Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author. SOURCES AND TRANSPORT OF PHOSPHORUS AND NITROGEN IN A STREAM DRAINING

A DOMINANTLY PASTURE CATCHMENT

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Soil Science at Massey University

# Andrew Neville Sharpley 1977

#### ABSTRACT

The literature relating to the sources and amounts of P and N forms transported in runoff types (surface, accelerated subsurface, and subsurface runoff) and in stream flow from catchments of varying land use was reviewed. There is a paucity of information available on this topic for New Zealand situations.

Concentration-flow relationships of P and N forms varied between different runoff types in the dominantly pasture catchment under study. Flow was the more important variable, however, in determining the P and N loadings in each runoff type. Because of more rapid fluctuations in P and N concentrations, surface and accelerated subsurface runoff, and storm flow in the stream, smaller sampling intervals were required than for subsurface runoff in order to obtain reliable estimates of P and N loadings.

An appreciably greater proportion of fertilizer P was transported in surface runoff from 13 and 6° undrained slopes (6.7 and 5.6% as TP, respectively) than from a 6° drained slope (1.0%) in four months following application (50kgP ha<sup>-1</sup>). This could be attributed to a four-fold reduction in the volume of surface runoff from drained slopes. Although 0.77 and 4.18kg ha<sup>-1</sup> of total P (TP) and total N (TN), respectively, were transported in surface runoff in four weeks as a result of grazing with dairy cattle, the effect of grazing was less sustained than that due to fertilizer P application.

Following the application of urea to the drained area of a 20-ha subcatchment, 2.3% of the applied N was lost as TN ( $^{0}7\%$  as NO<sub>3</sub>) in tile drainage in a four-week period. Although the volume of tile drainage was dramatically reduced following grazing, the concentrations of P and N forms increased. The effect of grazing on N concentrations in tile drainage was not as sustained as that of urea application.

Highly significant correlations were obtained between extractable soil P in surface soil (0-10cm) and the dissolved inorganic P (DIP) concentrations in surface runoff, and between extractable soil P and nitrate  $(NO_3)$  in the subsoil (40-50cm) and the DIP and  $NO_3$  loadings, respectively, of tile drainage.

A much greater amount of N (13.15 and 16.32kg ha<sup>-1</sup> y<sup>-1</sup> as NO<sub>3</sub> and TN, respectively) than of P (0.43 and 1.31kg ha<sup>-1</sup> y<sup>-1</sup> as total dissolved P (TDP) and TP, respectively) was transported in stream flow in 1975. Although surface runoff contributed the major proportion of P transported (13% for TP) by the runoff types, streambank crosion contributed 64 and 67%, respectively, of the TP and sediment transported in stream flow during 1975. The major proportion of stream flow (67%) and N transported (59% as TN), however, was contributed by subsurface runoff.

Earthworm casts contained appreciably more inorganic P (IP) than underlying soil, of which 90% of the additional IP was held by a more-physical sorption type and thus, readily released to solution. The data point to the importance of surface casts as a potential source of particulate material and P in surface runoff, and in the cycling of P in a soil under pasture. A differing ability of potential source and suspended-particulate materials to sorb and release IP from solution was observed and this was related, with some success, to field data.

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## SECTION 1

#### INTRODUCTION

Phosphorus (P) and nitrogen (N) are commonly regarded as the two primary nutrients which most frequently control the biological productivity of natural waters (Mackenthun, 1965; Vollenweider, 1968; Lee, 1970). Sawyer (1947), Sylvester (1961), and more recently Vollenweider (1968) have attempted to establish the critical concentrations of P and N in natural waters and found that concentrations of dissolved inorganic orthophosphate (DIP) and inorganic N in excess of 0.01 and  $0.3 \text{mg l}^{-1}$ , respectively, can increase the frequency and severity of obnoxious algal blooms in a lake. Because surface waters arising from minimally-disturbed catchments frequently contain more than 0.01 and  $0.3 \text{mg l}^{-1}$  of DIP and inorganic N, respectively (Hutchinson, 1957; White, 1972; Johnson <u>et al.</u>, 1976; Schreiber <u>et al.</u>, 1976), the addition of only a small amount of P or N, as a result of disturbance by human activity, is likely to dramatically increase biological activity.

The amounts and forms of P and N, and sediment transported in waters draining areas under varying land use have been studied extensively. Little attention has been directed, however, towards quantifying the relative sources and interactions between the dissolved and particulate forms of nutrients during transport, in an attempt to understand more fully the transport and losses of P and N in surface waters from catchments.

The aims of the study reported in this thesis were to determine the amounts of water, P and N forms, and sediment transported in stream flow from a dominantly pasture catchment, and the influence of fertilizer P and N applications, and grazing on these amounts. In addition, an attempt was made to investigate the relative contribution of runoff types to the P and N loadings of stream flow in the catchment. Laboratory studies were also carried out to investigate the interactions between DIP and potential source particulate materials in surface runoff and stream flow under conditions established in field monitoring studies.

#### REVIEW OF LITERATURE

The following review of literature will discuss the various sources of P and N to flowing waters and the amounts of these nutrients transported in the runoff types, surface, accelerated subsurface (tile drainage), and subsurface runoff, and stream flow. The modification of dissolved P concentrations by suspended particulate material and potential particulate source materials, such as surface soil, earthworm casts, and stream-bank material, during transport in the above runoff types and stream flow, will also be discussed.

#### 2.1 Sources of Phosphorus and Nitrogen Forms in Flowing Waters

The sources of P and N forms in flowing waters are frequently divided into those deriving from precipitation and from agricultural and urban activities (Lee, 1966; McCarty, 1967). Although agriculture is considered to be a major source of P and N to streams (Keup, 1968; Vollenweider, 1968; Ryden <u>et al.</u>, 1973; Viets, 1975), the relative contribution from agricultural, urban, and industrial sources is not well understood.

Based on their ease of quantification, McCarty (1967) categorised the various nutrient sources into point and diffuse sources. Point sources such as sewage and industrial effluent can be quantified more easily and consequently data are available on the amounts contributed by such sources to surface waters (Lee <u>et al</u>. 1969; Jaworski and Hetting, 1970; Johnson <u>et al</u>., 1976). On the other hand, diffuse sources such as precipitation, runoff, and drainage from agricultural land and urban areas, droppings from birds, and leaf fall, can only partially be estimated quantitatively. Diffuse sources can be divided further into surface and subsurface runoff, as defined by Langbein and Iseri (1960). Surface runoff is that part of precipitation which flows over the land surface to stream channels, whereas subsurface runoff is that part which infiltrates the soil and moves toward streams as ephemeral, shallow perched groundwater above the main ground-water level.

#### 2.1.1 Precipitation

In recent years it has clearly been shown that nutrients contained in precipitation can play an important part in the nutrient cycle of ecosystems on oligotrophic sites (Carlisle et al., 1966; Miller, 1961). Vaporised and uncontaminated, condensed water (precipitation) should contain no P or N (Keup, 1968). Most of the P and N in precipitation is the result of "washout" of atmospheric particulate material, the composition and quantity of which govern their concentrations in precipitation. Contamination of precipitation samples during collection may occur from insects, plant debris, and bird droppings, which may subsequently be leached by precipitation (Allen et al., 1968; Gore, 1968; Taylor et al., 1971). Unless adequate precautions are taken to guard against contamination of the collection vessel (Ryden et al., 1973), errors in the concentration of P and N forms in precipitation can be expected.

It is apparent that nutrient concentrations in precipitation can vary according to the geographical situation of the collection site and human activities. Olson <u>et al.</u> (1973) observed that the amounts of total N (TN) in precipitation ranged from 5.6 to 15.7kg ha<sup>-1</sup> y<sup>-1</sup> from west to east in an area of intensive livestock farming in Nebraska. In contrast, Taylor <u>et al.</u> (1971) attributed an increase in the nutrient concentration of precipitation at Coshocton, Ohio, over a ten-year period to an increase in automobile traffic in the several major population centres located within a 400-500km distance from Coshocton. Although variations in the concentration of P and N in precipitation during the year were measured by Allen <u>et al.</u> (1968) and Schuman and Burwell (1974), no seasonal trends were observed. In addition, these workers reported no consistent relationship between the quantity of precipitation and the concentrations of P and N in precipitation.

Although the amounts of N and particularly P in precipitation are small compared to the amounts of these elements frequently added annually in fertilizer to agricultural lands, their direct addition to waters may be sufficient to enhance algal growth in certain situations. Schnidler and Nighswander (1970) attributed most of the enrichment of Clear Lake in Haliburton County, Ontario, to precipitation containing concentrations of 0.018, 0.022, and  $0.198 \text{mg l}^{-1}$  of total dissolved phosphorus (TDP), total phosphorus (TP), and nitrate (NO<sub>3</sub>), respectively. Similar observations have also been made for several Wisconsin lakes by Lee (1973).

On reaching the soil surface, precipitation becomes an integral part of the soil-water ecosystem of any catchment and can consequently enter surface, subsurface, or groundwater runoff, and storage water or evapotranspiration. Surface, subsurface, and groundwater runoff can contribute to eutrophication by providing pathways of nutrient movement to streams and lakes. Movement through any part of the soil-water ecosystem can potentially affect P and N concentrations in the water as a result of interactions with soil components, fertilizer, vegetation, and animal wastes, as discussed below.

#### 2.1.2 Agricultural land

The sources of P and N forms in runoff from agricultural land can originate from soil, fertilizer applications, crop residues, and animal wastes.

2.1.2.1 <u>Soils</u>. The quantity of P in an unfertilized soil is mainly a function of the parent material from which the soil was developed. Although the TP content can exhibit a high variability within a particular rock type, it is generally assumed that basalt is the main source, with a decrease in P content with an increase in acidity of the rock (Landergren, 1962; Syers and Williams, 1977). The major P-bearing minerals, however, are of the apatite group, having the general formula  $(Ca_{10}(PO_4)_6 Y_2)$ , where Y can be F, OH, Cl, or  $\frac{1}{2}$  CO<sub>3</sub>. Small amounts of P can also be substituted into the lattice structure of many minerals (Koritnig, 1965).

Primary P-bearing minerals undergo dissolution at different rates to give secondary P forms. The dissolution of apatite, however, is pH dependent, being greater in acid soils. In the case of "lattice" P, the mobility of P ions is governed more by the solubility of the host mineral. Consequently, a large variation in the TP content of unfertilized soils can result from a difference in parent materials, environmental conditions effecting dissolution processes, and the age of the soil, governing the length of time during which these processes have been acting. In two soils of differing age (650 and 6500y BP) developed in greywacke alluvium in Canterbury, New Zealand, Syers <u>et al</u>. (1969) reported that the apatite content of the younger profile, which constituted the major proportion of TP, was 2.5 times greater than that in the older profile.

In the case of fertilized soils, the continued application of P fertilizer has been shown to significantly increase the TP content of the soil in the surface horizons (O-22.5cm; Warren and Johnston, 1963; Cooke and Williams, 1970).

It has been suggested that certain chemical processes are important in the formation of secondary inorganic P. Although precipitated Fe and Al phosphates were at one time thought to be important (Cole and Jackson, 1950; Huffman, 1962), it is now generally believed that sorption mechanisms explain more fully the chemistry of P in soils. Several studies have indicated that short-range order components, such as allophanic materials (Cloos et al., 1968) and crystalline oxides and hydrous oxides of Fe and associated Al (Saunders, 1965; Syers et al., 1971), are important in the chemisorption of P. These components are particularly important in P sorption because of their large surface area and number of -OH and -OH, groups in surface positions which can undergo ligand exchange with P ions. Consequently they have a high P sorption maxima. Many workers (Fox and Kamprath, 1970; Ryden et al., 1977a) have observed, however, that the sorption of P by soils exhibits an initially rapid reaction followed by a slower reaction which may continue for weeks or even months, such that a slow reaction may result from the diffusive penetration of P into soil components (Syers and Williams, 1977).

Similarly, the desorption of P from soils has been shown (Shapiro and Fried, 1959) to occur as a pseudo-first order displacement of soil P by OH ions, at an initially rapid rate. This quickly diminished with time, and proceeded at a slower rate,

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which became relatively constant with time. The two forms of P indicated may be distinguished by a difference in the binding energy of the P and soil component, such that one form is more tightly held than the other. In a fertilized soil, however, where precipitated fertilizer-reaction products, such as short-range order Fe and Al phosphates may occur (Section 2.1.2.2), dissolution of the reaction product may explain the release of P (Ryden <u>et al</u>., 1972b). It is unlikely, however, that these fertilizer reaction products will be as important as sorbed P in determining P equilibrium in fertilized and unfertilized soils because of their high solubility and, therefore, short life.

The sorption maxima, binding energy of a soil, and to a lesser extent the solubility of any reaction products will, therefore, determine the rate and extent of P sorption and desorption by a soil, and consequently the concentration of P in the soil solution and ultimately runoff waters.

In a soil where components with a high sorption maxima predominate, the capacity to remove P from solution will be greater than in a soil where components with a low sorption maxima predominate. If, however, the sorbents attain a high level of P saturation then the concentration of P maintained in solution will increase. This situation can arise in the surface horizons of many soils where an increased rate of mineralisation of organic P coupled with the addition of P fertilizer, may lead to a high saturation of P sorption sites in the surface soil.

In the case of an unfertilized soil, a lower saturation of the sorbing complex is expected than in a fertilized soil, such that the major proportion of P transported in surface runoff will be attached to soil particles (Munn <u>et al.</u>, 1973; Romkens <u>et al.</u>, 1973; Burwell <u>et al.</u>, 1974). Sorption or desorption of P may occur when the soil particles reach waters of higher or lower soluble P concentration, respectively. An increase in the concentration of P in surface runoff following the application of P fertilizer (Nelson and Romkens, 1971; Schuman <u>et al.</u>, 1973b; Burke <u>et al.</u>, 1974b) will result from the dissolution of fertilizer particles <u>per se</u> and of fertilizer reaction products and an increase in the saturation of P sorbing sites leading to a reduction

in the binding energy of some of the sorbed P.

The P sorbing complex of sub-soil material usually shows a lower level of P saturation, due to the limited movement of soluble P down the soil profile. Consequently, P will be sorbed with a higher binding energy (Shapiro and Fried, 1959) in the subsoil. Sorption thus predominates over desorption of P in sub-soils and P will be rapidly removed from percolating waters. The concentration of P in subsurface runoff is thus, much lower than that in surface runoff (Burwell <u>et al.</u>, 1974; Baker <u>et al.</u>, 1975; Johnson <u>et al.</u>, 1976).

Nitrogen in soil, particularly that in the surface horizon, occurs largely in organic combination (Harmsen and von Schreven, 1955; Kononova, 1961; Bremner, 1965; Stevenson, 1965). Thus, the accumulation of N in a soil bears a close relationship to the accumulation of organic material. This depends on such factors as climate, type of vegetation, nature of terrain, physical characteristics of the soil and activities of the microflora and fauna (Jenny, 1941).

The major forms of inorganic N, which are formed from organic N by mineralisation processes, are soluble in water and can be translocated easily by diffusion and mass flow of water through the profile. Mineralisation of organic matter by microorganisms results in the release of N in the ammonium  $(NH_4)$  form, which under soil conditions of good aeration and temperatures favourable for microbial activity, is oxidized to nitrite  $(NO_2)$  initially and then to NO<sub>3</sub> by the process of nitrification (Harmsen and Kolenbrander, 1965; Tomlinson, 1971). The step from NO<sub>2</sub> to NO<sub>3</sub> is usually faster than that from NH<sub>4</sub> to NO<sub>2</sub>, so that practically no NO<sub>2</sub> accumulates (Jacquemin and Berlier, 1956; Alexander, 1965). If nitrate is subsequently exposed to reducing conditions it will be converted to gaseous N forms and lost to the atmosphere, by the process of denitrification (Arnold, 1954; Cady and Bartholomew, 1960; Broadbent and Clark, 1965).

Ammonium ions are fixed (chemisorbed) by micaceous clay minerals present in many soils (Standford and Pierre, 1947; Allison <u>et</u> <u>al</u>., 1953; Brown and Bartholomew, 1962; Mortland and Wolcott,

1965). Further immobilisation of NH<sub>L</sub> may occur through plant uptake and the formation of complexes with oxidised lignin and various quinones, which are resistant to dissolution and enzyme action (Mortland and Wolcott, 1965; Broadbent and Clark, 1966). Consequently, the concentration of  ${\rm NH}_{\rm L}$  in the soil solution and groundwaters is usually very low (Nelson, 1953; Ray et al., 1957; Willrich, 1969; Zwerman et al., 1972; Gilliam et al., 1974). The NOz ion is non-specifically adsorbed and can move freely by diffusion and mass transport in the soil (Greenland, 1958; Gardner 1965; Harmsen and Kolenbrander, 1965). Consequently, if  $NO_3$  is not taken up by plant roots it can be quickly leached from the soil in drainage waters (Cooke and Williams, 1970; Standford et al., 1970; Terry and McCants, 1970; Tomlinson, 1971; Viets and Hageman, 1971; Kamprath <u>et</u> <u>al.</u>, 1973). As a result, the concentration of  $NO_3$ is high in groundwater (Willrich, 1969; Jackson et al., 1973; Gambrell et al., 1975) and low in surface runoff (White et al., 1967; Moe et al., 1968; Benoit, 1974; Hanway and Laflen, 1974; Gambrell et al., 1975).

The amounts of certain P and N forms in soils frequently exhibit seasonal fluctuations. Mack (1959) reported that "available" soil P was slightly higher during autumn than in summer, but decreased to a minimum during winter, because of low soil temperatures and high soil moisture contents. Blackmore (1966), however, was unable to observe any consistent seasonal variations in available soil P except when dung or fertilizer P was applied. Favourable conditions for the mineralisation of organic matter in spring will increase the potential for NO<sub>3</sub> leaching (Barnes, 1950; Viets, 1975). Because NO<sub>3</sub> accumulates in the soil during summer (Cooke and Williams, 1970; Tomlinson, 1970, 1971), the leaching of NO<sub>3</sub> may be significant in autumn. Similar seasonal variations in soil NO<sub>3</sub> levels and the NO<sub>3</sub> concentration in rivers in southern England, suggests that soils are a major source of NO<sub>3</sub> to rivers in this area (Tomlinson, 1970).

2.1.2.2 <u>Fertilizers</u>. Phosphate fertilizers range in chemical composition in terms of the P forms and supporting compounds present. Consequently, the dissolution of fertilizer particles and subsequent reactions with the soil will vary. The source of P in the commonly-used superphosphate fertilizer is present

as monocalcium P (MCP)  $(Ca(H_2PO_4)_2)$ . On application to a soil the particle of superphosphate will absorb water from the soil and the MCP will rapidly dissolve, to give a saturated or nearly saturated solution, which is continuously removed from the granule by diffusion (Lindsay and Stephenson, 1959; Taylor and Gurney, 1965). Lehr <u>et al.</u> (1959) found that within six days of applying superphosphate to a silt loam in Alabama no undissolved MCP was present in the particles and a highly porous residue of crystalline dicalcium phosphate (DCP) remained in place.

Up to 30%, however, of the P present initial as MCP may be precipitated as DCP (Ca HPO<sub>4</sub>) in the residue (Brown and Lehr, 1959; Lehr <u>et al.</u>, 1959; Taylor and Gurney, 1965). Dissolution of the residue will almost cease because of the low solubility of DCP (Brown and Lehr, 1959). Studies by Lindsay and Stephenson (1959) pointed to the importance of DCP as an initial fertilizer reaction product in the vicinity of MCP granules in soils. In soils of high calcium status, DCP assumed an even greater importance as a reaction product. Aluminium and Fe were considered to play secondary and tertiary roles, respectively, as initial reaction products, with the possibility of potassium taranakite  $(H_6K_5Al_5(PO_4)_8.18 H_2O)$  also being precipitated.

With DCP fertilizer, a much slower dissolution of the P source occurs. Because of this a greater residual effect of DCP has been observed, in comparison with superphosphate, in terms of plant uptake in field experiments (Bouldin <u>et al.</u>, 1960; Devine <u>et al.</u>, 1968; Larsen 1971).

Reactions of monoammonium P, the dissolution product of ammoniated superphosphate (Huffmann, 1968), with gibbsite and active magnesium (Mg) in soils leads to the formation of insoluble complexes and precipitates, such as ammonium taranakite in the case of gibbsite (Taylor and Gurney, 1965), and hannayite, schertelite, and struvite in the case of Mg (Frazier <u>et al.</u>, 1963). The most recently introduced phosphatic fertilizers are ammonium polyphosphates. Ammonium pyro- and tripolyphosphates dissolve Fe and Al from soils and inhibit the reprecipitation of these metals as orthophosphates (Philen and Lehr, 1967; Huffmann, 1968). With ammonium pyro- and tripolyphos-
phate, reactive Ca and Mg minerals rapidly form pyrophosphate precipitates that are effective sources of P for plant growth (Lehr et al., 1964; Brown et al., 1964).

. It appears that P fertilizers are a potentially important source of both particulate and dissolved P to surface waters, although the relative amounts of these two P forms will be dependent on the rate and extent of fertilizer dissolution and subsequent precipitation. Lehr et al. (1959) observed that the movement of solution into the soil from the dissolution of a fertilizer particle, appeared to be governed more by the rate of transport of moisture to the particle, than by the ability of the surrounding soil to remove the solution. Consequently, as soil moisture increases there will be a corresponding decrease in dissolution, probably because the nearly saturated soil zone impedes the movement of water to the fertilizer particle, thus restricting the formation of soluble P (Brown and Lehr, 1959). It is expected, therefore, that if the fertilizer is applied in early autumn, when the soils have not yet reached field capacity, the dissolution of fertilizer particles and consequently, the susceptibility of the soluble P released to be removed by surface and subsurface water movement and plant and soil uptake, will be enhanced. Following an application in mid-winter, when soil moisture is high, the loss of particulate P in surface runoff may be expected to be greater.

The majority of N fertilizers are water soluble, with the more important being ammonium sulphate, ammonium nitrate, and ammonium phosphate, ammonia, either anhydrous or in solution, and urea. If fertilizer N persists in the soil for any length of time,  $NH_4$  will be oxidised to  $NO_3$ , as discussed in the previous section (2.1.2.1). This process can be affected by the dramatic changes in pH in soils. With the high pH values (8.5) attained, the activity of  $NO_2$  oxidising bacteria is inhibited and  $NO_2$  tends to accumulate. This can be oxidised further, however, as it diffuses away from the high pH zone, except in highly calcareous soils (Russell, 1973). In contrast, a reduction in soil pH can occur in sandy soils of low cation exchange capacity with the formation of acids, inhibiting continued nitrification (Pesek <u>et al.</u>, 1971).

If N fertilizers are applied at a time of low vegetation cover or

growth, then uptake by vegetation will be at a minimum. Consequently, a large proportion of the NO<sub>3</sub> within the soil profile can potentially be removed by leaching (Cooke and Williams, 1970; Tomlinson, 1971; Klausner et al., 1974).

2.1.2.3 <u>Animals</u>. It has been shown that animal excreta can be a source of P and N to surface waters overseas (McCarty, 1967; Holt <u>et al.</u>, 1970; Owens, 1970). It has been suggested that this may also be the case in New Zealand where large areas of land are intensively grazed (O'Connor, 1968; During 1971; Elliot, 1971). The main route by which P and N derived from animal excreta may enter streams is by surface runoff (Ryden <u>et al.</u>, 1973), although a small contribution by subsurface and groundwater runoff may occur (Gilbertson <u>et al.</u>, 1970; Elliot <u>et al.</u>, 1972; McCalla <u>et al.</u>, 1972).

Based on field studies involving manure application to surface runoff plots during winter months, Lee <u>et al</u>. (1969) estimated that 60% of the TP lost in surface runoff to streams from rural land in the Lake Mendota (Wisconsin) watershed, was a result of manure applications to frozen ground in agricultural areas. Similarly, Cooke and Williams (1970) suggested that surface runoff losses can be serious, when liquid or solid manure is applied to frozen ground. Dung pats, particularly when dry, are susceptible to transport in surface runoff and will consequently transport P and N in both the dissolved and particulate forms. Because the amounts of P and N deposited in dung and urine are concentrated into small areas, leaching of both P and N may occur if heavy rain follows grazing.

Cooke and Williams (1973) reported that animal wastes spread thinly and uniformly over land, would not contribute more P or N than an equivalent application of P and N as fertilizer. Some application rates of animal waste, however, are so large as to cause concern that the capacity of the soil to retain nutrients against leaching is exceeded.

With the growth of intensive feedlot operations, where large numbers of animals are confined in a small area of land, disposal of waste becomes more difficult. Most of the feedlots in the midwestern and western states of the U.S.A. have a capacity of more than 1000 and feedlots of 80,000 to 100,000 head are now operating. In studies of the wastes from such feedlots in Nebraska, Gilbertson <u>etal.</u> (1970) and McCalla <u>et al</u>. (1972) reported that the quantities of P and N removed from the feedlot surface were directly proportional to stocking rate. Because many feedlots are located on slopes adjacent to streams, variable amounts of nutrients could be flushed into streams during periods of precipitation. In a separate study, McCalla <u>et al</u>. (1972) reported that 3 to 6% of the material deposited on a feedlot could be transported in surface runoff and observed concentrations of TP, ranging from 4 to 5200mg  $1^{-1}$ , with a mean of 36mg  $1^{-1}$ , of TN ranging from 11 to 8593mg  $1^{-1}$ , with a mean of 916mg  $1^{-1}$ .

In a study of 34 watersheds in the Iowa lake district, Jones et al. (1975) concluded that feedlots were a source of nutrients to the streams and lakes in the area. This was based on the significant positive correlations between both the concentration and losses of P and N in streams and the number of animal units in feedlots where surface or tile drainage occurred (one animal unit consisted of one beef steer, 0.7 dairy animal, 4.5 slaughter hogs, 35 feeder pigs, and 12 sheep or lambs, all producing a unit amount of waste, in terms of the BOD content). They showed that both the P and N concentrations significantly increased by 0.67  $\pm$  0.07mg l<sup>-1</sup> and 0.74  $\pm$  0.08mg l<sup>-1</sup>, respectively, for each animal unit per hectare in the watershed.

High concentrations of P and N in feedlot surface drainage waters have been reported in many streams (Miner <u>et al.</u>, 1966; Gilbertson <u>et al.</u>, 1970; Townshend <u>et al.</u>, 1970; E.P.A., 1971; McQuitty <u>et al.</u>, 1971; Taylor <u>et al.</u>, 1971; Edwards <u>et al.</u>, 1972). Other investigations have shown that feedlot drainage can be a high local source of these nutrients in streams (Frink, 1969; Taylor and Kunishi, 1971; Morris, 1973; Muir <u>et al.</u>, 1973; Burwell <u>et</u> al., 1974; Loehr, 1974).

2.1.2.4 <u>Crops</u>. Under certain conditions, leaching of the vegetative cover by precipitation and surface runoff water

can contribute substantial amounts of soluble P and N to surface waters. Field and laboratory studies in Minnescta (Timmons <u>et al</u>., 1968; Holt <u>et al</u>., 1970) have shown that the leaching of the dead tissue of forage crops resulted in considerable DIP and TN loss. Further work by Holt <u>et al</u>. (1970) showed that there was a substantial increase in the loss of P and N from the crops following a freeze-thaw-drying cycle. The magnitude of the susceptibility of P and N to leaching increased with the number of treatment cycles and was most marked for bluegrass and least for barley and oats. In fact, one freeze-thaw-drying cycle of bluegrass removed 80% of the total plant P as soluble P (of which 76% was DIP) and 7% of the total plant N as dissolved N. A similar treatment of barley and oats only released a maximum of 16% total plant P as dissolved P (21% DIP) and 14% total plant N.

Under field conditions, plants may become dehydrated due to water stress during the growing season or during dry summer months, and may be subject to freezing and thawing cycles during autumn. Heber (1967) suggests that the dehydration that accompanies freezing alters the permeability of biological membranes and states that the membranes bordering the protoplasm are no longer intact in frost-killed cells. Consequently, cell nutrients will be more readily leached from plant cells after they have been ruptured by frost or dehydration by severe water stress.

Several workers have indicated that seasonal fluctuations in the amount of P and N transported in runoff from various watersheds, may be due in part to the effect of the leaching of vegetation in different stages of decay (Cowan and Lee, 1971; Taylor et al., 1971; Kleusener, 1972; Wells et al., 1972; Gosz et al., 1973; Schuman et al., 1973b; Burwell et al., 1975; Singer and Rust, 1975). In addition, it has been suggested that differences in the P and N concentrations in runoff between different areas, may be partially due to the vegetation type and consequently the amounts of P and N leached (Muir et al., 1973; Schuman et al., 1973b; Burwell et al., 1974; Gburek and Heald,  $\sqrt{1974}$ ). In a study by White and Williamson (1973), it was suggested that variations in the P and N concentrations in surface runoff from grassed-runoff plots may have been caused by differences in grass maturation or in stages of decomposition. This was substantiated after further field work by White (1973), who

measured a differential release of P from vegetation collected from the plots.

It is apparent, therefore, that the leaching of certain crops by surface runoff waters could contribute substantial amounts of soluble P and N to lakes and streams.

## 2.1.3 Urban land

The large amounts of P and N added to surface waters in sewage effluent and industrial wastes have received much attention (Engelbrecht and Morgan, 1961; Weibel, 1969; Vollenweider, 1968). Sewage is generally derived from excreta, ground garbage, laundry and other cleaning wastes from households, wastes from commercial and industrial processes, and clean-up, and wash operations from inumerable industrial activities. With the increase in urbanisation, there will be a subsequent increase in the importance of human and animal wastes as potential sources of P and N to surface waters. In fact, Muir et al. (1973) reported that human and animal densities were the predominant influence on P and N concentrations in Nebraska waters. In New Zealand, Syers (1974) estimated that domestic sewage effluent amounted to 9 million kgP  $y^{-1}$ , based on the analysis of the discharge effluent from Palmerston North sewage works, in contrast to 2.5 million kgP  $y^{-1}$  assumed to be derived from fertilizer runoff.

Ryden <u>et al</u>. (1973) suggested that eroding soil was a potentially important source of P in urban drainage, especially in areas of urban development where large areas are cleared of vegetation and laid bare, thus increasing the potential for erosion by surface runoff. In addition, it was suggested that the leaching of DIP from leaves and seeds can be important, leading to high DIP concentrations in spring and autumn. Furthermore, because large amounts of P are readily leached from dead leaves (Holt <u>et al</u>., 1970; Cowan and Lee, 1971), Lee (1973) suggested that an efficient leaf pick-up during autumn might minimise the amounts of nutrients derived from this source in urban drainage.

Thus, drainage from urban lands can be a major source of P and N to natural waters. Urban drainage is a much more amenable source

to control by chemical and physical treatment, than are the diffuse runoff sources from agricultural land (Taylor, 1967; Syers, 1974).

2.2 Amounts of Phosphorus and Nitrogen Forms Transported in Runoff Types

2.2.1 Surface runoff

The transport of P and N forms in surface runoff will depend upon their movement in solution and on suspended soil particles. Consequently, the amounts transported will be determined by the intensity, duration, and amount of precipitation, and soil factors such as the rate of infiltration and percolation, soil texture, land slope, farming practice, vegetation type and cover, nature and distribution of native soil P, and P fertilization history. All of these factors vary considerably in relative importance over small areas, resulting in both the chemical and physical composition of surface runoff being highly heterogeneous (Ryden <u>et al.</u>, 1973; Gburek and Heald, 1974; Viets, 1975).

The losses of soil and of both particulate and dissolved forms of P and N in surface runoff have been studied extensively using experimental field plots. These plots are frequently of small area with high rates of artificial rainfall being applied. Gilchrist and Gillingham (1970) used plots of area 0.4m<sup>2</sup> and applied artificial rain at a rate of 7.5cm h<sup>-1</sup>, immediately after P fertilizer was added, in order to investigate the movement of P in surface runoff. Similarly, Munn et al. (1973) employed plots of area  $0.36m^2$  and artificial rain at a rate of up to  $12.7cm h^{-1}$ . Even so, the use of rainfall simulators can be justified on the grounds that experimental variables can be controlled more adequately and the accumulation of data can be hastened, reducing the high maintenance cost of such plots. The intensity of application, however, must be similar to natural rainfall intensities. Under these conditions, Young and Burwell (1972) have concluded that runoff and soil loss from simulated storms will reflect the loss that would occur from similar natural rainfall intensities.

Although larger plot areas of between 50 and 200m<sup>2</sup> have been

used (Barnett et al., 1972; Romkens et al., 1973; Burke et al., 1974a; Burwell et al., 1975; Singer and Rust, 1975), it is dangerous to extrapolate the data obtained from such plot experiments to whole catchments. This is due to the fact that small plots nearly always overemphasise nutrient and sediment losses, because they usually ignore redeposition of suspended particulate material that would occur with a reduction in velocity of surface runoff, as a result of a decrease in slope. In addition, it has been suggested by Betson (1964) and indicated by Ragan (1967) and Dunne and Black (1970) that surface runoff contributes to stream flow only in close proximity to the stream. Even though these limitations have been recognised (Munn et al., 1973 ; Ryden et al., 1973; Viets, 1975), surface-runoff plots provide a useful technique for the investigation of nutrient movement in relation to specific conditions, such as land slope, soil texture, cover and management, and rainfall factors. In the case of small-area plots, either all (Burwell et al., 1975; Singer and Rust, 1975) or a certain proportion of the total flow is collected and a representative sub-sample taken (Klausner et al., 1974). With larger experimental areas, flow is usually monitored continuously and samples are collected at intervals during the runoff event (Jackson et al., 1973; Romkens et al., 1973; Schuman et al., 1973a, b).

Little variation in concentration of DIP with flow was found by Nelson and Romkens (1971) during the latter part of a surfacerunoff event from unfertilized fallow and tilled plots. The concentration of DIP increased from  $0.05 \text{mg} \text{ l}^{-1}$  to  $0.5 \text{ and } 0.3 \text{mg} \text{ l}^{-1}$ after P fertilizer was applied at rates of 56 and 28kgP ha, respectively. Similar trends were observed by Timmons et al. (1973) for both DIP and NOz. Large variations in the concentration of particulate P and N with time, however, were observed by Barnett et al. (1972). With the collection of samples at infrequent intervals (Carter et al., 1971) and with the analysis of samples which have remained in the field for in excess of 24h (Munn et al., 1973; Burke et al., 1974b), resulting in a redistribution of P and N between particulate and soluble phases, misleading amounts of P and N transported in surface runoff can be obtained. Unfortunately, many studies do not report how frequently or when samples were taken during a runoff event (Timmons et al., 1968; White and Williamson, 1973).

Because the magnitude of flow change is much greater than variations in the concentration of P and N forms, in surface runoff, flow will be the more important variable in the calculation of the loadings of P and N forms (Taylor <u>et al.</u>, 1971). The volume of surface runoff is closely related to the infiltration capacity of the soil, such that the presence of surface seals and high antecedent soil moisture can result in increased volumes of runoff. Similarly, the volume of surface runoff can be reduced by the presence of mulches which increase the infiltration rate (Duley and Russell, 1941; 1942; Knoblauch <u>et al.</u>, 1942; Parr and Betrand, 1960; Batchelder and Jones, 1972).

By dissipating the impact energy of rainfall, crop cover has been shown to reduce the velocity and volume of surface runoff. Highly significant correlations have been observed for the relationship between percent bare soil and surface runoff (Branson and Owen, 1970; Masur and Hanif, 1972; Munn <u>et al.</u>, 1973). Dragoun (1969) measured a 90% reduction in surface runoff in two years after cultivated land was converted to native perennial grasses.

No data on the amounts of P and N forms transported in surface runoff from recently unfertilized New Zealand soils have been published. It is apparent, from overseas studies, however, that significant amounts of P and N forms can be transported in surface runoff from unfertilized land (Holt <u>et al.</u>, 1970; Klausner <u>et al.</u>, 1974). Harms <u>et al.</u> (1974) measured losses of 0.25, 0.40 and 1.12kg ha<sup>-1</sup> y<sup>-1</sup> of TP, NO<sub>3</sub>, and TN, respectively, from a sandy clay loam under pasture in South Dakota. These values are slightly lower than those measured by Burwell <u>et al.</u> (1975) who found that 0.39, 0.68, and 4.10kg ha<sup>-1</sup> y<sup>-1</sup> of DIP, TP, and TN, respectively, were lost from a loam soil under hay in west-central Minnesota. Lower annual losses of P forms and NO<sub>3</sub> were obtained by Timmons <u>et al</u>. (1973) from a fallow loam soil in Minnesota, where losses of DIP, TP, NO<sub>3</sub>, and TN of 0.01, 0.04, 0.07, and 8.02kg ha<sup>-1</sup> y<sup>-1</sup> were measured.

It has been recognised by other reviewers (Ryden <u>et al.</u>, 1973; Viets, 1975), that there is little information available on the losses of P and N forms in surface runoff from fertilized and unfertilized areas. With the application of fertilizer P and N, increased losses of P and N forms in surface runoff can be expected. Several New Zealand studies have demonstrated that fertilizer P can move in surface runoff. Using  $30 \text{ cm}^2$  plots and heavy artificial rainfall (6.6 to 13.3 cm h<sup>-1</sup>), Gilchrist and Gillingham (1970) found that 28% of the applied P (50 kgP ha<sup>-1</sup>) was transported up to a distance of 30 cm through an improved pasture vegetation cover. Studies using lower rates of artificial rainfall (5.8 cm h<sup>-1</sup>) on larger plots (0.004 ha) were carried out by Duncan (1972). The loss of TP in the first two storms of 30-min duration after fertilizer application were 0.049 and 0.37 kg ha<sup>-1</sup>, respectively.

In similar studies overseas, Schuman <u>et al</u>. (1973b) investigated the amounts of P forms transported in surface runoff from differentially-fertilized, contour-planted catchments in Iowa. Approximately 1.8 times more P in solution and on sediment was lost from the heavily-fertilized catchment (97kgP ha<sup>-1</sup> y<sup>-1</sup>) over a 3year period. The data indicated that the greater P loss was associated with the higher application of fertilizer P.

It appears that the major loss of TP in surface runoff is associated with sediment, due to the high sorption capacity of soil material for P discussed earlier (Section 2.1.2.1). Burwell <u>et al</u>. (1975) reported that particulate P accounted for 95% of the total P loss in surface runoff. Other workers have reported highly significant correlation coefficients between total nutrient losses and the quantity of soil eroded (Thomas <u>et al</u>., 1968; Munn <u>et al</u>., 1973; Schuman <u>et al</u>., 1973b). Further to this, Romkens <u>et al</u>. (1973) reported high correlation coefficients between the N and P content of runoff sediment and the clay content of runoff sediment, because of the high affinity of clay particles and related amorphous constituents for P. Thus, if soil erosion is reduced, movement of P and N from the soil surface will subsequently be reduced dramatically.

Because  $NO_3$  is highly soluble and will readily move into the soil,  $NO_3$  losses in surface runoff are normally low, except where considerable surface runoff occurs closely following fertilizer applications. Although no information is available on the movement of N forms in surface runoff after fertilizer N application in New Zealand, several overseas studies have shown that such applications can increase the loss of N in surface runoff. Romkens <u>et al</u>. (1973), found that the amount of  $NO_3$  transported in surface

runoff was greater from corn plots fertilized at a rate of 170kgN ha<sup>-1</sup>, than from unfertilized corn plots in Indiana. Schuman <u>et al</u>. (1973<sub>a</sub>) reported that the concentrations of particulate N in surface runoff were similar for contour-planted, corn-cropped catchments. receiving annual applications of 168 or 448kg ha<sup>-1</sup>, during a three-year period. Although the NO<sub>3</sub> content of surface runoff was low for each of the three years, a greater amount was lost from the heavily-fertilized catchment (3.05kg ha<sup>-1</sup> y<sup>-1</sup>) compared to the catchment fertilized at the recommended rate (1.89kg ha<sup>-1</sup> y<sup>-1</sup>).

The amounts of P and N forms, and sediment transported in surface runoff can vary greatly with crop type and conservation practice. Burwell et al. (1975) added 29kgP ha<sup>-1</sup> y<sup>-1</sup> to surfacerunoff plots under continuous corn, corn in rotation, and oats in rotation, and none to clean cultivated fallow and hay (alfalfa) in rotation. Although the loss of DIP in surface runoff was lower from the unfertilized, fallow plot than from the cropped plot, the loss from the unfertilized, hay plot was greater. This was due to the substantial amounts of dissolved P that could be leached from alfalfa (Timmons et al., 1970). On the other hand, particulate P losses from hay plots were insignificant (0.02kg ha<sup>-1</sup> y<sup>-1</sup>), whereas appreciable amounts of P were transported in surface runoff from oats (5kg ha<sup>-1</sup> y<sup>-1</sup>), corn in rotation (8.4kg ha<sup>-1</sup> y<sup>-1</sup>), continuous corn (18.2kg ha<sup>-1</sup> y<sup>-1</sup>), and fallow (33.15kg ha<sup>-1</sup> y<sup>-1</sup>). These differences emphasise the influence of vegetation cover in dissipating rainfall energy and reducing runoff, and consequently soil erosion. Corresponding differences in the amounts of soluble and particulate P and N forms transported in surface runoff were also reported by White and Williamson (1973) for the same crop types.

Reduced losses of both P and N after fertilizer application . were reported by Schuman <u>et al.</u> (1973a, b) with improved soil conservation practice. Both contour-cropped and level-terraced, cropped corn catchments received 448kgN ha<sup>-1</sup> y<sup>-1</sup> and 97kgP ha<sup>-1</sup> y<sup>-1</sup>. A reduction in the volume of surface runoff discharged and in soil erosion by level terracing, compared to unterraced slopes, resulted in a lower loss of DIP, NO<sub>3</sub>, and particulate P and N in surface runoff (0.049, 0.18, 0.085, and 2.62kg ha<sup>-1</sup> y<sup>-1</sup>, respectively) than from the contour-planted catchment (0.171, 1.050, 1.69, and 36.59kg ha<sup>-1</sup> y<sup>-1</sup>, respectively). The dramatic effect of mole drainage in

reducing the volume of surface runoff by increasing the rates of infiltration and percolation of water has been demonstrated by Rennes <u>et al.</u> (1977) who reported a four-fold decrease in the volume of runoff from undrained compared to drained land. Burke <u>et al.</u> (1974a) observed a thirty-fold decrease in a related study. Consequently, the amounts of P and N forms, and sediment transported from fertilized and unfertilized, drained plots were lower than those from corresponding undrained plots. A reduction of 90% in the P lost from drained, compared to undrained, fertilized clay soils on  $10^{\circ}$  slopes under pasture in Ireland was reported by Burke <u>et al.</u> (1974b).

Certain tillage methods which leave the land relatively undisturbed, or with a protective vegetation cover, can reduce the losses of P and N forms, and sediment in surface runoff. Romkens et al. (1973) showed that when the corn stalk and surface-applied fertilizer remained relatively undisturbed at the soil surface after tillage, the loss of particulate P and N in surface runoff was reduced, but this increased the loss of soluble P and N from the applied fertilizer (56kgP ha<sup>-1</sup> and 170kgN ha<sup>-1</sup>) remaining at the surface. When the corn residue and applied fertilizer particles were partially mixed with the surface soil, the losses of P and N were reduced but particulate P and N losses increased. The conventional system of completely turning over the surface soil, eliminating corn residues and fertilizer from the soil surface and loosening the soil structure, resulted in the highest losses of particulate P and N, but the lowest losses of soluble P and N. This emphasises the fact that by reducing the vegetative cover of the soil, increased losses of particulate P and N can result. By removing applied fertilizer particles from the soil surface, reduced losses of soluble P and N can result.

Although it has been suggested that grazing animals are a major source of P to natural waters in New Zealand (O'Connor, 1968; Elliot, 1971) no studies have reported the losses of P and N forms, and sediment in surface runoff as a result of grazing. It is probable that increased quantities of particulate P and N, and to a lesser extent dissolved P and N, will be transported in surface runoff from pasture that has been grazed. This may be due to the effect of surface pugging on infiltration, resulting in an increase

in the susceptibility of soil material at the soil surface to removal in surface runoff.

## 2.2.2 Subsurface runoff

Subsurface flow can contribute the major proportion of flow in many streams (Minshall <u>et al.</u>, 1969; Johnson and Moldenhauer, 1970; Carter <u>et al.</u>, 1971). Jackson <u>et al.</u> (1973) and Burwell <u>et al.</u> (1976) found that 80% of stream flow in small agricultural catchments in Georgia and Iowa, respectively, could be accounted for by subsurface flow.

Differences between the concentrations of P and N forms in surface and subsurface runoff are a result of the differing P and N soil-retention capacities. Whereas, soluble P is strongly sorbed by soil components (Williams <u>et al.</u>, 1958; Syers <u>et al.</u>, 1971), NO<sub>3</sub> is non-specifically sorbed and moves freely in percolating waters by diffusion and mass flow. Furthermore, because N from soil organic matter and fertilizer N is rapidly nitrified to NO<sub>3</sub>, and because NH<sub>4</sub> is fixed by certain soil components (Brown and Bartholomew, 1962), the major proportion of N transported in subsurface runoff is in the NO<sub>3</sub> form (Willrich, 1969; Erickson and Ellis, 1971; Jackson <u>et al.</u>, 1973; Baker <u>et al.</u>, 1975; Burwell <u>et al.</u>, 1976). In addition, because of the physical-seiving action of the soil profile, subsurface runoff contains only minor amounts of particulate material and consequently, particulate P and N (Burwell <u>et al.</u>, 197<sup>4</sup>; Hanway and Laflen, 1974; Viets, 1975).

Even though the concentration of P forms in subsurface runoff is much lower than that of N forms (Minshall <u>et al.</u>, 1969; Willrich, 1969; Baker <u>et al.</u>, 1975), subsurface runoff may make a major contribution to the P loadings of streams (Ryden <u>et al.</u>, 1973). Subsurface runoff frequently contributes the major proportion of the N loading in streams (Jackson <u>et al.</u>, 1973).

In many agricultural areas, percolating waters may be intercepted by artificial drainage systems, thus accelerating its movement into streams. This form of subsurface runoff is subsequently referred to as accelerated subsurface runoff. As a point source entering stream flow at discreet and identifiable locations, it is amenable to direct quantitative measurement. In contrast, subsurface runoff enters stream flow from diffuse sources (McCarty, 1967; Vollenweider, 1968; Ryden <u>et al.</u>, 1973) and can, therefore, only be partially estimated on a quantitative basis.

2.2.2.1 <u>Accelerated subsurface runoff</u>. No information is available on the concentrations and amounts of P and N forms transported in accelerated subsurface runoff from New Zealand soils, even though large areas of productive farmland are artificially drained. From the overseas studies reported, it is apparent that the concentration of DIP in accelerated subsurface runoff is lower than that in surface runoff because of the sorption of P when water moves through the profile as accelerated subsurface runoff. Hanway and Laflen (1974) measured annual average DIP concentrations of 0.004 and 0.018mg l<sup>-1</sup> from two sites in Iowa, whereas DIP concentration in surface runoff from the same sites varied from 0.013 to 0.240mg l<sup>-1</sup>. Other workers have reported lower concentrations of DIP in accelerated subsurface runoff than in surface runoff from the same experimental areas (Schwab <u>et al.</u>, 1973; Benoit, 1974; Burke <u>et al.</u>, 1974b).

Because NO<sub>3</sub> can move freely in percolating waters, studies (Benoit, 1974; Hanway and Laflen, 1974) have shown that the average NO<sub>3</sub> concentration of accelerated subsurface runoff is greater than that in surface runoff. For example, Jackson <u>et al.</u> (1973) observed that in three years following an annual fertilizer N application (168kgN ha<sup>-1</sup>) to a loamy sand planted in corn in Georgia, the average NO<sub>3</sub> concentration of accelerated subsurface runoff was 7, 10, and 9mg l<sup>-1</sup>, whereas the average concentration of NO<sub>3</sub> in surface runoff for the same three years was 0.2, 0.4, and 0.3mg l<sup>-1</sup>, respectively.

Furthermore, the concentration-flow relationships of P and N forms in accelerated subsurface runoff are different to those for surface runoff. Because of the low P concentrations in tile drainage, Baker <u>et al.</u> (1975) observed no relationship between variations in flow and concentration. Where higher concentrations of P forms in tile drainage resulted from high rates of manure applications

to the soil, Hergert <u>et al</u>. (1974) observed that the DIP concentration, which accounted for 90% of the TDP transported, increased with a rapid increase in flow, subsequently decreasing as flow diminished. Although the NO<sub>3</sub> concentration in tile discharge was constant from day to day, a rapid decrease in NO<sub>3</sub> concentration was found to correspond to an increase in tile flow (Baker <u>et al</u>., 1975).

Both the changes in P and N concentrations with variation in accelerated subsurface flow have been accounted for in part, by changes in the flow path of water to the tile line (Hergert <u>et al</u>., 1974; Baker <u>et al</u>., 1975). These workers suggested that during periods of high accelerated subsurface flow, the water table may rise above the tile drain, thus a greater proportion of drainage would be composed of soil water descending from higher levels in the profile and containing lower N and higher P concentrations. At lower flow rates, with a fall in the water table, water from lower levels containing lower P and higher N concentrations would move laterally to the tile line.

Any variation in the concentration of "extractable" soil P or NO<sub>3</sub> with depth between different soils (Murrman and Feech, 1969; Ryden et al., 1972b; Baker et al., 1975; Schuman et al., 1975) is potentially important in determining DIP and  $\mathrm{NO}_{\mathrm{Z}}$  concentrations in drainage water. Because the levels of "extractable" soil P and  $NO_{z}$  can be affected by a combination of factors such as fertilizer application (Blakemore, 1966; Nightingale, 1972), crop type (White and Greenham, 1967), soil temperature and moisture (Mack, 1959), and amounts of precipitation, the same factors will consequently influence losses of P and N in accelerated subsurface runoff. Hanway and Laflen (1974) found that the DIP concentration of tile drainage from several soils in Iowa, was directly related to the amount of "available" P in the soils, as extracted by ammonium fluoride and HCl. "Available" soil P levels of 13 to 20 and 2 to 4mgP  $\rm g^{-1}$  were measured for Creston and Carlson City soils, respectively, below the 61cm layer, whereas the average DIP concentration of accelerated subsurface runoff from these soils was 0.018 and 0.004mg 1<sup>-1</sup>, respectively. A similar relationship between soil NO<sub>3</sub> levels and the NOz concentration of tile drainage, however, was not observed for the same soils.

Few studies have adequately measured the effect of the application of P fertilizer on the concentration and amounts of P forms transported in accelerated subsurface runoff, because of the lack of a control, without fertilizer addition. The immobility of P in soils, however, suggests that fertilizer P should have little effect on the concentration and amounts of P transported in accelerated subsurface runoff. In studying P losses in tile drainage over a seven-year period, Bolton et al. (1970) observed that fertilizer application resulted in a small but consistent increase in P concentration of the drainage water from a clay soil in Ontario. The average annual concentration of DIP in tile drainage was 0.18 and 0.21mg 1<sup>-1</sup> from unfertilized and fertilized (29kgP ha<sup>-1</sup>) alfalfa, respectively, with an average annual loss of P from the unfertilized and fertilized crops of 0.12 and 0.19kg ha<sup>-1</sup>, respectively. Although Zwerman et al. (1972) did not report the loss of DIP in accelerated subsurface runoff from unfertilized cropped land, because they were very small, an increased rate of fertilizer application  $(12.2 \text{ to } 31.5 \text{kg ha}^{-1})$  did not result in any significant change in the DIP concentration of accelerated subsurface runoff from a silt loam planted in corn in New York. Furthermore, Hanway and Laflen (1974) found that although similar rates of fertilizer P (100kgP ha<sup>-1</sup>) were applied to three different sites, the amounts of DIP transported in accelerated subsurface runoff from these sites were very small  $(0 \text{ to } 0.004 \text{kg ha}^{-1})$ . When a smaller amount of P fertilizer was applied (38kgP ha<sup>-1</sup>) to a fourth site, the amount of DIP transported in tile drainage  $(0.005 \text{kg ha}^{-1})$  was higher than that from the other three sites. It may be concluded, therefore, that neither the concentration nor amounts of DIP transported in accelerated subsurface runoff can be related solely to the amounts of fertilizer applied.

Due to contrasting soil reactions, N fertilizer additions increase the loss of NO<sub>3</sub> in accelerated subsurface runoff from a soil to a varying extent (Meek <u>et al.</u>, 1969; Zwerman <u>et al.</u>, 1972; Gambrell <u>et al.</u>, 1975). The studies of Johnston <u>et al</u>. (1965), Doneen (1966), and Glandon and Beck (1969), all in the San Joaquin Valley, California, showed high NO<sub>3</sub> concentrations in drainage from fertilized, irrigated land. It is impossible, however, to determine how much of the NO<sub>3</sub> came from the applied N because the soils contained significant quantities of residual NO<sub>3</sub>. More recently, Jackson <u>et al.</u> (1973) monitored  $NO_3$  losses in accelerated subsurface runoff before and after fertilizer N application to a loamy sand under corn in Georgia. Nitrogen fertilizer had not been applied to the area during four years prior to the experimental fertilizer application and during the latter part of this period,  $NO_3$  concentrations in accelerated subsurface runoff averaged 4.8mg 1<sup>-1</sup>. Following the first application (168kgN ha<sup>-1</sup>  $y^{-1}$ ), the average annual  $NO_3$  concentration of the drainage water increased to 7.1, 10.3, and 9.3mg 1<sup>-1</sup> in the first, second, and third years, respectively. The data suggested that after three years, a maximum loss for the cropping system and fertilizer practice had been reached.

Although fertilizer N applications may increase the amount of NO3 transported in accelerated subsurface runoff, the conclusion cannot be drawn that the  $\mathrm{NO}_3$  is derived solely from the fertilizer. Losses of NO<sub>3</sub> clearly result from a combination of factors. Although some of the  $\mathrm{NO}_3$  losses reported may have been related to fertilizer applications, appreciable losses can occur without fertilizer application. Furthermore, the time of fertilizer N application can affect the concentration of  $NO_3$  in drainage waters. An increase in the NO<sub>z</sub> concentration of accelerated subsurface runoff can result from fertilizer N applications during wet periods before crops are sufficiently effective in terms of uptake (Cooke and Williams, 1970). If fertilizer N application does not exceed crop needs, no NO3 would be available for leaching (Pratt et al., 1972). Power and Alessi (1971) similarly concluded that as long as the fertilizer N application rate was less than the rate of total N removed by the harvested crop, it was unlikely that an increase in the NO<sub>3</sub> loss would occur.

In addition, because  $NO_3$  requirements will vary between different cropping systems, nutrient losses in accelerated subsurface runoff will also reflect the effect of the cropping system, as well as fertilizer application. In fertilizer N trial experiments in southern England, Tomlinson (1971) found that arable crops usually recovered no more than 50% of the N applied, whereas grass recovered up to 80%. Bolton <u>et al</u>. (1970) also reported that the  $NO_3$  concentration of accelerated subsurface runoff from a clay soil in Ontario was highest from unfertilized and fertilized (112kgN ha<sup>-1</sup>)

corn in rotation (8.5 and 14.0mg  $1^{-1}$ , respectively) and second year alfalfa sod (4.7 and 8.6mg  $1^{-1}$ , respectively), whereas it was appreciably lower in accelerated subsurface runoff from a field in bluegrass sod (0.3 and 0.7mg  $1^{-1}$ , respectively). Less specifically, Cooke and Williams (1970) observed higher NO<sub>3</sub> concentrations in accelerated subsurface runoff from arable areas (average concentration 22.5mg  $1^{-1}$ ) than from grassland (3.3mg  $1^{-1}$ ) at Woburn, England. In contrast, cropping systems have little or no effect on the concentration of P forms in accelerated subsurface runoff (Bolton <u>et al.</u>, 1970; Zwerman et al., 1972).

The literature indicates that P and N fertilizer application rates, and the type of crop and soil, can influence the amounts of P and N forms transported in accelerated subsurface runoff. There is consequently, a large variation in the amounts of P and N transported in accelerated subsurface runoff from different areas.

2.2.2.2 Natural subsurface runoff. The rate of water percolation through the soil profile as natural subsurface flow, will be markedly lower than that moving to the tile lines as accelerated subsurface runoff. Consequently, it is likely that the concentration of P and N forms in natural and accelerated subsurface runoff will not be the same. Several workers have in fact reported lower DIP and higher  $\mathrm{NO}_{\mathrm{Z}}$  concentrations in subsurface flow, than in tile drainage (Burwell et al., 1974; Gilliam et al., 1974; Thomas and Barfield, 1974). In the case of DIP, a longer time of contact between the subsoil material and natural subsurface runoff compared to accelerated subsurface runoff, will result in a greater removal of DIP from natural subsurface runoff. Lower NO<sub>z</sub> concentrations in accelerated compared to natural subsurface runoff, may be due to dilution as a result of a larger water discharge as accelerated subsurface runoff and a smaller depth of soil profile from which the NO3 can be leached before accelerated subsurface runoff leaves the soil profile.

Although the amounts of P and N forms transported in subsurface runoff cannot be measured quantitatively, it appears that marked variations in the concentrations of N forms, and to a lesser extent P forms, in subsurface runoff can occur, as a result of different fertilizer applications and cropping systems. No evidence has been reported to indicate that fertilizer application can increase either the concentration or losses of P forms in subsurface runoff, except in very sandy soils, where high rates of percolation and low P-sorption capacities of the soil can result in significant leaching of P (Cooke and Williams, 1970; Kurtz, 1970; Tomlinson, 1971; Viets, 1975).

In a study of the North Carolina coastal plain, Gilliam <u>et al</u>. (1974) reported that the concentration of  $NO_3$ , in subsurface runoff from cultivated and fertilized fields was greater than that from adjacent wooded areas. The data indicated, however, that the concentration of  $NO_3$  was not related to the crop grown, but to the degree of aeration, such that  $NO_3$  concentrations may be higher under the better drained sites than under adjacent wetter sites, due to an increased rate of N mineralisation and nitrification. Similarly, Nightingale (1972) obtained a positive correlation between the rate of fertilizer N application and  $NO_3$  concentrations in the soil solution. Although the  $NO_3$  concentration of subsurface flow increased, it was apparent that other factors were influencing the concentration of  $NO_3$  in subsurface flow.

Schuman <u>et al.</u> (1975) indicated that considerable  $NO_3$  leaching below the root zone could occur in a corn-cropped catchment in Iowa, when excessive rates of fertilizer N were applied and water percolated through the rooting zone. Once the N had moved below the crop root zone it is potentially a subsurface runoff pollutant. More recently, in a further report of the same study area in Iowa, Burwell <u>et al</u>. (1976) concluded that in order to control the losses of N in subsurface runoff, it was necessary to apply fertilizer N at rates that do not exceed crop needs.

# 2.3 Amounts of Phosphorus and Nitrogen Forms Transported in Stream Flow

The amounts of P and N forms transported in stream flow, as measured at the watershed outlet, represent an integration of all hydrological and chemical processes that affect water movement and modify P and N concentrations after their derivation from the various

sources.

In streams draining forest catchments, only minor fluctuations in the concentration of DIP, TP, and NO<sub>2</sub> have been reported. For both native and exotic forest catchments in New Zealand, White (1972) observed a mean DIP concentration of 0.011mg  $1^{-1}$  which varied only slightly (0.004 to 0.027mg  $1^{-1}$ ) with a change in the rate of stream discharge. Also, Schreiber <u>et al.</u> (1976) obtained mean annual DIP and NO<sub>2</sub> concentrations of 0.01 and 0.07mg  $1^{-1}$ , respectively, for stream flow in five pine catchments in Mississippi, which varied from only 0.008 to 0.015, and 0.03 to 0.1mg  $1^{-1}$  for DIP and NO<sub>3</sub>, respectively. Similar concentrations of P and N in streams from forested catchments have also been observed in other studies but with no apparent relationship to changing flow rate (Sylvester, 1961; Brink and Gustafson, 1970; Hobbie and Likens, 1973).

It appears that the concentration-flow relationships of P and N forms in forest streams are similar to those in subsurface flow. Eccause surface runoff will be minimal, due to canopy interception of precipitation (Syers and Ryden, 1973) the major proportion of stream flow draining stable forest catchments will be derived from subsurface runoff. In agreement with this, Johnson <u>et al.</u> (1976) found that the mean annual DIP and TDP concentration in stream flow from a forested catchment in New York, was 0.005 and 0.013mg  $1^{-1}$ , respectively, compared to average concentrations of 0.006 and 0.014mg  $1^{-1}$  in subsurface runoff, sampled in six wells in the same catchment.

The literature suggests that the concentrations of P and N forms in streams draining agricultural catchments generally increase with increasing flow rate (Muir <u>et al.</u>, 1973; Johnson <u>et al.</u>, 1976). McColl <u>et al.</u> (1975) observed that soluble P and N concentrations in a stream draining a gently-rolling pasture catchment in New Zealand, reached a maximum in the initial stages of a rapid rise in stream flow. These workers suggested that as flow rate increased, the potential for P and N to enter streams also increased. With a further increase in stream flow and subsequent recession, the reservoir of soluble P and N within the catchment, is depleted, with the result that stream concentrations rapidly decrease. A similar "flushing" of accumulated soluble nutrients during the initial

stages of storm flow has also been observed by Walling and Foster (1975) for several catchments in Devon, England. Both studies showed that the rise in the concentration of P and N forms, with an initial increase in stream flow, diminished with a subsequent secondary rise in flow, substantiating the idea that the sources of P and N are being gradually depleted during storm flows.

In catchments which have undergone urban development, surface runoff is expected to constitute the major proportion of stream flow (Ryden <u>et al.</u>, 1973). In contrast to forest streams, the concentrations of P and N forms in streams draining urban areas are generally high and show marked changes with flow rates. Although the particulate P concentrations of urban storm flow tend to increase with an increase in stream flow (Harris <u>et al.</u>, 1972), the concentrations of dissolved materials have been reported to decrease with increasing flow rate (Wang and Evans, 1970; Olsen <u>et al.</u>, 1973; Schreiber <u>et al.</u>, 1976).

Sampling the rise and fall of stream flow more intensively, Johnson et al. (1976) reported that the peak DIP concentration, which was up to two orders of magnitude greater than low-flow concentrations  $(0.01 \text{ mg l}^{-1})$ , preceded maximum flow, indicating that inputs from surface runoff and release from stream-bed sediments contributed to the increased DIP concentrations. Hydrograph analysis showed that maximum DIP concentrations coincided with a rapid but minor rise in flow, as a result of increased surface-runoff in-Further analysis showed that DIP concentrations were reasonputs. ably well correlated with the ratio of surface to total runoff. Consequently, during the initial stages of a rapid rise in stream flow, surface runoff, containing high P and low N concentrations (Section 2.2.1), will contribute the major proportion of water discharged in stream flow. As the rate of water discharged in surface runoff decreases, subsurface runoff, containing low P and high N concentrations (Section 2.2.2), will contribute an increasing proportion of the water discharged as stream flow. During stream flow recession, subsurface runoff will be the sole contributor. Catchment hydrology will, therefore, be of major importance in determining the fluctuations of P and N concentrations in stream flow.

The amounts of P and N forms transported in stream flow from

stable forested catchments, reflect the chemical and physical factors which affect P concentrations in groundwater and subsurface runoff, (Kyden et al., 1973), because of minimal amounts of surface runoff. Consequently, the amounts of P and N transported in streams draining stable, unfertilized forested catchments provide "background" or "natural" levels against which the amounts transported from forest catchments which have been cleared and developed into productive farmland and urban areas can be compared (Syers and Ryden, 1973; Johnson et al. 1976).

It is apparent that the amounts of P forms transported from forested catchments are lower than those from catchments of different land use. Ryden <u>et al.</u> (1973) cited six studies of P losses in streams draining forested catchments; the range in the amount of TP transported was from 0.2 to 0.68kg ha<sup>-1</sup> y<sup>-1</sup>. The amounts of N forms transported in streams draining forested and agricultural catchments, however, appear to be more variable than those of P forms from area to area. Because the concentration of N forms in precipitation is high compared to P forms (Section 2.1.1), the losses of N forms in streams draining forested catchments, and in some cases N-fertilized agricultural catchments, are dominated by the input of N in precipitation (Taylor <u>et al.</u>, 1971). Consequently, a variation in the composition and quantity of precipitation from area to area may account for the lack of any relationship between N losses and land-use and management in different areas.

As a result of the low loss of P forms in stream flow from forest catchments, and the large input of N forms in precipitation, stable forested catchments are normally conservative of both P and N forms. This is illustrated by the data presented by Schreiber <u>et al.</u> (1976) for five pine watersheds in Mississippi, which showed net gains of 0.02 and 2.8kg ha<sup>-1</sup> y<sup>-1</sup> of DIP and NO<sub>3</sub>, respectively, from precipitation. Taylor <u>et al.</u> (1971) reported that a woodland catchment in Coshocton, Ohio, which had received no P or N fertilizer in the past 35 years, accumulated 0.12kg ha<sup>-1</sup> y<sup>-1</sup> TDP and 18kg ha<sup>-1</sup> y<sup>-1</sup> TN. In addition, net gains of P and N by undisturbed forests have been reported by Hobbie and Likens (1973) and Likens <u>et al</u>. (1970), respectively. Although net gains of P and N forms can occur on an annual basis, Schreiber <u>et al</u>. (1976) reported that net gains of DIP and NO<sub>3</sub> decrease as runoff increased for individual

storm events in forested catchments.

The development of forestland results in an increase in the amounts of P and N forms transported in stream flow, especially in the initial stages of clear cutting. Aubertine and Patric (1974) observed that when one of two adjacent catchments in West Virginia, which had previously lost similar amounts of P and N, was clear cut, the amounts of water discharged and P and N forms, and sediment transported increased slightly. The increase in stream flow represented a reduction in water loss by evaporation. As reforestation continued, transpiration and rainfall interception by the developing regrowth increased, and stream flow and nutrient losses declined to precutting levels. In a similar study in New England, Marks and Borman (1972) found that nutrient losses were related to the rate of revegetation and that the losses rapidly returned to the steady-state observed before deforestation.

In contrast, Hobbie and Likens (1973) found significant increases in the loss of nutrients in stream flow after clear-cutting. When one of two comparable forested catchments at Hubbard Brook, New Hampshire, was cleared and regrowth stopped in the subsequent three years by herbicide treatment, an increase in stream flow of 40% in the first year and 26% by the third year occurred, compared to that from the undisturbed catchment. The loss of TP increased from 0.02kg ha<sup>-1</sup>  $y^{-1}$  to 0.20kg ha<sup>-1</sup>  $y^{-1}$  after clearing as a result of a 15-fold increase in particulate P transported. The latter P form contributed 90% of the TP transported after clearing, compared to only 57% prior to clearing. Consequently, there was a net gain of 0.06kg ha<sup>-1</sup>  $y^{-1}$ P in the undisturbed catchment, whereas after clearing a net loss of 0.10kg ha<sup>-1</sup>  $y^{-1}$  P was observed. The conversion of stable forested catchments to agricultural land is expected to cause a marked increase in the losses of P and N.

Although the losses of P and N in streams draining pasture catchments are greater than those from forested catchments (Taylor et al., 1971), they are usually lower than those from cropped catchments. From the sampling of several streams in Nebraska, Muir et al. (1973) observed that the losses of P and N were related to the intensity of cultivation and the proportion of land devoted to leguminous pasture growth. This correlation probably reflects the

greater vegetational covering of the ground with pasture, with a subsequent reduction in the P and N movement to the stream in soil particulates, and a lower amount of P and N leachable from pasture as opposed to crop residues (Timmons <u>et al.</u>, 1970; Muir <u>et al.</u>, 1973). Similarly, Olness <u>et al.</u> (1975) found that the losses of TP, DIP,  $NO_3$ , and TN were lower from a pasture catchment under rotational grazing than from three cropped catchments (Table 2.4). Significantly, higher losses of TP,  $NO_3$ , and TN (4.60, 1.80, and 7.87kg ha<sup>-1</sup> y<sup>-1</sup>, respectively), however, were lost from unfertilized pasture that was continuously grazed, than from rotationally-grazed pasture and in the majority of cases, fertilized crops. These results suggest that the losses of P and N formscan be appreciable from intensively-grazed pasture.

A number of studies have shown that increased losses of P and N in streams draining agricultural catchments are associated with fertilizer application. From studies carried out in New Zealand, Fish (1969) suggested that the eutrophication of lakes in the Rotorua area was accelerated by topdressing with superphosphate and measured a 100-fold increase in the concentration of DIP after aerial topdressing, in the Waingaeha stream which drains into Lake Rotorua. Because each sample was only collected at two-week intervals, it is not possible to obtain a reliable estimate of the P loading. It has also been suggested that an increased amount of reactive P transported into the Tomohawk Lagoon near Dunedin (Mitchell, 1971) and from the number five catchment at Taita (White, 1972), resulted from topdressing. An intensive sampling programme of stream flow in the Puketurua catchment, Whangarei, before and after two superphosphate applications was carried out by McColl et al. (1975). They estimated that in the first and second post-fertilizer floods, 1.4 and 0.55% of the applied P (56 and 62kg ha<sup>-1</sup> 15% potasic superphosphate, respectively) was lost. These amounts correlated well with the amount of fertilizer P falling in the dry-stream bed during application.

Kilmer <u>et al</u>. (1974) concluded that P and N losses in stream flow from two steeply-sloping, differentially-fertilized, grassed catchments in North Carolina, were not significantly increased by fertilizer additions. Annual losses of P were negligible and fertilizer P had no apparent effect on P losses in stream flow.

In the case of N, losses in drainage water over a four-year period from catchments receiving 112 kgN ha<sup>-1</sup> and 448 kgN ha<sup>-1</sup> amounted to 6 and 10% of that added. Such losses of N can hardly be considered insignificant. Although Olness et al. (1975) did not find any relationship between the losses of TP or TN in streams draining cropped catchments in Oklahoma and fertilizer application, losses were related to sediment transport. The loss of soluble P and NOz, on the other hand, appeared to be related to fertilizer application, even though the net loss of DIP and  $\mathrm{NO}_{\mathrm{X}}$  from any of the catchments was no more than 3 and 5% of the added fertilizer P and N, respectively. The amounts of DIP and NO<sub>z</sub> transported from eight hydrologically similar agricultural catchments in Kentucky were measured over two years by Thomas and Crutchfield (1974). The highest NO3 loss occurred in both years from a catchment which received little fertilizer and and was essentially all in bluegrass pasture. One intensivelycropped catchment showed rather high values for  ${\rm NO}_{\times}$  in stream water, whereas the others did not. Phosphorus contents of the waters were directly related to the geological formations through which the streams flowed. The highest P losses occurred in a stream draining a pasture catchment having soils developed from a limestone rich in P. Two streams draining intensively-cultivated catchments on alluvium and loess, low in native P, showed minimum P losses. The close relationship between catchment geology and P and N in streams, therefore indicates that this factor, even more than land use, can be of prime importance in determining the nutrient contents of waters.

The further development, by urbanisation, of catchments results in drastic changes in drainage patterns and increased losses of P and N in streams draining these catchments. Studies by Lee <u>et al</u>. (1969) and Lee (1973) of the amounts of P forms derived from various sources in Southern-Central Wisconsin showed that the conversion of undisturbed, forested catchments to cropped farmland resulted in an approximately ten-fold increase in TP losses. A further twentyfold increase was observed with the conversion of cropland to urban areas. In studying P losses from urban catchments in Madison, Wisconsin, Harris <u>et al</u>. (1972) and Kluesener (1972) suggested that the leaching of leaves and seeds, coupled with reduced infiltration, resulted in increased P losses from urban compared to agriculture catchments. Similar losses were observed by Wiebel <u>et al</u>. (1964) for an urban catchment in Cincinnati, Ohio. In addition, Kyden et al. (1973) indicated that urban development maximised the possibility of erosion, should surface runoff occur, by exposing large areas of bare soil. Consequently, high particulate P losses could be expected.

Point-source inputs of industrial and human effluents from sewage treatment plants can add significant amounts of P and N to urban streams. Engberg (1971) and Olson <u>et al.</u> (1973) reported that human density was the predominant influence on the P, N, and sediment losses in several streams studied in Nebraska. In a stream draining a rural catchment in central New York, Johnson <u>et</u> <u>al.</u> (1976) found that the Dryden sewage plant increased P and N losses in stream flow by a factor of 10 to 20-fold. For example, the flux of DIP up-stream of the sewage plant was about C.2kg  $day^{-1}$ , whereas a flux of 3.8kg  $day^{-1}$  was measured below the plant.

Information on the relative significance of runoff types to the P and N loadings of stream is limited. The overseas work that has been reported, suggests that subsurface flow can contribute the major proportion of flow and  $NO_3$ , but only a minor proportion of the P losses to a stream (Minshall <u>et al.</u>, 1969; Jackson <u>et al.</u>, 1973; Burwell <u>et al.</u>, 1974; 1976). In a more recent study, Johnson <u>et al.</u> (1976) proportioned the loss of DIP in a stream draining a rural catchment in central New York into three main sources. They estimated that of the DIP lost in the stream during the 18-month study, 44% was derived from natural biogeochemical processes, 22% was derived from diffuse sources in surface runoff associated with farming, and the remaining 34% was derived from point sources, mostly domestic sewage. This type of information is necessary where attempts are made to control P inputs into waters.

2.4 Modification of Phosphorus Concentrations in Surface Waters

It was apparent from the data reported in the previous section that the amounts of DIP added in precipitation to agricultural catchments are not the same as the output of DIP from the catchments in stream flow. There is, therefore, an interaction between the soluble P in the waters and the soils and sediments through which the waters pass, which may involve sorption, desorption, and dissolution reactions. These interactions thus determine the P concentration at the catchment outlet. According to Taylor and Kunishi (1971), and Kunishi <u>et al.</u> (1972), variables such as the source and amount of P available to be leached, the soils through which the water moves on its way to the stream, the types and amounts of sediments lining the stream channel and suspended in stream flow, and the velocity of the various runoff types and stream flow, can all affect modification of the DIP concentration during its movement in runoff through the catchment.

The types of reactions involved in the modification of DIP concentrations are believed to be the same regardless of whether they occur under conditions existing in surface runoff, streams, or in the soil profile, discussed earlier (Section 2.1.2.1) (Ryden and Syers, 1973). Consequently, these reactions will be of major importance in the modification of dissolved P concentrations by suspended particulate material in surface runoff and streams.

Because the concentration of DIP can vary as the rate of discharge of a stream changes (Taylor et al., 1971; Muir et al., 1973; McColl et al., 1975), there must be either a different source of P contributing when a catchment is hydrologically disturbed by precipitation, a different P sorption-desorption rate caused by a change in the relative importance of the runoff types to stream flow, differing soils and sediments contacted by the runoff waters, or some combination of these. Various studies have investigated the P sorption-desorption behaviour of soils under simulated stream flow conditions. The high levels of added inorganic P (IP) and narrow solution: solid ratios frequently used, do not adequately simulate the in-stream situation. In studies where soil materials have not reached equilibrium with the solution phase (Larsen and Court, 1950; Fordham, 1963; White, 1966), and where the levels of added IP are low (Ryden et al., 1972a, b), the release of 1P to solution from soil materials is dependent upon the solution:solid ratio. This is illustrated by the work of Ryden et al. (1972) who reported that at high levels of added IP and a solution: solid ratio of 50:1, a B1 horizon was able to sorb more IP than a C1 horizon, whereas the situation was reversed at lower levels of added IP. At a solution: solid ratio of 400:1, the two horizons behaved similarly.

The least complex situation appears to exist during subsurface flow, when consistently low DIP concentrations indicate that the sediment:water systems may be at an equilibrium (Gburek and Heald, 1974). Under these low flow conditions, the DIP concentrations reflect the P-sorbing characteristics of the sub-soil (Taylor and Kunishi, 1971).

The potentially important particulate materials in the sorption and desorption of IP in streams will be not only suspended sediment from surface runoff, but also eroded and in situ stream-bank material. In studying the amounts and forms of P transported in stream flow from a small, topdressed catchment in New Zealand, McColl et al. (1975) found that although topdressing increased the amounts of DIP and TP transported from a small catchment, no increase in these P forms was detected after the stream had passed through a larger catchment, similarly topdressed. The removal of DIP from solution P was attributed to uptake by stream-bank and stream-bed material, and suspended material in the stream. Sorption-desorption studies carried out by Taylor and Kunishi (1971) indicated that the high P-sorbing capacity of stream-bank material could account for a decrease in DIP concentrations downstream in a catchment in Pennsylvania. Further work by Kunishi et al. (1972) on the same rural catchment showed that different DIP concentrations during high and low stream flow, could be accounted for by a change in the relative contribution of the various sources of particulate material in the stream.

From the above discussion it appears that interactions between the particulate and dissolved phases will influence the DIP concentrations in streams draining agricultural catchments. It may be expected that particulate material from different sources within the catchment will exhibit a varying ability to sorb or desorb P in the stream environment.

# SECTION 3

#### GENERAL METHODOLOGY

#### 3.1 Description of the Catchment

The catchment under study is located adjacent to Massey University, Palmerston North, New Zealand. The catchment is long and narrow in shape (approximately 3800m long and 280m wide) and has an area of 112ha. This was determined by tracing the catchment boundaries on stereo-paired air photographs under a stereoscope and measuring the area with a planimeter.

The catchment consists of one soil type, Tokomaru silt loam (Pollok, 1975), and is situated on an elevated terrace, capped with loess blown up from the flood plain of the Manawatu River. Representative land slopes in the catchment were measured photogrammetrically and these were approximately one-third 4-7%, one-third 8-15%, and one-third 16-20% slopes. Although slopes are smooth and runoff is not impeded by local depressions, drainage is poor in the absence of artificial drainage. Some 60ha of the catchment are mole and tile drained.

The moderate fertility pasture of the catchment is used for fat lamb production, dairying, and beef cattle fattening, with some forage and grain crops grown for supplementary feed. Maintenance superphosphate applications (normally 375kg ha<sup>-1</sup>) are made.

A Lambrecht continuous recording raingauge was initially sited adjacent to the lower weir. This was removed after it was found that the amounts and intensities of rainfall were little different from those obtained using a similar raingauge sited approximately 1000m due east of the lower weir. Climatic data from DSIR Grassland Meteorological Station, 1km from the lower weir, showed that the average annual rainfall over the period 1936-1976 was 997mm, with an annual average of 180 raindays. Although no snow was recorded in the Massey Catchment in the study period, for convenience in comparing with other studies, the term precipitation is used to describe the rainfall entering the catchment.

The ephemeral stream draining the catchment is essentially a first-order stream with a subparalleled pattern of natural drainage. The first-order channel length is 5.3km with a meander factor of 1.3 and a channel fall of 67m. Flow data for the period 1971-1975 indicate that the stream flows for approximately 150 days per annum.

#### 3.2 Monitoring Installations

Stream flow was continuously monitored at two sites by compound weirs consisting of a 90° V notch flanked by wing walls of 3:1 slopes using Stevens F-type meters which continuously recorded stage measurements. The two weirs isolated a subcatchment of 20ha (Fig. 3.1) within the main catchment. The land within the subcatchment is owned by Massey University and was in permanent pasture for dairy farming during the study period. Stream samples were collected immediately upstream from each weir.

Two duplicate sets of surface-runoff plots (plots 1 to 4) were established adjacent to the stream in the subcatchment. Also two duplicate sets of surface-runoff plots (plots 5 to 8) were established on adjacent land although not within the catchment boundary. The slope, area, aspect, and management of these plots are summarised in Table 4.1. Each plot was delineated by vertical wooden boards, which were buried 20cm deep and protruded approximately 5cm above the ground surface to prevent up-slope and across-slope surface runoff from entering the plot. Access of cattle to the grazed plots (1-4) and the defaecation and urination behaviour of the cattle did not appear to be affected by the protruding boards. On each plot, surface-runoff water was directed by plastic guttering, sunk into the ground, to Childs' stage recorders which continuously monitored flow.

Approximately 14 of the 20ha subcatchment was mole and tile drained. The 7-cm diameter mole channels were spaced at 2-m intervals at a depth of 45cm in the profile, and discharged into ten tile lines at a depth of 75cm. Discharge from two lines, draining areas of 1.1 (area A) and 0.8ha (area B) of gently sloping  $(0 \text{ to } 1^{\circ})$  land were continuously monitored for flow by  $\frac{1}{4}$  90° V-



Fig. 3.1 Map of the subcatchment including surface runoff plots on  $13^{\circ}$  (1 and 2) and  $6^{\circ}$  (3 and 4) slopes, monitored tile lines draining 1.1ha (A) and 0.8ha (B), and upper (E) and lower (F) weirs on the stream. notch weirs, equipped with Stevens F-type stage recorders.

### 3.3 Sample Collection

#### 3.3.1 Earthworm casts

Production of surface casts of earthworms (dominantly <u>Allolobophora caliginosa</u>) in the catchment was measured by the collection at weekly intervals, of casts from the surface of duplicate  $0.090m^2$  plots. Cast production was represented by the oven dry weight ( $105^{\circ}C$ ) of sample collected.

#### 3.3.2 Water samples

Samples were collected in 500-ml polyethylene bottles used routinely for water sampling. Release of inorganic P from, and uptake by the container walls was shown to be negligible. Surface and accelerated subsurface runoff were sampled manually, whereas stream samples were collected manually or automatically with an ISCO automatic sampler. Details of the frequency of sampling used for each runoff type are discussed in the appropriate sections. The elapse time between sample collection and initial processing (filtration) never exceeded 2h. This was because the DIP concentrations of unfiltered runoff samples may change significantly after approximately 4h following collection when stream flow was high and the samples contained high concentrations of particulate material. The concentrations of DIP in filtered runoff samples were found to remain constant for at least 24h. Nevertheless, DIP was determined immediately after filtration. Filtered runoff samples for subsequent nitrogen (N) analyses were routinely stored under refrigeration at 1°C, whereas unfiltered runoff samples were frozen on arrival at the laboratory.

### 3.4 Analytical Procedures

Approximately 100ml of each runoff sample was initially

centrifuged at 15,000 rev.  $\min^{-1}$  for 5min at 23°C, using a Sorvall RC-2B high-speed, refrigerated centrifuge to facilitate Millipore filtration (< 0.45µm). Work in this laboratory has indicated that Millipore membranes released both DIP and dissolved organic nitrogen to solution. The membranes were, therefore, prewashed with distilled water before use.

The concentration of DIP was determined on a filtered sample, as was that of TDP after acid persulphate digestion following autoclaving at 15 p.s.i. for 45min and neutralisation of the solution (Environmental Protection Agency, 1971). Total P was determined on an unfiltered runoff sample following perchloric acid digestion for 1h, and neutralisation of the resulting extract (O'Connor and Syers, 1975). The method of Murphy and Riley (1962) was used for all inorganic P determinations, absorbance being measured at 712nm using a Unicam SP 1800B Spectrophotometer. Dissolved organic phosphate (DOP) was calculated by the difference between TDP and DIP, and particulate P by the difference between TP and TDP.

Analyses for N forms were carried out using a Technicon Autoanalysis system. The automated Griess-Ilosvay method following reduction by cadmium (Hendrikson and Selmer-Olsen, 1970) was used for the determination of NO<sub>3</sub> on a filtered sample. Total Kjeldahl N (TKN) was determined by the automated Kjeldahl digestion of an unfiltered sample (Terry, 1966). Total N was calculated from the sum of NO<sub>3</sub> and TKN. Netrale was measured as NO<sub>3</sub>-N but is Subsequently ufferred to as NO<sub>3</sub> for Onvenience.

The sediment concentration of samples was determined from the difference between the weights after evaporation to dryness at  $105^{\circ}C$  of a suitable aliquot of the unfiltered and filtered (< 0.45 $\mu$ m) samples.

#### 3.5 Data Processing

A computer programme was developed to process the data collected for the concentrations of P and N forms, and sediment at each sampling, and for water flow. Data were transformed to a form facilitating storage and manipulation, and to enable input

to either library packages for the direct plotting of curves and statistical analysis, or to curve-fitting programmes. The object programme was written in Fortran and implemented on a Burroughs B6700 computer at Massey University. The programmes developed were stored on magnetic tape and the flow and P and N data were stored as a tape file to assist availability, ease of handling, and flexibility of programme use.

The following programmes, with variations for print-out restrictions, were developed to:

- (a) validate the data card input, after the data for nutrient and sediment concentrations, water height, and time of collection of each runoff sample were transferred to cards for input to the computer.
- (b) calculate instantaneous and mean nutrient and sediment fluxes and flow rates from flow and concentration data, and total loading and total flow by numerical integration of the linearly interpolated nutrient flux-time and water flow-time curves, respectively, over periods of interest.
- (c) plot specific data variables, including water flow and the concentrations and fluxes of P and N forms and sediment using a Tektronics storage display terminal, with the facility to produce a photocopy of the screen plot. It was also possible to produce graphical output on a Calcomp plotter by either terminal or card input.
- (d) use the library packages for the statistical analysis of data on tape file.

The relative importance of concentration and flow in controlling the fluxes of P and N forms in surface, accelerated subsurface, and subsurface runoff, and in stream flow was assessed by multiple regression analysis. Nutrient flux was treated as the dependent variable. Because of the greater ease of partitioning variations among linearly-related components, the data were transformed to

logarithms.

The sampling interval required to reliably evaluate the loadings of P and N forms in surface, accelerated subsurface, and subsurface runoff, and in stream flow was investigated. For the three runoff types, the total loadings of P and N forms were calculated from a very intensive sampling of a runoff event to provide a best estimate standard. Estimate deviations are defined as the differences between estimated, using less intensive sampling, and the best estimate, with the difference being expressed as a percentage of the best estimate standard.

For each runoff type, proper subsets of the very intensive sampling were constructed using samples separated by defined time intervals. A number of such subsets, differing only in the time of the first sample, were used to obtain replicate estimates of the total nutrient loadings for each sampling interval during a runoff event. For each sampling interval and runoff type, the mean deviations and their confidence intervals were calculated.

# SECTION 4
# SOURCES AND TRANSPORT OF PHOSPHORUS AND NITROGEN IN SURFACE RUNOFF

#### 4.1 Introduction

Information relating to the inputs of P from fertilizer sources has usually been obtained from surface-runoff plots, (Stoltenberg and White, 1953; Nelson and Romkens, 1969; Weidner <u>et al.</u>, 1969). This approach was originally developed to evaluate soil fertility losses resulting from soil erosion. In New Zealand, Gilchrist and Gillingham (1970) have demonstrated that fertilizer P can move in surface runoff through improved pasture. Many surface-runoff studies, however, have employed small plots and high rates of artificial rainfall, with the result that it is frequently difficult to relate the data obtained to natural conditions.

Although the potential importance of dung as a source of P to surface-runoff waters in grazed catchments in New Zealand has been suggested (O'Connor, 1968; Elliot, 1971), no experimental data are available to determine the magnitude of this effect. In addition, there is no information available from which to determine the relative significance of soil, fertilizer, and animals as sources of P to surface runoff in New Zealand, as emphasised by Syers (1974).

A meaningful evaluation of the nutrient loadings of surface runoff entering streams requires determination of the requisite intermittent sampling frequency to satisfactorily estimate P and N losses in surface runoff. Initially, this requires some understanding of flow-concentration relationships for the forms of P and N in surface runoff. The sampling intervals used have differed appreciably in surface-runoff studies where nutrient inputs have been measured. Sampling intervals have ranged from 3min (Timmons <u>et al.</u>, 1973) to irregular intervals during a year (Carter <u>et al.</u>, 1971).

It would be expected that the losses of DIP in surface runoff

are related to the ease of release of P from the solid phase. If this is the case, then it may be possible to predict the loss of DIP in the surface-runoff environment. As a result of the appreciable cost involved in monitoring and sampling surface runoff, it is clear that laboratory extraction procedures which could be used to predict the losses of dissolved P in surface runoff would potentially be useful.

The aims of this part of the study relating to surface runoff were to (i) observe the interrelationships between flow, concentration, and flux of P and N forms, (ii) determine the effect of sampling frequency on estimates of the loadings of P and N forms, (iii) evaluate the relative significance of soil, fertilizer P, and grazing animals as sources of P and N forms as determined in field-plot studies under natural rainfall conditions, and (iv) investigate the potential of using soil extraction data to predict the loss of dissolved inorganic P in surface runoff.

#### 4.2 Material and Methods

Surface-runoff studies were conducted using the plots described in Section 3.2, details of which are summarised in Table 4.1. No fertilizer was added to the plots in 1974. In June 1975, powdered superphosphate at the rate of 50kgP ha<sup>-1</sup> was added by hand, as evenly as possible, to plots 2, 4, 6, and 8. Plots 1 to 4 were unfenced and animals had access to them during grazing events in the subcatchment. Plots 5 to 8 were fenced to prevent access of animals.

The sampling interval for surface runoff did not exceed 15min and was as small as 1min for rapid hydrograph changes.

To investigate the relationship between the amount of extractable soil inorganic P and the DIP concentration of surface runoff, soil samples from plots 5, 6, 7, and 8 were collected at monthly intervals, from depths of 0-5 and 5-10cm. The field-moist samples were passed through a 2-mm sieve and 2-g subsamples were shaken with 40ml of 0.1M NaCl for 40h at  $23^{\circ}$ C. After centrifugation at

10010				
		Plot n	umber	
	1 2	3 4	5 6	7 8
Slope	13° 30'	6° 30'	6° 30'	6° 30'
Area (m <sup>2</sup> )	55	55	41	41
Aspect	SW	SW	SW	ΝE
Drainage	Undrained	Undrained	Undrained	Drained
Land use	Grazed	Grazed	Ungrazed	Ungrazed

pasture pasture pasture pasture

Table 4.1 Details of the surface-runoff plots

15000rpm for 10min at 23<sup>°</sup>C and Millipore filtration, the extracts were analysed for DIP. Results were corrected for soil moisture content and bulk density.

### 4.3 Results and Discussion

# 4.3.1 Interrelationships between flow, concentration, and flux of phosphorus and nitrogen forms

The concentration of P and N in surface runoff and their relationships with flow during one low- (event 1, Fig. 4.1), two medium- (event 2, Fig. 4.2a, b; and event 3, Fig. 4.3a, b) and one high- (event 4, Fig. 4.4) intensity storm events are presented. These events cover the range of flows observed during two years of field monitoring.

The concentration of DIP showed little variation with flow during the storm of low-intensity (Fig. 4.1). During the storms of medium-intensity, however, DIP concentration (Fig. 4.2a, 4.3a) decreased slightly following peak flow, but gradually returned to the pre-peak flow value. During the high-intensity storm, DIP concentration varied little (Fig. 4.4). Similar trends were observed for NO<sub>3</sub> in the four storms considered, where the NO<sub>3</sub> concentrations decreased slightly at peak flow, due to dilution by increased water flow. A general decrease in NO<sub>3</sub> concentration with time was apparent, with the final concentration being slightly lower than in the early stages of the surface-runoff event. This probably reflects a dilution of the NO<sub>3</sub> source, as suggested by Barnett et al. (1972).

During surface runoff in these four events, variations in the concentrations of both DIP and NO<sub>3</sub> were small relative to the dramatic changes in flow. Consequently, the concentrations of DIP, TDP, and NO<sub>3</sub> were not significantly correlated to flow (Table 4.2, last column) in the medium-intensity event (event 2), typical of those observed, when the 17 samples collected during the event were used for the correlation analysis. Little variation in concentration with flow was also observed by Nelson and Romkens (1971)



Fig. 4.1 Variation in flow and concentrations of TP, DIP, TN, and  $NO_3$  for surface-runoff event 1.





Fig. 4.2 Variation in (a) flow and concentration of TDP, DIP, and NO<sub>2</sub>, and (b) flow and concentration of TP and TN for surface-runoff event 2.



400

3

Variation in (a) flow and concentration of DIP and NO3, Fig. 4.3 and (b) flow and concentration of TP, TN, and sediment for surface-runoff event 3.

Time (h)

1

2

40



Fig. 4.4 Variation in flow and concentration of TP, DIP, and sediment for surface-runoff event 4.

Table 4.2 Squared standard partial regression coefficients for the standard regression of log<sub>10</sub> flux on log<sub>10</sub> concentration and log<sub>10</sub> flow, and correlation coefficients for concentration with flow for P and N forms in surface-runoff event 2

P or N form	Squared standard regression coeff: for	partial icients	Correlation coeffi- cient for concen- tration with flow
	Concentration	Flow	
DIP	0.11**	0.83**	0.11
TDP	0.01**	0.94**	0.20
TP	0.11**	0.53**	0.76**
NO3	0.01**	0.91	0.30
TN	0.01**	0.82**	0.86**

\*\* Values significant at the 1% level.

for DIP and by Timmons et al. (1973) for both DIP and  $NO_3$ .

In contrast to the data obtained for DIP, TDP, and NO<sub>3</sub>, the concentrations of TP and TN increased as flow increased in all events (Fig. 4.1, 4.2b, 4.3b, and 4.4), resulting in the fact that both TP and TN concentrations were significantly correlated with flow (Table 4.2). It was also observed that sediment concentrations in surface runoff varied considerably with flow (Fig. 4.3a and 4.4) and that peak sediment concentration occurred near, and in most cases coincided with, peak water discharge. A similar relationship between sediment concentration and flow has been reported by Dragoun and Miller (1966).

Because the concentrations of DIP (Fig. 4.1, 4.2a, 4.3a, and 4.4), TDP (Fig. 4.2a), and NO<sub>3</sub> (Fig. 4.1, 4.2a, and 4.3a) were essentially constant until a point after peak flow, and because of the nature of the flow-concentration relationship for sediment, variations in TP and TN concentrations are due largely to variations in sediment concentration and to variations in particulate P and N concentrations. This is substantiated by the fact that correlation coefficients of 0.96 and 0.68 (both significant at the 1% level) were obtained for relationships between the amounts of particulate P and sediment, and TN and sediment, respectively, transported in surface-runoff events during the year. Similar high correlations between P and N, and sediment in surface runoff have been presented by Thomas <u>et al</u>. (1968), Munn <u>et al</u>. (1973), and Romkens <u>et al</u>. (1973).

The curves for flux of DIP and  $NO_3$  (Fig. 4.5a) were similar to those for flow in all events. Consequently, only the flux data for event 2 are presented. This similarity is confirmed by the significantly higher squared standard partial regression coefficients (Table 4.2, event 2) for flow than for DIP and  $NO_3$  concentration. In this analysis, the squared standard partial regression coefficients indicate the magnitude of the effects of flow and concentration on P and N flux. In addition, the flux of TP and TN (Fig. 4.5b) in surface runoff was more closely related to flow than to concentration (Table 4.2). Part of the variation in the concentrations of each P form between events is



Fig. 4.5 Variation in (a) flow and flux of DIP and NO<sub>3</sub>, and (b) flow and flux of TP and TN for surface-runoff event 2.

probably due to the varying elapse-time since the application of P fertilizer.

Because of the differing concentration-flow relationships for dissolved and total P and N, and the rapid change in P and N flux with flow during an event, it is apparent that the frequency of sampling required to reliably quantify the transport of P and N forms in surface runoff will vary. Consequently, it is important to investigate the effect of varying the sampling interval on loading estimates, in order to establish a meaningful sampling programme which enables the reliable estimation of loadings of both total and dissolved forms of P and N in surface runoff.

## 4.3.2 Sampling frequency

Details of the procedure used to establish the frequency of sampling of surface runoff have been presented in Section 3.5.

The deviation in estimates of P and N loadings generally increased with an increase in the sampling interval for the typical surface-runoff event (Table 4.3). The variability in the rate of change of concentration with time was greater for TP and TN (Fig. 4.2b) than for dissolved forms (DIP, TDP, and  $NO_3$ , Fig. 4.2a). Consequently, the deviations in loading estimates (Table 4.3) were invariably larger for TP and TN than for DIP, TDP, and  $NO_3$ . It is apparent that the deviation in loading estimates for  $NO_3$  was greater than that for dissolved P forms at the same sampling intervals, whereas the deviation for TP was less than for TN.

As a result of the significant correlations between flow and TP, and TN concentrations, surface runoff should be sampled whenever a significant change in flow rate occurs. The interval between base values and the maximum turning point for TP concentration is commonly of the order of 15min (Fig. 4.2b). Consequently, a sampling interval of greater than 15min is to be avoided for this region of the hydrograph. Deviations in loading estimates for samples taken at 30-min intervals, even when a sample at peak flow was included, were still greater than those obtained with a

Sampling	Num	per of	P or N	Deviatio	n in loading estimates
interval	Samples	Replicates	form		(%)
(min)				Mean	Confidence interval
					(95%)
2	42				
10	20	4	DIP	-1.09	(-2.12, 0.06)
			TDP	-0.33	(-1.51, 0.85)
			TP	-0.93	(-13.2, 11.3)
			NOz	-0.11	(-2.19, 1.97)
			TN	-2.97	(15.03, 9.09)
15	12	4	DIP	-0.76	(-3.0, 1.43)
			TDP	0.18	(-1.79, 2.15)
			ͲP	-4.7	(-15.3, 16.1)
			NOz	-3.85	(-7.51, -0.19)
			TN	-3.96	(-14.10, 6.18)
30 <sup>a</sup>	6	4	DIP	-1.21	(-5.1, 2.7)
			TDP	-1.15	(-5.0, 2.7)
			TP	-8.9	(-36.0, 18.1)
			NOz	-4.39	(-10.25, 1.47)
			TN	-7.05	(-19.0, 4.9)
b					
30-	5	4	DIP	-28.5	(-60, 4)
			TDP	-33.8	(-75, 10)
			TP	-65.7	(-93, -32)
			NO3	-42.1	(-96, 12)
			ΤN	-53.8	(-116, 10 )

Table 4.3 Deviations in loading estimates of P and N forms in surface-runoff event 2

a Sample at peak flow included.

b

Sample at peak flow not included.

15-min sampling interval (Table 4.3). At a flow-sampling interval of 15min, deviations in estimates of total water flow were less than 2%. Based on the data presented in Table 4.3 and a similar treatment of surface-runoff events 1 and 4, a maximum sampling time interval of 15min for both the concentrations of P and N forms, and flow was selected for subsequent studies, with the inclusion, where possible of a sample at peak flow.

Using the determined frequency of sampling (15min), estimate deviations of P and N loadings were obtained for eleven events studied. Estimate deviations (Table 4.4) were always less than 10%. The results are considered particularly acceptable in view of the rapid fluctuations in the flux of P and N forms in surfacerunoff events.

4.3.3 Phosphorus and nitrogen transport in surface runoff as influenced by soil, fertilizer phosphorus, and animals

Plot variability studies, conducted prior to the application of P fertilizer and in the absence of grazing cattle, indicated little variation in the volume of water discharged and amounts of dissolved P and N forms transported in surface runoff from plots 1 to 4 (all undrained), which differed only in slope, for the ten events studied (Table 4.5). Also, for the five events studied prior to fertilizer addition, plots 5 and 6 (undrained) replicated well, as did plots 7 and 8 (drained). Although only a small proportion of the total number of surface-runoff events were sampled in the year prior to fertilizer application, the fact that each of the four pairs of plots showed a similar behaviour in terms of the criteria considered, made a subsequent evaluation of the transport of P and N forms from the plots receiving different treatments.

4.3.3.1 <u>Soil</u>. The transport of P and N in surface runoff from undrained and drained Tokomaru silt loam resulting largely from soil, are represented by the data from plots 5 and 7,

Selected sampling	P or N	Deviation in loading estimates (%)				
interval (min)	form	Mean	Confidence interval (95%)			
15 <sup>a</sup>	DIP	-1.90	(-6.0, 2.1)			
	TDP	-0.24	(-1.9, 1.5)			
	TP	-3.10	(-7.1, 0.99)			
	NOz	-0.15	(-2.49, 2.19)			
	TN	-0.53	(-1.66, 2.82)			

Table 4.4Deviation in loading estimates of P and N formsin the eleven surface-runoff events studied

a Sample at peak flow included and flow data at 15-min intervals used.

Table 4.5Water discharged and forms of P and N, and sediment transported in surface runoff for<br/>ten (plots 1 to 4) and five (plots 5 to 8) events prior to fertilizer application

	Plot number									
Parameter	1	2	3	4	5	6	7	8		
Discharge (m <sup>3</sup> ha <sup>-1</sup> )	370	360	360	360	70	70	20	20		
DIP (kg ha <sup>-1</sup> )	0.23	0.23	0.21	0.23	0.016	0.016	0.004	0.004		
TDP "	0.35	0.36	0.33	0.34	0.018	0.019	0.005	0.005		
Particulate P (kg ha <sup>-1</sup> )	0.39	0.39	0.36	0.37	0.013	0.011	0.003	0.0014		
TP "	0.74	0.75	0.69	0.71	0.031	0.030	0.008	0.009		
NO 3 "	0.20	0.18	0.22	0.21	0.061	0.049	0.021	0.017		
TN "	0.61	0.63	0.56	0.58	0.10	0.09	0.030	0.028		
Sediment "	290	340	230	240	15	14	L <sub>4</sub>	4		

respectively (Table 4.6). Each of these plots was unfertilized and ungrazed. The amount of dissolved P (TDP) transported in surface runoff from the undrained plot was slightly greater than that of particulate P transported (C.48 and 0.37kg ha<sup>-1</sup> y<sup>-1</sup>, respectively). The losses of P forms in surface runoff are greater than those reported from similar management systems overseas, whereas the losses of TN are lower. Burwell <u>et al</u>. (1975) measured losses of 0.39, 0.68, and 4.10kg ha<sup>-1</sup> y<sup>-1</sup> for DIP, TP, and TN, respectively, from a loam soil under hay in westcentral Minnesota, and Harms <u>et al</u>. (1974) found losses of 0.25, 0.40, and 1.12kg ha<sup>-1</sup> y<sup>-1</sup> for TP, NO<sub>3</sub>, and TN, respectively, from a sandy clay loam under pasture in South Dakota. Even lower losses of P were obtained by Timmons <u>et al</u>. (1973) from a fallow loam soil in Minnesota, where annual losses of 0.01, 0.04, 0.07, and 8.02kg ha<sup>-1</sup> y<sup>-1</sup> for DIP, TP, NO<sub>2</sub>, and TN were measured.

The amounts of water discharged and P and N forms, and sediment transported in surface runoff from the unfertilized and ungrazed, drained plot (plot 7) were between 3 and 4 times lower (Table 4.6) than those from the unfertilized and ungrazed, undrained plot (plot 5). The very much lower volume of surface runoff from the drained, relative to the undrained plot supports the findings of Rennes <u>et al.</u> (1977) obtained using the same plots in the previous year and indicates the rather dramatic effect of mole and tile drainage on surface runoff. Burke <u>et al.</u> (1974a) observed that mole drainage virtually eliminated surface runoff. It is apparent, therefore, that the reduction in surface runoff volume, as a consequence of artificial drainage, leads to a decrease in the amounts of P and N forms, and sediment transported.

Although significant losses of P and N in surface runoff occur from land that has not recently received fertilizer P or recently been grazed, these losses cannot be attributed solely to soil, because of previous inputs of P and N from fertilizer and grazing animals. In addition, precipitation may contribute P and N both directly and indirectly to surface runoff. For convenience, precipitation as a source of P and N to surface runoff is considered in this section because it is regarded as a natural or background source. In this regard, precipitation is somewhat analogous to Table 4.6Annual amounts of water discharged and P and N forms, and sediment transported in surfacerunoff from the plots receiving the treatments indicated in Table 4.1

					Plot num	ber			
Parameter	-	1	2	3	l <sub>i</sub>	5	6	7	8
Discharge (m <sup>3</sup>	ha <sup>-1</sup> y <sup>-1</sup>	)1720	1720	1500	1500	1330	1330	440	440
DIP (kg ha <sup>-1</sup>	y <sup>-1</sup> )	0.71	2.18	0.49	1.83	0.33	1.66	C.10	0.42
TDP	н	1.08	2.68	0.94	2.38	0.48	1.91	0.13	0.46
Farticulate P	11	0.74	2.42	0.68	2.03	0.37	1.76	C.11	0.29
TP	11	1.94	5.19	1.62	4.41	0.85	3.67	0.24	0.75
NO3	11	0.56	0.60	0.48	0.45	0.46	0.43	0.18	0.21
TN	11	6.69	6.72	5.81	5.71	1.53	1.60	0.54	0.63
Sediment	11	980	990	880	830	670	610	180	170

soil, in contrast to fertilizer P or grazing animals.

The concentration of DIP, TP, and NO<sub>3</sub> in precipitation were measured in fifteen storms during the second year of study (Table 4.7). The mean concentrations of DIP, TP, and NO<sub>3</sub> were 0.008, 0.037, and 0.23mg 1<sup>-1</sup>, respectively, and showed little variation from observation to observation. The levels of TN in precipitation were too low for reliable data to be obtained. Allen <u>et al.</u> (1968) found no seasonal variation in the concentration of TP in precipitation collected at various sites in northern England, although the amounts of TP ranged from 0.009 to 0.002kg ha<sup>-1</sup> y<sup>-1</sup> at different sites.

The amounts of TP and NO<sub>3</sub> entering the catchment in a unit amount of precipitation were 0.004 and 0.023kg ha<sup>-1</sup> cm<sup>-1</sup>, respectively. Similar amounts (0.003 and 0.039kg ha<sup>-1</sup> cm<sup>-1</sup> of TP and NO<sub>3</sub>, respectively) were reported by Burke <u>et al.</u> (1974b) for precipitation in Ireland. Klausner <u>et al.</u> (1974) obtained values of 0.002 and 0.16kg ha<sup>-1</sup> cm<sup>-1</sup> of TP and NO<sub>3</sub>, respectively, in New York, whereas in New Sealand, Miller (1961) reported a TP input in precipitation of 0.0002 kg ha<sup>-1</sup> cm<sup>-1</sup> at Taita.

The amounts of DIP and TP added annually to the soil surface in precipitation (Table 4.7) were less than those transported in surface runoff from the unfertilized, ungrazed and undrained plot (plot 5). The amount of  $NO_3$  added in precipitation, on the other hand, was greater than that lost in surface runoff. It is of interest that Burwell <u>et al</u>. (1975) found more dissolved P and less  $NO_3$  in surface runoff than was contributed annually in precipitation.

It would appear that soil and plant material are more important sources than precipitation of the P transported in surface runoff in the present study. The reverse situation appears to be the case for NO<sub>3</sub>. Under certain conditions, leaching of litter material by surface-runoff water could contribute substantial amounts of dissolved P and N to surface waters. Timmons <u>et al</u>. (1970) reported that soluble P and N in leachates from alfalfa and bluegrass were greatly increased by drying or freezing, two processes which occur naturally in the field. The occurence of substantial amounts

Table 4.7	Mean concentrations	and annual	amounts	of DIP,	TP, and NO <sub>3</sub> in	n precipitation.	, and annual losses
	of DIP, TP, and NO3	in surface	runoff	from the	unfertilized,	ungrazed and us	idrained plot
	(rlot 5)						

	P and N forms in							
P or N form		Fred	Surface runoff					
	Mean concentration (mg l <sup>-1</sup> )	Confidence interval (95%)	kg ha <sup>-1</sup> cm <sup>-1</sup>	kg ha <sup>-1</sup> y <sup>-1</sup>	kg <sup>-1</sup> ha <sup>-1</sup> y <sup>-1</sup>			
DIP	0.008	(0.10, 0.06)	0.0C1	0.10	0.33			
TP	0.037	(0.040, 0.034)	0.004	0.39	0.85			
NO3	0.23	(0.25, 0.21)	0.023	2.23	0.46			

Total precipitation = 970mm.

of water-extractable inorganic P in pasture litter has recently been reported by Gillingham <u>et al</u>. (1976).

At certain times of the year, large numbers of earthworm casts were observed on the soil surface of the runoff plots and of surrounding pasture in the subcatchment. Because such casts may be enriched in P (Graff, 1970; Vimmerstedt and Finney, 1973), it is possible that they could be important sources of both particulate material and P in surface runoff. Surface cast production in the subcatchment exhibited distinct seasonal variations (Fig. 4.6). Maximum cast production was observed in early June, gradually decreasing to a minimum in mid-August, with a secondary rise in production in September. The factors, contributing to the seasonal variation in cast production are discussed in detail in Section 8.3.1. The mean concentration of sediment (obtained from total load divided by total flow) in each surface-runoff event during the casting period, showed similar seasonal variations to cast production (Fig. 4.6), with maximum concentrations in early June and late August and minimum values in July. Further evidence for the contribution of cast material to the sediment loading, and by inference to the particulate P loading of surface runoff, is indicated by the similar particle-size distribution of surface casts and the particulate material transported in surface runoff, discussed in Section 8.3.5.

The release of P from the surface (0-5cm) of Tokomaru silt loam and from earthworm casts has been studied in laboratory experiments and these results are also discussed in Section 8.3.3. It was observed that the surface soil was able to support a solution inorganic P concentration of approximately 10% of that usually present in surface runoff. In contrast, earthworm casts sustained solution inorganic P concentrations similar to that found in surface runoff.

4.3.3.2 <u>Fertilizer phosphorus</u>. Following the addition of superphosphate to plots 2, 4, 6, and 8 in the second year of the study, surface-runoff samples were collected during each of the runoff events in the period (approximately four months) when



Fig. 4.6 Mean sediment concentration in individual surface-runoff events (dashed line) and the quantity of earthworm casts produced at the soil surface (solid line).

surface runoff occurred. Losses of DIP from the fertilized plots (2, 4, 6, and 8) were approximately four times greater (Table 4.6) than from the corresponding unfertilized plots (1, 3, 5, and 7). The ratio of the amount of DIP lost from the fertilized relative to the unfertilized plots was usually greater than that for TDP and TP. No significant increase in the loss of 'TN and NO<sub>3</sub> was observed from plots (2, 4, 6, and 8) following the application of P fertilizer, compared to the unfertilized plots (1, 3, 5, and 7; Table 4.6). There was, however, a greater loss of NO<sub>3</sub> and TN from the steeper plots (1 and 2) compared to the less-steep plots (3 and 4).

The very good replication within each pair of plots before fertilizer application (Table 4.5), allowed estimation of the losses of fertilizer P in surface runoff by comparing the P data obtained from the fertilized and unfertilized plots (Table 4.8). Slightly more fertilizer P was lost as DIP (1.47kg ha<sup>-1</sup>) from the steeper, undrained plot than from the two less steep, undrained plots (1.34 and 1.33kg ha<sup>-1</sup> from plots 4 and 6, respect-Similar results were obtained for TDP and TP (Table 4.8). ively). The mean concentration of DIP, TDP, and TP in surface runoff over the four-month period, calculated from total loadings and total flow, were also slightly higher from the steeper, undrained plot (plot 2) than from the less steep, undrained plot (plot 4, Table 4.8). For example, the mean DIP concentration in surface runoff from plot 2 was  $1.34 \text{ mg l}^{-1}$ , compared to  $1.27 \text{ mg l}^{-1}$  from plot 4. Calculations indicate that 10 and 22% more dissolved P and particulate P, respectively, were lost from the steeper plot (plot 2) than from the less-steep plots (plots 4 and 6). An increase in slope would be expected to increase the velocity of surface runoff and hence its erosional power. Thus, it appears that increased slope will result in an increased loss of fertilizer P as particulate P and to a lesser extent as dissolved P in surface runoff. This is in agreement with the work of Duley and Hays (1932) and Munn et al. (1973) who observed an increase in the amount of particulate P lost as soil surface slope increased.

The lower amounts and mean concentrations of P forms, derived from fertilizer P, which were transported in surface runoff from Table 4.8 Amounts of P forms transported in surface runoff from fertilized plots, corrected for losses from corresponding unfertilized plots, and mean concentrations of P forms transported in surface runoff from fertilized plots during four months following fertilizer application

Plot number	Amount of fertilizer P transported			Percentage of added fertilizer P trans- ported as			Mean P concen- tration in sur- face runoff		
	DIP	TDP kg ha <sup>-1</sup> _	Τ̈́Ρ	DIP	I'DP - %	TP	DIP	'TDP mg l~1	TP
2	1.47	1.60	3.25	2.9	3.2	6.7	1.34	1.52	3.29
4	1.34	1.44	2.79	2.7	2.9	5.6	1.27	1.36	3.08
6	1.33	1.43	2.82	2.7	2.9	5.7	1.30	1.40	2.89
8	0.32	0.33	0.51	0.6	0.7	1.0	1.00	1.03	1.76

the drained, than from the undrained plot indicate that a higher proportion of fertilizer P entered the soil in the former situation. This is presumably a consequence of the lower volume of surface runoff lost from the drained plots (Table 4.6) and hence the greater volume of water infiltrating the drained soil. A reduction of 90% in the P lost from drained compared to undrained, fertilized clay soils on  $10^{\circ}$  slopes under pasture in Ireland was found by Burke <u>et al.</u> (1974b).

The proportion of added fertilizer P lost as TP in surface runoff from the undrained plots ranged from 5.6 to 6.7%, of which between 48 and 52% was in solution (TDP) and between 43 and 48% was in the dissolved inorganic (DIP) form. For the drained plot, only 1.0% of fertilizer P was lost, of which 70% was in the dissolved form and 60% was in the DIP form. In addition, both of the undrained, less-steep plots (plots 4 and 6) behaved remarkably similarly in terms of the proportion of fertilizer P lost (2.7 and 2.7%, respectively, as DIP; and 5.6 and 5.7%, respectively, as TP).

Thus, a single addition of fertilizer P to Tokomaru silt loam under pasture which had not been fertilized recently, at an application rate  $(50 \text{kgP ha}^{-1})$  similar to that normally used on this soil, increased substantially the amounts of P forms transported in surface runoff. The losses of fertilizer P from the undrained plots, where approximately 400mm of surface runoff occurred, were higher than those obtained by workers overseas. A loss of fertilizer P (56kgP ha<sup>-1</sup> added) of 1.2% as "soluble P" in 250mm of surface runoff from fallow and tilled plots during a three-month period was observed by Nelson and Romkens (1971). Smaller losses of fertilizer P (39kgP ha<sup>-1</sup> added) as "soluble P" (0.6%) and as TP (0.7%), were reported from pasture in a six-month period by Schuman et al. (1973b). Benoit (1974) also obtained an average annual TP loss of 0.9kg ha<sup>-1</sup> after a fertilizer application of 56 kgP ha<sup>-1</sup> to a silt loam on a 6° slope under pasture. Consequently, it appears that the data obtained in the present study for the losses of fertilizer P transported in surface runoff from undrained Tokomaru silt loam under pasture are greater than those reported in overseas studies involving similar land management.

4.3.3.3 Animals. Six weeks after P fertilizer was applied, 100 dairy cattle grazed a 4ha area, which contained plots 3 and 4, for a period of 24h as part of the normal grazing plan for the farm. The effect of animals on the losses of P and N forms, and sediment from plots 3 and 4 were isolated from the effect of fertilizer by using plots 5 and 6 (both undrained and ungrazed) as controls. This was considered acceptable because similar amounts of fertilizer P were transported in surface runoff from plots 4 and 6 (Table 4.8). The data in Table 4.9 suggest that the one grazing event of 24h duration resulted in significant losses of P and N forms, and sediment. Furthermore, similar amounts of P, N, and sediment were lost from the two grazed plots when the appropriate correction was made for the loss of fertilizer P from plot 4. Grazing animals had a major effect on the transport of DOP, where the loss of this P form in the four weeks following grazing (0.30kg ha<sup>-1</sup> from plot 3, Table 4.9) was twice that lost in four months from the corresponding ungrazed plots (0.15kg ha<sup>-1</sup> from plot 5, Table 4.6), and on the transport of particulate P, where a loss of 0.31kg ha<sup>-1</sup> was obtained (plot 3, Table 4.9) compared to 0.37kg ha<sup>-1</sup> in four months from the ungrazed plot (plot 5, Table 4.6). The relatively large loss of particulate P, attributable solely to grazing animals, is consistent with the large loss of sediment and the close correlation between particulate P and sediment discussed earlier.

Because dung has a higher P content than urine (During, 1972) the former probably contributes much of the P attributable to animals in surface runoff. It is also probable that increased quantities of particulate forms of P and N, and to a lesser extent dissolved forms, are transported in surface runoff from the grazed plots, because of the effect of surface pugging on infiltration, resulting in an increase in the susceptibility of soil material at the surface to removal in surface runoff.

The most significant loss attributable only to grazing animals was obtained for TN, where 4.18 and 4.11kg ha<sup>-1</sup> were lost from plots 3 and 4 in the four weeks following grazing (Table 4.9). This represents a three-fold increase in the amount of TN lost in four months from the ungrazed plot  $(1.53kg ha^{-1} from plot 5, Table 4.6)$ .

Table 4.9 Water discharged, and forms of P and N, and sediment transported in surface runoff from grazed, undrained plots, corrected for losses of P and N forms and sediment from corresponding ungrazed, undrained plots (plots 5 and 6) of the same slope during four weeks following grazing

	Plot number	
Parameter	3	а 4
Discharge (m <sup>3</sup> ha <sup>-1</sup> )	160	170
DIP (kg ha <sup>-1</sup> )	0.16	C.17
TDP "	0.46	0.47
Particulate P		
(kg ha <sup>-1</sup> )	0.31	0.27
ТР и	0.77	0.74
NO <sub>3</sub>	0.02	0.02
TN "	4.18	4.11
Sediment "	210	220

a Fertilizer added.

In contrast to TN, NO<sub>3</sub> losses in surface runoff due to grazing animals were very small (0.02kg ha<sup>-1</sup>). This may be attributed to the low NO<sub>3</sub> content of dung and urine and to the low soil temperatures during the winter months which would be expected to inhibit nitrification (Hedgwood, 1966). In addition, the high susceptibility of NO<sub>3</sub> to leaching (Greenland, 1958; Harmsen and Kolenbrander, 1965) by infiltration at the beginning of each runoff event to a depth below which surface soil is eroded (Timmons et al., 1973) would result in low NO<sub>3</sub> levels in surface runoff.

It is of interest to compare the loss of  $NO_z$  and TN in surface runoff in the four weeks following grazing with published data for losses of NO $_{\rm Z}$  and TN following the application of fertilizer N. Schuman et al. (1973a) reported an annual loss, averaged over three years, of 0.76 and 2.36kg ha<sup>-1</sup> y<sup>-1</sup> for NO<sub>3</sub> and TN, respectively, in surface runoff from a silt loam under pasture following an annual fertilizer N application of 168kgN ha<sup>-1</sup> as ammonium nitrate. This annual loss of TN resulting from N fertilizer addition was lower than that obtained following grazing in the present study (4.18kg ha<sup>-1</sup>, Table 4.9), although the reverse was the case for NO<sub>3</sub>. An annual loss of NO<sub>3</sub> over three years of O.30kg ha<sup>-1</sup> was observed by Jackson et <u>al</u>. (1973) after an annual application of 168kgN ha<sup>-1</sup> as liquid ammonium nitrate-urea to a sandy loam. This value is greater than the loss of NO3 obtained following grazing in the present study (0.02kg ha<sup>-1</sup>, Table 4.9). Moe <u>et al</u>. (1967) obtained losses of TN ranging from 5.8 to 33.8kg ha<sup>-1</sup> following the broadcast application of ammonium nitrate at a rate of 224kg ha<sup>-1</sup> to a silt loam of varying surface cover and antecedent moisture status. Consequently, it appears that under certain conditions the loss of TN in surface runoff following grazing with cattle may be greater than that resulting from fertilizer N addition.

It would be anticipated that because cattle grazed the fertilized plot (plot 4), subsequent losses of P may be due partly to an increase in the susceptibility of fertilizer particles to transport in surface runoff because of the disturbance of the soil surface. The fact that the increased losses of P and N forms in surface runoff in the four weeks following grazing were similar for fertilized (plot 4) and unfertilized plots (plot 5; Table 4.9), indicates that grazing animals did not increase the loss of fertilizer P in surface runoff. Consequently, the increase in amounts of P and N forms transported in surface runoff following grazing (Table 4.9), indicated by the plot studies (Table 4.9), is attributed to grazing, rather than to an enhancement of fertilizer P loss.

4.3.3.4 <u>Relative significance of soil, fertilizer phone</u><u>phorus and animals</u>. Because there was no effect of fertilizer P application on N losses in surface runoff (Section 4.3.3.2) and because the relative significance of soil and grazing animals on the transport of N in surface runoff has already been discussed (Section 4.3.3.3), this subsection is concerned with P. The application of fertilizer P and a grazing event with dairy cattle both resulted in an increased loss of both particulate and dissolved P and N in surface runoff. Comparison of the persistence of the effects of soil, fertilizer P and grazing cattle on the amounts of P forms in surface runoff can be achieved by using mean concentration data (obtained from total loading divided by total flow) for each event. Mean concentrations of DIP and particulate P in surface runoff from the undrained, fertilized (plot 6) and grazed (plot 3) plots showed different trends with time.

The grazing event resulted in increased mean concentrations of DIP and particulate P in runoff for a shorter period than did a fertilizer application (Fig. 4.7 and 4.8). Although the mean DIP concentration of surface runoff increased from approximately 0.2 to 1.8mg  $1^{-1}$  immediately following the grazing of plot 3, the mean DIP concentration returned to approximately 0.2mg  $1^{-1}$  after 25 days (Fig. 4.8). The mean particulate P concentration in surface runoff from the fertilized plot increased to a maximum value of 2.8mg  $1^{-1}$  immediately following fertilizer application and decreased much more gradually than that of DIP from the same plot (Fig. 4.7). Although the mean DIP concentration in runoff from the fertilized plot after 40 days following fertilizer application was approximately twice that from the control plot, the mean particulate P concentration in surface runoff from the same plot was



Fig. 4.7 Mean DIP concentrations in surface runoff for events before and after the addition of phosphate fertilizer, and before and after grazing.



Fig. 4.8 Mean particulate P concentrations in surface runoff for events before and after the addition of phosphate fertilizer, and before and after grazing.

five times greater than that from the control. Burke <u>et al</u>. (1974b) also noted that the DIP concentration in surface runoff decreased to negligible levels 40 days after fertilizer application (30kgP ha<sup>-1</sup>) to a clay soil on a  $10^{\circ}$  slope.

These results suggest that the addition of fertilizer P had a more sustained effect on the movement in surface runoff of particulate P than of DIP. This is not surprising given the generally high affinity of most soils for phosphate ions (Ryden <u>et al.</u>, 1973). With soils which have a greater ability to sorb P, than the rather low P-sorbing Tokomaru silt loam (discussed in Section 8.3.3), an even greater disparity between the losses of fertilizer P as particulate P, compared to DIP, could be expected.

It was shown earlier that two of the less-steep, undrained plots (plots 5 and 6) behaved remarkably similarly with respect to P and N losses prior to fertilizer application (Table 4.5). In addition, almost identical losses of fertilizer P were measured from plots 4 and 6 (Table 4.8). Consequently, it is reasonable to assume that similar losses of P and N would have occurred from plots 4 and 5 if the former had not been grazed during the study year. Data for plot 5 are used to give the values for soilderived P and N in Table 4.10, although as discussed previously, these would also include P and N from precipitation, plant leachates, and previous fertilizer and animal effects. As discussed in Section 4.3.3.1, the surface casts of earthworms also constitute a major potential source of P to surface-runoff waters. For convenience at this stage, earthworm casts are regarded as soil. The losses of P and N forms due to fertilizer P application and grazing cattle from plot 4 have, however, been established with some degree of reliability.

From the total annual loss of P and N forms, and sediment from plot 4 it is possible to calculate the proportion of annual P transported in surface runoff from soil, fertilizer P, and grazing cattle sources (Table 4.10). Although the annual loss of P and N forms in surface runoff from the fertilized, grazed, and undrained plot (plot 4) are presented in Table 4.10, the data are used in conjunction with data from the unfertilized, ungrazed, and undrained

Table 4.10 Contribution of soil, fertilizer P, and grazing animals to the annual amounts of P and N forms transported in surface runoff from a fertilized, grazed plot, and undrained plot (plot 4)

	Amount transported d			due to	Percent ported	Percentage of annual loss t ported due to		
Parameter	(kg ha <sup>-1</sup> y <sup>-1</sup> )	Soil	Fertilizer P kg ha <sup>-1</sup> y <sup>-1</sup>	Animals	Soil	Fertilizer F	Animals	
DIP	1.83	0.33	1.34	0.17	17	73	9	
TDP	2.38	0.48	1.44	0.47	20	бз	16	
Particulate P	2.03	0.37	1.35	0.27	17	63	17	
TP	4.41	0.85	2.79	0.74	19	63	17	
NO3	0.45	0.46	-0.03	0.02	102	-7	4	
TN	5.71	1.53	-0.10	4.11	27	-2	72	
Sediment	830	670	-41	220	80	-5	26	

plot (plot 5) to obtain estimates of the contribution of soil, fertilizer P, and animals to the annual loss of P and N forms in surface runoff (Table 4.10). As a result the total percentage contribution of soil, fertilizer P, and animals to the annual amounts of P and N forms transported will not equal 100.

It can be seen that the major losses of both dissolved and particulate P forms resulted from fertilizer P application. The annual losses of DIP and NO<sub>3</sub> attributable to grazing are lower than those from soil alone. Essentially all of the NO<sub>3</sub> in surface runoff was soil derived (102% Table 4.10), compared to grazing animals (4%), whereas approximately half the DIP was derived from animals (9%) compared to soil (17%). Grazing cattle, however, were responsible for 72% of the total annual loss of TN. It is apparent, therefore, that grazing caused greater losses of particulate N, compared to NO<sub>3</sub>, presumably due to the high sediment loss after grazing.

Although the amount of P deposited by animals as dung during one day may amount to between 0.05 and 0.2kgP ha<sup>-1</sup> (During, 1971), the losses in four weeks after a grazing event ranged from 13%(DIP) to 27% (particulate P), of the corresponding P forms lost during the four-month period after fertilizer P application.

It should be noted, however, that grazing animals were only present on the plots for 24h. During the winter months when surface runoff occurs, pasture growth is slow and consequently the grazing rotation is correspondingly longer. For example, in the period June to August the grazing rotation on the farm where the subcatchment is located is approximately 60 days, whereas in September it is approximately 30 days. Thus in the period June to September, when surface runoff occurs, two or at the most three, grazing events would be the normal practice. The data suggest, however, that although losses of P in surface runoff resulting from grazing animals are appreciable, they are lower than those resulting from fertilizer addition.

4.3.4 Prediction of the amounts of dissolved phosphorus transported in surface runoff using soil extraction data

Preliminary results indicated that because NO<sub>3</sub> concentrations in surface runoff from the ungrazed plots were consistently low during the sampling period, little predictive ability could be gained from soil extraction data for N.

The amounts of inorganic P extracted by 0.1M NaCl (subsequently referred to as "extractable soil P") from the upper 5cm of the four surface-runoff plots throughout the winter of 1975 are shown in Fig. 4.9a and 4.11a. There was little difference in the extractable soil P levels between the two unfertilized plots, and the amounts decreased gradually with time during the sampling period. Although the soil sampled at the 5-10cm depth contained lower amounts of extractable soil P, similar trends were observed for the undrained (Fig. 4.10a) and drained (Fig. 4.10b) plots. A similar decrease during winter in the amounts of P extracted from soils under established pasture has been reported by Caunders and Metson (1971). The application of superphosphate (50kgP ha<sup>-1</sup>) in late June resulted in a sharp increase in the amounts of extractable soil P. Although this fertilizer effect decreased with time, it was still apparent at the end of the sampling period, some four months following fertilizer application.

Similar mean DIP concentrations were obtained for surface runoff from the undrained and drained, unfertilized plots for all storms during the period when surface runoff occurred (Fig. 4.9b and 4.11b). In contrast, the mean DIP concentrations in surface runoff from both fertilized plots increased dramatically in the first runoff event after fertilizer application. Comparison of the mean DIP concentrations in surface runoff and the amounts of extractable P in surface soils from the fertilized plots indicated an obvious relationship between these two parameters. This relationship was investigated further using regression-correlation analysis, the results of which are presented in Fig. 4.12 and 4.13. For the purpose of this statistical analysis, extraction data for a particular soil sampling were paired with the data for the run-



Fig. 4.9 Seasonal variation in (a) amount of inorganic P extracted by 0.1<u>M</u> NaCl (extractable soil P) from the surface (0-5cm) of undrained, fertilized and unfertilized soils, and (b) mean DIP concentration of surface runoff from undrained, fertilized and unfertilized soils.


Fig. 4.10 Seasonal amounts of inorganic P extracted by 0.1<u>M</u> NaCl (extractable soil P) from the 5-10cm depth of (a) undrained and (b) drained fertilized and unfertilized soils.



Fig. 4.11 Seasonal variation in (a) amount of inorganic P extracted by 0.1<u>M</u> NaCl (extractable soil P) from the surface soil (0-5cm) of drained, fertilized and unfertilized soils, and (b) mean DIP concentration of surface runoff from undrained, fertilized and unfertilized soils.



Fig. 4.12 Relationship between mean DIP concentration in surface runoff and amount of inorganic P extracted by 0.1<u>M</u> NaCl (extractable soil P) from the surface (0-5cm) of drained and undrained, unfertilized soils.



Fig. 4.13 Relationship between mean DIP concentration in surface runoff and amount of inorganic P extracted by 0.1<u>M</u> NaCl (extractable soil P) from the surface (0-5cm) of drained and undrained, fertilized soils.

off event immediately following it.

Linear relationships with highly significant correlation coefficients were obtained for all plots. No significant relationships were obtained for extractable soil P at the 5-10cm depth for the drained situation (r = 0.56 and 0.55 for unfertilized and fertilized plots, respectively). Similarly, no significant correlation was obtained for the undrained, fertilized plot (r = 0.65). A highly significant correlation, however, was obtained for the unfertilized, undrained situation (r = 0.93, significant at the 1% level), where extractable soil P at the 5-10cm depth was similar to that for the 0-5cm sampling interval (Fig. 4.9a).

The regression lines for the undrained and drained plots (Fig. 4.12) sampled at O-5cm were identical in slope and differed only slightly in intercept. Surface runoff from the undrained, unfertilized plots, however, contained consistently higher mean DIP concentrations, for given levels of extractable soil P, than did that from the corresponding drained plot. It is possible that the desorption of P from the higher sediment concentrations present in surface runoff from the undrained site, shown earlier, would give rise to the greater DIP concentrations observed.

Regression lines of widely different slope were obtained for the fertilized plots (Fig. 4.13). The relationship obtained for the drained, fertilized plot is similar in both slope and intercept to those obtained for the unfertilized plots. This is the case in spite of the very much higher DIP concentrations in surface runoff and soil extracts. That this relationship applies over three types of land management involving large differences in both the quantities of surface runoff and its DIP concentration, suggests that it may be possible to predict DIP concentrations in surface runoff using soil extraction data.

The markedly different regression equation obtained for the fertilized, undrained plot is thought to have arisen from the soil sampling procedure used. In this procedure the O-5cm soil samples are passed through a 2-mm sieve, during which process the

herbage together with much of the upper 0.5-cm layer of soil is left behind. It is this surface layer, however, which may be expected to contribute most to the P carried in surface runoff. Therefore, in situations where the P status of this surface layer of soil and plant material differs markedly from the soil immediately below, poor prediction of the DIP concentration in surface runoff would be expected. Such a situation would arise on recently fertilized, undrained plots where a lower rate of infiltration than on the drained plots, would lead to a reduced incorporation of fertilizer P into the soil.

The results obtained in the present study appear to be substantially in agreement with those reported in a recent abstract (Calvert <u>et al.</u>, 1975) where, for an orchard soil, relationships were found between DIP losses in surface runoff and DIP concentrations in the soil solution of the surface soil. Romkens and Nelson (1974) also obtained a linear relationship between DIP concentrations in surface runoff and extractable inorganic P levels in a cultivated soil. The relationships obtained in the present study relate not only to a different system of land use, namely intensive grassland farming, but also point to the effects of drainage on the transport of DIP in surface runoff, as influenced by extractable P levels in the soil.

## 4.4 General Discussion

The data obtained from the runoff plots provide useful information relating to the amounts of P and N forms transported in surface runoff as a result of soil, fertilizer P, and animals. Up to now, this information has been lacking in New Zealand (Syers, 1974). Although the dangers of extrapolation from surface-runoff plot losses are recognised, the plots are useful in studying the relationship between the concentration and flux of P and N forms and flow, and in comparing the effects of different treatments on the losses of P and N in surface runoff.

It was apparent that marked fluctuations in the discharge rate of surface runoff occurred over short periods of time, whereas

the concentrations of P and N, during the same storm, remained relatively constant. In calculating the P, N, and sediment loads of surface runoff, therefore, flow data should be included more frequently than concentration data. After studying the concentration-flow relationships in runoff from an agricultural watershed in Ohio, Taylor et al. (1971) also concluded that flow was more important than concentration in determining nutrient loads.

The fact that appreciable errors in the loading estimates of P and N can occur when the sampling interval is increased, suggests that unreliable estimates of P and N loadings are obtained with infrequent sampling. For this reason, a maximum sampling interval of 15min was employed in the present study of surface runoff.

The greater losses of P in surface runoff obtained in the present study, than in corresponding overseas studies (Burwell <u>et</u> <u>al</u>., 1975; Timmons <u>et al</u>., 1973; Harms <u>et al</u>., 1974), may be attributed to the heavier applications of fertilizer P and the more intensive grazing of pasture in New Zealand. Consequently, the annual amounts of P transported in surface runoff from recently unfertilized and ungrazed soil were greater than that input in precipitation, whereas the same soil was conservative of N. A similar situation was also found by Burwell <u>et al</u>. (1975) for both P and N.

In approximately four months following the application of superphosphate to Tokomaru silt loam under pasture at a rate normally used on this soil, 2.9 and 6.7% of the added P was transported as DIP and TP, respectively, in surface runoff from an undrained  $13^{\circ}$  slope. These losses were greater than those measured by Nelson and Romkens (1971) (1.2% as DIP from fallow and tilled plots), Schuman <u>et al.</u> (1973b)(0.6 and 0.7% as DIP and TP, respectively, from pasture), and Benoit (1974) (1.6% as TP from pasture).

The artificial drainage of Tokomaru silt loam by mole and tile lines reduced the volume of surface runoff and amounts of P, N, and sediment transported in surface runoff from fertilized and unfertilized pasture. Although the fertilized, undrained  $6^{\circ}$ 

slope lost 12% less fertilizer P as TP than the fertilized, undrained  $13^{\circ}$  slope, a 67% reduction in the transport of TP was observed when the fertilized  $6^{\circ}$  slope was artificially drained. An even greater reduction in the transport of P from drained compared to undrained, fertilized soil was observed by Burke <u>et al</u>. (1974b). Consequently, artificial drainage could be an important method of controlling the losses of P and N from unfertilized and fertilized soils in certain areas, in addition to improving soil aeration and increasing infiltration rates.

In four weeks following a grazing event of 24h duration of pasture on Tokomaru silt loam at the normal stocking rate for the farm, significant losses of P, N, and sediment were observed. This was most marked for particulate P and N, where in the case of particulate P, the maximum mean concentration of approximately 3.0mg 1<sup>-1</sup> was observed in the surface-runoff event immediately following grazing, a value greater than the maximum mean particulate P concentration following fertilizer addition. The mean dissolved and particulate P concentration in surface-runoff events following grazing, however, decreased to the pregrazing levels more quickly than the corresponding concentrations following fertilizer applications, with the result that the loss of P attributed to fertilizer P application (73% DIP and 63% TP) was greater than the loss attributed to grazing (9% DIP and 17% TP). The substantial loss of TN following grazing (4.18kg ha y -1) was greater than that observed in surface runoff following fertilizer N application to a silt loam under pasture (2.36 kg ha y , Schuman et al., 1973a) in Ohio.

Although the data relate only to surface runoff in the catchment under study, they do indicate that significant amounts of P can be transported in surface runoff from P fertilized, undrained pasture and that N, and to a lesser extent P, can be transported from grazed, undrained pasture.

Because highly significant correlations were obtained between soil extraction data and P concentrations in surface runoff, soil extraction data appear to be useful in predicting DIP concentrations in surface runoff. This was the case for three types of land management, involving large differences in both the volumes and concentrations of DIP in surface runoff discharged.

The data obtained in the surface-runoff studies presented in this section are used in subsequent sections to determine the relative contribution of the runoff types to the amounts of water discharged and P and N forms transported in stream flow.

# SECTION 5

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## SOURCES AND TRANSPORT OF PHOSPHORUS AND NITROGEN IN ACCELERATED SUBSURFACE RUNOFF

### 5.1 Introduction

Artificial drainage systems increase the amounts and rates of infiltration and percolation, thus reducing the contact times between the soil solution and soil components capable of sorbing inorganic P from solution. Because of the large volumes of water discharged in drainage waters and the higher concentrations of both P and N, than in natural subsurface runoff, this runoff type, accelerated subsurface runoff, potentially may be of greater importance to the nutrient loadings of N an forms in an ephemeral stream. The work of Kohl <u>et al.</u> (1972) demonstrated that at peak NO<sub>3</sub> concentration in stream flow, a major proportion originated from tile drainage. In addition, the losses of P and N in tile drainage can increase due to the application of P (Bolton <u>ct al</u>., 1970) and N fertilizer (Nelson and Weaver, 1971; Zwerman <u>et al</u>., 1972), and animal wastes (Cooke and Williams, 1970).

The purpose of this part of the study relating to accelerated subsurface runoff was to (i) observe the relationships between flow, concentrations, and fluxes of P and N forms, (ii) determine the effect of sampling frequency on the estimates of the loading of P and N forms, (iii) estimate the annual losses of P and N forms and to investigate the effect of P and N fertilizer application, and grazing animals on the amounts of P and N forms transported, and (iv) evaluate the potential of using laboratory extraction data to predict the losses of DIP and NO<sub>3</sub> in this runoff type.

#### 5.2 Materials and Methods

Nitrogen was applied as urea (46% N) in early autumn (April, 1975) at a rate of 60kgN ha<sup>-1</sup> to the 14ha of drained land within the subcatchment. In June 1975, a second application of urea (60kgN ha<sup>-1</sup>) was made to the area drained by tile line A only (Fig. 3.1).

Although both drained areas received one application of fertilizer N, the area (area A) which received a second application in June is subsequently referred to as fertilized and ungrazed, although the area had been grazed previously. Area E which only received one application of fertilizer N in April but was grazed in August, is subsequently referred to as unfertilized and grazed.

Flow from the two tile lines, draining areas of 1.1ha (area A) and 0.8ha (area B) (Fig. 3.1) was collected at each outfall. The sampling interval did not exceed 1h and was as low as 5min for rapid hydrograph changes.

The relationship between extractable inorganic P and NO<sub>3</sub> in the soils and the DIP and NO<sub>3</sub> concentrations of tile drainage was investigated by collecting soil samples from the drained areas at 10-cm increments to a depth of 60cm, at monthly intervals for 6 months. Field-moist soil samples were passed through a 2-mm sieve and 2-g subsamples were shaken with 40ml of 0.1<u>M</u> NaCl for 40h at 23°C. After centrifugation at 15,000rpm for 10min at 23°C, and Millipore filtration, the extracts were analyzed for inorganic P and NO<sub>3</sub>. The results were corrected for soil moisture content and bulk density.

#### 5.3 Results and Discussion

5.3.1 Interrelationships between flow, concentration, and flux of phosphorus and nitrogen forms

Relationships between the concentration and flux of P and N forms and flow in accelerated subsurface runoff during a low-(event 1, Fig. 5.1a, b; 5.2a, b; 5.3), a medium- (event 2, Fig. 5.4a, b) and a high- (event 3, Fig. 5.5a, b) intensity storm event are presented. The events cover the range of storm intensities observed during two years of field monitoring. During the low-, medium-, and high-intensity events, an initial rapid rise in flow was associated with an increase in DIP concentration (Fig. 5.1a, 5.4a, 5.5a), which subsequently decreased rapidly and consistently with time before peak flow occurred. A secondary increase





Fig. 5.1 Variation in flow and (a) DIP concentration and flux, and (b) NO<sub>3</sub> concentration and flux for accelerated subsurface-runoff event 1.





Fig. 5.2 Variation in flow and (a) TP concentration and flux, and (b) TN concentration and flux for accelerated subsurfacerunoff event 1.



Fig. 5.3 Variation in flow and sediment concentration and flux for accelerated subsurface-runoff event 1.



Fig. 5.4 Variation in flow and (a) DIP and NO<sub>3</sub> concentrations, and (b) TP, TN, and sediment concentrations for accelerated subsurface-runoff event 2.

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Fig. 5.5 Variation in flow and (a) DIP and NO<sub>3</sub> concentrations, and (b) TP, TN, and sediment concentrations for accelerated subsurface-runoff event 3.

in flow was also associated with an increase in DIP concentration (Fig. 5.1a). These relationships resulted in a greater variation of DIP concentration within a storm event for accelerated subsurface runoff (0.03 to 0.24mg  $1^{-1}$ , Fig. 5.3a) compared to surface runoff (0.30 to 0.33mg  $1^{-1}$ ) in the same high-intensity storm (Fig. 4.4).

The concentration of  $NO_3$  increased with an initial increase in flow but decreased slightly at peak flow (Fig. 5.1b, 5.4a, 5.5a). As flow decreased, however,  $NO_3$  concentration gradually increased to the prepeak flow value. A subsequent increase in flow resulted in a decrease in  $NO_2$  concentration (Fig. 5.1b).

The concentration of TP increased with an initial increase in flow (Fig. 5.2a, 5.4b, 5.5b), reaching a maximum before peak flow. The similar variation in concentration with flow for both DIP and TP contrasts with the situation for surface runoff (Section 4.3.1). During a low-intensity event (Fig. 5.2b) the concentration of TN varied in a similar manner to that of TP. During events of greater flow, however, the TN concentration remained essentially constant throughout the event (Fig. 5.4b, 5.5b). With the exception of NO<sub>3</sub>, the concentration of P and N forms were significantly related to flow (Table 5.1) in event 2, which was considered typical of those studied.

Both the primary and secondary increase in TP concentration (Fig. 5.2) during the storm event were associated with an increase in sediment concentration (Fig. 5.3). For DIP this secondary increase in concentration may be due to the release of inorganic P to solution from the increased concentration of particulate P in the discharge. On the other hand, a secondary increase in flow was associated with a slight increase in TN and a decrease in  $\text{NO}_3$ . A small increase in particulate N may account for the variation in TN concentration, whereas the decrease in  $NO_{\chi}$  may be the result of dilution. Kohnke (1941) reported that nutrient concentrations were higher at the beginning of accelerated subsurface-runoff events than at peak discharge. It is probable that the decrease in DIP and  $\mathrm{NO}_3$  concentration at peak flow may be the result of dilution by increased water volume. Similar concentrationflow relationships to those observed in the present study have

Table 5.1 Squared standard partial regression coefficients for the standard regression of log<sub>10</sub> flux on log<sub>10</sub> concentration and log<sub>10</sub> flow, and correlation coefficients for concentration with flow for P and N forms in accelerated subsurface-runoff event 2

P or N form	Squared standard partial regression coefficients for		Correlation coefficient for concentration with flow
	Concentration	Flow	
DIP	°•12	0.52**	0.61**
TDP	0.04**	0.67**	0.73**
TP	0.19**	0.37**	0.75**
NO3	0.11**	0.84**	0.15
TN	0.13**	0.77**	0.44**

\* \*

Values significant at the 1% level.

also been reported by Hergert <u>et al.</u> (1974) for DIP, and by Baker <u>et al.</u> (1975) for  $NO_3$ .

Sediment concentration increased with increasing flow, reaching a maximum value before peak flow, with a subsequent gradual decrease in concentration (Fig. 5.3, 5.4b, 5.5b). A secondary increase in flow resulted in an increase in sediment concentration, which again peaked before flow (Fig. 5.3). The variation in sediment concentration in accelerated subsurface runoff was small compared to that found for surface runoff, as can be seen in the highintensity event presented. A range of 300 to 900mg  $1^{-1}$  in sediment concentration was observed in accelerated subsurface runoff (Fig. 5.5b) compared to a range of 400 to 2100mg  $1^{-1}$  in surface runoff (Fig. 4.4).

The fluxes of DIP, TDP, TP, NO<sub>3</sub>, and TN were significantly (1% level) more related to flow than to concentration (Table 5.1). The fluxes of P forms, however, were significantly less closely related to flow than to concentration, than was the case for surface runoff (Table 4.2).

The data reported indicate that flow was significantly more important than concentration in controlling the flux of P and N forms in accelerated subsurface runoff. Consequently, to obtain reliable estimates of P and N loadings, a greater emphasis must be placed on including more frequent flow measurements than concentration values. As flow measurements are normally recorded continuously, they should be included in loading calculations as frequently as is practicable.

### 5.3.2 Sampling frequency

Details of the procedure used to establish the frequency of sampling of accelerated subsurface runoff have been presented in Section 3.5.

The deviation in estimates of P and N loadings generally increased with an increase in the sampling interval for flow event 2, which was considered typical of the accelerated subsurface-

runoff events studied (Table 5.2). An increase in sampling interval from 8 to 60min did not result in large deviations in loading estimates. When a sample at peak flow was not included, however, deviations for the 60-min sampling interval were greater than those for the 120-min sampling interval. A sampling interval of 240min resulted in unacceptably high deviations in loading estimates (Table 5.2). In contrast to the data obtained for surface runoff (Table 4.3), a reduction in sampling interval from 8 to 30min had less effect on the deviation in P and N loading estimates for accelerated subsurface runoff (Table 5.2). This is attributed to the smaller variations in the rates of change in P and N concentrations with time (Fig. 5.1 to 5.5) than was observed for surface runoff (Fig. 4.1 to 4.4).

Because the variations in P and N concentrations were most rapid before peak flow (Fig. 5.1 to 5.5), tile drainage samples should be taken more frequently over this initial period, in order to decrease the deviations in loading estimates. Therefore, a maximum sampling time interval of 60min was employed before peak flow, and this was increased to 120min after peak flow, where the rate of change of concentration and flow became small and consistent with time. This approach to sampling is relevant to different storms because a definable point, peak flow, is used to determine changes in sampling frequency.

With the above sampling interval and by including flow measurements every 15min, deviations in the estimates of P and N loadings for the six events studied in detail were less than 15% (Table 5.3). Unless adequate attention is paid to the sampling time interval, however, appreciable errors in the estimates of the loadings of P forms in accelerated subsurface runoff can result.

As discussed for surface runoff, the data presented relate only to accelerated subsurface runoff in the watershed under study. With infrequent sampling (Bolton <u>et al.</u>, 1970; Carter <u>et al.</u>, 1971) and without estimates of the accuracy of the resulting nutrient loadings (Kolenbrander, 1969) the data reported for the nutrient loadings and their relative significance can be difficult to interpret.

Sampling	Number of		Parameter	Deviation in loading estimates (%)		
interval	Samples Replicates					
(min)				Mean	Confi	dence
					interva	1 (95%)
8	1 <sup>1</sup> +4					
30	36	4	DIP	-0.54	(-3.50,	2.40)
			TDP	-0.75	(-3.20,	1.73)
			TP	-0.61	(-1.09,	-0.13)
			NOz	-3.83	(-6.23,	-1.43)
			TN	-2.09	(-4.60,	C.42)
			Sediment	-0.46	(-2.36,	1.44)
60	18	4	DIP	0.11	(6.6,	6.8)
			TDP	-0.02	(-6.2,	6.2)
			TP	-0.34	(-8.6,	9.3)
			NOz	-3.21	(_8.64,	2.22)
			I'N	-1.56	(8.84,	5.72)
			Sediment	-4.76	(-9.23,	-0.29)
60 <sup>a</sup>	16	4	DIP	0.88	(-8.3,	9.2)
			TDP	1.00	(-6.6,	7.6)
			TP	0.22	(-11.3,	11.5)
			NOz	-3.34	(-20.1,	14.5)
			TN	2.62	(-21.6,	24.2)
			Sediment	-6.6	(-32.6,	19.4)
120	9	4	DIP	-1.01	(-8.3,	6.2)
			TDP	1.31	(-4.9,	7.5)
			TP	0.95	(-9.8,	11.7)
			NOz	-3.13	(-14.6,	7.3)
			TN	-3.48	(-17.1,	9.2)
			Sediment-	27.44	(-58.6,	5.8)

Table 5.2Deviation in loading estimates of P and N forms, andsediment in accelerated subsurface-runoff event 2

Sampling	Number of		Parameter	Deviati	on in loading
interval	Samples	Replicates		est	imates (%)
(min)				Mean	Confidence
					interval (95%)
240	4	4	DIP	-7.5	(-47, 32)
			TDP	-5.4	(-46, 35)
			TP	-2.9	(-38, 32)
			NOz	-2.5	(-18, 13)
			TN	-11.3	(-47, 24)
			Sediment	41.7	(-20, 103)

a Sample at peak flow not included.

Selected sampling	Parameter	Deviat	ion in loading	estimate (%)
interval (min)		Mean	Confidence in	iterval (95%)
60/ <sup>a</sup>	910	-4 7	(-10.2	0.75)
120	TDP	-1.6	(-11.6,	8.5)
	ΤP	-1.0	(- 5.1,	4.0)
	NO 3	-0.28	(-1.28,	0.72)
	TN	-0.30	(-2.22,	1.62)
	Sediment	-4.8	(-10.3,	0.7)

Table 5.3 Deviation in loading estimates of P and N forms, and sediment in six accelerated subsurface-runoff events studied

a Sampling interval of 60min prior to, and 120min following peak flow, with a sample at peak flow included.

Flow data at 15-min intervals used.

5.3.3 Transport of phosphorus and nitrogen forms in accelerated subsurface runoff as influenced by fertilizer nitrogen and animals

Variability studies conducted in the two months prior to the second application of urea and in the absence of grazing cattle, indicated little variation in the volume of water and in the concentration and amounts of dissolved P and sediment transported in accelerated subsurface runoff from both areas (Table 5.4). Slightly greater amounts of particulate P, NO<sub>3</sub>, and TN were transported in drainage from the smaller area (area B).

5.3.3.1 <u>Fertilizer nitrogen</u>. Because both areas behaved similarly in terms of the loss of P and N forms during the first two months of tile drainage discharge (May and June), it was possible to evaluate the effect of a second fertilizer N addition to area A and of the grazing of area B, on the transport of P and N in accelerated subsurface runoff by using one of the drained areas as a control.

Mean NO<sub>3</sub> (Fig. 5.6) and TN (Fig. 5.7) concentrations in each accelerated subsurface-runoff event during the year (calculated from the total loadings and total flow for each area) were highest in May when the drains first started flowing. The initial fertilizer N application of 60kgN ha<sup>-1</sup> was made in April, 1975. After the second urea application in early July, mean  $\mathrm{NO}_{z}$  and TN concentrations in the discharge increased, reaching a maximum value two weeks after the application (Fig. 5.6, 5.7). Subsequently, concentrations gradually and consistently decreased, returning to the pre-fertilizer concentrations approximately ten weeks after application. Libois (1968) also reported elevated NO3 concentrations in tile drainage for eight weeks following fertilizer N addition. The mean NOz and TN concentrations of accelerated subsurface runoff from the unfertilized area (area B), however, decreased gradually over the same period (Fig. 5.6, 5.7). In contrast, mean DIP and TDP concentrations in accelerated subsurface runoff from the fertilized area showed no response to urea application (Fig. 5.8), decreasing from maximum values in early autumn (April) and then remaining constant during the period from June

Table 5.4 Discharge of water and amounts of P and N forms, and sediment transported in accelerated subsurface runoff during four weeks after the second urea application to area A

	Area A		Arca	В
Parameter	Mean	Total	Mean	Total
COr	ncentration	loading	concentration	loading
(	(mgl <sup>-</sup> ) (gha	4 weeks)	(mg l <sup>-'</sup> ) (g	ha <sup>-1</sup> 4 weeks <sup>-1</sup> )
Discharge (m <sup>3</sup> ha <sup>-1</sup> 4 v	veeks <sup>-1</sup> ) 670		74	0
DIP	0.064	42.6	0.059	43.5
מתח	0.005	67 6	0.084	
	0.092	0.0	0.004	01.7
Particulate P	0.084	56.5	0.070	51.5
TP	0.177	118.9	0.152	112.6
NOz	4.2	2850	2.2	1660
TN	4.7	3140	2.3	1750
Sediment (kg ha <sup>-1</sup> 4 w	130 veeks <sup>-1</sup> )	90	140	101



Fig. 5.6 Mean NO<sub>3</sub> concentration in accelerated subsurface runoff before and after the second urea application and grazing (dashed line, area A; solid line, area B).



Fig. 5.7 Mean TN concentration in accelerated subsurface runoff before and after the second urea application and grazing (dashed line, area A; solid line, area B).



Fig. 5.8 Mean DIP concentration in accelerated subsurface runoff before and after the second urea application and grazing (dashed line, area A; solid line, area B).

to September.

The amounts of P and N forms transported in tile drainage during July after the second urea application are presented in Table 5.4. The amounts of NO<sub>2</sub> and TN transported from the fertilized area (2.85 and 3.14kg ha<sup>-1</sup> 4 weeks<sup>-1</sup>, respectively, area A, Table 5.4) were greater than those transported from the unfertilized area (1.66 and 1.75kg Ma<sup>-1</sup> 4 weeks<sup>-1</sup>, respectively, area B, Table 5.4). The increase in loss of NO<sub>2</sub> and TN from the fertilized area in 4 weeks (1.2 and 1.4kg ha<sup>-1</sup> 4 weeks<sup>-1</sup>, respectively) accounted for 2.0 and 2.3%, respectively, of the applied fertilizer N. The major proportion (87%) of the increased loss in N after fertilizer application was transported as NO<sub>3</sub>. The amounts of both particulate and dissolved P transported in accelerated subsurface runoff from both areas were similar.

5.3.3.2 <u>Animals</u>. The unfertilized area (area E) was grazed by 100 dairy cattle at a stocking rate of 300 cattle ha<sup>-1</sup> at the beginning of August, for 12h as part of the normal grazing plan for the farm. Because both areas lost very similar amounts of P forms in the three months prior to grazing (Table 5.4, 5.5), it is possible to evaluate the effect of grazing on P forms transported in tile drainage by difference between the two areas.

A rapid increase in the mean concentrations of NO<sub>2</sub>, TN, DIP, and particulate P in accelerated subsurface runoff (Fig. 5.6, 5.7, 5.8, and 5.9, respectively) was observed after the grazing event. The increase in NO<sub>3</sub> and TN concentration (12.0 and 16.0mg 1<sup>-1</sup>, respectively), however, was not as great as the increase in DIP and particulate P concentration (C.23 and O.70mg 1<sup>-1</sup>, respectively). Whereas the N concentrations remained elevated for three`weeks, the P concentrations started to decrease only one week after grazing, as a result of the low mobility of P in accelerated subsurface runoff. At this time, the concentrations of NO<sub>3</sub> and TN in discharge from the fertilized area (area A) had only just reached the prefertilizer levels, a period of ten weeks after fertilizer application (Fig. 5.6, 5.7). It is apparent, therefore, that the grazing event had a less sustain effect on NO<sub>3</sub> and TN concentrations in accelerated subsurface runoff than the application of urea.

Table 5.5 Discharge of water and amounts of P and N forms, and sediment transported in accelerated subsurface runoff during May and June prior to the second urea application and grazing

Area A			Area 1	3
Parameter co	Mean Incentratio (mg l <sup>-1</sup> )	Total n loading (g ha <sup>-1</sup> 4 weeks <sup>-1</sup> )	Mean concentration (mg 1 <sup>-1</sup> ) (g	Total loading ha <sup>-1</sup> 4 weeks <sup>-1</sup> )
Discharge (m <sup>3</sup> ha <sup>-1</sup> 4	weeks <sup>-1</sup> )	110	100	)
DIP	0.056	6.2	0.057	5.7
TDP	0.068	7.5	0.072	7.2
Particulate P	0.015	1.6	0.024	2.4
ΤP	0.082	9.1	0.097	9•7
NOz	10.6	1170	12.3	1230
'I'N	12.7	1410	14.7	1470
Sediment (kg ha <sup>-1</sup> 4	130 weeks <sup>-1</sup> )	28	120	25



Fig. 5.9 Mean particulate P concentration in accelerated subsurface runoff before and after the second urea application and grazing (dashed line, area A; solid line, area B).

Although the major proportion of P transported in tile drainage was in the dissolved form (80% as TDP, Table 5.6), grazing also resulted in a two-fold increase in the loss of particulate  $P(46.9g ha^{-1} 4 weeks^{-1}, Table 5.6)$  compared to DIP (23.1g ha^{-1}) 4 weeks<sup>-1</sup>, Table 5.6). The greater effect of grazing on particulate P in discharge was associated with a 50% increase in the amount of sediment carried, although the volume of water was reduced (Table 5.6). This is probably the result of the destruction of arainage channels in the soil profile and surface "pugging", which resulted in a reduced infiltration capacity of the soil. At this time, surface runoff was observed to occur from the gently sloping land  $(0-1^{\circ} \text{ slope})$ , a situation which was not apparent prior to the grazing event. As a result, accelerated subsurface flow increased more gradually from the grazed area during the first drainage event after grazing, than from the ungrazed area (Fig. 5.10b). In addition, peak flow from the grazed area (area B, Fig. 5.10b) was very much less well-defined in contrast to drainage from the ungrazed area (area A, Fig. 5.10b), and for both areas during the pre-grazing drainage event (Fig. 5.10a). The accelerated subsurface-flow hydrograph for the grazed area was still dissimilar to the flow hydrographs for runoff events from the pre-grazed and ungrazed areas three weeks after grazing (Fig. 5.10c).

The volume of water and amounts of P and N forms, and sediment transported in accelerated subsurface runoff in four weeks after the grazing of area B were significantly greater than those transported from the ungrazed area A (Table 5.6).

Because the losses of N forms from area A (Table 5.6) include fertilizer losses, it is not possible to quantitatively evaluate the effect of grazing on the transport of N. The increased loss of NO<sub>3</sub> from the grazed compared to the ungrazed area (2.1kg ha<sup>-1</sup> 4 weeks<sup>-1</sup>, Table 5.6) in four weeks is, however, greater than that lost following fertilizer application (1.2kg ha<sup>-1</sup> 4 weeks<sup>-1</sup>, Table 5.4), in the same time period. The data in the present study indicate that in four weeks, larger amounts cf NO<sub>3</sub> and TN may be transported in accelerated subsurface runoff after grazing than after urea application. Because urea application has a more sustained effect on the concentration of N in tile drainage,

Table 5.6 Discharge of water and amounts of P and N forms, and sediment transported in accelerated subsurface runoff during four weeks following grazing of area B

	A	rea A	Area .	В	
Parameter	Mean	Total	Mean	·Total	
C 0 )	ncentratio (mg 1 <sup>-1</sup> )	on loading (g ha <sup>-1</sup> 4 weeks <sup>-1</sup> )	concentration (mg l <sup>-1</sup> ) (g	loading ha <sup>-1</sup> 4 weeks <sup>-1</sup> )	
Discharge (m <sup>3</sup> ha <sup>-1</sup> 4	weeks <sup>-1</sup> )	7.	750		
DIP	0.049	44.6	0.090	67.7	
TDP	0.074	66.8	0.118	88.8	
Particulate P	0.053	47.5	0.126	94.4	
ΥΡ	0.124	112.5	0.244	183.2	
NO3	4.0	3590	7.5	5650	
ΤN	5.2	4700	9.7	7330	
Sediment (kg ha <sup>-1</sup> 4 y	110 weeks <sup>-1</sup> )	100	200	 151	



Fig. 5.10 Water discharge rate from an ungrazed (area A) and grazed (area B) tiled area in a flow event (a) 1 week before grazing, (b) 1 week after grazing, and (c) 3 weeks after grazing.

the loss of N from urea in ten weeks may be greater than that lost as a result of grazing.

5.3.3.3 <u>Annual amounts of phosphorus and nitrogen</u> <u>transported</u>. Due to the lack of adequate controls, the amounts of P and N forms transported in accelerated subsurface runoff from unfertilized and ungraph of Tokomaru silt loam could not be measured. Consequently, the relative significance of soil, fertilizer N, and grazing animals as sources of the forms of P and N transported in accelerated subsurface runoff cannot be calculated. The mean concentrations, the range of observed concentrations, and the annual amounts of P and N forms transported in accelerated subsurface runoff from both areas are given in Table 5.7.

The mean concentrations of N forms in accelerated subsurface runoff were much greater than those of P forms, although the mean concentrations of dissolved forms of P and N were greater than those of particulate forms. The mean concentration of TDP was slightly greater than that of particulate P (0.083 and 0.066mg 1<sup>-1</sup>, area A, Table 5.7), whereas the mean concentration of NO<sub>3</sub> constituted 83% of TN. The average range in the concentration of P forms in tile drainage during 1975 (Table 5.7), was much greater than the range observed during surface-runoff events during the same year (Fig. 4.1 to 4.4).

The concentrations of DIP, TP, and NO<sub>2</sub> observed in accelerated subsurface runoff in the present study, were similar to those obtained in overseas studies. Baker <u>et al.</u> (1975) found mean concentrations of 0.038, 0.182, and 10mg 1<sup>-1</sup> for DIP, TP, and NO<sub>2</sub>, respectively, from a silt loam receiving 122kgN ha<sup>-1</sup> every two years. Also Erickson and Ellis (1971) measured a range in DIP concentration of 0.01 to 0.3mg 1<sup>-1</sup> and in NO<sub>3</sub> concentration of 0.2 to 11mg 1<sup>-1</sup>, in tile drainage from agricultural land in Michigan. In a study of accelerated subsurface runoff from a silt loam, to which different amounts of P and N fertilizer had been applied, Zwerman <u>et al.</u> (1972) obtained increased NO<sub>3</sub> concentrations associated with higher rates of fertilizer application, whereas DIP concentration was less affected.
Table 5.7 Annual discharge of water and amounts of P and N forms, and sediment transported in accelerated subsurface runoff from fertilized area (A) and fertilized and grazed area (B)

		Area A			Area B	
Parameter C	Concentr (mg l alculated mean	ration Lo -1) (kg h d Observed range	ading 1a <sup>-1</sup> y <sup>-1</sup> )	Concentr (mg 1 <sup>-</sup> Calculated mean	ation Lo 1) (kg Observed range	bading ha <sup>-1</sup> y <sup>-1</sup> )
Discharge (m <sup>3</sup> ha <sup>-1</sup> y	-1)	1820			1900	
DIP	0.058	0.560-0.016	0.11	0.072	0.353-0.011	0.13
TDP	0.083	0.580-0.026	0.16	0.097	0.404-0.025	0.18
Particulat P	e 0.066	0.650-0.001	0.13	0.094	1.049-0.007	0.17
TP	0.135	1.007-0.037	0.26	0.173	1.363-0.033	0.32
NO3	5.57	49.2 - 1.1	10.6	6.52	26.4 - 1.0	11.9
TN	6.68	56.3 - 1.4	12.7	9.50	32 <b>.</b> 1 - 1.3	14.0
Sediment	157	926 - 26	283	163	983 - 23	297

The annual amounts of P and N forms, and sediment transported in accelerated subsurface runoff from the grazed area (area B), receiving only one fertilizer N application, were slightly greater than those transported from the ungrazed and fertilized area (area A, Table 5.7). The amounts of N forms lost from both areas, however, were greater than the amounts of P forms. Of the TN transported,  $NO_3$  accounted for 80%, whereas in the case of P 61% was transported in the dissolved form. This is in contrast to surface runoff, where there was a greater transport of P and N in the particulate, compared to the dissolved form. In addition, the amounts of P forms transported were greater than those of the N forms.

The basic differences between the transport of P and N in accelerated subsurface runoff are a result of the differing P and N soil retention capacities. Whereas soluble P is readily sorbed by soil components, because NO<sub>z</sub> is a non-specifically sorbed anion, it moves freely by diffusion and mass transport with soil water movement (Harmsen and Kolenbrander, 1965) through the soil profile. The nitrification of N derived from soil organic matter and urea fertilizer may be enhanced in a drained soil during winter, where there would be less chance of reducing conditions occurring, resulting in a potentially large pool of  $\mathrm{NO}_{\mathrm{Z}}$  accumulating in the soil. Furthermore, the fixation of  $NH_{L}$  by vermiculite, which is the dominant clay mineral in Tokomaru silt loam (Pollok, 1975), would also favour the predominance of NOz in accelerated subsurface runoff. Low to negligible amounts of  $\mathrm{NH}_4$  and high  $\mathrm{NO}_3$  have widely been observed in accelerated subsurface runoff (Willrich, 1969; Erickson and Ellis, 1971; Hanway and Laflen, 1974).

The annual losses of DIP and TP (0.11 and 0.26kg ha<sup>-1</sup> y<sup>-1</sup>, respectively, Table 5.7) in accelerated subsurface runoff from the ungrazed, fertilized area (area A) were greater than those found by Baker <u>et al.</u> (1975) (0.03 and 0.18kg ha<sup>-1</sup> y<sup>-1</sup>, of DIP and TP, respectively) in accelerated subsurface runoff from an ungrazed, N fertilized silt loam. In contrast, slightly greater losses of DIP (0.18kg ha<sup>-1</sup> y<sup>-1</sup>) in accelerated subsurface runoff from a clay loam also receiving no fertilizer P were measured by Bolton <u>et al.</u> (1970).

Losses of NO<sub>3</sub> from the fertilized, ungrazed (12.7kg ha<sup>-1</sup> y<sup>-1</sup>, area A) and from the fertilized, grazed (14.0kg ha<sup>-1</sup> y<sup>-1</sup>, area B) obtained in the present study were less than the average annual loss over four years of NO<sub>3</sub> (31kg ha<sup>-1</sup> y<sup>-1</sup>) in a study conducted by Baker <u>et al</u>. (1975) on a silt loam receiving 112kgN ha<sup>-1</sup> of fertilizer every two years. In contrast, the losses of NO<sub>3</sub> (13.1kg ha<sup>-1</sup> y<sup>-1</sup>) in tile drainage after a much heavier application of 225kgN ha<sup>-1</sup> to a silt clay in California, obtained by Johnston <u>et al</u>. (1965), were similar to those in the present study (Table 5.7).

5.3.4 Prediction of dissolved phosphorus and nitrogen losses in accelerated subsurface runoff using soil extraction data

The amounts of inorganic P extracted by O.1M NaCl from soil samples collected from the grazed and ungrazed areas decreased gradually with sample depth. Maximum values were obtained from the O-10cm depth and minimum values from the 50-60cm depth. (Fig. 5.11 and 5.12). The amounts of extractable soil P in the ungrazed area (Fig. 5.11) were slightly higher at all depths in autumn (May) and gradually decreased over the sampling period, to reach a minimum in September when soil temperatures were low and soil moisture content high. Extractable soil P from area B (Fig. 5.12) decreased similarly until grazing occurred in August, when a rise in extractable soil P was observed in the top 20cm (Fig. 5.12). Blackmore (1966) also observed little seasonal variation in extractable soil P, except when dung or fertilizer P were applied, resulting in an increase in the extractable soil P levels in both the surface and subsurface soil. Particularly significant is the fact that similar trends in the mean DIP concentration of accelerated subsurface runoff were obtained (Fig. 5.8) during the same period.

The amounts of  $NO_3$  extracted by  $O.1\underline{M}$  NaCl (subsequently referred to as extractable soil  $NO_3$ ) decreased with sample depth in both areas, as was the case for extractable soil P (Fig. 5.13 and 5.14). The amounts of extractable soil  $NO_3$  were greatest in May, after urea application, but gradually decreased at all depths until a second urea application was made in July. A soil sampling one



Fig. 5.11 Amounts of extractable soil P at 10-cm intervals in the soil profile from area A during the period when accelerated subsurface runoff occurred, and urea was applied in early July.



Fig. 5.12 Amounts of extractable soil P at 10-cm intervals in the soil profile from area B during the period when accelerated subsurface runoff occurred, and the area was grazed in early August.



Fig. 5.13 Amounts of extractable soil NO<sub>3</sub> at 10-cm intervals in the soil profile from area A during the period when accelerated subsurface runoff occurred, and urea was applied in early July.



Fig. 5.14 Amounts of extractable soil NO<sub>3</sub> at 10-cm intervals in the soil profile from area B during the period when accelerated subsurface runoff occurred, and the area was grazed in early August.

week after the application of urea showed increased extractable soil NO<sub>3</sub> levels at all depths in the profile, with the maximum concentration at the 10-20cm depth (Fig. 5.13). One month later the amounts of extractable soil NO<sub>3</sub> at the 10-20cm depth had decreased from 48 to 9.0kg ha<sup>-1</sup> 10cm<sup>-1</sup> and the profile distribution of extractable soil NO<sub>3</sub> was similar to that before the second fertilizer application. Subsequently, a gradual decrease in extractable soil NO<sub>3</sub> levels occurred until October. Extractable soil NO<sub>3</sub> levels remained fairly constant during June and July, but a grazing event in August resulted in an increase in extractable soil NO<sub>3</sub> in the surface 20cm (Fig. 5.14).

Extractable soil  $\mathrm{NO}_{\mathsf{X}}$  levels obtained one month after the first urea application in April were similar to the levels one month after the second application in July (Fig. 5.13). The maximum NO<sub>z</sub> concentration in tile drainage from the fertilized area (area A), however, was greater in May (20.6mg 1<sup>-1</sup>, Fig. 5.6), one month after the first application of urea, than the maximum  $NO_z$  concentration measured after the second application of urea (16.6mg 1<sup>-1</sup>, Fig. 5.6). This suggests a more rapid hydrolysis and nitrification of urea, and a greater mobility of  $NO_z$  within the soil profile in May than in July. In April, soil temperature is higher and moisture content at an optimum for hydrolysis and nitrification within the soil because field capacity has not yet been reached. In July, however, soil temperatures are lower and the degree of aeration decreased because of increasing water content. Thus, the conversion of  $NH_4$  to  $NO_7$  would occur at a much slower rate than during April. Consequently, the NOz concentration of tile drainage is expected to be greater after an application of urea in April than in July.

Similar variations in the mean NO<sub>3</sub> concentration of tile drainage events (Fig. 5.6) and extractable soil NO<sub>3</sub> (Fig. 5.13, 5.14) were observed. It is apparent, therefore, that a relationship exists between extractable soil P and N and the amounts of P and N discharged in accelerated subsurface runoff. This relationship was investigated further using regression correlation analysis.

The concentration of DIP in tile drainage from established pasture varies considerably during a particular flow event (Fig.

5.1 to 5.5). Consequently, it is difficult to establish a single parameter to describe the transport of DIP in accelerated subsurface runoff. The two parameters selected for this purpose were (i) mean DIP concentration, calculated from total loading and total flow data for each event, and (ii) the total loading of DIP transported during an 8-h period of maximum hydrograph change during each event. In contrast to surface runoff, soil extraction data (Table 5.8, 5.9) were not significantly correlated (Table 5.10) with mean DIP concentrations in tile drainage. Total loadings of DIP, however, were better correlated with the amounts of extractable P in the subsoil from both areas, particularly at 40-50cm, which was the depth of the mole channels. The fact that loadings rather than concentrations of DIP in tile drainage were so well correlated with extractable soil P levels, suggests that extraction with 0.1M NaCl removes a pool of readilyleachable inorganic P which is normally exhausted during a flow event, but replenished between events. The source of such a pool of inorganic P is not clear. One possibility is the mineralisation of soluble organic matter leached down the profile during the preceding rainfall event.

Correlation coefficients for the relationship between the amounts of extractable soil  $NO_3$  (Table 5.11, 5.12) at various depths in the profile and the mean concentration and total loading of  $NO_3$  in accelerated subsurface runoff are presented in Table 5.13. As was the case for DIP, mean  $NO_3$  concentrations in the discharge were not significantly correlated with the amounts of extractable  $NO_3$  at all depths, for both areas. Total loadings of  $NO_3$ , however, were more closely correlated with extractable soil  $NO_3$  data than was the case for DIP, with highly significant correlations again being obtained at the 40-50cm depth. The correlation coefficients obtained for the grazed, unfertilized area (area B), were generally higher than those for the ungrazed, fertilized area (area A).

The loadings of P and N in accelerated subsurface runoff showed the closest correlations with extractable soil P and N at the 40-50cm depth. This is to be expected because the mole channels are situated at this depth and would be the final point of contact between the soil and percolating soil water entering

Table 5.8 Amounts of extractable soil P at various depths in the profile throughout the year (1975) and mean DIP concentration and total DIP loading in accelerated subsurface runoff in storm events immediately following soil sampling of area A

Soil			Sampling	date						
depth										
(cm)	23.5.75	13.6.75	8.7.75	4.8.75	2.9.75	6.10.75				
			Extractable soil	P (kg ha <sup>-1</sup> )						
0-10	1.61	2.67	2.79	1.48	1.19	2.04				
10-20	0.68	1.09	1.53	0.69	0.55	0.45				
20-30	0.29	0.60	0.69	0.46	0.18	0.27				
30-40	0.26	0.43	0.69	0.34	0.16	0.28				
40-50	-	0.33	0.55	0.20	0.57	0.14				
50-60	-	0.40	0.33	0.30	0.14	0.12				
Total pr	ofile 2.84	5.52	6.52	3.47	2.79	3.23				
0-00		Mean DIP Concentration (mg 1 <sup>-1</sup> )								
	0.10	0.07	0.09	0.06	0.02	0.12				
			Total DIP Los	ading (g ha <sup>-1</sup> )						
	1.30	2.62	l <sub>+</sub> • 52	2.43	6.84	0.31				

Table 5.9 Amounts of extractable soil P at various depths in the profile throughout the year (1975) and mean DIP concentration and total DIP loading in accelerated subsurface runoff in storm events immediately following soil sampling of area B

Soil				Sampling	date			
Depth (cm)	23.9.74	16.10.74	23.5.75	13.6.75	8.7.75	4.8.75	2.9.75	6.10.75
			Ext	ractable soil	L P (kg ha	1)		
0-10	0.60	1.16	2.79	1.48	2.59	2.07	1.49	1.25
10-20	0.33	0.48	0.95	0.92	1.08	0.74	0.66	0.57
20-30	0.11	0.70	0.55	0.60	0.69	0.38	0.42	0.22
30-40	0.09	0.21	0.27	0.37	0.56	0.40	0.29	0.18
40-50	0.06	0.59	_	0.42	0.43	0.19	0.08	0.12
50-60	0.04	0.11	-	C.32	0.04	0.23	0.10	0.20
Total pro	file 1.23	3.25	-	4.11	5.39	3.81	3.04	2.34
0-60			Meas	n DIP Concent	tration (mg	1 <sup>-1</sup> )		
	0.062	0.149	0.145	0.051	0.033	0.113	0.037	0.086
				Total DIP Lo	bading (g ha	a <sup>-1</sup> )		
	0.18	4.06	1.76	3.14	2.76	2.69	0.30	1.30

Table 5.10 Relationship between mean DIP concentration and DIP loading of accelerated subsurface runoff and amounts of extractable soil P at different depths expressed as correlation coefficients

		Relationship between							
Soil Depth (cm)	Mean DIP con discharge and soil	centration of d extractable l P	DIP loading of discharge and extractable soil P						
	Area A	Area B	Area A Area B						
0-10	0.465	0.154	0.172 0.276						
10-20	0.082	-0.178	0.263 0.358						
20-30	0.164	0.156	0.010 0.780*						
30-40	0.200	-0.428	0.130 0.461						
40-50	0.656	0.331	0.951 0.920						
50-60	-0.225	0.171	0.041 0.356						
Total prof	ile 0.147	0.272	0.161 0.403						

Significant at 5% level.

\*\* Significant at 1% level.

Table 5.11 Amounts of extractable soil NO<sub>3</sub> at various depths in the profile throughout the year (1975) and mean NO<sub>3</sub> concentration and total NO<sub>3</sub> loading in accelerated subsurface runoff in storm events immediately following soil sampling of area A

	-#II.	ine a					
Soil		ALC TOPS	Sampling	data		2. 2.	
Depth (cm)	28.5.75	13.6.75	8.7.75	4.8.75	2.9.75	6.10.75	
			Ext <b>ractable so</b> il	1 NO <sub>3</sub> (kg ha <sup>-1</sup> )			
0 - 10	7.56	3.16	12.22	6.57	5.86	3.98	
10 - 20	4.62	2.19	23.53	4.87	5.87	1.61	
20 - 30	2.97	1.82	16.15	4.74	2.07	1.68	
30 - 40	2.68	2.24	15.55	1.88	4.00	1.60	
40 - 50	-	1.83	13.94	0.86	1.36	1.09	
50 - 60	- # ~	2.27	9.58	1.12	3.38	0.79	
Cotal profi	ile					A. Francisco	
0 - 60	17.83	13.51	90.97	20.04	22.54	10.75	
		:	Mean NO <sub>3</sub> concen	tration (mg $L^{-1}$	)	1	
Egt.	20.00	14.00	12.30	8.90	1.11	1.38	* <sup>53</sup>
			Total NO <sub>3</sub> Loadi	ng (g ha <sup><math>-1</math></sup> )			
	916	884	1324	313	675	630	

The second

Table 5.12 Amounts of extractable soil NO<sub>3</sub> at various depths in the profile throughout the year (1975) and mean NO<sub>3</sub> concentration and total NO<sub>3</sub> loading in accelerated subsurface runoff in storm events immediately following soil sampling of area B

Soil	Sampling date								
Depth (cm)	Cem) 23.5.75 13	13.6.75	8.7.75	4.8.75	2.9.75	6.10.75			
			Extractable so:	1 NO <sub>z</sub> (kg ha <sup>-1</sup> )					
0-10	9.15	7.59	9.17	13.73	10.60	5.18			
10-20	7.82	4.91	8.58	9.50	6.59	5.37			
20-30	4.89	2.66	5.87	6.15	6.11	3.91			
30-40	4.00	3.20	4.32	6.08	3.52	3.84			
40-50	-	10.08	3.88	8.53	3.57	3.72			
50-60	-	4.18	2.88	7.78	1.44	2.45			
Total pr	ofile								
0-60	25.86	32.62	34.70	51.77	32.43	24.47			
			Mean NOz concer	ntration (mg 1 <sup>-1</sup>	)				
	22.08	7.20	6.70	7.10	1.70	1.50			
			Total NO <sub>2</sub> 1	pading (g ha <sup>-1</sup> )					
	222	363	102	317	32	86			

	as correlati	on coefficients		L.				
	Relationship between							
Soil N Depth ( (cm)	Mean NO <sub>3</sub> con discharge an soil 1	centration of d extractable NO <sub>3</sub>	NO <sub>3</sub> loading of dischar and extractable soil <sup>NO</sup> 3					
	Area A	Area B	Area A	Area B				
0-10	0.317	0.129	0.608	0.257				
10-20	0.178	0.326	0.724	0.066				
20-30	0.227	0.095	0.670	0.481				
30-40	0.154	0.070	0.789	0.282				
40-50	0.123	-0.424	0.868*	0.988**				
50-60	-0.003	-0.335	0.879**	0.792*				
Total profil	e 0.171	-0.161	0.734	0.446				

Table 5.13 Relationship between mean  $NO_3$  concentration and  $NC_3$ loading of accelerated subsurface runoff and amounts of extractable soil  $NO_3$  at different depths expressed as correlation coefficients

Significant at 5% level.

\*\* Significant at 1% level.

#### 5.4 General Discussion

Although large areas of productive farmland in New Zealand are artificially drained, there is no published information on the amounts and forms of P and N transported in accelerated subsurface runoff in New Zealand. The data obtained from the present study using "field-size" drainage areas, indicate that significant amounts of P and N may be transported in this runoff type.

Marked fluctuations over short periods of time were obtained for the discharge rate of tile drainage but these were not as rapid as those observed for surface runoff. The initial rise in the discharge rate of accelerated subsurface runoff, resulting in a corresponding increase in the concentration of discolved and particulate P and N, contrasted with the concentration-flow relationships obtained for surface runoff. Similar fluctuations in the concentration of P and N with changes in the discharge rate of accelerated subsurface runoff were also observed by Kohnke (1941), Hergert et al. (1974), and Baker et al. (1975).

It was apparent that flow was significantly more important than concentration in determining the flux of P and N forms in accelerated subsurface runoff. Thus, in the calculation of P, N, and sediment loads, flow data should be included more frequently than concentration data. As the changes in the discharge rate of accelerated subsurface runoff were not as rapid as those in surface runoff, a lower intensity of sampling than that used for surface runoff gave a similar accuracy for the P, N, and sediment loadings during accelerated subsurface runoff.

The fact that the concentration and amounts of N transported in accelerated subsurface runoff were appreciably greater than those of P, with NO<sub>3</sub> constituting the major proportion of N transported, is consistent with the data obtained in many studies (Willrich, 1969; Erickson and Ellis, 1971; Zwerman <u>et al.</u>, 1972; Burwell <u>et al.</u>, 1974; Hanway and Laflen, 1974). This reflects the differing mobility of P (Ryden <u>et al.</u>, 1973) and N (Brown and Bartholomew, 1962; Harmsen and Kolenbrander, 1965) within the soil.

Similar concentrations of P and N forms in accelerated subsurface runoff were observed in the present study to those reported in overseas studies (Erickson and Ellis, 1971; Zwerman et al., 1972; Baker et al., 1975). Variations in the annual volume of water flowing through the soil to the tile line, and the path by which the water reaches the tile line, appear to result in large variations in the amounts of P and N transported annually from area to area (Hergert et al., 1974). Furthermore, variations in the amounts of P and N transported in accelerated subsurface runoff from soils of similar management, may be due to differences in soil texture and the P and N status of the soil. Losses of both P and N by leaching have been shown to be greater for sandy soils which have a lower P and water retention capacity, than soils with a high clay content (Kolenbrander, 1969; Olsen and Watanabe, 1970). The factors involved in P and N losses in tile drainage are complex and it is, therefore, not surprising that the amounts of P and N transported in this runoff type vary in different studies, and show no relationship to the amounts of P and N applied through fertilizer and grazing cattle (Johnston et al., 1965; Bolton et al., 1970; Baker et al., 1975).

The proportion of fertilizer N transported as NO<sub>3</sub> (2%) in tile drainage following an application in July was greater than that measured in similar studies overseas. In one year Bolton <u>et al</u>. (1970) observed a 0.6% loss of fertilizer N in accelerated subsurface runoff from a clay loam under continuous bluegrass. Meek <u>et al</u>. (1969) also reported that low amounts of NO<sub>2</sub> were discharged from tile lines in a heavily fertilized (280kgN ha<sup>-1</sup>) cotton field in California, where the NO<sub>3</sub> leached amounted to only 1.5% of the N applied.

The data obtained in the present study suggest that as well as fertilizer applications, grazing animals must be regarded as a significant potential source of P and N to accelerated subsurface runoff. In addition, grazing animals may reduce the efficiency of the drainage system as a result of surface pugging. Less significant correlations were obtained between the concentrations and amounts of DIP and NO<sub>3</sub> transported in accelerated subsurface runoff and the amounts of extractable P and NO<sub>3</sub>, respectively, in the subsoil, than between the corresponding relationships for surface runoff and surface soil. Although significant correlations were obtained between the amount of NO<sub>3</sub> transported in accelerated subsurface runoff and extractable soil NO<sub>3</sub> at the depth at which mole channels were situated, the otherwise insignificant correlations were probably due to a more complex, and longer period of interaction between soluble P and N, and soil material than is the case for surface runoff. High correlations between the concentration of P and N in tile drainage and subsoil, however, were obtained by Hanway and Laflen (1974) and Calvert et al. (1975).

Although it is recognised that the data obtained relate only to the area studied, they de indicate that significant losses of P and N can occur in accelerated subsurface runoff. Some of the data presented in this section are used in subsequent sections, to determine the relative contribution of the runoff types to the amounts of water discharged and P and N forms transported in stream flow.

# SECTION 6

£3

## SOURCES AND TRANSPORT OF PHOSPHORUS AND NITROGEN IN STREAM FLOW

### 6.1 Introduction

Stream flow can be divided into storm flow and subsurface flow. The former represents a part of stream flow resulting from storm rainfall, reaching an observation point within a relatively short period of time, whereas the latter lags storm rainfall by a longer period of time than storm flow (Guy, 1964). Stream flow is usually separated into the components of storm and subsurface flow by empirical analysis of the runoff hydrograph. The general concepts of such an analysis are illustrated in Fig. 6.1, where ABCD represents the total runoff and AECD represents the amount of subsurface flow (Wisler and Brater, 1949). The reversal in direction of subsurface flow (AE, Fig. 6.1) results from a greater hydrostatic pressure in the stream than in the banks, as a consequence of a more rapid increase in the height of water in the stream channel during stream flow than that in the water table. As soon as the stream level starts to fall, the direction of flow reverses and as a result of the water accumulated in the stream bank, the subsurface contribution to the stream is considerably increased for a short period of time. When the bank storage is drained out, subsurface flow follows the normal depletion curve.

Because it is not possible to determine the actual position of the line AECD, subsurface flow is separated from storm flow by the straight line AC (Fig. 6.1). Although the exact location of C cannot usually be determined, this is not important as long as a consistent procedure is used to determine the point.

Annual loadings of nutrients in flowing waters have often been calculated by assuming concentration values between samples taken at arbitary intervals. For a range of nutrients, however, several studies have demonstrated the dependence of concentration upon flow (Wang and Evans, 1970; Kunkle and Comer, 1972; McColl <u>et al.</u>, 1975). Because variations in either flow or nutrient concentrations cause variations in nutrient fluxes, it is desirable tc



Fig. 6.1 Components of a stream flow hydrograph.

determine their relative significance in influencing nutrient loadings. This information is necessary to establish the frequency of sampling required to reliably estimate P and N loadings of both storm and subsurface flow in streams. In the past, sampling intervals used for streams and rivers have ranged from 5min or less (Frere, 1971; White, 1972) through to one week (Englebrecht and Morgan, 1961), and even one month (Smith, 1959).

The aims of this part of the study were to (i) observe the relationship between flow and concentrations, and fluxes of P and N forms in stream flow, (ii) determine the effect of sampling frequency on the loading estimates of P and N forms, and (iii) estimate the amounts of water, and P and N forms transported in subsurface flow, storm flow, and stream flow from the catchment under study.

#### 6.2 Materials and Methods

Stream flow samples were collected immediately upstream of each of the compound weirs in the catchment. The sampling interval varied according to the hydrograph, being as small as 2min for rapid hydrograph changes and as large as 12h for the subsurface component of stream flow. The data presented in this chapter relate to samples collected at the lower weir only.

#### 6.3 Results and Discussion

#### 6.3.1 Stream flow

6.3.1.1 <u>Relationship between precipitation and stream</u> <u>flow</u>. Stream flow in the catchment is considered to originate solely from precipitation because no surface or subsurface water is believed to enter the catchment from outside the catchment boundary. Stream flow, however, is restricted to the cooler, winter months (May to October), when approximately 75% of the annual precipitation occurs. During these months, the proportion of precipitation appearing as stream flow in the catchment during the two years of study can be calculated. This information is presented in Table 6.1.

	19	74	1975		
Month	Precipitation (mm)	Stream flow %	Precipitation (mm)	Stream flow %	
January	31	0	37	0	
February	56	0	30	0	
March	21	0	53	0	
April	111	0	71	0	
May	121	8.1	130	6.0	
June	40	11.8	65	49.1	
July	251	96.2	128	82.7	
August	82	39.2	161	87.4	
Septembe	r 116	79.1	56	45.2	
October	128	31.7	83	0.1	
November	53	0.4	54	0	
December	78	0	102	0	
Total	1088	36.9	970	32.2	

Table 6.1 Amounts of water entering the catchment as precipitation and the percentage leaving the catchment as stream flow in each month during 1974 and 1975

In May, when soil moisture is still low and the amounts, and frequency of precipitation are also usually low, a small percentage of precipitation leaves the catchment as stream flow. Similarly, in June, the soils have not usually reached field capacity and are still capable of retaining a high proportion of the precipitation as soil water. When field capacity is reached in mid-winter, however, due to prolonged periods of precipitation and minimal evaporation losses due to low air and soil temperatures, a high proportion of the water entering the catchment leaves as stream flow. In July 1974 and August 1975, a maximum of 96.2 and 87.4%. respectively, of the monthly precipitation could be accounted for by stream flow (Table 6.1). Although soil temperatures were low during August, 1974, the small amount of precipitation during this month permitted some drying of the soil, resulting in only a small proportion of the precipitation appearing as stream flow (39%, Table 6.1).

In late winter and early spring (September to November) the amounts of precipitation are gradually decreasing, whereas soil temperatures are increasing. Consequently, the moisture content of the soil within the catchment gradually decreases, with the result that an increasing proportion of precipitation is retained in the soil profile.

Remarkably similar proportions of the total precipitation falling between May and November could be accounted for by stream flow in 1974 (50.7%) and in 1975 (51.2%, Table 6.1), even though a greater amount of precipitation fell during this period in 1974 (791mm), compared to the same period in 1975 (677mm). A similar proportion of the annual precipitation also appeared as stream flow in 1974 (36.2%) and in 1975 (32.2%, Table 6.1).

Overseas workers have reported a varying proportion of the annual precipitation appearing as annual stream flow from catchments of similar area, land slope, soil type, and land use to those of the Massey Catchment. For example, in a study of an ephemeral stream in Georgia which flowed for approximately nine months of the year, Jackson <u>et al.</u> (1973) reported that 47% of the annual precipitation (1178mm) appeared as stream flow, whereas Burwell <u>et al.</u> (1974) could account for only 17% of the 780mm of precipitation averaged over four years, in a perennial stream, in south-west Iowa. 6.3.1.2 Effects of grazing on the concentration of phosphorus and nitrogen in stream flow. In July 1975, 100 dairy cattle block-grazed the undrained area of the 20ha subcatchment in which the stream channel is situated at a stocking rate of 25 cattle ha<sup>-1</sup> for ten days. The grazing event occurred during a period of subsurface flow when the concentrations of both particulate and dissolved P and N forms, and sediment were low and remained relatively constant. The concentrations of DIP and particulate P (Fig. 6.2), and sediment (Fig. 6.3) in stream flow increased dramatically following the introduction of cattle to the area. At the same time, the concentration of TN increased only slightly, whereas that of NO<sub>3</sub> increased after one day (Fig. 6.3).

The most dramatic increase in concentrations were observed for particulate P (Fig. 6.2) and sediment (Fig. 6.3), where an increase of approximately 0.30 and 300mg  $1^{-1}$ , respectively, was observed in approximately 10h following the onset of grazing. The effect was less pronounced for DIP concentration, where an increase of approximately 0.06mg  $1^{-1}$  was observed in the same period of time. Although NO<sub>3</sub> concentrations remained virtually constant for the first 24h after the start of grazing, the slight increase in TN concentration could be attributed to an increase in particulate N.

Because surface and accelerated subsurface runoff did not occur during the time that animals were grazing the subcatchment and the concentrations of P and N forms, and sediment, measured at the upper weir in stream flow entering the subcatchment were essentially constant over this period (Fig. 6.4 and 6.5), the observed increase in concentrations of P and N forms can be attributed to the movement of cattle in the stream channel, stirring up bottom sediments, and depositing excreta in the stream. The increases in the concentrations of P and N forms in the stream, however, were short-lived (Fig. 6.2 and 6.3) and were not maintained at the initially high concentrations during the whole period of grazing. After two days, the concentrations of particulate P and sediment had decreased by approximately 0.27 and 170mg 1, respectively. The lack of any sustained effect of grazing in maintaining high concentrations of P and N forms, and sediment



Fig. 6.2 Variation in flow and in DIP and particulate P concentrations at the lower weir, during subsurface flow, before and after grazing.



Fig. 6.3 Variation in flow and in TN, NO3, and sediment concentrations at the lower weir, during subsurface flow, before and after grazing.



Fig. 6.4 Variation in flow and in TP, DIP, and sediment concentrations at the upper weir, during subsurface flow, before and after grazing.



Fig. 6.5 Variation in flow and in TN and NO<sub>3</sub> concentrations at the upper weir, during subsurface flow, before and after grazing.

in stream flow results from the fact that the cattle were grazed in blocks of approximately 3ha, beginning adjacent to the lower weir and gradually moving up the catchment over the ten-day period. Consequently, as the distance between the area being grazed and the lower weir increased, the degree of settling of suspended particulate material, and possibly the resorption of DIP by suspended particulate material and stream-bank material (Section 8.3.3), would be expected to increase. The data presented confirm previous suggestions that increases in nutrient and sediment concentrations in stream base flow can result from grazing cattle (Lusby <u>et al</u>., 1971; Minshall <u>et al</u>., 1969).

#### 6.3.1.3 Amounts of phosphorus and nitrogen transported

in stream flow. The mean concentration of DIP and TDP (calculated from total loadings and total flow) were lower than the mean concentration of particulate P, during 1974 and 1975 (Table 6.2). Because N analyses were only conducted towards the end of 1974, mean concentrations and annual loadings of N forms are not presented for 1974.

It was apparent from data obtained in the second year that the mean concentrations of N forms were always greater than those of P forms. The mean annual concentrations of dissolved P forms (DIP and TDP) were remarkably similar for both 1974 and 1975 (Table 6.2), although the observed concentration ranges were smaller in 1975. The mean concentrations and observed concentration ranges of particulate P, TP, and sediment, however, were slightly greater in 1975 than in 1974. This may result from the fact that high-intensity storm flow was more frequent in 1975 than in 1974 (15-min rainfall intensities in 1975 exceeded the maximum intensity observed during 1974 (25mm 15min<sup>-1</sup>) or twelve occasions). Consequently, the potential for particulate material and particulate P to be detached and transported in surface runoff and stream flow was greater in 1975.

It was apparent that approximately 60% of the annual stream discharge of P and N forms, and sediment occurred during the months of highest stream flow in both 1974 and 1975, although the annual amounts transported were lower in 1975 than in 1974

		1974	1975				
Parameter	Concentra	tion (mg l <sup>-1</sup> )	Loading	Concentrati	Concentration (mg 1 <sup>-1</sup> )		
	Calculate	d Observed	$(kg ha^{-1} y^{-1})$	Calculated	Observed	(kg ha <sup>-1</sup> y <sup>-1</sup> )	
	mean	range		mean	range		
Discharge						F1	
(m <sup>3</sup> ha <sup>-1</sup> y	-1)	0 - 1.05 <sup>a</sup>	4030		0 - 1.36 <sup>a</sup>	3100	
DIP	0.097	0.013 - 0.716	0.39	0.098 0	0.019 - 0.446	0.31	
TDP	0.131	0.035 - 0.972	0.53	0.137	0.037 - 0.517	0.43	
Particulate	e P 0.247	0.010 - 0.984	0.99	0.276 0	.005 - 2.246	0.87	
TP	0.378	0.068 - 1.737	1.52	0.413 0	0.052 - 2.446	1.31	
NO3b	-	-	-	3.24 1	- 9.3	10.25	
<sup>d</sup> ИТ	-	-	-	5.16	1.3 -11.4	16,32	
Sediment	290	11 - 2100	1150	310	20 - 2650	980	

Table 6.2 Annual amounts of water discharged, and P and N forms, and sediment transported in stream flow during 1974 and 1975

Observed discharge range expressed as m Sec . No N analyses in 1974.

(Table 6.2). In 1974 this was July, and in 1975 both July and August. During these months of high flow, particulate P contributed 70% of the TP transported. This contrasts with the data obtained in the months of low flow (May), where only 48% of the TP was in the particulate form. In the case of N, NO<sub>3</sub> contributed 73% of the TN transported in July and August 1975, whereas in the months of low flow it contributed 76%.

Lower annual losses of DIP, particulate P, TP, NO<sub>3</sub>, and TN (0.19, 0.21, 0.45, 0.19, and 0.61kg ha<sup>-1</sup> y<sup>-1</sup>, respectively) from a pasture and cropped catchment in Iowa, of similar area, soil type, and land slope to those in the present study, were measured by Burwell et al. (1974), even though fertilizer applications of 28kgP ha<sup>-1</sup> and 127kgN ha<sup>-1</sup> were made. Harms <u>et al.</u> (1974) obtained losses of TP, TN, and NO<sub>z</sub> of 0.23, 1.45, and 0.27kg ha<sup>-1</sup> y<sup>-1</sup>, respectively, in a stream draining a sandy clay loam under pasture in eastern South Dakota. In a similar study in North Carolina, Kilmer et al. (1974) reported particulate P losses of 0.15kg ha<sup>-1</sup>  $y^{-1}$ , and TN and NO<sub>3</sub> losses of 3.28 and 2.36kg ha<sup>-1</sup>  $y^{-1}$ , respectively, in stream flow from a catchment which included cropped land and heavily-grazed pasture to which 48kgP ha<sup>-1</sup> and 112kgN ha<sup>-1</sup> of fertilizer were applied. Even when 192kgP ha<sup>-1</sup> was applied, an annual particulate P loss of only 0.27kg ha<sup>-1</sup> was observed, compared to a loss of 0.87kg ha<sup>-1</sup> y<sup>-1</sup> (Table 6.2, 1975) in the present study.

In addition, the annual loss of TDP in stream flow in the present study (0.53 and 0.43kg ha<sup>-1</sup> y<sup>-1</sup>, for 1974 and 1975, respectively, Table 6.2) is greater than that found by Taylor <u>et al.</u> (1971) (0.20kg ha<sup>-1</sup> y<sup>-1</sup>) from a catchment in Ohio, of soil type silt loam, under permanent pasture and cropping, to which 16.2kgP ha<sup>-1</sup> was added as fertilizer over four years.

### 6.3.2 Subsurface flow

6.3.2.1 <u>Interrelationships between flow, concentra-</u> <u>tion, and flux of phosphorus and nitrogen in subsurface flow</u>. Relationships between the concentration of P forms and flow (Fig. 6.6a and 6.7a) and the concentrations of N forms and sediment and



Fig. 6.6 Variation in flow and (a) TP, TDP, and DIP concentrations, and (b) TN, NO<sub>3</sub>, and sediment concentrations for subsurfaceflow event 1.



Fig. 6.7 Variation in flow and (a) TP, TDP, and DIP concentrations, and (b) TN, NO<sub>3</sub>, and sediment concentrations for subsurfaceflow event 2.

flow (Fig. 6.6b and 6.7b), transported during two subsurface-flow events, are presented. Relationships between the flux of P forms and flow (Fig. 6.8b) in the first of these two subsurface-runoff events are also given. The events are representative of those observed during two years of field monitoring.

The discharge rate and concentrations of DIP, TDP, TP, NO<sub>3</sub>, and TN varied within narrow limits, decreasing gradually during both events. Slight variations in the concentrations of P and N forms between the events are apparent, however, due to the preceding discharge of surface, accelerated subsurface, and subsurface runoff, and soil moisture and temperature conditions.

As a result of the small variations in the concentration of P and N forms, and in flow, the concentrations of P and N forms were significantly correlated to subsurface flow (Table 6.3, where the data presented relate to event 1). The significant correlations obtained contrast with the much lower correlations for the relationship between the concentration of P and N forms, and flow in the other runoff types studied, where marked changes in concentration occurred with flow. For example, correlation coefficients of r = 0.76, 0.75, and 0.85 (significant at the 1% level) for TP concentration, and r = 0.11, 0.61, and 0.97 (significant at the 1% level) were obtained for the relationship between DIP concentration and flow for surface, accelerated subsurface, and subsurface runoff, respectively. Similar concentration-flow trends have been observed by Minshall et al. (1969) and Gburek and Heald (1974) who also observed that P and N concentrations attained rather constant values during prolonged periods of subsurface flow. The intensity and duration of the preceding storm, however, may result in concentration differences between subsurface flow events.

The flux of P and N forms was significantly (1%) more closely related to flow than to concentration (Table 6.3). The flux of TN, however, had a significantly higher squared regression coefficient (r = 0.96) than that for TP (r = 0.72) when the relationship with flow was considered. Because of the highly significant correlation coefficients between the concentrations of P and N forms, and flow, the regression coefficients for the flux of P and N forms and subsurface flow (r = 0.72 and 0.96, for TP and TN,



Fig. 6.8 Variation in flow and (a) TP, TDP, and DIP flux, and (b) TN, NO<sub>3</sub>, and sediment flux for subsurface-flow event 1.
Table 6.3 Standard partial regression coefficients for the standard regression of log<sub>10</sub> flux on log<sub>10</sub> concentration and log<sub>10</sub> flow, and correlation coefficients for concentration with flow for P and N forms in subsurface flow for event 1

P or N form	Squared standard regression coeffi	partial cient for	Correlation coefficient for concentration with flow
	Concentration	Flow	
DIP	0.07**	0.55**	0.97**
TDP	0.04**	0.67**	0.82**
TP	0.04**	0.72**	0.85**
NO3	0.03**	0.92**	0.54**
ΤN	0.01**	0.96**	0.66**

\*\* Values significant at the 1% level.

respectively) were significantly higher than for either surface (r=0.53 and 0.82, for TP and TN, respectively) or accelerated subsurface runoff (r=0.37 and 0.77, for TP and TN, respectively).

The soil-water-sediment system can be said to have reached a hydrological equilibrium under these low flow conditions, when there is no input of water to the system through precipitation and negligible amounts of suspended sediment in subsurface flow. In this state, P and N concentrations are influenced only by the deeper subsoils through which subsurface flow moves, and by the stream-bank and bottom sediments which stream flow contacts. A steady state for dissolved P and N output could then be expected.

The data suggest that it is not necessary to collect samples of subsurface flow as frequently as for the other runoff types to obtain a similar accuracy of loading estimates. This arises because of the very small variation in flow, and in the concentration and flux of P and N forms, over long periods of time.

6.3.2.2 Sampling frequency. The methods by which the frequency of sumpling of subsurface flow was established have been given in Section 3.5. Deviations in the estimates of loadings of P and N forms in subsurface-runoff event 1 were low (Table 6.4), reflecting the small variability in the rate of change of P and N concentrations and fluxes. Furthermore, an increase in the sampling interval from 60 to 720min had only a slight effect on the deviation of loading estimates. In contrast, an increase in the sampling interval of surface and accelerated subsurface runoff from 8 to 30 and 8 to 240min, respectively, resulted in a dramatic increase in the deviation of loading estimates (Tables 4.3 and 5.2). In contrast to surface and accelerated subsurface runoff, it is apparent that the variability in loading estimate of DIP during subsurface flow at a specific sampling interval (12.9% at 1440min, Table 6.4), was greater than that for TP (5.3% at 1440min, Table 6.4). Maximum sampling intervals of 720min for P and N concentrations, and 15min for water flow were found to give deviations in estimates of P and N loadings within 15% (Table 6.5). These sampling intervals were thus used in later studies.

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Sampling	Numi	per of	Parameter	Deviation in loading estimates				
interval	Samples	Replicates		-	(%)			
(min)				Mean	Confidence i	nterval 95%		
60	120	6						
360	120	6	DIP	-1.12	(-3.2,	1.02)		
			TDP	-0.89	(-3.2,	1.45)		
			TP	-0.94	(-2.1,	0.24)		
			NOZ	-0.01	(-0.1,	0.08)		
			ΤN	0.02	( 0.01,	0.03)		
			Sedimen	t 0.9	(-1.3,	3.1)		
720	10	6	DIP TDP TP NO <sub>3</sub> TN· Sedimer	-1.73 -0.89 -0.62 -0.03 0.08	(-4.5, (-5.12, (2.39, (-0.19, (-0.14, (-3.0,	1.08) 2.9) 1.15) 0.13) 0.30) 6.2)		
1440	5	6	DIP TDP TP NO <sub>3</sub> TN Sedimen	-3.2 -1.42 -0.73 -0.03 0.17 t 2.7	(-9.6, (-7.1, (-3.4, (-0.29, (-0.25, (-0.9,	3.3) 4.3) 1.9) 0.23) 0.6) 6.3)		

Table 6.4	Deviation	in	loading	estimat	ces	of	Ρ	and	Ν	forms,	and
	sediment	in	subsurfac	ce-flow	eve	ent	1				

Selected	Parameter	Deviation	in loading estimates (%)
sampling time (min)		Mean	Confidence interval 95%
720 <sup>a</sup>	DIP	0.9	(-2.1, 5.3)
	TDP	3.1	(1.5, 12.7)
	TP	2.7	(-10.3, 9.9)
	NO -	-1.0	(-2.8, 0.8)
	TN	-0.9	(-0.7, 2.5)
	Sediment	1.3	(-1.4, 4.0)

Table 6.5 Deviation in loading estimates of P and N forms, and sediment in six subsurface-runoff events studied

a Flow data at 15m intervals used.

# 6.3.2.3 Amounts of phosphorus and nitrogen transported

in subsurface flow. Subsurface flow was estimated using hydrograph resolution, as discussed previously (Fig. 6.1). Two criteria were used to establish when the hydrograph curve was represented by subsurface flow alone (points A and C, Fig. 6.1). The first method (subsequently referred to as Method 1) involved estimating the point of greatest curvature on the recession limb of the hydrograph (point C, Fig. 6.1), at which point the calculated value of the ratio of discharge at one time to the discharge one hour earlier became constant. Point A (Fig. 6.1) was considered to be the point where an initial marked increase in stream flow occurred. In the second method (subsequently referred to as Method 2), point A (Fig. 6.1) was taken as the point when accelerated subsurface flow started and natural subsurface flow was no longer the sole source of stream flow. Similarly, point C (Fig. 6.1) was considered to be the point when accelerated subsurface runoff stopped and natural subsurface runoff was the sole source of stream flow again (point C, Fig. 6.1).

It was also assumed that the P and N concentrations of subsurface flow during storm flow changed constantly from the subsurface flow concentrations immediately preceding storm flow (point A, Fig. 6.1) to the concentrations following storm flow (point C, Fig. 6.1). The annual amounts of water discharged, P and N forms, and sediment transported in subsurface flow were calculated using both of the above methods. It can be seen that both methods gave similar estimates of the amounts of P and N forms transported in subsurface flow (Table 6.6). The estimate of the volume of water discharged, however, was slightly greater for Method 1. Because the two different methods gave similar estimates of annual losses of P and N, only the data obtained using Method 1 are discussed.

The mean concentrations of P forms in subsurface flow were appreciably lower than the concentrations of N forms. For both P and N, a greater proportion of the amounts transported was in the dissolved form (60 and 74% for TDP and NO<sub>3</sub>, respectively, Table 6.6). Although the mean concentration of dissolved and particulate P in subsurface flow (0.024 and 0.016mg  $1^{-1}$  for TDP and particulate P, respectively, Table 6.6) were much lower than those observed in surface runoff from the unfertilized plots (0.248

Table 6.6 Annual water discharge and amounts of P and N forms, and sediment transported in subsurface flow from the catchment as measured by hydrograph resolution

		Method 1		Method 2
Parameter -	Concentration Calculated mean	n (mg l <sup>-1</sup> ) Observed (kg range	Loading ; ha <sup>-1</sup> y <sup>-1</sup> )	Loading (kg ha <sup>-1</sup> y <sup>-1</sup> )
Discharge (m <sup>3</sup> ha <sup>-1</sup> y <sup>-1</sup> )	)		1700	1500
DIP	0.015	0.019-0.044	0.03	0.03
TDP	0.024	0.037-0.070	0.04	0.05
Particulate F	0.016	0.005-0.070	0.03	0.03
TP	0.040	0.052-0.140	0.07	0.07
NO.3	4.73	1.1 -9.3	8.08	8.18
TN	6.39	1.3 -11.4	10.92	11.03
Sediment	21	20 - 67	40	30

and 0.278mg  $1^{-1}$  for TDP and particulate P, respectively, plot 5, Table 4.6), the mean concentration of N forms in subsurface flow (4.73 and 6.39mg  $1^{-1}$  for NO<sub>3</sub> and TN, respectively) were greater than these in surface runoff (0.35 and 1.15mg  $1^{-1}$  for NO<sub>3</sub> and TN, respectively, plot 5, Table 4.6).

The mean annual concentrations of P and N forms in subsurface flow (Table 6.6) were also lower than the corresponding concentrations in accelerated subsurface runoff (Table 5.7). A reduction in the contact time between the soil solution and soil components capable of sorbing inorganic P (Section 8.3.3) is expected for accelerated subsurface runoff. This is because the drainage system accelerates the movement of water through the soil profile. For example, the mean DIP concentration of subsurface flow (Table 6.6) was 0.043mg 1<sup>-1</sup> lower than the mean concentration of the same P form in accelerated subsurface runoff (Table 5.7).

In the case of N forms, the lower mean NO<sub>3</sub> concentration in subsurface flow, compared to accelerated subsurface flow, suggests dilution by increased water discharge in subsurface flow. The nutrient concentrations in accelerated subsurface runoff measured by Burwell <u>at al</u>. (1974) were consistently greater than those in subsurface flow samples collected at the same time.

Although there was little variation in the P and N concentrations within a particular period of subsurface flow, variations were observed between flow periods during the year (Table 6.6). For example, DIP concentrations ranged from 0.019 to 0.044mg  $1^{-1}$  and TP concentrations from 0.052 to 0.140mg  $1^{-1}$ , whereas a greater variation in NO<sub>2</sub> and TN concentrations were observed (1.1 to 9.3 and 1.3 to 11.4mg  $1^{-1}$ , respectively).

The range in DIP concentration in subsurface flow observed in the present study is consistent with that found by Gburek and Heald (1974), from a small catchment primarily under cropping and forest in Pennsylvania (0.01 to 0.03mg l<sup>-1</sup>). In a three year study of subsurface flow from a cropped sandy loam in Georgia, Jackson <u>et al</u>. (1973) reported a mean annual NO<sub>3</sub> concentration of 8.92mg l<sup>-1</sup>, with concentrations ranging from 5 to 10mg l<sup>-1</sup>, when 168kgN ha<sup>-1</sup> was applied annually as fertilizer.

The annual amounts of N forms transported in subsurface flow were much greater than the annual amounts of P forms transported. An appreciably greater proportion of the TP and TN transported in subsurface flow (60 and 74% for TDP, and NO3, respectively, Table 6.6) was in the dissolved form compared to surface runoff (56 and 30% for TDP, and NO3, respectively, plot 5, Table 4.6). Thus, the higher proportion of particulate P and N in surface runoff was a result of the approximately 20-fold greater quantity of sediment in surface runoff (640kg ha<sup>-1</sup> y<sup>-1</sup>, average of plot 5 and 6, Table 4.6) than in subsurface flow (40kg ha<sup>-1</sup> y<sup>-1</sup>, Table 6.6). These differences in the forms of P and N transported reflect the differing characteristics of the transport processes involved in the two runoff types. The difference between the amounts of P and N forms transported in subsurface flow result from the fact that  $NO_3$  is able to move freely through the soil by diffusion and mass water transport, whereas DIP is rapidly removed from solution by sorption.

A similar amount  $(0.043 \text{kg ha}^{-1} \text{ y}^{-1})$  of TDP to that in the present study  $(0.04 \text{kg ha}^{-1} \text{ y}^{-1})$  was transported in base flow, equivalent to subsurface flow in the Massey Catchment, from a perennial stream draining a catchment of similar soil type and slopes to those in the Massey catchment (Burwell <u>et al.</u>, 1974). Losses of NO<sub>3</sub> from the same catchment, however, were only 0.35kg ha<sup>-1</sup> y<sup>-1</sup>, in spite of the fact that 127kgN ha<sup>-1</sup> was applied to the cropped area. Slightly higher annual losses of TP and NO<sub>3</sub> (0.11 and 1.2 kg ha<sup>-1</sup> y<sup>-1</sup>, respectively) were measured by Minshall <u>et al.</u> (1969) in base flow from 36 drainage areas in south-western Wisconsin, where the area of cropped land equalled that under pasture. An even greater difference between the annual loss of DIP (0.3kg ha<sup>-1</sup> y<sup>-1</sup>) and NO<sub>3</sub> (33kg ha<sup>-1</sup> y<sup>-1</sup>) was observed by Carter <u>et al.</u> (1971) in subsurface flow from a cropped silt loam in southern Idaho.

6.3.3 Storm flow

6.3.3.1 <u>Interrelationships between flow, concentration</u>, and flux of phosphorus and nitrogen in storm flow. The relation-

ship between concentration and flux of P and N forms, and flow in storm flow for a low- (event 1, Fig. 6.9a, b, Fig. 6.10a, b and Fig. 6.11a, b), a medium- (event 2, Fig. 6.12a, b), and a high-(event 3, Fig. 6.13a, b) intensity event are presented. The events represent the range of intensity of storm flow observed during two years of field monitoring. The concentration of DIP in the event of low-intensity (Fig. 6.9a) decreased with an initial rise in flow. During the medium- and high-intensity events (Fig. 6.12a and Fig. 6.13a), however, no decrease in the DIP concentration was observed during the initial stages of the event. Thus, it appears that the DIP concentration of initial storm flow was higher in the low-intensity event  $(0.15 \text{mg l}^{-1})$  when compared to the medium- and high-intensity events (0.08 and 0.03mg 1<sup>-1</sup>, respectively). The data suggest, therefore, that when DIP concentrations increase prior to storm flow, dilution of the DIP concentration may occur, depending on the DIP concentration of the initial runoff water. With a further increase in flow, the concentration of DIP showed similar variations for the low-, medium-, and highintensity events, where DIP concentration increased, reaching a maximum value before peak flow. Subsequently, concentrations gradually and consistently decreased, and a secondary flow increase was accompanied by a slight rise in DIP concentration (Fig. 6.9a).

In the low-, medium-, and high-intensity events (Fig. 6.10a; 6.12b; and 6.13b, respectively), TP concentrations increased with a rise in flow at approximately the same rate as the rate of flow increase. The TP concentration reached a maximum value before peak flow and subsequently decreased at a much faster rate than flow. The concentrations of DIP, TDP, and TP were significantly correlated to flow (Table 6.7) during event 1, which was considered typical of those studied.

The concentrations of NO<sub>3</sub> decreased gradually with an increase in flow during the low- and high-intensity events (Fig. 6.9b and Fig. 6.13a, respectively). During the medium-intensity event, however, NO<sub>3</sub> concentration increased slightly with an initial rise in flow, but in all events decreased at peak flow. This was most marked for the low- and high-intensity events. With the recession of flow, NO<sub>3</sub> concentrations gradually increased reaching a concentration greater than that at the beginning of the event.



Fig. 6.9 Variation in flow and (a) DIP concentration and flux, and (b) NO<sub>3</sub> concentration and flux for storm-flow event 1.





Fig. 6.10 Variation in flow and (a) TP concentration and flux, and (b) TN concentration and flux for storm-flow event 1.

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Fig. 6.11 Variation in flow and in sediment concentration and flux for storm-flow event 1.



Fig. 6.12 Variation in flow and (a) DIP and NO<sub>3</sub> concentrations, and (b) TP, TN, and sediment concentrations for stormflow event 2.

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Fig. 6.13 Variation in flow and (a) DIP and NO<sub>3</sub> concentrations, and (b) TP, TN, and sediment concentrations for stormflow event 3.

Table 6.7 Standard partial regression coefficients for the standard regression of  $\log_{10}$  flux on  $\log_{10}$  concentration and  $\log_{10}$  flow, and correlation coefficients for concentration with flow for P and N forms in storm event 1

P or N form	Squared standard regression coeffi	l partial cient for	Correlation coefficient for concentration with flow				
	Concentration	Flow					
DIP	0.10**	0.53**	0.84**				
TDP	0.14**	0.48**	0.73**				
ЧT	0.14**	0.44**	0.84**				
NO3	0.30**	0.32**	0.37				
ΤN	0.34**	0.36**	0.29				

\*\* Values significant at the 1% level.

In the initial stages of the low-, medium-, and high-intensity events, the concentration of TN showed similar fluctuations to that of TP, increasing rapidly with an increase in flow (Fig. 6.10b, 6.12b, and 6.13b). The maximum TN concentration, however, was observed earlier than that of TP. This difference results from the fact that because NO<sub>3</sub> constituted the major proportion of the TN transported, a decrease in NO<sub>3</sub> concentrations with increasing flow due to dilution, will be reflected in a corresponding decrease in TN concentration with increasing flow. A minimum TN concentration was obtained at peak flow. As the flow decreased, TN concentrations gradually increased, becoming greater than at the beginning of the event. It is apparent from Table 6.7 that NO<sub>3</sub> and TN concentrations were not significantly correlated to flow during event 1.

It was observed previously (Section 4.3.3.1) that  $NO_z$  concentrations in surface runoff were low and that particulate N accounted for the major proportion of TN. In contrast, NO<sub>x</sub> concentrations in accelerated (Section 5.3.3.3 ) and natural subsurface runoff (Section 6.3.2.3 ) were high, contributing 80% of the TN in both runoff types. Because the response of surface flow is much more rapid than that of either accelerated or natural subsurface flow, the initial rise in stream flow at the beginning of an event will be mainly the result of surface runoff. Consequently, the initial variation in TN concentrations in stream flow will be due mainly to variations in particulate N. Surface runoff, however, is normally of short duration and particulate N concentrations will rapidly decrease. As the contribution of subsurface flow to stream flow increases,  $\mathrm{NO}_{_{\rm X}}$  will contribute the major proportion of TN in stream flow. The variations in TN concentration following peak concentration will, therefore, be mainly a result of variations in  $NO_3$  concentration and should show similar flow-concentration relationships to subsurface runoff (Section 5.3.1 and 6.3.1).

The concentration of sediment in the low-, medium-, and highintensity events (Fig. 6.11, 6.12b, 6.13b, respectively) increased with an increase in flow, with maximum concentrations preceding peak flow. With a decrease in flow, sediment concentrations gradually and consistently decreased. A secondary increase in flow resulted in a further increase in sediment concentration. These variations in sediment concentration are partly due to the large contribution of surface runoff to stream flow during the early stages of an event and to an increase in the area of croding bank contacted by the stream as stream flow increases.

As was the case for TP, sediment concentrations increased at a similar rate to stream flow during the rising stage, but decreased much more rapidly during flow recession. The result is that for a given value of discharge, sediment and TP concentrations were higher on the rising limb, than on the falling limb of the hydrograph. This suggests both a decrease in the availability of sediment as the storm event continues, and an increase in the contribution of subsurface flow, containing low TP and sediment concentrations. It is thus apparent that the relationships between flow and P, N, and sediment concentrations during storm flow are complex, as a result of both surface and subsurface runoff operating at and over different portions of the storm hydrograph.

Partial regression coefficients from the analysis of event 1 (Table 6.7), however, indicate that flow was significantly (1% level) more important in determining the flux of P forms than was concentration, although the coefficients were lower than those obtained for surface runoff (Table 4.2). In the case of N, however, flow and concentration were equally important in determining the flux of N forms (Table 6.7).

Variations in TP and TN concentrations, similar to those obtained within an event in the present study, were observed by Muir <u>et al.</u> (1973) in major streams in Nebraska, where concentrations increased during periods of maximum flow. In contrast, McColl <u>et al.</u> (1975) reported that the "soluble P" concentrations in stream flow from a catchment under pasture in the North Island of New Zealand, decreased during a flood event, mainly as a function of the time elapsed since the flood started. Minor increases in soluble P concentrations were observed, however, and were associated with an increase in flow rate.

Variations in P, N, and sediment concentrations between consecutive events were apparent in the present study and also in studies conducted by Walling and Foster (1975) in southern England and McColl <u>et al.</u> (1975) in New Zealand. These variations are attributed to the time interval between events, such that a long period may allow a larger pool of "leachable" nutrients to accumulate, antecedent moisture, maximum stream flow, and the proportion of surface and subsurface runoff contributing to stream flow.

The variations in sediment concentration in the present study are similar to those obtained in catchment studies overseas, where an increase in stream flow resulted in a corresponding increase in sediment concentration which peaked before flow (Vice <u>et al</u>., 1968; Guy and Ferguson, 1970). Also the finding that more particulate material is carried on the rising compared to the falling limb of the hydrograph, at a given flow rate, is consistent with the work of Kunkle and Comer (1972) and Walling (1974) for streams draining permanent pasture.

6.3.3.2 <u>Sampling frequency</u>. The procedure used to investigate the frequency of sampling of storm flow has been outlined in Section 3.5.

The deviation in estimates of the loading of P and N forms in storm flow (in event 1) increased as the sampling interval increased (Table 6.8). When the sampling interval exceeded 60min, the errors became unacceptably large. The use of flow measurements at 15-min intervals was found to give less than 1% deviation in estimates of total water discharge. As was the case for surface and accelerated subsurface runoff, inclusion of a sample collected at peak flow significantly decreased the deviations in loading estimates.

Because rapid flow and nutrient concentration changes occurred before peak flow, more frequent sampling should be employed over the initial stages. Similar findings were obtained with accelerated subsurface runoff (Section 5.3.2). Based on these data and the significant correlations (Table 6.7) of concentration upon flow, samples were collected at a sampling-time interval of 60min until half-peak flow was reached on the recession hydrograph. The sampling interval was subsequently increased to 120min as flow and concentration variability decreased. For nine runoff events,

Sampling	Num	ber of	Parameter	Deviation in loading estimates				
interval	Samples	Replicates		-	(%)			
(min)				Mean	Confidence interval 95			
8	144							
30	36	4	DIP	-0.35	(-2.7, 1.95)			
	-		TDP	-0.51	(-2.3, 1.30)			
			TP	-0.51	(-1.92, 0.90)			
			NO_	0.10	(-0.03, 0.23)			
			3 TN	0.14	(-1.02, 1.30)			
			Sediment	0.16	(-1.34, 1.66)			
60 <sup>a</sup>	18	4	DIP	4.2	(-1.3, 9.7)			
			TDP	1.1	(-2.6, 4.8)			
			TP	8.0	(-2.3, 18.3)			
			NO3	3.6	(-2.0, 9.2)			
			TN	7.0	(-2.4, 16.4)			
			Sediment	6.9	(-0.3, 13.1)			
60 <sup>b</sup>	17	4	DIP	-1.26	(-3.5, 1.00)			
			TDP	-2.6	(-10.9, 5.7)			
			TP	-1.78	(-4.8, 1.20)			
			NO3	0.49	(-2.18, 3.16)			
			TN	0.04	(-3.67, 3.75)			
			Sediment	12.62	(-3.88,29.12)			
120 <sup>b</sup>	9	4	DIP	-2.3	(-6.3, 1.8)			
			TDP	-2.2	(-31 26.2)			
			TP	-2.04	(-18.0,14.0)			
			NO3	1.19	(0.14, 2.24)			
			TN	0.53	(-7.63, 8.89)			
			Sediment	50.7	(9.3,92.1)			

Table 6.8	Deviation	ir	l loadi	ing e	stima	ates	of	Ρ	and	Ν	forms,	and
	sediment	in	storm	flow	for	ever	nt '	1				

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Sampling	Number of		Parameter	Deviation in loading estimates				
interval	Samples	Replicates			(%)			
				Mean	Confidence	interval 95	5%	
240 <sup>°</sup>	4	4	DIP	-3.9	(-10.	9,3.0)		
			TDP	-12.6	(-45,	19.9 )		
			ΤP	-8.2	(-31,	14.3)		
			NO3	3.42	(-1.8	9, 8.73)		
			TN	-2.56	(-14.8	89,9.77)		
			Sediment	91.7	(22.3	, 161.1)		

a Sample at peak flow not included.

b Sample at peak flow included.

this sampling interval gave deviations in the loading estimates of P and N forms, and sediment of within 15% (Table 6.9).

Although several studies have involved frequent sampling of stream flow (Burm et al., 1968; Walling and Teed, 1971; McColl et al., 1975), it is essential when choosing a sampling frequency to state not only the frequency and number of samples taken but also to give an indication of the accuracy of the loading estimates obtained. With infrequent sampling of small catchment streams (Smith, 1959; Taylor et al., 1971), however, the data reported for the annual nutrient loadings are difficult to interpret. For estimates of the nutrient output in streams over longer periods of time (up to 20y), one sample per week was reported as being sufficient by Edwards and Thornes (1973).

6.3.3.3 Amounts of phosphorus and nitrogen trans-

ported in storm flow. The annual amounts of P and N forms, and sediment transported in storm flow were calculated as the difference between the annual amounts transported in the stream and in subsurface flow (Table 6.10). The mean annual concentrations of both dissolved and particulate P forms (obtained from total loadings and total flow) were substantially greater than those in subsurface flow (Table 6.6). For example, the mean DIP and particulate P concentrations in storm flow were 0.203 and 0.580mg  $1^{-1}$ , respectively, compared to 0.015 and 0.016mg  $1^{-1}$ , respectively, in subsurface flow. In contrast, the mean concentrations of TN and NO<sub>3</sub> (3.71 and 1.49mg  $1^{-1}$ , respectively) were lower than those in subsurface flow (6.39 and 4.73mg  $1^{-1}$ , respectively, Table 6.6).

It was observed previously (Section 6.3.2.1) that marked fluctuations in the concentration of P forms occurred within storm flow events. The concentration of DIP in storm flow during the year varied from 0.061 to 0.446mg  $1^{-1}$  and of particulate P from 0.070 to 2.246mg  $1^{-1}$ . Because of the heterogeneous nature of storm flow with respect to the contributions of the runoff types and their markedly different concentrations of P forms, variations in the concentrations of P forms in storm flow were greater than those in the more homogeneous subsurface flow. On the other hand, the concentrations of N forms did not vary as much as in subsurface

Selected sampling interval	Parameter	Deviation in loading estimates (%)					
(min)		Mean	Confidence interval 95%				
60/120 <sup>a</sup>	DIP	1.6	(-2.1, 5.3)				
	TDP	7.1	( 1.5, 12.7 )				
	TP	-0.20	(-10.3, 9.9)				
	NO3	-C.41	(-3.07, 2.25)				
	ΊN	1.81	(-1.09, 4.71)				
	Sediment	3.64	(-4.59,11.87)				

Table 6.9 Deviation in loading estimates of P and N forms, and sediment in nine storm-flow events studied

a Sample at peak flow included and flow data at 15min intervals used.

Parameter	Concentrati	lon (mg 1 <sup>-1</sup> )	Loading
	Calculated	Observed	$(kg ha^{-1} y^{-1})$
	mean	range	
Discharge (m <sup>3</sup> ha <sup>-1</sup> y <sup>-1</sup> )			1400
DIP	0.203	0.061-0.446	0.28
TDP	0.271	0.082-0.517	0.39
Particulate P	0.580	0.070-2.246	0.84
TP	0.850	0.518-2.446	1.24
NO3	1.49	1.0 -6.0	2.17
TN	3.71	1.3 -7.3	5.40
Sediment	650	380 -2650	940

Table 6.10 Annual water discharged and amounts of P and N forms, and sediment transported in storm flow

runoff.

Although the annual amount of water discharged in storm flow  $(1400m^3 ha^{-1} y^{-1})$ , Table 6.10) was less than in subsurface flow  $(1700m^3 ha^{-1} y^{-1})$ , Method 1, Table 6.6), the amounts of P forms transported in storm flow were appreciably greater (Table 6.10). For example, 0.28 and 0.03kg ha<sup>-1</sup>  $y^{-1}$  DIP and 0.84 and 0.07kg ha<sup>-1</sup>  $y^{-1}$  TP were transported annually in storm and subsurface flow, respectively. In addition 66% of the TP transported in storm flow was in the particulate P form, compared to only 40% in subsurface flow. The amounts of TN and  $NO_3$  transported in storm flow (5.40 and 2.17kg ha<sup>-1</sup> y<sup>-1</sup>, respectively, Table 6.10) were lower than those in subsurface flow (8.08 and 10.92kg  $ha^{-1} y^{-1}$ , respectively, Table 6.6). Also the proportion of TN transported as NO<sub>z</sub> in storm flow (26%) was lower than in subsurface flow (74%). These differences in the amounts and forms of P and N transported in storm and subsurface flow result from the fact that storm flow includes surface runoff, which has been shown to transport large amounts of DIP and particulate P (Table 4.9) but low amounts of  $\mathrm{NO}_3$  , relative to subsurface flow. It is apparent, therefore, that although lower amounts of N forms are contributed to annual stream loadings by storm flow, than by subsurface flow, storm flow contributes the major proportion of the annual P loading in the stream. Similar observations for P, but contrasting in the case of N, were obtained by Olson et al. (1973) and Walling and Foster (1975), who found that storm flow contributed large amounts of P and N to surface waters in catchment studies in Nebraska and southern England, respectively.

The relative contributions of surface, accelerated subsurface, and subsurface runoff to stream flow are discussed in detail in the next Section (Section 7.3).

# 6.4 General Discussion

As was the case for both surface and accelerated subsurface runoff, there is a shortage of data for the losses of P and N forms in stream flow from catchments in New Zealand. Furthermore, little attempt has been made both in New Zealand and overseas to separate stream flow into surface and subsurface flow to investigate the relative importance of these two components to the P and N loadings of streams.

Although a greater amount of precipitation fell during 1974 compared to 1975, a similar proportion of the annual precipitation left the catchment as stream flow in both years of the study. When the present data are compared with those obtained in overseas studies it can be seen that differences in the proportion of precipitation which leaves a catchment as stream flow, is influenced by the drainage characteristics of the soils within the catchment. For example, Taylor et al. (1971) calculated that an average of 37% of the 870mm of precipitation per year appeared as stream flow in Ohio during four years, from a catchment in which a shallow soil mantle (1.5 to 2m) overlay impermeable bedrock. In addition, Jackson et al. (1973) reported that 47% of the annual precipitation (1178mm) appeared as stream flow from a tile-drained catchment. A corresponding situation in the Massey Catchment exists, where an impermeable fragipan (Pollok, 1975) is present at a depth of approximately 70cm and where approximately 50% of the catchment is artificially drained. In these situations, soil water will move more readily to the stream channel than in the situation where there is no drainage impedance or artificial drainage. Consequently, a greater proportion of the precipitation will appear as stream flow. In a catchment in southwest Iowa, containing a freely draining soil, Burwell et al. (1974) could account for only 17% of the 780mm of precipitation, averaged over 4 years.

Subsurface flow was characterised by little change in flow or in the concentration of P and N forms, and sediment. During periods of storm flow, however, fluctuations in the concentration of P and N forms, and sediment were associated with rapid changes in stream flow reflecting variations in the volumes of surface and accelerated subsurface runoff input into the stream. Although the stream draining the Massey Catchment is ephemeral, similar concentration-flow relationships have been observed by Minshall et al. (1969) and Muir et al. (1973) during periods of subsurface flow and by McColl et al. (1975) and Walling and Foster (1975) during periods of storm flow in catchments drained by perennial streams. From studies of variations in nutrient concentrations and flow, Frere (1971) and Taylor <u>et al</u>. (1971) concluded that flow was the more important variable than concentration for computing nutrient loading. This is in agreement with the generally significant correlations between flow and concentration of P and N forms in the present study, indicated by the fact that selective sampling for concentration based on changes in stream flow would give an improved estimate of loadings. Consequently, the sampling interval needed to obtain accurate estimates of the P, N, and sediment loading of stream flow, was appreciably greater for storm flow (60min) than for subsurface flow (720min).

From the data presented it appears that the annual amounts of N forms transported in storm and subsurface flow were much greater than the amounts of P forms transported, even though there was an approximately 10-fold and 20-fold greater transport of DIP and TP, respectively, in storm compared to subsurface flow. A similar difference in the annual amounts of P and N transported in stream flow has been observed in overseas catchments of varying land use (Minshall <u>et al.</u>, 1969; Carter <u>et al.</u>, 1971; Burwell <u>et al.</u>, 1974).

The annual amounts of P and N forms transported in stream flow in the present study were greater than those measured in many overseas studies from catchments of similar size, soil type, and land use where fertilizer P and N applications were made during the year of study. The annual losses of DIP, particulate P, TP, NO3, and TN in stream flow from a catchment in Iowa, receiving fertilizer applications of 28 kgP ha<sup>-1</sup> y<sup>-1</sup> and 127 kgN ha<sup>-1</sup> y<sup>-1</sup> (Burwell <u>et al.</u>, 1974), were only 61, 24, 34, 2, and 4%, respectively, of the annual amounts transported in stream flow in the Massey catchment. Similarly, the annual losses of particulate P, NOz, and TN obtained by Kilmer et al. (1974) from a catchment in western North Carolina, which included heavily grazed pasture to which 48kgP ha-1 and 112 kgN ha<sup>-1</sup> of fertilizer were applied, were only 48, 23, and 20%, respectively, of those obtained in the present study. In spite of a very much greater level of fertilizer P (192kgP ha<sup>-1</sup>) applied in the studies of Kilmer et al. (1974), the annual amounts of particulate P transported in stream flow were similar to those in the Massey Catchment.

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The much greater loss of  $NO_3$  in stream flow in the Massey Catchment than in overseas studies, points to the importance of N fixation by clover and the effect of grazing animals on the losses of  $NO_3$ . The regular use of fertilizer P in the past and the intensive grazing of the catchment would explain the greater losses of P. Similar thinking could apply to New Zealand, where high rates of P fertilizer application and grazing could contribute to a unique situation in terms of the transport of P and N in stream flow. SECTICN 7

RELATIVE SIGNIFICANCE OF THE RUNOFF TYPES AS SOURCES OF PHOSPHORUS AND NITROGEN TO THE STREAM

## 7.1 Introduction

Little information has been reported in the literature on the losses of P or N forms in runoff types and their relative contribution to stream flow in the same catchment. Exceptions to this are the studies of Jackson <u>et al.</u> (1973) and Burwell <u>et al</u>. (1974). Various reviewers have drawn conclusions regarding the relative contribution of surface and subsurface runoff, as sources of P and N forms to streams using data from different catchments (Zubriski <u>et al.</u>, 1971; Ryden <u>et al.</u>, 1973). Such conclusions, however, must be treated with caution, because of the conciderable variations in the amounts of P and N forms transported in the runoff types from different catchments.

To gain a better understanding of the transport and subsequent modifications of P and N forms in runoff types and stream flow, the relative contribution of the runoff types to stream flow and thus the paths by which water moves through the catchment, must initially be determined. In the catchment under study, surface and accelerated subsurface runoff were monitored in an isolated area, where the input and output of stream flow was also monitored.

The aim of this part of the study was to estimate the amounts of water, P and N forms, and sediment contributed by surface, accelerated subsurface, and subsurface runoff to stream flow in the subcatchment.

### 7.2 Materials and Methods

Stream flow was continuously monitored at two sites in the catchment, isolating a 20-ha subcatchment between the two weirs. The input of runoff from the subcatchment into the stream could, therefore, be monitored continuously. Within the subcatchment, surface and accelerated subsurface runoff were continuously monitored. In this way, it was possible to evaluate the relative significance of runoff types as sources of P and N forms, and sediment to the stream.

#### 7.3 Results and Discussion

7.3.1 Amounts of water discharged, phosphorus and nitrogen forms, and sediment transported into and out of the subcatchment in stream flow

The contribution of surface, accelerated subsurface, and subsurface runoff to the P, N, and sediment loading of stream flow in the subcatchment was calculated as the difference between the P, N, and sediment loading, respectively, of stream flow at the lower and upper weirs which isolated the subcatchment. There was an increase in the amount of water discharged and P and N forms, and sediment transported in stream flow from the subcatchment as a result of the input of the various runoff types during all months of stream flow (Table 7.1). This increase was most marked during the months of highest flow (July and August) when 86% of the total annual flow and 96% and 85% of the annual TP and TN loading, respectively, were transported. An appreciably greater proportion of the TP transported during the months of highest flow was in the particulate form (71% in July and August, Table 7.1), compared to the months of low flow (58% in May and September, Table 7.1). These observations are discussed later in relation to the relative inputs of runoff types during these months.

The amounts of DIP and TP added to the subcatchment in precipitation during the months of low stream flow (May and September) were greater than the amounts of DIP and TP discharged in the runoff types from the subcatchment (Table 7.1). In contrast, the amounts of DIP and TP entering the subcatchment in precipitation were less than the amounts discharged in stream flow during the months of continuous stream flow. The annual input of DIP in precipitation (1.55kg, Table 7.1) was approximately four times lower than the DIP output from the subcatchment in stream flow (6.47kg). On the other hand, there was a net annual loss of 31.62kg of TP from the subcatchment in stream flow compared to the input of TP in precipitation. Table 7.1 Amounts of water discharged, and P and N forms, and sediment transported in runoff from the subcatchment to stream flow, and amounts of DIP and TP added to the subcatchment in precipitation during 1975

Month	Discharge	DIP	TDP	TP	NO3	ΤN	Sediment	Precipi	tation
	2							DIP	TP
	(m <sup>-</sup> )	-			( kg .	)			
May	1360	0.07	0.19	0.26	5.7	7.4	200	0.21	0.96
June	6330	0.47	0.69	1.27	18.6	24.2	640	0.26	1.22
July	30410	2.77	5.74	20.73	128.7	162.5	15740	0.20	0.95
August	47700	2.92	4.55	14.38	122.9	154.6	8820	0.26	1.19
September	5090	0.23	0.83	2.15	15.5	23.1	2600	0.09	0.14
October	10	0.01	0.01	0.01	1.0	1.4	1	0.13	0.61
Total (kg	y <sup>-1</sup> )90900 <sup>a</sup>	6.47	12.01	33.80	292.4	373.1	28020	1.55	7.18
'Total per area (kg h	unit 4550 <sup>b</sup> .a <sup>-1</sup> y <sup>-1</sup> )	0.32	0.60	1.94	14.6	18.7	1400		
a Units m	3 y-1	b Unit	$s m^3 ha^{-1}$	y-1					

In a similar study, Olness <u>et al.</u> (1975) found that slightly more DIP and TP were discharged in stream flow (0.13 and 1.27kg ha<sup>-1</sup>  $y^{-1}$  of DIP and TP, respectively) than were added in precipitation (0.20and 0.32kg ha<sup>-1</sup>  $y^{-1}$  of DIP and TP, respectively) to a catchment under pasture in Oklahoma, when no fertilizer P was added. Because of the changes in the forms of P added in precipitation during movement through the catchment however, it is difficult to evaluate the effect, of the forms of P carried in precipitation, on the corresponding loading of P forms in runoff.

The discharge of water from the 20-ha subcatchment during  $1975 (4550m^3 ha^{-1} y^{-1})$ , Table 7.1) was slightly greater than from the whole catchment  $(3100m^3 ha^{-1} y^{-1})$ , Table 6.2) during the same period. This may be the consequence of a greater proportion of the subcatchment (70%) being artificially drained by mole and tile drains, compared to the whole catchment (50%). In addition, the losses of TDP, TP, NOz, TN, and sediment from the subcatchment (0.60, 1.94, 14.6, 18.7, and 1400 kg ha<sup>-1</sup> y<sup>-1</sup>, respectively, Table7.1) in stream flow, were slightly greater than those from the whole catchment during the same year (0.43, 1.31, 10.25, 16.32, and 980kg ha<sup>-1</sup> y<sup>-1</sup>, respectively, Table 6.2), whereas losses of DIP were very similar (0.31 and 0.32kg ha  $^{-1}$  y  $^{-1}$  from the sub-and whole catchment, respectively). The differences in the amount of P and N forms, and sediment transported can be attributed to the difference in the amount of water discharged, because the mean annual concentrations of TDP, TP, NO3, and sediment in water discharged from the subcatchment (0.132, 0.426, 3.21, and  $308 \text{mg l}^{-1}$ , respectively) were remarkably similar to those from the whole catchment during 1975 (0.139, 0.419, 3.29, and  $314 \text{mg l}^{-1}$ , respectively).

7.3.2 Estimation of the inputs of water, phosphorus and nitrogen forms, and sediment in the runoff type to stream flow in the subcatchment

7.3.2.1 <u>Assumptions</u>. The total input of water, P and N forms, and sediment in surface, accelerated subsurface, and subsurface runoff to the stream can be estimated if a number of assumptions are made.

It was assumed that surface runoff occurred only from the undrained area in the subcatchment. The drained area (14ha) varied in slope from 0 to 1° and surface runoff was only observed when heavy rain immediately followed a grazing event (100 cattle ha<sup>-1</sup> for 48h). The undrained area of land (6ha) in the subcatchment had approximately equal areas of 0 to  $3^{\circ}$ , 3 to  $8^{\circ}$ , and 8 to 13° slopes, with the runoff plots located on the medium and maximum slopes in the area. It must be assumed, however, that the amounts of water discharged and P, N, and sediment transported in surface runoff from the plots are representative of those from all parts of the undrained area. Furthermore, because approximately  $\frac{1}{2}$  of the undrained area of the subcatchment had slopes of 0 to  $\frac{3}{2}$ , from which little surface runoff originated, based on observations during storm events, it was assumed that  $\frac{2}{3}$  of the undrained part of the subcatchment would contribute surface runoff, as measured by the  $6^{\circ}$  surface runoff plots, to stream flow. These two assumptions are potentially dangerous, as it is well established that surface-runoff plots frequently over-emphasise nutrient losses. This is a result of the fact that field plots usually ignore redeposition of suspended particulate material that would occur on a catchment basis, where a decrease in the angle of slope would cause a reduction in the velocity of surface flow. In addition, because vegetation cover and soil chemical and physical properties are not constant with regard to the whole catchment, the composition of surface runoff would be expected to be highly heterogeneous (Viets, 1971; Ryden et al., 1973). Consequently, these factors lead to errors in nutrient loading estimates by assuming a constant composition of surface runoff.

In the case of accelerated subsurface runoff, it was assumed that the amounts of water discharged and P, N, and sediment transported in this runoff type from the two monitored tile lines, were similar to the amounts transported from the eight unmonitored tile lines. The validity of this assumption cannot be substantiated.

7.3.2.2 <u>Validity of using surface-runoff plots to</u> <u>estimate surface-runoff inputs into the stream</u>. The validity of estimating the amounts of water discharged and P, N, and sediment transported in surface runoff from the subcatchment using surfacerunoff plot data was evaluated. This was carried out by comparing estimates of the amounts of water discharged and P, N, and sediment transported in surface runoff, obtained by hydrograph analysis of stream flow in the subcatchment, with the amounts calculated from field plot data, using the previously mentioned assumptions.

The following equation was used to calculate the amounts of P, N, and sediment contributed to stream flow in the subcatchment from surface runoff, by accounting for inputs from accelerated subsurface and subsurface runoff:

SRO = (A - B) - (ASRO + SSRO)

The symbols A and B represent the amounts of water discharged and P, N, and sediment transported in stream flow at the lower and upper weirs, respectively, during the time that surface runoff was The term A - B, therefore, is the total contribution occurring. of surface, accelerated subsurface, and subsurface runoff to stream flow and P, N, and sediment loadings over this period in the subcatchment. The symbols, ASRO and SSRO represent the amount of water discharged and P, N, and sediment transported in accelerated subsurface and subsurface runoff, respectively, over the same period of time, when surface runoff was occurring. The amounts of water P and N forms, and sediment contributed by accelerated subsurface runoff were estimated from the data obtained from the two tile lines in the subcatchment, whereas the amounts contributed by subsurface runoff were estimated by hydrograph resolution (Method 1), discussed in Sections 6.1 and 6.2.3.2. SRO, thus represents the amounts of water discharged, and P, N, and sediment contributed by surface runoff to stream flow and nutrient loading in the subcatchment. These are considered to represent reasonable estimates of the contribution of surface runoff to stream flow and P and N, and sediment loadings. The amounts of water discharged and P, N, and sediment transported in surface runoff, estimated by this method (referred to as "calculated" in Table 7.2) and from field plot data, are presented in Table 7.2.

Estimates of the amounts of water discharged and dissolved P (DIP and TDP) transported in surface runoff from the subcatchment during eight surface-runoff events, obtained using surface-runoff

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Table 7.2 Amounts of water discharged and P and N forms, and sediment transported in surface runoff as determined using surface-runoff plots (measured) and by hydrograph analysis (calculated) for eight surface-runoff events

Parameter	Amount	(kg ha <sup>-1</sup> )	Deviation	Measured estimate
	Measured	Calculated	%	95% C.i.
Discharge <sup>a</sup>	120	130	-7.7	(-12.3, 4.3)
DIP	0.02	0.02	0	(- 8.4, 8.4)
TDP	0.03	0.03	0	(- 7.2, 7.2)
ТР	0.08	0.07	+14.3	(-16.8, 4.8)
NO3	0.06	0.07	-14.3	(-30.5, 4.1)
ΤN	3.7	3.6	+2.8	(- 8.6, 13.0)
Sediment	790	850	7.1	(-18.6, 5.4)

a Discharge expressed as m<sup>3</sup> ha<sup>-1</sup>.

b 95% Confidence interval.

plots (measured) and by hydrograph analysis (calculated) were sediment, however, the field remarkably similar. For plots yielded slightly lower estimates than hydrograph analysis, whereas the reverse was the case for TN During individual events, estimates of the amounts of water discharged and P forms and TN transported in surface runoff obtained using field plots deviated by approximately 15% from the calculated values. In the case of  $\mathrm{NO}_{\mathrm{X}},$  the discrepancy between the two methods, was greater (35%, Table 7.2). Because the amounts of NO3 transported in surface runoff were very low, compared to subsurface runoff (Table 4.6 and 6.6), this discrepancy was considered unimportant with respect to the NOz loading of the stream. It has been suggested that surface-runoff plots overestimate the contribution of surface runoff to the P, N, and sediment loading of stream flow (Section 2.2.1). This does not, however, appear to be the case in the present study. Because estimates of surface runoff obtained by hydrograph analysis did not exclude the contribution of P and N forms, and sediment from stream bank erosion, it is possible that the surface-runoff plots overestimate the amounts of P, N, and sediment contributed by surface runoff to stream flow by an amount equal to that contributed by stream bank erosion.

Consequently, the surface-runoff plots established in the subcatchment appear to provide acceptable estimates of the amounts of water discharged and P, N, and sediment transported in surface runoff during both individual surface-runoff events and over a number of events. In addition, the data validate the assumptions used to estimate the contribution of surface runoff from the subcatchment to stream discharge and P, N, and sediment loading of the stream.

7.3.2.3 Estimation of the input of water, P and N forms, and sediment in subsurface runoff to the stream from field monitoring and hydrograph analysis methods. Because it was possible to estimate the annual amounts of water discharged and P, N, and sediment transported in surface and accelerated subsurface runoff in the subcatchment with some degree of reliability, the difference between the sum of these two inputs and the total amounts transported in stream flow during the year, was considered to represent
the input from subsurface runoff in the subcatchment. Remarkably similar estimates of the amounts of water discharged into the stream as subsurface flow were given by the three methods, suggesting that they each measured the same portion of stream flow within the subcatchment. There was some discrepancy, however, between the amounts of P, N, and sediment transported in subsurface runoff determined by this method and the two methods of hydrograph resolution as can be seen from the data in Table 7.3. This was most marked for particulate P and sediment, where an approximately 20-fold greater loss in the annual amounts transported were observed using field data (21.35 and 20800kg y<sup>-1</sup>, for particulate P and sediment, respectively), compared to hydrograph analysis (1.16 and 1100kg y<sup>-1</sup>, for particulate P and sediment, respectively, using Method 1). The differences between the methods were greatest during periods of high flow (July and August), where an approximately 40- and 45-fold greater amount of particulate P and sediment, respectively, was transported during the two months in subsurface runoff, obtained by difference using field data, than those measured by hydrograph analysis (Method 1). In contrast, during the months of low flow (May and September) only an approximately 3- and 5-fold greater transport of particulate P and sediment, respectively, was obtained from field data compared to hydrograph analysis (Table 7.3). Furthermore, during May and September, the estimate of the amount of DIP transported in subsurface runoff, obtained from field data (0.11kg, Table 7.3), was lower than the amount estimated from hydrograph analysis (0.21kg, by Method 1, Table 7.3). This difference in the amount of DIP transported may be attributed to P sorption by suspended particulate material in the stream. It has been suggested (Kunishi et al., 1972; Ryden et al., 1973; Gburek and Heald, 1974) that such a modification of DIP concentration by particulate material may occur during stream flow.

The difference, between the two methods, in the amounts of P forms and sediment transported in subsurface runoff can be attributed to the erosion and resuspension of stream bank and bottom sediments by stream flow, which is not included in the estimates obtained by hydrograph analysis. During the months of high stream flow, erosion and resuspension will be at a maximum. Also, grazing cattle moving in the stream channel, during this period, would further enhance the discrepancy.

Table 7.3 Amounts of water discharged and P and N forms, and sediment transported annually in subsurface runoff in the subcatchment from field monitoring and hydrograph analysis methods

	Amounts	in subsurface	runoff	as estimated by
Parameter	Hydrograph	resolution		By difference from
	Method 1	Method 2		field measurements
			- kg	
Mav				
Discharge	a 740	650		800
DIP	0.04	0.03		0.03
TDP	0.12	0.10		0.13
TP	0.15	0.14		0.16
NO.,	5.8	5.4		2.3
2 TN	7.2	6.7		2.3
Sediment	80	70		90
June				
Discharge	4150 <sup>4</sup>	4300		4860
DIP	0.30	0.25		0.34
TDP	0.45	0.37		0.53
TP	0.69	0.58		0.97
NO3	16.7	14.3		12.1
TN	20.9	18.2		14.0
Sediment	200	150		470
July				
Discharge	17700	16400		18000
DIP	0.15	0.49		0.33
TDP	0.26	0.89		1.69
ΤΡ	0.71	1.32		13.48
NO3	76.6	78.9		82.8
TN	85.9	90.4		101.6
Sediment	220	150		12600

	Amounts	in subsurface	runoff as estimated by
Parameter	Hydrograph	resolution	By difference from
	Method 1	Method 2	field measurements
			- kg
August			
Discharge	a 34400	34400	32300
DIP	0.51	0.44	1.71
TDP	0.83	1.01	2.57
TP	0.92	1.39	10.65
NOz	75.2	63.1	56.3
TN	84.7	68.6	67.6
Sediment	180	140	5400
September			
Discharge	a 4000	3600	2900
DIP	0.17	0.10	0.08
TDP	0.32	0.13	0.64
ЧР	0.67	0.33	1.65
NOz	18.9	19.9	10.2
TN	20.2	24.0	12.6
Sediment	400	260	2300
Annual tota	1		
Discharge	a 61090	60200	58900
DIP	1.17	1.31	2.49
TDP	1.98	2.50	5.56
TP	3.14	3.76	26.91
NOz	190	180	170
TN	220	210	200
Sediment	1100	780	20200

Table 7.3 (Continued)

a Discharge expressed as m<sup>3</sup>.

It is thus possible to estimate the effect of erosion and resuspension of stream bank and bottom sediments in terms of the annual amounts of P and sediment transported in stream flow as a result of these processes, by the difference between the two methods (field measurements and hydrograph analysis, Method 1, Table 7.3). Using this approach, it was calculated that there was an annual input of DIP, particulate P, TP, and sediment of 1.32, 20.19, 23.77, and 19700kg, respectively, into the subcatchment (Table 7.3), as a result of these erosion processes. ln the case of particulate P, TP, and sediment, these amounts accounted for 79, 64, and 67%, respectively, of the annual amounts transported by the stream in the subcatchment (Table 7.1). In addition, 50% of the annual DIP loading of the stream could be accounted for by inputs from the release of P from suspended and resuspended particulate material.

## 7.3.3 Contribution of the runoff types to the amounts of water discharged, and P and N forms, and sediment transported in stream flow

The change in the rate of discharge of stream flow at the two weirs and of surface and accelerated subsurface runoff in the subcatchment, along with the intensity of precipitation over the same period of time, for a typical storm event are presented in Fig. 7.1.

Surface runoff occurred shortly after the onset of rainfall (15min). Further fluctuations in precipitation intensity were quickly followed by corresponding fluctuations in the rate of discharge of surface runoff. By the time precipitation had stopped, surface runoff had virtually decreased to zero. In contrast to surface runoff, the response of accelerated subsurface runoff to fluctuations in precipitation intensity was not as rapid, and minor fluctuations in precipitation intensity did not result in a corresponding flow change. Accelerated subsurface runoff continued for a longer period of time than surface runoff.

As a result of the difference in flow paths of water as surface and subsurface runoff, stream flow responded more slowly



Fig. 7.1 Rainfall (a), stream (b, lower weir, solid line; upper weir, dashed line), accelerated subsurface (c), and surface (d) flow data from a typical storm event.

to precipitation intensity, and reached a peak after both that of surface and accelerated subsurface runoff. Due to the prolonged contribution of subsurface runoff to stream flow after precipitation has stopped, the recession limb of the stream hydrograph decreased gradually (Fig. 7.1). Peak storm flow at the upper weir preceded peak flow at the lower weir. Similar trends were observed for stream flow at the two weirs and for surface and accelerated subsurface runoff for all other events during the study year.

During the time that precipitation intensity exceeds the infiltration capacity of the soil, water moves over the surface as surface runoff. When precipitation ceases, water drains from the surface and upper few centimetres of the soil within a short period of time and the rate of surface runoff decreases dramatically. Movement of excess water in the soil profile by gravity, however, continues and a gradual recession of accelerated subsurface runoff and stream flow results. Consequently, in the event presented (Fig. 7.) a greater amount of water infiltrated the soil and emerged as accelerated subsurface runoff than flowed over the surface. It was calculated that surface runoff contributed 7% and accelerated subsurface runoff 40% of stream flow.

The amounts of water discharged, and P and N forms, and sediment transported from the subcatchment, during each month of stream flow are presented in Table 7.4. The amounts transported in surface and accelerated subsurface runoff were estimated using field measurements, as discussed previously (Section 7.3.2.1). Because the contribution of subsurface runoff was estimated from hydrograph analysis methods, the sum of the contribution of the runoff types to stream flow does not equal the total amount transported in stream flow (Table 7.4).

The amount of water discharged as subsurface runoff was greater than that discharged as surface and accelerated subsurface runoff for all months of stream flow. This was the case even though the amount of water discharged varied appreciably from month to month. Of the total surface runoff, 82% was discharged during July and August. In addition, the amount of water discharged as accelerated subsurface runoff during each month was approximately three times greater than that discharged as surface

Table 7.4 Estimated monthly inputs of water, P and N forms, and sediment from surface and accelerated subsurface runoff obtained from field measurements, and from subsurface runoff obtained from hydrograph analysis, to stream flow in the subcatchment

				Runo	ff inputs		
Parameter	Difference between		Surface	Acceler	ated subsurface	SI	ubsurface
	the two weirs (kg)	Loading	%	Loading	%	Loadin	g %
		(kg) Co	ntribution	(kg)	Contribution	(kg) (	Contribution
May							and diversion on the other strength of the str
Discharge	e <sup>a</sup> 1360	150	11	410	30	740	54
DIP	0.07	0.01	14	0.03	43	0.03	43
TDP	0.19	0.02	10	0.04	21	0.13	68
TP	0.26	0.04	15	0.06	23	0.16	62
NO <sub>3</sub>	5.7	0.1	2	3.4	60	5.8	102
TN	7.4	0.8	11	4.3	58	7.2	97
Sediment	210	20	10	100	48	80	38
June							
Discharg	e <sup>a</sup> 6330	290	5	1180	19	4150	66
DIP	0.47	0.07	15	0.06	13	0.30	64
TDP	0.69	0.08	12	0.08	12	0.45	65
TP	1.27	0.12	9	0.13	10	0.69	54
NOz	18.6	0.2	1	6.3	34	16.7	90
TN	24.2	1.0	4	9.2	38	20.9	86
Sediment	640	50	8	120	19	200	31

Table 7.4 (Continued)

		Runoff inputs							
Parameter	Difference between		Surface		ted subsurface	Subsurface			
	the two weirs (kg)	Loading	%	Loading	%	Loading	76		
		(kg) Co	ntribution	(kg) Co	ontribution	(kg) C	ontribution		
July					n a fan de ser en gemeente de fan de seren fan de seren ander ge				
Discharge	e <sup>a</sup> 30410	2330	8	10040	33	17700	58		
DIP	2.77	1.82	66	0.62	22	0.15	5		
TDP	5.74	3.14	55	0.91	16	0.26	5		
TP	20.73	4.74	23	1.50	7	0.71	3		
NOz	128.7	0.5	1	45.4	35	76.6	60		
TN	162.5	12.2	8	48.7	30	85.9	53		
Sediment	15750	1820	12	1360	9	220	1		
August									
Discharg	e <sup>a</sup> 47700	3070	6	12340	26	34400	72		
DIP	2.92	0.48	16	0.73	25	0.51	17		
TDP	4.55	0.91	20	1.07	24	0.83	18		
ΤP	14.38	1.75	12	1.97	14	0.92	6		
NOz	122.9	1.2	1	64.4	52	75.2	61		
TN	154.6	9.2	6	77.9	50	84.7	55		
Sediment	8820	1760	20	1700	19	180	2		

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				Runo	off inputs			
Parameter Difference the two we	Difference between	Surf: ce		Acceler	Accelerated subsurface		Subsurface	
	the two weirs (kg)	Loading (kg)	%	Loading (kg)	% Contribution	Loading (kg) C	% ontribution	
September								
Discharge	a 5100	510	10	1700	33	4000	78	
DIP	0.23	0.06	26	0.09	39	0.17	74	
TDP	0.83	0.07	8	0.12	14	0.32	39	
TP	2.15	0.24	11	0.16	7	0.67	31	
NO3	15.5	0.1	1	5.3	34	18.9	122	
TN	20.1	1.8	9	8.7	43	20.2	100	
Sediment	2600	150	6	170	- 7	400	15	
October								
Discharge	a 10					10	100	
DIP	0.01					0.01	100	
TDP	0.01					0.01	100	
TP	0.02					0.02	100	
NOz	1.0					1.0	100	
TN	1.4					1.4	100	
Sediment	1					1	100	

# Table 7.4 (Continued)

**a** Discharge expressed as m<sup>3</sup>.

runoff. Numerous other studies have also reported that subsurface flow (Minshall <u>et al.</u>, 1969; Johnson and Moldenhauer, 1970; Burwell <u>et al.</u>, 1976) and accelerated subsurface and subsurface runoff (Carter <u>et al.</u>, 1971; Jackson <u>et al.</u>, 1973; Burwell <u>et al.</u>, 1974), can contribute the major proportion of flow in both ephemeral and perennial streams.

The data indicate that 86% of the annual amount of water discharged as stream flow occurred in the months of July and August. In addition, the calculated mean DIP, TP, and sediment concentrations during these two months increased to 0.091, 0.681, and 518mg  $1^{-1}$ , respectively, from 0.074, 0.192, and 102mg  $1^{-1}$ , respectively. in June. Consequently, the amounts of P and N forms, and sediment transported in the three runoif types were greatest during July and August. Even though the proportion of the total stream discharge contributed by the three runoff types was similar during all months of stream flow, there was an increased contribution of P forms to stream flow from surface runoff during July (66% DIP and 22% TP), with a subsequent decrease in the proportion of subsurface runoff (5% DIP and 3% TP) compared to the other months (surface runoff contributed 14% DIP and 15% TP, and subsurface runoff 43% DIP and 62% TP of that transported in the stream in May). Furthermore, the contribution of surface runoff to the sediment loading of the stream during July and August was greater than that from accelerated subsurface runoff. During the other months of stream flow, accelerated subsurface runoff contributed a greater proportion of the sediment load of the stream than surface runoff (Table 7.4).

The increased proportion of particulate P and sediment contributed by surface runoff to the loading of the stream during July and August can be attributed to a higher rainfall intensity during this period than during the remaining months of stream flow. The precipitation intensity exceeded 2.5mm 15min<sup>-1</sup> on twelve occasions during July and August, whereas in May, June, September, and October, this value was only exceeded on three occasions. Furthermore, grazing of the subcatchment, during July caused an increase in the transport of particulate P and sediment in surface runoff (Section 4.3.3.3). A negligible proportion of the  $NO_3$  transported in stream flow was contributed by surface runoff. A slightly greater proportion of particulate N than  $NO_3$  was contributed by surface runoff to stream flow during all months, with accelerated subsurface and subsurface runoff contributing the major proportions of N forms (Table 7.4). The proportions of N forms contributed by subsurface runoff to stream flow during the months of high stream flow (July and August) were  $60\% NO_3$  and 53% TN, and  $61\% NO_3$  and 55% TN, when the major proportion of the annual surface and accelerated subsurface runoff was discharged. These proportions were lower than during the months of low stream flow (102% NO<sub>3</sub> and 97% TN in May, Table 7.4).

The data in Table 7.5 indicated that of the three runoff types, surface runoff was the main source of both dissolved (38%) and particulate P (10%) to the annual P loading of the stream. Surface runoff contributed approximately twice as much dissolved and particulate P as subsurface runoff. In fact, surface runoff contributed a remarkably similar proportion of P (35% TDP and 18% TP, Table 7.5) to that contributed by accelerated subsurface plus subsurface runoff (35% TDP and 18% TP, Table 7.5), even though surface runoff contributed only a minor proportion of the water discharged annually as stream flow (7%, Table 7.5).

The major proportion of the annual N loading of the stream was contributed by subsurface runoff (both accelerated and natural, Table 7.5). This is to be expected from the fact that  $NO_3$  can move freely within the soil in drainage waters, as discussed previously (Section 4.3.4). It has frequently been reported that the major proportion of P transported in stream flow from catchments under varied land use is contributed by surface runoff, whereas that of N is contributed by subsurface runoff (Minshall <u>et al</u>., 1969; Carter <u>et al</u>., 1971; Viets, 1971; Burwell <u>et al</u>., 1974; Baker <u>et al</u>., 1975).

#### 7.4 General Discussion

Although the amounts of P and N forms transported in stream flow from several catchments in New Zealand have been evaluated

Table 7.5 Estimated annual inputs of water, P and N forms, and sediment from surface and accelerated subsurface runoff, obtained from field measurements, and from subsurface runoff, obtained from hydrograph analysis, to stream flow in the subcatchment

		-		Runof	f inputs		
Parameter	Difference between	S	urface	Accelera	ted subsurface	Subs	urface
	the two weirs (kg)	Loading	% of	Loading	% of	Loadirg	% of
-		(kg)	difference	(kg)	difference	(kg)	difference
Discharge <sup>a</sup>	90900	6350	7	25660	28	61090	67
DIP	6.47	2.44	38	1.57	24	1.18	18
TDP	12.01	4.22	35	2.24	19	1.98	16
Particulate	P 26.79	2.67	10	1.58	6	1.16	4
TP	38.80	6.89	18	3.82	10	3.14	8
NO3	292	2	1	125	43	190	65
TN	373	25	7	149	<sup>1</sup> + O	220	59
Sediment	28020	3810	14	3450	12	1080	4

a Discharge expressed as m<sup>3</sup>.

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(Fish, 1969; Mitchell, 1971; White, 1972; McColl et al., 1975), no attempt has been made to investigate the importance of precipitation and the relative contribution of runoff types to the losses of P and N. The net loss of P forms in stream flow from the Massey subcatchment compared to the input in precipitation, was greater than that reported by Harms et al. (1974) and Olness et al. (1975) from unfertilized catchments under pasture in South Dakota and Oklahoma, respectively, and by Taylor et al. (1971) from a fertilized (16kgP ha<sup>-1</sup>) catchment under pasture and cropping in Ohio. Furthermore, overseas studies have shown that undisturbed forest catchments, having no additional input of P other than in precipitation, are conservative of P forms (Hanway and Laflen, 1974; Schreiber et al., 1976). The high net loss of P forms in stream flow from the Massey Catchment, compared to the input in precipitation probably reflects the recent addition of P fertilizer to the catchment and grazing.

Although it has frequently been suggested that stream-bank erosion may contribute significant amounts of P and sediment to stream flow (Kunishi et al., 1972; Kunkle and Comer, 1972; Ryden et al., 1973; Gourek and Heald, 1974), the data in the present study indicate that 50, 79, 64 and 67% of the DIP, particulate P, TP, and sediment, respectively, transported annually in stream flow from the subcatchment, can be attributed to an input of stream-bank and stream-bed material. The fact that 50% of the annual DIP loading of the stream could be accounted for by the release of P from resuspended and in situ particulate material, suggests that the release of P to solution from particulate material is more important than the sorption of P by particulate material. Such a process, whereby suspended particulate material can modify both the DIP and particulate P concentration in the stream by sorption and desorption of P, depending on the DIP, particulate P, and sediment concentration in the stream'at any one time, has frequently been suggested (Kunishi et al., 1972; Ryden et al., 1973; Gburek and Heald, 1974; McColl et al., 1975).

The major proportion of stream flow in the Massey catchment was contributed by subsurface flow (67% of the annual stream discharge). Minshall <u>et al.</u> (1969) observed that over a period of 25y, subsurface runoff accounted for 60% of the annual flow in

the Platte River, Wisconsin, whereas Burwell <u>et al.</u> (1976) reported that subsurface runoff contributed 88% of the annual stream flow in a catchment under pasture in Iowa. In a smaller catchment, drained by an ephemeral stream, Jackson <u>et al.</u> (1973) observed that surface runoff accounted for 80% of the total annual runoff.

Because of the interaction between particulate material and dissolved P and N in stream flow, and the settling of suspended particulate material, the amounts of particulate and dissolved P and N entering the stream in surface, accelerated subsurface, and subsurface runoff may be modified during transport to the lower weir. Consequently, estimates of the proportion of particulate and dissolved P and N, contributed by the three runoff types to the stream loading in the subcatchment, will be less reliable than those of TP and TN.

Because of the differing soil P and N retention capacities, subsurface runoff contributed the major proportion of N forms transported annually in stream flow (65 and 59% of the  $NO_{x}$  and TN, respectively). In contrast, much smaller proportions of P forms (17 and 8% of the TDP and TP, respectively) were contributed by subsurface runoff. Surface runoff contributed the major proportion of P forms (35 and 18% of the TDP and TP, respectively) compared to the other runoff types. Similar trends have been observed by Burwell et al. (1974) in a cropped, level-terraced catchment in Iowa, where 78 and 18% of the  $\mathrm{NO}_3$  and DIP, respectively, discharged in stream flow was contributed by subsurface runoff. Jackson et al. (1973) found that 99% of the  $NO_{z}$  transported in total runoff from a catchment in Georgia, planted in corn, was in the form of subsurface flow, whereas in the Platte River, Wisconsin, subsurface runoff contributed only 10% of the TP lost in surface runoff annually (Minshall et al., 1969). Minshall et al. (1969), however presented data showing opposite trends for N, with subsurface runoff only contributing 25% of the  $\mathrm{NO}_3$  loading of the stream. Thus, it appears from the data obtained in the present study, and from the literature, that it is dangerous to generalise about the relative importance of the runoff types to the P and N loading of a stream by the extrapolation of data from one catchment to another.

# SECTION 8

### INTERACTION OF PHOSPHORUS SOURCES IN SURFACE RUNOFF AND STREAM FLOW

#### 8.1 Introduction

The potential sources of sediment transported in stream flow are surface soil (Munn et al., 1973), streambank material (Kunkle and Comer, 1972; Kunishi et al., 1972), and earthworm casts deposited on the soil surface. The deposition at certain times of the year, of large numbers of earthworm casts on the soil surface in the catchment, and their disappearance after heavy rainfall, suggests that casts could be an important source of both particulate material and P to surface runoff. Because earthworm casts may also be enriched in "available" P (Barley, 1961; Gupta and Sakal, 1967; Graff, 1970; Vimmerstedt and Finney, 1973), it is possible that they may be a significant potential source of both particulate and dissolved P to runoff water. No work has been reported, however, on the chemical nature of P in casts. Although large amounts of soil can be brought to the surface in the form of earthworm casts, studies of the seasonal variation of casting activity have largely been based on earthworm numbers (Nielson, 1953; Waters, 1955; Nielson and Hole, 1964; Zajonc, 1970). Less attention has been directed towards surface cast production as an index of earthworm activity.

In previous sections, earthworm casts were regarded, for convenience, as soil material in the discussion of their effect on P levels in surface runoff (Section 4.3.3.1). Because surface casts may behave differently from underlying soil materials, in terms of the uptake and release of inorganic P (IP), cast material will subsequently be discussed separately.

Based on laboratory sorption studies it has been suggested that suspended stream particulate material can modify DIP concentrations (Kunishi <u>et al.</u>, 1972). The high levels of added inorganic P and narrow solution:solid ratios used in many studies, however, probably do not adequately simulate the stream environment (Ryden <u>et al.</u>, 1972a, b). Preliminary laboratory data obtained with the same systems as those used for P sorption studies, and theoretical considerations of the interaction of  $NO_3$  with soil materials, indicated that negligible amounts of  $NO_3$  would be removed from solution by soil materials. Consequently, any modifications in  $NO_3$  concentration during  $NO_3$  movement in the catchment are probably a result of biological transformations. Thus, only data for the uptake and release of P are presented in this section.

The aims of this part of the study were to investigate (i) the seasonal variations in surface-cast production by earthworms and the amounts and release to solution of P forms in earthworm casts and underlying soil materials, (ii) the chemical nature of IP in casts, (iii) the ability of various potential source materials, which contribute to suspended stream and surface-runoff sediment, to modify DIP concentrations in simulated systems, and (iv) the ability of these laboratory systems to adequately simulate the field situation, by comparison of data obtained from laboratory studies with data obtained from field monitoring studies under various flow conditions.

#### 8.2 Materials and Methods

#### 8.2.1 Materials

Surface casts of earthworms (dominantly <u>Allolobophora</u> <u>caliginosa</u>) were collected at weekly intervals from duplicate  $900 \text{ cm}^2$  plots on each of 6 and  $13^\circ$  slopes in the catchment. At the same time, approximately 50g of freshly-deposited casts and underlying soil material (0-10cm) were collected from an adjacent area, sieved (< 2mm), and frozen.

In addition, casts were removed and discarded from the soil surface at several sites adjacent to the undrained surface-runoff plots in the subcatchment. Casts deposited in the 14h following clearance of the sites were collected, bulked, sieved (< 2mm), and frozen. Soil materials were collected at depths of 0-5, 8-12, and 18-22cm underlying these sites and treated similarly.

Further soil samples were collected from the subcatchment for simulated stream studies. Surface soil was sampled at a depth of 0-5cm. Stream-bank material was also sampled at a depth of 10-20cm, discarding the outer 1cm of material, where the bank was exposed when the stream was not flowing. The soils were passed through a 2-mm sieve, air dried, and stored for later use.

A 22-1 sample of stream water, which contained a high suspended sediment concentration, was collected at peak flow during a highintensity storm. Similarly, a 22-1 sample of surface runoff was collected from one of the runoff plots in the study area at maximum flow. In each case, the sediment was concentrated by continuous centrifugation at 15,000rev. min<sup>-1</sup>, using a Sorvall RC-2B with the inflow of the suspension to the centrifuge controlled so that the outflow was sediment free. The concentrated sediment was stored as a sludge at  $4^{\circ}$ C for later use.

#### 8.2.2 Methods

A sub-sample of casts collected from the field plots was dried at  $105^{\circ}$ C and weighed to determine the weekly production of casts, on an oven-dried basis. Sub-samples of underlying soil and casts from the adjacent area were treated similarly for moisture content determination. Particle-size distribution was determined by sieving or decantation (Jackson, 1968) following water dispersion of samples on an end-over-end shaker for 24h at 23°C. In addition, the amounts of < 4µm material were determined by centrifugation following dispersion of separate samples with sodium hexametaphosphate. Samples of the < 30µm fraction of surface soil and cast material were isolated by settling and decantation (Jackson, 1968) of the whole sample, dispersed by end-over-end shaking in distilled water for 1h.

Total P (TP) and total inorganic P (TIP) in whole samples of casts, soils, and sediments, and in particle-size separates, obtained by water dispersion, were determined by extraction of ignited and non-ignited samples with 0.5M H<sub>2</sub>SO<sub>4</sub> (Walker and Adams, 1958), organic P (TOP) being calculated by difference.

The release of IP and organic P (OP) by casts and surface soil to  $0.1\underline{M}$  NaCl and the removal of IP from  $0.1\underline{M}$  NaCl, distilled water, and filtered stream water containing  $0.1 \text{mgP} \text{ l}^{-1}$  at a solution:solid ratio of 400:1 over 24h was also determined with a view to establishing a suitable solution phase for simulated system studies. Similarly, the release of IP and OP to  $0.1\underline{M}$  NaCl and the removal of IP from  $0.1\underline{M}$  NaCl containing  $1 \text{mgP} \text{ l}^{-1}$  were used to investigate the method of storage of earthworm casts. Samples of recently-deposited (<14h) casts were retained in a fresh condition (untreated), frozen and then thawed, or air dried. Samples were shaken at a solution:solid ratio of 400:1 for varying periods of time on an end-over-end shaker at 23°C and the release of P investigated.

Seasonal variation in the release of IP and OP from freshlydeposited casts (<14h) and underlying soil to 0.1M NaCl was determined by shaking thawed samples at a solution:solid ratio of 400:1 for 24h on an end-over-end shaker at  $23^{\circ}C$ .

The amounts of exchangeable P in casts and underlying soil were determined as a function of time of shaking following the addition of 2.0µCi of carrier-free <sup>32</sup>P. In addition, the amounts of rapidly-exchangeable P(1h) in casts and surface soil were determined by shaking these materials with 0.1M NaCl at a solution: solid ratio of 400:1. After the initial 24-h shaking period, 2µCi of carrier-free <sup>32</sup>P was added and shaking continued for a further 1h. Solution <sup>32</sup>P concentration was determined by adding a 3-ml aliquot of filtered supernatant to 10ml of Triton-toluene scintillation cocktail for counting with a Packard Tricarb scintillation spectrometer. The Triton cocktail was prepared by dissolving 4g of PPO and 0.1g of MP\_POPOP in 667ml of toluene and then adding 333ml of Triton X-100. Blank aqueous extracts of each soil material were used for quench correction. The amounts of exchangeable P for each time of shaking were determined from isotope dilution theory.

The release of IP and OP from freshly-deposited, unfrozen casts and surface soil incubated at  $16^{\circ}C$  and  $4^{\circ}C$  for varying periods of time, was evaluated by extraction (1h) with 0.1<u>M</u> NaCl at a solution: soil ratio of 400:1. At each time of sampling,

phosphatase activity was determined on separate samples by the colorimetric estimation of the p-nitrophenol released from p-nitrophenol phosphate substrate, when 1g of soil material was incubated with 5ml of buffered (pH 6.5) sodium p-nitrophenyl phosphate solution and 0.25ml toluene at  $37^{\circ}$ C for 1h. The p-nitrophenol released was extracted by 1ml of 0.5M CaCl<sub>2</sub> and 4ml of 0.5M NaOH. The stable colour developed was measured spectro-photometrically at 410µm (Tabatabai and Bremner, 1969).

To investigate the chemical nature of additional IP in casts, the release of IP from casts and underlying soil to 0.5<u>M</u> NaHCO<sub>3</sub> (pH 8.5), at a solution: solid ratio of 50:1, during 30min (Olsen <u>et al.</u>, 1954), and in two sequential 1-h extractions with water (Ryden and Syers, 1977b) at a solution: solid ratio of 400:1, was also evaluated.

In order to study the uptake and release of IP under conditions simulating the runoff environment, earthworm casts, stream-bank material, surface soil, surface-runoff sediment, and stream sediment were shaken in  $0.1\underline{M}$  NaCl containing varying levels of added IP, at varying solution:solid ratios and for different periods of time on an end-over-end shaker at  $23^{\circ}$ C. In the case of casts and surface-runoff and stream sediment, equivalent weights of oven-dry material were used. The solution:solid ratios and added IP levels used in all cases approximated the maximum and minimum values obtained for DIP concentrations in surface, accelerated subsurface, and subsurface runoff and stream water presented in Sections 4.3.1, 5.3.1, 6.3.2.1, and 6.3.3.1, respectively.

#### 8.3 Results and Discussion

8.3.1 Earthworm casts

8.3.1.1 <u>Cast production</u>. The quantity of surface casts produced showed marked changes during 1975 (Fig. 8.1a). Between October and May, cast production was negligible. A sharp increase in cast production was observed in May and this reached a maximum in early June. Subsequently, cast production decreased steadily to a minimum in mid-August, after which time a secondary



Fig. 8.1 Seasonal production of casts (oven-dried basis) on 6 and 13<sup>°</sup> slopes (a), and seasonal variation in soil moisture (A) and temperature (B) in the top 10cm of underlying soil (b).

peak was observed. Cast production on the  $6^{\circ}$  and  $13^{\circ}$  slopes was remarkably similar and thus no attempt has been made in Fig. 8.1a to distinguish between the data for each slope. The total quantity of casts produced during the study year (1975) was 25tonnes ha<sup>-1</sup>. This value is similar to that (30tonnes ha<sup>-1</sup> y<sup>-1</sup>) estimated for the same experimental plots in the previous year. Guild (1955) gave an estimate of surface cast production of 27tonnes ha<sup>-1</sup> y<sup>-1</sup>, a value lower than that (up to 62tonnes ha<sup>-1</sup> y<sup>-1</sup>) reported by Evans (1948) for old pasture at Rothamsted.

Seasonal variations in the gravimetric moisture content and temperature of the surface soil are shown in Fig. 8.1b. The data indicate that in the warmer months preceding May, soil conditions were too dry for earthworm activity at the soil surface. As soil moisture levels increased during May, however, surface cast production also increased. Maximum cast production occurred in early June and this coincided with high, although slightly declining soil temperature and adequate soil moisture. Although soil moisture levels remained high during late June and July, lower soil temperatures appeared to limit cast production. When soil temperature increased in August, an increase in cast production was observed. The generally higher soil temperatures and lower soil moisture contents between October and the following April were associated with essentially zero cast production during this period.

The data suggest that seasonal variations in soil moisture and temperature resulted in optimum conditions for surface cast production in early June, but as soil temperature decreased, cast production also decreased. Similar observations have been made by Gerard (1967), who reported that casting activity was affected by soil temperature when soil moisture levels were at field capacity. This may result from a reduction in motor activity of the earthworm, counteracting the lethal effect of soil temperature extremes on the earthworm. Variation in the quantity of food available to the earthworm, such as decomposing roots (Lindquist, 1941) and plant litter, could also be expected to influence earthworm activity and cast production (Waters, 1955; Barley, 1961). Although no quantitative data are available on the amount of plant debris available throughout the year in the study area, this appears to be at a maximum in the May-June period. Consequently, soil temperature and moisture will both directly (Evans and Guild, 1947; Lee, 1959) and indirectly affect cast production.

8.3.1.2 Particle-size distribution and phosphorus content of casts and underlying soil. Earthworm casts contained a higher proportion of finer particles than underlying surface soil (Table 8.1). The proportion of the finest fraction recovered (< 4µm) following water dispersion increased from 6% in the surface soil (0-5cm) to 20% in the casts. The probability of increased aggregate formation and water stability in casts (Dutt, 1948), due to the production of mucilages (Russell, 1973) or to the presence of fungal hyphae (Parle, 1963), was investigated using sodium hexametaphosphate as the dispersant. The proportion of the <  $4 \mu m$ fraction recovered from casts dispersed in this way increased to 32%, whereas the corresponding value for surface soil was 13%. Although dispersion in water simulates the surface runoff environment more closely than does dispersion in sodium hexametaphosphate, the former procedure underestimates the enrichment of  $< 4 \, \mu m$  material in casts. The higher proportion of < 4µm material in casts may be attributed to the selective feeding by the earthworm on finer soil particles (Russell, 1973), and the mechanical breakdown of particles by the grinding action of the earthworm's gut (Basalik, 1913). Blank and Giesecke (1924, cited by Barley, 1961) showed that after 2y in a controlled pot experiment the amount of < 2µm particles in a loam soil increased significantly, whereas the proportion of  $< 60 \mu m$  material decreased.

The amounts of TIP and TOP in casts collected in early May of the first year of study (1974) were considerably greater than those in underlying soil collected at the same time (whole sample, Table 8.2). The enrichment of TIP in the casts was restricted to the finest (20-4 and < 4 $\mu$ m) and coarsest fractions (2000-250 $\mu$ m) separated by water dispersion, whereas only the finer fractions were enriched in TOP.

Although the proportion of the <20µm fraction in casts and underlying soil (all depths) was approximately similar (Table 8.1), the amounts of TIP and TOP in this fraction separated from the casts were appreciably higher than in those separated from under-

Particle size	Particle size distribution (%) of							
fraction (µm)			Soil at					
	Casts	0-5	8-12	18-22	Stream-bark material	Surface-runoff		
		(cm)	(cm)	(cm)	(10-20cm)	sediment		
2000-250	4	17	12	6	6	1		
250-63	20	32	20	15	32	12		
63-20	34	27	37	39	31	17		
20-4	22	18	19	24	19	36		
< 4	20(32) <sup>a</sup>	6(13)	12(22)	- 16(24)	12	34		

Table 8.1 Particle-size distribution of water-dispersed samples of casts, underlying soil, stream-bank material, and surface-runoff sediment

a Numbers in parentheses are for samples dispersed with sodium hexametaphosphate.

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Particle size	Inorganic P (µg g <sup>-1</sup> ) in					Organic $P(\mu g g^{-1})$ in			
fraction (µm)		Sc	oil at	(cm)			So	il at	(cm)
,	Casts	0-5	8-12	18-22		Casts	0-5	12	18-22
Whole sample	461	257	137	80		352	246	213	89
2000-250	571	396	215	155		405	682	172	80
250-63	165	206	114	43		159	206	94	33
63-20	98	91	58	28		117	97	69	24
20-4	583	265	139	109		864	451	210	98
< 4	971	427	200	69		1370	731	310	173

Table 8.2 Amounts of inorganic and organic P in whole samples and in particle-size separates of casts and underlying soil obtained by water dispersion

lying soil (Table 8.2). This suggests incorporation of P into casts during passage of soil, plant material, and possibly dung through the earthworm. For fractions coarser than 20µm, there was less difference between the TIP and TOP contents of casts and underlying soil materials.

During the period of surface casting in the second year of study (1975), the TP content of the casts remained rather constant (Fig. 8.2). In contrast, the TIP content of casts gradually decreased from a maximum in April and May to a minimum in August. Consequently, TOP levels showed a reverse trend over the same period. Variations in the amounts of TIP and TOP in the surface soil were very much less pronounced than in the casts, indicating that seasonal changes in the distribution of P forms in the underlying soil could not explain those obtained for the casts.

The progressive decrease in the level of TIP and the corresponding increase in the level of TOP in casts in the May-August period and the subsequent increase in the proportion of inorganic P, with increasing soil temperature in August and September (Fig. 8.2), may be attributed to the effect of temperature on phosphatase enzyme activity. It is well established that enzyme catalysed reactions are temperature dependent (Skujins, 1967). Thus, the decrease in TIP and increase in TOP from mid-May is probably due to a reduction in the conversion of TOP to TIP, because of lower microbial and phosphatase enzyme activity as a result of declining soil temperature (Fig. 8.1b).

Although significant quantities of TIP (9kg ha<sup>-1</sup>) and TOP  $(13kg ha^{-1})$ , respectively, were accumulated in surface casts during the study year, it must be emphasised that the TP content of the casts cannot be greater than the TP content of plant litter. It has recently been shown that the major proportion (59-83%) of TP in litter from New Zealand pastures is present in the inorganic form (Gillingham <u>et al.</u>, 1976). As the major proportion of P in the casts is organic, there may, in fact, be an increased conversion of IP to OP as a result of passage of litter, dung, and soil through the earthworm.



Fig. 8.2 Seasonal variation in amounts of total P in casts (A), of organic P in casts (B) and in underlying (0-10cm) soil (D), and of total inorganic P in casts (C) and in underlying (0-10cm) soil (E).

#### 8.3.1.3 Release and uptake of phosphorus by casts

Preliminary studies indicated that the P release and and soil. uptake characteristics of freshly-collected casts changed with time, thus methods of storing cast materials were evaluated. A bulked sample of casts, stored in a manner which would cause minimal changes in P release and uptake characteristics, was required for the experiments described subsequently. Of the two methods investigated, freezing immediately after collection and thawing prior to use was found to give comparable results, in terms of P release and uptake, to fresh casts (Table 8.3). Consequently, a bulk sample of freshly-collected casts was frozen and sub-samples were allowed to thaw for 24h as required before analysis. Speir and Ross, (1975) have indicated that storage of field-moist samples at 4°C is preferable to air-drying for retaining phosphatase activity. As discussed later, the time of storage of non-frozen samples at room temperature has a considerable bearing on the amounts of IP and OP released to solution.

Because the intention was to study the uptake and release of IP by cast material under conditions simulating the runoff environment, it was necessary to use a medium which was reasonably similar to that of filtered surface runoff or stream water. The use of filtered surface runoff or stream water as the support medium presented problems in maintaining a constant chemical composition, both from the standpoint of storage over long periods of time and the variation in samples taken at different times of the year. It was observed that both earthworm casts and surface soil released very similar amounts of IP and OP to 0.1M NaCl and filtered stream water (Table 8.4). The use of distilled water as the support medium resulted in a greater release of IP and OP, and lower removal of IP from solution by casts and surface soil than from filtered stream water (Table 8.4). This is consistent with the effect of ionic strength on the sorption (Ryden et al., 1977b) and desorption (Ryden and Syers, 1977a) of P by soils. Therefore, 0.1M NaCl was used as the support medium in subsequent simulated stream and runoff studies.

Although the TIP content of casts (whole samples) collected in early May, was approximately twice that of the underlying surface soil (Table 8.2), the release of IP from the same casts to

Table 8.3 Release of inorganic and organic P, and uptake of inorganic P by casts from 0.1<u>M</u> NaCl at a solution: solid ratio of 400:1 during 24h as influenced by method of storage

Storage	Releas	e of	Uptake (µg g <sup>-1</sup> )		
method	Inorganic P (µg g <sup>-1</sup> )	Organic P (µg g <sup>-1</sup> )	of inorganic P <sup>a</sup>		
Untreated (fresh)	31.4	16.9	36.9		
Frozen-thawed	31.8	16.2	38.8		
Air dried	28.4	14.4	54.6		

<sup>a</sup> Added P concentration was 400 $\mu$ gP g<sup>-1</sup>, i.e., 1mgP l<sup>-1</sup>.

Table 8.4 Release of inorganic and organic P, and uptake of inorganic P by fresh casts and surface soil from 0.1<u>M</u> NaCl, distilled water, and filtered stream water at a solution:solid ratio of 400:1 during 24h

Support	Releas	e of	Uptake (µg g <sup>-1</sup> )		
medium I	norganic P (µg g <sup>-1</sup> )	Organic P (µg g <sup>-1</sup> )	of inorganic P <sup>a</sup>		
Casts					
0.1 M NaCl	31.5	17.0	36.7		
Distilled water	35.4	19.7	31.3		
Filtered-stream wate	r 32.6	17.6	34.9		
Soil Surface (O-5cm)					
O.1M NaCl	8.3	9.3	61.3		
Distilled water	9.4	10.1	57.3		
Filtered-stream wate	r 8.6	9.2	60.1		

<sup>a</sup> Added P concentration was 400µgP g<sup>-1</sup>, i.e., 1<sub>mgP l<sup>-1</sup></sub>.

 $0.1\underline{M}$  NaCl after 24h (32.1µgP g<sup>-1</sup>, lower half, Fig. 8.3) was approximately four times greater than that from the surface soil (8.0ugP g<sup>-1</sup>, lower half Fig. 8.3). More than half of this inorganic P was released from the casts in less than 1h (Fig. 8.3). In contrast, casts removed less added IP from solution than underlying surface soil (upper part of Fig. 8.3). The difference between the amounts of added IP removed from solution by surface soil and casts was approximately equal to the difference between the amounts of IP released to solution by the materials for times of shaking in excess of 8h. The greater release of IP (Fig. 8.3) and higher proportion of < 4µm material (Table 8.1) in casts relative to underlying soil, indicated that the difference in T1P and T0P distribution between casts and underlying soil material (Table 8.2), is not a direct result of material from lower depths being brought to the surface by the earthworm.

As the proportion of TIP and TOP in the casts varied during the casting period (Fig. 8.2), the amounts of inorganic and organic P released to solution may also be expected to vary. It was observed that casts deposited in April, May, and most of June, released appreciably more IP than OP to 0.1M NaCl (Fig. 8.4a). The difference between the amounts of IP and OP released to solution increased until the beginning of June, after which time progressively less IP and more OP was released to solution. The release of OP reached a maximum value in mid-July. It is of interest that the amounts of rapidly exchangeable IP in casts (Fig. 8.4b) showed similar trends to the release of TP (Fig. 8.4a). The amounts of rapidly exchangeable P increased to a maximum in early June and then decreased gradually and remained fairly constant for the remainder of the casting season.

In contrast, the amounts of IP and OP (Fig. 8.4a) released to  $0.1\underline{M}$  NaCl and of rapidly exchangeable P in the surface soil (Fig. 8.4b), were very much lower than those released from casts and were essentially constant throughout the year.

Preliminary studies indicated that the relative proportion of IP released to solution by freshly-deposited, unfrozen casts increased with temperature and time of storage. Subsequently, the release of inorganic and organic P from fresh casts and surface









Fig. 8.4

Seasonal variation in (a) the release to 0.1<u>M</u> NaCl of inorganic P from casts (A) and underlying soil (0-10cm) soil (C), and of organic P from casts (B) during 1h at a solution:solid ratio of 400:1, and (b) the amounts of rapidly-exchangeable (1h) inorganic P in casts (A) and in underlying (0-10cm) soil (B). soil to  $0.1\underline{M}$  NaCl,at a solution:solid ratio of 400:1,was evaluated as a function of temperature of incubation at  $16^{\circ}$ C and  $4^{\circ}$ C. It was observed that the amount of IP released from casts incubated at  $16^{\circ}$ C was greater than for a corresponding incubation at  $4^{\circ}$ C (Fig. 8.5). Also phosphatase activity in casts incubated at  $4^{\circ}$ C, as indicated by the release of p-nitrophenol,was appreciably lower than that in the same material incubated at  $16^{\circ}$ C. In contrast, the release of IP and phosphatase activity in surface soil was little affected by temperature of incubation and, therefore, the data are not presented.

The effect of time of incubation on the release of IP and OP from fresh casts and surface soil to 0.1M NaCl at a solution:solid ratio of 50:1 was evaluated at an incubation temperature of  $16^{\circ}C$ . The release of total P (IP plus OP) from fresh casts to solution (in 24-h extractions) was essentially constant with time of incubation. In contrast, the release of IP from casts increased from approximately  $16\mu gP g^{-1}$  to  $50\mu gP g^{-1}$  after incubation at  $16^{\circ}C$  for 5 days (Fig. 8.6). Organic P release decreased systematically from a maximum value of  $59\mu gP g^{-1}$ , mirroring the increase in IP release. It is significant that all of the IP generated in the casts during incubation is released to solution. Phosphatase activity increased rapidly to a maximum following incubation for 18h, when the amount of OP released to solution had decreased from 59 to  $21 \mu g F g^{-1}$ . It is of interest that this maximum release of p-nitrophenol preceded the maximum value for inorganic P release. The data suggest, therefore, that the conversion of OP to IP in the casts is the result of phosphatase enzyme activity. Although the same trends were observed for the release of IP, OP, and p-nitrophenol from surface soil, they were of appreciably lower magnitude (Fig. 8.6b) and could not, therefore, account for the differences observed with cast material.

Consequently, the potential of casts for the DIP enrichment of surface runoff is expected to be influenced by the elapse-time between cast deposition and the onset of a rainfall event resulting in the release of IP. Under rainfall conditions where the infiltration rate is not exceeded, however, IP could be leached from the casts into the underlying soil. In such situations, surface casts may represent a significant source of directly-available P



Fig. 8.5 Release of inorganic P to 0.1M NaCl from casts incubated at  $16^{\circ}C$  (A) and  $4^{\circ}C$  (B), and release of p-nitrophenol from casts incubated at  $16^{\circ}C$  (C) and  $4^{\circ}C$  (D) as a function of time of incubation.



Fig. 8.6 Release of total P (A), inorganic P (B), and organic P (D) to 0.1<u>M</u> NaCl, and p-nitrophenol released (C) as a function of time of incubation at 16<sup>o</sup>C of fresh casts (a) and surface soil (b) at a solution:solid ratio of 50:1.
for plant growth.

The fact that the seasonal variations in the release of P to 0.1M NaCl (Fig. 8.4a) and the amounts of rapidly exchangeable P in the casts (Fig. 8.4b) were more closely related to cast production (Fig. 8.1) than to changes in the relative amounts of IP and OP in the casts (Fig. 8.2), indicated a varying mobility of P which is largely independent of the amount of P present. The data indicate that the impact of earthworm casting on P cycling will be greatest during May and June. Although phosphatase enzyme activity did not vary during the casting period, temperature had a pronounced effect on phosphatase activity in freshly-deposited The amounts of IP released to solution, however, were casts. very much less influenced by the temperature of incubation. Thus, it would appear that temperature differences, alone, do not explain the seasonal variation in the amounts of P released to solution (Fig. 8.4a). Significantly, neither the seasonal changes in the relative amounts of IP and OP in casts, nor their release to solution, can be attributed to similar seasonal variations in these parameters in the underlying soil.

8.3.1.4 Nature of inorganic phosphorus in casts.

Information relating to the nature of the IP in casts was obtained from further chemical extraction and isotopic exchangeability studies. Sequential extractions of casts and underlying soil materials with 0.1<u>M</u> NaCl provided additional information on the kinetics of release of IP. In the first 15-min extraction period, casts released 9µgP g<sup>-1</sup> (Fig. 8.7), whereas the underlying soil surface material released 2.1µgP g<sup>-1</sup> (Fig. 8.7). Appreciably smaller amounts of IP were released from the soil at 8-12 and 18-22cm (1.7 and 1.2µgP g<sup>-1</sup>, respectively) during the first 15-min extraction period. During eight successive extractions over 3h, casts released  $62\mu$ gP g<sup>-1</sup>, whereas the surface soil only released  $13\mu$ gP g<sup>-1</sup>.

The rate of release of IP from the casts was initially greater than that from underlying soil materials. The rate of P release from the casts, however, gradually decreased and was similar to that from underlying soil materials after approximately 2h. The



Fig. 8.7 Rate of release of inorganic P to 0.1<u>M</u> NaCl by casts (A) and underlying soil at 0-5cm (B), 8-12cm (C), and 18-22cm (D) plotted against cumulative extraction time at a solution:solid ratio of 400:1.

rate of release of IP from the three soil materials was similar. When the rate of IP release was plotted against cumulative release (Fig. 8.8), it was possible to identify three apparently distinct reactions for the release of IP from casts and two for the underlying soils. With the exception of the first reaction relating to a rapid release of IP from the casts, the slopes for the four materials were similar, suggesting similar release mechanisms.

The fact that casts, but not underlying soil, contain a pool of loosely-bound inorganic P, which is readily released to solution, implies a greater isotopic exchangeability of the inorganic P which is incorporated into the casts. Although the amount of inorganic P in the casts was approximately twice that present in the surface soil (Table 8.2), the amount of exchangeable P was three times greater (90 and 30µgP  $g^{-1}$ , respectively) for the two materials when a 6-day period was used for exchange (Fig. 8.9). Thus, the IP in the casts has a higher exchangeability than that in the surface soil. In contrast, soil materials at 8-12 and 18-22cm contained very much lower amounts of exchangeable P. In addition, the amounts of rapidly-exchangeable (1h) IP in casts were appreciably greater than in underlying soil (Fig. 8.4).

Barley (1961) considered that the increase in pH of earthworm casts was responsible for the higher "solubility" of nutrients in casts. The pH of casts used in the present study, however, was only slightly greater than that of the surface soil (6.22 and 5.86, respectively). It is generally accepted that pH has only a small effect on P sorption by soils in the range of 4 to 6.5 (Barrow, 1970; Ryden and Syers, 1975). Consequently, there is little reason to believe that a pH increase of 0.36 would dramatically affect the desorption of P. The greater release of P from casts is more readily explained in terms of the additional P incorporated into casts having a lower binding energy, as indicated by a higher isotopic exchangeability. Inorganic P sorbed with a lower binding energy is more readily desorbed (Ryden and Syers, 1977a).

The amounts of IP extracted from casts at varying times of the year by the Olsen bicarbonate reagent  $(0.5M \text{ NaHCO}_3)$ , water, and 0.1M NaCl were very closely related (Fig. 8.10). More IP



Fig. 8.8 Rate of release of inorganic P to 0.1<u>M</u> NaCl by casts (A) and underlying soil at 0-5cm (B), 8-12cm (C), and 18-22cm (D) plotted against cumulative release at a solution: solid ratio of 400:1. The scale on the left-hand y axis relates to casts (A) and that on the right-hand y axis relates to underlying soil (B, C, D).



Fig. 8.9 Amounts of isotopically exchangeable P in casts (A) and underlying soil at 0-5cm (B), 8-12cm (C), and 18-22cm (D) as a function of time allowed for exchange at a solution:solid ratio of 400:1. The scale on the lefthand y axis relates to casts (A) and 0-5cm soil (B), that on the right-hand y axis to soil at 8-12 (C) and 18-22cm (D).



Fig. 8.10 Relationship between amounts of inorganic P extracted by 0.5<u>M</u> NaHCO<sub>3</sub> in 30min (A) or by two sequential 1-h extractions with water (B) and that extracted by 0.1<u>M</u> NaCl in 1h from freshly-deposited casts collected at different times of the year. In each case the solution: soil ratio used was 400:1.

was extracted by NaHCO, than by water from each sample of casts. Also very much more IP was extracted by NaHCO<sub>3</sub> than by 0.1M NaCl. For example, the amounts of 1P extracted from a sample of casts collected in early June, 1975 by 0.5M NaHCO<sub>3</sub>, water, and 0.1M NaCl were 157, 128, and 33 $\mu$ g g<sup>-1</sup>, respectively. The very much greater amounts of IP extracted from casts by 0.5M NaHCO<sub>3</sub> than by 0.1M NaCl (Fig. 8.10) is attributed to the effect of hydroxyl ions on the desorption of P. The pH of the 0.5M NaHCO<sub>3</sub> reagent is 8.5 and this is appreciably greater than that of a suspension of casts in 0.1M NaCl. Significantly, less IP was extracted by water than by 0.5M NaHCO<sub>3</sub> and this difference (approximately 30µg g<sup>-1</sup>) was essentially constant throughout the year. Ryden and Syers (1977b) have demonstrated that water quantitatively removes inorganic P from soils which is sorbed by a more-physical type of sorption, whereas IP which is chemisorbed is not extracted. Consequently, 0.5M NaHCO<sub>3</sub> removed approximately 30µg g<sup>-1</sup> of chemisorbed P from casts. This chemisorbed P would have a lower potential plant availability than the more-physically sorbed P.

The very much lower amounts of IP extracted from casts by O.1<u>M</u> NaCl than by water is consistent with the potential-determining mechanism involved in the more-physical type of sorption, which is influenced by ionic strength (Ryden <u>et al</u>., 1977b). A progressive decrease in the ionic strength of NaCl used as an extractant resulted in a corresponding increase in the amount of IP extracted from soils (Ryden and Syers, 1977b). Because waterextractable IP accounts for approximately 90% of the difference between TIP in the casts and underlying soil, essentially all of the additional IP in the casts is sorbed by a more-physical sorption type. The high isotopic exchangeability of P present in casts is also consistent with this observation because a high isotopic exchangeability is characteristic of more-physically sorbed P (Ryden and Syers, 1977a).

8.3.1.5 <u>Implications</u>. The implications of the results obtained for the particle-size distribution, the forms and amounts of P, the P release and uptake characteristics, and the nature of P in earthworm casts, to the P enrichment of surface runoff waters and plant nutrient availability, are several. Casts deposited on

the soil surface are more readily transported in surface runoff than is underlying soil. The higher proportion in casts of finer particles (Table 8.1), which are transported preferentially in surface runoff (Ryden <u>et al.</u>, 1973), coupled with their higher P content (Table 8.2), accentuate the "enrichment ratio" effect for particulate P in surface runoff (Massey and Jackson, 1952; Stoltenberg and White, 1953). In addition, the finding that casts release appreciable quantities of IP and OP to solution and remove less IP from solution (Fig. 8.3) than underlying soil materials, suggests that casts may enhance the dissolved P levels in surface runoff.

Russell (1973) has emphasised that the consequence of earthworm casting on the distribution of plant nutrients in the soil has received little attention. The data presented, however, suggest that a high proportion of the IP in casts is available to plants following desorption. Because of the rapid release of IP from casts to solution, the rate of desorption is not expected to be a limiting step in determining the plant availability of IP in casts. It must be noted, however, that the considerable variation in the relative proportions of IP and OP in casts during the period of casting activity, indicate that adequate consideration should be given to the time of sampling in studies relating to P forms in casts.

Surface casting activity in the study area occurs during the autumn to spring period. Significantly, this coincides with the the period when surface runoff occurs, namely in the months of April to September. In addition, the fact that peak surface cast production (Fig. 8.1a) coincides with maximum release of IP to solution (Fig. 8.4a), suggests that the importance of surfacecasting earthworms in the cycling of P is greatest at this time. This is substantiated by the fact that both the mean DIP and sediment concentrations (total load divided by total flow) of individual surface-runoff events from unfertilized, ungrazed plots, during the casting period, showed similar seasonal variations to cast production (Fig. 4.6).

Further evidence for the contribution of casts to the loading of particulate material in surface runoff, and by inference to the loading of particulate P, has been obtained from the similarity in particle-size analyses of discharge collected from surface-runoff plots and of earthworm casts. The major proportion (80%) of particulate material carried in surface runoff was less than 63µm (Table 8.1), as was the case for surface-cast material (76%) in comparison to underlying soil material, where only 51% was less than 63µm.

Although the data indicate that surface-casting earthworms may be a potentially important source of both particulate material and particulate P in surface runoff, the accelerated incorporation of plant litter into the soil by earthworms may remove a potentially greater source of DIP to surface runoff than that present in cast material. Further work presently being carried out at Massey University, suggests that this in fact may be the case. Furthermore, Stockdill (1966) has shown that in the absence of earthworms, a thick mat of plant litter can build up at the surface of soils under pasture in Otago, consequently reducing infiltration rates. The major role of surface-casting earthworms in decomposing and mixing plant material with the soil, thus accelerating the rate of cycling of P in the pasture situation, cannot be ignored.

8.3.2 Effects of solution:solid ratio on the release and uptake of inorganic phosphorus by potential particulate source materials

The release of IP from soil surface, stream-bank, and earthworm cast material to 0.1<u>M</u> NaCl with time showed a dependence upon solution:solid ratio (Fig. 8.11). As the solution:solid ratio decreased (sediment concentration increases), more IP was released to solution. It was observed that this relationship was not linear. Below a solution:solid ratio of 1000:1, variations in the ratio had a greater effect on P release than at wider ratios (Fig. 8.11). This effect was most marked for cast material (Fig. 8.11a). It was calculated, however, that the release of IP to solution per unit weight of soil increased as the solution: solid ratio increased. Work reported by Larsen and Court (1960), Fordham (1963), and White (1966) also showed that at disequilibrium, release of IP to solution from soil material was dependent upon



Fig. 8.11 Release of IP to 0.1<u>M</u> NaCl (no added IP) from earthworm casts (a), soil surface (0-5cm) (b), and stream-bank material (c) as a function of solution:solid ratio.

solution:solid ratio. Hope and Syers (1976) have recently shown that solution:solid ratio effects on P sorption are kinetic in origin. It is reasonable to suggest that a similar explanation applies to the release or desorption of P.

With initial P concentrations of 0.2 and  $0.5mgP l^{-1}$ , the data indicated that as the solution:solid ratio increased, sorption of IP by surface soil material decreased, with the result that the final solution P concentration increased (Fig. 8.12, curves b and c, respectively). Similar trends were observed for streambank and cast material and the data are, therefore, not presented. The decrease in P sorption with an increase in solution:solid ratio results from the fact that as the solution:solid ratio increases, the number of P sorbing sites in the system decreases, whereas the solution P concentration remains constant. The sorption of P per unit weight of soil was greater as the solution:solid ratio increased.

Under low stream-flow conditions, therefore, when sediment concentrations are also low, release or uptake of IP by suspended particulate material will be at a minimum. In contrast, under high stream-flow conditions, when sediment concentrations are high, an extensive modification of DIP concentrations is likely.

In the present study, P was added to systems of varying solution:solid ratios, such that the initial solution P concentration was the same in each system, irrespective of the amount of soil material present. This was done in order to investigate the effect of sediment concentration on the DIP concentrations obtained from stream monitoring studies. In contrast, however, Hope and Syers (1976) added different levels of P to obtain the same initial P concentration per unit weight of soil in the systems studied, with the result that at narrower solution:solid ratios the initial solution P concentration was higher than at the wider ratios. In doing so, these workers were able to isolate the effect of solution:solid ratio from that of initial solution P concentration.

The fact that surface soil was able to sorb more P per unit weight of solid material at wider solution:solid ratios arises from the fact that as the ratio increases, the initial solution P



Fig. 8.12 Uptake of IP by and release of IP from surface soil (0-5cm) to 0.1<u>M</u> NaCl containing O (A), 0.2 (B), and 0.5mg l<sup>-1</sup> (C) of IP, as a function of time at a solution:solid ratio of 100:1 (a), 800:1 (b), and 4000:1 (c).

concentration per unit weight of soil in the system increases. Consequently, there is a corresponding increase in the amount of P per unit number of sorption sites.

The data suggest that as the solution:solid ratio decreases, as would occur with increasing stream flow, the rate and extent of modification of DIP concentration by suspended particulate material in the stream will increase. Under low stream-flow conditions, however, a steady state of DIP concentration would occur.

It would appear from the data presented in Fig. 8.11 that the simulated systems are not at equilibrium because of the continued release of P to solution after 24h. This is in agreement with work of Ryden and Syers (1975) who also showed that true equilibrium could only be estimated by extrapolation of kinetic data to an infinite shaking time. Over the shorter shaking times, which are relevant to the contact time between soil material and runoff waters in the field situation, a more steady state in terms of solution P concentration is attained after a shorter period of time at wider solution:solid ratios.

## 8.3.3 Release and uptake of inorganic phosphorus in simulated runoff systems

In addition to investigating the P uptake and release characteristics of stream and surface-runoff sediments, similar experiments were carried out using the source materials of these suspended sediments. The potential source materials considered were surface soil, casts, and stream-bank material.

8.3.3.1 <u>Potential source materials</u>. The amount and rate of IP release from cast material to 0.1<u>M</u> NaCl containing no P, was appreciably greater than that from either surface soil or stream-bank material at solution:solid ratios of 400:1 and 2000:1 (Fig. 8.13 and 8.14). After 4h, casts had released four times more IP than surface soil and five times more than stream-bank material.



Fig. 8.13 Release and uptake of IP from 0.1<u>M</u> NaCl (no added IP) by stream-bank material (a), surface soil (0-5cm) (b), prewashed earthworm casts (c), untreated earthworm casts (d), suspended-stream sediment (e), < 30 µm surface soil (f), suspended surface-runoff sediment (g), and < 30 µm earthworm casts (h), as a function of time at a solution:solid ratio of 400:1.



Fig. 8.14 Release and uptake of IP from 0.1<u>M</u> NaCl (no added IP) by stream-bank material (a), surface soil (0-5cm) (b), prewashed earthworm casts (c), untreated earthworm casts (d), suspended-stream sediment (e), < 30 µm surface soil (f), suspended surface-runoff sediment (g), and < 30 µm earthworm casts (h), as a function of time at a solution:solid ratio of 2000:1.

Approximately 80% of the IP released to solution from surface soil and stream-bank material after 4h was released in the first hour at solution:solid ratios of 400:1 and 2000:1 (Fig. 8.13, 8.14, respectively). Even after 30min, approximately 75% of the release of IP after 4h was attained. This rapid release of IP is expected to be important, considering the short contact times between surface-runoff waters and the soil surface, and between stream water and stream-bank material. Although appreciably more IP was released to solution from casts than from underlying soil materials, only 56% of the IP released after 4h was released after 1h.

When casts were prewashed with  $0.1\underline{M}$  NaCl to remove readilyextractable P, a situation which would occur in the surface-runoff environment, and then shaken with  $0.1\underline{M}$  NaCl containing no IP, the amount of IP released to solution was reduced only slightly relative to the unwashed casts (Fig. 8.13 and 8.14).

Both untreated and prewashed casts released IP to  $0.1\underline{M}$  NaCl containing  $0.1 \text{mgP} \text{ l}^{-1}$  at solution:solid ratios of 400:1 and 2000:1 (Fig. 8.15, 8.16, respectively). The rate of release of IP to solution, however, decreased with time compared to the rate of release in the absence of added P. At the narrower ratio (400:1) casts sustained higher DIP levels (Fig. 8.15) than at the wider ratio 2000:1 (Fig. 8.16). In contrast, surface soil and streambank material removed IP from solutions containing 0.1 mgP 1<sup>-1</sup> at solution:solid ratios of 400:1 and 2000:1 (Fig. 8.15 and 8.16, respectively). The rate of IP removal by both surface soil and streambank material at a solution:solid ratio of 400:1 was greater than at 2000:1. For example, surface soil and streambank material at 2000:1, 0.004 and  $0.018 \text{mgP} 1^{-1}$ , respectively, during 4h at 400:1, whereas at 2000:1, 0.004 and  $0.018 \text{mgP} 1^{-1}$ 

The data suggest that the release of IP from surface soil and cast material may occur in surface runoff in view of the low DIP concentration in precipitation. If surface runoff did not contribute to stream flow, because of a reduction in land slope, but joined subsurface flow, then subsoil material (corresponding to stream-bank material) would be able to remove IP from solution



Fig. 8.15 Release and uptake of IP from  $0.1\underline{M}$  NaCl containing  $0.1 \text{mg l}^{-1}$  of IP by stream-bank material (a), surface soil (0-5cm) (b), prewashed earthworm casts (c), untreated earthworm casts (d), suspended-stream sediment (e), < 30  $\mu$ m surface soil (f), suspended surfacerunoff sediment (g), and < 30  $\mu$ m earthworm casts (h), as a function of time at a solution:solid ratio of 400:1.



Fig. 8.16 Release and uptake of IP from 0.1<u>M</u> NaCl containing 0.1mg 1<sup>-1</sup> of IP by stream-bank material (a), surface soil (0-5cm) (b), prewashed earthworm casts (c), suspended-stream sediment (d), untreated earthworm casts (e), <30 µm surface soil (f), suspended surface-runoff sediment (g), < 30 µm and earthworm casts (h), as a function of time at a solution: solid ratio of 2000:1.</p>

resulting in low DIP concentrations in subsurface flow (Section 6.3.2.1.

When the potential source materials were shaken with 0.1MNaCl containing  $0.25mgP l^{-1}$  of DIP at solution:solid ratios of 400:1 and 2000:1, all removed IP from solution (Fig. 8.17 and 8.18, respectively). The rate of sorption of IP was much greater for stream-bank material than for surface soil or casts. When the initial 0.1M NaCl solution contained a P concentration of  $0.25mg l^{-1}$ , 25% of the added P was sorbed after 30min at a solution:solid ratios ratio of 400:1 (Fig. 8.17). After the same time, however, surface soil sorbed only 8% and casts 4% of the added P (Fig. 8.17). Furthermore, stream-bank material had an appreciably greater capacity to sorb IP from solution than surface soil or cast material.

When the potential source materials and suspended sediments were shaken in 0.1M NaC1 containing  $0.5mg l^{-1}$  of IP at solution: solid ratios of 400:1 and 2000:1, similar trends for the uptake and release of IP were observed (Fig. 8.19 and 8.20, respectively) as with 0.25mgP 1<sup>-1</sup> of added IP (Fig. 8.17 and 8.18). Even at the high initial IP concentration  $(0.5mgP l^{-1})$ , which was recorded only occasionally in runoff waters, IP was released by the < 30µm fraction of casts  $(0.07mgP l^{-1}$  released after 4h, Fig. 8.19h) and suspended surface-runoff sediment  $(0.06 \text{mgP} \text{ 1}^{-1} \text{ released after 4h},$ Fig. 8.19g) at a solution: solid ratio of 400:1. In contrast, stream-bank material, surface soil, and untreated casts were able to remove 40, 12, and 8% of the added IP, respectively, under corresponding conditions. Similar observations were made at the wider ratio of 2000:1, where the  $\prec$  30µm fraction of casts and suspended surface-runoff sediment released 0.029 and 0.026mgP 1<sup>-1</sup>, respective-(Fig. 8.20h and 8.20g, respectively), whereas streamly, bank, surface soil, and casts removed 16, 9, and 4% of the added IP. Thus, the data indicate the potential of the < 30µm fraction of cast material and suspended surface-runoff sediment to release IP to solution and of stream-bank and surface-soil material to remove IP from solutions containing high IP concentrations.

It is apparent, therefore, that if runoff occurred when the stream was at low flow, characterised by low DIP and sediment concentrations (Section 6.3.2.1), the particulate material (surface



Fig. 8.17 Release and uptake of IP from 0.1<u>M</u> NaCl containing 0.25mg 1<sup>-1</sup> of IP by stream-bank material (a), surface soil (0-5cm) (b), prewashed earthworm casts (c), untreated earthworm casts (d), suspended-stream sediment (e), < 30 µm surface soil (f), suspended surface-runoff sediment (g), and < 30 µm earthworm casts (h), as a function of time at a solution:solid ratio of 400:1.



Fig. 8.18 Release and uptake of IP from 0.1<u>M</u> NaCl containing 0.25mg l<sup>-1</sup> of IP by stream-bank material (a), suspendedstream sediment (b), surface soil (0-5cm) (c), prewashed earthworm casts (d), untreated earthworm casts (e), < 30 µm surface soil (f), suspended surface-runoff sediment (g), and <30 µm earthworm casts (h), as a function of time at a solution:solid ratio of 2000:1.



Fig. 8.19 Release and uptake of IP from 0.1<u>M</u> NaCl containing 0.50mg 1<sup>-1</sup> of IP by stream-bank material (a), suspendedstream sediment (b), surface soil (0-5cm) (c), prewashed earthworm casts (d), untreated earthworm casts (e), < 30 µm surface soil (f), suspended surface-runoff sediment (g), and <30 µm earthworm casts (h), as a function of time at a solution:solid ratio of 400:1.



Fig. 8.20 Release and uptake of IP from 0.1<u>M</u> NaCl containing 0.5 mg l<sup>-1</sup> of IP by stream-bank material (a), surface soil (0-5cm) (b), prewashed earthworm casts (c), suspendedstream sediment (d) untreated earthworm casts (e) < 30 µm surface soil (f), suspended surface-runoff sediment (g), and < 30 µm earthworm casts (h), as a function of time at a solution:solid ratio of 2000:1.

soil and cast material) contributed in surface runoff would release IP to solution. Because the concentration of DIP in surface runoff from unfertilized, ungrazed pasture is low (Section 6.3.3.1), the observed rise in DIP concentration, with a unit rise in stream flow (Section 6.4) may be attributed to a release of IP from suspended-particulate material. In contrast, under conditions of high stream flow and increased DIP concentration, <u>in situ</u> streambank and suspended-stream sediment derived from bank erosion (Section 7.3.2.3), should remove substantial amounts of IP from solution.

Using potential source materials from a catchment in Pennsylvania in systems simulating field conditions, Taylor and Kunishi (1971) obtained similar results to those in the present study, although the amounts of IP released to, and sorbed from solution were different, due to the differing extractable soil P levels of the potential source materials. These workers were able to show that stream-bank material, and to a lesser extent surface soil, had a very large capacity to sorb IP from the stream. The ability of sorption-desorption studies, using potential source materials from the Massey Catchment, to provide reasonable estimates of DIP concentrations in the stream under various flow conditions, is discussed in a later section (Section 8.3.4).

8.3.3.2 Suspended stream and surface-runoff particu-

<u>late material</u>. The uptake and release of IP by suspended stream and surface-runoff sediments were investigated using the same systems as those used for potential source materials. Stream sediment sustained higher DIP concentrations in 0.1M NaCl in the absence of added IP, than did any of the other three source materials (Fig. 8.13 and 8.14). At higher initial P concentrations  $(0.5mg l^{-1})$  and at a solution:solid ratio of 400:1, casts and stream sediment behaved similarly.

Surface-runoff sediment released substantially more IP to  $0.1\underline{M}$  NaCl containing no IP, than did casts (Fig. 8.13 and 8.14). After 4h at 400:1, surface-runoff sediment released  $0.28mgP l^{-1}$ , whereas casts released only  $0.067mgP l^{-1}$  (Fig. 8.13). Similar trends were also observed at the wider ratio of 2000:1, although

the surface-runoff sediment concentrations observed in fieldmonitoring studies seldom fell below 500mg  $1^{-1}$  (2000:1 solution:solid ratio). From the data presented, it appears that the P uptake and release characteristics of the surface soil and cast material are not analogous to those of surface-runoff sediment. Surface-runoff sediment, however, contained no material greater than 250µm (Table 8.1) and 70% was less than 20µm. Consequently, the P uptake and release characteristics of the < 30µm fraction of casts and surface soil were investigated. The <30µm fraction of casts released slightly more IP to 0.1M NaCl after 4h than surface-runoff sediment at all levels of added IP and at both solution: solid ratios (Fig. 8.13 to 8.18). Initially, however, the rate of release of IP to solution from surface-runoff sediment was greater than that from < 30µm cast material.

Approximately 25 and 50% of the whole sample of surface soil and casts, respectively, was <30µm. Consequently, in systems using the <30µm fraction there would be a four- and two-fold greater amount of <30µm material than in the system using whole samples of surface soil and cast material, respectively. This, coupled with the fact that the <30µm size fraction is enriched in IP compared to the more coarse fractions (Table 8.2), would lead to the <30µm material sustaining an appreciably higher DIP concentration than whole samples. This is the case, even though IP release would have occurred during the separation of <30µm from the surface soil and casts.

The data indicate that <30µm surface soil and cast material, and suspended surface-runoff and stream sediment, maintains higher DIP concentrations than whole surface soil or cast material samples. This provides a better understanding of the concentrations of DIP observed in surface runoff (as discussed in a later section, Section 8.3.4). Although Taylor and Kunishi (1971), Kunishi <u>et al.</u> (1972), and Ryden <u>et al.</u> (1972a, b) conducted similar experiments using whole samples of surface and subsoil material, no work has been reported which evaluates the sorption and desorption of IP by certain size fractions of particulate source materials contributing to surface-runoff and stream sediment.

## 8.3.3.3 Mixtures of potential source materials in

<u>surface runoff</u>. Because surface-runoff sediment is primarily derived from casts and surface soil, mixtures of these two materials were shaken in 0.1<u>M</u> NaCl containing no added IP at a solution: solid ratio of 400:1 in order to investigate the ability of surface soil to sorb IP released.

It has previously been shown that casts release more IP to solution and remove less IP from solution than surface soil. As the contribution of casts increased, the amounts of P released to 0.1M NaCl increased correspondingly (Fig. 8.21). The increase in DIP concentration after 4h was not directly proportional to the increase in the percentage of cast material in the mixture. For example, an increase in the DIP concentration of 0.013mg  $1^{-1}$ was obtained when the amount of cast material in the mixture was increased from zero to 10%. With each subsequent increase of 20% in the proportion of cast material in the mixtures up to 90%, the increase in DIP concentration maintained became smaller (Fig. 8.21). For example, an increase in DIP concentration of 0.011mg  $l^{-1}$  at 4h was obtained when the proportion of casts in the mixture was increased from 10 to 30%, whereas an increase of only 0.005mg  $1^{-1}$ at 4h was observed when the proportion of cast material was increased from 70 to 90% (Fig. 8.21). Surface soil can apparently only buffer the release of IP by casts when the amount of IP released by the casts is greater than a value which results in P sorption by the surface soil and supression of P release.

The removal of IP from solution by mixtures of casts and surface soil was similarly investigated using a shaking time of 30min and a solution:solid ratio of 400:1. The data are presented in the form of a nomogram (Fig. 8.22), developed by plotting sorption isotherms for a range of ratios of cast and surface soil material. This approach was used by Ryden <u>et al.</u> (1972b) to investigate and predict the potential of soil horizons for the P enrichment of streams. Ryden <u>et al.</u> (1972b) constructed parallel lines through points corresponding to the same initial P concentration on all isotherms, because the solution:solid ratio was constant (400:1). These lines crossed the abcissa at a final solution P concentration equal to the initial P concentration; that is, where there was no net change of P between the solid and aqueous phases.



Fig. 8.21 Release of IP from mixtures of earthworm casts (A) and surface soil (B) to 0.1M NaCl (no added IP) as a function of time at a solution:solid ratio of 400:1.



Fig. 8.22 Uptake of IP by 1.0 to 0.0 (a), 0.9 to 0.1 (b), 0.7 to 0.3 (c), 0.5 to 0.5 (d), 0.3 to 0.7 (e), 0.1 to 0.9 (f), and 0.0 to 1.0 (g) mixtures of casts and surface soil, from 0.1M NaCl containing 0, 0.1, 0.25, and 0.5mg 1<sup>-1</sup> of added IP after 30min, at a solution:solid ratio of 400:1.

Consequently, it is possible to predict the effects of varying mixtures of casts and surface soil on the DIP concentration at different initial P concentrations, under experimental conditions simulating surface runoff.

It was observed that the gradients of the constructed lines representing the same initial P concentration (dashed, Fig. 8.22) were equal to 400:1, thus being proportional to the solution: solid ratio. Thus, by constructing lines of varying slope, it is possible to estimate the DIP concentration after a contact time of  $30_{min}$ between particulate material and the solution at specified initial P concentrations, solution: solid ratios, and mixtures of cast and soil material. These estimates are only valid if the P sorption isotherms for the range of soil mixtures do not change relative to one another with a change in solution: solid ratio (Ryden <u>et al</u>., 1972b).

By constructing a line equivalent to a solution:solid ratio of 2000:1, it is predicted that surface soil material can sorb  $1.8\mu$ gP g<sup>-1</sup> soil (0.001mg l<sup>-1</sup>) from an initial P concentration of 0.10mg l<sup>-1</sup> after 30min. It was observed earlier that 2.0µgP g<sup>-1</sup> (0.001mg l<sup>-1</sup>) was sorbed by surface soil (Fig. 8.16) from 0.1<u>M</u> NaCl after 30min at a solution:solid ratio of 2000:1. If the data from simulated studies using mixtures of the different potential source materials contained in surface runoff or stream flow are presented as a nomogram, it should be possible to estimate the effect of these mixtures on the DIP concentrations observed in surface runoff and stream flow at various solution:solid ratios by extrapolation from the nomogram for one ratio.

It has been shown that stream and surface-runoff sediment and potential sediment-source materials exhibit widely differing P release and uptake characteristics (Fig. 8.13 to 8.18). In the case of surface runoff, surface soil and casts released significant quantities of IP to solutions containing negligible DIP concentrations, such as those in precipitation. The concentration of DIP, however, will be modified further during periods of high stream flow due to the high P sorption capacity of stream-bank material operating <u>in</u> <u>situ</u> or transported in suspension (Section 7.3.2.3). 8.3.4 Comparison of field and simulated systems data

In an attempt to estimate and explain the changes in DIP concentrations during stream flow, the data obtained from field monitoring studies, under various stream flow conditions, were compared with those obtained from simulated systems.

During the high-intensity storm described earlier (event 3, Sections 5.3.1 and 6.3.3.1, for accelerated subsurface and storm flow, respectively) a DIP concentration of  $0.1 \text{mgP} \text{ l}^{-1}$  was observed in accelerated subsurface runoff entering the stream following peak tile discharge (Fig. 5.5a). One hour later, a DIP concentration of  $0.16 \text{mgP} \text{ l}^{-1}$  was observed in stream flow (Fig. 6.13a). The sediment concentration of stream flow, however, only decreased from 2000 to 1750mg l<sup>-1</sup> (a solution:solid ratio of approximately 500:1) over this period (Fig. 6.13b). It was shown in the previous section that when stream sediment was shaken with 0.1M NaCl containing  $0.10 \text{mgP} \text{ l}^{-1}$  of added IP at a solution:solid ratio of 400:1  $(2500 \text{mg l}^{-1})$ , a DIP concentration of 0.15 mgP l<sup>-1</sup> was maintained after 1h (Fig. 8.15). Considering that in situ stream-bank material will remove some IP from solution, the DIP concentration maintained in the simulated system is remarkably similar to that from field observations.

Surface runoff primarily originates directly from precipitation with minor amounts of subsurface flow emerging at the surface and contributing to surface runoff (Dunne and Black, 1970). It can be assumed, therefore, that surface-runoff water initially has a low DIP concentration (0.008mgP 1<sup>-1</sup>, Section 4.3.3.1) before contact with the surface soil. During a high-intensity storm (Fig. 4.3b), a maximum sediment concentration of 2000mg 1<sup>-1</sup> was observed in surface runoff, whereas very little variation in the DIP concentration of 0.18 mgP  $1^{-1}$  (Fig. 4.3a) was observed during the event. By reference to the simulated system, in which surface-runoff sediment was shaken with solutions containing no added IP at a solution: solid ratio of 400:1 (2500mg  $1^{-1}$ ), a DIP concentration of 0.18mgP  $1^{-1}$  was measured after 30min (Fig. 8.13). The data indicate that the experimental conditions used in the laboratory studies adequately simulate the surface-runoff environment, although the contact time between sediment and water of 30min is

arbitrary, and shorter or longer contact times may occur in the field. Romkens and Nelson (1974) also obtained similar data for the concentration of DIP in surface runoff and the concentration maintained by surface soil material from surface-runoff plots, when shaken with 0.1<u>M</u> NaCl at a solution:solid ratio of 50:1 for 16h.

In a storm event (event 1, Sections 5.3.1 and 6.3.3.1, for accelerated subsurface and storm flow, respectively) of lower stream discharge rate than in the first event discussed (event 3) a DIP concentration of  $0.1 \text{mgP} \ 1^{-1}$  in accelerated subsurface runoff was observed during the decrease in flow (Fig. 5.1a). One hour later, a DIP concentration of  $0.08 \text{mgP} \ 1^{-1}$  was observed in stream flow (Fig. 6.9a), whereas over this period the sediment concentration of stream flow decreased from 500 to  $300 \text{mg} \ 1^{-1}$  (a mean solution: solid ratio of 2000:1). The low concentration of suspended sediment in the stream will modify DIP concentrations to a small extent only (Fig. 8.16). When stream-bank material was shaken with 0.1 MNaCl containing  $0.10 \text{mgP} \ 1^{-1}$  of added IP, at a solution:solid ratio of 2000:1 a DIP concentration of  $0.09 \text{mgP} \ 1^{-1}$  was attained after 1h (Fig. 8.16).

If subsurface runoff, with low suspended sediment concentration, is assumed to originally have a similar DIP concentration to that of surface runoff (average of approximately 0.10mgP  $1^{-1}$ from unfertilized, ungrazed plots in the monitoring studies, Section 4.3.3.1) the uptake and release of IP by subsoil material (streambank material) can account for the concentration of DIP observed in subsurface flow. During one subsurface flow event (Fig. 6.3a), the DIP concentration only varied between 0.030 and 0.035mgP 1 and the suspended sediment concentration remained negligible over a period of nine days. The DIP concentration of subsurface flow is, therefore, influenced by the subsoil through which the water moves, and the stream-bank material and bottom sediments that the stream contacts during its passage. Stream-bank material (subsoil exposed at the stream-bank) was able to support a DIP concentration of 0.035mgP 1<sup>-1</sup> at the narrower solution:solid ratio (400:1) after a 4-h shaking period (Fig. 8.15).

Taylor and Kunishi (1971) were also able to closely simulate

DIP concentrations during base flow of a stream draining a small agricultural catchment in Pennsylvania, using P sorption data obtained with potential source materials from the catchment. They observed that DIP concentrations during base flow of the stream were in the range of 0.040 to  $0.060 \text{mg l}^{-1}$ , concentrations close to those predicted from P sorption studies using stream-bank and subsoil material. Further work by Kunishi <u>et al.</u> (1972) on the same catchment showed that eroded stream-bank material exhibited a high P-sorption capacity which resulted in a decrease in the DIP concentration in stream flow under conditions of high water flow and mixing.

Consequently, simulated systems using potential source materials and suspended sediment, at solution:solid ratios and initial IP concentrations similar to those observed in the field, can to a large extent account for the changes in DIP concentrations observed in the field.

## 8.4 General Discussion

The data obtained for the seasonal variation in earthworm activity, and for the amounts and release to solution of P forms from earthworm casts, have been discussed earlier (Section 8.3.1.5), along with the chemical nature of IP in casts, in terms of the potential contribution of casts to the loading of P forms and sediment in surface runoff. In the following discussion, however, casts will be evaluated along with surface soil and stream-bank material as potential source and sink materials of IP under conditions which simulate the runoff environment. In terms of the stream environment, surface-runoff and stream sediment, and streambank material were used as the solid materials in the simulated systems.

As emphasised by Ryden <u>et al.</u> (1972a), and as is apparent from the present study, the levels of IP added and solution:solid ratios used in simulated systems affect the concentration of IP maintained in solution by potential source materials. When the solution: solid ratio was increased (sediment concentration decreased), the rate of P sorption and desorption decreased much more rapidly and thus, a steady-state P concentration was maintained in a shorter period of time for surface soil, cast, and stream-bank material. A dependence of the amount of IP released to solution on the solution:solid ratio was also found by several workers using various soils (Larsen and Court, 1960; Fordham, 1963; White, 1966). Work by Hope and Syers (1976), however, has shown that the relationship between solution:solid ratio and IP sorption is kinetic in origin. It is conceivable that similar thinking applies to P release.

In systems simulating the runoff environment, casts released more IP than surface soil, which in turn released more than streambank material. This sequence was reversed, however, with respect to the ability of the materials to remove IP from solution. The data suggest, therefore, that the IP which is released by cast and surface-soil material to solution under conditions which simulate the surface-runoff environment, can be removed from solution by stream-bank material under conditions which simulate the stream environment. Other workers have reported that subsoil or material exposed at the stream-bank is able to remove IP released by surface soil (Taylor and Kunishi, 1971; Ryden et al., 1972b).

In contrast, surface-runoff sediment was able to maintain higher IP concentrations than potential source materials. Little work has been reported, however, on the ability of suspended particulate materials to modify the concentration of DIP under conditions simulating the stream and surface-runoff environments. Kunishi <u>et al</u>. (1972) demonstrated that suspended-stream sediment sorbed IP from solution in amounts that were consistent with the uptake and release characteristics of the potential source materials.

In a study of the sorption of IP by suspended particulate material from the Illinois and Spoon rivers in Illinois, Wang (1974) observed that the rates of IP sorption by the two sediments were essentially the same at similar initial P concentrations. Particulate material from the Illinois river, however, was able to sorb approximately seven times more IP per unit weight of material than that from the Spoon river. This was attributed to a dissimilarity in particle size, mineralogy, and organic matter content of the materials.

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Attempts to account for the concentrations of DIP in surface and subsurface runoff and in stream flow, using data for the uptake and release of IP by suspended surface-runoff and stream sediment and potential source materials, were reasonably successful. In the case of surface runoff, a remarkably similar concentration of IP was maintained by suspended surface-runoff sediment, after only a short period of contact with a solution of negligible initial IP concentration, to the DIP concentration obtained in field studies. It is of interest that Romkens and Nelson (1974) were able to estimate the concentration of DIP in surface runoff from a fertilized silt loam using sorption-desorption studies.

The ability of subsoil or stream-bank material to remove large amounts of IP from solution is consistent with the low DIP concentrations observed in subsurface flow when the only particulate material in contact with stream flow was stream-bank material. This can be attributed to a lower saturation of the P sorption complex in stream-bank material than in the other potential source and suspendedsediment materials used.

A similar agreement between the concentration of IP maintained by subsoil material and that observed during stream-base flow was found by Taylor and Kunishi (1971). With an increase in stream flow, however, a more complex situation arises with the variable contribution of potential source material to suspended-stream sediment. Even so, it was possible in the present study, to account for a change in the concentration of DIP in the accelerated subsurface runoff input into stream flow after a certain period of time, considering the uptake and release of IP by suspended-stream sediment and stream-bank material. Kunishi et al. (1972) also observed that the suspended sediment from a stream at high flow in Pennsylvania sustained higher DIP concentrations than suspended sediment from the stream at low flow. This difference was attributed to a much higher proportion of top soil in the suspended material from the high-flow event contributed by surface runoff, giving a composite sample of lower P-sorbing capacity than in the low-flow event. The very high sorption capacity of suspended material from the low-flow event is consistent with the presence of a high proportion of streambank material. Furthermore, these workers suggested from sorptiondesorption studies that surface runoff from agricultural land can

contain 0.05 to 0.20mgP  $1^{-1}$  DIP, but with movement down stream and mixing with sediments derived from subsoil or stream-banks, these concentrations are reduced to 0.010 to 0.015mgP  $1^{-1}$ .

The data obtained indicate that IP sorption and desorption by potential source materials and suspended sediment, using initial P concentrations and solution:solid ratios similar to those obtained in field monitoring studies, provide a meaningful evaluation of the modification of DIP concentration in surface and stream flow. The work presented in this thesis may be summarised as follows:

1. A review of the literature indicated that little data have been reported on the sources and amounts of P and N forms transported in runoff types (surface, accelerated subsurface, and subsurface runoff) and in stream flow from catchments in New Zealand. Furthermore, little attempt has been made to evaluate the relative contribution of runoff types to the P and N loadings of streams draining catchments both in New Zealand and overseas.

2. Although relationships between flow and concentration of P and N forms varied between the different runoff types, flow was the more important variable in determining the P and N loadings in each runoff type. As a result of more rapid fluctuations in the concentration of P and N forms, and in flow during surface and accelerated subsurface runoff, and in storm flow in the stream draining a dominantly pasture catchment, a greater frequency of sampling of these runoff types was required to obtain reliable estimates of P and N loadings, than was the case for subsurface runoff.

3. The application of fertilizer P (50kgP ha<sup>-1</sup>) to surfacerunoff plots in the catchment in June 1975, dramatically increased the concentrations and amounts of P forms transported in surface runoff. The amounts of P forms transported in surface runoff from both unfertilized and fertilized pasture in the present study were greater than those reported in similar overseas studies. Low amounts of dissolved N forms were transported in surface runoff.

4. Although grazing with dairy cows resulted in a significant increase in the transport of P forms in surface runoff, the effect of grazing was not as sustained as that due to fertilizer application. In the case of N, however, grazing resulted in a greater loss of N forms than that reported in surface runoff studies overseas, including several which have involved fertilizer N applications.
5. Highly significant correlations were obtained between the concentration of DIP in surface runoff and the amounts of extractable P in the surface soil (0-5cm) of unfertilized and fertilized, drained and undrained surface-runoff plots. Remarkably similar regression equations, predicting the losses of DIP in surface runoff, were obtained for all treatments except the fertilized, undrained situation. The data obtained suggest that the soil-sampling procedure used could be improved. The use of the laboratory extraction procedure for predicting the losses of DIP in surface runoff from a surface soil, differing greatly in the amounts of extractable soil P, appears to be a feasible proposition.

6. Applications of urea to the drained area of the subcatchment resulted in a dramatic increase in the loss of N forms in accelerated subsurface runoff. The concentrations of both P and N forms, in this runoff type also increased following grazing, although the effect of grazing on N concentrations was less than that of urea application. In addition, tile discharge was dramatically reduced following grazing, as a result of surface pugging.

7. Significant correlations were obtained between the concentrations of DIP and NO<sub>3</sub> in accelerated subsurface runoff and the amounts of extractable soil P and NO<sub>3</sub> in the subsoil at 40-50cm. This depth corresponded to that of the mole channels.

8. Appreciably greater amounts of N forms than P forms were transported annually in stream flow from the Massey Catchment. The amounts of P and N forms transported, however, were greater than those reported in overseas studies, even though in many cases higher fertilizer P and N application rates were used than in the present study.

9. The amounts of water discharged and P and N forms, and sediment transported in stream flow were separated into those transported during subsurface and storm flow using hydrograph analysis. Although a greater amount of water and N forms was discharged annually in subsurface flow than in storm flow, a larger amount of P forms was transported in storm flow. This is attributed to the appreciably higher proportion of TN occurring

in the dissolved form.

10. Of the three runoff types, surface runoff contributed the major proportion of the annual P loading of the stream in the subcatchment, whereas subsurface runoff contributed\_the major proportion of the water discharged and the annual N loading. It appears, however, that stream-bank erosion and the resuspension of bottom sediments contributed the major proportion of the annual loading of P forms and sediment in the stream.

11. Earthworm casts contained an appreciably greater amount of IP and OP than underlying soil material from which the casts were derived. The additional IP in the casts was sorbed by a more-physical sorption type and, as a consequence, was released more readily to solution than the IP in underlying soil. The importance of earthworms in increasing the rate of P cycling in a soil under pasture is indicated.

12. The fact that peak cast production coincided with periods of increased surface runoff suggests that earthworm casts may be a potential source of both particulate material and particulate P to surface runoff.

13. The ability of the potential sources of particulate material in the stream (surface soil, stream-bank material, and earthworm casts) to sorb IP from solution and release IP to solution, under conditions which simulate the surface-runoff environment, varied appreciably. Earthworm casts, and to a lesser extent surface soil, released IP to solution, whereas a rapid and extensive sorption of IP by stream-bank material indicated a possible buffering during transport in the stream of the IP released to solution in the surface-runoff environment.

14. A study of the sorption and release of IP by potential source materials and suspended-stream and surface-runoff sediments with time, at specified solution:solid ratios and amounts of added IP, appeared to simulate reasonably well the modification of IP concentrations in both surface runoff and stream flow.

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