Langmuir equation. The probable reason for the lower correlation coefficient when the phosphorus adsorption data in these series of tests is plotted according to the Langmuir isotherm probably lies with the non-uniformity between soil samples used in the adsorption experiments. It must be remembered that two consolidated soil samples, one sample comprised of soil material passing a 2 mm sieve and one sample of material not passing a 2 mm sieve, were each prepared by adding together the ten individual heterogeneous soil samples collected from the vicinity of the location of the ten lysimeter plates. The individual soil samples used in the phosphorus adsorption experiments varied in total weight from 1 g up to 100 g, with each soil sample composed of 40% greater than 2 mm and 60% less than 2 mm in diameter of soil from the two consolidated samples. Recognizing the soil heterogeneity involved in these consolidated samples, it would be very unlikely that each soil sample in the phosphorus adsorption experiments contained the same percentages of the same soil microscopic particles. Alternately, the possibility exists that the phosphorus adsorption data was not entirely describable by the Langmuir adsorption isotherm.

The major advantage of describing the phosphate adsorption data by the Langmuir equation is that a phosphorus adsorption maximum can be calculated. Such maximum values for the adsorption of ortho and total phosphate by the soil from

the forested plot are given in Table 8.

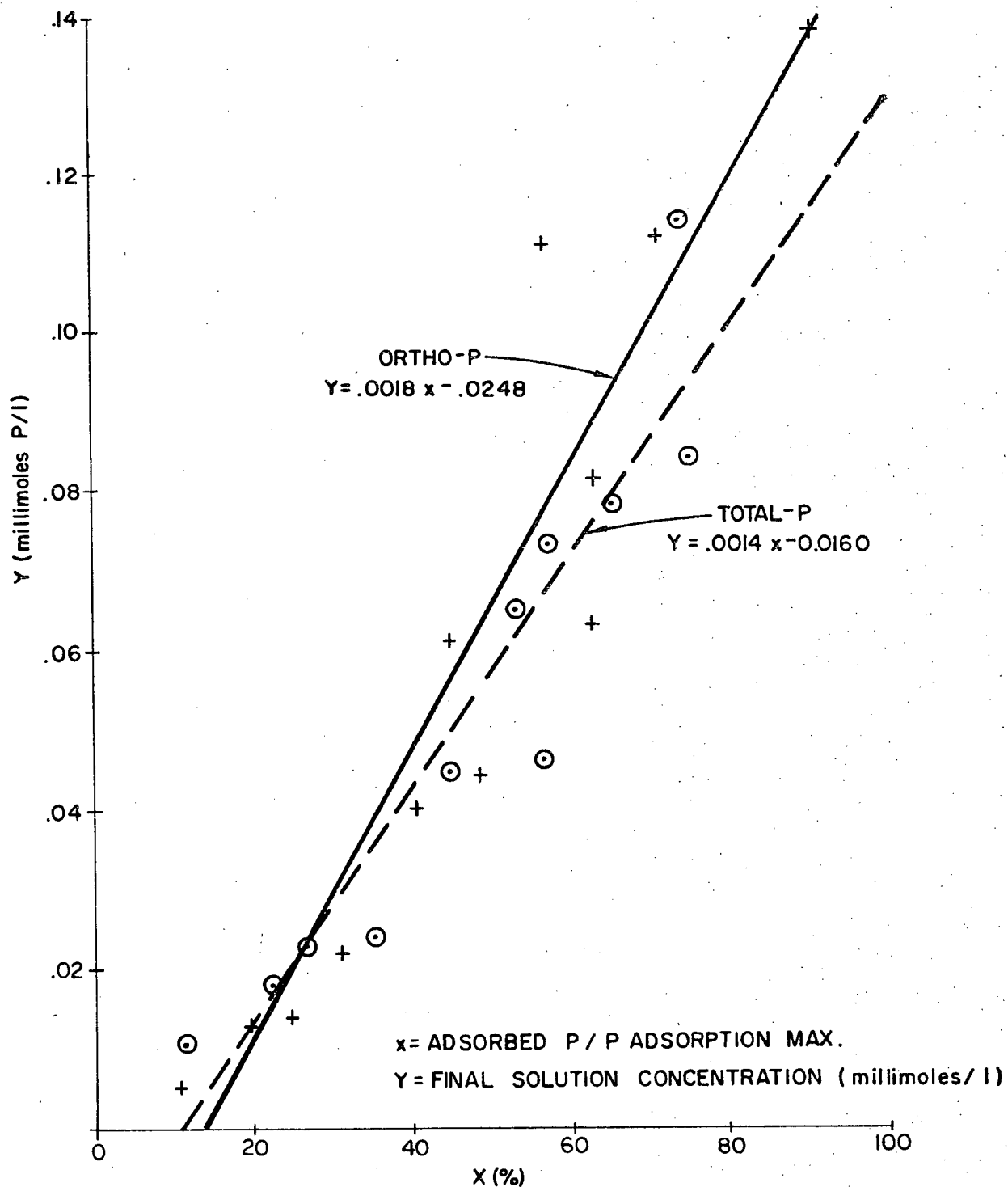
The theoretical ortho and total phosphorus adsorption maximums are similar in value. This results from the fact that the total phosphorus contained in the sewage samples tested, consisted mostly of the orthophosphate species. The original orthophosphate concentration in the sewage sample was 4.70 mg/l P whereas the original total phosphorus concentration was 5.04 mg/l P. The discrepancy between the two adsorption values probably involves the non-uniformity in the soil samples used in the preparation of the two Langmuir isotherms.

The Langmuir isotherm is based on the assumption that phosphorus is adsorbed by discrete points situated on the adsorbing material. In theory, as these discrete adsorption sites are progressively occupied with phosphorus, further additions of phosphorus will result in an increase in the phosphorus concentration in the soil leachate. As shown in Fig 23, a close relationship exists between the percentage saturation of the adsorption maximum as predicted from the Langmuir equation and the final solution concentration. The significant correlation coefficients of .928 and .939 between the final solution concentration and the percentage saturation of the adsorption maximum for orthophosphate and total phosphate respectively indicate the equilibrium concentration of ortho and total phosphate in a soil suspension closely reflects the degree of phosphate saturation of the potential adsorbing sites. As was pointed out earlier, the Langmuir isotherm, upon which

Table 8: Phosphorus Adsorption Maxima for the Forest Soil  
as Predicted by the Langmuir Isotherm  
(for calculations see Appendix D)

	Adsorption Maximum
Total Phosphorus	403 <u>micrograms total-P</u> gram of soil
Ortho Phosphorus	426 <u>micrograms ortho-P</u> gram of soil

**FIGURE 23**  
**RELATIONSHIP BETWEEN THE FINAL SOLUTION**  
**CONCENTRATION AND PERCENTAGE SATURATION**  
**OF THE ADSORPTION MAXIMUM**





the relationships in Fig 23 are based, only accounts for the initial rapid adsorption reaction of phosphorus.

The ortho and total phosphorus adsorption data plotted according to the Freundlich adsorption equation are presented in Fig 24. On Table 9 the equations of the lines of best fit and the respective correlation coefficients by the method of least squares fit are given. The data show that satisfactory agreement with the Freundlich isotherm was obtained for both total and ortho phosphorus contained in the domestic effluent.

It was pointed out earlier that the adsorption of phosphorus by soil particles involves an initial rapid phosphate removal step followed by a slower phase that may take years for an equilibrium state to be achieved. The initial fast reaction is looked upon as an adsorption reaction while the slower reaction involves the release of iron and aluminum ions from the lattice of the amorphous compounds and the subsequent nucleation and growth of a new crystal. The initial reaction reaches a definite end point within a matter of hours while the slow reaction continues by the gradual increase in the crystal size of the precipitated iron and aluminum phosphates, with the metal ions being contributed by the gradual breakdown of clay minerals and hydrous oxides.

The phosphorus adsorption maximum based on the Langmuir adsorption data represents the maximum amount of phosphorus that can be truly adsorbed by the soil particles over the term of initial rapid reaction. It in no way represents the maximum

Table 9: Freundlich Adsorption Isotherm Equations of Lines of Best Fit for Ortho and Total Phosphate Determination

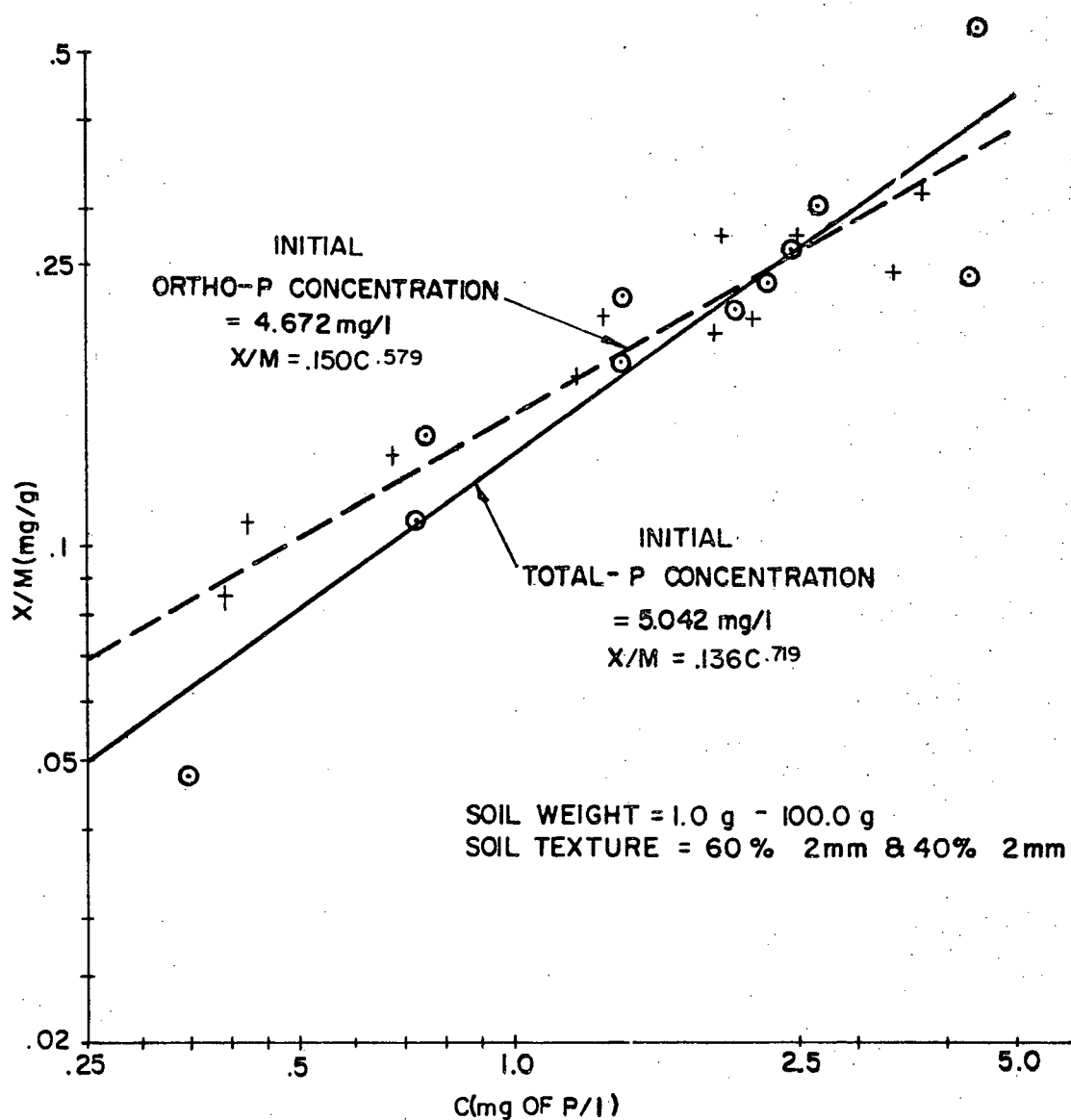
	Equation of line of best fit	Correlation Coefficient
Ortho P	$(X/M) = .150C^{.579}$	.973
Total P	$(X/M) = .136C^{.719}$	.936

Where C is phosphorus equilibrium concentration (milli-  
miles/l)

(X/M) is phosphorus adsorbed/g of soil (mgP/g  
of soil)

**FIGURE 24**  
**PHOSPHORUS REMOVAL ISOTHERM**  
 (PLOTTED ACCORDING TO FREUNDLICH EQUATION)

C = TOTAL PHOSPHORUS EQUILIBRIUM CONCENTRATION (mg/l)  
 X = WEIGHT OF PHOSPHORUS REMOVED (mg)  
 M = WEIGHT OF OVEN DRIED SOIL (g)



amount of phosphorus that could be adsorbed by soil constituents if effluent were continually applied to the forest podzol soil. The second stage of the fixation of phosphorus will result in a further immobilization of the applied phosphorus, an amount not accounted for in the theoretical adsorption fixation maximum based on the Langmuir adsorption isotherm data. Chen et al (1973b) found that successive additions of phosphate on a short time scale (20 to 60 hours) resulted in a decreased capacity for phosphate removal but on a long time scale (70 days in their experiment) the total amount removed and its rate of removal were the same for the second addition as the first. More important is the work of Kao and Blanchar (1973). They found that the P adsorption capacities of fertilized and unfertilized silt loam soils were the same. Their data indicated that the soil fertilized with P for 82 years had nearly double the total P content, but the ability of the soil to adsorb additional P was the same. For example, they found the P adsorption maximum of P-treated and untreated soil in the soil A horizon was the same value of 116 micrograms P/gram soil. In the soil B horizon, the P adsorption maximum values of the treated and untreated soil were 288 and 335 micrograms P/gram soil respectively. Beek et al (1977) found that even after 30 to 50 years of applications of domestic sewage to a podzol soil the phosphorus was still retained in the top 50 cm of the soil profile.

A consideration of the phosphorus concentration trends

in the soil leachate samples resulting from the regular application of domestic effluent to the forest soil in conjunction with a consideration of the phosphorus adsorption results raise several points. First, the use of the Langmuir adsorption maximum to predict the theoretical amount of phosphorus that could be adsorbed by a soil will lead to a very conservative design of an effluent recycling system. The Langmuir isotherm does not take account of the slower long term phosphorus fixation process which may have a substantial influence on the immobilization of phosphorus over a long time span. For the movement of phosphorus through the soil and the possible renovation life time of the soil, several models are presented in the literature (Enfield and Bledsoe, 1975; Shah et al, 1975; Novak and Adriano, 1975; Novak et al, 1975; Sawhney, 1977; Harter and Foster, 1976; and Zarnett, 1976). Secondly, the use of a phosphorus removal criterion as a basis for the application of domestic sewage to land rather than a conventional water balance criterion may be possible. During the term of this research the soil water content was continually above the water content of the so-called soil field capacity because of the abnormally high amount of rainfall. On a strictly water balance criterion, no effluent would have been applied to the forested plot. Despite this soil water condition, no phosphorus was detected in the soil leachate samples collected by the tension lysimeters. It is clear that the presence of the amorphous hydrous oxides in the podzol soil and the

rapidity of the initial phosphorus adsorption reaction limited the mobility of the phosphorus despite the water movement in the soil. These results suggest that a phosphorus balance may be a better operating criterion than a water balance. In particular, the fast reaction time between phosphorus and the soil and the high capacity of the podzol soil to remove phosphates over the long term may allow the addition of phosphates to the soil to be the primary focus of the irrigation of domestic effluent, with the addition of water a secondary concern. Such a plan would involve evaluating the phosphate requirements over the growing season of the crop, and meeting these requirements with the application of phosphates in the effluent. A sound management policy of phosphate removal by crops and soil constituents during the growing season may allow the effluent to be applied to the land on a long term basis.

## 5.0 SUMMARY AND CONCLUSION

The primary aim of the research reported herein was to observe the trend over time of the concentration of specific soil leachate constituents contained in domestic effluent applied to a forested area. From July 15, 1976 to November 12, 1976, 2 cm of domestic effluent, to which commercial fertilizer had been added, was spray-irrigated twice weekly to a 900 m<sup>2</sup> plot situated on a mountain slope. Ten porous plate tension lysimeters, installed at various depths and locations in the podzol soil profile, continuously extracted the resulting soil leachate. The soil water samples collected twice per week over the duration of the study, as well as the applied effluent samples, were analysed for chloride, nitrate and total Kjeldahl nitrogen, and total and orthophosphorus.

The chloride ion concentration in the soil leachate samples collected by the tension lysimeters increased in magnitude over the duration of the study until it eventually equalled the value of the chloride concentration in the applied domestic effluent. This trend, and not the sudden increase in the chloride concentration in the soil leachate as predicted by the research reported in the literature, was thought to be due to the substantial anion exchange capacity (AEC) in the low pH podzol type soil found on the forested plot.

From a consideration of the results of the chloride concentration trend over time, the sampled soil leachate was a direct result of the application of domestic effluent. The

monitoring of the chloride concentration in the soil leachate collected by one lysimeter also indicates that the applied effluent may, for a short distance in the soil, bypass the soil matrix through channels possibly formed by decayed tree roots.

The TKN and nitrate nitrogen concentration trends with time suggest that microbiological immobilization was playing a major role in the removal of the nitrogen contained in the applied effluent. A microbiological population level sufficient to sustain a degree of activity associated with a particular amount of applied effluent would be built up. The addition of a larger amount of nitrogen would not be immobilized by the microbiological population present and a fraction of this nitrogen would move with the effluent through the soil profile. In response to this increased amount of readily available nitrogen, the microbiological population would immediately begin to increase in numbers until a level was reached that could be sustained by the amount of nitrogen being applied to the forested plot. This was reflected by a decrease in the nitrate nitrogen and total Kjeldahl nitrogen concentration levels in the soil leachate samples collected by the tension lysimeters.

While it is recognized that the vegetation on the irrigation site would assimilate a portion of the readily available nitrate nitrogen and TKN, the trend in the nitrate nitrogen and TKN concentrations in the soil leachate samples was shaped by microbiological activity in the LFH horizon of the forest



floor.

Clearly, if the domestic effluent is applied during the warm season to a forested plot containing a litter zone similar to the one found on the plot in this research, then a nitrogen balance may be used as an operating criterion rather than a water balance criterion. Despite a soil water content continually above the field capacity, little nitrogen was found in the soil leachate samples except on the occasions noted above. This demonstrates that a nitrogen balance based on microbiological and vegetation assimilation may be a possible design and operating criterion for the recycling of domestic effluent to a soil similar to the one found at the research site. Over a long time span the rate of nitrogen mineralization would probably begin to equal the rate of nitrogen immobilization and reduced N removal would occur.

In the research results reported herein, no phosphorus was detected in the soil leachate samples collected by the lysimeters situated in the forest soil profile. There are several reasons for this phenomenon. The high carbon content in the decaying organic matter comprising the LFH horizon would sustain an increased microbiological population in the presence of the readily assimilated nitrogen and phosphorus compounds in domestic effluent. Also, the applied phosphorus would be immobilized by the amorphous iron and aluminum compounds found in the Ae and B horizons of the podzol soil profile. These compounds comprise a sizeable weight fraction of

the podzol soil.

In order to investigate the reactions between phosphorus and the iron and aluminum compounds in a podzol soil, batch scale tests were undertaken. It was immediately obvious from the phosphorus time-adsorption results that the phosphorus reaction with the amorphous iron and aluminum compounds is very fast. Not only was this reinforced by similar results reported in the literature, but the literature indicated that a second slower reaction occurs in which iron and aluminum are released from the lattice of amorphous compounds and react with phosphorus to form a new crystal. The phosphorus adsorption maximum, as calculated by the Langmuir isotherm, represents the maximum amount of phosphorus that can be truly adsorbed by the soil particles over the term of the initial reaction. Since it does not take account of the slower fixation of phosphorus, the Langmuir adsorption maximum will predict a lower value of the amount of phosphorus than that which will in fact be fixed by the podzol soil.

The reaction of phosphorus with the constituents of a podzol soil indicate that it may be possible to irrigate domestic effluent based on a phosphorus balance criterion rather than on a water balance criterion.

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## APPENDIX A

## Haney Research Forest Plot

## Soil Description

Slope: : 30°

Aspect : West

Parent

Material : Ablation till\* overlying compacted till

Sub-group : Ferro-humic podzol

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
LFH	4 - 0	Shallow undecomposed coniferous material and moss litter overlying black (5YR 2/1 moist) well to partially decomposed coniferous material. Few medium to fine roots. Abrupt boundary.
Aej	0 - 1	Brown (7.5 YR 5/2 moist) sandy-loam. Structureless. Very friable when moist. Thin, and discontinuous horizon thickness. Few medium to fine roots. Abrupt boundary.
Bfh I	1 - 24	Dark reddish-brown (2.5 YR 3/4) sandy-loam. Structureless. Very friable when moist. Common medium to fine roots. Wavy boundary.
Bfh II	24 - 49	Dark reddish-brown (2.5 YR 3/4) Sandy-loam. Structureless. Very friable when moist. Common medium to fine hard shot. Plentiful medium to fine roots. Gradual boundary.
Bf	49 - 71	Reddish-brown (5YR 4/4) sandy-loam. Structureless. Very friable when moist. Common medium to fine hard shot. Few fine roots. Gradual boundary.

\* Colluvium present in the first 25 cm of the profile. Fragments vary from fines to boulders.

APPENDIX A Continued  
Soil Description Continued

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
BC	71 - 95	Reddish-brown (5YR 4/4) sandy-loam. Structureless. Very friable when moist. Common medium to fine hard shot. Few medium to fine roots. Diffuse boundry.
II B1	95+	Reddish-brown (5YR 4/4) sandy-loam with grayish-brown 10YR 5/2 fine sandy loam pseudo-blocks which grade to massive structure at depth. Structureless matrix with very firm (moist) pseudo-blocky fragments. Few medium roots.

Classification\*: Ferro-Humic Podzol. Closely resembling description given for Cardinal Series in "Soil Survey of Mission Area" Preliminary Report No. 9 B.C.D.A. Kelowna 1968.

\* Classification Scheme used was the Canadian System of Soil Classification as ratified by C.S.S.C. in 1976

## APPENDIX B

Available Water Storage Capacity of Soil  
Samples From Around Lysimeters

Lysimeter Location	Depth below Soil Surface (cm)	Particle Size Analysis (% of weight 2 mm)			Available Water* Storage Capacity** (Cm <sup>3</sup> /Cm <sup>3</sup> )
		Sand	Silt	Clay	
A1	13.5	52	47	1	.160
A2	47.3	60	35	5	.136
A3	6.0	58	38	4	.157
B4	39.5				.141
B5	44.5	58	31	11	.129
B6	20.0				.157
B7	15.2	52	41	7	.148
C8	20.3				.255
C9	15.1	56	42	2	.213
C10	26.5	48	45	7	.161

Average AWSC (average over 10 locations) = .166 (Cm<sup>3</sup>/Cm<sup>3</sup>)

\*Available Water Storage Capacity (AWSC) =  
 Water Content @ -1/3 Bar (Field capacity) -  
 Water Content @ -15 Bar (Permanent Wilting  
 Point)

\*\*See Figures 6, 7 and 8

## APPENDIX C

Water Content Measurement at Lysimeter Location B ( $\text{cm}^3/\text{cm}^3$ )

Date		Depth Below Soil Surface (cm)			
		15	30	50	70
July 19/76	BSS	.375	.345	.450	.370
July 20/76	BSS	.395	.340	.445	.365
	ASS	.440	.375	.475	.370
July 23/76		.415	.355	.490	.365
July 26/76	BSS	.385	.345	.440	.365
	ASS	.425	.370	.490	.365
July 29/76	BSS	.400	.350	.465	.365
	ASS	.410	.370	.485	.360
August 3/76	BSS	.385	.345	.455	.375
	ASS	.425	.390	.500	.370
August 6/76	BSS	.400	.370	.480	.360
	ASS	.420	.385	.490	.360
August 9/76		.400	.370	.480	.355
August 12/76	BSS	.400	.360	.470	.360
	ASS	.430	.390	.515	.365
August 16/76	BSS	.420	.385	.495	.365
	ASS	.425	.395	.505	.370
August 19/76	BSS	.400	.365	.480	.365
	ASS	.420	.395	.520	.380
August 24/76	BSS	.410	.380	.505	.390
	ASS	.455	.410	.530	.390
August 27/76	BSS	.410	.380	.490	.360
	ASS	.435	.405	.500	.405



## APPENDIX C Continued

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Date		Depth Below Soil Surface (cm)			
		15	30	50	70
August 31/76	BSS	--	--	--	--
	ASS	.420	.390	.500	.375
Sept.7/76	BSS	.400	.375	.505	.385
	ASS	.425	.390	.500	.390
Sept.10/76	BSS	--	--	--	--
	ASS	.425	.395	.410	.370
Sept.14/76	BSS	.410	.370	.490	.360
	ASS	.420	.380	.495	.360
Sept.17/76	BSS	.400	.370	.495	.385

Neutron scaler no longer working

BSS - Before spraying sewage

ASS - after spraying sewage

## APPENDIX D

Sample Calculation of Phosphate Adsorption Maximum

Langmuir adsorption equation  $X/M = \frac{Kbc}{1+Kc}$

or in linear form  $\frac{c}{(X/M)} = \frac{1}{Kb} + \frac{c}{b}$

Where  $c$  = final solution concentration (equilibrium concentration) - millimoles/l

$X/M$  = mg P adsorbed per g of soil

$b$  = adsorption maximum

$K$  = A constant related to the bonding energy of the soil colloids for the phosphorus

a) Adsorption maximum for total phosphate

From a linear regression of the total phosphate adsorption data according to the Langmuir isotherm

$$\frac{c}{(X/M)} = 2.481 \cdot C + .136 \quad (\text{see page 152})$$

$$\frac{c}{(X/M)} = \frac{c}{b} + \frac{1}{Kb} \quad \text{or} \quad 2.481 \cdot C = \frac{c}{b} \Rightarrow b = .403 \frac{\text{mg total P}}{\text{g of soil}}$$

$$\text{or} \quad b = .403 \frac{\text{mg total P}}{\text{g of soil}} \cdot \frac{1 \text{ g}}{1000 \text{ mg}} \cdot \frac{10^6}{1 \text{ g}} \text{ microg P}$$

$$b = 403 \frac{\text{micrograms total P}}{\text{gram of soil}}$$

Adsorption Maximum =  $b$  is  $403 \frac{\text{micrograms total P}}{\text{gram of soil}}$

b) Adsorption maximum for ortho phosphate from linear regression of ortho phosphate adsorption data according to the Langmuir isotherm

$$\frac{c}{(X/M)} = 2.349 \cdot c + .122 \quad (\text{see page 152})$$

$$\frac{c}{X/M} = \frac{c}{b} + \frac{1}{Kb}$$

## APPENDIX D Continued

$$\text{or } 2.349 * c = \frac{c}{b} \Rightarrow b = .426 \frac{\text{mg ortho P}}{\text{g of soil}}$$

$$\text{or } b = .426 \frac{\text{mg ortho P}}{\text{g of soil}} \cdot \frac{1 \text{ g P}}{1000 \text{ mg P}} \cdot \frac{10^6 \text{ microg P}}{1 \text{ g P}}$$

$$b = 426 \frac{\text{micrograms ortho P}}{\text{gram of soil}}$$

Adsorption maximum - b is  $\frac{426 \text{ micrograms ortho P}}{\text{gram of soil}}$