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FIELD AND LABORATORY STUDIES
OF THE MOVEMENT AND REACTIONS
OF PHOSPHORUS IN SOILS

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

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1978

ABSTRACT

Low and stable concentrations of phosphorus (P) forms and sediment were obtained in stream flow from two small, adjacent, scrub-covered, and minimally-disturbed catchments near Palmerston North, New Zealand. In contrast, higher and irregular concentrations and loadings were obtained following land clearing, P fertilizer application, and the establishment of grazed pasture. The need for intensive stream sampling, as well as complete hydrograph data in order to obtain reliable information on stream loadings, is emphasised.

High and fluctuating concentrations of P forms and sediment were obtained following the change in land use. A high proportion of the P and sediment loss occurred in the storm runoff component of stream flow. The estimated losses of fertilizer P in stream flow (approximately 1% of that added) were very small from an agronomic standpoint but they represent large proportional increases in the loadings of P forms in stream flow.

The high amounts of water-extractable P present in the soils of the catchment (field soils), immediately following the aerial application of fertilizer P, declined rapidly to lower, more stable values. This pattern of decline for field soils was replicated using small pots established in the field (pot soils) and containing fertilized soil representative of the catchments. Close correlations were obtained between water-extractable P in the upper 1cm of field and pot soils, and mean dissolved inorganic P (DIP) concentrations in the surface runoff component of stream flow in closely-following storms. The possibility of predicting DIP losses in surface runoff from soils using a water-extraction technique is thus indicated.

The decrease with time in the amounts of water-extractable P observed after superphosphate addition to field and pot soils was reproduced in the laboratory. This relationship validated the use of laboratory studies to examine the rate and extent of interaction of fertilizer P occurring in field soils and to predict the potential movement of fertilizer P from soils to waters.

The decline in water-extractable P closely paralleled the decrease in plant uptake of P with time following fertilizer P addition to two contrasting soils. This suggested that water extraction may be a useful soil-testing procedure for predicting P availability to plants, as well as the movement of P in surface runoff from soils.

The rate of decline in water-extractable P in a given soil was proportional to both the amount of P added and the amount initially extractable immediately following P addition. This suggests that the rate and extent of P sorption in a soil is directly related to soil solution P concentration. Differences were obtained, however, between three contrasting soils in the relative rate and extent of P sorption.

A kinetic model based on the Langmuir equation was developed to simulate the decline in water-extractability of P added to three soils. Three populations of sites were assumed and the appropriate sorption maxima and binding energy constants were derived from sorption isotherm studies. The model provided a satisfactory prediction of the fate of different amounts of fertilizer P. It is probable that the further development of this model would provide a useful basis for predicting the fate of P added to soils and the potential movement of added P in surface-runoff waters.

ACKNOWLEDGEMENTS

I would like to express my gratitude to a number of people without whose help and support this thesis would never have eventuated. In particular I would like to thank:

My supervisor, Professor Keith Syers, to whom I am deeply indebted for his bouyant enthusiasm, encouragement, and friendship. Further to this, his rigorous standards of scientific thoroughness and presentation, while sometimes trying, have been highly rewarding.

Mr. Russell Tillman, to whom I am particularly grateful for his friendship, patience, and continual assistance during the planning, execution and presentation of this study.

Other members of the Department of Soil Science staff, both teaching and technical, and my colleagues who provided assistance and good humour.

Julie, for her patience over the long duration of the study and her forebearance of difficulties.

Dianne, for producing first-class typescript.

The University Grants Committee for a post-graduate scholarship for three years.

The Faculty of Agricultural and Horticultural Science, Massey University, for a Massey post-graduate scholarship.

The Waikato Valley Authority for time and encouragement to complete this thesis.

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CHAPTER 1

REVIEW OF LITERATURE

This review of literature discusses the importance of phosphorus (P) forms and concentrations in natural waters and the influence of factors affecting P enrichment of surface waters and water quality. Particular attention is given to the relative contribution of different systems of land use in increasing concentrations of P above background levels to potentially eutrophic levels. The movement of P from soils to water is discussed with specific reference to surface and subsurface runoff, and to the potential effect of changing land use on the quantities of P movement. Reactions which influence P movement within and from soils are reviewed with reference to the potential applications of modelling to predict the fate of added P in soils. The value of estimating the potential movement of fertilizer P from agricultural soils to water is also discussed.

1.1 Importance of Phosphorus Forms and Concentrations in Surface Waters

The biological productivity of natural waters is often determined by the amounts of specific nutrients present. Phosphorus (P) has been widely implicated as a primary nutrient limiting this productivity (Vollenweider, 1968; Lee, 1970; Kilmer, 1972). Although it has been recognised that other nutrients may limit productivity, e.g., nitrogen (Vollenwieder, 1968; Keeney, 1973), many studies have demonstrated that P is the most wide-spread limiting element in natural waters (Vollenweider, 1968; Schindler, 1971). The role of P limitations in New Zealand waters, however, has not been so well established.

This limitation of biological productivity may be undesirable in some cases, e.g., commercial or recreational fishing. Moyle (1956) estimated fish production in Minnesota lakes to be 100, 167, and 413 kg ha^{-1} yr^{-1}, respectively, from waters containing 0.03, 0.06, and 0.12 mg l^{-1} of total phosphorus (TP). Increases in the nutrient inputs into lakes, however, may have adverse effects on fish yields. Fish (1963) examined three lakes near Rotorua, New Zealand. One of these lakes had streams draining minimally-disturbed catchments of scrub and native bush, while the other two lakes had streams draining catchments dominantly converted to grazed pasture and urban development. Although all three lakes had similar trout populations the lake with streams draining minimally-disturbed catchments yielded trout with greater growth rates and maturity sizes. He suggested that high total P (TP) concentrations in streams draining the agricultural and urban catchments (up to 0.20 mg l^{-1}) led to higher primary production, an increased population of bottom fauna, and a reduction in oxygen supply for the fish. Another effect of increased nutrient inputs into surface water can be the accelerated growth of large aquatic weed plants, e.g., willows, rushes, and floating plants which may reduce the volumes of lakes and capacities of channels, leading to flooding and sediment deposition. Attention has generally been focused, however, on the excessive productions of algae and phytoplankton in association with increased inputs of P to waters (Owens and Wood, 1968; Vollenweider, 1968). Frequently, when such blooms of algae die the depletion of oxygen accompanying decomposition can cause foul odours and the death of fish.

Because of the widely-accepted importance of P to primary production in natural waters, attempts have been made to establish critical concentration limits of P below which algal blooms are unlikely to occur and above which such risks are severe. Several workers (Sawyer, 1947, 1952; Sylvester, 1961; Vollenweider, 1968) agree that the risk of accelerated productivity is slight at concentrations of biologically available P below 0.01 mg l^{-1} and that at concentrations between 0.03 and 0.05 mg l^{-1}, risks may be severe. Holt et al. (1970) have reviewed a number of studies reporting on the P concentrations of some lakes and streams. Despite inconsistencies in the forms of P measured it was shown that concentrations of dissolved inorganic P (DIP) ranged from 0.018 to 0.180 mg l^{-1} (i.e., at or above critical levels) and total dissolved P (TDP) concentrations ranged from 0.015 to 1.40 mg l^{-1} but were frequently between 0.020 and 0.10 mg l^{-1}. In several recent studies, where the concentrations of P in streams draining minimally-disturbed catchments have been measured, similar values have been presented (Singer and Rust, 1975; Timmons et al., 1977). These studies have shown that background concentrations of P forms can approach or exceed the values in the range of 0.01 to 0.05 mg l^{-1} regarded as critical to advanced eutrophication. Where P is the limiting nutrient, the sensitivity of receiving water to small increases in concentrations of biologically-available P forms is likely to be high.

Little information is available on the concentrations of P forms in New Zealand waters. The few studies in New Zealand reporting actual data indicate that concentrations of P in surface waters may also be lower than or close to the critical concentrations of P discussed by other workers. Fish (1969) has suggested that although it is possible that few New Zealand lakes and rivers are affected by eutrophication, a small number (in particular some coastal lakes and the Waikato River) are in an advanced state of eutrophication. Although Mitchell (1975a) has suggested that concentrations of inorganic nitrogen could be low in New Zealand lakes relative to those found in lakes on the North American continent and in Europe, the small amount of available evidence suggests that if P is the limiting nutrient, only small increases in P inputs could increase productivity quite markedly. Data on the background concentrations of P forms in natural waters and the influence of land disturbances on these concentrations in New Zealand are scarce. It seems likely, however, that water quality in New Zealand may be sensitive to quite small changes in concentrations and amounts of P moving into surface waters.

1.2 Factors Influencing Phosphorus Enrichment of Surface Waters

Phosphorus enrichment of surface water can potentially occur naturally from either non-surface sources, e.g. precipitation and wind drift of dust, or from surface and subsurface sources, e.g., vegetation, animals, and soil parent materials. This enrichment gives rise to background concentrations of P in surface water. It is the acceleration of these processes, or the involvement of additional processes, particularly as a result of man's activities, that is of principal concern in accelerated eutrophication. Man particularly increases P inputs to waters by such activities as urban land development with the production of associated domestic and industrial effluents, changes in land use leading to increased erosion, the intensification of livestock farming leading to higher concentrations of animal wastes in runoff, and the use of fertilizers and chemicals on land and water.

1.2.1 Natural or background phosphorus concentrations

Although evaporated and condensed water (theoretically pure precipitation) contains no P (Keup, 1968), surface waters invariably do contain low concentrations of P. Two main general sources account for this. The first of these is a non-surface input. Precipitation may become contaminated with atmospheric materials, e.g., smoke, industrial fumes, or dust particles (Keup, 1968). White (1972) found that although the mean DIP concentration in rainwater over a long time period could be as high as 0.02 mg l^{-1}, concentrations of 0.003 mg l^{-1} in showers were probably more likely. Walker and Syers (1976) have agreed that the annual atmospheric return of P in New Zealand commonly amounts to 0.1 kg ha^{-1}. It is also possible for wind drift to deposit particulate material directly into surface water, e.g., loessial drift (Walker, 1972) or plant material. There may also be miscellaneous contamination by animals directly into water, e.g., bird excrement or insect bodies.

The second input of P forms into water is from surface and subsurface sources. Native vegetation can yield P in leaf drip, stem wash, and percolation through dead litter on soil surfaces (White et al., 1973; Singer and Rust, 1975). Native animals may also contribute to natural inputs of P. Dung has a significantly higher P content than urine (During, 1972). Both O'Connor (1968) and Elliot (1971) have implicated dung as a potential source of P to waters from pasture although few data have been presented to substantiate this. The ability of earthworms to substantially modify the movement of P from pasture in surface runoff has recently been illustrated by Sharpley et al. (1978c). Although surface-casting earthworms increased the movement of particulate P in surface runoff, the loss of DIP was reduced due to litter incorporation. Similar modifications, to a lesser extent, may also occur on native sites.

In a recent study Singer and Rust (1975) observed TDP concentrations of 0.05 to 1.20 mg l^{-1} in surface runoff from an area of 0.01 ha under deciduous forest in Minnesota over a 12-month period. Measuring nutrient losses from an undisturbed aspen-birch forested catchment in Minnesota, Timmons et al. (1977) obtained TP concentrations of 0.33 mg l^{-1} and DIP concentrations of 0.19 mg 1^{-1}. These losses of TP, however, were several times greater than those reported by other workers from climax hardwoods in eastern Ontario, Canada (Schindler and Nighswander, 1970) and from deciduous hardwood and pine in Ohio, U.S.A. (Taylor et al., 1971).

All of these studies have shown that concentrations of P forms in waters originating from minimally-disturbed catchment sources can approach or exceed values in the range of 0.01 to 0.05 mg 1^{-1} regarded as critical to advanced eutrophication. Where P is the limiting nutrient, the sensitivity of receiving water to small increases in concentrations of biologically-available P forms is likely to be high.

Little information is available on the concentrations of P forms in New Zealand waters. Several recent studies have indicated that background concentrations of P forms are close to the proposed critical range. White (1972) measured concentrations of dissolved "reactive" P (filtered at 0.45 μm and measured by the method of Murphy and Riley (1962) without digestion) in a stream draining a small, native-forested catchment at Taita, New Zealand; values of between 0.007 and 0.020 mg 1^{-1} were obtained. In a similar stream draining an exotic forested catchment, concentrations ranged from 0.004 to 0.027 mg 1^{-1}. In a study of the chemistry and trophic status of seven New Zealand lakes near Rotorua, McColl (1972) found that for four of these lakes, described as mesotrophic or oligotrophic and surrounded by catchments largely under native bush, scrub, and grass, "reactive" P concentrations were commonly 0.003 to 0.008 mg 1^{-1} and TP concentrations were commonly 0.010 to 0.020 mg 1^{-1}.

The soils in minimally-disturbed catchments are expected to contain relatively large amounts of organic P (OP) resulting from significant litter return and decomposition. The mobility of OP through a soil has also recently been demonstrated (Rolston et al., 1975). The contribution of OP to natural waters may be considerable but has not been extensively studied.

1.2.2 Urban land use

Runoff from urban land and the outputs of domestic and industrial effluents have been recognised as major sources of P to surface waters (Owens and Wood, 1968; Ryden et al., 1973; Syers, 1974; Johnston et al., 1976). In summarising the results of specific urban runoff studies, Ryden et al. (1973) showed that there was reasonable agreement between the different studies. Concentrations of TP between 0.21 and 0.55 mg l^{-1} were obtained and concentrations of DIP between 0.08 and 1.12 mg l^{-1} were reported. Where large numbers of trees were present in the study area the leaching of seeds, leaves, and debris was thought to contribute significantly to these high values.

Although the concentrations of P recorded in urban runoff are higher than those commonly found in natural waters draining minimally-disturbed catchments (discussed in Section 1.2.1), it is probable that P transported in surface runoff from urban areas amounts to only a small percentage of that contributed by municipal and industrial wastes. Taylor (1967) has suggested that domestic sewage may contain up to 5.0 mg l^{-1} of P. The TP concentration in effluent from the sewage treatment plant at Palmerston North, New Zealand, has been measured (Syers, 1974) as 4.5 mg l^{-1}. Owens and Wood (1968) have presented data which show that TDP concentrations in sewage effluent discharging into the Great Ouse Basin in Britain vary between 3.0 and 14.0 mg l^{-1}. Similar concentrations have been reported by McCarty (1967) and Fergusson (1968) (discussed in Ryden et al., 1973) who estimated that P concentrations in domestic sewage in the United States were between 3.5 and 9.0 mg l^{-1}. Such concentrations of P are commonly between 10 and 1,000 times greater than those found in natural waters. The volumes of these discharges may be small, however, and as point sources of P discharges they are more amenable to identification and control than diffuse sources.

1.2.3 Rural land use

Several workers (Webber et al., 1968; Barnett, 1972; Seim et al., 1972) have argued that the contribution of agriculture to the P enrichment of waters is insignificant relative to that of effluents and sewage, and relative to the benefits of increased agricultural production. Zubriski et al. (1971) has suggested that non-agricultural sources of P in North Dakota, U.S.A. may be sufficient to maintain a eutrophic state of water, despite a reduction in P inputs from agricultural sources. It is widely agreed, however, (Taylor, 1967; Vollenweider, 1968; Kilmer, 1972; Ryden et al., 1973; Syers, 1974), that erosion, direct addition of fertilizers to waters, and intensified animal rearing can all contribute to increased P enrichment of waters. Although data to support these claims are scarce, a brief review of available data relating to specific rural land uses is presented.

1.2.3.1 Forestry

Few studies have examined the concentrations of P in stream discharge originating from catchments under native or production forests. In a comparison of streams draining catchments under native forest, exotic forest, scrub cover, and grazed pasture at Taita, New Zealand, White (1972) obtained mean concentrations of dissolved reactive P in 34 samples from two storms of 0.011, 0.011, 0.017, and 0.018 mg 1^{-1}, respectively. The concentrations of P in streams from both forests were essentially similar but only two thirds of those found in streams from the other two catchments. Higher concentrations of TDP in surface runoff were obtained from an area under deciduous forest in Minnesota (Singer and Rust, 1975), with values ranging from 0.040 to 1.20 mg l^{-1} over a year. High values were attributed to autumn leaf fall and spring decomposition of litter. Studying surface runoff from a catchment under aspen-birch forest in Minnesota, Timmons et al. (1977) obtained average concentrations of TP and DIP of 0.33 and 0.18 mg l^{-1}, respectively. These high values, relative to other studies, could also be due to autumn leaf fall and cycles of freezing and thawing. Freezing causes cell rupture and increases leaching of P (Cowan and Lee, 1971). The streams draining two watersheds, one undisturbed and the other clear-cut, which were each initially under birch, beech, and maple forest, were studied in New Hampshire, U.S.A. by Hobbie and Likens (1973). Mean TP concentrations of 0.0012 and 0.0016 mg l^{-1}, respectively, were obtained for the two catchments in a one-year study. These low values suggested that the catchments were conservative of P relative to inputs from precipitation and the annual turnover of P in forest litter.

Forms and concentrations of P found in stream runoff from forested watersheds in the U.S.A., Europe, and New Zealand have been summarised by Syers and Ryden (1973). Mean concentrations of DIP were frequently within the range of 0.007 to 0.011 mg l^{-1} and TP concentrations were in the range of 0.041 to 0.069 mg l^{-1}.

The small amount of data available indicates that the concentrations of P forms, particularly DIP, are frequently low in streams originating from land under native or managed forest. This is probably due to minimal erosion or movement of particulate P (PP) from such areas. Deciduous forests, with heavy leaf fall in autumn, probably yield higher P concentrations in stream runoff in autumn and spring than coniferous and evergreen forests. It appears that forests on unstable or eroding soil and those that are felled without adequate conservation measures (e.g., minimal logging track construction and buffer strip maintainance along stream banks (Aubertin and Patric, 1974)) will yield far higher concentrations of TP in streams draining the catchments than the figures presented. It seems unlikely that carefully managed, unfertilized forests contribute significantly to increased P enrichment of surface waters.

1.2.3.2 Livestock farming

Livestock farming usually involves either grazed pasture or feedlot systems. Grazed pasture farming is extensively practiced in New Zealand in sheep, cattle, and dairy farming. Despite extensive use of land for these purposes the influence of grazing animals on the movement of P in runoff waters has not been established. O'Connor (1968) and During (1971) have emphasised the importance of dung as a potential source of P to waters but provide no data. Sharpley (1977) has reviewed work by Lee et al. (1969) which showed that 60% of the TP lost to streams in surface runoff from rural land in the Lake Mendota (Wisconsin) watershed resulted from manure applied to frozen ground in agricultural areas. Losses from frozen ground, however, are of little relevance to the New Zealand situation. In a recent study, Sharpley and Syers (1976) have shown that the presence of 100 dairy cows grazing a 4-ha area for 24 hours, as part of the regular farm grazing rotation at Massey University, New Zealand, increased mean concentrations of DIP and PP in surface runoff originating from plots within the 4-ha area. Control concentrations of DIP and PP before grazing were both consistently close to 0.20 mg l^{-1} but after grazing, the mean concentrations in surface runoff from storm events increased to 1.80 and 3.0 mg l^{-1}, respectively. After approximately 20 days the concentrations of both P forms had returned to pre-grazing values. It seems likely that the influence of grazing animals on soil composition and increased surface runoff will also increase P losses from pasture. Although grazing animals are a potentially important source of P to natural waters their influence is still not fully understood.

Feedlot raising of animals in New Zealand is not yet practiced to any meaningful extent but the concentration of animals for several hours (milking and drenching), days (holding pads), or even months (overwintering barns) is widespread. Syers (1974) has pointed out that up to 64,000 kg of P may require disposal annually from 20,000 dairy sheds. Because such wastes are either discharged into streams or returned, at unusually high concentrations, to small areas of pasture from which losses may be high, the intensification of stock can significantly increase P inputs to water. Extremely high concentrations of DIP in the drainage discharge from a cattle wintering yard near Massey University have also recently been reported (Tillman et al., 1978). In a similar study, Edwards et al. (1972) isolated a 0.17-ha area of barnlot (used as a beef-cattle barnlot for 25 years) in east-central Ohio, U.S.A. and sampled the storm runoff from the area for three years. Mean monthly concentrations of TP in runoff water ranged from 1.40 to 13.90 mg l^{-1} in 1968; mean annual concentrations of TP in runoff water in the three years 1968, 1969, and 1970 were 3.20, 4.60, and 7.20 mg l^{-1}, respectively. These concentrations of P are similar to those found in domestic sewage. Despite the small volumes involved, discharges from confined animal operations may be an important source of P to waters in some situations.

1.2.3.3 Cropping

Soil losses and the movement of particulate and dissolved P forms have been studied extensively because row-cropping and soil cultivation are widely practiced, particularly in the U.S.A. Attempts to isolate the influence of soil cultivation and cropping from that of fertilizer on P movement in runoff forms from arable land have involved study areas ranging from small runoff plots to whole catchments. Comparisons between these studies are difficult, however, because of widely differing cropping practices, soil types, slopes, rainfall characteristics, sampling of runoff, and P forms measured. The movement of eroded soil material, which may be enriched in P (Rogers, 1941; Ryden et al., 1973), will potentially have a greater effect on the P concentrations of streams than the P which moves in percolating ground water (Taylor, 1967). In studying concentrations of P forms in drainage water from a wide variety of crops in the Coachella Valley, California, Oertli and Bradford (1973) found that dissolved P in drainage water from the cropped land was commonly less than 0.10 mg 1^{-1}. In a study in California, Johnston et al. (1965) reported that drainage waters from fertilized crops frequently had a mean P concentration of 0.08 mg 1^{-1}. Although concentrations reported from both these studies represent low proportional losses of P added as fertilizer P (Ryden et al., 1973), they significantly exceed the suggested critical concentrations discussed in Section 1.1. The losses of P and sediment in surface runoff from four field-sized experimental watersheds in Iowa, U.S.A. were studied by Schuman et al. (1973). Two of these watersheds were row-cropped with corn, one being contour-planted and the other level-terraced. For a period of three years of surface runoff sampling, solution P concentrations averaged 0.220 and 0.513 mg 1^{-1} from the contoured and terraced watersheds, respectively. Concentrations of PP were between 1.0 and 3.0 mg 1^{-1} over the same period from the two watersheds. These concentrations of dissolved P are high relative to the background levels of P in natural waters;

the concentrations of PP are extremely high. The influence of clean fallow, corn, oats, and hay crops on the movement of P in surface runoff in Minnesota was studied by Burwell et al. (1975). Using natural rainfall erosion plots established on 6% slopes, they found that up to 95% of all P lost in surface runoff from cultivated cropping systems was lost as PP. Nelson and Romkens (1971) examined concentrations of DIP in surface runoff from unfertilized and fertilized fallow and cultivated plots. The concentrations of DIP increased from approximately 0.05 mg 1^{-1} to 0.50 and 0.30 mg 1^{-1}, respectively, after P fertilizer was applied at rates of 56 and 28 kg P ha^{-1}. Although concentrations of PP were not reported the concentrations of sediment in surface runoff were found to be as high as 7,000 mg 1^{-1}. The finding of Schuman et al. (1973) that PP concentrations may exceed DIP concentrations by a factor of approximately 6 when large concentrations of sediment are present in surface runoff, may indicate that PP concentrations could have been as high as 3.0 mg 1^{-1}. Such losses of P from fertile, cultivated soils, and sediment concentrations of up to 7,000 mg 1^{-1} in surface runoff may not be uncommon. Because the concentrations discussed, notably those for PP, are high relative to those for natural waters, cropping may be a major source of P enrichment in waters, particularly where conservation practices are inadequate.

1.2.3.4 Fertilizer

It has been emphasised widely that the use of fertilizer and appropriate land management systems may contribute positively to water quality by promoting and maintaining an erosion-resistant vegetation cover on marginal or unstable land (Kilmer, 1972; Viets, 1971; Syers, 1974; Walker, 1975). The reduction in erosion and in the movement of PP that can result from fertilizer application is the main rationale for such claims.

Fertilizer P, however, has been implicated as an important source of P moving into natural waters from rural land (Fish, 1969; Mitchell, 1971). Despite this claim, there have been few studies which have specifically examined the influence of P fertilizers added to agricultural land on the amounts and concentrations of P moving into water. Holt et al. (1970) have presented some data from the unpublished work of Timmons (1969) who investigated the influence of superphosphate, incorporated into cultivated surface soils, on the concentrations of DIP in surface runoff. Concentrations of 0.08 mg l^{-1} for DIP in surface runoff from a control plot and 0.09, 0.16, and 0.30 mg l^{-1} for DIP in surface runoff from plots on which fertilizer was broadcast and deep-ploughed, disked into the surface, and surface-applied without incorporation, respectively, were obtained in this study. To investigate the effect of mixing P fertilizer with soil, Romkens and Nelson (1974) added 0, 56, and 113 kg P ha^{-1} to replicate runoff plots of cultivated Russell silt loam. Concentrations of DIP in surface runoff water were found to be 0.07 mg l^{-1} from the control and 0.24 and 0.44 mg l^{-1} from the plots fertilized at the two rates of P, respectively. Nelson and Romkens (1971) found a loss of fertilizer P (56 kg P ha^{-1} added) of 1.2% in 250 mm of surface runoff from fallow and tilled plots during a 3-month period whereas Schuman et al. (1973) reported a 0.6% loss (39 kg P ha^{-1} added) from pasture in a 6-month period. Although these amounts are regarded as being agronomically insignificant, the concentrations of dissolved P appearing in surface runoff are high relative to the background levels discussed in Section 1.2.1.

The movement of P in drainage and seepage water, from fertilizers applied to the soil surface, is often believed to be small due to the low mobility of P in soils (Taylor, 1967; Ryden et al., 1973). Bolton et al. (1970) reported that P concentrations in tile drainage water from soils under various crops were only slightly affected by fertilizer P addition and concentrations of 0.20 mg 1^{-1} were commonly obtained. Although the movement of fertilizer P within soils may be limited, such values are also high relative to background concentrations.

In spite of pastoral farming on steep land, the occurrence of winter surface runoff, and extensive superphosphate fertilizer application in New Zealand, data on the influence of fertilizer P addition on the P concentrations in runoff waters are very limited (Syers, 1974). Gilchrist and Gillingham (1970) have shown that up to 28% of added P may be transported over 30 cm (the length of the small plots used) through improved pasture under very heavy artificial rainfall applications (6.6 and 13.3 cm $hour^{-1}$). How much of this 28% of fertilizer P actually moves over longer distances into a stream is unknown. It has been pointed out (Syers, 1974) that fertilizer falling directly into a stream or channel can increase P concentrations significantly. In examining the influence of fertilizer application on P concentrations in storm runoff from a newly-cleared catchment at Puketurua, Whangarei, McColl et al.(1975) noted that P losses in storms occuring shortly after fertilizer application corresponded closely to the amounts of P calculated to have fallen into the stream channel. The aerial application of superphosphate to pasture was considered (Fish, 1969) to have increased TDP concentrations in a stream draining a fertilized area, from 0.09 mg 1^{-1} before application to 8.9 mg 1^{-1} in samples taken immediately after application. In a study at Tomahawk Lagoon, near Dunedin, in May - June, 1965, Mitchell (1971) suggested that the large amounts of soluble "reactive" P entering the Lagoon resulted from aerial topdressing. A recent study by Sharpley and Syers (1976) has shown that DIP and PP concentrations in surface runoff from grazed pasture at Massey University increased, following the application of 50 kg P ha^{-1}, from control values of 0.20 mg l^{-1} to 3.3 and 2.8 mg l^{-1}, respectively. Although the mean concentrations in surface runoff from successive storm events declined progressively throughout the year, they remained between 2 and 5 times greater than those obtained with the control plot. Despite the fact that the losses of DIP and TP represent only 2.9% and 6.7% of total P added, respectively, the concentrations of P obtained in surface runoff are high relative to the data discussed in Section 1.2.1.

1.2.4 Relative importance of factors influencing the phosphorus enrichment of waters

A review of the background concentrations of P forms found in surface waters originating from natural or minimally-disturbed catchments overseas has shown that dissolved P concentrations of approximately 0.01 to 0.05 mg l^{-1} commonly occur. These values are supported by limited data from New Zealand studies and are close to or within the range of dissolved P concentraions which is internationally recognised as the threshold for the development of algal blooms.

Urban runoff, with TP concentrations of between 0.20 and 0.50 mg l^{-1}, and sewage and effluent discharges with TP concentrations of between 5 and 15 mg l^{-1}, may contribute substantially to the P concentrations in receiving waters. Their influence, however, is localised and probably amenable to control, relative to the widespread, diffuse contributions from rural land uses.

Although P movement from unfertilized forests is insignificant relative to background concentrations, concentrations of DIP and PP in surface runoff from intensively-grazed pasture may be as high as 0.20 mg l^{-1}, i.e., ten times higher than background concentrations. Even higher DIP concentrations (up to 0.50 mg l^{-1}) and PP concentrations (up to 3.0 mg l^{-1}) in surface runoff may occur from cropped soils. Although cropping is less extensive in New Zealand than pastoral farming, its increasing role makes it a potentially important source of P movement into surface water.

The application of P fertilizer to soil is an integral part of arable or pastoral farming. Although several studies have indicated that only a small proportion of fertilizer P added to soil is lost in surface runoff (often as little as 1%), and even less lost in drainage water, such movement of P may be widespread and have a major influence on the P concentrations found in receiving waters.

The significance of rural land, relative to urban land, in increasing P concentrations in surface waters may be large, particularly in New Zealand. Such a diffuse P source is difficult to identify and even more difficult to control. It is apparent, however, that although very much higher P concentrations in receiving water may result from point discharge sources, the "critical" P concentrations discussed previously may be widely and frequently exceeded in waters receiving runoff water from rural land.

1.3 Movement of Phosphorus from Soils to Surface Waters

Although the relative importance of factors influencing the extent of P enrichment of surface waters has been discussed in Section 1.2, specific sources of water and P require clarification.

1.3.1 Sources of water and phosphorus

The movement of P into receiving waters may originate from point sources and diffuse sources (Ryden et al., 1973). Although industrial and sewage effluents are obvious point sources, P movement into surface water from rural land usually takes the form of diffuse sources.

Studies of the movement of P forms from soil to water have ranged from the sampling of surface runoff from small, precisely-defined runoff plots (Gilchrist and Gillingham, 1970; Nelson and Romkens, 1971) to the sampling of rivers draining areas of land, partly or wholly under a particular land use (Oertli and Bradford, 1973; Burwell et al., 1974). This has meant that the fractions of runoff responsible for P movement from land have either been incompletly studied or else not well identified, making it difficult to establish sources of P for comparative or prediction purposes. Further to this, as pointed out by Ryden et al. (1973), many studies have measured different P forms in runoff water, e.g., only TP or specific P forms. In studies where there have been inadequate or incomplete flow data (discussed by Taylor et al., 1971) or inadequate sampling (discussed by Sharpley et al., 1976), actual loadings of nutrient forms from specific sources may have been difficult to quantify even if the sources of flow had been established. Kilmer (1972) has proposed the following parameters as being ideal for field experiments designed to study the sources and amounts of nutrient movement to water from soils and fertilizers:

1) A drainage system permitting the quantitative measurement of water discharge volumes (surface, subsurface, and base flow) from an area whose dimensions are accurately established.

2) A continuous water-sampling system that takes samples proportional to flow volume.

3) Monitoring instruments to measure nutrient inputs in precipitation and dry fallout.

4) Provisions for obtaining nutrient transport data under unfertilized or control conditions.

5) Facilities for preserving water samples during the period between collection and chemical analysis.

In attempts to establish the influence of land use and related factors on P movement from soils to water it is essential to establish sources of water which carry P, forms of P transported, and reliable loading calculations for P forms. In particular, in measuring P additions to water from rural land and diffuse sources, the isolation of contributions from surface and subsurface runoff is useful.

1.3.1.1 Surface runoff

Surface runoff is that part of precipitation which flows over the land surface to stream channels. Discussion of concentrations of dissolved and particulate P forms in Sections 1.2.3 and 1.2.4 has indicated that high concentrations of DIP, TDP, PP, and sediment can be transported over at least short distances in surface runoff. Although lower concentrations of P forms and sediment are often found in surface runoff from whole catchments than from small runoff plots, because small plots often measure only localised relocation of P and fail to account for net movement , it has been shown that surface runoff from rural land can contain high P concentrations, especially of PP. Romkens et al.(1973) obtained high correlation coefficients between the PP and clay contents of runoff sediment, probably because of the high affinity of clay particles and related amorphous constituents for P, resulting in the "enrichment ratio" effect (Rogers, 1941). Thus if soil erosion is reduced, movement of P from the surface soil may be greatly reduced.

The lower saturation of the P sorbing complex in unfertilized soils would tend to result in a greater proportion of the P transported in surface runoff remaining attached to soil particles (Munn et al., 1973; Burwell et al., 1975). Sorption or desorption of P may occur when the soil particles enter waters of higher or lower DIP concentrations, respectively, than those in surface runoff water. Increased P concentrations in surface runoff following the application of P fertilizer (Schuman et al., 1973) may result from both the dissolution of fertilizer particles and reaction products, and an increase in the saturation of the P sorbing complex, with the P on sorption sites of lower binding energy maintaining higher dissolved P concentrations in solution. Because the movement of soil P in surface runoff is often closely related to that of sediment movement, an understanding of the reactions of P with soils and soil components should be useful in explaining and predicting the concentrations of DIP maintained in solution by PP and sediment transported in surface runoff.

1.3.1.2 Subsurface runoff

Subsurface runoff is that part of precipitation which infiltrates the soil and moves towards streams as ephemeral, shallow-perched groundwater above the main groundwater level. Drainage discharge may be regarded as a form of accelerated subsurface runoff (Sharpley et al., 1976). In many situations subsurface runoff may contribute a major portion of stream flow (Minshall et al., 1969; White, 1972). Several studies have shown that a very low proportion of fertilizer P applied to the soil surface appears in accelerated subsurface runoff (Bolton et al., 1970; Cooke and Williams, 1970), and that lower concentrations of DIP are found in drainage water than in surface runoff from the same experimental areas (Benoit, 1974). Two main reasons account for this. Firstly, P is often strongly sorbed by soil components (Syers et al., 1971; Ryden et al., 1977a). This is in contrast to anions such as NO_3^- and Cl^- which usually move freely through the soil profile in drainage water and often appear in relatively high concentrations in subsurface runoff. The P-sorbing complex of subsoil material usually shows a lower saturation than that of surface soil, due to the accumulation of P in surface soil. Consequently, P will be sorbed with a higher binding energy (Ryden and

Syers, 1977a) in the subsoil. Secondly, because of the physical sieving action of the soil profile, subsurface runoff contains only small amounts of particulate material and, consequently, of PP (Ryden et al., 1973). Recent experiments by Rolston et al. (1975) have shown that organic P compounds may move more readily through the soil profile than inorganic P to depths of up to 12 cm before hydrolysis. The movement of organic P, which may become biologically available (Berman, 1970), in subsurface and drainage water has not been studied extensively. An increased understanding of the reaction rates of P with soils and the potential release of P to water moving through the soil is required.

1.3.2 Potential influence of changes in land use on phosphorus movement to water

The literature reviewed in Section 1.2 has suggested that the potential P enrichment of water can partly be related to land use practices. Several authors have suggested that a change in land use may increase (Benoit, 1974; McColl, 1972) or decrease (Viets, 1971; Kilmer, 1972) the amounts and concentrations of P forms moving into surface water. Although several studies have compared the influence of different land use on P losses in runoff (White, 1972; Schuman et al.1973) almost no data are available from studies designed to measure P losses from land undergoing a specific use change. Such data are particularly scarce in New Zealand, despite extensive land clearing.

Several studies have suggested that a change in land use may not affect P losses greatly and may have a conservative effect on the movement of water and sediment from cleared land. Toebes et al. (1968) has shown that following oversowing and topdressing of unimproved pasture in a small catchment at Makara, New Zealand, there was a decrease in annual runoff, a probable increase in infiltration, and an increase in surface detention.

This could indicate a decrease in sediment movement and PP in surface runoff. Aubertin and Patric (1974) reported no increases in nutrient or sediment losses from a clear-cut watershed in West Virginia in which a buffer strip was left along the main stream channel. In a New Zealand study of yellow-brown pumice soils under grazed and ungrazed pasture, and scrub, Selby (1972) showed that with careful management and complete soil cover, erosion losses from grazed pasture could be less than those from scrub. It is possible that nutrient losses, especially particulate forms, may be reduced where adequate precautions accompany changing land use.

It has also been suggested (Fish, 1971; Mitchell, 1975b) that the development of grazed pasture has led to increased P concentrations in streams draining such catchments. Fish (1971) suggested that pasture catchments were the major sources of P entering Lake Rotorua, relative to inputs from catchments under scrub and bush. Similar claims have been made by Mitchell (1975b) for a small catchment contributing stream flow to Lake Mahinerangi after the catchment was developed to grazed pasture.

It is now recognised (Scarseth and Chandler, 1938; Burwell et al., 1975) that major losses of P can occur from land during and following a change in land use. A critical period threatening P enrichment probably occurs during the clearing operation when bare, disturbed soils and fertilizer are susceptible to movement in surface runoff. Where the burning of debris in stream beds or catchments is practiced, higher concentrations of P forms in early winter flow events seem probable (White et al., 1973). It has also been pointed out (Fish, 1969; Syers, 1974; Mitchell, 1975a) that during and following the land development operation direct contamination of waterways by aerially-applied superphosphate can increase P concentrations in water. Despite the fact that such operations are widespread in New Zealand, quantitative data for their effects are unavailable. These are required to support land use management recommendations.

The fact that the composition of runoff from cleared and fertilized soil is influenced by soil P reactions, both in the soil profile and in suspensions of sediment and runoff water, has been well established (Taylor and Kunishi, 1971; Ryden et al., 1972a,b). A consideration of the forms of P present in soils and their reactions seems essential to an understanding of the potential movement of P within and from soil. In particular, the reaction rates and mechanisms of P added to soils may control the persistence of labile P and the potential mobility of P from soil into water.

1.4 Forms and Reactions of Phosphorus in Soils

The potential of a soil to contribute to P enrichment of surface and subsurface water is partly dependent on its P status. The forms and reactions of P in soil, determining its P status, are subsequently reviewed. It is convenient to distinguish between organic P (OP) and inorganic P (IP) and further to divide IP into primary and secondary forms. Because fertilizer P added to soils essentially influences secondary IP forms and reactions, these will receive major attention.

1.4.1 Organic phosphorus in soils

The quantitites of OP found in soils can vary widely. It has been reported (Syers and Williams, 1978) that between 20 and 90% of TP in soils may be present as OP and this range may even be exceeded in some cases. The diversity and complexity of OP forms has meant that the subject is rather poorly understood, despite considerable investigation. Several authors (Anderson, 1967; Cosgrove, 1967) have reviewed the nature, sources, properties, and metabolism of soil OP. Three main groups of phosphate esters that have been identified in soils are inositol phosphates, nucleic acids, and phospholipids.

Inositol phosphates are esters of orthophosphoric acid and the cyclic polyol, inositol. Their amounts in soils may vary, forming between 5 and 58% of OP, but they occur widely. It has been suggested that the mobility of inositol P in soils may be controlled by both sorption and precipitation reactions.

Nucleic acids are high molecular weight polymers of two types: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Their widespread occurrence is due to the presence of DNA and RNA in the nuclear material of all living cells. This extensive occurrence, however, is of little significance to the P status of soils in view of the small amounts found.

Phospholipids form a group of phosphate esters which is poorly defined and only very small amounts are present in mineral soils. Apart from their presence little is known about their interactions with soils.

Despite their poor characterisation it has been suggested that OP compounds play a significant role in the P chemistry of soils (Sinha, 1971). The total amounts of OP and IP present in a soil reflect the balance between the processes of formation (addition) and mineralization (decomposition) (Syers and Williams, 1978). The mineralization of soil OP has been studied extensively under field and laboratory conditions (reviewed by Cosgrove, 1967). In a field study, Dormaar (1972) reported a rapid decline of soil OP in spring following a winter accumulation. The winter accumulation and rapid spring decline of OP has widely been observed and attributed to increased microbial activity with increased spring temperatures and soil aeration. In an experiment to monitor the decline in "labile" IP in soil, which was expected to accompany the large increase in plant uptake in spring pasture growth, Saunders and Mettson

(1971) found no significant difference in the labile pool of IP over this period. They concluded that the pool of plant-available IP was maintained, despite removal from it, at a stable level by increased mineralization of soil OP. In a leaching experiment Rolston et al. (1975) found that IP added to the soil surface remained in the top 2 cm but OP moved up to 12 cm down through the soil before mineralization. This mobility could be an important factor in P cycling within soils and the movement from soils.

Because the amounts and forms of OP in soils vary greatly and the rates of mineralization and formation appear to depend on many factors (Thompson and Black, 1948; Eid et al., 1951; Cosgrove, 1967) it is possibly not surprising that the role of OP in the P dynamics of soils remains unclear. While it is difficult to estimate the net contribution of OP mineralization to the pool of IP in soil, it is clear that under certain environmental conditions the contribution can be significant. This may be an important consideration in assessing the potential of the soil to supply P for plant uptake and to contribute to the P enrichment of surface and subsurface water.

1.4.2 Inorganic phosphorus in soils

1.4.2.1 Primary inorganic phosphorus

Primary IP occurs in soils as the mineral apatite. Minerals of this group have the formula $Ca_{10}(PO_4)_6X_2$ where X = F, OH, Cl, or $\frac{1}{2}$ CO_3. Fluorapatite is the most stable of these forms and occurs widely in igneous and metamorphic rocks (up to 95% of P in igneous rocks). Generally, apatite is stable, except under acid conditions, although weathering can be more rapid in topsoils where temperature and microbial activity are greater, and further advanced in older soils. Although apatite is initially the major source of P in virgin soils, the rate of weathering is generally too slow to provide adequate P for plant growth, unless the plant species have a low P requirement.

1.4.2.2 Secondary inorganic phosphorus

Secondary IP has widely been considered to consist of three groups: soil solution P, precipitated P forms, and sorbed P forms.

Soil solution IP generally comprises only a small fraction (commonly approximatley 0.1%) of TP in soil. Despite this, DIP along with DOP is potentially the most mobile form of P in soil. It is probable that a balance between DOP and DIP in the soil solution is maintained (discussed in Section 1.4.1) by quite rapid mineralization of DOP (phosphatase enzymes) and assimilation of DIP (biological uptake) within soils. The pool of DIP present in the soil solution forms the only known source of directly plant-available P. It is also believed to be in equilibrium with other forms of IP in the soil.

Much work has been published on studies of precipitated P forms in soils. During this century there have been alternations between the arguments for sorbed P and slightly-soluble, precipitated P as the forms controlling soil solution P concentrations. Prior to 1916, soil IP was thought to be in the form of slightly-soluble P compounds maintaining low solution P concentrations. Studies by Russell and Prescott (1916) and Mattson (1930, 1931) led them to propose a sorption mechanism which was widely accepted until 1950. Cole and Jackson (1950) and Haseman et al. (1950) were some of the first workers to show that a number of crystalline P compounds could be identified when soils were reacted with concentrated P solutions, often at elevated temperatures. It was thought that compounds of the variscite ($AlPO_4.2H_2O$), barrandite ($(Fe, Al)PO_4.2H_2O$), and strengite ($FePO_4.2H_2O$) isomorphous series controlled the retention and release of P in neutral and acid soils via solubility equilibria.

The reaction of fertilizer P with soils or soil components, following high P addition rates, has allowed the identification of a large range of such compounds (Huffman, 1962; 1968). Despite the identification, by x-ray diffraction, of such compounds from high P concentration systems (Haseman et al., 1950) they were not detectable in soils fertilized at normal rates. The extremely small size of the crystals was suggested as the reason for this (Haseman et al., 1950). Kittrick and Jackson (1955) showed that the concentrations of P maintained in solution by discrete-phase compounds were higher than those found in soils, except near to fertilizer particles. Although this did not exclude the possibility that such compounds may form following fertilizer addition to soil, it seemed less likely that the solubility of discrete P compounds alone controlled the pool of IP in the soil solution. The suggestion that high soil solution concentrations of Fe and Al would suppress the dissolution of P compounds was shown (Hsu, 1964) to be unfounded. Bache (1963; 1964) also questioned the stability of crystalline variscite and strengite in soils. Although many crystalline P compounds and several short-range order precipitates may be identified as immediate fertilizer reaction products (Lindsay et al., 1962) it is now generally believed that the solubility equilibria of such minerals do not adequately explain the chemistry of P in soils (Syers and Williams, 1978). The proposal that sorption reactions, rather than precipitation reactions, are likely to control soil solution P concentrations is now considered more likely.

Sorption reactions refer loosely to both the processes of adsorption and absorption which are difficult to distinquish and probably occur simultaneously. Adsorption refers to the development of a higher species concentration at the surface of the solid phase than occurs in the solution phase. Absorption refers to the more or less uniform penetration of a species into the solid. Because it is possible that both adsorption and absorption involve similar mechanisms, Syers and Williams (1978) have suggested that absorption can be considered as adsorption on internal surfaces, making a distinction important in terms of rates only.

The ability of a soil to sorb P is essentially influenced by both the amounts and types of P-sorbing components present. Of particular importance are poorly structured, short-range order compounds, in contrast to highly structured, crystalline compounds. One short-range component usually found in soils contaminated by volcanic ash is allophane-like material which has been shown (Cloos et al., 1968) to be extremely effective in P sorption. Short-range order Fe and Al hydrous oxides and hydroxy-oxides have large surface areas and are also capable of sorbing large amounts of P (Bache, 1964; McLaughlin et al., 1977). Bache (1963) showed that poorly-ordered Fe and Al hydroxides can sorb up to 20 times more P than crystalline Al hydroxide. Where such short-range order materials occur as coatings on other soil components, e.g., clay minerals, it has been suggested (Ryden et al., 1973) that they, together with the greater surface area of the clay fraction, explain the higher TP content of clay fractions in soils. The higher sorption maxima of short-range order components, extensively found in soils, is attributed to greater surface areas and numbers of $-OH$ and $-OH_2$ groups in surface positions which can undergo ligand exchange reactions with P.

It is apparent that if sorption and desorption processes in soils control solution P concentrations, an understanding of the mechanisms involved should contribute to the prediction of the P status of a soil and the fate of fertilizer P in soil. Although such mechanisms have been proposed their usefulness in describing P forms and reactions in soils has still not been extended to a practical field interpretation.

1.5 Modelling the Reactions and Reaction Rates of Phosphorus Added to Soils and the Movement of Phosphorus from Soils

1.5.1 Reactions

The sorption of IP by soils and soil components has been shown to follow a distinct pattern (Hsu, 1964; Rajan and Fox, 1972; Ryden et al., 1976). This has been described as an initial rapid reaction followed by a very much slower reaction which can proceed for many days and even months. Several interpretations of the mechanisms involved in P sorption have subsequently been made. Hsu (1964) considered that the "fast" reaction was due to rapid surface sorption and the "slow" reaction involved progressive build-up of P on newly-formed surfaces. Cloos et al. (1968) concluded that two diffusion processes were involved.

A number of workers have analysed experimental data by the use of sorption isotherms. Although the results obtained from isotherm resolution do not prove that sorption mechanisms, as distinct from precipitation mechanisms, are operating they can provide useful information which, in association with other experimental results, may provide evidence for reaction mechanisms.

1.5.1.1 Isotherm resolution of data

The relationship between adsorbed and unadsorbed species at a given temperature may be described by a sorption isotherm. Because absorption may be regarded as a form of adsorption, it is possible that both adsorption and absorption reactions can be described by a sorption isotherm.

The simplest form of isotherm commonly used to describe P sorption data involves plotting the amount of P sorbed against the amount remaining in solution. Attempts have been made to obtain more quantitative data from such simple isotherms by the use of isotherm equations, e.g., Freundlich or Langmuir, or by division of the simple isotherm into distinct regions by inspection (Bache, 1964; Muljadi et al., 1966). More recent work by Syers et al. (1973) showed that the breaks obtained by resolution of experimental data did not correspond to the breaks obtained by "inspection" and the validity of the inspection procedure has been questioned.

The Freundlich equation takes the form:

$$x/_m = kC^{\frac{1}{n}}$$

or $$\log x/_m = \log k + \frac{1}{n} \log C$$

where x = weight of P removed by a weight m of solid, C = the equilibrium concentration of P in solution, and k and n are constants. Although the equation was developed to describe the sorption of gaseous species by a solid, it has been used to describe the sorption of P from solution by soils (Low and Black, 1950) and soil components (Kuo and Lotze, 1973). It has been found (Bache and Williams, 1971), however, that good fit between sorption data and the Freundlich equation is not always achieved. It has been suggested (Sawhney, 1974) that progressive sorption of anions (e.g., P) leads to increasing negative charge on sorption surfaces with a corresponding net decrease in the heat of sorption for latterly-sorbed species. It has been largely for this reason that the Freundlich equation, which assumes a logarithmic decrease in the heat of adsorption with increasing surface cover, has been favoured.

The Langmuir equation may take the form:

$$x/_m = K_1 K_2 C/(1 + K_1 C)$$

where x, m, and C are the same as in the Freundlich equation and K_1 and K_2 are constants related to the binding energy and sorption maximum, respectively. This equation assumes that the heat of sorption remains constant with changing surface cover, implying uniform sorption sites and no interaction between sorbed species, and that monolayer sorption is the maximum possible. Despite these strict conditions, the Langmuir equation has yielded good fit to experimental data and been useful in describing P sorption by soils.

The first detailed study of the application of the Langmuir equation to describe sorption of P by soils was reported by Olsen and Watanabe (1957) using the linear form:

$$C/{}^{x}/_{m} = 1/K_1 K_2 + C/K_2.$$

Although close fit of the data with the equation was achieved, their data indicated that two linear relationships were present. Since then many similar studies have been undertaken (Muljadi et al., 1966; Syers et al., 1973; Holford et al., 1974; Rajan and Fox, 1975).

Another rearranged form of the Langmuir equation which has been used recently(Ryden et al., 1977a) is in the form of:

$$1/_{x} = 1/_{K_1K_2C} + 1/_{K_2}.$$

It can be shown that K_1 as derived from this equation, is equivalent to the equilibrium constant of the sorption reaction. A linear relationship is obtained for data conforming to this reciprocal form of the equation such that values for K_1 and K_2 can be calculated. Use of the reciprocal form of the equation has been criticised (Veith and Sposito, 1977) because small errors in the measurement of solution P concentration can result in large numerical errors in the value of $^{1}/_{C}$. Careful analytical procedures and reliable data, however, permit the use of this equation form to evaluate P sorption at low solution P concentrations.

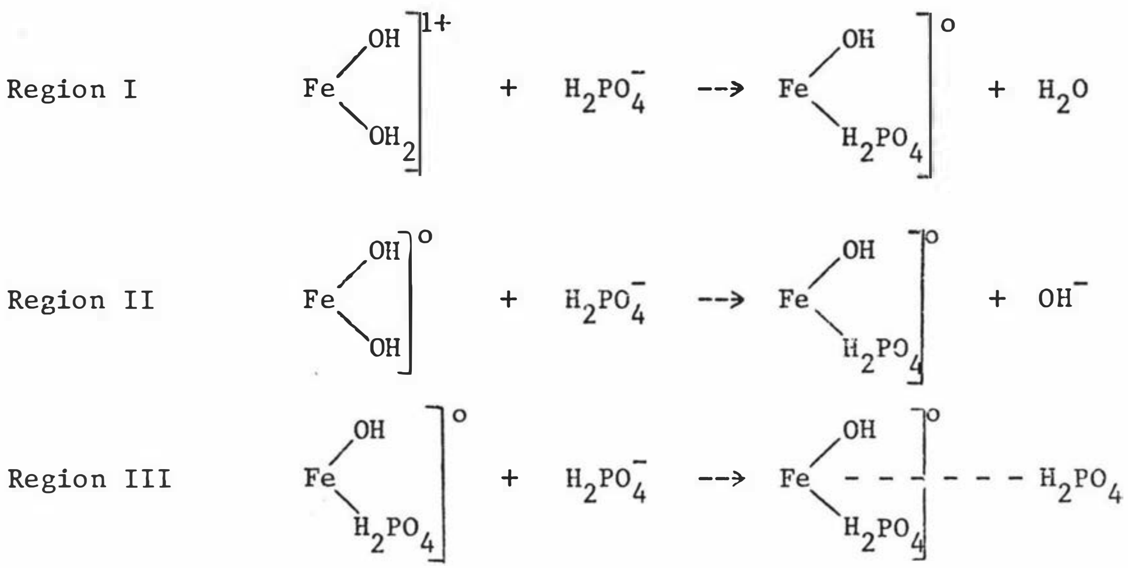
1.5.1.2 Reaction mechanisms

Sorption isotherm equations have been used in conjunction with other experimental evidence to study P sorption reactions in soils and to propose reaction mechanisms. Sorption of P has recently been investigated (Ryden et al., 1977a) over a wide range of solution P concentrations, including less than 3 μmole l^{-1}, for which there have been little data available. It was found necessary to determine equilibrium isotherms for P sorption (Ryden and Syers, 1975) in order to obtain true estimates of the sorption maxima, and also to correct the isotherms for "native" P already on surfaces prior to P addition. When the reciprocal form of the Langmuir equation was applied to the corrected equilibrium isotherm it was found that at least 5 linear portions were apparent on the overall isotherm over a final P concentration range of 0 - 650 μmole l^{-1}. A single linear relationship could only be obtained over a very restricted concentration range. Multiple linear relationships implied that P was sorbed concurrently at more than one distinct K_1 value. Therefore a procedure of successive approximation was developed (Ryden et al., 1977a) to resolve the experimental data obtained. It was subsequently shown that three distinct relationships or regions (I, II, and III), each conforming to a particular Langmuir equation, described the overall P sorption isotherm. For each region it was possible to determine a value for K_1 and K_2, where K_1 was equated to the free energy of sorption (ΔG) by the equation:

$$\Delta G = - RT \ln K_1 \quad \text{(Graham, 1953).}$$

It was found that the values of ΔG were extremely similar for a particular region, not only for contrasting soils but also for Fe gel. Differences in sorbants used were reflected only in the magnitude of the sorption maxima (K_2 values). The magnitudes of the ΔG values were such that a more chemical type bond (chemisorption) was suggested for the first two regions whereas the third region had a relatively low ΔG value suggesting a more-physical sorption type. Further evidence for the sorption types was provided by the observation that although sorption in regions I and II was independent of ionic strength, sorption in region III was dependent on ionic strength.

The charge relationships of P sorption obtained for Fe gel were consistent with those for soils, permitting a more detailed evaluation of the mechanisms of sorption involved. In regions I and III the negative charge on the sorbant increased whereas no change in charge occured for region II sorption. Solution pH showed no change with sorption in regions I and III. From this information, three different reaction mechanisms for these three regions were proposed:



These proposed mechanisms were found to be in agreement with all the other experimental evidence and data obtained. They are similar to those proposed by Hingston et al. (1972) but contrast in that Hingston et al. (1972) proposed reactions which exclusively involved ligand exchange and also suggested that all sorption mechanisms always rendered the sorbing surface more negatively charged. An important aspect of the three regions or mechanisms, as proposed by Ryden et al. (1977a), is that the ΔG values, the K_2 values, and the breaks in the three regions are calculated by isotherm resolution of actual experimental data.

Several criticisms of the applicability of the Langmuir equation to describe sorption isotherms have recently been made. These include the suggestion by Harter and Baker (1977) that with increasing sorption of anions, e.g., $H_2PO_4^-$, at surfaces the reactions involved displace competing anions, e.g., OH^- into solution. They suggested that at high saturations of the sorbing complex it is necessary to adjust solution concentrations of the sorbed species to take account of increasing concentrations of competing anions. Recent studies in this laboratory have shown, however, (Tillman, R.W., pers. comm.) that at high saturations of sorbing complexes in soils no corresponding pH change is observed in solution, indicating that in whole soils, rather than pure systems, buffering of the solution occurs to balance the increasing OH^- concentration, as suggested by Ryden et al. (1977a). More fundamental criticism of the Langmuir equation approach to sorption isotherm analysis has been made by Bowden et al. (1977). They suggested that increasing saturation of the sorbing complex by anions renders the net charge on the surface more negative, thus reducing ΔG for the reaction, which is not taken into account by the equation. It has been argued, however, by Brunauer et al. (1967) that lateral interaction energies between physically-adsorbed molecules increase the heat of adsorption. This implies that the greater the number of adsorbate molecules on the surface, the greater the contribution to the heat of adsorption. This may result in an effective balancing of the decreasing heat of adsorption due to increasing net negative charge and thus result in the ΔG of sorption remaining essentially constant with increasing saturation of the sorption complex. Further to this, it has been shown that the free energy of sorption (ΔG) can be arbitrarily split (Huang, 1975) into contributions from chemical interactions ($\Delta G_{\text{chemical}}$) and coulombic attractions ($\Delta G_{\text{coulombic}}$) (net surface charge) as follows:

$$\Delta G = \Delta G_{chemical} + \Delta G_{coulombic}$$

Because $\Delta G_{coulombic}$ is related to the net charge on the surface, and because this may change with increasing sorption of anions, the value of $\Delta G_{coulombic}$ varies as sorption increases. If, however, $\Delta G_{chemical}$ is far greater than $\Delta G_{coulombic}$ it may be expected that overall values of ΔG for sorption will remain essentially constant and the Langmuir equation would be obeyed. It has been suggested that this is the case (Aveyard and Haydon, 1973) for chemisorption reactions where there is a major contribution to ΔG for sorption from $\Delta G_{chemical}$. Huang (1975) has calculated the magnitude of $\Delta G_{chemical}$ and $\Delta G_{coulombic}$ for sorption of P by Al gel at final P concentrations corresponding to region III showing the contribution of $\Delta G_{coulombic}$ to the overall ΔG to be small. This effect would be even less significant for sorption in regions I and II.

Although the successful use of the Langmuir equation in the study of Ryden et al. (1977a) does not, by itself, imply that sorption mechanisms are operating exclusively, the consistent fit of data and agreement with other experimental results make the proposed mechanism a useful model.

1.5.2 Reaction rates

Sorption of P by soils has been extensively studied. The decline in water-extractable P in soil following P addition has commonly been observed (Larsen et al., 1965; Barrow, 1973). This has been attributed (Barrow and Shaw, 1975a; Overman and Chu, 1977a) to the transformations of added IP from water-extractable to "less-soluble" forms. It has been suggested that the number of "less-soluble" forms of P in soils may be large and the interrelationships of their reactions complex (Larsen, 1967). Ryden et al. (1973) have proposed four major phases of secondary IP in soils, viz., (i) soil solution P, (ii) physically-sorbed P, (iii) chemisorbed or occluded P closely bound to surfaces (and possibly derived from physically-bound P in a subsequent reaction step), and (iv) precipitated forms of P compounds of varying solubility. The concentration of DIP probably controls the forward reactions to adsorbed, absorbed, and precipitated forms where these occur. Although it is generally believed that these changes in P forms, following P addition to soil, occur as a complex series of multistep kinetic reactions (Schuffelin, 1974), there appears to be a lack of experimental data to describe the rate coefficients of such reactions. The importance of P reaction rates in soils to such processes as leaching losses and plant uptake of added P has not been studied extensively.

A number of kinetic studies have described the rate of interaction of P with soil components (Kuo and Lotze, 1973; McLaughlin et al., 1977) and whole soils (Larsen et al., 1965; Barrow, 1973) following P addition to soil. In fact many of these studies have not actually monitored the rates of P reactions but the rate of decline in a parameter, e.g., plant recovery of P from soils sampled as a function of time following fertilizer P addition (Larsen et al., 1965) or soil solution P concentration (Barrow and Shaw, 1975a). Mansell et al. (1977) proposed a mechanistic, multistep model, using chemical kinetics and mass transport theory, to describe orthophosphate transformation and movement in soil. No experimental data were used in the construction of this model. Soil P was assumed to be present in four phases, viz., (i) solution P, (ii) physically-sorbed P, (iii) chemisorbed P, and (iv) precipitated P. A range of arbitrarily-chosen rate factors describing the reaction kinetics between any two phases were fitted and the equations were solved to describe the amounts and movements of P in a hypothetical soil profile. Barrow (1973) and Barrow and Shaw (1975a) have also described the decline in soil solution P concentrations following fertilizer P addition to soil. Decreasing plant-availability of P, particularly as influenced by the temperature of soil incubation, was plotted on a log scale of "relative effectiveness" of P against time of incubation and the experimental data points were described approximately by mathematically-derived curves. The equation variables however, were without meaning in real terms, i.e., experimentally-determined data on soil parameters. This approach was extended (Barrow and Shaw, 1975a) to the concept that soil P reactions could be described by the model:

$$A \rightleftharpoons B \rightleftharpoons C$$

where "compartment A" contains soil solution P, "compartment B" contains P adsorbed at soil surfaces and controlling solution P in A according to a sorption isotherm, and "compartment C" contains P converted into a form not directly in equilibrium with "compartment A". With the assumptions that P transfer from A to B follows the Freundlich sorption isotherm and that the transfer rate from B to C was similar to that found in the plant-availability experiment, good fit to the equation was obtained for soil solution P concentration data experimentally obtained. The mechanistic basis of this model, however, is empirical and not derived from experimentally-determined data which elucidate reaction mechanisms. A series of publications by Overman and Chu (1977a, 1977b, 1977c) discuss the developement of a model involving Langmuir-type adsorption followed by a second reaction (a "fast" and a "slow" reaction) to describe "steady state fixation" of P with soils in a batch reactor. The non-specific term "fixation" was defined in this study to mean a fast, complex solution/surface sorption followed by a slower first-order chemical reaction. The proposed reaction scheme was:

$$P + S \underset{kd}{\overset{ka}{\rightleftharpoons}} A \xrightarrow{kr} F + S$$

where P = concentration of P in solution

S = concentration of adsorption sites in the soil

A = concentration of adsorbed P

F = concentration of "fixed" P

ka = rate coefficient for adsorption

kd = rate coefficient for desorption

kr = rate coefficient for reaction.

According to the above model the adsorption sites in the soil act in a catalytic manner, either by recycling of existing sites or generation of new sites in association with the reaction step. Differentiation of the above equation produces the equation for changes in P concentration with time:

$$\frac{dP}{dt} = - ka\ SP + kd\ A$$

which indicates that the rate of P adsorption from solution depends on the quantity of adsorbent (site population) and solution P concentration. Subsequent development of this mathematical model to describe an open-batch reactor (constant P addition rate) achieved good fit of predicted solution P concentrations to actual data obtained from a 6-hour experiment. The model was based in principle on the observation that solution P declines rapidly initially and then more slowly following P addition to soil, suggesting a fast step followed by a slower step. No quantitative data were presented with respect to the relative rates of these two steps and evidence for two mechanisms was not presented. Further to this the results suggested that an unidentified process in soil, other than adsorption sites, contributed to the removal of P from solution. This same suggestion has been examined in more detail by McLaughlin et al. (1977) in the development and evaluation of a kinetic model to describe P sorption by Fe gel. Isotherms for P sorption were described by a three-equation Langmuir sorption model. Each equation described sorption within a distinct concentration range or region (I, II, and III) of the overall isotherm (studied by Ryden et al. (1977a) and discussed in Section 5.1.1.2). With increasing sorption time, up to 28.7 days, the extent of sorption in region I (chemisorption) increased by more than 30% despite no detectable increases in 0.1M NaOH-extractable (surface-sorbed) P. The data indicated that the increasing chemisorption of P with increasing sorption time involved the diffusion of sorbed P into the bulk of the Fe gel particles. This process could be the "unidentified process" involved in soil removing P from solution, as concluded by Overman and Chu (1977a).

Although it is implicit in the proposal that sorption equilibria control solution P concentrations that a desorption process operates concurrently with sorption (Bache, 1963), the desorption process has been less frequently studied. Shapiro and Fried (1959) proposed a kinetic equation for the desorption of P from soils by hydroxyl anions which assumed a pseudo first-order reaction. The rates of release suggested that sorbed P was present in two forms, i.e., a rapidly-released form which quickly diminshed with time and a more-slowly released form which was relatively constant with time. More recently it has been shown that the rate and extent of P desorption is partly dependent on the extent of saturation of the sorbing complex (Woodruff and Kamprath, 1965; Ryden et al., 1977a) and the time allowed for sorption prior to desorption (Evans and Syers, 1971; Barrow and Shaw, 1975b). The differing ease of P desorption has been interpreted (Muljadi et al., 1966) to reflect P sorbed on sites of differing energies with P adsorbed at sites of greatest energy being non-reversible and P at sites of low energy being readily reversible. Ryden and Syers (1977b) have recently shown that more-physically sorbed P, which is the dominant sorbed form initially, is readily reversible with respect to concentration while chemisorbed P is far less so at iso-pH.

The practice of dividing sorption of P in soils into a "fast" reaction and a "slow" reaction, based on the inspection of curves which plot declining solution P concentration with time following P addition, is similar to isotherm division into regions by inspection (Muljadi et al., 1966). It is important to emphasise that the mechanisms of P sorption and desorption ascribed to such regions have been without the analysis of actual experimental data and the break between "fast" and "slow" reactions has been imposed arbitrarily.

The approach to modelling the rates of P sorption from the soil solution, as previously reviewed, has depended upon theoretical and simple models of soil P reactions to describe mathematically the decline in solution P or plant-available P. Further to this, no experimental data are incorporated into the rate factors which are arbitary and are adjusted until approximate fit to data is obtained. Work by Ryden et al. (1977a) has shown that it is possible to obtain for three distinct reaction mechanisms, data such as sorption maxima (K_2 values), equilibrium constants (K_1 values), and relative bonding energies (ΔG values) for each region. This information, and the fact that the equilibrium constant for each region, K_{eqm}, is comprised of a balance between a forward rate constant (K_f) and a reverse rate constant (K_r) may permit the construction of a model, based on experimental data, which describes the reactions of P controlling solution P concentrations in soils more realistically.

Such an approach to modelling would seem useful in the prediction of rates of decline in potentially-mobile or plant-available P in soils following fertilizer P addition.

1.5.3 Prediction of phosphorus movement from soils and catchments to water

The need for suitable water quality models, particularly for agricultural watersheds, has recently been reviewed by Nicholson (1975). Emphasis is placed on the need to control pollution from agricultural activities, including forestry, much of which enters surface and ground water from diffuse sources. The preservation of favourable water quality often requires forecasting the impact of specific agricultural practices on river-basin scales so that preventative management steps may be planned and implemented. It is suggested that the production of prediction models, based on events that occur in and on the soil both during and within rainfall events, should be useful in such planning. Some of these models, e.g., Bailey et al. (1974) take into account factors influencing the fate of numerous agricultural chemicals in the soil.

An intergrated approach to whole-catchment modelling with respect to the movement of water, suspended load, and dissolved chemicals originating from point and diffuse sources and land under different systems of management is still in its infancy. A currently used computer model, limited to the prediction of water movement in runoff from a catchment (USDAHL - 74 Model of Watershed Hydrology) is based on parameters of soils and vegetative cover as well as rainfall. A recent supplementary modification to this model has been proposed in an attempt to predict the movement of pesticides as well as water in runoff from catchments.

Although several studies with such models are as yet incomplete a recent mathematical modelling approach (Novotny et al., 1978) has achieved good agreement between predicted and observed flows and loadings of sediment, dissolved P, and TP movement from several watersheds in south-east Wisconsin. Representative data for 102 soils gathered from the literature were selected for statistical analysis. Sorption of P by these soils had been described by a linear form of the Langmuir sorption isotherm. In a summary of the findings it was shown that maximum multiple regression correlations were obtained between sorption maxima values and soil contents of Al, Fe, clay, organic matter, and soil pH. A soil-adsorption model including P inputs, P adsorption in the soil A horizon, potential P movement with sediment, P adsorption in the lower soil horizons, and potential P movement in groundwater was proposed and described mathematically. The sorption maximum of the soil, calculated from the regression equation developed from the 102 soils discussed above, was one of the factors of the general kinetic model developed to describe P movement. The soil adsorption model was incorporated into a dynamic hydrological sediment transport model termed LANDRUN. The LANDRUN model estimated the runoff quantity, suspended load, and organic load, whereas the soil adsorption segment furnished information on the concentrations of dissolved and adsorbed P transported.

The movements of P from soils into water and the concentrations of P obtained in both surface and subsurface water have been studied by several workers. Soil material can influence the P concentration in the aqueous phase by sorption, desorption or dissolution reactions. Sorption isotherms have been used (Taylor and Kunishi, 1971; Ryden et al., 1972a; 1972b) to evaluate the effects of eroded soil materials on DIP concentrations in streams. By the careful selection of soil:solution ratios and P addition rates relevant to stream runoff environments, it has been possible to show that surface soil material can release IP into solution (Ryden et al., 1972a; 1972b) while subsurface soil material can remove IP from solution during stream flow (Taylor and Kunishi, 1971). Reasonable estimates of DIP concentrations in streams have been achieved by this technique.

Several attempts have also been made to establish relationships between nutrient forms and amounts in soils under different land use and forms and amounts subsequently appearing in specific runoff types. Sharpley et al. (1977) have used a 0.1M NaCl-extraction procedure with soils to predict losses of DIP in surface runoff and tile drainage. They obtained close linear relationships between amounts of IP extracted from surface soils (0-5cm) and mean DIP concentrations observed in surface runoff from grazed pasture plots. The relationships differed in slopes and intercepts between drained and undrained, and fertilized and unfertilized plots but linear relationships were always obtained. In contrast to surface runoff, soil extraction data from discrete depths in the profile were not well correlated with mean DIP concentrations in tile drainage during storm events. Total loadings of DIP, however, were better correlated with the amounts of extractable P in the subsoil, particularly at the depth of the mole channels (40 - 50 cm). This correlation has suggested that extraction with 0.1M NaCl removes a pool of readily-extractable IP which is normally exhausted during a flow event but replenished between events. The potential of such an extraction procedure to predict the movement of DIP in drainage water seems considerable. The results of this study were found to be in agreement with the findings of Nelson and Romkens (1971) who obtained a linear relationship between DIP concentrations in surface runoff and extractable IP amounts in a cultivated soil. In a more recent study, Sharpley et al. (1978b) have shown that superior correlations between 0.1M NaCl-extractable P in soil and mean DIP concentrations in surface runoff can be obtained from soil samples restricted to the top 1 cm of pasture. Furthermore, the slopes and intercepts were essentially the same for the different treatments.

Because fertilizer P is commonly applied to soils, particularly in New Zealand, an appreciation of P reaction mechanisms in soils, as they influence the movement of P within and from soils, is essential in understanding and predicting the movement of P from soils to surface and ground waters. In particular, the rates at which such reactions proceed need to be established to predict the possible extent of P movement subsequent to fertilizer P addition. This predictive ability is presently not available but the potential for achieving it seems reasonable.

1.6 General Conclusions and Research Needs

A number of general conclusions are possible from the material presented in this review of literature and several aspects requiring further research have emerged. These general conclusions and research needs are briefly outlined.

It has been well established internationally, although not so completely in New Zealand, that P is frequently the nutrient in natural waters which most limits the growth of algae and aquatic macrophytes at concentrations of below or between 0.01 and 0.05 mg l^{-1}. Natural background concentrations of P in New Zealand waters are poorly documented and additional information is required. Because many studies of P in waters have measured only some or unspecified P forms, comparison between studies is difficult.

Although it is well established that different systems of land use can influence the amounts of P moving into surface water, e.g., urban and rural land uses, little information is available in New Zealand on the relative importance of land use practices to the P enrichment of water. In particular, the effect of clearing land and the development of grazed pasture accompanied by P fertilizer use, which is widespread in New Zealand, on the movement of P into waters has not been established and requires further evaluation.

The relative importance of surface and subsurface runoff in contributing to P losses from soil to water is reasonably well established overseas, particularly for cultivated and cropped soils, and for drained soils. This has not been established in New Zealand and has often been neglected in runoff studies which do not identify runoff fractions in the stream flow sampled. Studies designed to evaluate the relative importance of sources of water and P to P losses from New Zealand soils are required and these studies should recognise the runoff types monitored in the calculation of P loadings.

It is apparent from the literature that the forms and reactions of P in soils have been extensively studied. Although the forms and reactions of OP in soils are poorly understood, due to their extremely complex nature, the situation for IP in soil is very much better understood. The reactions of IP in soils, particularly following fertilizer P addition, are not established with certainty, although it is now believed that sorption reactions, rather than precipitation reactions, control the amounts and concentrations of IP in the soil solution.

Although it is believed that sorption reactions control the concentration of IP in soil solution and the transfer of P to a form which is non-available to plants, only recent studies have established probable reaction mechanisms for P sorption in soils. Reaction rates of P sorption have been studied only to a limited extent and this has involved a parameter-monitoring approach rather than an approach based on a understanding of P sorption forms and reaction mechanisms. There is a need to study rates of P sorption and desorption using both observed results and reaction mechanism models derived from actual experimental data.

Few studies have attempted to extend the results of kinetic experiments and modelling of P reaction rates in soils from the laboratory to a field situation. There is a need to model and predict the rate of P reactions in soils and to interpret these results in terms of field situations regarding the potential movement of P from soils to water and the plant availability of P in soils. In particular, the ability to predict the fate and reaction rates of fertilizer P added to soils would be useful in making land management decisions where the movement of P from soil to water potentially threatens water quality.

CHAPTER 2

GENERAL MATERIALS AND METHODOLOGY

2.1 Description of the Catchments

2.1.1 Topography, geology, and soils

The two adjacent catchments used for this study are located approximately 12 km east of Massey University, Palmerston North. Their general location in the North Island of New Zealand is shown in Fig. 2.1 and an enlargement of the inset area is shown in Fig. 2.2. A more precise location may be obtained from N149/179314* and N.Z. Soil Bureau map 102/179314 (Cowie et al., 1972). Cowie (1972) has also compiled an extended legend for map 102, refered to above, which provides detailed information on the soils of the area.

The two catchments were aerially photographed in 1974 before clearing and in 1975 after clearing. Paired photographs for each year were examined under a stereoscope. Catchment boundaries were subsequently traced on the photographs, areas calculated by grid count after adjustment for photo scale, and slopes estimated and channel characteristics identified. Both catchments have narrow ridges and steep slopes, varying from 50% in the upper regions to 100% in the lower regions. The larger catchment has an area of 22 ha and is drained by an ephemeral stream, essentially first-order, with a channel length of 1.3 km, a meander factor of 1.2, and an overall fall of 65 m. The smaller catchment has an area of 6 ha and is drained by a first-order ephemeral stream with a channel length of 0.8 km, a meander factor of 1.2, and an overall fall of 55 m.

The streams are two of a number of tributaries to major rivers which dissect the high terraces of the Manawatu. These high terraces abut

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* Grid reference based on the National thousand-yard grid of the 1:63,360 topographical map series (N.Z.M.S. 1, 1973).

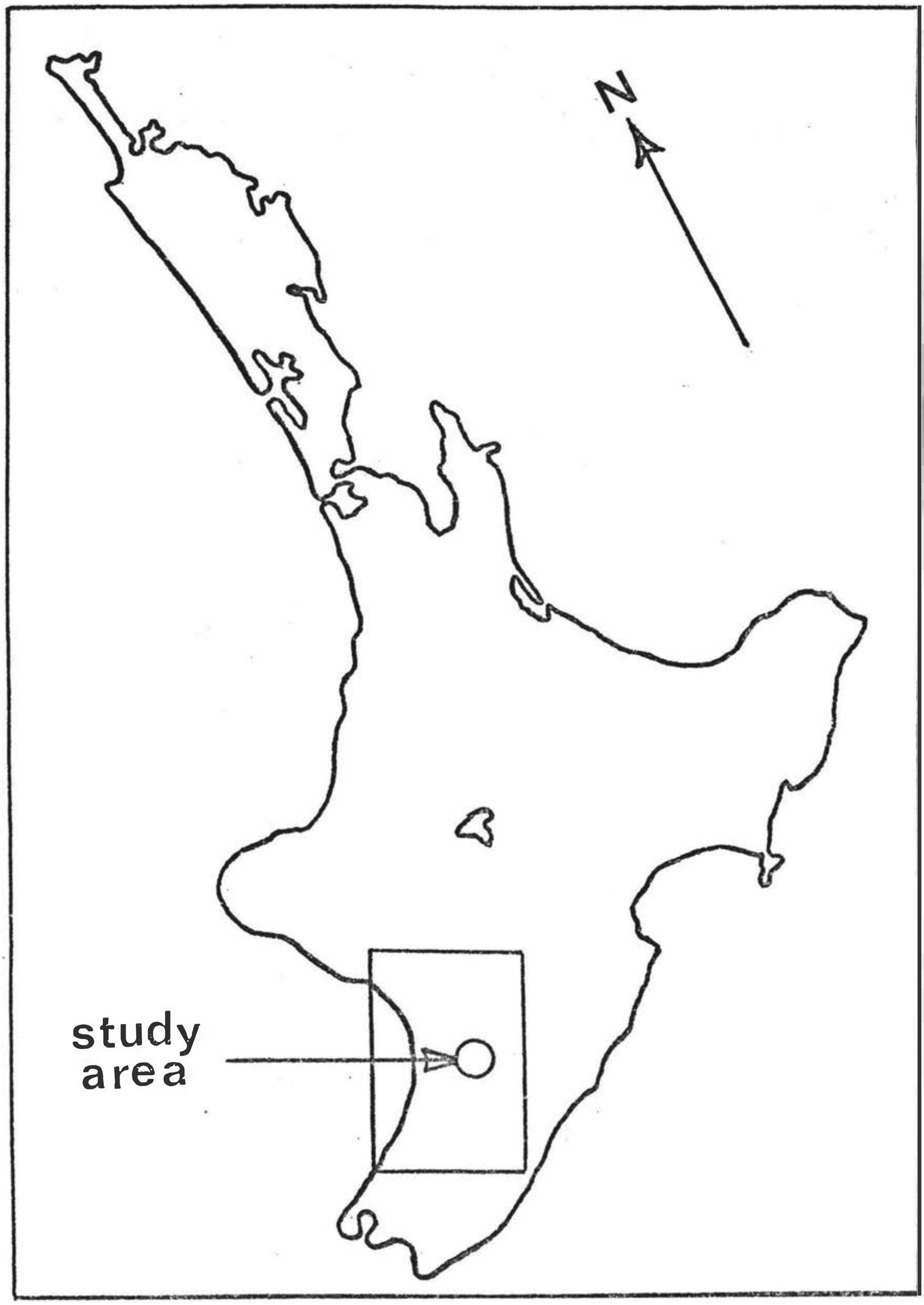


Fig. 2.1 Map of the North Island of New Zealand showing the general location of the study area in the inset.

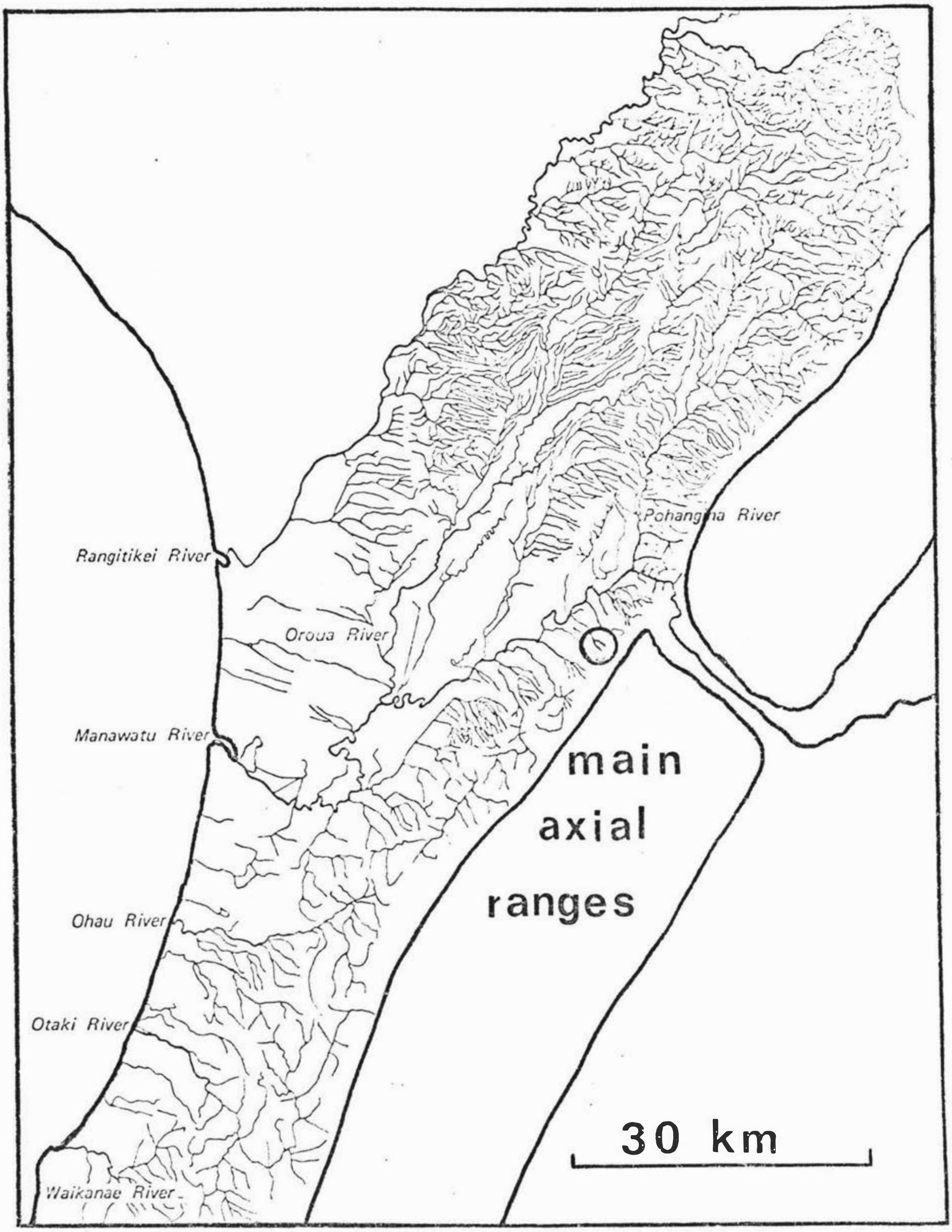


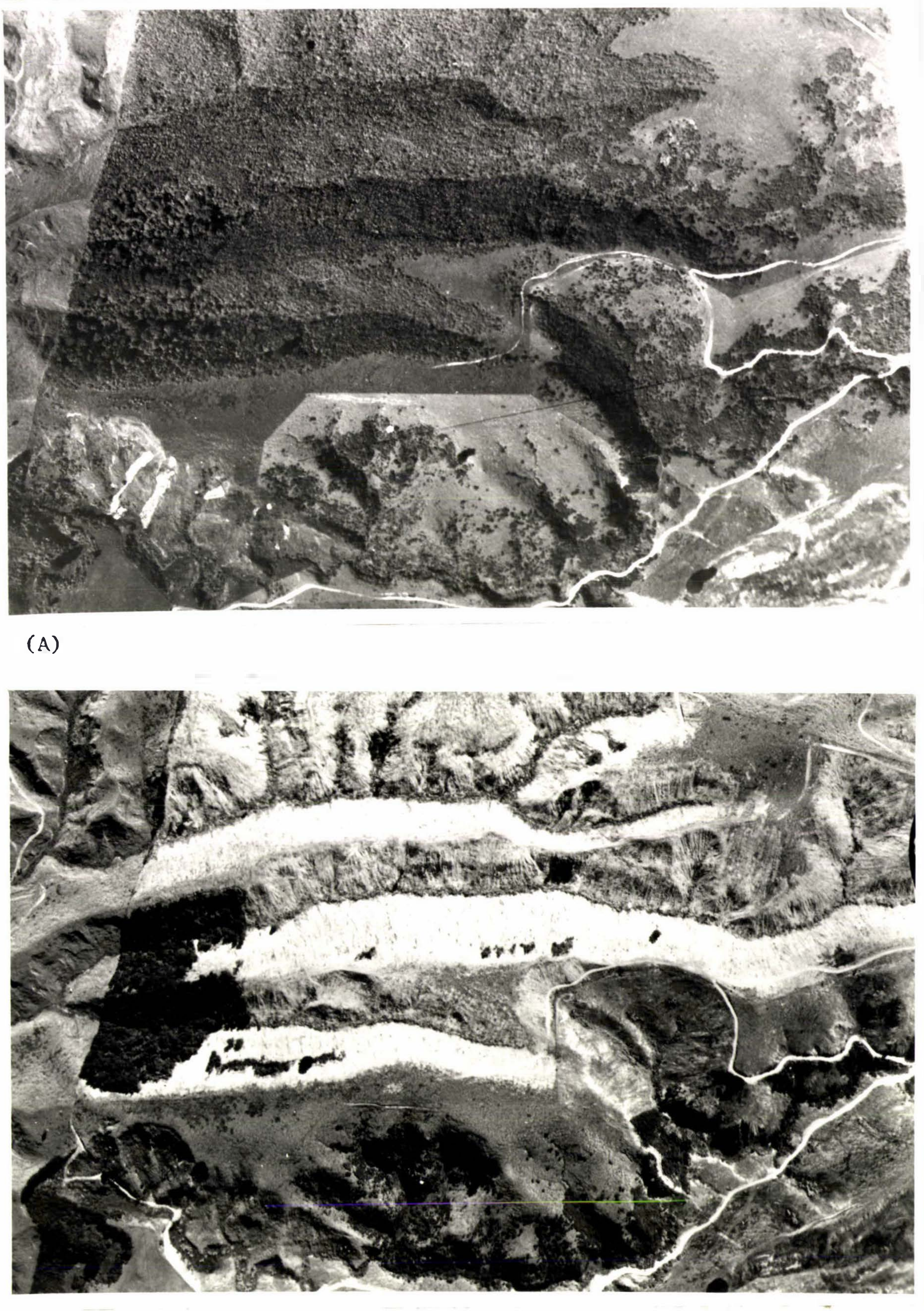
Fig. 2.2 Map of the study area (from inset on Fig. 2.1) showing location of catchments (circle), local drainage networks, and indicating topography.

against the greywackes of the main axial ranges further to the east beyond the catchments' boundaries. Four metres of loess beds, apparent on crests, overlie Lower Quaternary greywacke gravels, which in turn overlie a 10-m thick sequence of nearby flat-lying Castlecliffian sands and gravels which are exposed on lower slopes. These sands and gravels are highly susceptible to erosion because they are loose and unconsolidated. Widespread surface slips and slumps are visible on surrounding hillsides, where these have been cleared of native vegetation cover or scrub.

The soil on the ridge crests, locally known as Shannon silt loam, is formed on older loess, exhibits poor internal drainage, and shows some clay movement and mottling within the profile. The soil is an Inceptisol, probably mainly an Aquic Dystric Eutrochrept intergrading to a Ruptic-Alfic Eutrochrept (U.S. Soil Taxonomy, 1975). The soil on the catchment slopes locally known as Raumai hill soils, is formed on loose sands and gravels. The soil is an Inceptisol, probably mainly an Aquic Dystrochrept. intergrading to Ruptic-Alfic Dystrochrept (U.S. Soil Taxonomy, 1975). Comprehensive details of these two soils, compiled by Cowie (1972), are presented in Appendix 1.

2.1.2 Vegetation and land clearing

Prior to January 1975, the catchments were vegetated predominantly with secondary growth of manuka (Leptospermum scoparium) and gorse (Ulex europaeus), with small areas of grasses on the ridge crests and native bush near the outfalls of the streams. In January 1975, the catchments were cleared by bulldozers, which scraped vegetation, roots, and a mixture of surface and sub-surface soils from the ridges and slopes onto the valley floors. Vertical aerial photographs taken in 1974 (before clearing) and in 1975 (after clearing) are presented in Fig. 2.3; these



(A)

(B)

Fig. 2.3 Vertical aerial photographs of the two catchments before (A) and after (B) clearing.

show the areas cleared and the small areas of native bush remaining at the outfalls. Further detail of the cleared catchments is shown in the colour aerial photography taken in March 1975 (Fig. 2.4) in which the debris in valley floors and channels is apparent. This debris, along with the disturbed soil surfaces and steep catchment slopes, is shown more clearly in Fig. 2.5 in a ground photograph taken within the 22-ha catchment. In March 1975, superphosphate fertilizer was applied by air at the rate of 375 kg ha^{-1}. Lime was also applied by air at the rate of 1250 kg ha^{-1}. The catchments were then sown to a pasture of perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) and in August 1975, received their first light grazing by sheep. In October 1975, a second application of superphosphate (250 kg ha^{-1}) was made. The catchments were subsequently grazed throughout 1976 by sheep and small numbers of beef cattle as part of the grazing pattern of the farm.

2.2 Monitoring Equipment

Rainfall was monitored in the two catchments for three successive years of the study, by a Lambrecht 30-day continuous rainfall recorder, centrally situated on the ridge between the two catchments. Stream flow was monitored for the same three years by 60^{o} V-notch weirs and flow meters installed in the stream channel at the lower limits of each catchment. An H-S flume was placed in the 6-ha catchment and an H flume in the 22-ha catchment. Each flume was fitted with a Stevens F-type flow meter which recorded continuous stage heights. The H-S flume and flow recorder on the 6-ha catchment stream are shown in Fig. 2.6.

Fig. 2.4 Vertical aerial photograph of the two catchments showing cleared slopes and debris deposition following clearing.

Fig. 2.5 Ground photograph in the 22-ha catchment after clearing showing soil surface disturbances, steepness of slopes, and debris in stream channel.

Fig. 2.6 H-S flume and Stevens F-type flow recorder operating on the stream draining the 6-ha catchment.

2.3 Sample Collection

2.3.1 Water samples

Stream samples were collected in 600-ml polyethylene bottles routinely used for water sampling. Although regular samples, at not less than 7-day intervals, were taken during low flow between storm events, the sampling interval was as low as 15 min for rapid changes in hydrograph movement, i.e., storm events. Samples were taken either manually or with an ISCO automatic sampler. Initial laboratory processing (filtration) was done as soon as possible and usually within 2 hours of sampling.

2.3.2 Soil samples

Samples of surface soils considered to be representative of the two catchments were taken, from depths of 0-2 cm, at intervals during the winter of 1975. In 1976, soil sampling was concentrated in the 6-ha catchment and samples were taken weekly although the sampling interval was extended later in the winter. Three representative areas were sampled in both years although these were not the same in each year. In 1975 one area was located on the central ridge between the two catchments, one was on a catchment slope (60%) in the 6-ha catchment, and the third was on a catchment slope (30%) in the 22-ha catchment. In 1976 three representative areas in the 6-ha catchment were sampled, one being on the valley floor adjacent to the stream, the second on a catchment slope (100%), and the third on the crest of the central ridge. For each site a grid 5 m by 5 m (i.e., 25 m^2) was set out. It was found that 25 samples per site, each sample taken randomly from within 1 m^2, gave a deviation value at the 95% confidence level which was small enough for valid comparisons between sampling times to be made. Soil samples were restricted to the period from March to November, i.e., the winter period during which runoff and stream flow occured.

2.4 Analytical Procedures

Approximately 100 ml of each stream sample was initially centrifuged at 13,000 rev min^{-1} for 5 min at 23^{o}C, using a Sorvall RC-2B high-speed, refrigerated centrifuge, followed by Millipore filtration ($< 0.45\mu$m). The membranes were pre-washed with distilled water to eliminate the possible release of dissolved inorganic P (DIP) to the filtrate.

The concentration of DIP was determined on a filtered sample, as was that of total dissolved P (TDP) after acid persulphate digestion by autoclaving at 15 p.s.i. for 45 min and neutralization of the solution (Environmental Protection Agency, 1971). Total P (TP) was determined on an unfiltered sample following perchloric acid digestion for 1 hour, and neutralization 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 Pye Unicam SP 1800B Spectrophotometer. Dissolved organic P (DOP) was calculated as the difference between TDP and DIP, and particulate P (PP) was calculated as the difference between TP and TDP.

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

2.5 Data Processing

Use was made of a computer programme developed in this laboratory to process the data collected for the concentrations of P and N forms, and sediment at each sampling and 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, P, and sediment data were stored as a tape file to assist availability, ease of handling, and flexibility of programme use.

The two main programmes used in this study were:

(a) A CHECK programme, to validate the data card input, after the data for nutrient and sediment concentrations, stage height, and time of collection of each stream sample were transferred to cards for input to the computer.

(b) A TOTAL programme, to calculate instantaneous and mean P and sediment fluxes and flow rates from flow and concentration data, and total loadings and total flow by numerical intergration of the linearly interpolated nutrient flux-time and water flow-time curves, respectively over periods of interest.

CHAPTER 3

MOVEMENT OF WATER, SEDIMENT, AND PHOSPHORUS FORMS FROM TWO SMALL, ADJACENT CATCHMENTS UNDER CHANGING LAND USE

3.1 Introduction

Annual fertilizer topdressing of pasture in New Zealand occurs largely on the 64% of land that can be categorised as mountainous or hill country (Bowler, 1971). This now usually involves in excess of 2 million tonnes of superphosphate and 6 million hectares of land (Syers, 1974). Because the role of phosphorus (P) in the accelerated growth of aquatic nuisance plants has been documented extensively (Mackenthun, 1965; Vollenwieder, 1968; Lee, 1970; Kilmer, 1972), phosphate fertilizer has been directly implicated in eutrophication in New Zealand (Fish, 1969; Mitchell, 1971). Other workers (e.g., McColl et al., 1975) have found that only small amounts of fertilizer P added to soils move into water, although these amounts could significantly increase P concentrations. The observation of O'Connor (1968) that increased fertility of land is likely to yield drainage water of an increased fertility, seems pertinent.

The responses of hydrology, erosion, and water quality to changes in land use within catchments have been discussed by several workers (Chow, 1964; Burton, 1966; Boughton, 1968). Other workers have investigated the quality of water originating from land under specific uses, e.g., urban (Harris et al., 1972), forestry (Cooper, 1969), mixed cropping (Kunishi et al., 1972), and grazed pasture (Kilmer, 1972; Sharpley, 1977). Many of these investigations, however, have been of a qualitative, general nature and provide little actual data on which realistic predictions can be based.

The conversion of steep catchments from native and secondary scrub and bush to improved grassland, grazed by sheep and beef cattle, has been practised extensively in New Zealand. Such conversion typically involves bulldozer crushing with the removal of vegetation from crests and slopes, and an accumulation of debris in the valley floors, where it may be burnt. It is also common to aerially apply approximately 1250 kg of lime per hectare in the first year after clearing and 375 kg ha^{-1} superphosphate in the first and each subsequent year, along with a seeding mixture of ryegrass and white clover. There are still extensive areas in New Zealand with the potential to undergo a change of land use in this manner. Many of these areas presently form catchment sources of high quality water.

It has been suggested (Fish, 1969; Mitchell, 1971; McColl, 1972) that in New Zealand the conversion of land from scrub and bush to agricultural use, together with the use of P fertilizer, has increased the nutrient content of runoff waters and may have accelerated the deterioration of water quality in streams and lakes. Other workers (Campbell, 1952; Poole, 1973; Syers, 1974; Walker, 1975) have suggested that, after land clearing, the use of fertilizer and sound grazing management may have increased soil stability and thus reduced erosion relative to the native or undisturbed state. The extent to which water quality deterioration is directly attributable to such activities, however, remains uncertain, and requires more comprehensive evaluation (White, 1972; Syers, 1974; McColl et al., 1975).

Although experimental work has shown that fertilizer P can be transported over short distances in surface runoff waters (Gilchrist and Gillingham, 1970; Sharpley and Syers, 1976), relatively few studies have been designed to measure the effects of fertilizer use on water quality under field conditions, not only in New Zealand, but also overseas (Kilmer, 1972). This aspect of the study is concerned with an evaluation of the effects of scrub clearing and subsequent pasture establishment on the loadings of sediment and P forms in the streams draining two small adjacent catchments. Particular attention was given to detailed sampling and the forms of P measured. It is believed that the results obtained are relevant to many parts of New Zealand.

3.2 Materials and Methods

The catchments and monitoring equipment used in this study are described in detail in Chapter 2. Stream sampling and flow monitoring were undertaken during 1974 before scrub clearing and continued in conjunction with soil sampling throughout 1975 and 1976. Details of the scrub clearing operation, fertilizer application, and pasture establishment are given in Chapter 2.

Data obtained in 1974 and 1975, and presented in Section 3.3 of Chapter 3, indicated that the two catchments were hydrologically similar. This facilitated an evaluation of the effect of P fertilizer addition on the movement of P forms in stream water. In March, 1976, the third year of the study, an application of 375 kg ha^{-1} of superphosphate was aerially spread on the 6-ha catchment (referred to as the "fertilized catchment") but withheld from the 22-ha catchment ("unfertilized catchment"). Procedures for stream sample collection and analysis are described in Chapter 2.

Before discussing the method of stream hydrograph resolution used to obtain data for runoff components, it is necessary to define some terms and provide some background. Stream flow can be divided into storm flow and subsurface flow. Storm flow is that part of flow which results from storm rainfall within the catchment boundaries and which reaches an observation point within a relatively short period of time. Subsurface flow results from rainfall within the catchment and appears at an observation point significantly delayed behind storm flow (Guy, 1964).

Stream flow is usually divided into storm and subsurface flow by empirical analysis of the runoff hydrograph. A schematic approach to such an analysis is presented in Fig. 3.1, where ABCD represents the total runoff and AECD represents the amount of subsurface flow (Wisler and Brater, 1959). During the early rise of the hydrograph some back-flow occurs into potential water-storage capacity in stream banks. This results in an apparent reduction in base flow (shown at E in Fig. 3.1) during stream hydrograph rise. During recession in stream level from peak flow, excess water drains out from stream banks, thus increasing the apparent subsurface flow. Because the actual position of the line AECD is difficult to determine, and differs between streams and storms, an approximate separation between storm flow and subsurface flow can conveniently be made by the line AC. The exact position of C is not critical if a consistent procedure is adopted (Sharpley, 1977).

Although the entire area ABC can be regarded as storm flow, it is possible that the rising part of the hydrograph represents flow dominated by a "primary surface runoff" while the receding portion of the hydrograph represents flow comprised of an increasing proportion of water appearing from subsurface seepage onto catchment slopes and then moving as surface runoff to the stream, i.e., as "secondary surface runoff". For the purpose of establishing relationships between water-extractable P in surface soils and P in surface runoff water, "primary surface runoff", represented by area ABF, is likely to give the most accurate results.

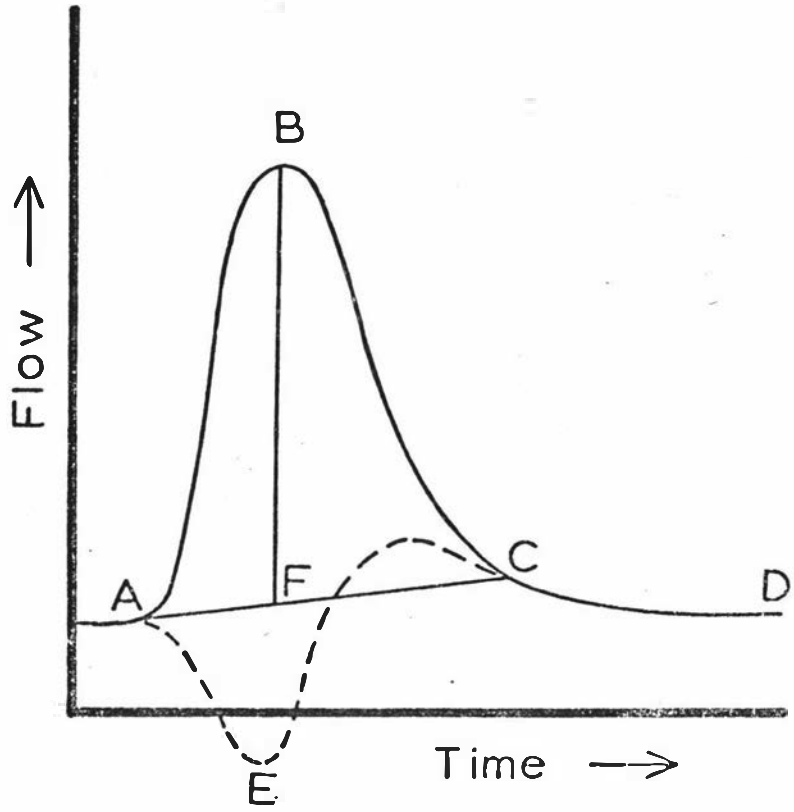


Fig. 3.1 Components of a stream hydrograph.
Points A, B, C, D, E, and F are discussed in text.

In this section the term discharge is frequently used instead of flow because the former can be applied to water, sediment, and P movement, whereas flow refers only to water movement. The separation of stream flow is confined to total stream flow, stream flow within storm events only, storm flow (stream flow within storm events but exclusive of the subsurface flow component), and subsurface flow within or between storm events.

3.3 Results and Discussion

3.3.1 Flow-concentration relationships

Before land clearing and fertilizer application in 1974, the concentrations of DIP, DOP, PP, and sediment in storm events were very stable and similar both in subsurface and storm flow events, and from one storm event to another. This is illustrated in Fig. 3.2 and Fig. 3.6 in which flux and flow data for a typical hydrograph (24/6/1974) are presented. Concentrations of PP and sediment fluctuated approximately 2- to 3-fold within the storm event shown in Fig. 3.2. Concentrations of DIP and DOP fluctuated even less (approximately 1.5- to 2-fold) within the same storm event (Fig. 3.6). Further to the low proportional changes, the concentrations of P forms and sediment were very low before, during, and after the storm event, despite large and rapid changes in flow. Consequently, in a stable, undisturbed catchment, it is essential to have reliable hydrograph flow data with close interval flow points in order to estimate total loadings of sediment and nutrients accurately. Because changes in flow in storm events were large and rapid, whereas concentrations of sediment and P forms were low and stable, the contribution of flow to total loadings of sediment and P forms was substantial. This finding supports the work of Taylor et al. (1971) and Sharpley et al. (1977)

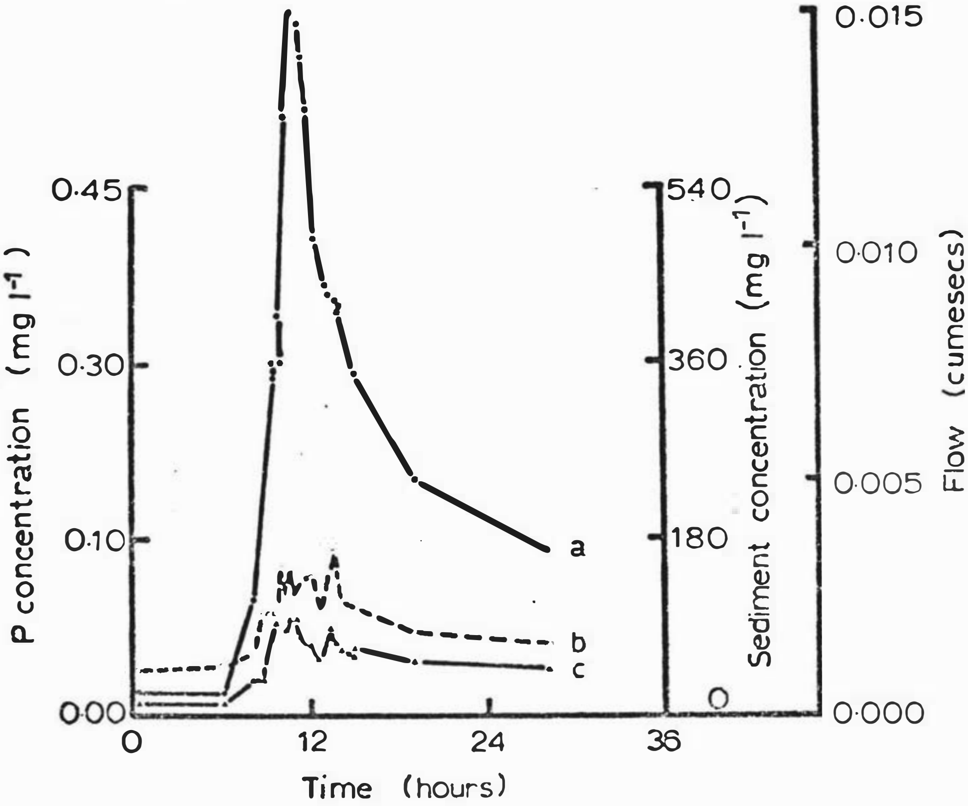


Fig. 3.2 Variation in flow and concentrations of PP and sediment in storm discharge from the 22-ha catchment during the storm event of 24-25/6/1974 before land clearing.
a = flow, b = sediment concentration, and
c = PP concentration.

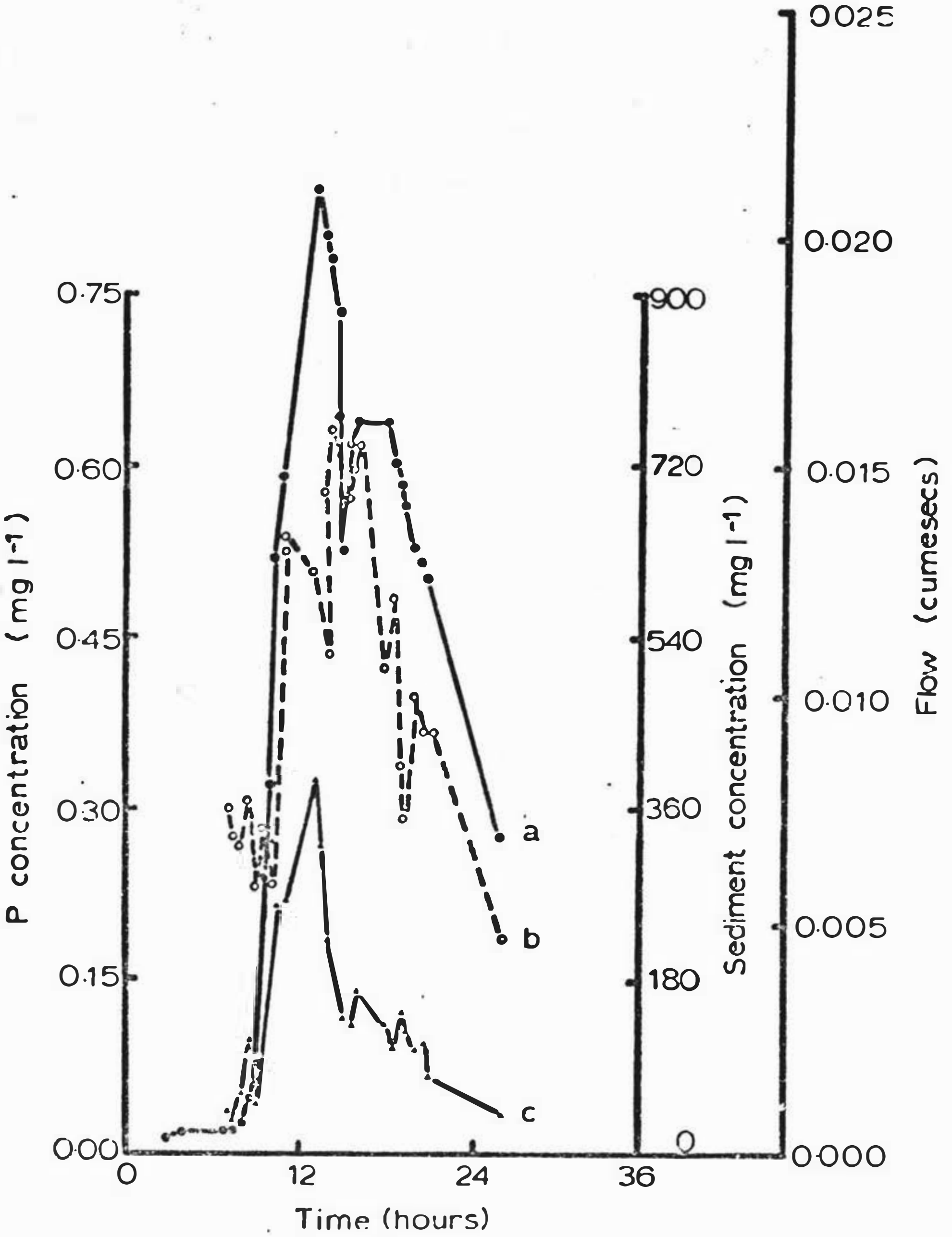


Fig. 3.3 Variation in flow and concentrations of PP and sediment in storm discharge from the 22-ha catchment during the storm event of 26/5/1975 after land clearing.
a = flow, b = sediment concentration, and c = PP concentration.

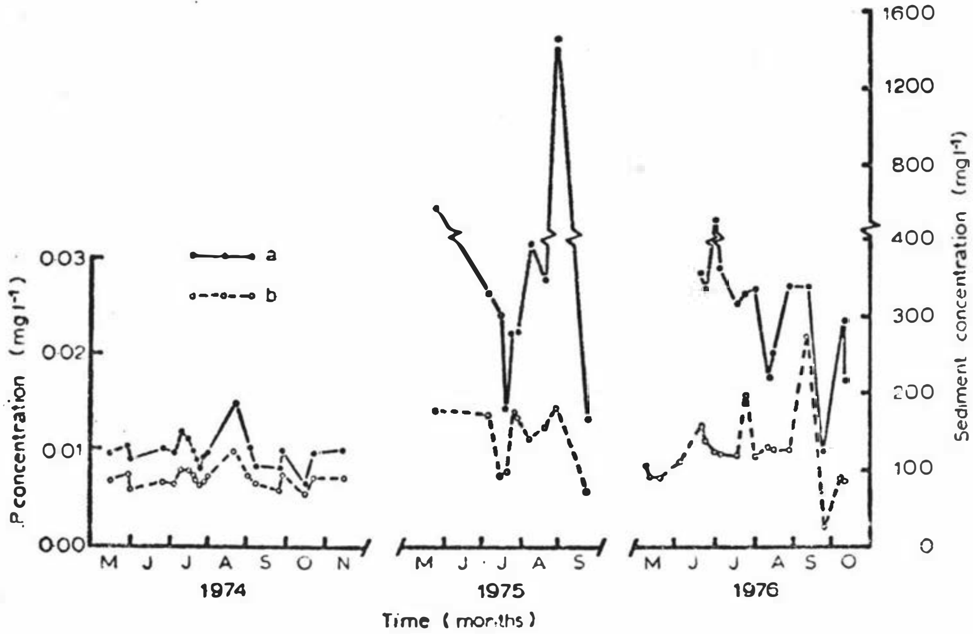


Fig. 3.4 Variations in mean concentrations of sediment and PP in the storm discharge of successive storm events throughout 1974, 1975, and 1976 for the 22-ha catchment.

a = sediment concentration and b = PP concentration.

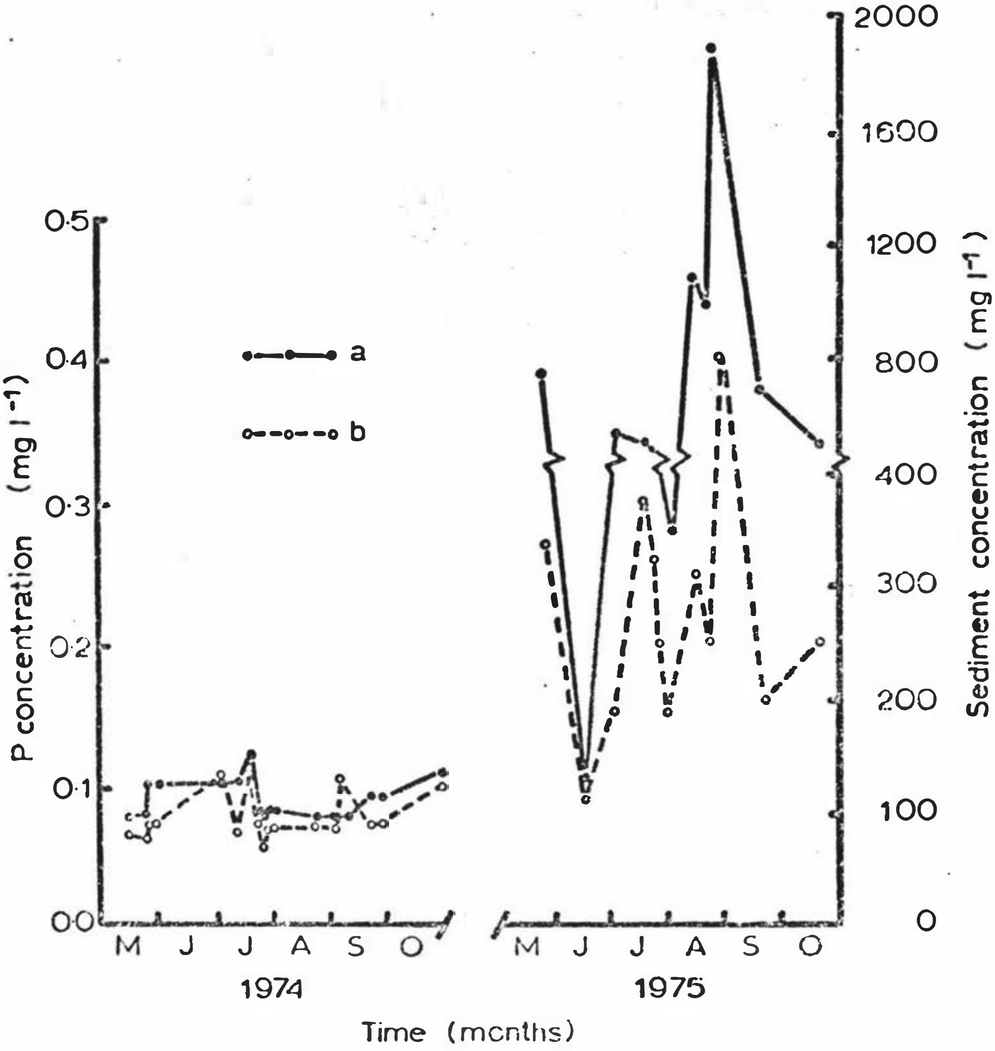


Fig. 3.5 Variations in mean concentrations of sediment and PP in the storm discharge of successive storm events throughout 1974 and 1975 for the 6-ha catchment. a = sediment concentration and b = PP concentration.

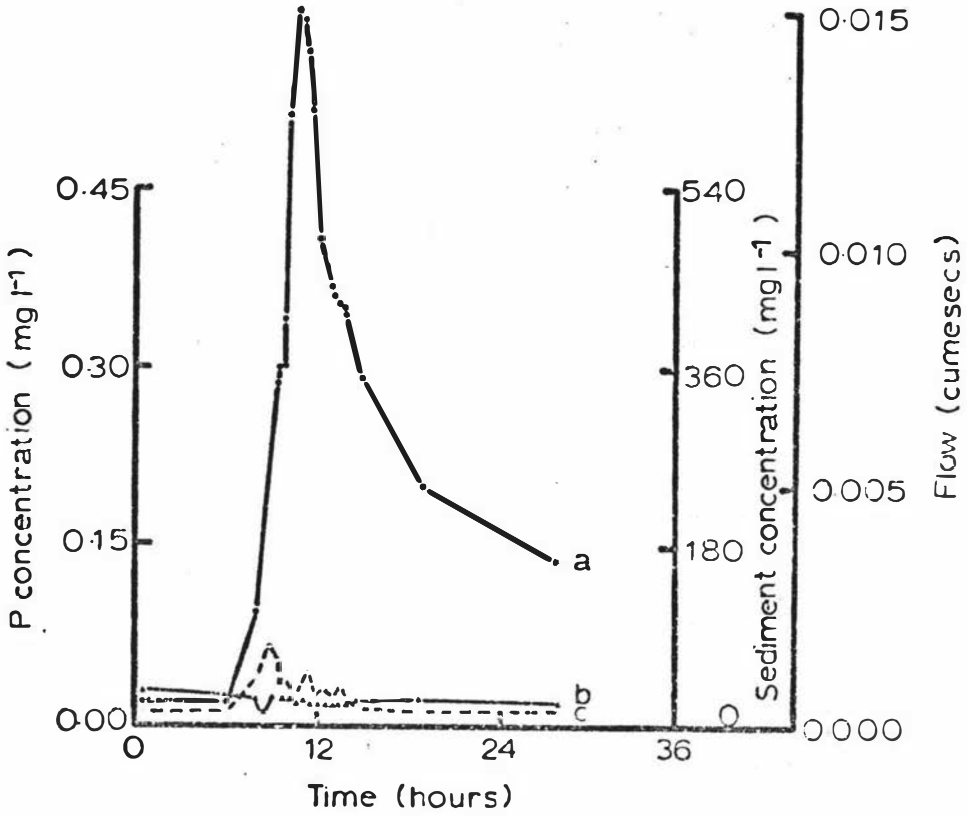


Fig. 3.6 Variation in flow and concentrations of DIP and DOP in storm discharge from the 22-ha catchment during the storm event of 24-25/6/1974 before land clearing.
a = flow, b = DIP concentration, and c = DOP concentration.

for the concentration-flow relationships in streams draining agricultural watersheds.

The essentially stable concentrations of sediment and P forms in 1974, before clearing, changed dramatically in 1975. Following catchment clearing and fertilizer application, the concentrations of DIP, DOP, PP, and sediment in the stream showed large and rapid fluctuations, particularly within storms. These changes are shown in Fig. 3.3 and Fig. 3.7 in which flux and flow data for a typical hydrograph (26/5/1975) are presented. Concentrations of PP and sediment fluctuated widely within the storm flow event (Fig. 3.3). A similar relationship applied to DIP and although DOP concentrations appeared more stable and relatively low, fluctuations were still significant (Fig. 3.7). Also, the changes in concentrations occurred in conjunction with major changes in flow so that both changes in flow and concentrations made major contributions to the total loadings of sediment and P forms.

3.3.2 Sources of water, sediment, and phosphorus forms

A comparison between the hydrograph characteristics and flow yields for each of the three years of the study showed that the catchments behaved in an essentially similar manner, despite rainfall differences between years. Annual flows from the two catchments are presented in Table 3.1 for the three years 1974, 1975, and 1976. Similar ratios of discharge, on a per-hectare basis, were obtained for the two catchments in each year. Because of the longer channel and greater area, peak flow occurred later in the 22-ha catchment.

The division of flow into fractions related to the source of water was useful for subsequent discussion of sources of sediment and P forms.

Stream flow for the entire year is referred to as annual stream flow. Although rainfall data for 1974 were incomplete (Appendix 2), it was found

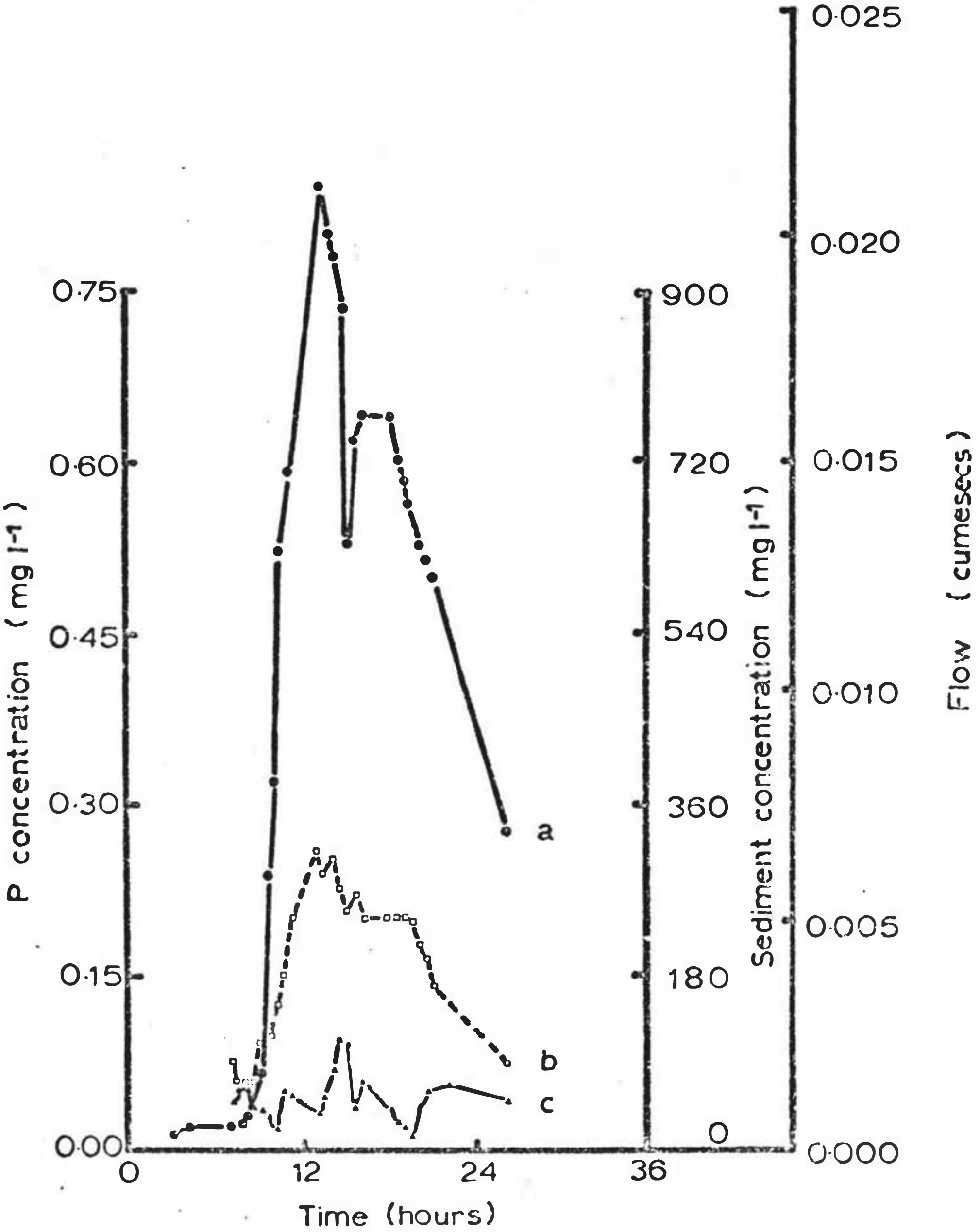


Fig. 3.7 Variation in flow and concentrations of DIP and DOP in storm discharge from the 22-ha catchment during the storm event of 26/5/1975 after land clearing.
a = flow, b = DIP concentration, and c = DOP concentration.

Table 3.1 Flow from the 22-ha and 6-ha catchments for the years 1974, 1975, and 1976, showing total annual outputs of four forms of flow

Catchment	Annual stream flow	Annual stream flow within storm events	Annual storm flow	Annual subsurface flow
1974				
22-ha (m^3)	32,670	21,750	17,640	15,030
(m^3ha^{-1})	1,480	990	800	680
6-ha (m^3)	7,230	5,340	4,160	3,070
(m^3ha^{-1})	1,210	890	690	510
Ratio 22/6	1.23	1.11	1.16	1.34
1975				
22-ha (m^3)	25,760	16,240	13,980	11,790
(m^3ha^{-1})	1,170	740	640	540
6-ha (m^3)	6,570	4,020	3,460	3,100
(m^3ha^{-1})	1,090	670	580	520
Ratio 22/6	1.07	1.10	1.10	1.04
1976				
22-ha (m^3)	36,000	26,520	24,600	11,400
(m^3ha^{-1})	1,640	1,210	1,120	520
6-ha (m^3)	8,740	6,140	5,460	3,280
(m^3ha^{-1})	1,460	1,020	910	550
Ratio 22/6	1.12	1.18	1.23	0.95

that annual stream flows were 14.6% and 13.7% of rainfall, respectively, for the 22-ha and 6-ha catchments in 1975; and 15.0% and 13.0% of rainfall, respectively, for the 22-ha and 6-ha catchments in 1976. The importance of annual stream flow is that it represents the total input of water and loads to receiving waters.

It can be calculated (Table 3.1) that for the 22-ha catchment, annual stream flows within storm events for the years 1974, 1975, and 1976 were 67%, 63%, and 74%, respectively, of annual stream flows, and for the 6-ha catchment, 74%, 61%, and 70%, respectively. Although annual stream flow within storm events is a variable combination of storm flow and subsurface flow (Fig. 3.1), it is significant that approximately two thirds of annual steam flow occurs within storm events in the three years of study. The importance of detailed stream sampling during storm events is illustrated by the observation that approximately 20 storm events occurred per year with an average storm flow duration of approximately two days. Flow within storm events would be expected to carry a large proportion of sediment and P forms from surface soils.

Storm flow in the stream is essentially surface runoff water. Thus it might be expected that this form of discharge is most influenced by surface soil in the catchment. Annual storm flow was only slightly less than annual stream flow within storm events and comprised approximately 55% of the total annual stream flow (Table 3.1). Where storm flow can reliably be identified, it can probably be regarded as the main component carrying sediment and P forms from surface soils.

Annual subsurface flow, added both between and within storm events, comprised approximately 45% of annual stream flow (Table 3.1). Subsurface flow is probably the form of flow which is the least dependent on surface soils in the catchment, and may be expected to carry little sediment and only low concentrations of dissolved P forms.

3.3.3 Impact of land clearing and changing land use on sediment and phosphorus movement

Significant changes in the loadings and concentrations of sediment and P forms were observed after catchment clearing and fertilizer application. This is illustrated by analysis of individual storms, mean concentrations in storm discharge events for the three years of study, and annual discharges in the different runoff types.

3.3.3.1 Movement of sediment and particulate phosphorus

Following the change in land use, significant differences were found in the concentrations of sediment and PP in the flow from a single storm event. The sediment concentrations before and within a storm event in the 22-ha catchment early in 1974 (24-25/6/1974) before clearing (Fig. 3.2) showed initial low values of 50 mg 1^{-1}, with a 3-fold increase at peak flow to 150 mg 1^{-1}, which decreased rapidly with decreasing flow to a stable 65 mg 1^{-1} recession value. This stability of values at low concentrations was also shown by PP, which increased from approximately 0.020 mg 1^{-1} to 0.060 mg 1^{-1}, returning to recession values of approximately 0.040 mg 1^{-1}. These low concentration values contrast sharply with values obtained during a storm event in early 1975 (26/5/1975) after clearing (Fig. 3.3) in which sediment and PP concentrations are shown within a storm event similar to, although slightly greater than that shown in Fig. 3.2. Initial sediment concentrations (approximately 0.250 - 0.300 mg 1^{-1}) were 7-times greater than in the 1974 storm (Fig. 3.3) and increased erratically to peak values of approximately 0.60 mg 1^{-1}. These concentrations fell during flow recession to approximately 0.20 mg 1^{-1}. Values for PP were initially approximately 0.050 mg 1^{-1} but increased rapidly to peak values of 0.30 mg 1^{-1}, with a recession decrease to between 0.050 and 0.10 mg 1^{-1}. After clearing, sediment and PP concentrations in storm flow increased dramatically and showed major fluctuations in both relative and absolute values.

The increases in concentrations of sediment and P forms within storm flow following clearing, in addition to the increased variability of concentrations, also characterised successive storm flow events throughout the year following clearing. Mean sediment and PP concentrations in the storm flow of successive storm events for the three years of the study are shown in Fig. 3.4 (22-ha catchment) and for two years only in Fig. 3.5 (6-ha catchment). Despite differences in the size of storms and flow discharges, definite trends are apparent. As indicated previously, the mean sediment and PP concentrations in successive storms were relatively low and stable before clearing (1974). Mean storm flow concentrations were often less than twice the subsurface flow concentrations. In 1975 and 1976 a number of contrasts were apparent. The sediment concentrations were generally far higher, being up to 15 times those of 1974. The values also varied widely between storms, so that an 8-fold range was obtained in 1975 and a 5-fold range in 1976. Mean concentrations of PP showed a general increase over 1974 and an increase in range of values of up to 5-fold in both 1975 and 1976. Although these mean values ignore differences in the sizes of storm flow events they illustrate the increased variability in sediment and PP concentrations in storm flow after clearing. Similar major changes were observed in the sediment and PP concentrations in storm flow from the 6-ha catchment. The initially low, stable values persisting throughout 1974 were followed by high values in 1975 (after clearing). Mean sediment concentrations in 1975 increased by up to 20 times those of 1974, and showed a similar range in values between storms.

For PP, a 10-fold increase over the 1974 concentrations in storm flow and a similar range between storm events was obtained. From the data obtained for both catchments it is evident that the clearing operation and fertilizer application had two major effects. Firstly, there was a substantial increase in the variability of mean sediment and PP concentrations in the storm flow of successive storm events. Secondly, mean concentrations of sediment and PP in storm flow events were generally far higher after clearing.

Because of the differences in annual rainfall from year to year, and consequently differences in annual flow discharges, it is difficult to compare losses of sediment and P forms on a per-hectare basis (Tables 3.2 to 3.9). It is more convenient to compare results from year to year or between the two catchments by examining mean concentrations of sediment and P forms in annual flows.

Apart from significant increases in sediment and PP concentrations in individual storm flows, large increases in annual discharges within annual stream flows were also observed (Table 3.2). Both the 22-ha and the 6-ha catchments showed large increases in annual mean sediment concentrations from 1974 (107 and 82 mg l^{-1}, respectively) to 1975 (653 and 838 mg l^{-1}, respectively). Although there was a decrease in annual mean sediment concentrations in flow from the 22-ha catchment in 1976 (331 mg l^{-1}), probably due to an increase in soil stability with early pasture development, the mean sediment concentrations in flow from the 6-ha catchment were even higher in 1976 (1,590 mg l^{-1}) than in 1975. This was specifically due to slumping and slipping in the 6-ha catchment in 1976 and this is discussed in more detail in Section 3.3.4. The initial increase in annual mean sediment concentration following clearing was probably partly the direct result of the soil debris which was bulldozed

Table 3.2 Discharge of water, sediment, particulate P (PP), and total P (TP) from the two catchments in annual stream flow before land clearing (1974) and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	kg ha^{-1}	Discharge	% of TP	Mean conc. (mg l^{-1})	kg ha^{-1}
1974								
Flow (m^3)	32,670				7,230			
Sediment (kg)	3,500	-	107	159	590	-	82	99
PP (kg)	2.080	53	0.064	0.094	0.540	60	0.074	0.090
TP (kg)	3.940	100	0.121	0.179	0.900	100	0.124	0.150
1975								
Flow (m^3)	25,760				6,570			
Sediment (kg)	16,840	-	653	765	5,510	-	838	917
PP (kg)	2.55	50	0.099	0.116	1.06	63	0.161	0.176
TP (kg)	5.08	100	0.198	0.231	1.67	100	0.254	0.278
1976								
Flow (m^3)	36,000				8,740			
Sediment (kg)	11,910	-	331	541	13,870	-	1,590	2,310
PP (kg)	3.59	54	0.100	0.163	4.91	84	0.561	0.818
TP (kg)	6.70	100	0.186	0.304	5.71	100	0.652	0.951

into the stream bed, as well as the movement from catchment surfaces in storm flow. This result illustrates the potential impact of sediment movement into water during the transition period of changing land use when loose soil material is exposed. The mean concentration of sediment in annual stream flow from the 22-ha catchment in 1976 was 3 times greater than that in 1974, before clearing. This may be a closer reflection of sediment movement in surface runoff than the 1975 result because concentrations were probably less influenced by temporary debris in the stream channel.

Mean concentrations of PP in annual stream flow from both catchments (Table 3.2) showed increases from 1974 (0.064 and 0.074 mg l^{-1}) to 1975 (0.099 and 0.161 mg l^{-1}), respectively, for the 22-ha and 6-ha catchments. In the case of the 22-ha catchment, the mean PP concentration in annual stream flow in 1976, two years after clearing, was similar to that in 1975 (0.100 mg l^{-1}) although there was a reduction in mean sediment concentration. This implies that the sediment carried in 1976 was richer in P than that carried in 1975, possibly due to selectivity for fine materials (Rogers, 1941; Ryden et al., 1973) after the coarser debris material in the stream bed had been carried away in 1975. This effect is more clearly shown in Table 3.10. The mean concentration of PP in annual storm flow from the 22-ha catchment increased only 2-fold from 1974 to 1975, despite a 10-fold increase in sediment concentration, indicating a net reduction in the P concentration of sediment. The net P concentration of sediment in 1976 showed a 2.5-fold increase over that obtained in 1975. Consequently, mean PP concentrations in 1976 stream flow were similar to those in 1975, despite a reduction in mean sediment concentrations in 1976, relative to 1975.

Increases in sediment and PP losses following clearing are more apparent in the data for annual stream flow within storm events (Table 3.3). The discharge of water, sediment, PP, and TP from both uncleared catchments in 1974 were all approximately 60 to 70% of the annual stream discharge values, i.e., the discharges of sediment and PP were in close proportion to flow. Following clearing, however, up to 99% of sediment and 94% of PP appeared in stream flow within storm events, despite only 60% of annual stream flow appearing within storm events. These high proportions of annual sediment and PP losses and annual flow occurred within a relatively small proportion of the annual stream flow duration. This emphasises the importance of detailed sampling during storm events, as discussed by Sharpley et al. (1976) and in Section 3.3.1. This is further supported by the observation that increases in the mean sediment concentration in 1975, relative to 1974 (Table 3.3), as shown in annual stream flow, are more apparent in flow within storm events. The 22-ha and 6-ha catchments showed increases in annual mean sediment concentrations of 10- and 19-fold, respectively, over those observed before clearing.

Discharges of PP in stream flow within storm events only, showed similar increases from 1974 to 1975 (Table 3.3) to those obtained for sediment. For the 22-ha catchment, mean PP concentrations increased from 0.059 mg 1^{-1} before clearing to 0.113 mg 1^{-1} in the first post-clearing year, and to 0.118 mg 1^{-1} in the second post-clearing year. Again, the slight increase from 0.113 to 0.118 mg 1^{-1} was accompanied by a reduction in sediment concentration over the same period from 1,030 mg 1^{-1} to 413 mg 1^{-1}, reflecting increased P-enrichment of sediment. The increases in annual mean PP concentrations in stream flow within storm events for the 6-ha catchment from before to after clearing, showed a similar pattern.

Table 3.3 Discharge of water, sediment, particulate P (PP), and total P (TP) from the two catchments in annual stream flow within storm events before land clearing (1974) and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual discharge	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual discharge
1974								
Flow (m^3)	21,750			67	5,340			74
Sediment (kg)	2,330	-	107	67	379	-	71	64
PP (kg)	1.28	53	0.059	61	0.39	60	0.073	72
TP (kg)	2.43	100	0.112	62	0.65	100	0.122	72
1975								
Flow (m^3)	16,240			63	4,020			61
Sediment (kg)	16,730	-	1,030	99	5,370	-	1,340	98
PP (kg)	1.83	48	0.113	72	1.00	62	0.248	94
TP (kg)	3.83	100	0.236	75	1.53	100	0.381	92
1976								
Flow (m^3)	26,520			74	6,140			70
Sediment (kg)	10,950	-	413	92	13,530	-	2,200	98
PP (kg)	3.12	54	0.118	87	4.87	88	0.793	99
TP (kg)	5.77	100	0.218	86	5.55	100	0.894	97

Storm flow was separated from subsurface flow, as shown in Fig. 3.1. For these calculations it was assumed that sediment and P concentrations in subsurface flow within a storm event maintained the same low values obtained between storm events and from samples taken immediately before and after storm flow. Subsequently calculated annual storm flows are presented in Table 3.4. There were small flow reductions relative to stream flow within storm events (Table 3.3) due to the loss of the subsurface component of flow. It is apparent from Table 3.4 that between 80 and 90% of annual stream flow within storm events (Table 3.3) is actually storm flow. Also, between 82 and 99% of sediment and P forms carried in annual stream flow within storm events is carried in storm flow. The differences in annual mean sediment and PP concentrations in stream flow before and after clearing are most apparent in storm flow. Because storm flow is the most closely identified with surfaces in the catchment, changes in land surfaces are most readily apparent in such flow. It is within this fraction of stream flow, i.e., storm flow, that the mean sediment and PP concentrations in individual storm events were calculated (Fig. 3.4 and 3.5). In both annual storm flow and individual storm flow the increases in sediment and PP concentrations following the change in land use are clearly illustrated. Mean sediment concentrations in annual storm flow from the 22-ha catchment (Table 3.4) showed an increase from 115 mg l^{-1} before clearing to 1,110 mg l^{-1} in the first post-clearing year and to 436 mg l^{-1} in the second post-clearing year. These large changes in sediment concentration, despite low flow values for 1975, resulted in major increases in sediment discharge. Thus it was observed that storm flow after clearing and fertilizer application carried 7 times the sediment load per hectare in the first year after clearing, relative to the pre-clearing year, and 5 times the load in the second post-clearing year.

Table 3.4 Discharge of water, sediment, particulate P (PP), and total P (TP) from the two catchments in annual storm flow before land clearing (1974), and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual stream discharge within storm events	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual stream discharge within storm events
1974								
Flow (m^3)	17,640			81	4,160			78
Sediment (kg)	2,020	-	115	87	350	-	83	92
PP (kg)	1.13	52	0.064	88	321	60	0.077	82
TP (kg)	2.19	100	0.123	90	533	100	0.128	82
1975								
Flow (m^3)	13,980			86	3,460			86
Sediment (kg)	15,560	-	1,110	93	5,260	-	1,510	97
PP (kg)	1.74	49	0.124	95	0.83	65	0.239	83
TP (kg)	3.53	100	0.252	92	1.28	100	0.368	83
1976								
Flow (m^3)	24,600			93	5,460			89
Sediment (kg)	10,730	-	436	98	13,360	-	2,450	99
PP (kg)	2.87	54	0.117	92	4.65	88	0.852	96
TP (kg)	5.29	100	0.215	92	5.29	100	0.970	95

A similar pattern is apparent from the data relating to the 6-ha catchment where, in the first post-clearing year, a 15-fold increase in sediment loss per hectare was observed relative to the 1974 pre-clearing data.

The annual mean concentrations of PP in storm flow from the 22-ha catchment increased from 0.064 mg 1^{-1} in 1974 to 0.124 mg 1^{-1} in 1975 and to 0.117 mg 1^{-1} in 1976 (Table 3.4). The data presented in Table 3.10 show that, despite a reduction in sediment concentration in storm flow in 1976, relative to 1975, the mean concentration of PP was maintained, due to a higher P concentration in the sediment in 1976. The mean concentrations of PP in storm flow from the 6-ha catchment increased from 0.077 mg 1^{-1} before clearing to 0.239 mg 1^{-1} after clearing, i.e., a 3-fold increase.

Although there were major increases in the mean concentrations and losses per hectare of sediment and PP in storm flow following the change in land use, the mean concentrations and losses in subsurface flow (Table 3.5) were essentially unaffected. Subsurface flow within storm events commonly comprised only 20% of annual subsurface flow (calculated from Tables 3.3, 3.4, and 3.5). Stream flow between storm events (subsurface flow) was sampled regularly to obtain concentration data. Errors in the estimation of mean sediment and PP concentrations in subsurface flow within storm events would therefore have only a small effect on calculations of annual mean concentrations. Mean sediment concentrations in the annual subsurface flow from the 22-ha catchment (Table 3.5) were essentially the same for all three years. The mean concentrations of sediment in subsurface flow from the 6-ha catchment over the 3 years show similar stable values during the change in land use.

Table 3.5 Discharge of water, sediment, particulate P (PP), and total P (TP) from the two catchments in annual subsurface flow before land clearing (1974), and following clearing and fertilizer application (1975 and 1976)

Parameter	22-ha catchment				6-ha catchment			
	Discharge	% of TP	Mean conc. ($mg\ l^{-1}$)	kg ha^{-1}	Discharge	% of TP	Mean conc. ($mg\ l^{-1}$)	kg ha^{-1}
1974								
Flow (m^3)	15,030				3,070			
Sediment (kg)	1,470	-	98	67	240	-	79	41
PP (kg)	0.95	54	0.063	0.043	0.22	60	0.069	0.037
TP (kg)	1.76	100	0.117	0.080	0.37	100	0.117	0.061
1975								
Flow (m^3)	11,790				3,100			
Sediment (kg)	1,270	-	108	58	270	-	87	45
PP (kg)	0.81	51	0.069	0.037	0.23	59	0.073	0.038
TP (kg)	1.60	100	0.136	0.073	0.39	100	0.125	0.065
1976								
Flow (m^3)	11,400				3,280			
Sediment (kg)	1,180	-	103	54	310	-	94	52
PP (kg)	0.72	51	0.063	0.032	0.25	60	0.076	0.042
TP (kg)	1.41	100	0.123	0.063	0.41	100	0.126	0.070

Similar low, stable annual mean concentrations of PP were observed in subsurface flow (Table 3.4) throughout the study. For the 22-ha catchment, mean PP concentrations were 0.063 mg l^{-1}, 0.069 mg l^{-1}, and 0.063 mg l^{-1}, respectively, in 1974, 1975, and 1976. Similar values were obtained from the 6-ha catchment. Generally, the transport of sediment and PP in subsurface flow was uneffected by the land-clearing operation and any slight increases observed initially were not apparent one year after clearing.

3.3.3.2 Movement of dissolved inorganic and organic phosphorus

Following land clearing, major differences were observed in the DIP and DOP concentrations in flow within storm events. Before clearing, concentrations of DIP in storm flow were only slightly higher than those in flow between storm events and concentrations were always low. Concentrations in storm flow from the 22-ha catchment in a storm event in early 1974 (24-25/6/1974, Fig. 3.6) were initially low (0.020 mg l^{-1}) and increased to only 0.030 mg l^{-1} at peak flow, with a rapid return to the pre-peak value of 0.020 mg l^{-1}. Concentrations of DOP in storm flow of the same event (Fig. 3.6) were also low and increased from a initial value of 0.010 mg l^{-1} to a maximum of 0.060 mg l^{-1}, but rapidly decreased to a steady value of approximately 0.020 mg l^{-1}. Although DOP concentrations within storm flow fluctuated more than those of DIP, both forms showed stable, low values, despite major flow changes.

Following clearing, substantial fluctuations and high concentrations were observed in flow within storm events. This is illustrated by the data for DIP and DOP concentrations obtained for storm flow in an event in early 1975 (26/5/1975, Fig. 3.7). Concentrations of DIP were at an initially high level of 0.050 mg l^{-1} (2-3 times greater than initial values in Fig. 3.6) and increased rapidly to approximately 0.250 mg l^{-1} at peak flow. Values remained at approximately 0.20 mg l^{-1} throughout storm flow and finally decreased late in the event to approximately 0.075 mg l^{-1}. Although DOP concentrations in storm flow did not reach such high values as DIP, they showed major fluctuations during the storm event within a range of 0.01 to 0.10 mg l^{-1}. This was probably due to the heterogeneous nature of the new stream bed after clearing and the organic matter transported from the severely-disturbed, old stream system. Both DIP and DOP concentrations showed large increases in variability within a storm event. In particular, DIP concentrations showed major increases over values obtained in storm flow before land clearing.

Major changes were observed in the mean concentrations of DIP and DOP in storm flow in successive storm events following land clearing. These changes are shown in Fig. 3.8 (22-ha catchment) and Fig. 3.9 (6-ha catchment). During 1974, before clearing, mean DIP and DOP concentrations in the storm flow of successive storm events remained essentially similar throughout the year. Values were relatively low, rarely exceeding those for subsurface flow, and showed little variation in concentrations from storm to storm. In 1975 and 1976, mean concentrations of DIP in storm flow from the 22-ha catchment (Fig. 3.8) were up to 7 times greater than those obtained in 1974. The values also varied widely between storms so that up to a 4-fold range occurred in 1975 and a 3-fold range in 1976. Mean DOP concentrations in storm flow showed no general increases following clearing (Fig. 3.8). Although the mean DOP concentration remained similar to that in 1974, large fluctuations occurred from storm to storm in both 1975 and 1976. This could have been caused by irregular decomposition rates of post-clearing debris (e.g., different weather conditions and time intervals between storms) or the influence of grazing

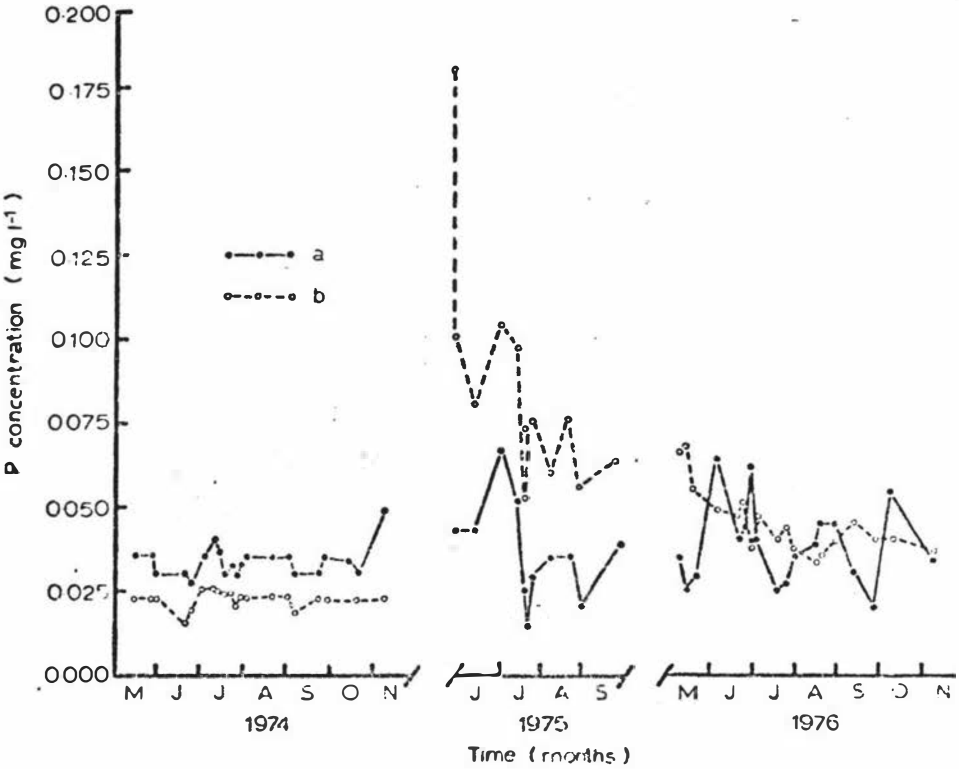


Fig. 3.8 Variation in mean concentrations of DIP and DOP in the storm discharge of successive storm events throughout 1974, 1975, and 1976 for the 22-ha catchment.

a = DOP concentration and b = DIP concentration.

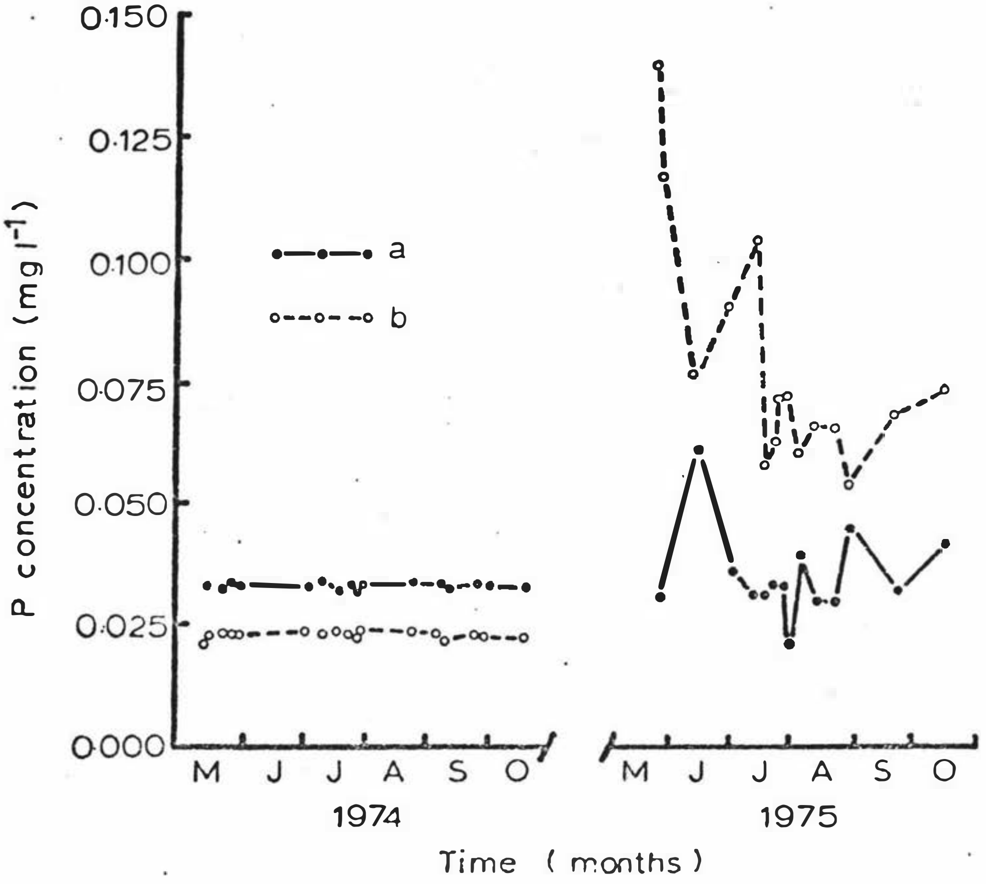


Fig. 3.9 Variation in mean concentrations of DIP and DOP in the storm discharge of successive storm events throughout 1974 and 1975 for the 6-ha catchment. a = DOP concentration and b = DIP concentration.

animals (e.g., dung deposition in the stream bed before or during storm events). These observations with respect to DIP and DOP in storm flow were supported by data from the 6-ha catchment (Fig. 3.9). The initially low, stable mean DIP and DOP concentrations in storm flows throughout 1974 contrasted markedly with the results obtained in 1975 after clearing. Mean DIP concentrations increased greatly over those obtained in 1974, and showed significant fluctuations between storms. Mean DOP concentrations were approximately similar to 1974 values but showed increased variability from storm to storm.

Mean concentrations of DIP in storm flow from both catchments were extremely high for the first storm events in 1975 (immediately after clearing) and followed a gradual, erratic decline throughout the year. For the 22-ha catchment, this gradual decline continued into 1976 (Fig. 3.8) so that at the end of the second post-clearing year, mean DIP concentrations fluctuated less and began to stablize at approximately twice the pre-clearing values. Concentrations of DOP, however, continued to fluctuate up to two full years following clearing. It is apparent that the land clearing operation and fertilizer application had a major effect on the mean DIP and DOP concentrations in storm flow for at least two years, and probably longer.

The annual discharge of DIP in stream flow following clearing and fertilizer addition showed large increases, although the discharge of DOP remained relatively constant (Table 3.6). In flow from the 22-ha catchment, the annual mean DIP concentration increased from 0.023 mg l^{-1} in 1974 to 0.062 mg l^{-1} in 1975 and to 0.041 mg l^{-1} in 1976. A similar effect was observed from the 6-ha catchment after clearing, where the annual mean DIP concentration increased from 0.024 mg l^{-1} to 0.055 mg l^{-1} in the first post-clearing year. The initial 3-fold increase in DIP

Table 3.6 Discharge of water, dissolved inorganic P (DIP), dissolved organic P (DOP), and total P (TP) from the two catchments in annual stream flow before land clearing (1974) and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	kg ha^{-1}	Discharge	% of TP	Mean conc. (mg l^{-1})	kg ha^{-1}
1974								
Flow (m^3)	32,670				7,230			
DIP (kg)	0.76	19	0.023	0.035	0.17	19	0.024	0.029
DOP (kg)	1.10	28	0.034	0.050	0.19	21	0.026	0.031
TP (kg)	3.94	100	0.121	0.129	0.90	100	0.124	0.150
1975								
Flow (m^3)	25,760				6,570			
DIP (kg)	1.59	31	0.062	0.072	0.36	22	0.055	0.061
DOP (kg)	0.94	19	0.037	0.043	0.22	15	0.037	0.041
TP (kg)	5.08	100	0.198	0.231	2.67	100	0.406	0.444
1976								
Flow (m^3)	36,000				8,740			
DIP (kg)	1.48	22	0.041	0.067	0.45	8	0.051	0.075
DOP (kg)	1.63	24	0.045	0.074	0.35	6	0.040	0.059
TP (kg)	6.70	100	0.186	0.304	5.71	100	0.652	0.951

concentration was probably partly due to P fertilizer falling directly into the stream bed, giving rise to very high DIP concentrations in flow from the first storm events following application, as well as to P movement from catchment surfaces in surface runoff. The 2-fold increase in the second post-clearing year probably reflected P movement in surface runoff and a reduction in the mobility of P from surface soil.

Annual mean DOP concentrations in storm flow from the 22-ha catchment showed almost no change following clearing (0.034 mg l^{-1} up to 0.037 mg l^{-1} in the first year) but showed a slight increase in the second year (up to 0.045 mg l^{-1}). There was a slight increase in annual mean DOP concentrations in storm flow from the 6-ha catchment from 0.026 mg l^{-1} before clearing to 0.037 mg l^{-1} after clearing. It is probable that the source of DOP changed, however, from leaf and debris litter before clearing, to decaying vegetation bulldozed into the stream bed. The increase in DOP concentrations in the second post-clearing year could be related to initial pasture establishment, giving rise to litter at the soil surface or to dung from grazing animals.

Increases in annual mean DIP and DOP concentrations following clearing are more evident in annual stream flow within storm events (Table 3.7). It is also apparent from Table 3.7 that the percentages of annual discharge of DIP and DOP appearing in stream flow within storm events were similar to those found for sediment and PP. In 1974, before clearing, approximately 60 - 70% of annual discharge of water, DIP, and DOP appeared in stream flow within storm events. In 1975 and 1976, however, the percentages of DIP and DOP increased to approximately 86 to 97% and 60 to 95%, respectively, despite the fact that only 60 - 70% of water discharge appeared in storm events, as found for 1974. For the 22-ha catchment, the annual mean DIP concentrations in stream flow within

Table 3.7 Discharge of water, dissolved inorganic P (DIP), dissolved organic P (DOP), and total P (TP) from the two catchments in annual stream flow within storm events before land clearing (1974) and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual discharge	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual discharge
1974								
Flow (m^3)	21,750			67	5,340			74
DIP (kg)	0.49	20	0.023	64	0.12	19	0.023	71
DOP (kg)	0.66	27	0.030	60	0.14	21	0.026	74
TP (kg)	2.43	100	0.112	62	0.65	100	0.122	72
1975								
Flow (m^3)	16,240			63	4,020			61
DIP (kg)	1.44	38	0.089	91	0.35	23	0.088	97
DOP (kg)	0.56	15	0.034	60	0.23	15	0.058	95
TP (kg)	3.83	100	0.236	75	1.53	100	0.381	92
1976								
Flow (m^3)	26,520			74	6,140			70
DIP (kg)	1.33	23	0.050	90	0.39	7	0.063	86
DOP (kg)	1.32	23	0.050	81	0.29	5	0.048	84
TP (kg)	5.77	100	0.218	86	5.55	100	0.894	97

storm events increased by a factor of approximately 4 from 0.023 mg l^{-1} before clearing to 0.089 mg l^{-1} in the first post-clearing year and by a factor of 2 up to 0.050 mg l^{-1} in the second post-clearing year. Similar results were observed in flow from the 6-ha catchment with an increase from 0.023 mg l^{-1} in 1974 up to 0.088 mg l^{-1} in 1975.

The increases in mean concentrations of DOP resulting from clearing are shown more distinctly in annual stream flow within storm events (Table 3.7). In flow from the 22-ha catchment, the mean DOP concentrations increased slightly from 0.030 mg l^{-1} before clearing to 0.034 mg l^{-1} in the first post-clearing year, and to 0.050 mg l^{-1} in the second post-clearing year. A similar trend was observed in flows from the 6-ha catchment where mean DOP concentrations showed a greater increase following clearing (from 0.026 mg l^{-1} in 1974 to 0.058 mg l^{-1} in 1975).

Because most of the annual discharge of DIP and DOP is lost within storm events, as with sediment and PP, it is useful to separate storm flow from subsurface flow. Changes in mean DIP and DOP concentrations and discharges in storm flow, following clearing and fertilizer application, are shown in Table 3.8. As with PP and sediment discharges (Table 3.4), a high percentage (80 to 90%) of water, DIP, and DOP discharged in stream flow within storm events appears in storm flow itself.

For the 22-ha catchment, mean DIP concentrations in storm flow increased form 0.025 to 0.093 mg l^{-1} in the first post-clearing year and to 0.049 mg l^{-1} in the second post-clearing year. Mean concentrations of DIP in storm flow from the 6-ha catchment increased similarly from 0.024 to 0.080 mg l^{-1} in the first post-clearing year. This 3- to 4-fold increase in mean DIP concentrations in storm flow from both catchments shows that the change in land use had a major impact on the movement of DIP in surface runoff, in particular.

Table 3.8 Discharge of water, dissolved inorganic P (DIP), dissolved organic P (DOP), and total P (TP) from the two catchments in annual storm flow before land clearing (1974) and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual stream discharge within storm events	Discharge	% of TP	Mean conc. (mg l^{-1})	% Total annual stream discharge within storm events
1974								
Flow (m^3)	17,640			81	4,160			78
DIP (kg)	0.45	21	0.025	91	0.10	19	0.024	80
DOP (kg)	0.61	28	0.034	93	0.11	21	0.027	81
TP (kg)	2.19	100	0.123	90	0.53	100	0.128	82
1975								
Flow (m^3)	13,980			86	3,430			86
DIP (kg)	1.30	37	0.093	90	0.28	22	0.080	78
DOP (kg)	0.49	14	0.035	88	0.17	13	0.049	73
TP (kg)	3.53	100	0.252	92	1.28	100	0.368	83
1975								
Flow (m^3)	24,600			93	5,460			89
DIP (kg)	1.21	23	0.049	91	0.36	7	0.066	93
DOP (kg)	1.21	23	0.049	91	0.28	5	0.051	94
TP (kg)	5.29	100	0.215	92	5.29	100	0.970	95

Mean DOP concentrations in storm flow showed no increase in the first year after clearing (0.034 to 0.035 mg l^{-1}) but a moderate increase in the second year to 0.049 mg l^{-1}. In storm flow from the 6-ha catchment, there was a greater increase in mean DOP concentrations in the first post-clearing year (0.027 up to 0.049 mg l^{-1}), possibly due to differences in amounts and decomposition rates of vegetative debris in the channels of the two catchments.

Despite major changes in the movement of DIP and DOP in storm flow or surface runoff, very small differences in subsurface flow concentrations were observed (Table 3.9). It is evident that the influence of land clearing and fertilizer application on mean concentrations of DIP in flow from the catchments was essentially confined to surface runoff water. This conclusion is supported by the mean concentrations of DOP in subsurface flow, shown in Table 3.9, and the mean concentrations of DOP in storm flow, shown in Fig. 3.8 and Fig. 3.9.

3.3.4 Influence of phosphorus fertilizer on the movement of phosphorus forms from the catchments

The losses of water, sediment, and P forms from the two catchments were similar following land clearing and fertilizer application (discussed in Section 3.3.3). This allowed a further P fertilizer application to be made to the 6-ha catchment in 1976 while leaving the 22-ha catchment as a control (discussed in Section 3.2).

Consistent and appreciable differences in mean DIP concentrations in storm flows were subsequently observed for the fertilized catchment, relative to the unfertilized catchment (Fig. 3.10A). The mean DIP concentrations in storm flow from the first storms in 1976 were lower than those for the first storms in 1975. This was because in 1975 the soils in the catchments were rather dry until the first storm, which was

Table 3.9 Discharge of water, dissolved inorganic P (DIP), dissolved organic P (DOP), and total P (TP) from the two catchments in annual subsurface flow before land clearing (1974) and following clearing and fertilizer application (1975 and 1976)

	22-ha catchment				6-ha catchment			
Parameter	Discharge	% of TP	Mean conc. (mg l^{-1})	kg ha^{-1}	Discharge	% of TP	Mean conc. (mg l^{-1})	kg ha^{-1}
1974								
Flow (m^3)	15,030				3,070			
DIP (kg)	0.32	18	0.021	0.014	0.07	20	0.024	0.012
DOP (kg)	0.50	28	0.033	0.023	0.07	20	0.024	0.012
TP (kg)	1.76	100	0.117	0.080	0.37	100	0.117	0.061
1975								
Flow (m^3)	11,790				3,100			
DIP (kg)	0.34	21	0.029	0.016	0.09	22	0.028	0.015
DOP (kg)	0.45	28	0.038	0.016	0.07	19	0.024	0.012
TP (kg)	1.60	100	0.136	0.073	0.39	100	0.125	0.065
1976								
Flow (m^3)	11,400				3,280			
DIP (kg)	0.27	19	0.024	0.012	0.09	22	0.027	0.015
DOP (kg)	0.42	30	0.037	0.019	0.08	18	0.023	0.013
TP (kg)	1.41	100	0.124	0.063	0.41	100	0.126	0.070

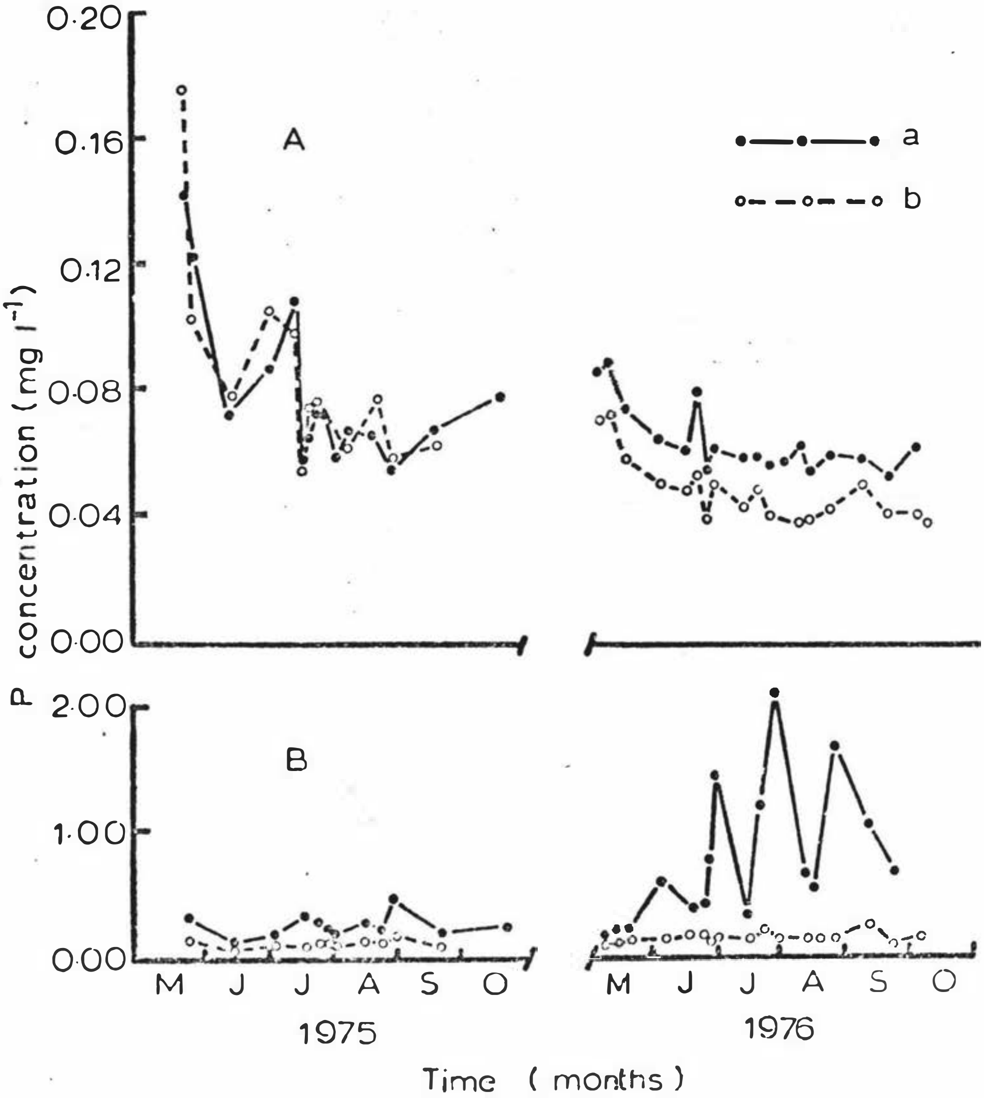


Fig. 3.10 Influence of fertilizer P application on the variation in mean concentrations of DIP (A) and PP (B) in the storm discharge of successive storm events from two adjacent catchments, both of which were fertilized in 1975 but only one of which was fertilized in 1976.

a = 6-ha catchment fertilized in both 1975 and 1976, and b = 22-ha catchment fertilized in 1975 only.

intense and probably transported some of the fertilizer which had fallen directly into the stream bed. A similar effect has been reported by McColl et al. (1975) in a study of recently-cleared, fertilized land at Puketurua, New Zealand, and has been commented on by Fish (1969) and Syers (1974). In 1976, there was light summer and autumn rain after fertilizer application, which was insufficient to cause flow but may have been sufficient to allow some P to dissolve and to interact with surface soil. It has been shown that following moisture addition, an appreciable part of the monocalcium phosphate in superphosphate can rapidly revert to dicalcium phosphate which is less soluble (Lehr et al., 1959). The interaction with the soil and reduced solubility could account for lower mean DIP concentration values in early storm flows in 1976. The data indicate, however, that as a result of fertilizer application the initial mean concentrations of DIP in 1976 storm flows were higher than the final concentrations in 1975 and that the higher concentrations persisted throughout 1976 for the fertilized catchment, (Fig. 3.10A). In contrast, the mean DIP concentrations in early 1976 storm flows from the unfertilized catchment were essentially the same as those at the end of 1975 and showed a continuing decline throughout 1976 (Fig. 3.10A). Mean DIP concentrations in storm flow from the fertilized catchment were commonly close to 0.060 mg 1^{-1} at the end of 1976 whereas mean DIP concentrations in storm flow from the unfertilized catchment were commonly approximately 0.040 to 0.045 mg 1^{-1} over the same period. It is also apparent that this difference of approximately 0.015 to 0.020 mg 1^{-1} was consistently observed throughout 1976. This relationship is shown as a regression between mean DIP concentrations in storm flow from the two catchments in 1975 and 1976 (Fig. 3.11). The regression line for 1975 (both catchments similar) shows an essentially 1:1 relationship

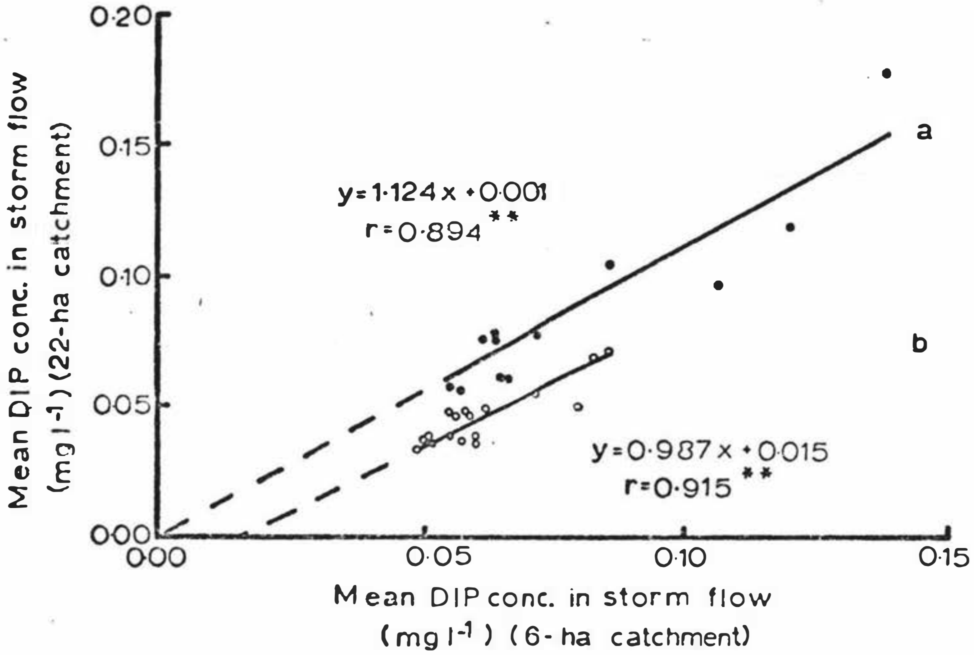


Fig. 3.11 Regression between mean concentrations of DIP in storm flow from the 22-ha and 6-ha catchments in 1975 (both catchments fertilized) and in 1976 (6-ha catchment only fertilized).
a = 1975 data and b = 1976 data.

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between mean DIP concentrations in storm flow from the two catchments, with a highly significant correlation coefficient and an intercept value close to zero. The regression line for 1976 (6-ha catchment, fertilized) shows a similar slope to the 1975 line but an intercept value of 0.015 mg l^{-1}, reflecting the consistent difference between the two catchments in mean DIP concentrations in storm flows.

The appreciable difference in DIP losses from the two catchments is shown in Table 3.11 and is expressed on a weight per hectare basis. Despite slightly less storm flow per hectare from the fertilized catchment, the higher DIP concentrations in storm flow accounted for higher losses of DIP per hectare from the fertilized catchment.

Changes in mean PP concentrations in storm flow, following fertilizer application to the 6-ha catchment in 1976, were also observed (Fig. 3.10B). In 1975, mean PP concentrations in storm flow from the two catchments were essentially the same, although the values for the 6-ha catchment were slightly higher, due to slightly higher sediment loads. In 1976, however, mean PP concentrations in storm flow from the fertilized catchment increased to between 5 and 10 times those obtained for the unfertilized catchment. This was partly due to the slipping and slumping which occurred in 1976 in the fertilized catchment only, therefore increasing sediment loads. Increased losses of sediment alone, however, do not account for increases in PP losses from the fertilized catchment in 1976. Sediment concentrations in storm flow in 1976 were approximately twice those in 1975 but PP concentrations were almost 4 times greater than those in 1975 (Table 3.4), i.e., there was a 2-fold increase in the mean P concentration in transported sediment. It can also be seen from Table 3.4 that sediment losses per hectare were 3 times greater than those in 1975, whereas PP losses per hectare were 6 times greater than those in

1975. This reflects the same 2-fold increase in P enrichment of sediment transported in 1976 compared to the PP to sediment ratio observed in 1975. This P enrichment of transported sediment following fertilizer addition is further illustrated in Tables 3.10 and 3.11. By comparison of data from the two catchments in 1976 (Table 3.11), it can be calculated that the annual mean PP concentration in storm flow from the fertilized catchment was approximately 7 times greater than that from the unfertilized catchment. This relationship is shown by the data presented in Table 3.10. In storm flow from the two catchments in 1974 (before clearing) mean PP concentrations and mean sediment concentrations were each generally similar between the two catchments and the ratios of PP to sediment were high. In 1975, PP concentrations in storm flow from both catchments increased approximately 2 - 3 times over the 1974 values and sediment concentrations increased by approximately 10 - 15 times, thus effectively reducing the mean PP to sediment ratios to approximately one fifth of the 1974 ratios. This may have been due to the increased erosion of subsurface soil material, low in P, dominating the greatly increased sediment load. For the 22-ha catchment, the mean PP concentration in storm flow in 1976 was essentially the same as in 1975, despite a reduction in sediment concentration to approximately one third that of 1975. This resulted in a 2.5-fold net increase in the P enrichment of transported sediment, possibly due to greater erosion selectivity for finer, P-enriched material. This is consistent with the work of Rogers (1941) and Ellison (1952), both of whom showed that sediment in runoff can be enriched in fine materials, which contain a higher concentration of nutrients, relative to the source soil. Ryden and Syers (1973) have also suggested that fine fractions and clay coatings on particles carried in runoff may have very high capacities to sorb and carry P from surface soils. The P enrichment of

Table 3.10 Mean concentrations of particulate P (PP) and sediment, and amounts of PP associated with sediment in annual storm flow from the 22-ha and 6-ha catchments in 1974 (before clearing) and in 1975 and 1976 (following clearing and fertilizer application)

Year	22-ha catchment			6-ha catchment		
	PP (mg l^{-1})	Sediment (mg l^{-1})	PP/Sediment (µg g^{-1})	PP (mg l^{-1})	Sediment (mg l^{-1})	PP/Sediment (µg g^{-1})
1974	0.064	115	557	0.077	83	928
1975	0.124	1,110	111	0.239	1,512	158
1976	0.117	436	268	0.852	2,450	348

Table 3.11 Losses of P forms and sediment from fertilized (6-ha) and unfertilized (22-ha) catchments in 1976 showing losses per hectare, proportions of P forms lost, and mean concentrations in annual storm discharge

	22-ha catchment (Unfertilized, 1976)			6-ha catchment (Fertilized, 1976)		
Storm flow (m^3 ha^{-1})	1,118			910		
	Losses (kg ha^{-1})	% of TP	Mean conc. (mg l^{-1})	Losses (kg ha^{-1})	% of TP	Mean conc. (mg l^{-1})
DIP	0.055	23	0.049	0.060	7	0.066
DOP	0.055	23	0.049	0.046	5	0.051
PP	0.131	54	0.117	0.776	88	0.852
TP	0.241	100	0.215	0.882	100	0.970
Sediment	488	-	436	2,260	-	2,450

transported sediment is even more apparent in data from the 6-ha catchment in 1976 (Table 3.10). There was a 4-fold increase in the annual mean PP concentration in storm flow in 1976, relative to 1975, in association with a 2-fold increase in sediment concentrations, resulting in a 2-fold increase in the PP to sediment ratio. This enrichment occurred despite an increase in mean sediment concentrations in 1976, illustrating the effect of further fertilizer application in 1976.

In 1974, before clearing, significant correlations were obtained between the mean concentrations of sediment and PP in storm flows from each catchment (0.740^{**} and 0.713^{**} for the 22-ha and 6-ha catchments, respectively). Following clearing (1975) there were no significant correlations between mean concentrations of sediment and PP for either catchment (0.550 and 0.630 for the 22-ha and 6-ha catchments, respectively). In 1976, the correlation coefficient between mean concentrations of sediment and PP increased very slightly for the unfertilized 22-ha catchment ($r = 0.583^{*}$) whereas the correlation coefficient for the fertilized 6-ha catchment was significantly increased ($r = 0.899^{**}$) relative to the values obtained in 1975 (Fig. 3.12A and 3.12B).

No significant correlation was obtained between mean concentrations of sediment and DIP in storm flows, however, for either catchment in any of the three years of the study. If sediment had released P to solution or removed P from solution, such correlations might have been expected. Sediment concentrations did not appear to significantly influence the mean concentrations of DIP in storm flow. The time interval between peak rainfall intensity and peak flow from the 6-ha catchment was approximately 20 minutes, whereas that for the 22-ha catchment was approximately 60 minutes. In addition, the soil:solution ratios in storm flow were commonly very wide (mean sediment concentrations of 100 to 2,000 mg l^{-1} or

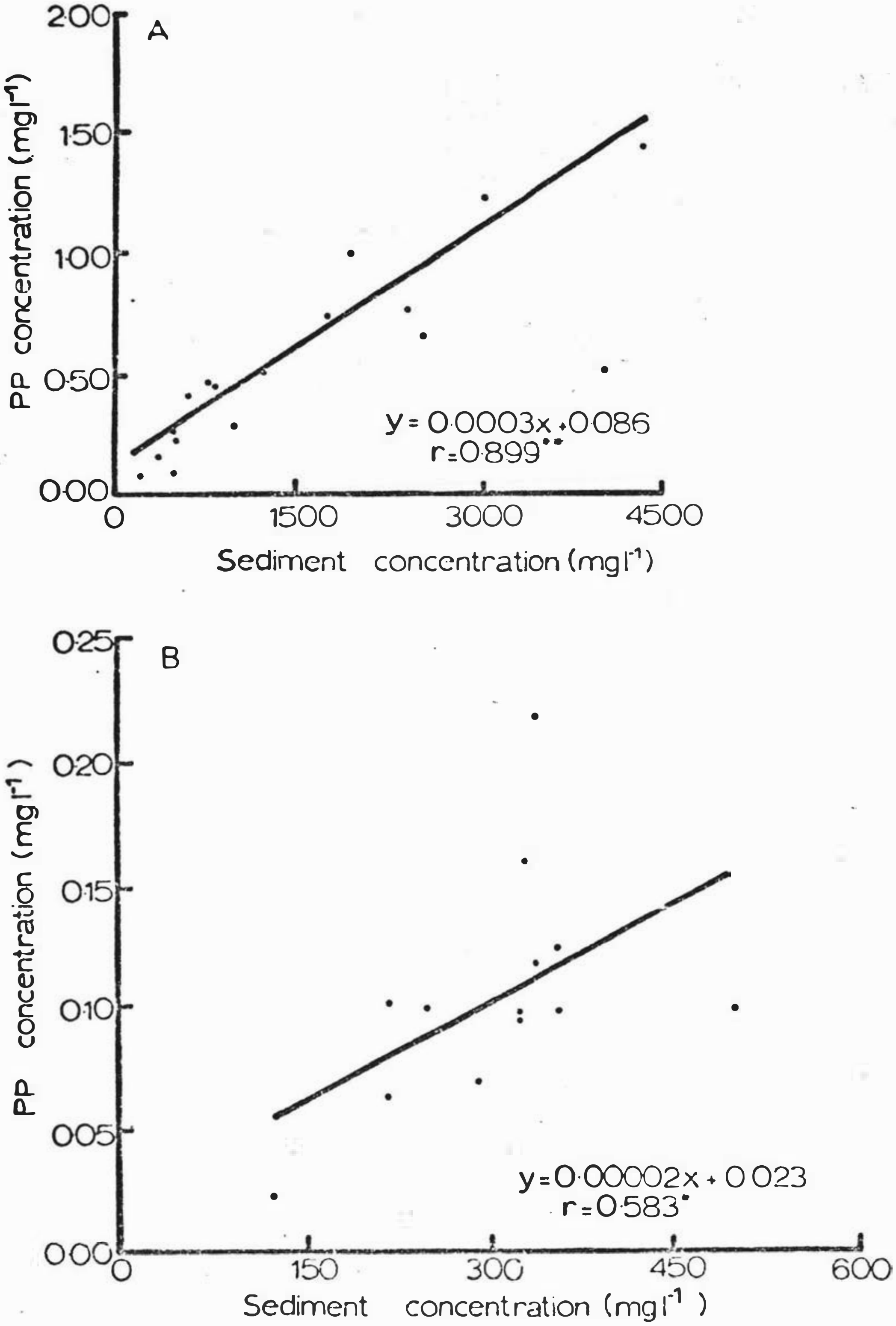

Fig. 3.12 Regression between mean PP and sediment concentrations in storm flow from the 6-ha catchment (A) and the 22-ha catchment (B) in 1976 following fertilizer addition to the 6-ha catchment only.

soil:solution ratios of 1:10,000 to 1:500). Because wider soil:solution ratios increase only the rate at which a sorption-desorption reaction for P comes to equilibrium, and not the final equilibrium value (Hope and Syers,1976; Gillingham, 1978), it may be expected that relationships between concentrations of DIP and sediment in storm flow would have become apparent at the sampling point after 20 to 60 minutes of mixed flow at a wide soil:solution ratio. The fact that no close relationship was obtained suggests that mean DIP concentrations could be largely independent of sediment concentrations.

Losses of DOP per hectare and mean concentrations of DOP in storm flow (Table 3.11) were essentially the same for both catchments in 1976, or independent of fertilizer application in the short term. It is possible that long-term fertilizer application would lead to increased DOP losses from catchments, similar to the increased losses obtained for DIP and PP. This is potentially important because, although the chemistry and biological availability of soil OP is relatively poorly understood (Cosgrove, 1967), it has been shown that OP can be utilised by algae (Berman, 1970) under certain conditions.

It can also be calculated from Table 3.2 and the fertilizer P application rate that TP loss from the two catchments was between 0.68 and 0.82% of fertilizer P added in 1975, and between 0.90 and 1.41% of P added in 1976. Although these values represent small agronomic losses, they represent large proportional increases in the P loadings of the streams draining the two catchments.

3.4 General Discussion

The data obtained in this study provide useful information relating to the movement of sediment and P forms from minimally-disturbed catchments, the impact of a land-clearing operation and pasture establishment on the movement of sediment and P forms, and the influence of P fertilizer application on the discharge of P forms. Such detailed quantitative information has been unavailable in New Zealand previously (Syers, 1974; Walker, 1975). Because the pre-clearing vegetation cover, topography, method of land-clearing, fertilizer and grass-seed applications, and farm management in this study were all reasonably similar to situations and practices widespread in New Zealand, it is likely that the data presented are relevant to many other areas and potential land-clearing operations.

It has been established (Sylvester, 1961; Vollenweider, 1968) that concentrations of biologically-available P in natural waters of less than 0.010 mg l^{-1} may limit algal growth; concentrations in excess of 0.030 to 0.050 mg l^{-1} frequently represent abundant P. Consequently, it is useful to know the background P concentrations of natural water to establish the sensitivity of such water to incremental additions of P forms and the risk of algal bloom formation, assuming that P is the limiting nutrient. Such information is limited in New Zealand. It is apparent from the data obtained in 1974, before clearing, that the mean concentration of DIP in stream flow, subsurface flow, and storm flow was commonly between 0.020 and 0.025 mg l^{-1}. Mean concentrations of DOP were commonly between 0.030 and 0.035 mg l^{-1} so that mean TDP concentrations of approximately 0.050 mg l^{-1} were common. White (1972) has reported "reactive" P concentrations of 0.027 mg l^{-1} in a small stream at Taita, New Zealand. If such dissolved P concentrations occur widely in New Zealand, then only small additions of biologically-available P to water could exceed the critical range of concentrations discussed. Although other nutrients in natural water may be limiting algal and phytoplankton growth, e.g., nitrogen (Vollenweider, 1968; Keeney, 1973), it is possible that some New Zealand waters may be highly sensitive to small additional increases in P concentrations.

The data presented in Fig. 3.2 and 3.6 for a single storm event and Figs. 3.8 and 3.9 for successive storm flow events illustrate the steady-state nature of concentrations persisting within single and successive storm events. In such a situation, which may be typical of many low fertility, minimally-disturbed catchments under scrub cover in New Zealand, it is evident that large changes in flow may be accompanied by only small changes in sediment and P concentrations. This finding emphasises the need for accurate flow data in calculating total loadings and is in agreement with the findings of Taylor et al. (1971) and Sharpley et al. (1976).

Sharp contrasts were observed in data obtained in 1975 and 1976 following land clearing. There were rapid, major fluctuations in the concentrations of sediment and P forms both within and between storm events. Because the land-clearing operation involving soil exposure on steep slopes without conservation measures, e.g., contouring, appears to be unique to New Zealand in land development for grazed pasture, it is difficult to compare the results obtained with data from overseas studies. Aubertin and Patric (1974) observed no increases in sediment or nutrient loadings in a small stream draining a catchment which was clear-felled of forest without soil disturbance and when vegetation "buffer" strips were left along stream banks. It has been shown in the present study that the highly erratic variations in sediment and P concentrations are related to surface runoff or storm flow. This result further emphasises the need for intensive stream sampling within storm events, as well as good hydrograph data. Sharpley et al. (1976) have also discussed the need for intensive sampling within storm events, where stream flow includes surface runoff from nutrient-rich soils, if reliable data for nutrient loadings in the stream are to be obtained. It seems likely that a number of studies of nutrient losses in stream flow(Fish, 1969; Kunishi et al., 1972; Burwell et al., 1974) have underestimated this requirement.

Subsequent to the clearing operation and pasture development, overall higher concentrations and losses of sediments and P forms were observed from both catchments. The data show that losses of sediment before clearing were commonly 100 to 160 kg ha^{-1}. Studying a similar catchment under native bush 10 km away from this study, Bargh (1976) reported sediment losses of 157 kg ha^{-1}. Against such background losses, which may be common in New Zealand for minimally-disturbed catchments, the losses of sediment following clearing of 540 to 2,300 kg ha^{-1} from the two catchments in this study are high. It has also been shown (Sharpley, 1977) that sediment losses in surface runoff from grazed, essentially undrained pasture may be as high as 830 to 990 kg ha^{-1}. In a study of a partly grazed and partly cultivated catchment, Bargh (1976) obtained values for sediment losses of 1,400 kg ha^{-1} yr^{-1}. Consequently, both the land-clearing operation and new land use (grazed pasture), in the short term, can greatly increase sediment concentrations and losses in runoff waters.

The TP losses from the two catchments in 1974 were 0.18 and 0.15 kg ha^{-1} (Table 3.2). Losses of TP from a similar bush-covered catchment in New Zealand (Bargh, 1976) were 0.13 kg ha^{-1}. Similar low values have been reported in overseas studies. Campbell and Webber (1969) reported an annual TP loss of 0.08 kg ha^{-1} from rangeland in Southern Ontario, Canada, and Singer and Rust (1975) have reported annual

TP losses from deciduous forest in Minnestoa, U.S.A., of 0.09 kg ha^{-1}. Against these background values of TP losses from stable, vegetated catchments, the TP losses of between 0.23 and 0.95 kg ha^{-1} shown in Table 3.2, following clearing, are high and represent a major increase in TP movement into surface waters. Despite these increases in TP losses, it is of interest to note that Sharpley (1977) has shown that TP losses from a grazed catchment under improved pasture near Massey University, Palmerston North, were 1.51 and 1.31 kg ha^{-1} yr^{-1} in 1974 and 1975, respectively. Almost half of the TP lost was as PP, in association with sediment losses of approximately 1,000 kg ha^{-1} yr^{-1} in both 1974 and 1975. These values suggest that the high initial losses following clearing and pasture establishment reported in the present study may continue in the presence of grazing animals. The fact that up to between 52 and 60% of TP losses were as PP may be significant to the biological productivity of receiving waters. A varying but often substantial proportion of PP may be available to algae, as recently demonstrated by Hedley (1978).

With the data obtained from two catchments, this study has demonstrated that the addition of fertilizer P to soil can have a direct, appreciable and continuing effect on the movement of P into surface water. Although a number of studies have examined P movement from fertilizer over short distances on runoff plots (Gilchrist and Gillingham, 1970; Nelson and Romkens, 1971; Sharpley and Syers, 1976) the influence of P fertilizer addition on amounts and forms of P in water originating from a whole catchment has not been studied intensively. The fact that between 0.68 and 1.41% of added P may be lost in stream flow implies that management techniques which reduce surface runoff, e.g., contouring, will not only reduce sediment losses but also fertilizer P movement into water. Although such movement may be insignificant from an agronomic standpoint, it may contribute significantly to the P enrichment of water.

CHAPTER 4

FATE OF APPLIED PHOSPHORUS ADDED TO SOILS AND MOVEMENT IN RUNOFF WATER

4.1 Introduction

An understanding of the movement of P in surface runoff water and within soils, and the immobilization of added P in soils, would be useful in predicting the P loadings of streams and the persistence of plant-available P in soil systems. Little work has been published in the literature on the movement of added P within soils. Several studies have been confined to laboratory conditions involving columns packed with both surface and sub-surface soils (Cho et al., 1970; Mansell et al., 1977). Other studies have been conducted in the field and have involved artificial drainage systems (Bolton et al., 1970; Cooke and Williams, 1970).

The reactions of added P, particularly in shaken systems, have been studied extensively under laboratory conditions using soils (Rajan and Fox, 1975; Ryden et al., 1977a) and soil components (Muljadi et al., 1966; Kuo and Lotze, 1972; Rajan et al., 1974). Comparatively few studies of the reactions of P in soils have been undertaken under field conditions. The work of Saunders and Metson (1971) showed no significant changes in 0.1M $CaCl_2$- extractable IP in soil over 14 months. They suggested that mineralization of the IP, arising from the pool of OP built up in the soil during winter, was balanced by more rapid plant uptake of IP in spring. This accumulation of soil OP during winter, and its mineralization in spring, was also reported in a field study by Dormaar (1972). Neither study, however, examined the rates and mechanisms of P reactions within soils or the fate of added fertilizer P.

The rate at which "labile" or plant-available P is immobilized in soils has been the subject of several studies. Larsen (1967) has emphasized the need to study reaction rates of mobilization and immobilization between "non-labile" and "labile" P in soils and has presented some experimental field data (Larsen et al., 1965). The rates of decline of plant-available P following P addition to soils in a pot experiment have been shown (Barrow, 1973) to be related to the soils' ability to adsorb P. The nature and persistence of "labile" P in soils has also been defined theoretically (Ryden et al.,1976). In the latter study the rate of decrease in the pool of labile P in soil, following fertilizer P addition, was described using data obtained from both shaken tube and soil incubation systems.

The significance of results obtained in the laboratory for the fate of P added to soils and the movement of P in soils, to the P enrichment of waters and even to agronomic requirements, is poorly established. The purpose of this part of the study was to examine the changing pattern of water-extractable P in soil in the field following fertilizer P application and to relate this to the concentrations of dissolved inorganic P (DIP) in stream waters. To arrive at a better understanding of P movement within the soil, and to reduce field sampling variability, pots of soil to which fertilizer P was added were established in the field and examined concurrently with field soil samples.

4.2 Materials and Methods

Work carried out in this part of the study consisted of a preliminary investigation in 1975 and a more detailed investigation in 1976. In addition, a supplementary study was also conducted in the laboratory in 1976.

4.2.1 Preliminary investigation

Three sites within each of the two catchments were chosen in 1975 as potential sampling areas to represent each catchment (Fig. 4.1). Two of the areas were one on each side of the central ridge between the two catchments and near their outfalls; a further two were approximately half-way along the length of the 6-ha catchment with one site half-way down each of the two slopes of the central ridge; and the third pair was near the upper reaches of each catchment and near their respective valley floors.

Each site covered an area of 5-m square ($25m^2$) and was divided into 25 x 1-m square plots. Adjacent to each site, an area of 10 m^2 was covered during fertilizer addition and subsequently sampled as a control site.

Initially, an estimate was made of the evenness of distribution of superphosphate in the two catchments. Three transect lines were chosen across the two catchments (Fig. 4.1) and a series of collection containers (17cm square and 20cm deep) were placed along them (locations shown in Fig. 4.2). An estimate was also made of the distribution of superphosphate surrounding each potential sampling area to determine how representative the site was of the catchment as a whole. Six containers were placed around each site to estimate the P application rate. Immediately following aerial topdressing, the containers were transported to the laboratory and total P per container was measured by digestion of the collected material with perchloric acid (O'Connor and

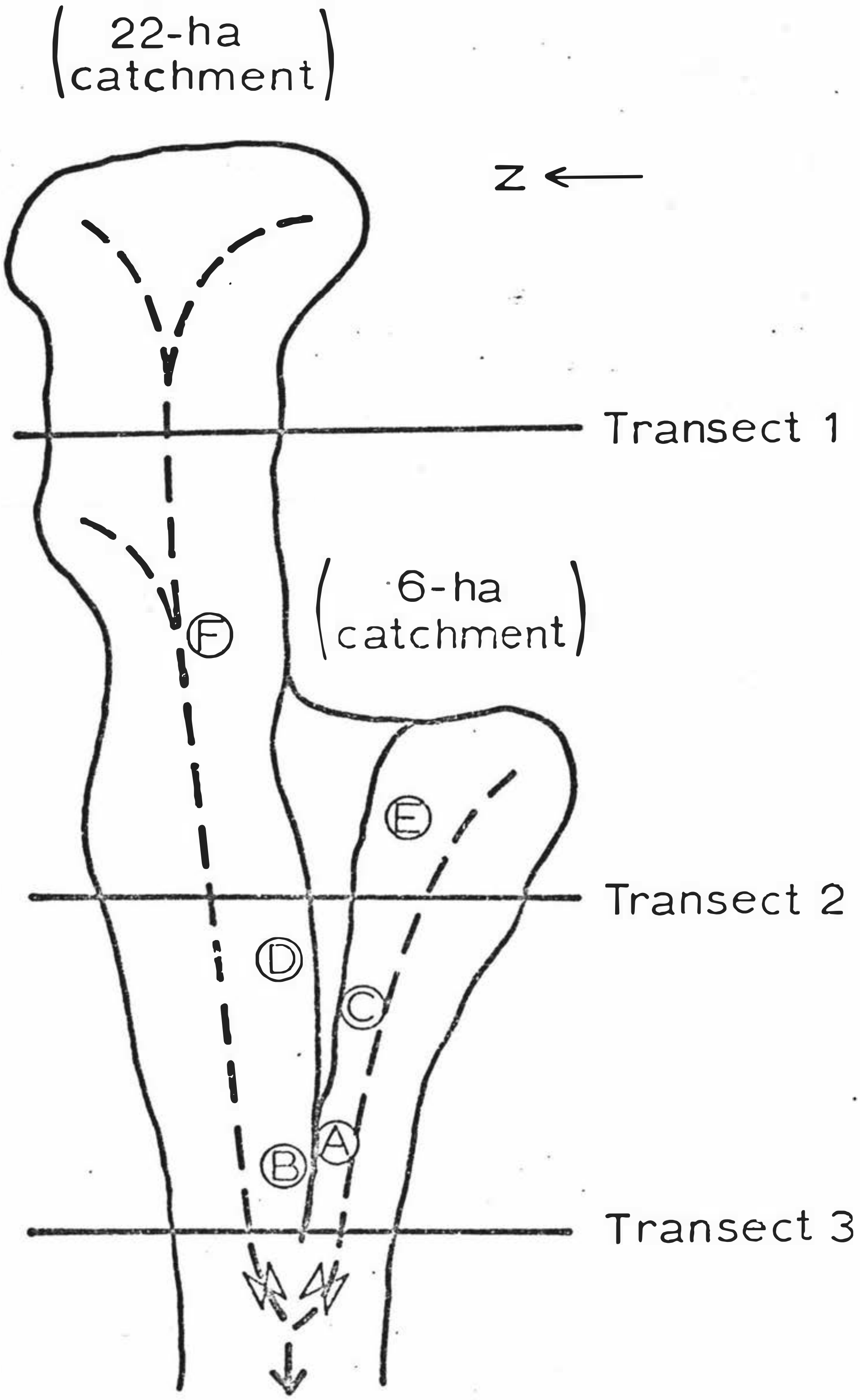

Fig. 4.1 Plan of the two catchments showing the location of 6 sites for soil sampling in 1975 (A, B, C, D, E, and F) and the three transect lines for placement of pots to estimate the mean superphosphate application rates in the catchments.

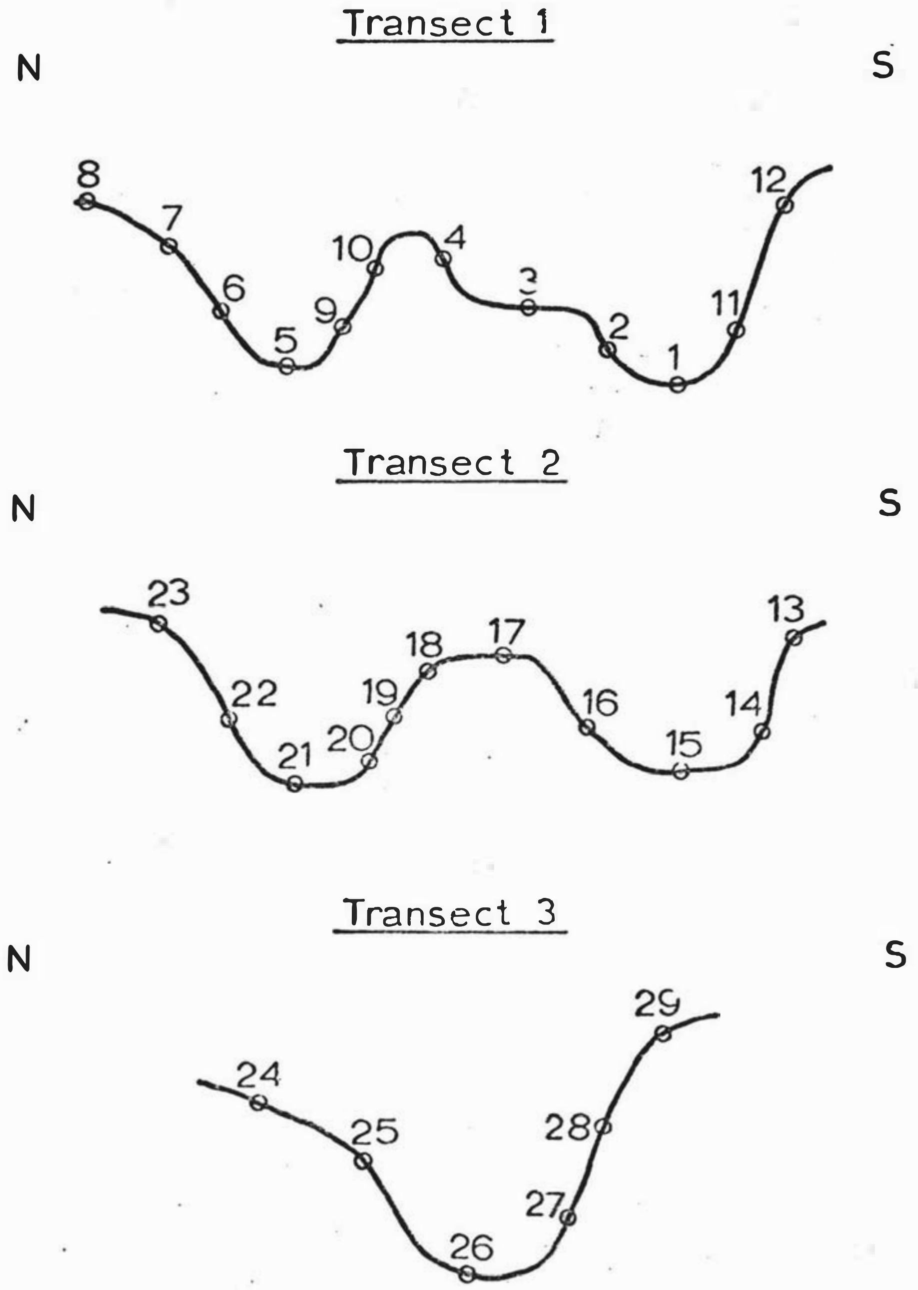

Fig. 4.2 Transverse section of the three transect lines shown in Fig. 4.1 showing the location of pots placed in the catchments to estimate the application rate of superphosphate.

Syers, 1975). This was considered more satisfactory than simply weighing the contents of each container because it provided data pertaining to the actual P addition rate to the soil surface. A sample of the superphosphate was also analyzed for TP and water-soluble P. This was considered important because superphosphate produced in New Zealand has been shown (R.W. Tillman, pers. comm.) to be variable in both TP and water-soluble P content.

To investigate the fate of added fertilizer P, sample cores, 5cm in diameter and 2cm in depth, were taken at random from each of the 1-m^2 plots within both the fertilized and control areas of each of the selected sites. A total of 25 cores was taken from each fertilized area and 10 cores from each unfertilized area. Samples were taken at monthly intervals throughout 1975.

4.2.2 Detailed investigation

Soil samples were taken from the 6-ha catchment only in 1976, at a sampling interval of approximately one week. In February 1976, three new sites were chosen within this catchment; these sites were considered to be representative of the soils and topography of the catchment (J.A. Pollock, pers. comm.). As described in Section 4.2.1, each site was 5-m square and 25 soil samples were taken from each site on each sampling occasion. The control sites used in 1975 were retained in 1976. As in 1975, sampling containers were placed around each site prior to fertilizer application; nine containers were used per site. The control sites were covered to prevent contamination with superphosphate. Soil samples were collected immediately following fertilizer application and thereafter were taken at weekly intervals until November, 1976. A statistical analysis of the variability of the 25 soil samples from each site was done on the first samples taken and the deviation from the mean at the 95% confidence level calculated. Regular sampling involved sieving ($<$ 2mm) of the 25 bulked cores, mixing, and moisture determination by overnight drying at 105°C. The freshly-sieved field soil was corrected by weight to an oven-dry equivalent basis for P extraction.

For P extraction, samples were shaken at a soil:solution ratio of 1:400 with distilled water in 240-ml polyethylene bottles on an end-over-end shaker at 23°C for 17 hours. Subsamples of the suspension were centrifuged, at 13,000 r.p.m. at 23°C, filtered ($<$ 0.45μm) and the supernatant solution analyzed for DIP in the usual way. Extracted P is expressed as μg P g^{-1} soil on an oven-dry basis.

To reduce the variability in field soil samples, and to evaluate several different treatments involving fertilizer application, a series of experimental "pots" were established in the field, in conjunction with the field sampling programme. The pots were constructed from light gauge, clear plastic, and were 12-cm long, 10-cm wide, and 3.5-cm deep. Surface soil was used for the experiment and this was taken from approximately 30 random sites throughout the two catchments, from a depth of 0 - 5cm, before fertilizer application. The soil was shredded, passed through a 2-mm sieve, mixed, and air-dried. A 2-cm depth of soil (approximately 200g of oven-dry material) was placed in each pot which had a series of drainage holes punched in the bottom. Several treatments were used for fertilizer addition to the soils:

Treatment 1 - no superphosphate added and used as controls

Treatment 2 - superphosphate ($<$0.5-mm material) mixed throughout the 2-cm depth of soil at a rate of 0.336g $200g^{-1}$ soil

(161 μg P g^{-1} based on a TP analysis of 9.6% for the superphosphate). This rate is equivalent to 336 kg ha^{-1} of superphosphate, assuming mixing in the top 1cm of the soil.

Treatment 3 - addition of 0.336g of superphosphate per 200g of soil spread evenly over the surface of the pot.

Treatment 4 - as for treatment 3 except that a piece of nylon gauze was placed on the surface of the lower 1-cm layer of soil before the upper 1-cm of soil was added. Superphosphate was applied to the surface as in treatment 3. This technique allowed the soil in the pot to be divided into the upper and lower 1-cm layers prior to extraction and analysis of P in order to monitor the movement of water-extractable P downwards from the surface application of fertilizer.

The pots were installed in the field adjacent to area C (Fig. 4.1), with the surface of the pot being at the same level as that of the field soil. Thus, the soil in the pots experienced environmental conditions which were as similar as possible to those experienced by field soils. At each soil-sampling event, replicate pots of each treatment were transported to the laboratory and analyzed for water-extractable P.

4.2.3 Supplementary study

Because it was found in 1975 that the mean DIP concentration in storm flow often showed large differences from storm to storm, a study of the short-term changes in soil water-extractable P was initiated in the laboratory. Twenty pots (treatment 2) were brought into the laboratory from the field. The pots were collected on November 1, 1976, following two weeks of dry weather. They were placed on the bench in a light, sunny position. Distilled water was applied to simulate a rainfall event (25mm of water added in small increments to the soil surface over a period of 2.5 hours) and the leachate from each pot collected. The treatment was repeated on the same pots 24 hours later, and then again 10 days later after the pots had been standing at ambient temperature without further moisture addition. Watering and leachate collection occurred on November 1, 2, and 11, 1976. On each occasion the leachate from each pot was analyzed for DIP.

4.3 Results and Discussion

4.3.1 Changes in water-extractable phosphorus in soil from fertilized and control field sites within the catchments

In the preliminary investigation in 1975, it was found that the distribution of P in superphosphate around each of the six potential sampling sites was highly variable (Table 4.1). The intended mean application rate for the two catchments was 375kg ha^{-1}. This rate, based on a TP analysis of 9.6% for the superphosphate applied, is equivalent to 360 μg P cm^{-2}. If it is assumed that interaction between the added P and soil is confined to the upper 2cm of soil, and the mean bulk density of the soil is 1.0g cm^{-3}, this rate of addition is equivalent to 180 μg P g^{-1}. It was considered from the distribution data (Table 4.1) that the three sites A (446 μg P cm^{-2}), C (226 μg P cm^{-2}), and F (120 μg P cm^{-2}) were representative of the range of values obtained, and also gave a reasonable distribution about the mean catchment value of 302 μg P cm^{-2}, which was reasonably close to the intended application rate of 360 μg P cm^{-2} or 36 kg P ha^{-1}.

Table 4.1 Application rate of fertilizer P at the soil surface obtained from sampling containers surrounding six potential soil-sampling sites in the preliminary investigation of 1975

	Application rate of P (μg cm^{-2}) at sampling sites						
Replicate	A	B	C	D	E	F	Catchment
1	374	420	156	132	326	108	(29 samples)
2	418	374	184	58	204	164	
3	374	216	374	96	144	120	
4	400	374	204	70	554	118	
5	554	302	192	122	192	84	
6	556	276	240	252	252	118	
Average (6 containers)	446	328	226	122	280	120	302

The first soil-samples from all six sites were collected in late March (1975) before the application of superphosphate, lime, and grass seed, but after clearing. Samples were taken three days following fertilizer application from sites A, C, and F, the weather being warm and the soil dry. Very high values for water-extractable P were obtained immediately following fertilizer application but at the time of the second sampling one month later (7/5/1975), the values at all sites had decreased considerably (Table 4.2 and Fig. 4.3). Although there was an overall decrease in water-extractable P values during the year, it is evident from the data presented that some variation occurred between samples. This could have been the result of sampling error (sample numbers too small) or a reflection of real fluctuations in water-extractable P in the soil over time. Two studies (Saunders and Metson) 1971; Dormaar, 1972) have suggested that 0.01M $CaCl_2$-extractable or soil-solution P values do not fluctuate widely throughout the year. The tendency, however, for water-extractable P values at all three sites in the present study to follow a similar pattern (Fig. 4.3) suggests that real, short-term fluctuations could occur in the field.

Consequently, a more detailed sampling programme was adopted for the more-detailed investigation in 1976. Three new sampling sites were chosen in the 6-ha catchment, although the same three control sites used in 1975 were retained. Because a new aerial application of superphosphate was made in March 1976, fertilizer P addition rates to the soil were again established before soil sampling began. For the top site (near C, Fig. 4.1) the mean addition rate was 326 μg P cm^{-2}, that for the sloping site was 626 μg P cm^{-2}, and that for the bottom site was 158 μg P cm^{-2}. These values are equivalent to 163, 313, and 79 μg P g^{-1}, respectively, for the

Table 4.2 Amounts of water-extractable P in soils from sites A, C, and F (Fig. 4.1) and control sites on 24/3/1975 (before fertilizer application) and at various times after fertilizer was applied on 5/4/1975

	Water-extractable P ($\mu g\ g^{-1}$) in soil at site				
Date	A	C	F	Average	Control
24/3/75	4.4	3.7	3.3	3.8	3.6
8/4/75	189.7	41.2	10.8	80.6	3.5
7/5/75	78.7	27.7	7.3	37.9	4.3
25/6/75	50.2	27.5	7.0	28.3	3.2
23/7/75	72.7	31.3	8.0	37.3	3.0
20/8/75	60.0	33.5	12.7	35.4	4.7
24/9/75	35.4	10.9	3.8	16.7	3.9
20/10/75	41.0	12.7	2.9	18.9	4.6
28/11/75	38.1	19.8	3.6	20.5	4.1

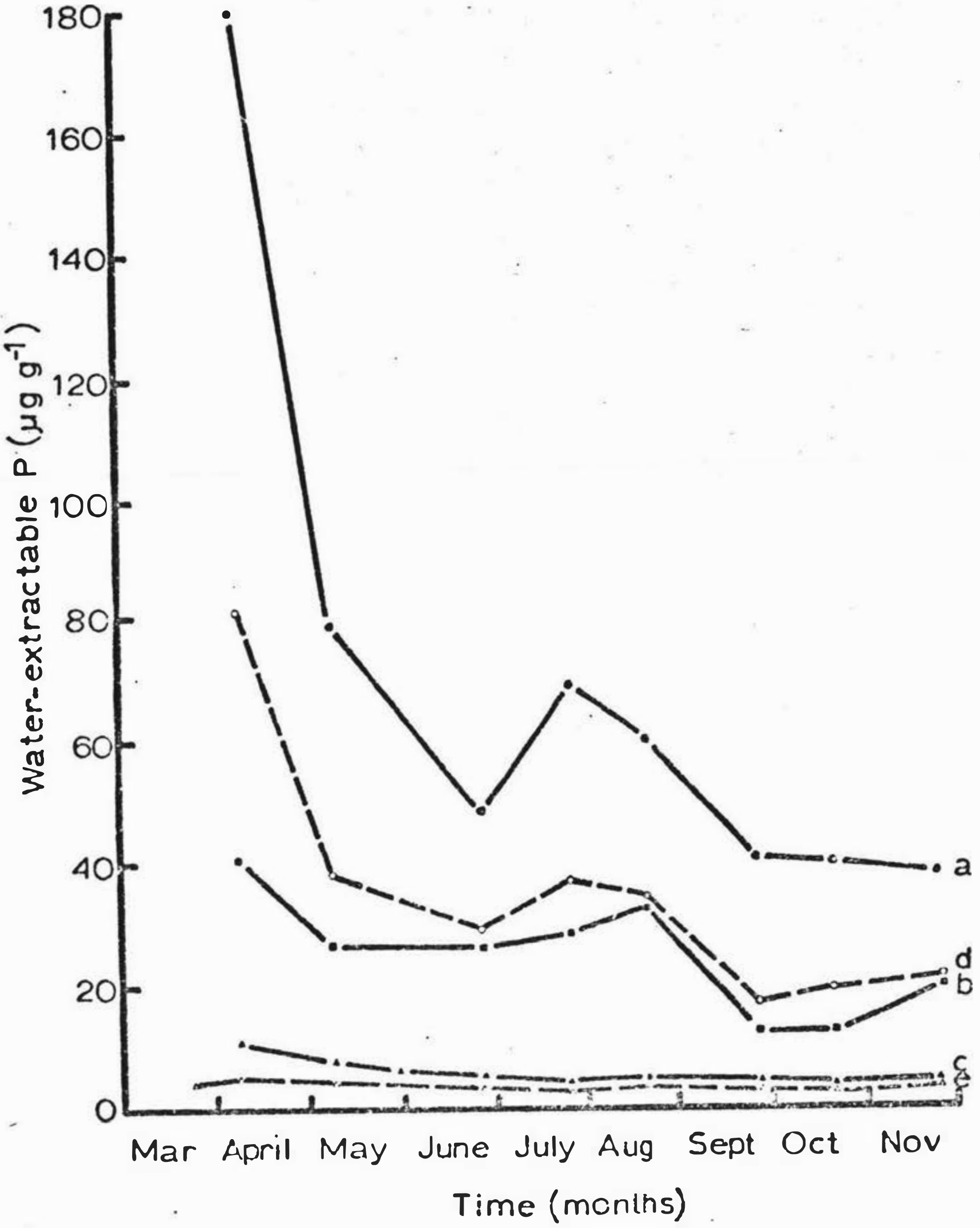

Fig. 4.3 Decline in water-extractable P in soils with time following fertilizer P addition at three fertilized sites and from three control sites in 1975.
a = site A, b = site C, c = site F, d = average of sites A, C, and F, and e = average of three control sites.

three sites, assuming interaction with the upper 2cm of soil and a mean soil bulk density of 1.0g cm^{-3}. Twenty-five soil samples from each site were collected several hours after fertilizer application. Mean water-extractable P values were 83µg P g^{-1} for the top site, 146 µg P g^{-1} for the sloping site, and 91µg P g^{-1} for the bottom site. The fact that the first two of these values were lower than those predicted, whereas the third was higher than predicted, could be related to resorption or desorption of P during extraction; this is discussed later.

An estimate of the error of the mean water-extractable P values (obtained from 25 soil samples) was made following the calculation of variance for each group of 25 samples (Snedecor and Cochran, 1967). Deviations at the 95% confidence level were found to be 83 ± 19 µg P g^{-1} (16 at 90%) for the top site, 146 ± 32 µg P g^{-1} (27 at 90%) for the sloping site, and 91 ± 18 µg P g^{-1} (16 at 90%) for the bottom site. Because all of these deviations were less than the expected decreases throughout the year, it was accepted that 25 samples were sufficient to monitor changes in water-extractable P in surface soils. It was also initially anticipated that variability would decrease with time, as the fertilizer P became more evenly distributed through the upper 2cm of soil.

Subsequent to this initial sampling, soil samples were taken at all three sites and control sites at weekly intervals during winter through to November, 1976. The progressive decrease in water-extractable P values is shown in Fig. 4.4. It is apparent that not only the trends, but also the actual values were similar to those obtained in 1975 (Fig. 4.3). This is seen more clearly when the averaged data for the three sites in 1975 and in 1976 are presented together (Fig. 4.5). The first data point on the 1975 curve was lower (82µg P g^{-1}) than that on the 1976

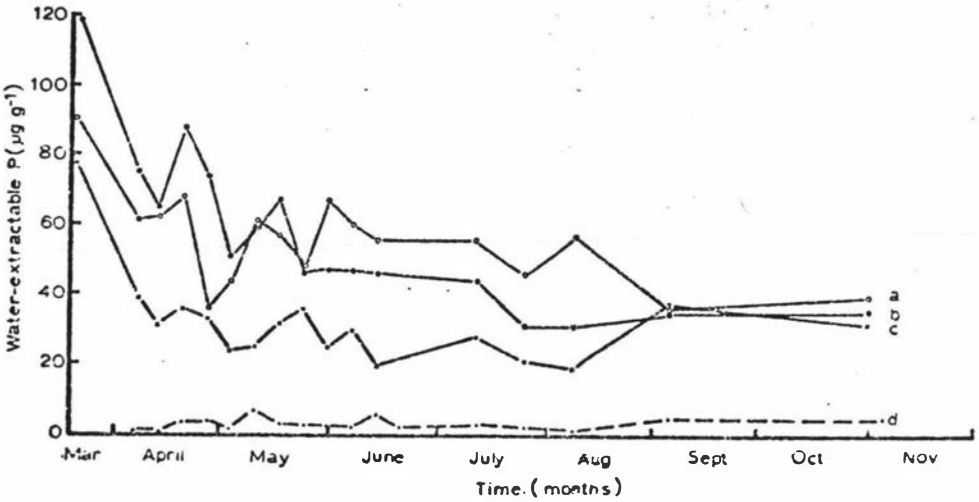

Fig. 4.4 Decline in water-extractable P in soils with time following fertilizer P addition at three fertilized sites and from three control sites in the 6-ha catchment only in 1976.

a = bottom site, b = sloping site, c = top site, and d = average of three control sites.

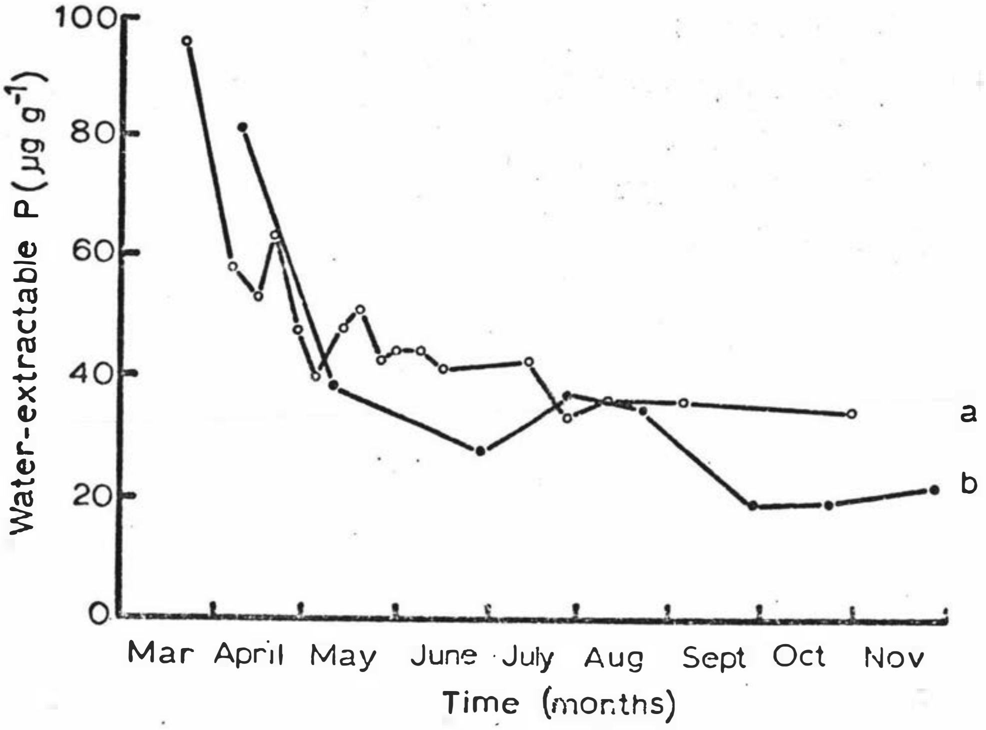

Fig. 4.5 Decline in water-extractable P in soils with time following fertilizer P addition at three fertilized sites in the 6-ha catchment only in 1976 and three fertilized sites in both catchments in 1975.

a = 1976 average of three sites and

b = 1975 average of three sites.

curve (98 μg P g^{-1}). This may have been due to the lower average fertilizer P application rate to the sites in 1975 (132 μg P g^{-1}) than in 1976 (165 μg P g^{-1}), although there may also have been some effect of residual fertilizer P in early 1976 from the 1975 application. Despite this difference, the initial rate of decrease of both curves was similar. Between June and October, the 1976 data points were usually higher than those for 1975. This is possibly due to higher initial values and to the increased saturation of the sorption complex, leading to higher sustainable values in solution. When successive water-extractable P values are expressed as a proportion of the initial extraction values (Fig. 4.6), the proportional rates of decline for the two years are essentially the same.

Soil samples taken prior to fertilizer application in March 1976 gave water-extractable P values of 4 μg P g^{-1} for the top site, 4 μg P g^{-1} for the sloping site, and 49 μg P g^{-1} for the bottom site. These results suggest that there could be a net down-slope movement of P with time in the catchment. The data in Fig. 4.4 support this suggestion. Although the sloping site received the highest fertilizer P addition rate and gave the highest initial water-extractable P values, the bottom site which received the lowest P addition rate gave a higher water-extractable P value than the top site. After 60 days, the bottom site yielded the highest water-extractable P values. The persistent high values for the bottom site, despite a concurrent decline in values for the sloping and top site, together with the initial high value, implies a net down-slope movement of P. This movement could be as particulate P (PP) or as dissolved P transported downslope in surface runoff.

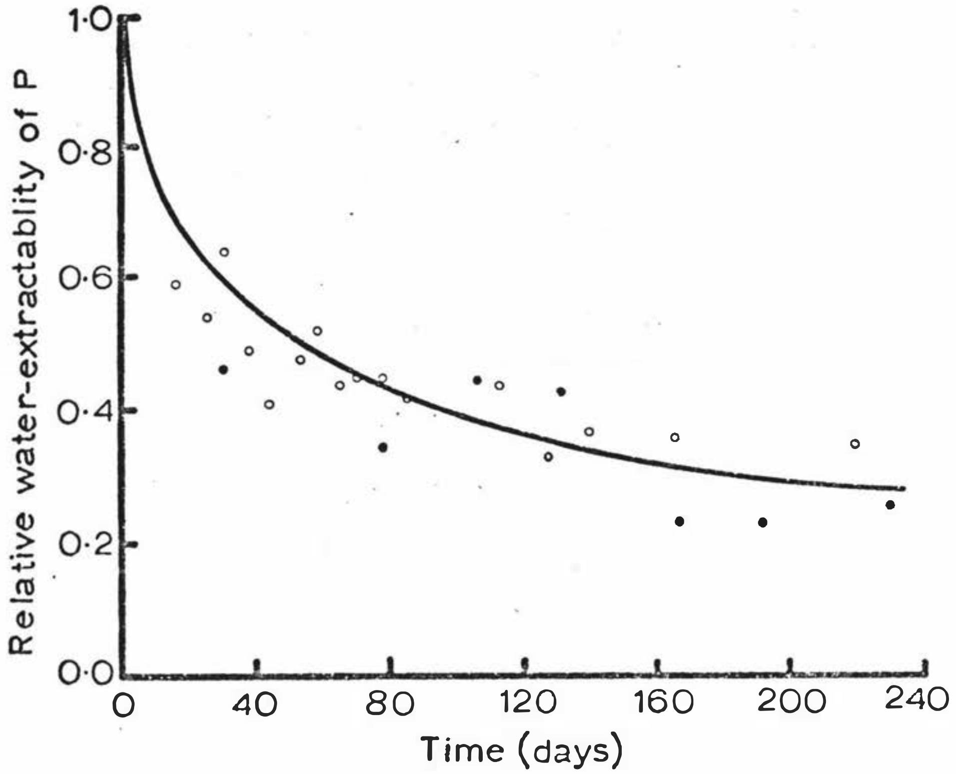

Fig. 4.6 Relative water-extractability of P, expressed as a proportion of the initial extraction value, with time following fertilizer P addition at three fertilized sites in the 6-ha catchment only in 1976 and three fertilized sites in both catchments in 1975.

Open symbols = 1976 average of three sites and closed symbols = 1975 average of three sites.

4.3.2 Changes in water-extractable phosphorus in soil from fertilized and control pots in the field

4.3.2.1 Treatment differences and phosphorus movement from the upper 1cm

The pots to which superphosphate was added were sampled simultaneously with the fertilized field soils to monitor the decline in water-extractable P as a function of time following P addition. Because the soil in the pots had been mixed, and was thus more homogeneous than field soil, and because fertilizer P was added in the laboratory, less variation in water-extractable P values was apparent in the results. The treatment which most closely resembled the field sites was treatment number 3, with fertilizer P uniformly distributed over the surface. The decrease in water-extractable P for both the surface application (treatment 3) and the mixed treatment (treatment 2) was essentially the same throughout 1976 (Fig. 4.7). Both gave similar initial values and although the mixed treatment appeared to show a greater initial rate of decline, there was no detectable difference between the two treatments at the third sampling (18 days). Small fluctuations between data points can probably be accounted for by variations in sampling. The very rapid initial decline in water-extractable P during approximately the first 10 days was followed by a slower rate of decrease which persisted for the remainder of the year. The results from treatment 4, however, showed a different pattern. With fertilizer added to the surface, the upper 1cm of soil gave an initial water-extractable P value which was twice that obtained with treatments 2 and 3. The rate of decrease, relative to this initial value, was essentially the same as that for the other two treatments but actual values were consistently twice as high

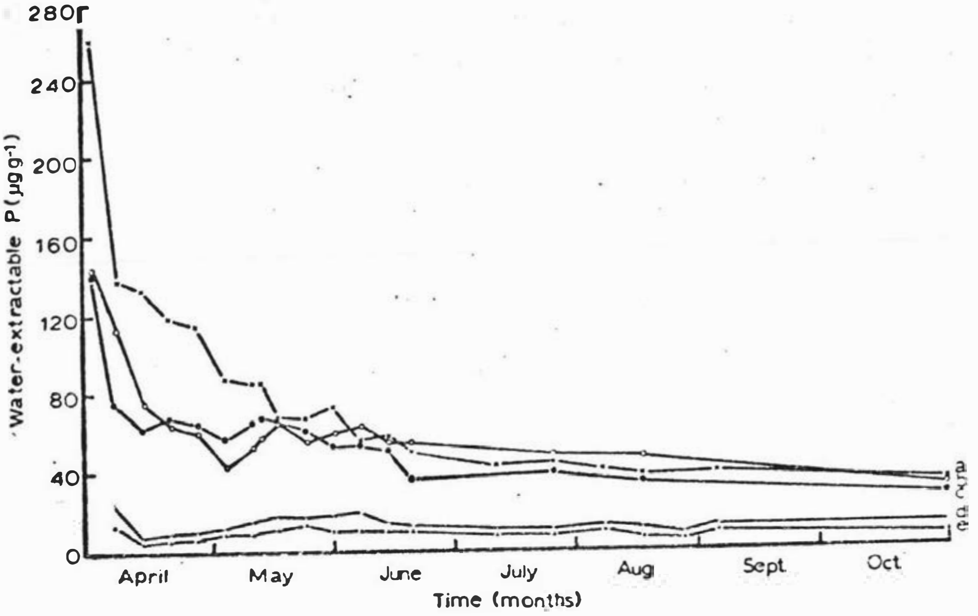

Fig. 4.7 Decline in water-extractable P with time, following fertilizer P addition, in soil from field pots.
a = mixed treatment, b = surface 2-cm treatment, c = surface upper 1-cm treatment, d = surface lower 1-cm treatment, and e = unfertilized control.

for approximately the first 40 days. In contrast, the lower 1cm of soil in this treatment, which was not in direct contact with fertilizer P, gave consistently low values for the whole year; in fact these were indistinguishable from the control. The fact that the pattern of decline in the upper 1cm was essentially the same as that for the 2cm surface treatment (treatment 3) and the mixed treatment (treatment 2), except that the values were doubled for the first 40 days, suggested that the rate of P removal from a water-extractable form was directly related to P concentration in the soil solution. This implies that there were differences in the rates of P sorption between the surface application and the mixed treatment, but that these differences were masked by the procedure of sampling the soil to a depth of 2cm in each case, i.e., maintaining the same P:soil ratio. Taking only the upper 1cm effectively doubles the P:soil ratio and thus the rate of P sorption in absolute terms, although the relative rates are the same (Fig. 4.8).

There was no evidence for the downward movement of P from the upper 1cm to the lower 1cm, even after 200 days in the field (Fig. 4.7). Although this result is in agreement with that of other workers, e.g., Cho et al. (1970), it may be to some extent an artefact resulting from the use of disturbed soils. Recent work (Scotter et al., 1978) has shown that P may move through undisturbed soils which have continuous pores. The extensive soil disturbances occurring within catchments during land clearing operations, however, may permit extrapolation of the pot experiment results to the field situation immediately following land clearing.

The tendency for water-extractable P values to converge after approximately 40 days (May, 1976; Fig. 4.7) was possibly due to a feature

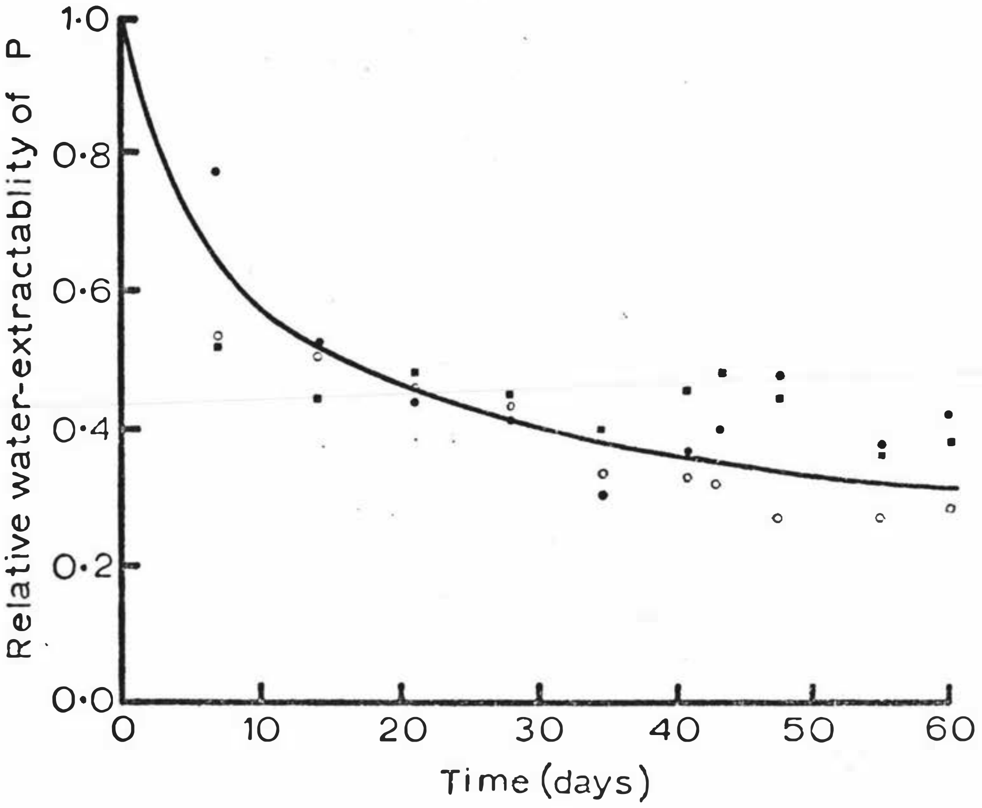

Fig. 4.8 Relative water-extractability of P, expressed as a proportion of the initial extraction value, with time following fertilizer P addition to soil in field pots.
Closed square symbols = mixed treatment, closed circle symbols = surface 2-cm treatment, and open circle symbols = surface upper 1-cm treatment.

of the field experimental technique used. When the pots were established in the field they were placed into the soil on a slightly sloping site. After approximately 40 days, the soil in the pot tended to assume a horizontal surface, possibly because of rainfall splash or water movement. The migration of material from the up-slope to the down-slope surface almost certainly moved fertilizer P from the upper 1-cm section to the 2-cm section (left-hand side in Fig. 4.9B) of the pot. This probably accounts for the decrease in water-extractable P values in soil from the upper 1cm down to, and even below, values for the other two treatments. It may also explain the levelling off, followed by an increase in water-extractable P values for soil in the 2-cm treatment to values above those for the other treatments (Fig. 4.7). The redistribution of surface material may also account for the scatter of data points about the relative water-extractable P decline curve (Fig. 4.8) 40 days after P addition. The gradual removal of P from the upper 1cm would result in a progressive decrease in values with time, whereas P accumulation on the surface of the 2cm section would result in a progressive increase in values with time. The small-scale redistribution of P observed is in agreement with the suggested down-slope surface movement of P to the bottoms of catchment slopes. Although several workers, e.g. Ellison (1944, 1954), have shown that sediment can move down-slope by rainfall splash and that such sediment may contain high nutrient concentrations (Rogers, 1941; Ellison, 1952), the data obtained in the present study suggest that fertilizer P added to catchment soils may move down steep slopes relatively quickly.

4.3.2.2 Relationships between water-extractable phosphorus data obtained for soils from fertilized field sites and pots

A close relationship was obtained between the water-extractable

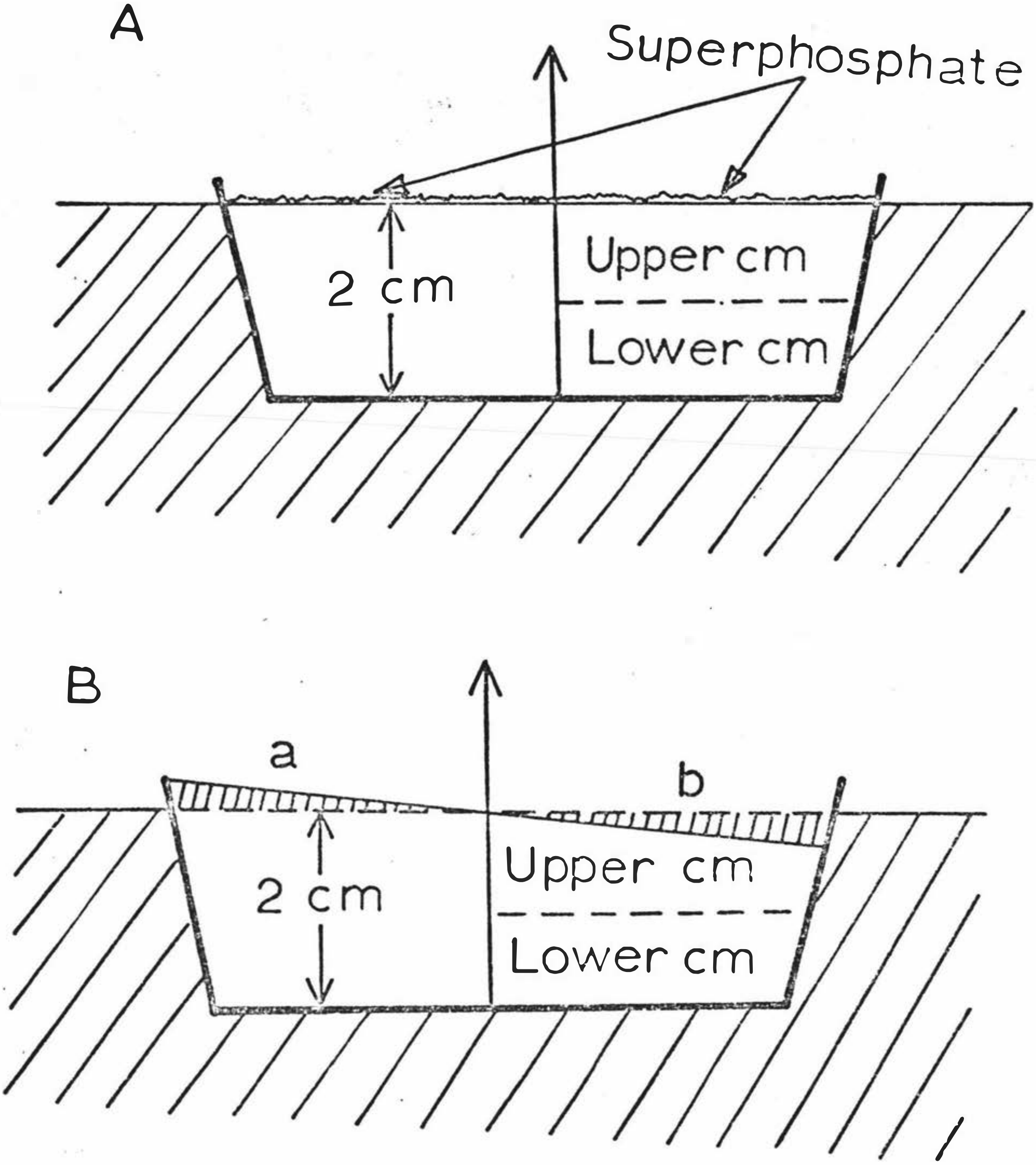

Fig. 4.9 Field pots involving "divided" soil treatments showing condition at time of fertilizer placement and after 40 days in the field.

A = pot as initially prepared, B = pot after 40 days in the field showing redistribution of surface soil and superphosphate.

P values for soils from the field sites and from the experimental pots. The decline in water-extractable P with time following fertilizer P addition is shown in Fig. 4.10. The 1975 values for field sites are generally low, due partly to a lower rate of fertilizer P addition in 1975. The 1976 pot values are generally higher than the 1976 field site values, due in part to the transfer of P across the pot surface during May and June (discussed Section 4.3.2.1). Despite the differences in values, there is a close similarity in the pattern of data for the two sets of samples. Correlations for the data are presented in Fig. 4.11 and Fig. 4.12. Correlation coefficients for the two regressions between 1976 field site data and pot data were 0.978^{**} for the surface 2-cm treatment and 0.944^{**} for the mixed treatment. The regressions suggest that the experimental field pots could be useful in estimating water-extractable P values for an overall catchment, provided that the catchment is reasonably uniform in soil type and that P fertilizer addition rates can be replicated in the pots.

Insufficient soil samples were available from treatment 4 (before P redistribution occurred, as discussed in Section 4.3.2.1) to calculate regressions between data from this treatment and the field site. The basic 2:1 relationship between values from the upper 1-cm treatment and the surface 2-cm treatment, obtained during the first 40 days following P addition (Fig. 4.7), suggests that the simple relationship of increased soil water-extractable P values being proportional to the increased P addition rates could be extended to the field situation.

4.3.2.3 Regeneration of the water-extractable phosphorus pool in soils

It was observed that when two storms closely followed one another, e.g., within approximately 1-2 days, the second event showed a

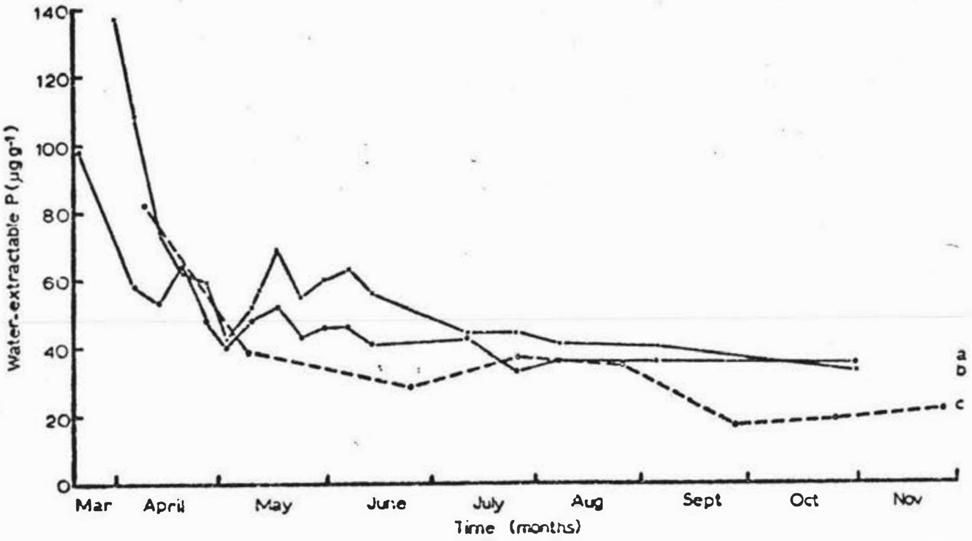

Fig. 4.10 Decline in water-extractable P with time, following fertilizer P addition, in soil from fertilized sites in the field and pots in the field.
a = 1976 average of three field sites, b = surface 2-cm pot treatment, and c = 1975 average of three field sites.

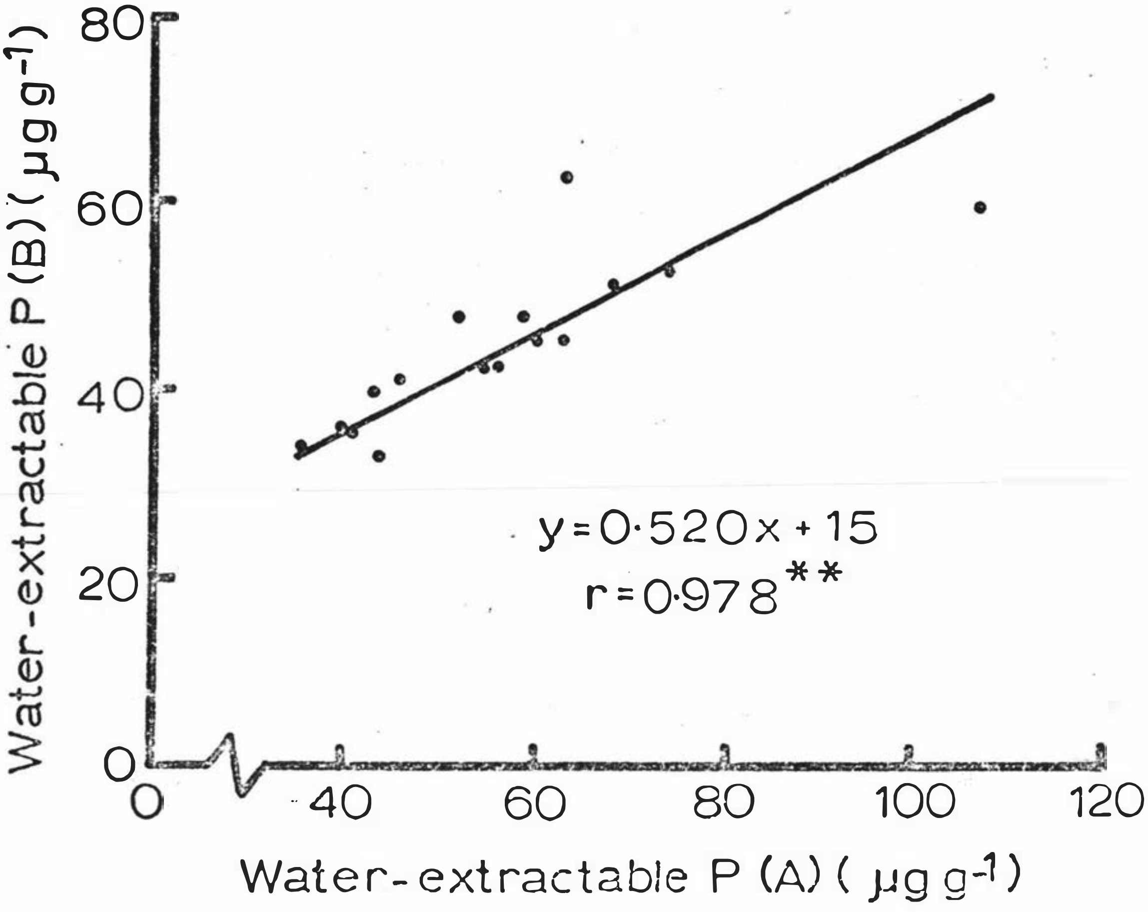

Fig. 4.11 Regression between water-extractable P in soil from fertilized field sites (B) and from surface 2-cm pot treatment (A). All data for the 6-ha catchment in 1976.

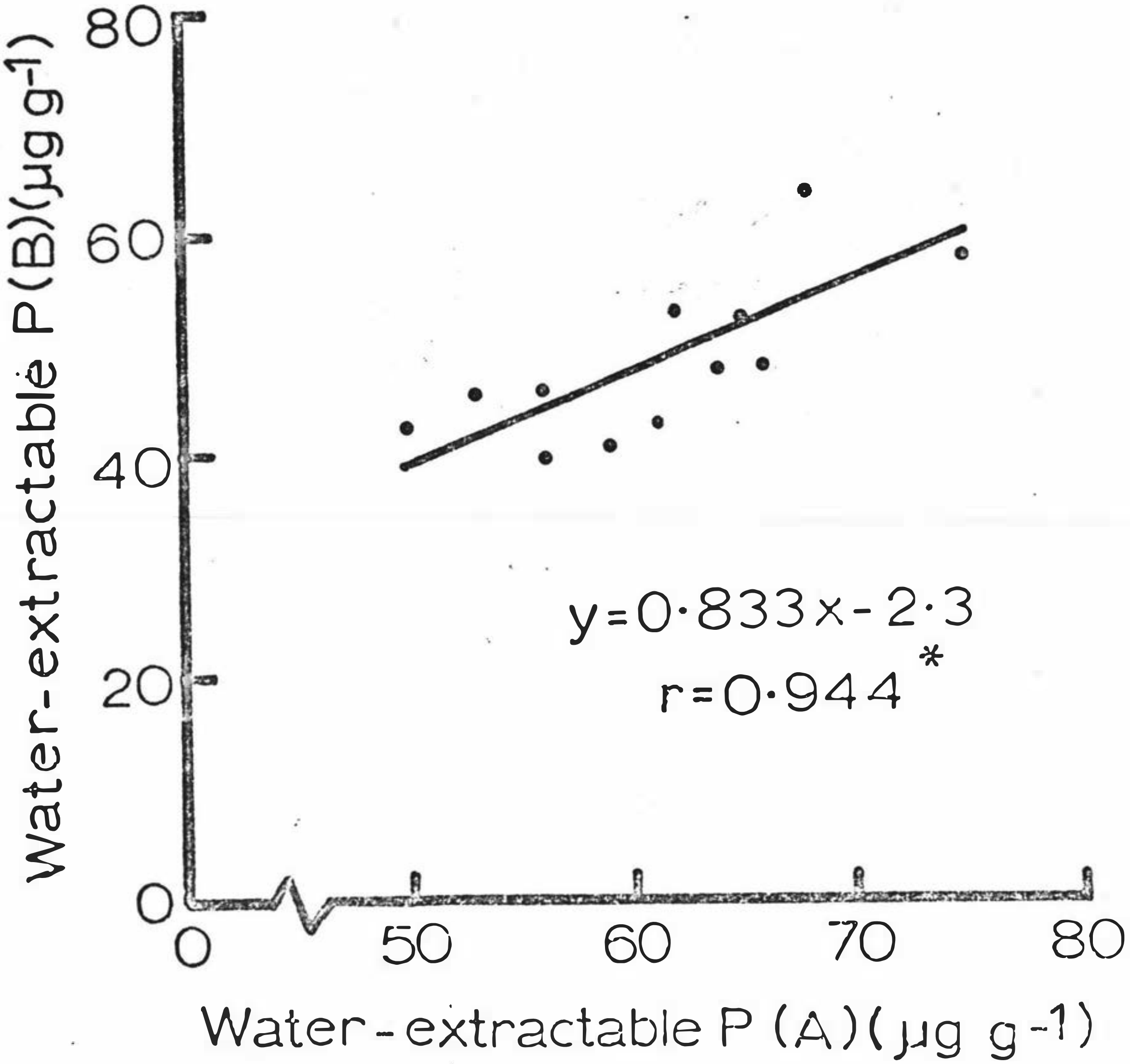

Fig. 4.12 Regression between water-extractable P in soil from fertilized field sites (B) and from mixed pot treatment (A). All data for the 6-ha catchment in 1976.

lower mean DIP concentration in storm flow than was obtained in storm flow of the first event. A third storm event up to 10 days later often showed a recovery of mean DIP concentrations in storm flow to approximately those obtained in storm flow in the first event. For example, in storm flow for an event on 14th August, 1976, mean DIP concentrations were 0.067 and 0.056 mg P l^{-1} for the 6-ha and 22-ha catchments, respectively. For a storm on the 16th August, 1976, mean DIP concentrations of 0.043 and 0.038 mg P l^{-1}, respectively, were obtained in storm flow from the two catchments. A significant recovery in the values was observed for a third storm event on the 26th August when mean DIP concentrations in storm flow were 0.056 and 0.051 mg P l^{-1}, respectively, for the two catchments. A possible explanation for this may have been that the loss of DIP from the surface soil in surface runoff in the first event resulted in lower mean DIP concentrations in the storm flow of the second event. The increase in mean DIP concentrations in the third event may have resulted from the mineralization of OP to water-extractable IP or from a redistribution of sorbed IP in soil to re-establish equilibria with soil solution P.

To examine this further, 20 of the treatment 2 (mixture) pots were leached in the laboratory, as described in Section 4.2.2. It was found that the DIP concentrations in the leachates from the first leaching were all within the range of 0.050 to 0.100 mg l^{-1}, with a mean value of 0.081mg l^{-1}. In the leachates from the second leaching 24 hours later, DIP concentrations were within the range of 0.025 to 0.075 mg l^{-1}, with a mean value of 0.051 mg l^{-1}. In the leachates from the third leaching 10 days later, DIP concentrations were widely different, ranging from

0.050 to 0.450 mg l^{-1}. Although the DIP concentration values in the third leaching were usually greater than those obtained for the same pot in the first leaching, the changes in values were often large and irregular.

The regression analyses and correlation coefficients given in Fig. 4.13 show the relationships between data obtained in the first leaching and those obtained in the second leaching (A), and those obtained in the third leaching (B). The lower values for DIP concentrations obtained in the second leaching are related to the initial amounts of DIP present in the soil and reflect a proportional dilution or "wash out" of the water-extractable pool of IP in the soil (Fig 4.13A). The data presented in Fig. 4.13B indicate that the DIP concentrations in the leachate obtained after 10 days of warm, dry weather are independent of the initial values and presumably the size of the pool of water-extractable IP in the soil. It seems possible that the recovery of DIP values after leaching can be attributed to the mineralization of part of the OP pool in the soil.

The concentrations of DOP in the leachates of the first leaching were low and rather similar, with a mean value of 0.047 mg l^{-1}. In the second leaching the mean value was approximately 0.029 mg l^{-1}, whereas in the third leaching the mean value was 0.045mg l^{-1}. Although there was some recovery of DOP concentrations it seems unlikely that the recovery of DIP values was due to the conversion of DOP to DIP. It is possible that microorganisms may have liberated some DIP from particulate OP.

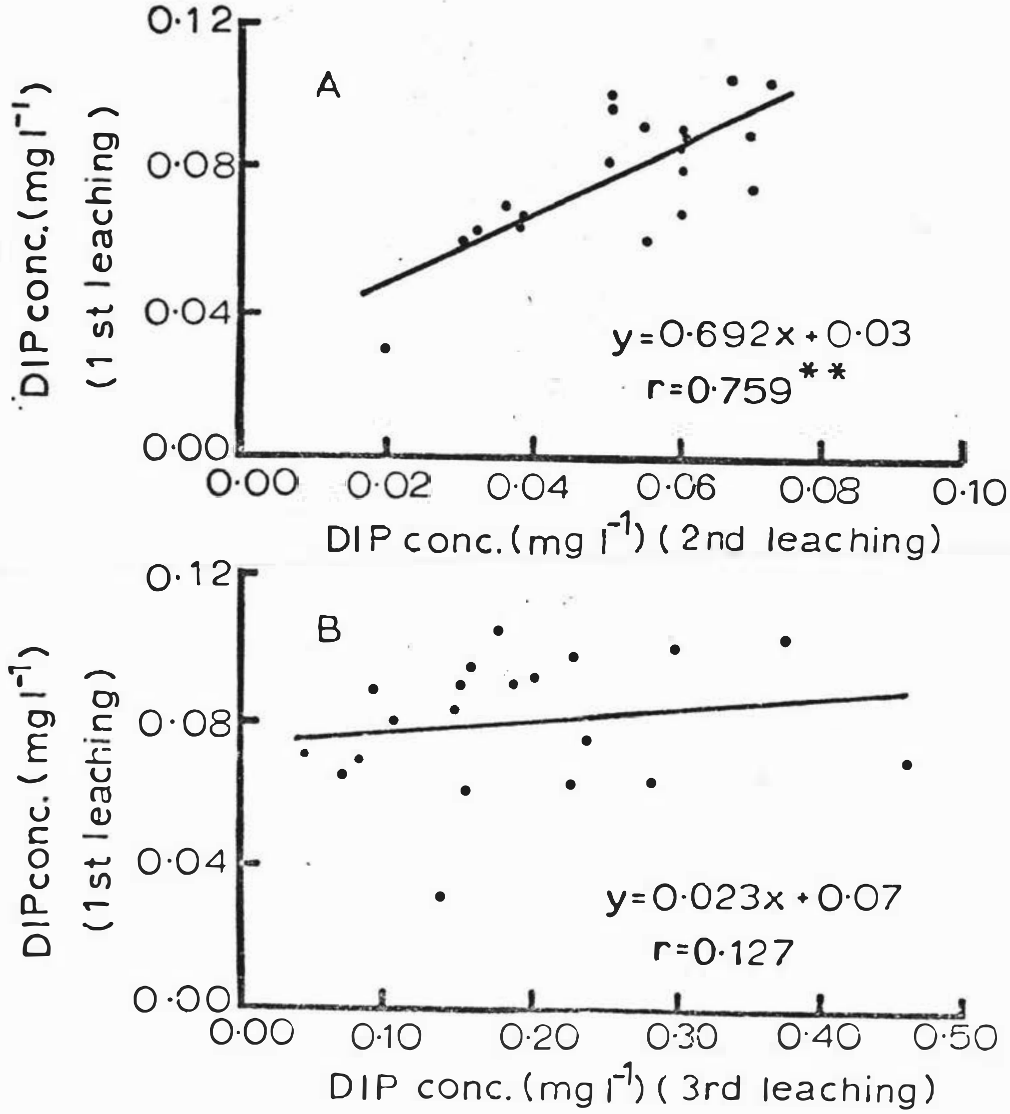

Fig. 4.13 Regression between DIP concentrations in the leachates from 20 pots (mixed treatment after 7 months in the field) obtained by successive leachings.
A = regression between DIP concentrations in the first leachate and the second leachate 24 hours later,
B = regression between DIP concentrations in the first leachate and the third leachate 10 days later.

4.3.3 Relationships between mean dissolved inorganic phosphorus concentrations in surface runoff and water-extractable phosphorus values obtained for soils from fertilized field sites and pots

It seemed likely that the best regression analysis results would be achieved if relationships were established between water-extractable P values in the top 2cm of soil and the mean DIP concentrations in that portion of stream flow most closely representing surface runoff. It has previously been suggested (Section 3.2 and Fig. 3.1) that storm flow, as distinct from subsurface flow, may be regarded as surface runoff. The portion of storm flow appearing within the rising portion of the hydrograph may most closely approximate true or "primary" surface runoff. This is the fraction of storm flow which will subsequently be referred to as surface runoff and used in regression analyses in this Section.

Data obtained from the preliminary study in 1975 (Fig. 4.14) showed that there was a general decline in both water-extractable P values in field soils and in mean DIP concentrations in surface runoff following fertilizer P addition. The pattern of decline for both showed high initial values, with a rapid decline followed by lower values and a slower decline rate in the later part of the year. Although there were some differences between the mean DIP concentrations in surface runoff from the 22-ha and 6-ha catchments, they were generally similar throughout the year. Despite some fluctuations, the water-extractable P values in soil from the field sites showed the same general pattern throughout the year. In view of the possible rapid changes in water-extractable P which may occur in soils, possibly resulting from microbial activity (discussed in Section 4.3.2.3), it appears that more frequent soil sampling could

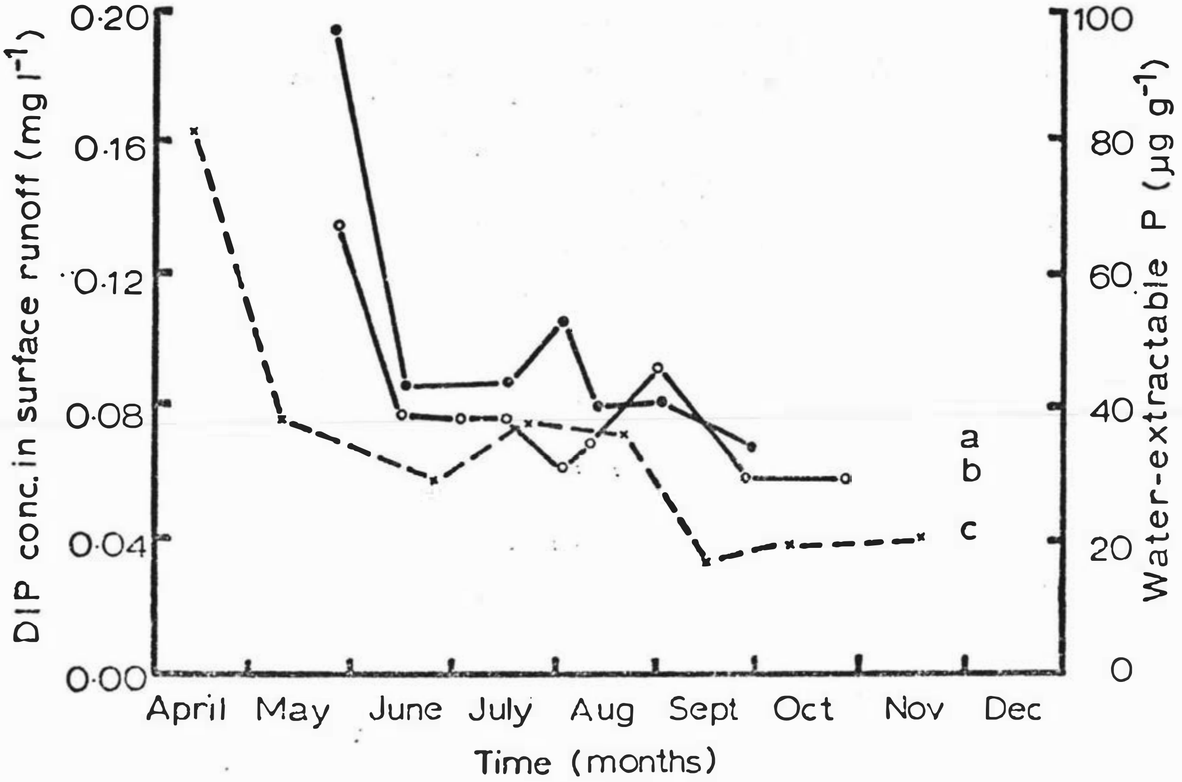

Fig. 4.14 Relationship between mean DIP concentrations in the surface runoff component of storm flow from the two catchments and water-extractable P in soil from fertilized field sites in 1975.

a = 22-ha catchment storm flow, b = 6-ha catchment storm flow, and c = 1975 average of three field sites.

improve the precision of data points available for regression analysis. Also, because the soil sampling interval was large (1 month), few samples could be paired with closely-following storm events for which the mean DIP concentration in surface runoff was obtained. The few data points for each catchment which could be paired in this way, however, indicated a linear relationship between water-extractable P values for soil and the mean DIP concentrations in surface runoff from storm events closely following the soil sampling. Correlation and regression analyses between runoff data and soil data were similar for both catchments (Fig. 4.15). Although the correlations were not strong or highly significant, probably due to the few data points, the similarity of the regressions suggested that with more frequent soil sampling, the regressions and correlations could be improved.

In the more detailed investigation of 1976, soil sampling was intensified (Fig. 4.4. and Fig. 4.5) and storm flow was sampled more intensively on the rising portion of the hydrograph for every storm event for the 6-ha catchment. A similar relationship between water-extractable P values for soil and mean DIP concentrations in surface runoff (Fig. 4.16) was obtained to that shown in Fig. 4.14 but the relationship was supported by far more data points. Because water-extractable P values from field sites generally remained higher in 1976 than in 1975 (Fig. 4.5), the regression and correlation analyses shown in Fig. 4.17 for 1976 data involved only a restricted range of values in the x axis. When the data for 1976 were combined with those for 1975 (Fig. 4.18), it was shown that the 1976 data supported and extended the relationship obtained in 1975 (Fig. 4.15). The regression analyses for data obtained from each catchment in 1975, from the 6-ha catchment only in 1976, and from the 6-ha

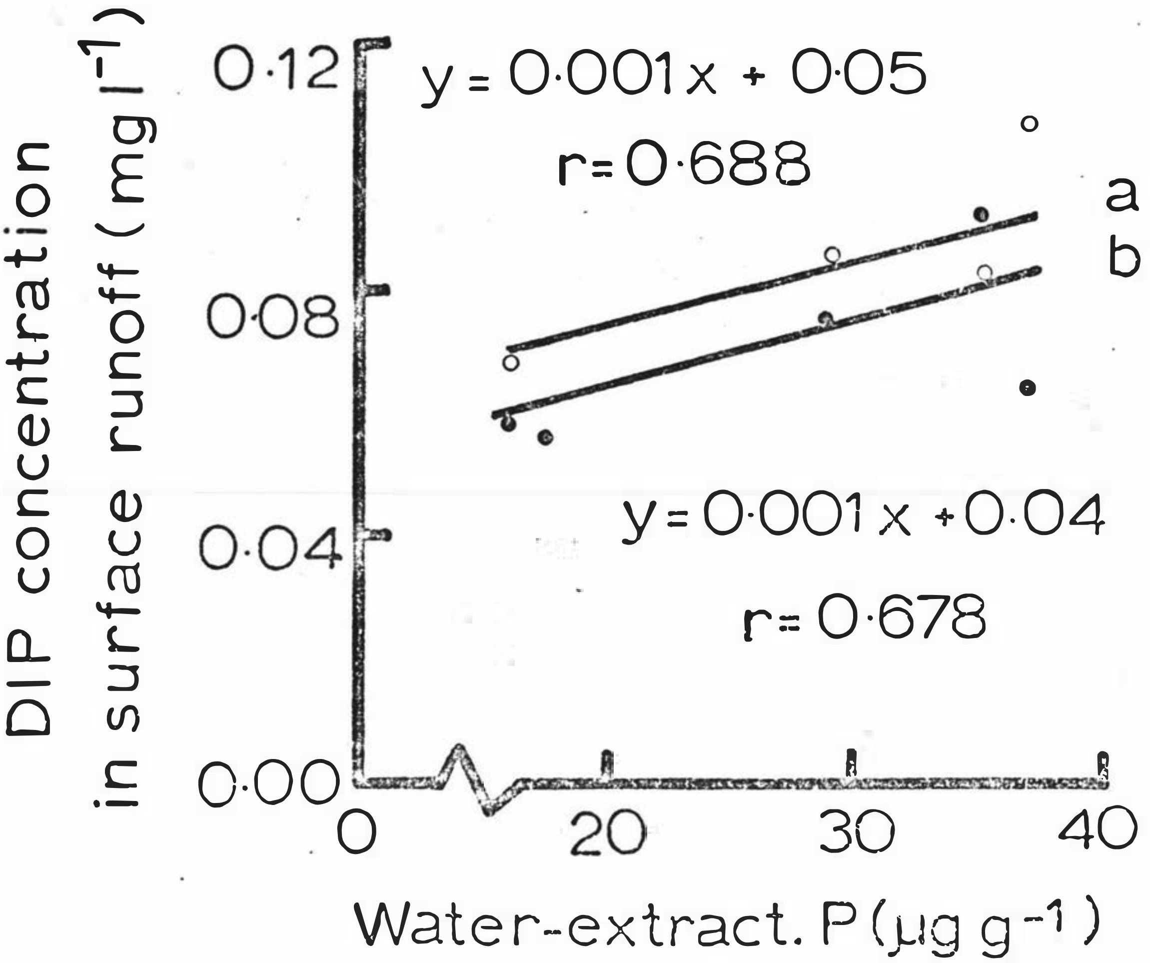

Fig. 4.15 Regression between mean DIP concentrations in the surface runoff component of selected storm flow and water-extractable P in soil from fertilized field sites in 1975. a = 22-ha catchment and b = 6-ha catchment.

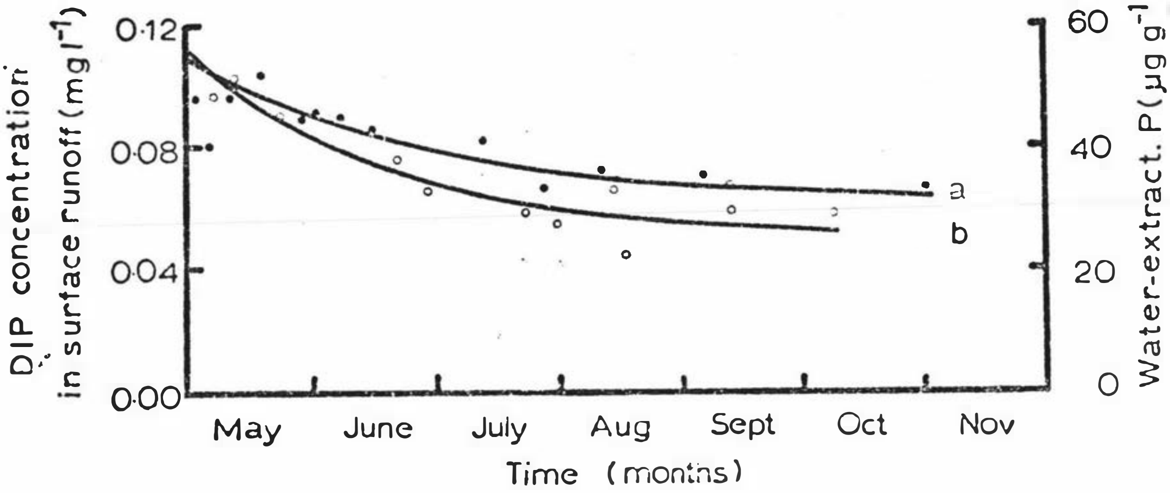

Fig. 4.16 Relationship between mean DIP concentrations in the surface runoff component of storm flow from the 6-ha catchment and water-extractable P in soil from fertilized field sites in the 6-ha catchment in 1976. a = storm flow and b = soil extraction values.

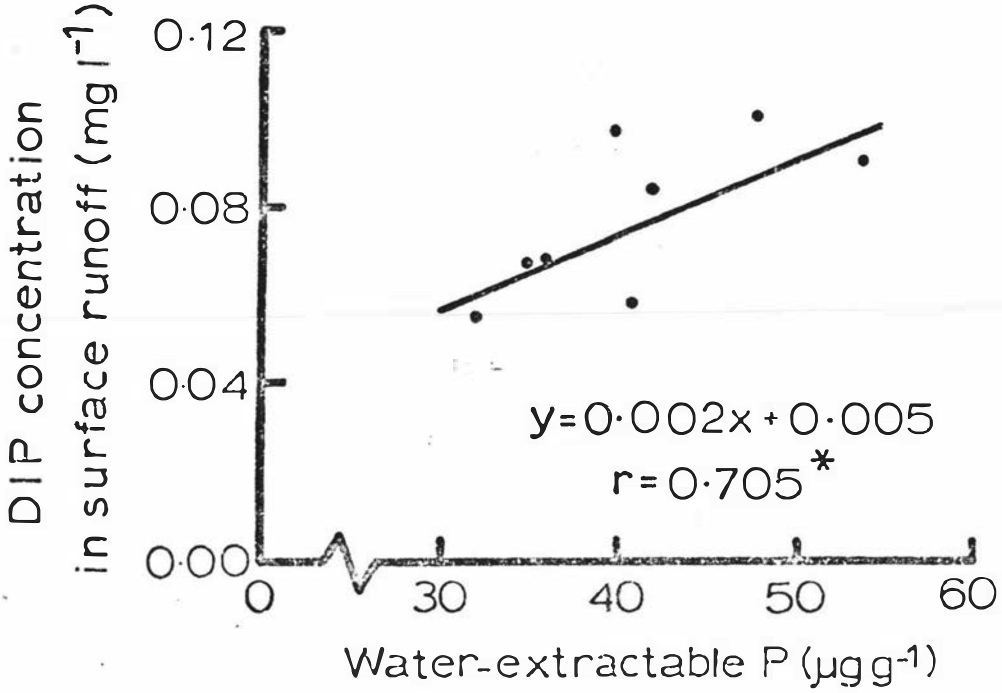

Fig. 4.17 Regression between mean DIP concentrations in the surface runoff component of storm flow from the 6-ha catchment and water-extractable P in soil from fertilized field sites in the 6-ha catchment in 1976.

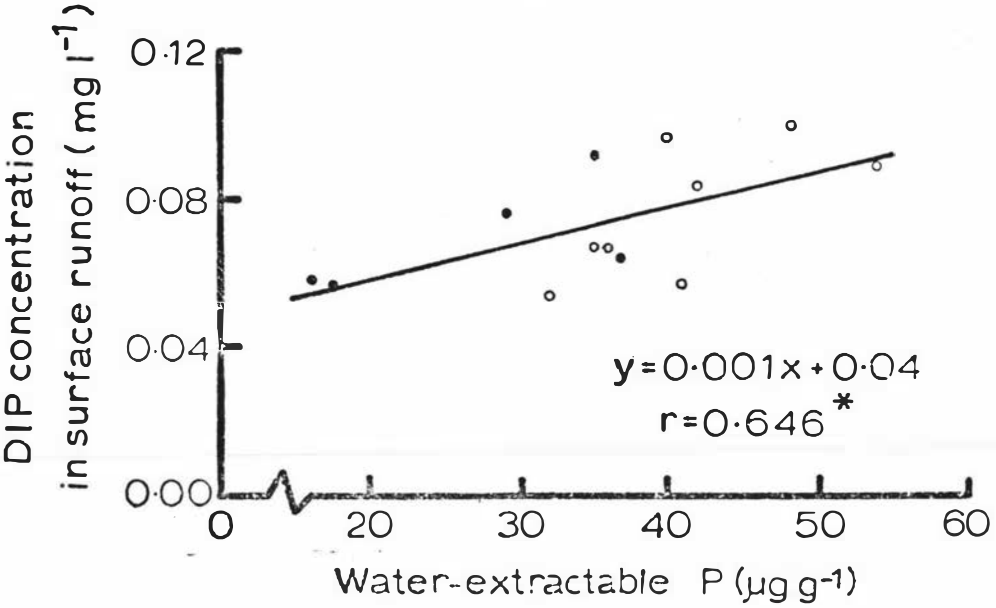

Fig. 4.18 Regression between mean DIP concentrations in the surface runoff component of storm flow and water-extractable P in soil from fertilized field sites in the 6-ha catchment combining 1975 and 1976 data.
Closed circles = 1975 data and open circles = 1976 data.

catchment in 1975 and 1976 combined, are summarized in Table 4.3.

Because it has already been shown that water-extractable P values for soils from the field sites and experimental pots following fertilizer P addition were closely related (Section 4.3.2.2), it was expected that data from the experimental pots could be useful in predicting mean DIP concentrations in surface runoff. It was found that the prediction potential given by regression analysis between data from both the surface 2-cm treatment pots and the mixed treatment pots, and mean DIP concentrations in surface runoff was similar to that given by data for the soils from the field sites. Fewer data were available from the surface 2-cm treatment pots because of the error in values obtained later in the year, caused by soil and fertilizer movement within the pots (discussed in Section 4.3.2.1).
The data available from the early part of the experiment however, gave a similar regression to that obtained with field site data (Fig. 4.19), although the correlation obtained ($r = 0.383$) was lower. The regression obtained with data from the mixed pot treatment (Fig. 4.20) gave a much higher correlation ($r = 0.934$). Because this treatment was not affected by fertilizer movement over the surface, due to homogeneous mixing of P with the soil, it had the highest potential for predicting mean DIP concentrations in the surface runoff component of stream flow.

4.4 General Discussion

The data obtained for fertilizer P addition to the catchments showed that fertilizer distribution was uneven between sites but approximately averaged the intended application rate of 375 kg ha^{-1}. For the three sites studied in 1975 and 1976, it was found that high values of water-

Table 4.3 Regression analyses between amounts of water-extractable P in soils and mean DIP concentrations in the surface runoff component of stream flow for the two catchments during the two years of study

Study	Regression analysis
1975	$y = 0.001x + 0.042$
(6-ha catchment)	$r = 0.678$
1975	$y = 0.001x + 0.051$
(22-ha catchment	$r = 0.688$
1976	$y = 0.002x + 0.005$
(6-ha catchment)	$r = 0.705$*
1975 and 1976	$y = 0.001x + 0.038$
(6-ha catchment)	$r = 0.646$*

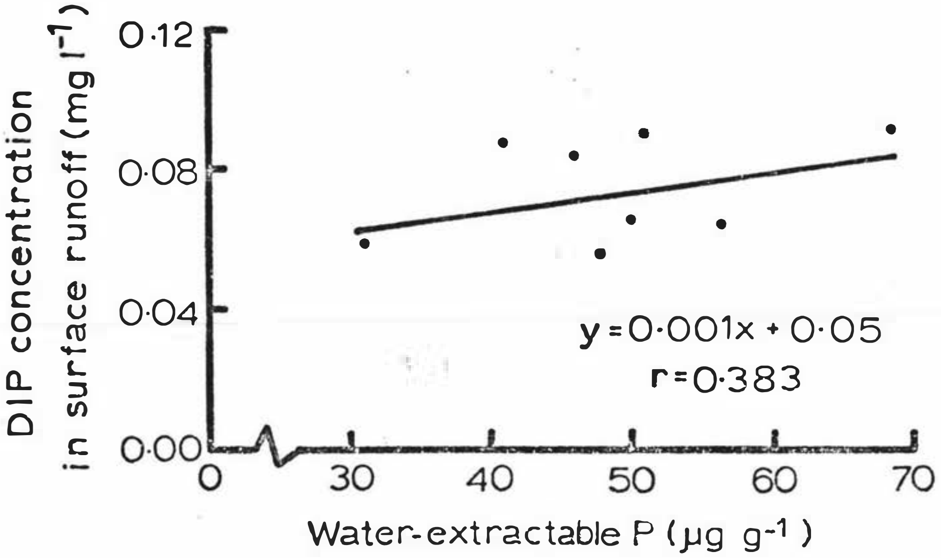

Fig. 4.19 Regression between mean DIP concentrations in the surface runoff component of storm flow from the 6-ha catchment in 1976 and water-extractable P in soil from surface 2-cm pot treatments.

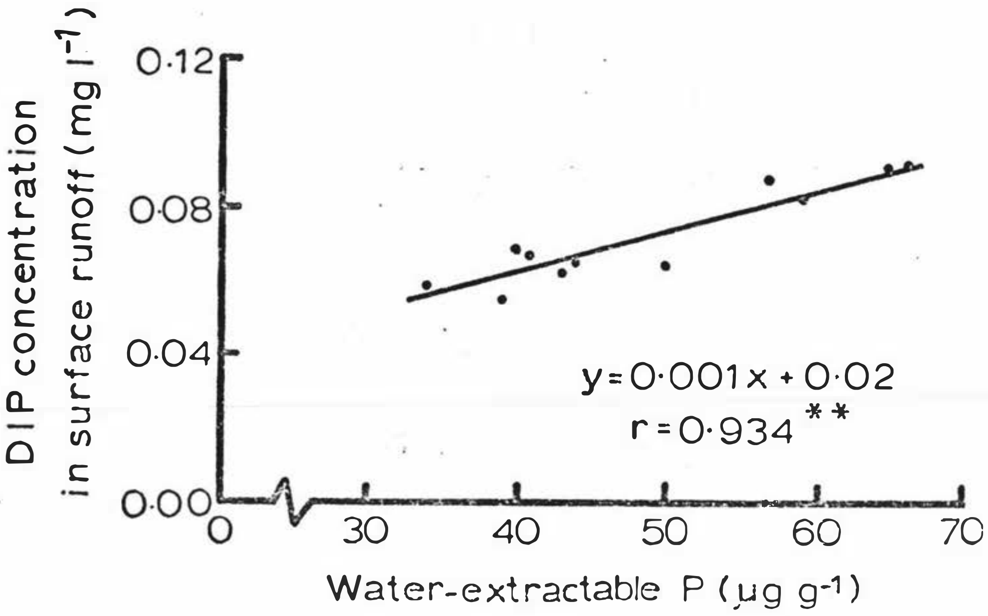

Fig. 4.20 Regression between mean DIP concentrations in the surface runoff component of storm flow from the 6-ha catchment in 1976 and water-extractable P in soil from the mixed pot treatments.

extractable P from soil were obtained immediately following fertilizer application, but that there was a rapid subsequent decrease in these values. A similar pattern of decline in water-extractable P in soil with time following P addition has been reported by other workers. McLaughlin et al. (1977) observed such a decline in solution P concentrations with time following P addition to Fe gel in a shaken-tube system. A similar pattern of decrease in solution (in NaCl) P over six days has been reported by Fox and Kamprath (1970) in P sorption studies. Ryden et al. (1977b) obtained essentially the same pattern of decline in water-extractable P for soils shaken in tubes and incubated in pots at field capacity, following P addition. In another study, Barrow (1974) observed a similar, although less well-defined pattern of decreasing plant uptake of P with time following fertilizer P addition to soils in pots. Despite widely differing experimental conditions, all of these studies have shown that following P addition to soil components or soils the high levels of readily-extractable P initially present decline rapidly to more stable, lower levels which tend towards equilibrium levels. This basic relationship has not previously been studied in a field situation and its significance to the potential movement of P from fertilized soils in runoff waters has not previously been demonstrated.

It has been shown (Williams, 1971) that the extremely rapid dissolution of monocalcium phosphate (MCP) present in superphosphate particles, following contact with moist soil is followed, within 24 hours, by the precipitation of anhydrous dicalcium phosphate (DCP). It is possible that the formation of DCP, with a lower P solubility, may partly explain the pattern of declining water-extractable P found in field soil. In a very recent study, Sharpley et al. (1978a) have shown that superphosphate released a high proportion of the P present in one water extraction whereas DCP released a lower but consistent amount of P in each of the seven sequential extractions made. Correspondingly, the proportionate loss of P as DIP in surface runoff was greater from the plot receiving superphosphate (4.6%) than from the plot receiving DCP (3.3%). The data reported in Chapter 5 indicate that changes in the nature of sorbed P with time may also be directly relevant to the field situation.

Despite some variation in the values obtained in this study for water-extractable P in soils following different P addition rates to different sites, the proportional rate of decrease (relative to the first extraction value following P addition) was similar for all sites. The data obtained in both 1975 and 1976 could be described by a single curve which was essentially common to all P addition rates to soil. This common proportional decline curve is supported by the findings of Ryden et al. (1977b) and the suggestions of Rajan (1976) and Overman and Chu (1977a) who have reported that the rate of immobilization of P in soils following P addition is directly proportional to the P addition rate to soil, or the P concentration in the soil solution. This supports the suggestion that laboratory studies to examine the mechanisms and factors influencing the rates of P immobilization have implications to the field situation.

It has been shown in this study that the amounts of water-extractable P in soils are reduced, following a storm event, apparently due to the leaching of DIP from surface soil in surface runoff water. The recovery of water-extractable P values within a period of 7 to 10 days has been observed. Experimental data have suggested that the mineralization of particulate OP may provide for relatively stable levels of water-extractable

P in soils. Dalal (1976) has indicated that OP may be more important to the P status of soils than is often recognised. This view is supported by the suggestion of Saunders and Metson (1971) that conversion of soil OP to IP by microbial action in spring may balance increased plant uptake of IP from the soil solution. The possibility that such conversion may influence both the amounts of P forms in soils and DIP concentrations in runoff waters is suggested by the results obtained in the present study.

Data obtained from a series of pots involving mixed soil and fertilizer treatments have shown that it is possible to replicate the field situation reliably with minimal sampling. For three treatments (a surface application to a 1-cm and a 2-cm depth of soil, and a mixed application through 2 cm of soil), a similar pattern of initially high values of water-extractable P followed by a rapid decline in the first 1 to 3 weeks and a subsequent slower decline, was observed. This pattern was essentially the same as that observed with the field soil samples. For all three treatments in the pot experiment and for the field soils, a plot of relative water-extractable P values, expressed in relation to the initial value, as a function of time, fell on essentially the same curve. The fact that this was common to a range of concentrations supports the suggestion that the extent of P immobilization or shift from a water-extractable form is essentially proportional to the amount of P added. Several workers (Fox and Kamprath, 1970; Ryden et al., 1977b; McLaughlin et al., 1977) have described this decline of readily-extractable P in terms of changes in the nature of sorbed P. This suggests that studies of the mechanisms and rates of P immobilization involving sorption may be valuable in modelling the fate of P added to field soils.

Data obtained from the division of a 2-cm depth of soil into two 1-cm layers, with fertilizer being applied to the surface of the upper 1cm, revealed that water-extractable P did not move down into the lower 1-cm layer, even after 9 months in the field. This result suggests that there is very little movement from the upper 1-cm of a disturbed soil following fertilizer P application. It has recently been shown, (Scotter et al., 1978), however, that P can move substantial distances through a soil where continuous vertical pores of appropriate diameter are present. It has also recently been shown that close correlations can be obtained between 0.1M NaCl-extractable P in the top 5 cm of established pasture soil and mean DIP concentrations in surface runoff from pasture (Sharpley et al., 1977). Despite the findings of Scotter et al. (1978) that P may be distributed below the upper 1-cm of soil, Sharpley et al. (1978b) have observed that the correlations obtained with 5-cm depth soil samples were improved when a 1-cm sampling depth was used. Further to this, sampling from the upper 1-cm depth only led to a common linear relationship between soil water-extractable P and mean DIP concentrations in surface runoff from both drained or undrained and fertilized or unfertilized soils. It seems probable that the upper 1-cm depth of soil is most active in influencing DIP transport in surface runoff in fertilized soils and may be the most useful depth to sample for prediction studies.

The data obtained in this study in 1975 indicated that water-extractable P values for soil and mean DIP concentrations in surface runoff followed a similar pattern. The initial high values after fertilizer application were followed by a more gradual decline later in the year.

Although only a small number of data points were available for soil samples which could be paired with closely-following storm events, a linear relationship was suggested. Data obtained in 1976 extended this relationship and confirmed a linear relationship between water-extractable P in soil samples from a 2-cm depth and mean DIP concentrations in the surface-runoff component of successive storm events. The fact that similar linear relationships have been observed by other workers (Römkens and Nelson, 1974; Sharpley et al., 1977, 1978b) suggests that extraction procedures employing water or neutral salt solutions may be useful to predict the movement of DIP in surface runoff from differing situations. The similarity of regression lines obtained between water-extractable P in both field soils and soils from experimental pots, and mean DIP concentrations in surface runoff suggest that pot experiments involving fertilizer P addition to soils may be useful for predicting the potential losses of P from catchments where soil types are similar. The possibility of modelling the decline in water-extractable P in soil following P addition appears useful for such predictive purposes.

CHAPTER 5

THE RATE AND EXTENT OF PHOSPHORUS REACTIONS IN SOILS

5.1 Introduction

The data presented and discussed in Chapter 4 indicate that the amounts of water-extractable P in soils of the catchments during one year following fertilizer P addition, were closely correlated with the mean DIP concentrations measured in the surface runoff component of storm flow from the catchments. Extraction procedures using water or dilute salt solutions have been used by other workers to predict concentrations of P forms in runoff water (Ryden et al., 1972a, b; Romkens and Nelson, 1974; Sharpley et al., 1977, 1978b) and also to estimate plant-available P (Bingham, 1949; Hagin et al., 1963; van der Paauw, 1971). Although good correlations have been obtained between the amounts of P extracted from soil and both the P concentrations in runoff types and plant uptake of P, these studies have not always involved the same extraction procedures. The amounts of P extracted are influenced by factors such as the soil: solution ratio and the time of shaking (Hope and Syers, 1976). The substitution of distilled water for dilute salt solutions, e.g., 0.1M NaCl or 0.01M $CaCl_2$, also influences the amounts of P extracted (Ryden and Syers, 1977a). The lack of a non-empirical definition of the labile pool of extractable P has made comparisons between the above studies and the data obtained in this study and discussed in Chapter 4 difficult.

Labile P in soils has been defined non-empirically (Ryden and Syers, 1977a) as being equivalent to P which is more-physically sorbed on surfaces in soils, totally isotopically exchangeable during 30 min, and readily plant-available. These workers suggested that the amounts of more-physically sorbed P corresponded closely to the amounts of P extracted by two successive 1-hour water extractions at a soil:solution ratio of 1:40. It was also suggested (Ryden et al., 1976) that the amount of water-extractable P as determined above may be a good indicator of directly-available P for plants which is independent of soil type. This suggestion has recently been supported in a glasshouse study by Luscombe (1976) who obtained close correlations between water-extractable P in soils and plant uptake of P. In attempting to establish relationships between water-extractable P in soils and mean DIP concentrations in runoff types or plant uptake of P from soils, it would be useful to adopt an extraction procedure developed from an understanding of the nature of the pool of labile P in soil.

It has been shown (Chapter 4) that the decline in water-extractable soil P, after fertilizer P addition in the field, follows a characteristic pattern of a rapid initial decline followed by a more gradual decline approaching equilibrium. This pattern of declining water-extractable P is consistent with observations from other studies (Hsu, 1964; Probert and Larsen, 1972; Rajan and Fox, 1972; Barrow, 1974). Although several models have been proposed to describe this decline (Barrow, 1974; Mansell et al., 1977; Overman and Chu, 1977a,b,c) such models have been mathematical and have incorporated arbitrary factors to describe the decline in monitored P forms in soils. In contrast, it has been suggested by Ryden et al. (1977a) that P sorption in soils can be described by three Langmuir-type equations, thus enabling estimates of the sorption maxima and binding energy constants to be made. Other workers have challenged the use of the Langmuir equation for this purpose (Bowden et al., 1977; Veith and Sposito, 1977), claiming that the conditions of P sorption in soils differ so markedly from the initial Langmuir assumptions that no significance can be attached to any values derived from the equations.

Consequently, it is of interest to test the ability of a model incorporating sorption parameters derived using the approach of Ryden et al. (1977a) to predict actual experimental data.

5.2 Materials and Methods

5.2.1 Comparison of extraction techniques to estimate labile phosphorus in soils

Nine soils with differing fertilizer histories and P retention characteristics were chosen to relate the P extraction technique used in the field study (Chapter 4) to that proposed by Ryden and Syers (1977a). Soil samples (1g) were shaken for 17 hours in 400 ml of distilled water and the extracted P measured as described previously (Section 4.2). Concurrently, soil samples (1g) were shaken with 40ml of distilled water for 1 hour, centrifuged, and extracted P determined in the supernatant solution. Following addition of a further 40 ml of distilled water the sample was shaken again for 1 hour and extracted P determined. Total extracted P was expressed as the sum of P removed in each of the two extractions. Following a correlation-regression analysis of the data obtained from the two procedures, the sequential 1-hour extraction procedure was adopted for all further studies of water-extractable P in soils.

5.2.2 Soils used in subsequent laboratory studies

Three surface soils with contrasting P retention characteristics were chosen for this part of the study. The soils were:

(1) Pahiatua soil from the study catchments (and described in Appendix 1). The soil is an Inceptisol, probably a Eutrochrept intergrading to a Dystrochrept.

(2) Dannevirke soil a silt loam taken from a minimally-disturbed site. The soil is an Andic Dystrochrept.

(3) Egmont brown soil a silt loam taken from an improved pasture site. The soil is an Entic Dystrandept.

Some of the more important background data for the soils are presented in Table 5.1. Soil pH was measured using a combination electrode following the mixing of 10g soil with 25 ml of distilled water and overnight equilibration. Retention of P was determined by shaking 5g of soil for 16 hours in 25 ml of a P solution containing 1000 mg P l^{-1} in a sodium acetate-acetic acid solution buffered at pH 4.65. Retention of P (%) was calculated by difference between P added and P removed from solution. Bicarbonate-extractable P (Olsen et al., 1954) was measured following shaking of soil (1g) for 30 min in 20 ml of $\overset{0\cdot 5\,M}{0.1M}$ $NaHCO_3$ solution buffered at pH 8.5 and analysis of the supernatant solution following centrifugation, filtration, and neutralization. Water-extractable P was calculated following two sequential 1-hour shakes (described in Section 5.2.1).

5.2.3 Preliminary laboratory studies of the decline in water-extractable phosphorus following phosphorus addition to one soil

As a preliminary experiment, the effect of differing P addition rates to soil on the decline in water-extractable P with time following addition was examined using the Pahiatua soil. Fertilizer P (sieved

Table 5.1 Background data for three soils used in laboratory studies

Parameter	Soil		
	Pahiatua intergrade	Dannevirke silt loam	Egmont brown loam
Sampling depth (cm)	0-15	0-15	0-15
Fertilizer history	Slight	Nil	Moderate
pH	5.67	5.76	5.45
P retention %	23	43	81
Olsen-extractable P (μg g^{-1})	11.5	12.0	22.0
Water-extractable P (μg g^{-1})	4.5	2.0	2.5

superphosphate, <250 µm) was thoroughly mixed with sieved (<2 mm) air-dried soil. Plastic pots, 10 cm in diameter and 6 cm deep, were each filled with 200g of the fertilized soil. The superphosphate used had a TP content (O'Connor and Syers, 1975) of 9.0% and a water-soluble P content (Fertilizer Regulations, 1969) of 2.2%. The rates of P addition were 0.45, 1.35, and 2.70g of superphosphate per pot (200g soil) which were equivalent to 224, 672, and 1,344 kg of superphosphate ha^{-1}, respectively, assuming interaction with the upper 1cm of soil (discussed in Section 4.3.2.1). Each pot was moistened to field capacity (0.40g of water g^{-1} soil) and incubated at 10°C. Duplicate samples were taken at two- and three-day intervals for 17 days to monitor water-extractable P.

5.2.4 Laboratory and glasshouse studies of the decline in water-extractable and plant-available phosphorus in contrasting soils following phosphorus addition

Following the preliminary study, a further experiment was established to characterise the decline in water-extractable P in more detail over a longer time period and to assess changes in the plant-availability of P. The two soils used in this study (Pahiatua and Egmont) were low and high P sorbing soils, respectively (Table 5.1). Superphosphate (< 250 µm) was added as previously described at rates of 0.0, 0.67, and 1.35g per pot (200g soil). To investigate the effect of a slow-release P source on the amounts of water-extractable P in soils, Christmas Island "A-grade" rock phosphate (< 250 µm) was added to the soils in separate pots at a TP addition rate equivalent to 0.67g of superphosphate per pot. Although the TP content of this rock phosphate was 16%, water-soluble P was only 0.001%. Triplicate samples were taken 0, 2, 7, 13, 27, 42, 65, and 100 days after P addition and analysed for water-extractable P.

To measure changes in the plant availability of added P in contrasting soils with time following fertilizer P addition, the technique of Stanford and De Ment (1957) was used on triplicate soil samples taken on the above sampling dates from those treatments receiving 0.67g superphosphate per 200 g soil or equivalent amounts of rock phosphate (based on TP addition). This technique facilitated very rapid plant uptake of P to occur at varying times following P addition to soils. Small plastic pots, 10cm in diameter and 6cm deep, with their bases removed, were placed within similar intact pots and the resulting pair partly filled with 200g of washed river sand. Approximately 20 seeds of perennial rye-grass (Lolium perenne) were placed in each pot which was regularly watered with a complete, but minus P nutrient solution (Middleton and Toxopeus, 1973). Following a 50-day growth period, 20g (air-dry equivalent of incubated pot soil was spread evenly on the bottom of a new pot. The inner pot of sand and grass was lifted from its enclosing pot and the exposed root mat placed in contact with the soil layer in the new pot. Watering with P-deficient nutrient solution continued and herbage cuts were taken after 50 days. Plants were germinated to allow 50 days of growth before placement on the soils at the sampling intervals indicated above. Herbage was oven-dried (36 hours at 60°C), weighed, ground, and analysed for TP (Murphy and Riley, 1962) following digestion with nitric-perchloric acid (Jackson, 1968). Relationships between plant-available P (plant uptake) and soil P (water-extractable or bicarbonate-extractable) were subsequently established using linear regression analysis.

5.2.5 Comparisons between solid and liquid additions of phosphorus to soils

To compare liquid and solid P additions to soil, superphosphate was dissolved and the P solution obtained was used, at an appropriate concentration, to moisten the soil to field capacity. Superphosphate (sieved, <250 μm) was also added to soil in another pot at the rate of 0.67g per pot (200g soil). Consequently, each soil received 75 μg P g^{-1} soil of water-soluble P but the amount of solid P added was 302 μg TP g^{-1} soil. Both soils were sampled in triplicate following incubation for up to 60 days and water-extractable P determined as described in Section 5.2.1.

5.2.6 Detailed studies of the decline in water-extractable phosphorus in soils

In the previous experiments, differences were observed between the rate and extent of decline in water-extractable P in the Pahiatua and Egmont soils. Because it seemed possible that these differences could be related to the P sorption (Langmuir) constants, further incubation studies were conducted using the Pahiatua, Dannevirke, and Egmont soils. All P additions were made using liquid P which improved the eveness of mixing through the soil and reduced sampling variability. Three P addition rates were used (75, 150, and 300 μg P g^{-1} soil) with the Pahiatua soil and two P addition rates were used (75 and 150 μg P g^{-1}) with the Dannevirke and Egmont soils. The soils were moistened to field capacity (0.40, 0.45, and 0.50g g^{-1} soil for the Pahiatua, Dannevirke, and Egmont soils, respectively) with solutions of appropriate P concentrations. Samples were taken in triplicate at increasing time intervals for up to 100 days following incubation and water-extractable P determined (described in Section 5.2.1).

Equilibrium P sorption isotherms were obtained in order to calculate values for the P sorption constants. Samples (1g) of soil were shaken with 40ml of 10^{-1} M NaCl containing different amounts of added P, as NaH_2PO_4, in 50-ml polycarbonate centrifuge tubes on an end-over-end shaker at 23°C. The appropriate amounts of P were added in 5-ml aliquots at 0, 24, 48, and 72 hours after commencing to shake 1-g samples of soil with 35 ml of 0.1M NaCl. Shaking was continued for 144 hours. Consequently, the total shaking time for each system was the same but the times of contact between soil and added P were, respectively, 144, 120, 96 and 72 hours. After shaking, the suspensions were centrifuged (13,000 r.p.m. at 23°C for 5 min), filtered (<0.45 μm), and analysed for inorganic P (Murphy and Riley, 1962). Equilibrium solution P concentration was estimated by a graphical procedure (Ryden and Syers, 1975).

Native sorbed P was determined at four time intervals by a method similar to that described above. Carrier-free ^{32}P was added to soils in shaken systems (Ryden et al., 1977a) and native exchangeable P for each time of contact was determined by isotope dilution theory. Equilibrium values were estimated graphically (Ryden and Syers, 1975). The value obtained for each soil was added to all values of added P sorbed to give the values of "total sorbed P" which were used to prepare equilibrium P sorption isotherms.

The sorption isotherms were evaluated using the rearranged form of the Langmuir equation:

$$\frac{1}{x} = \frac{1}{Kbc} + \frac{1}{b}$$

where x = amount of P sorbed (total sorbed P), c = solution P concentration (equilibrium value), b = sorption maximum, and K = a constant related to the sorption energy. A procedure for resolving compound isotherms into their separate components, as proposed by Ryden et al. (1977a), was adopted.

It was possible to determine equilibrium values of K and b for each of three distinct sorption regions for each of the three soils studied. The symbols K and b have been used in preference to K_1 and K_2, respectively, (Chapter 1) to avoid confusion.

The derivation of values for K and b for each of three sorption regions allowed the development of a model to describe P sorption from solution by soils and the redistribution of sorbed P on sorbing surfaces. The model assumes that solution P tends towards an equilibrium with P being sorbed concurrently in three regions. The equilibrium relationship for each region may be considered as a balance between a forward reaction (P sorption at vacant sites in that region) and a reverse reaction (P desorption from occupied sites in that region). There are several assumptions implicit in the operation of this model:

(1) There is a finite number of P sorption sites in each region.

(2) Each site within a region is equivalent to other potential reaction sites.

(3) At a particular solution P concentration, some sites in each region will be occupied (one phoshate ion per site) and the remaining vacant sites constitute the potential reaction sites for further forward reaction.

(4) In each region the rate of forward reaction is controlled by solution P concentration, a rate factor or constant (KF), and the number of vacant sites, this may be written as:

$$\text{Solution P} \xrightarrow{\text{KF x Soln [P] x vacant sites}} \text{Sorbed P}$$

(5) In each region the rate of the reverse reaction is controlled by a rate factor or constant (KR) and the number of occupied

sites; this may be written as:

$$\text{Sorbed P} \xrightarrow{\text{KR} \quad \text{x} \quad \text{occupied sites}} \text{Solution P}$$

(6) The equilibrium constant of reaction in each region, for the balance between forward and reverse reactions within each region, is numerically equal to the ratio between the forward rate constant (KF) and the reverse rate constant (KR), and to the value of K obtained from the linear form of the Langmuir equation (Graham, 1953; Shapiro and Fried, 1959), i.e.,

$$K_I = KF1/KR1$$

$$K_{II} = KF2/KR2$$

$$\text{and} \quad K_{III} = KF3/KR3$$

Although the ratio of the rate constants for the sorption and desorption reactions were equated to the experimentally-derived Langmuir constants, the magnitude of these constants was estimated to produce modelled curves of similar shapes to those obtained for the decline in water-extractable P in incubation experiments.

The following rate reactions were incorporated into an overall kinetic model of P sorption in soils:

Region I
Sorption = KF1 x solution [P] x time x vacant sites
Desorption = KR1 x time x occupied sites

Region II
Sorption = KF2 x solution [P] x time x vacant sites
Desorption = KR2 x time x occupied sites

Region III
Sorption = KF3 x solution [P] x time x vacant sites
Desorption = KR3 x time x occupied sites

The overall model was operated as a Continuous Systems Modelling Programme (C.S.M.P) and executed on a Burroughs B6700 computer. The time interval for each step was made very small (0.005 day) and the initial soil solution P concentration, entered at time = 0 (beginning of incubation), was calculated from the fertilizer P addition rate. The sorption model was allowed to run for 60 days, with print-out every two days showing the amounts of P sorbed in regions I, II, and III, and soil solution P concentration. To determined water-extractable P at times during the incubation, e.g., after 10, 30, or 60 days, the sorption programme was stopped at that time, soil:solution ratio adjusted to 1:40, solution P concentration equated to zero, and the programme run for 1 hour. After 1 hour, the programme was stopped, soil solution P returned to zero, and the programme run for a further 1 hour. The final amounts of P present in 40 ml water after each 1-hour equilibration were added together and expressed as μg P g^{-1} soil extracted. All rate constants during the extraction procedure were increased by a factor of 10. This was done because it is known that the rate at which desorption proceeds increases at wider soil:solution ratios (Ryden and Syers, 1977b) and also to achieve a desorption equilibrium within 1 hour, as demonstrated by Gillingham (1978). It was also considered that reactions would proceed faster in a shaken system than in incubated soil where ionic movement between solution and solid phases occurs by diffusion only. Different fertilizer P addition rates were simply modelled by an appropriate increase in the initial soil:solution concentration at the beginning of the incubation.

5.3 Results and Discussion

5.3.1 Comparison of extraction techniques

A close, linear relationship was obtained between the amounts of P extracted from soils using the two water-extraction procedures (Fig. 5.1). Shaking for 17 hours at a soil:solution ratio of 1:400, however, extracted approximately 50% more P from the same soil than did 2 x 1-hour sequential extractions at a soil:solution ratio of 1:40. This relationship enabled the water-extraction data obtained in laboratory studies with incubated soil to be related to water-extraction data (one extraction 17 hours and 1:400) obtained from field studies in previous years. Also, the use of the 2 x 1-hour water extraction procedure would allow comparison of results with those of other workers (Luscombe, 1976; Ryden et al., 1976; Ryden and Syers, 1977a) who have defined the amount of P extracted theoretically. The 2 x 1-hour sequential water-extraction procedure was subsequently used in this study.

5.3.2 Decline in water-extractable phosphorus following phosphorus addition to one soil

Water-extractable P in soil following fertilizer P addition and incubation at field capacity, followed a similar pattern of decline for three different P addition rates (Fig. 5.2). The three values obtained for P extracted in the first extraction (beginning of incubation) were proportional to the three fertilizer P addition rates. Also, the values on each curve at subsequent extraction times were in the same ratio to each other as the initial extraction values and, thus, also to the P addition rates. This relationship is shown in Fig. 5.3 where each

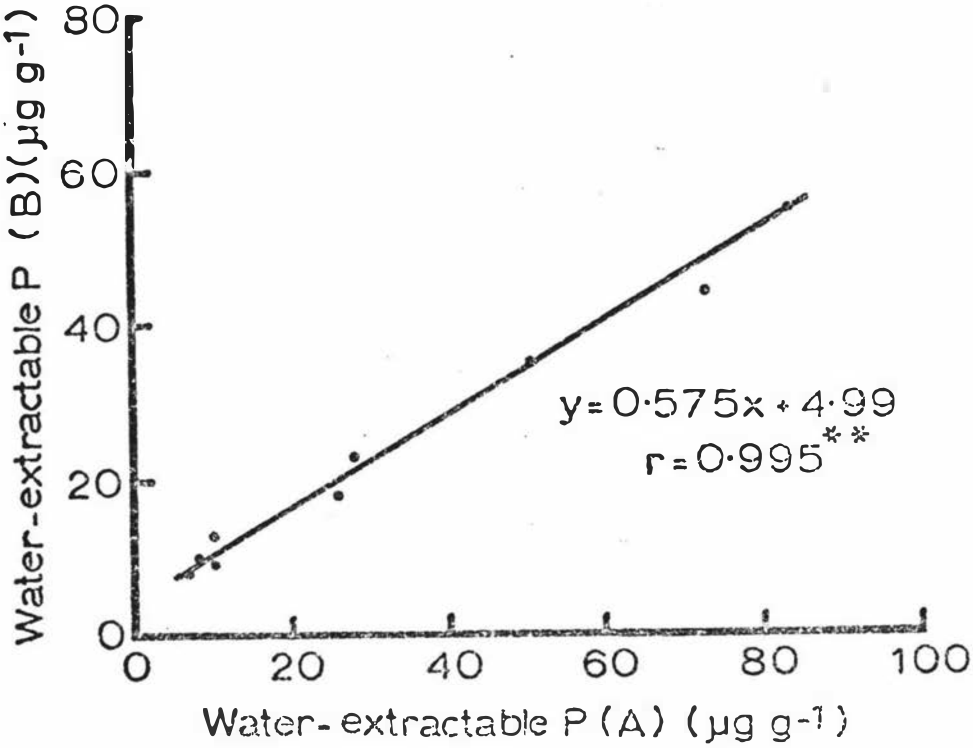

Fig. 5.1 Regression between water-extractable P values obtained in two sequential water extractions (each of 1 hour duration at a soil:solution ratio of 1:40) (B) and in one water extraction (17 hours duration and at a soil:solution ratio of 1:400) (A).

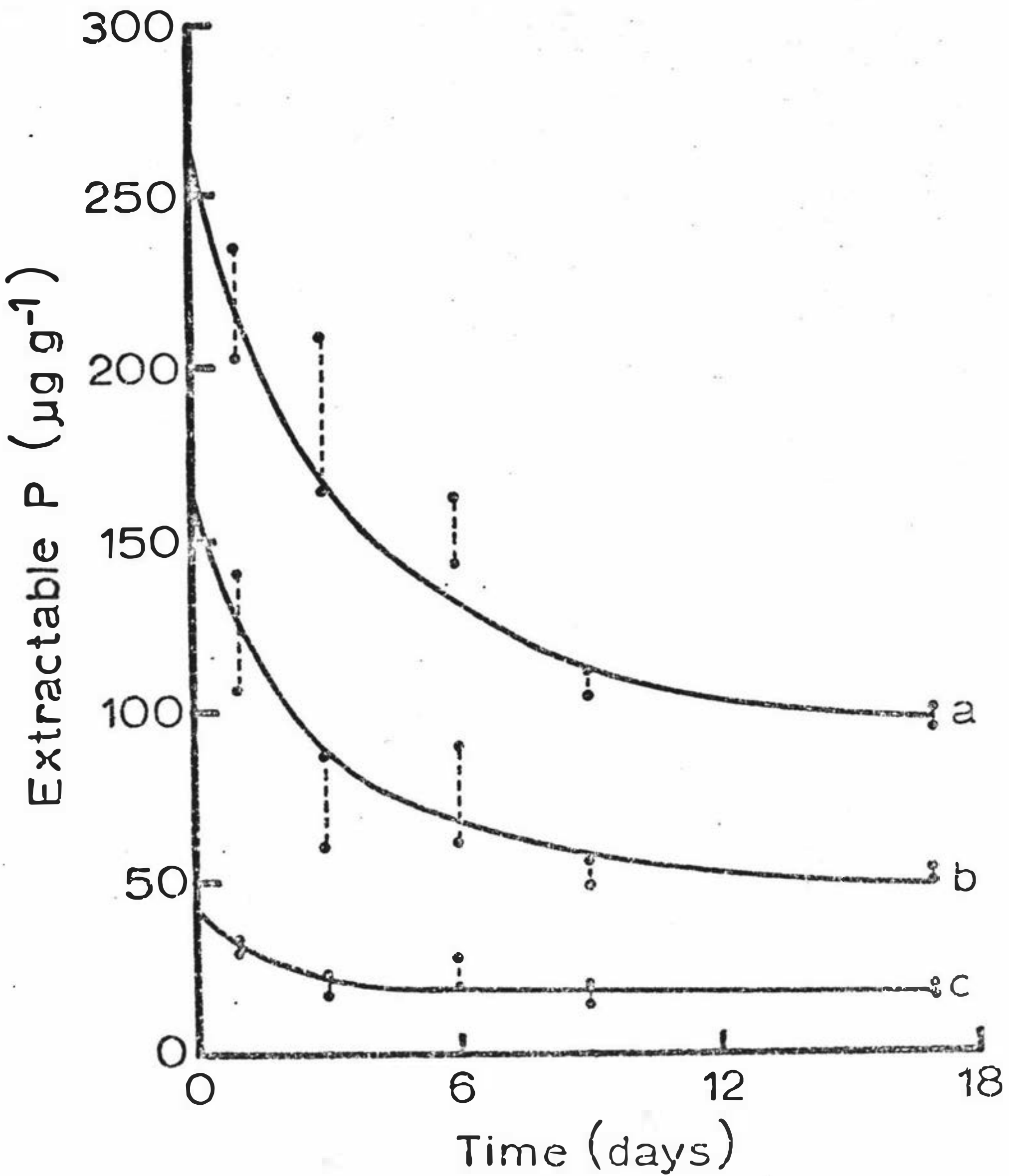

Fig. 5.2 Decline in water-extractable P (two 1-hour extractions at a soil:solution ratio of 1:40) with time from soil incubated in pots following fertilizer P addition.
a = 300 μg P g^{-1}, b = 150 μg P g^{-1},
c = 50 μg P g^{-1}.

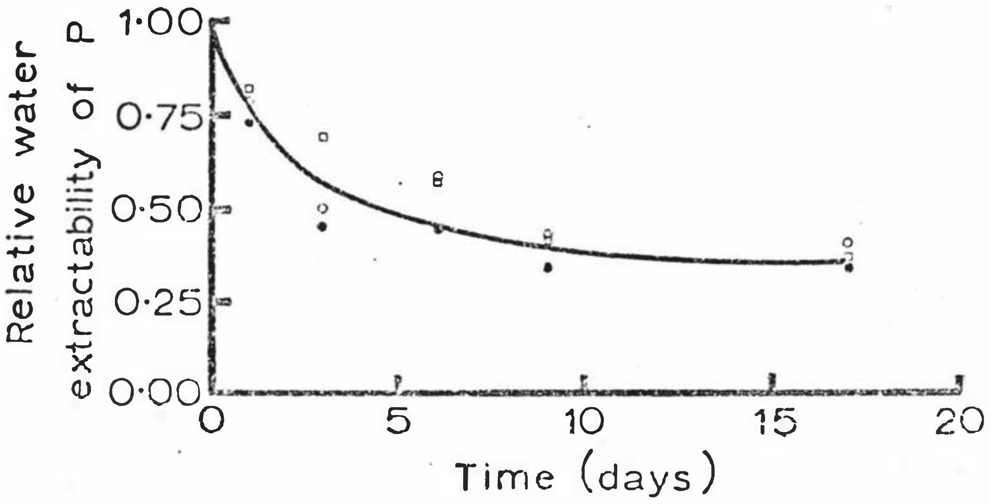

Fig. 5.3 Relative water extractability of P, expressed as a proportion of the initial extraction value, with time following P addition at three rates. Open circles = 50 μg P g^{-1}, closed circles = 150 μg P g^{-1}, and open squares = 300 μg P g^{-1}.

successive extraction value is plotted as a proportion of the initial extraction value, i.e., a proportional decline curve of water-extractable P for each addition rate. It is apparent from Fig. 5.3 that the proportional decline curve is common to all three rates of P addition to soils. Ryden et al. (1976) suggested that a similar relationship was common to all soils but did not study the effect of different fertilizer P addition rates to soils. This preliminary study suggests that both the pattern of decline in water-extractable P and the influence of P addition rates on this decline require more detailed examination.

The decline in water-extractable P shown in Fig. 5.2 is essentially similar to that shown in Fig. 4.3, 4.5, 4.7, 4.10, and 4.14 which describe the declining water-extractable P values obtained for soils of fertilized catchments and field pots. It is also similar to the pattern observed for mean DIP concentrations in the surface runoff component of storm flows (Fig. 4.14 and 4.16). A more detailed study of the declining water-extractable P pattern shown in Fig. 5.2, over a longer time period may provide verification of this relationship and allow tne data obtained from laboratory studies to be used in describing field situations.

5.3.3 Decline in water-extractable and plant-available phosphorus in contrasting soils following phosphorus addition

The decline in water-extractable P (observed in Section 5.3.2) is characterised more accurately over a longer time period (up to 65 days) for a low P-sorbing soil (Pahiatua) and a high P-sorbing soil (Egmont) in this section.

5.3.3.1 Characteristics of the decline in water-extractable phosphorus in soils of contrasting phosphorus sorption properties

The relationship $y = 0.575x + 5.0$, derived by regression analysis from the data shown in Fig. 5.1, was used to express water-extractable P values from the laboratory study using Pahiatua soil on a similar basis to data obtained in previous years in the field. The decline in water-extractable P obtained from the field pot study and from field soils during 1975 and 1976, following superphosphate P addition to the catchments, are shown in Fig. 5.4. Despite differences in values obtained, because of different fertilizer P application rates, the pattern of declining water-extractable P following P addition was essentially the same. This result has two important implications. Firstly, the observation made from Fig. 5.2 and 5.3, that differing amounts of P added to soil affect only the amounts of water-extractable P subsequently obtained but not the fundamental pattern of decline in water-extractable P, is supported. Secondly, the similarities of the data validate the use of laboratory studies with incubated soils to examine the reactions in soils following fertilizer P addition in the field.

Close correlations were also obtained between water-extractable P values from field soils and mean DIP concentrations in the surface runoff component of storm flows in 1975 and 1976 (discussed in Chapter 4). The relationship shown in Fig. 5.4 suggests that data obtained from laboratory studies with representative field soils may also be useful to predict the potential movement of DIP in surface runoff water.

Using superphosphate as a source of P, it was found that there was a large difference between the Pahiatua and Egmont soils in the initial rates of decline in water-extractable P and also in the final amounts of water-extractable P remaining in the soil after 65 days. The data presented in Fig. 5.5 show that following P addition to Egmont soil,

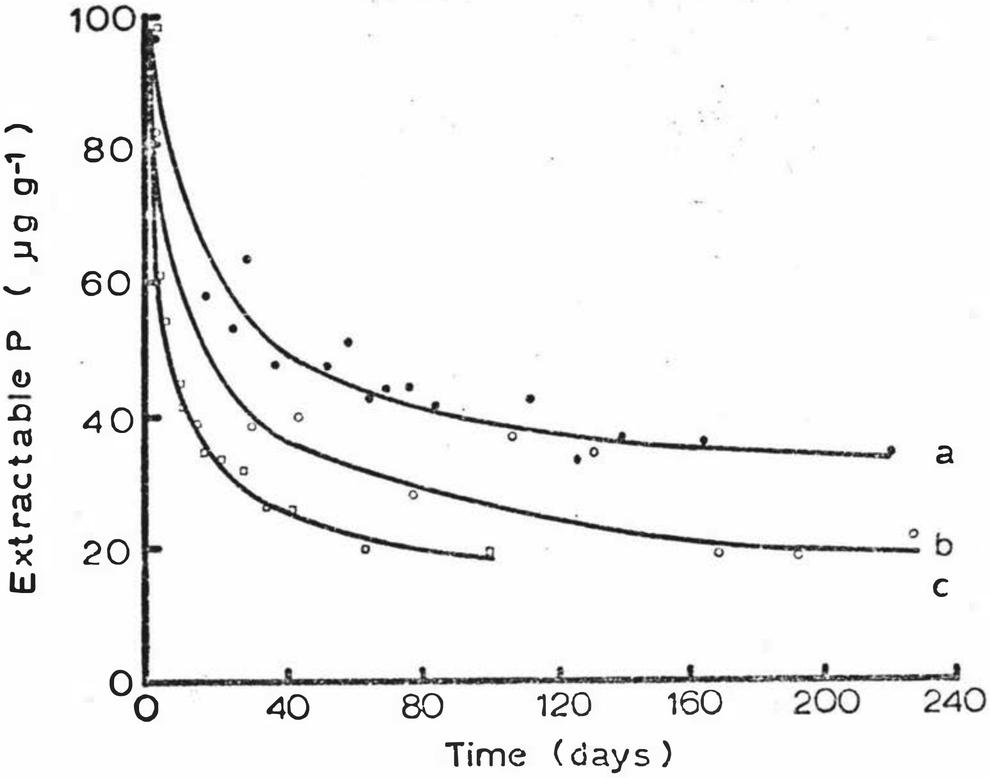

Fig. 5.4 Decline in water-extractable P in catchment field soils and in incubation pots of the same soil following fertilizer P addition.

a = catchment sites (1976 average of three sites),

b = catchment sites (1975 average of three sites),

and c = incubation pots.

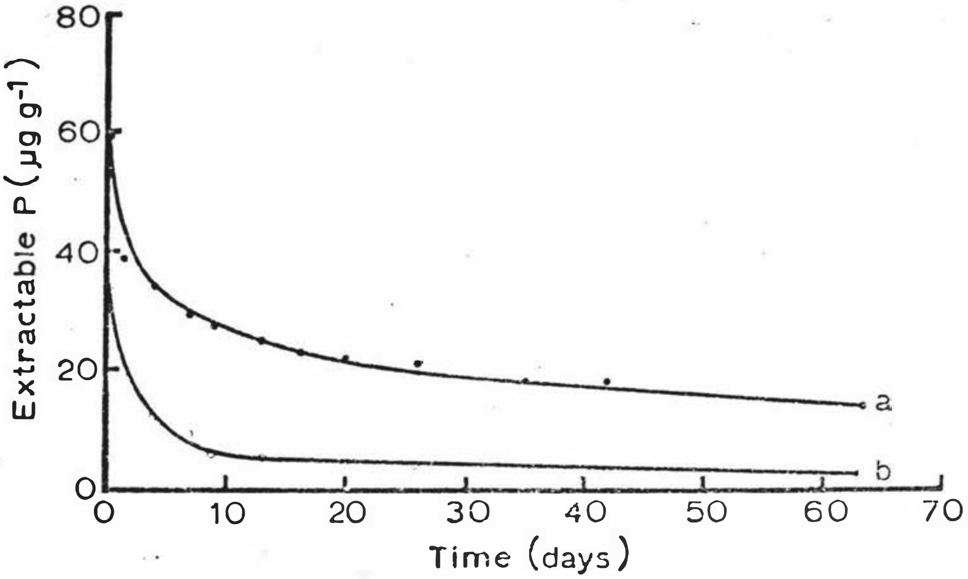

Fig. 5.5 Decline in water-extractable P from Pahiatua and Egmont soils with time following incubation and fertilizer P addition.

a = Pahiatua soil and b = Egmont soil.

water-extractable P declined rapidly, to a very low value after approximately 10 days and remained stable at this low value, which was probably close to equilibrium. Water-extractable P from the Pahiatua soil, however, showed a slower initial rate of decline following P addition and also maintained higher values after 65 days. Also, the value at 65 days was not an equilibrium value and the slow decline was continuing.

It was considered that the initially rapid decline in water-extractable P (Fig. 5.5) might be modified by the use of a low solubility source of P, e.g., a rock phosphate, which might release P over a longer time period. The addition of Christmas Island A phosphate to soil resulted in an initial water-extractable P value which was only slightly higher than the control for both the Pahiatua soil (Fig. 5.6) and the Egmont soil (Fig. 5.7). The increases for Egmont soil were obtained for the first 5 to 10 days only and subsequent values were essentially the same as control values. This result is consistent with the observation (A.M. Posner, pers. comm.) that rapid initial release of water-soluble P from Christmas Island A grade rock phosphate may be followed by a very slow release to solution in a continuous-flow system. It has been suggested by Posner that the initial dissolution of surface P is responsible for this effect. It is also possible, however, that any very fine particles in the sample would dissolve rapidly, with larger particles releasing P to solution only slowly.

5.3.3.2 Decline in water-extractability of phosphorus in soil and the availability of phosphorus to plants

For each of the two soils studied the pattern of declining

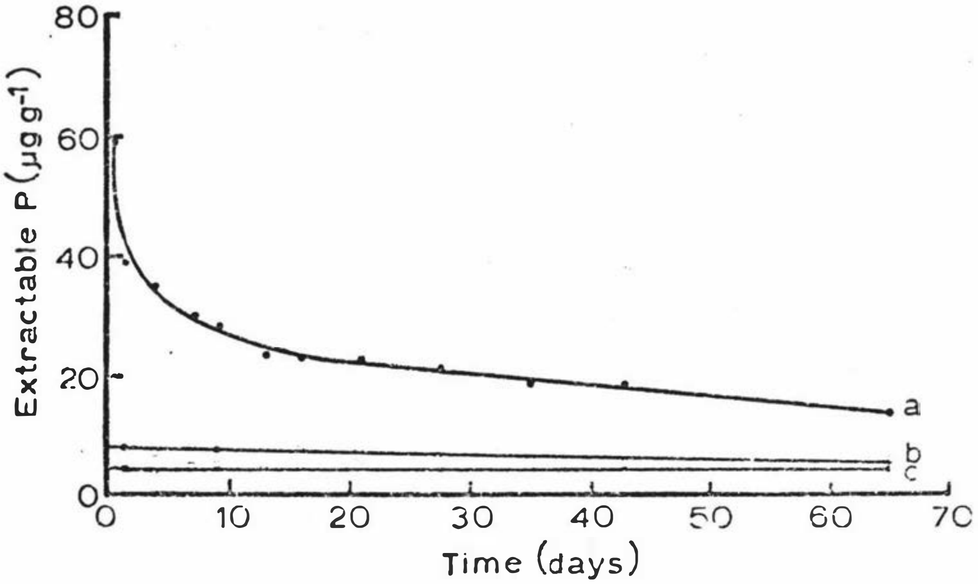

Fig. 5.6 Decline in water-extractable P from Pahiatua soil with time following incubation and fertilizer P addition.

a = superphosphate, b = rock phosphate, and c = control.

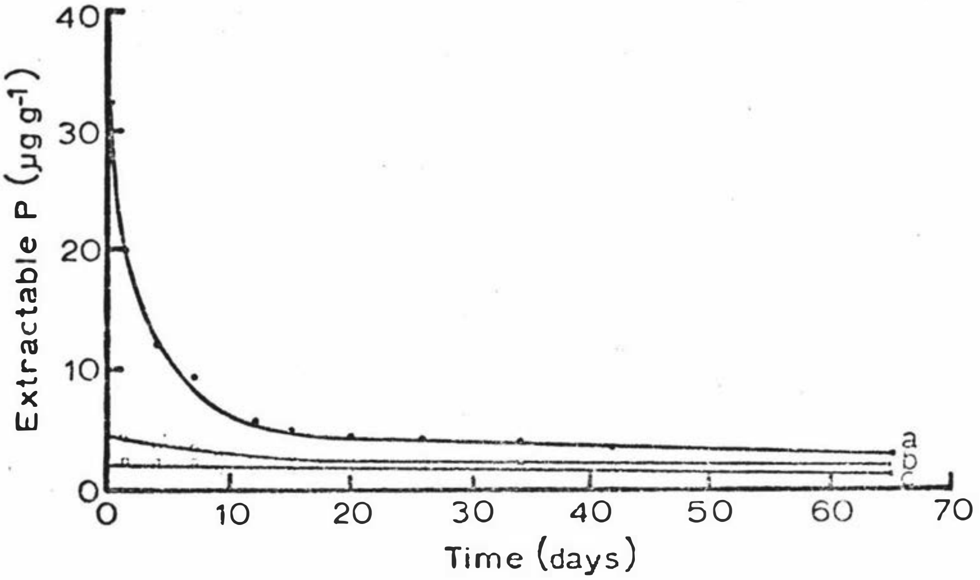

Fig. 5.7 Decline in water-extractable P with time following fertilizer P addition and incubation of Egmont soil.

a = superphosphate, b = rock phosphate, and c = control.

water-extractable P and decreasing plant recovery of P with time following P addition were similar (Fig. 5.8 and 5.10). For the low P-sorbing Pahiatua soil the decrease in P recovery by herbage showed only a slow initial decline (Fig. 5.8) with relatively high values being maintained up to 100 days after P addition to soil. There was a closer correlation (Fig. 5.9A, $r = 0.957^{**}$) between water-extractable P and plant uptake than between Olsen-extractable P and plant uptake (Fig. 5.9B, $r = 0.791^{*}$). Further to this, the regression line obtained for water-extractable P passed through a point close to the origin (Fig. 5.9A), whereas for Olsen-extractable P values, the line intercepted the x axis at a point close to 30 μg P g^{-1} soil for zero plant uptake (Fig. 5.9B).

Essentially the same relationships were obtained for the high P-sorbing Egmont soil (Fig. 5.10), with a steeper decline in plant recovery of P corresponding with a steeper decline in water-extractable P. Regressions and correlations between plant uptake of P and water-extractable P (Fig. 5.11A, $r = 0.938^{**}$) and Olsen-extractable P (Fig. 5.11B, $r = 0.707$) were also similar to those obtained for the Pahiatua soil. This similarity is shown in Fig. 5.12 (A and B) where data for both soils are presented on the one figure, The parallel slopes and high correlation coefficients imply that either of the extraction procedures may be useful in predicting plant-available P in soil. The two procedures differ, however, in their intercept values with the x axis. This indicates that although both extractions provide an estimate of plant-available P in soil over a range of soil P values, the Olsen extraction removed approximately 30 μg P g^{-1} soil more than the water extraction. The fact that the slope of neither regression line is equal to one or the intercept equal to zero indicates that neither extraction predicts the actual amount of P which is plant available.

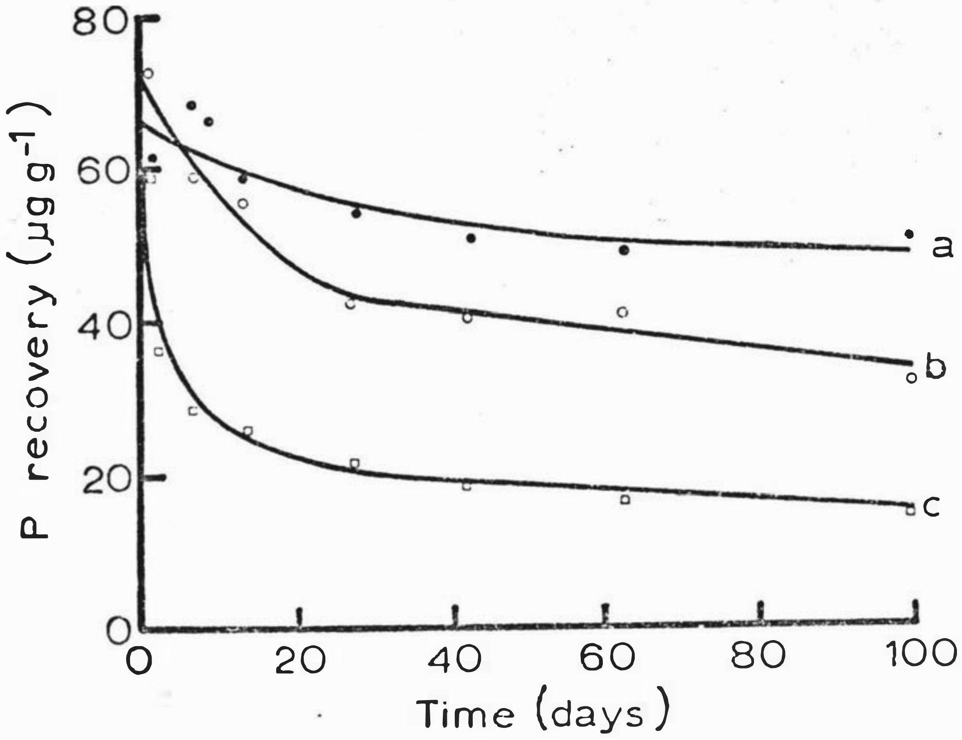

Fig. 5.8 Decline in recovery of P from Pahiatua soil with time following superphosphate addition and incubation.

a = Olsen P, b = plant uptake of P and

c = water-extractable P.

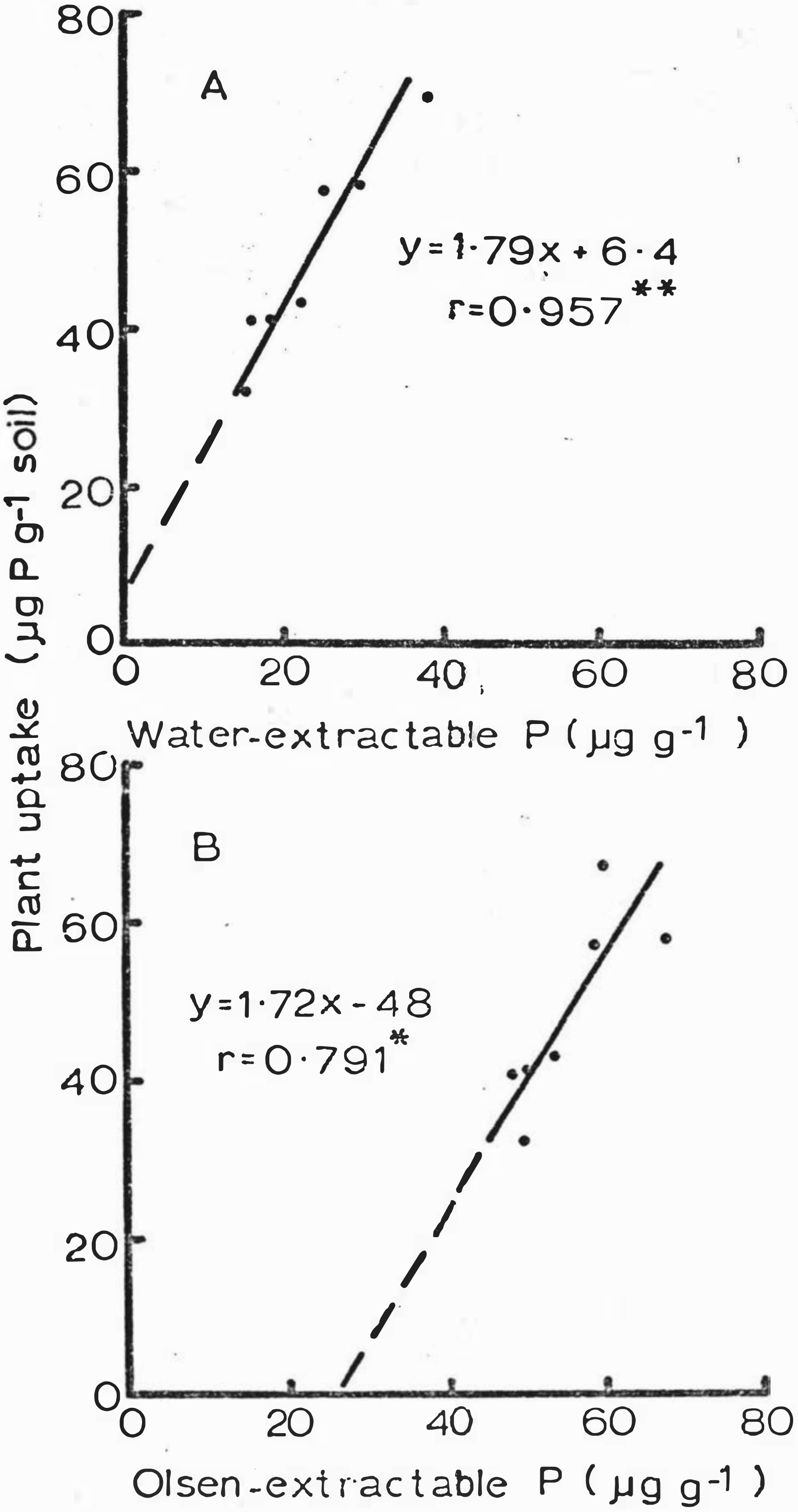

Fig. 5.9 Regression between plant uptake of P from Pahiatua soil following superphosphate addition and incubation, and amounts of extractable P.

A = water-extractable P and B = Olsen P.

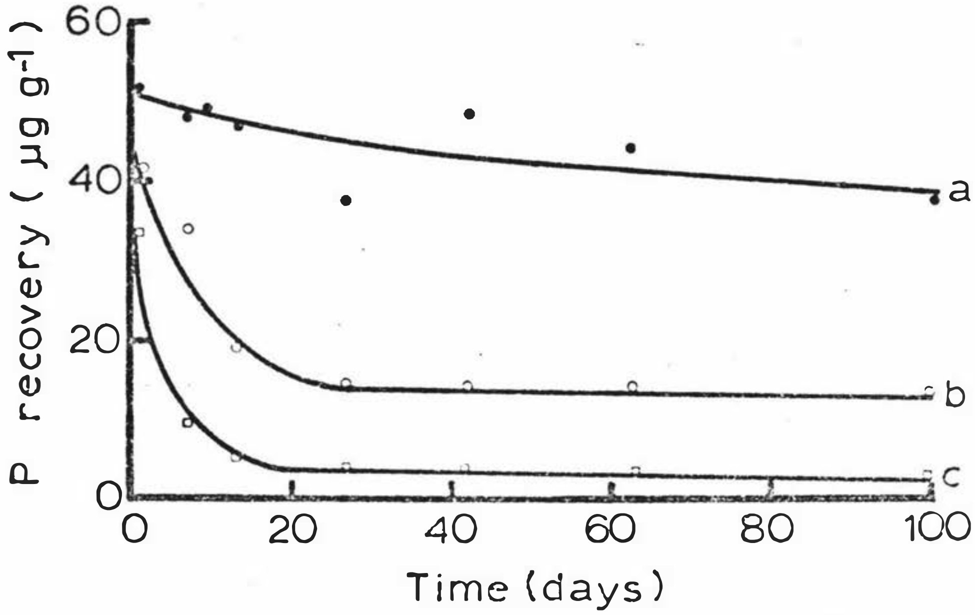

Fig. 5.10 Decline in recovery of P from Egmont soil with time following superphosphate addition and incubation.
a = Olsen P, b = plant uptake of P, and
c = water-extractable P.

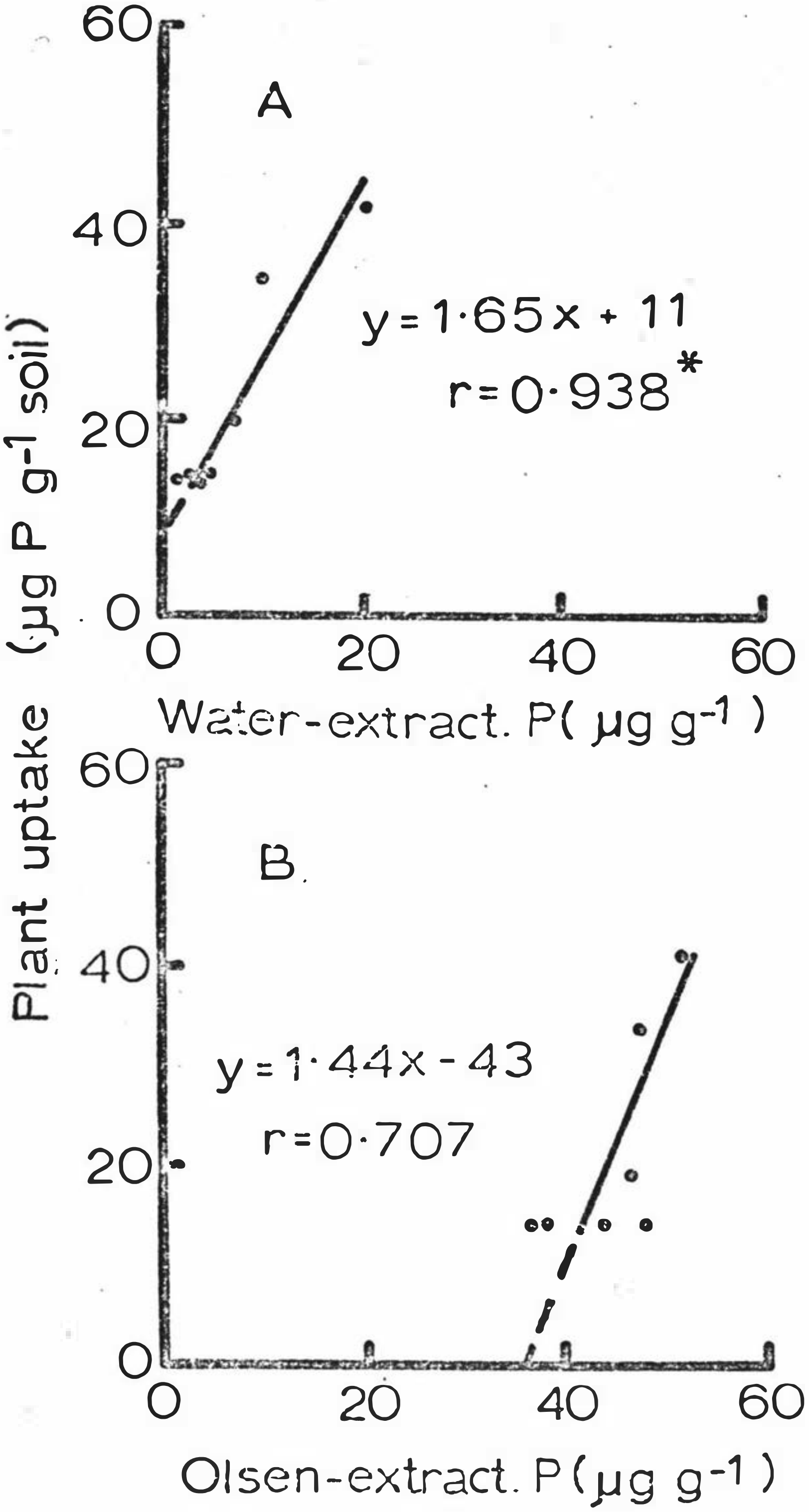

Fig. 5.11 Regressions between plant uptake of P from Egmont soil samples following superphosphate addition and incubation, and amounts of extractable P.

A = water-extractable P and B = Olsen P.

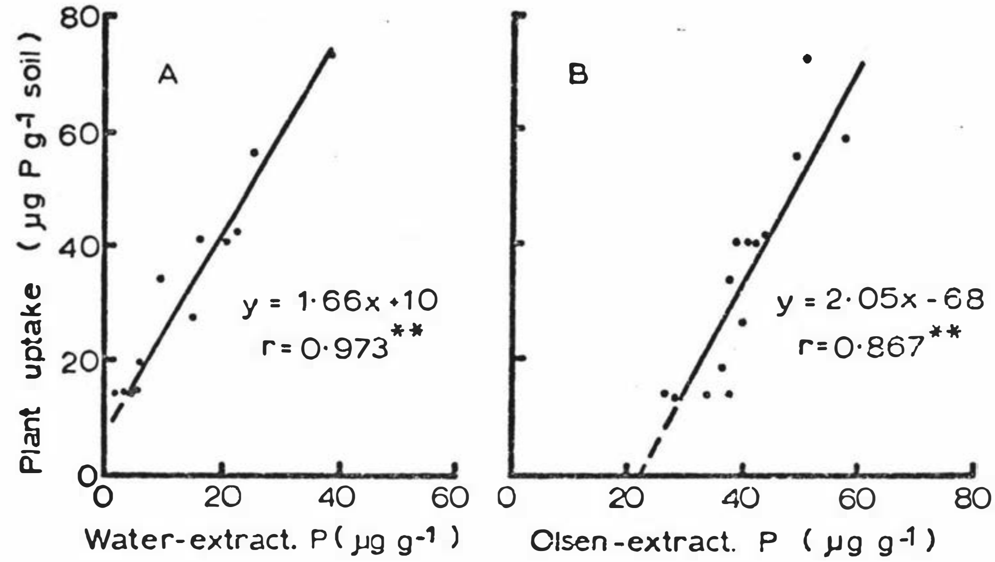

Fig. 5.12 Regression between plant uptake of P from Pahiatua and Egmont soils following superphosphate addition and incubation, and extractable P. A = water-extractable P and B = Olsen P.

Recovery of P by herbage or by extraction from soils to which rock phosphate had been added, was low with only slight changes in values up to 100 days after P addition (Fig. 5.13 and 5.14). The values obtained were similar to those from unfertilized control soils, indicating that the P in rock phosphate which is not extracted from soil by either water or bicarbonate is also not available for plant uptake, at least under the conditions of the experiment. The absence of significant correlations between either water- or Olsen-extractable P values and plant uptake P values (Table 5.2) may have been due to the small spread of data points.

The total amount of P added to each soil as fertilizer P was 302 μg P g^{-1} soil. It is evident from Fig. 5.8 and 5.10 that not more than 60 and 40 μg P g^{-1} were recovered from Pahiatua and Egmont soils, respectively, by either extraction procedure or by plant uptake, even immediately following P addition. These amounts represent approximately 20 and 15% of TP added, respectively. It is possible that some of the added P may have reacted very quickly with soil components and become unavailable either to plants or the extractant. It is therefore of interest to examine the extractability of P from soil following the addition of solid and solution P forms.

5.3.4 Influence of solid or dissolved phosphorus addition to soil on the decline in water-extractable phosphorus

Two samples of Pahiatua soil received solid and solution P additions of 75 μg solution P g^{-1} soil and 302 μg solid P (75 μg water-soluble P) g^{-1} soil, respectively. The rate and extent of the decline in water-extractable P from soil were identical for both forms of P

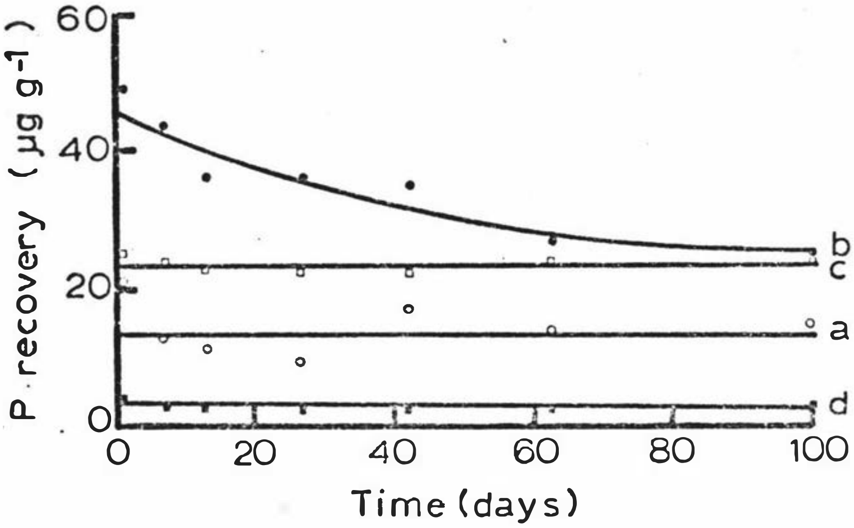

Fig. 5.13 Decline in recovery of P from Pahiatua soil with time following rock phosphate addition and incubation.

a = plant uptake (1 cut), b = plant uptake (2 cuts), c = Olsen P and d = water-extractable P.

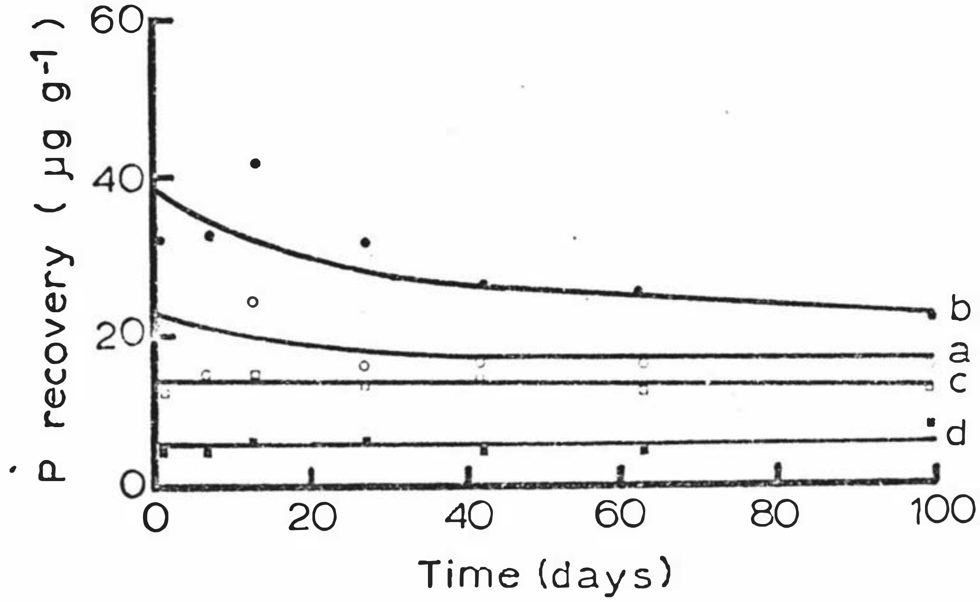

Fig. 5.14 Decline in recovery of P from Egmont soil with time following rock phosphate addition and incubation.

a = plant uptake (1 cut), b = plant uptake (2 cuts), c = Olsen P, d = water-extractable P.

Table 5.2 Correlation coefficients between plant uptake of P after 50 days growth in Pahiatua and Egmont soils fertilized with superphosphate and rock phosphate and amounts of water-extractable P and Olsen-extractable P.

	Correlation coefficients between plant uptake of P and	
Soil	Water-extractable P	Olsen-extractable P
	Superphosphate	
Pahiatua	0.957**	0.791**
Egmont	0.938**	0.707
	Rock phosphate	
Pahiatua	0.556	- 0.565
Egmont	0.666	- 0.498
	Control	
Pahiatua	- 0.354	0.009
Egmont	0.729	- 0.460

addition (Fig. 5.15). The close similarity in the behaviour of dissolved P and water-soluble solid P at times of up to 60 days following P addition indicates that the initially water-insoluble P in superphosphate (77% of TP in the sample used) did not become soluble with time in the soil. Although approximately 90% of both solution P and water-soluble solid P added to soil was initially water-extractable in the soil system (Fig. 5.16) only 20% of the TP added as a solid was water-extractable in the soil system. The data obtained and discussed previously (Section 5.3.3.2) suggest that the water-insoluble fraction of TP in superphosphate may also remain unavailable to plants for periods of up to 100 days following superphosphate addition to soils, at least under conditions similar to the present experiments.

The data presented subsequently in this Chapter were obtained using incubated soils to which solution P derived from superphosphate was added, as in the above experiment. This procedure reduced the possibility of incomplete mixing of P with the soil and the variability between replicate samples.

5.3.5 Detailed studies of the decline in water-extractable phosphorus in soils and an approach to modelling soil phosphorus reactions

Three contrasting soils (Table 5.1) were incubated, following the addition of P at different rates, to obtain suitable data which provided a base against which the modelling of soil P reactions could be tested. Once again, differences were obtained between soils in the rate of the initial decline in water-extractable P and the final values persisting after 60 days (Fig. 5.17, 5.18, and 5.19), confirming and extending the observations discussed in Section 5.3.3.1. It was also observed that

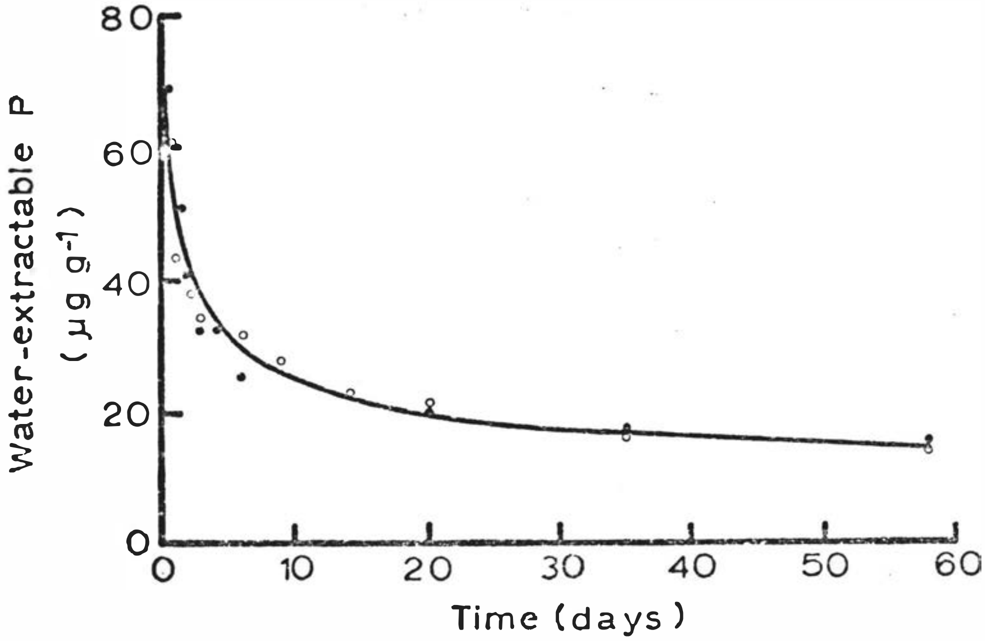

Fig. 5.15 Decline in water-extractable P from Pahiatua soil with time following fertilizer P addition at 75μg P g^{-1} in solid and liquid forms.
Solid circles = solid P and
open circles = liquid P.

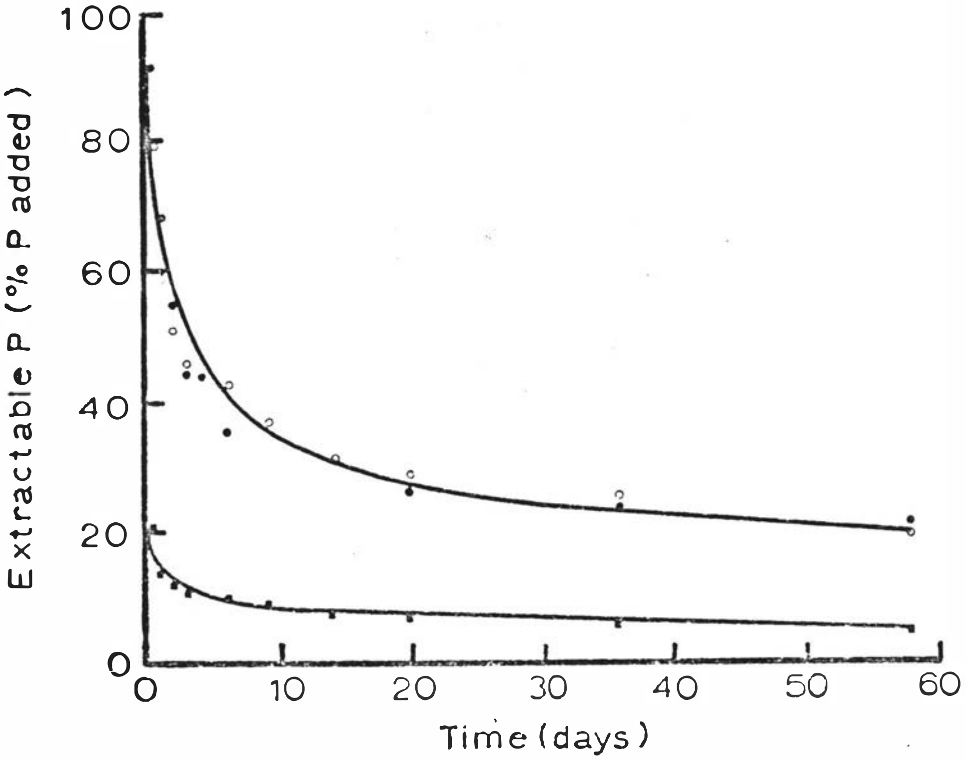

Fig. 5.16 Decline in water-extractable P from Pahiatua soil following fertilizer P addition and incubation. Extractable P is expressed as % of water-soluble P added as solid superphosphate (closed circles), % of TP added as a solution of superphosphate (open circles), and % of TP added as solid superphosphate (closed squares).

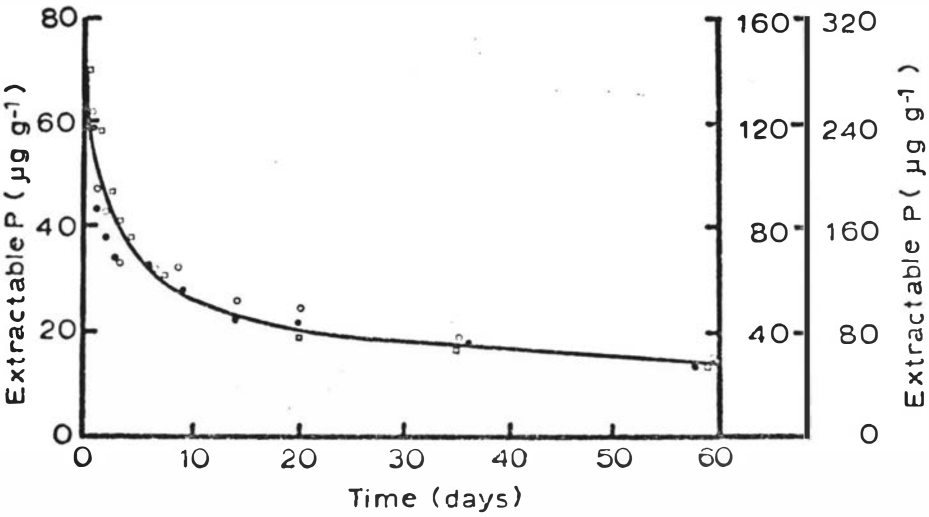

Fig. 5.17 Decline in water-extractable P with time from Pahiatua soil following fertilizer P addition and incubation at three rates of addition. Closed circles = 75 µg P g^{-1}, open circles = 150 µg P g^{-1}, and open squares = 300 µg P g^{-1}.

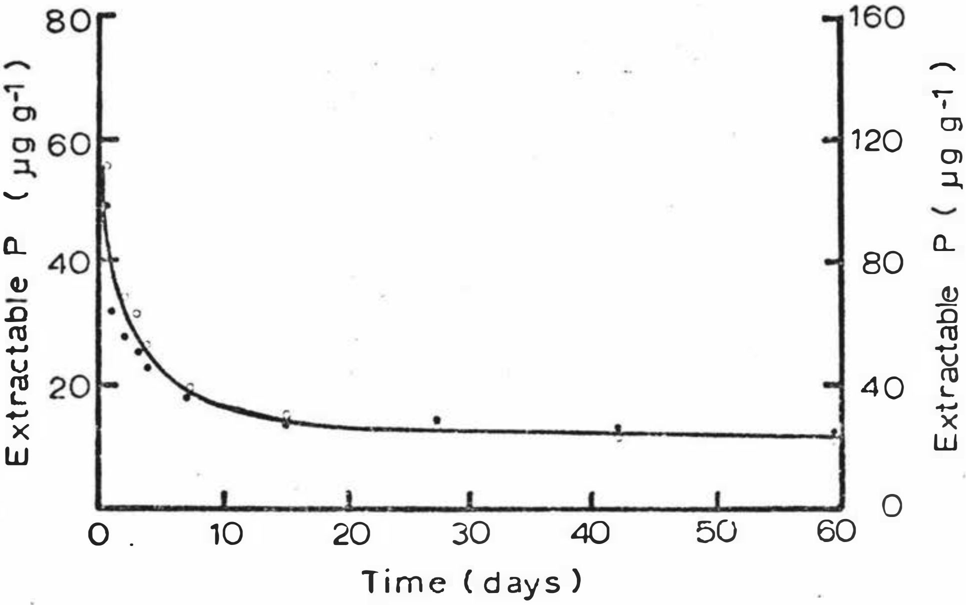

Fig. 5.18 Decline in water-extractable P with time from Dannevirke soil following fertilizer P addition and incubation at two rates of addition. Closed circles = 75 µg P g^{-1} and open circles = 150 µg P g^{-1}.

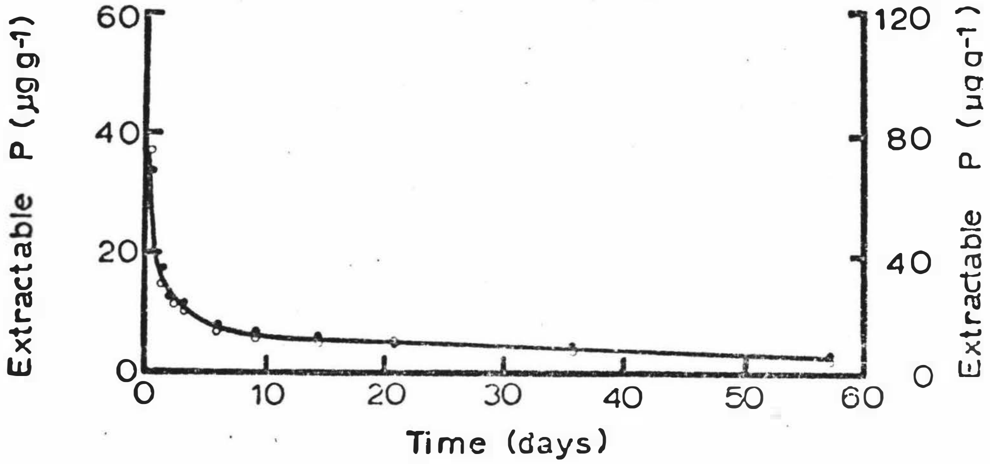

Fig. 5.19 Decline in water-extractable P with time from Egmont soil following fertilizer P addition and incubation at two rates of addition. Closed circles = 75 µg P g^{-1} and open circles = 150 µg P g^{-1}.

for each soil the values of water-extractable P were directly proportional to the P addition rate. This is shown in Fig. 5.17, 5.18, and 5.19 where the water-extractable P values, following different P addition rates, are superimposed after scale adjustment proportional to the rates of P addition.

The decline in water-extractable P for each soil can also be expressed relative to the amount of P extracted in an initial extraction 40 hours after P addition (Fig. 5.20). It is evident that soils with a higher P-sorbing capacity remove a greater proportion of initially-extractable P from a water-extractable form more rapidly than soils of lower P-sorbing capacity. This result differs from that obtained by Ryden et al. (1976) who suggested that the relative water-extractability of P following P addition was essentially common to different soils. It is possible, however, that the scatter of data points about a generalised decline curve, as obtained by Ryden et al. (1976), could accommodate the discrete curves shown in Fig. 5.20.

Total amounts of native P present in each soil are shown in Table 5.3; these amounts were added to all values for equilibrium P sorbed. The equilibrium P sorption isotherms were subsequently resolved using the linear form of the Langmuir equation (described in Section 5.2.6 and by Ryden et al., 1977a). Sorption constants describing three regions of P sorption for the three soils are presented in Table 5.4 It has been shown (Graham, 1953; Shapiro and Fried, 1959) that the equilibrium constant of a sorption reaction is equivalent to the value of K obtained from the linear form of the Langmuir equation. Values of K_I, K_{II}, and K_{III} are therefore presented as the equilibrium constants of reaction for P sorption in each region (Table 5.4). Values of K_I, K_{II}, or K_{III}

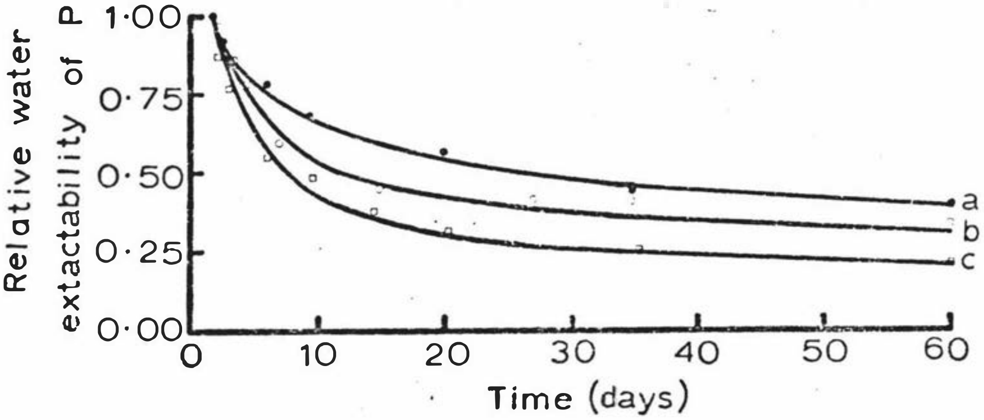

Fig. 5.20 Decline in relative water extractability of P, expressed as a proportion of the extraction value obtained after 40 hours, with time following fertilizer P addition and incubation.

a = Pahiatua, b = Dannevirke, and c = Egmont.

Table 5.3 Amounts of total "native" P, determined using ^{32}P, and the amounts of P present in each region, calculated from solution P concentration at equilibrium with no P addition and the Langmuir equation for each region

Soil	Amount of P Total	 Region I	 Region II	 Region III
	$\mu g\ P\ g^{-1}$			
Pahiatua	80	67.2	11.1	1.6
Dannevirke	101	94.7	5.9	0.4
Egmont	700	639	57	4

Table 5.4 Sorption constants describing the three (I, II, and III) regions of P sorption for three soils; K and b are the equilibrium constant of reaction and the sorption maximum, respectively, for a particular region

Soil	K value for each region			b value for each region		
	K_I	K_{II}	K_{III}	b_I	b_{II}	b_{III}
	ml μg^{-1}			μg P g^{-1}		
Pahiatua	51	0.77	0.059	89	286	520
Dannevirke	113	1.09	0.041	154	372	785
Egmont	131	1.06	0.054	870	1515	2220

are similar for different soils. There are major differences, however, between K_I and K_{II} values or K_{II} and K_{III} values within the soil. A similar relationship has been obtained for contrasting soils by Ryden et al. (1977a). These workers suggested that the large differences between K values within a soil (related to the ΔG of reaction) are evidence for different P sorption mechanisms operating within soils and common to different soils. This implies that differences in the rate and extent of P sorption in soils are dependent essentially upon the number of vacant sites and the distribution of vacant sites between the three regions.

Although the equilibrium constant of reaction may be regarded as a balance or ratio between the forward and reverse rate constants, the Langmuir sorption constants obtained (Table 5.4) do not indicate values for the rate constants. Rate constants were estimated (Table 5.5) keeping the ratio of the forward to reverse value (KF/KR) equal to the Langmuir K value by assuming a common KR (desorption) constant for each region or mechanism but some variation in the KF value. It is possible that both parameters for one region vary slightly between soils, which may reflect relatively small, but possibly real, differences in the binding energy of a given mechanism operating in different soils. The estimated rate constants for region III are generally higher than those for region II, and both are higher than those for region I. This progression of rate constant values is based on the work of McLaughlin et al. (1977) who showed that P sorption in region III by hydrous ferric oxide gel, was initially rapid but was followed by redistribution of sorbed P and slower, continuing sorption in regions II and I.

These values, together with the sorption maxima values (Table 5.4), the amounts of P initially present on sites in each region (Table 5.3),

Table 5.5 Estimated rate factors for forward (KF) and reverse (KR) reactions in each of three (I, II, and III) regions of P sorption in three contrasting soils. Rate factors are expressed as ratios of the forward to reverse reaction rate constants for each region, the ratios being numerically equal to the equilibrium constant of reaction (K_I, K_{II}, K_{III}) shown in brackets and in Table 5.3

Soil	$\frac{KF_I}{KR_I}$	(K_I)	$\frac{KF_{II}}{KR_{II}}$	(K_{II})	$\frac{KF_{III}}{KR_{III}}$	(K_{III})
Pahiatua	$\frac{0.014}{0.00027}$	(51)	$\frac{0.031}{0.04}$	(0.077)	$\frac{0.062}{1.05}$	(0.059)
Dannevirke	$\frac{0.031}{0.00027}$	(113)	$\frac{0.044}{0.04}$	(1.09)	$\frac{0.043}{1.05}$	(0.041)
Egmont	$\frac{0.035}{0.00027}$	(131)	$\frac{0.042}{0.04}$	(1.06)	$\frac{0.057}{1.05}$	(0.054)

and initial soil solution P concentration (related to fertilizer addition rate and soil moisture), were incorporated into the model shown in Fig. 5.21. Operation of the model (described in Section 5.2.6) allowed concurrent P sorption from solution in all three regions, although most of the initial sorption took place in region III (more physical sorption), followed by a subsequent redistribution of P into regions I and II (chemisorption), and accompanied by declining solution P concentration. Initial sorption was rapid but was followed by a more gradual, subsequent sorption and redistribution, tending towards an equilibrium. The computer programme of the model for each soil is shown in Appendix 3, accompanied by the appropriate print-out showing P distribution in each region and soil solution P concentrations following P addition. Simulated water-extraction (desorption) was modelled for two successive 1-hour shaking times at appropriate intervals following P addition, e.g., 10, 30, and 60 days.

Close fit was obtained between the experimental data and the predicted data for the rate and extent of decline in water-extractable P (Fig. 5.22) for the three soils studied. The Egmont and Dannevirke soils gave a particularly close fit, although the predicted equilibrium value for the Pahiatua soil was greater than the experimental value. It is interesting to note that the K_I value obtained for Pahiatua soil was relatively low (51 compared to 113 and 131 for Dannevirke and Egmont soils, respectively). The tendency for sorption to proceed in region I relative to regions II and III, as modelled for the Pahiatua soil, is therefore disproportionately less than that for region I in the Dannevirke and Egmont soils, giving rise to a higher water-extractable P value.

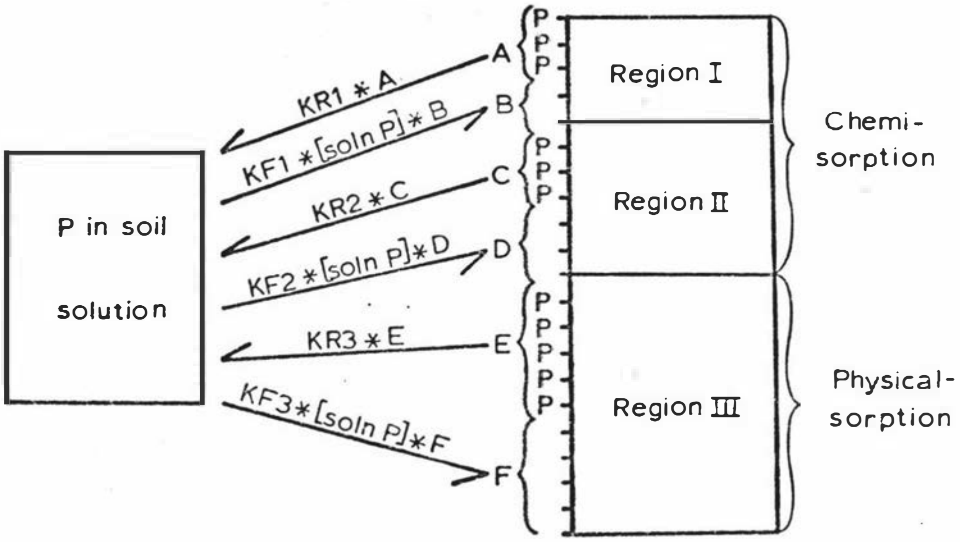

Fig. 5.21 Schematic representation of the proposed reaction mechanisms involved in P sorption and desorption. Symbols are discussed in the text.

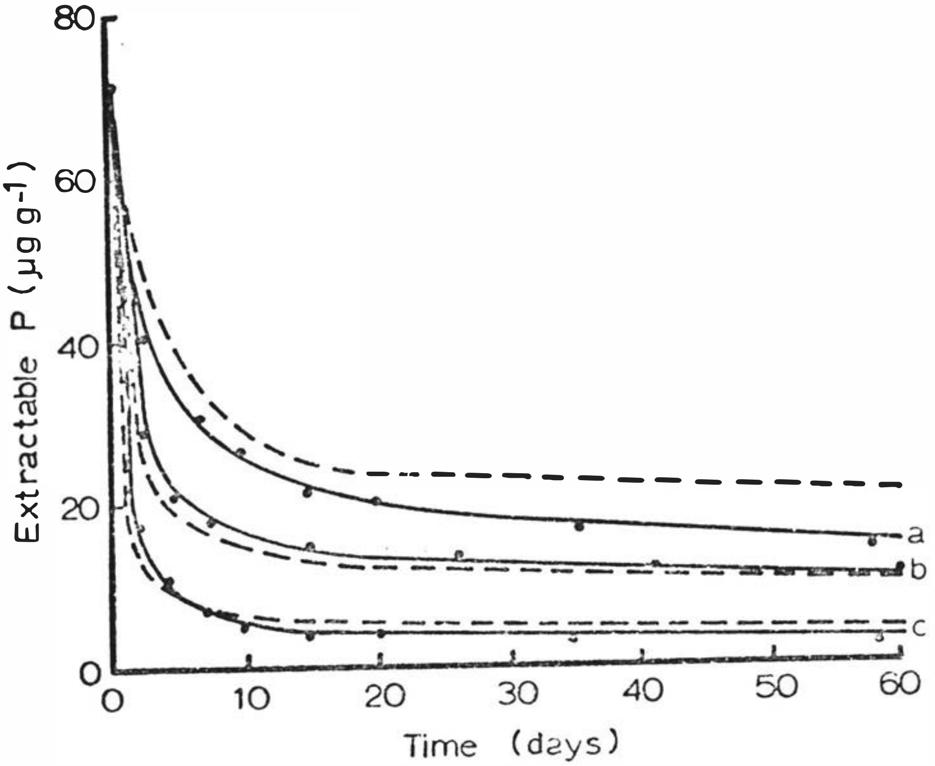

Fig. 5.22 Predicted (---) and measured (——) decline in the amounts of water-extractable P in Pahiatua (a), Dannevirke (b), and Egmont (c) soils with time after the fertilizer P addition.

Both Ryden (1976) and Hope (1978) observed similar differences in K_I values between soils but regarded them as insignificant, relative to the far larger differences between K_I, K_{II}, and K_{III} values within soils. The poorer fit of predicted data for Pahiatua soil introduces the possibility that there may be some error in the measured values of K_I. If it was accepted that the K value for a particular region was common to all soils, as suggested by Ryden et al. (1977), the model predicted very closely the decline in water-extractable P in all three soils.

Because it has been observed experimentally that the amounts of water-extractable P in a soil folloiwng P addition are directly proportional to the amount of P added, i.e., initial soil solution P concentration, this effect was tested in the model. A doubling of the initial soil solution P concentration led to a similar doubling of the water-extractable P value in the soil with time and consistent close fit between the predicted and the experimental data. This effect is shown in Fig. 5.23, 5.24, and 5.25 for Pahiatua, Dannevirke, and Egmont soils, respectively.

5.4 General Discussion

Changes in the extractability of P added to soils and soil components with time after addition have been described by several workers (Larsen et al., 1965; Barrow, 1973; Barrow and Shaw, 1975b; Overman and Chu, 1977a,b,c). There have been, however, inconsistences in the extraction procedures used for soil P and hence the nature of soil P measured. In fact the lack of an adequate definition of the nature of the soil P extracted has made interpretation of the decline in

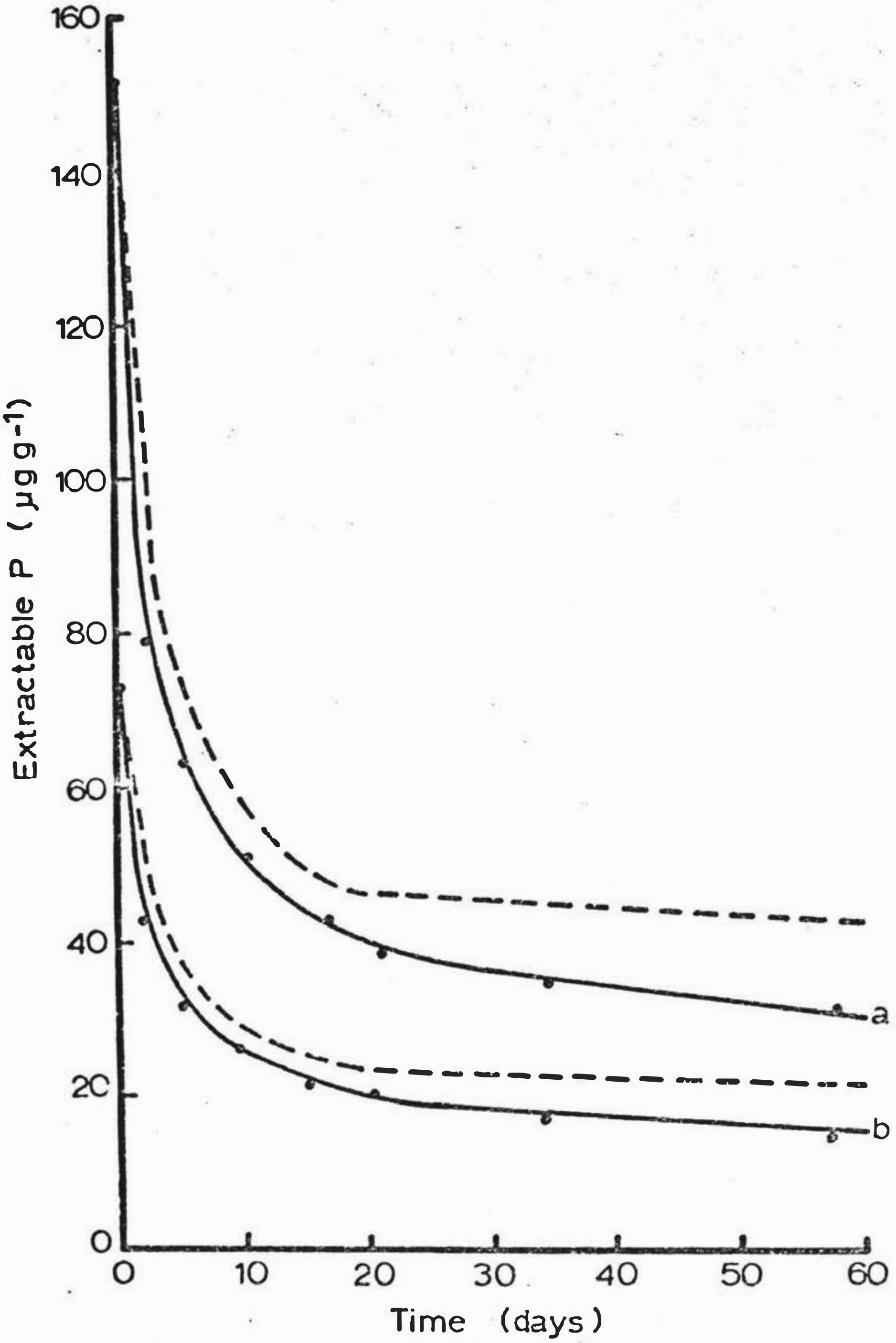

Fig. 5.23 Predicted (---) and measured (——) decline in the amounts of water-extractable P in Pahiatua soil with time after fertilizer P addition at rates of 150 µg P g^{-1} (a) and 75 µg P g^{-1} (b).

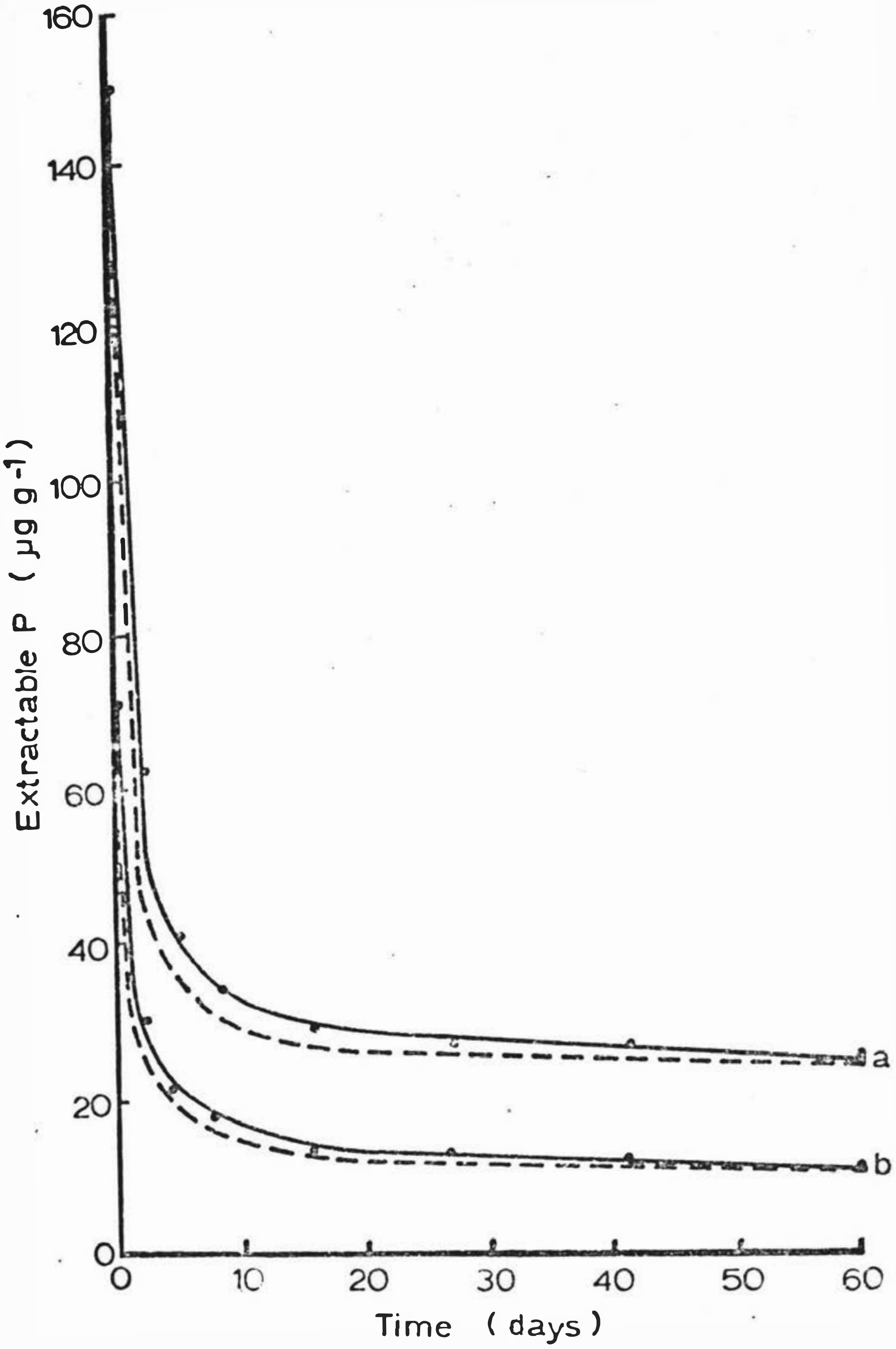

Fig. 5.24 Predicted (---) and measured (——) decline in the amounts of water-extractable P in Dannevirke soil with time after fertilizer P addition at rates of 150 µg P g^{-1} (a) and 75 µg P g^{-1} (b).

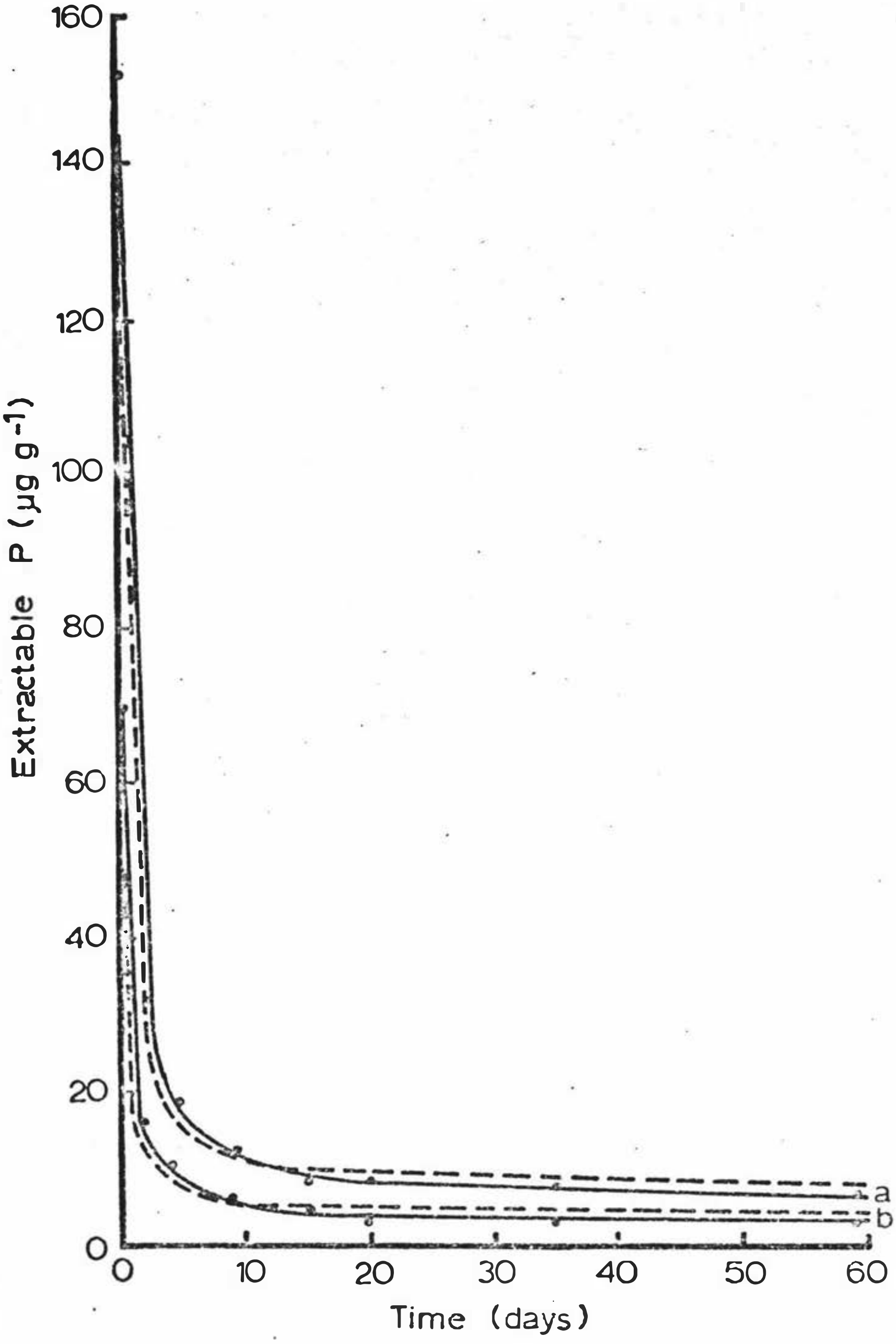

Fig. 5.25 Predicted (---) and actual (——) decline in the amounts of water-extractable P in Egmont soil with time after fertilizer P addition at rates of 150 µg P g^{-1} (a) and 75 µg P g^{-1} (b).

extractable P difficult to interpret. The study by Ryden and Syers (1977a), suggesting that a 2 x 1-hour sequential water extraction procedure removes an amount of P from soils equivalent to the more-physically sorbed P, is one of the very few which places a theoretical meaning on the fraction of extracted P. Because a linear relationship was obtained between this extraction procedure and that used in the field soil studies (Chapter 4), it has been possible to show that the pattern of decline of water-extractable P in soil following P addition was similar both in the field and in the laboratory. Also, the close correlations obtained between water-extractable P in field soils and mean DIP concentrations in the surface runoff component of storm flow (Chapter 4) suggest that laboratory studies may be useful in predicting the potential movement of added DIP from soil into surface waters.

The rapid decline in water-extractable P in soils corresponded closely to the decline in plant-available P. A number of workers have suggested that water-extractable P in soils may be a good indicator of plant-available P (Bingham, 1949; van der Paauw, 1971; Luscombe, 1976). Although the Olsen reagent extracted more P from a given soil than distilled water, both procedures may correlate closely with plant-available P, although neither has been found to estimate the actual amount of P which is plant-available.

The data obtained in this study for contrasting soils and different rates of P addition show that the rate of P reaction in soil is related to the initial soil solution P concentration or P addition rate. This is consistent with the mathematical model proposed by Overman and Chu (1977a,b,c) and the suggestion of Rajan (1976). It has been of interest, however, to observe that although the proportional decline in water-extractable P (relative to an initial extraction value) was common to one soil for different P addition rates, different curves were obtained for different soils when one rate of P addition was used. This finding differs from that of Ryden et al. (1976) who suggested that one proportional decline curve was common to both different soils and different P addition rates. Their suggestion was explained in terms of a common overall sorption isotherm for different soils (Ryden and Syers, 1977a) which expressed the amount of P sorbed at each solution P concentration as a fraction (Θ) of the overall sorption maximum. Although they suggested that the relative sizes of the chemisorption and more-physical sorption maxima accounted for the scatter of data about the overall sorption isotherm, and also about the common proportional decline curve (Ryden et al.,1976), this suggestion has not been further examined. The data obtained in the present suggest that the rate and extent of P sorption reactions in different soils may differ.

Several other workers have studied the interaction of P with soil components (Kuo and Lotze, 1973; McLaughlin et al., 1977) and with whole soils (Larsen et al., 1965; Barrow, 1974). These studies, however, have not examined the reaction mechanisms occurring, nor have they incorporated experimental data into the models describing the decline in extractable P following P addition. Such models have often been of the type proposed by Mansell et al. (1977), involving a mathematical model without experimental data. Barrow and Shaw (1975b) have suggested that P reacts in soils in three stages from 'A' (solution P) to 'B' (sorbed P) and then to C (essentially non-exchangeable P). Similarly, Overman and Chu (1977a,b,c) have described P sorption from solution in two stages, i.e., a "fast" reaction (sorption) followed by a "slow" reaction (fixation). The evidence, however, for a fast reaction followed by a different, slow reaction has not been conclusive.

In contrast to the above models, which have been conceptual rather than experimentally derived, Ryden et al. (1977a) have suggested that sorption of P occurs simultaneously in each of three regions and that each of these sorption reactions can be described by a Langmuir equation. The significant advantage of this approach to mechanism modelling is that it has allowed the calculation of values for the binding energy and sorption maximum which have been useful in the subsequent prediction of soil phosphate sorption behaviour.

The use of the Langmuir equation has been criticised by several workers (Bowden et al., 1977; Veith and Sposito, 1977). These workers have not denied that experimental P sorption data can be fitted to straight line Langmuir equations. They have argued, however, that because the conditions of P sorption on soils may vary widely from the initial Langmuir assumptions, the derived values for K and b have no real physical meaning. The use of the K and b values, derived experimentally for soils (Ryden et al., 1977a), in a model based essentially on the original Langmuir theory has therefore provided a useful test for the application of the Langmuir equation to describe P sorption by soils.

Close fit to experimental data was achieved for all soils studied, although slightly poorer fit was acheived for low P-sorbing soil. It is possible that deviations between predicted and actual values are due to errors in the measurement of K values for a particular region between soils. The predictive ability of the model was very good if it was assumed that the K value for a particular region was common to the three soils. This would be expected if the reaction mechanisms for each region is common to all soils. A further study of differences in K values for each region between soils would therefore be useful.

It is also of interest to observe that an increase in the amount of fertilizer P added in the model resulted in proportional increases in the rates of P sorption. From a practical standpoint, the results suggest that doubling the rate of P addition to soils would double the amount of water-extractable P, at least during the time period considered in the present experiment. It would only be when region III becomes more fully saturated (region I and II also saturated) that high P application rates would increase the amounts of water-extractable P disproportionately.

The successful developement and operation of the above model has a number of important implications. The resolution of sorption isotherm data using the Langmuir equation, despite its suggested limitations (Bowden et al., 1977; Veith and Sposito, 1977), has allowed the estimation of values of K (equilibrium constant of sorption) and b (sorption maximum) and their incorporation into the model. Although the successful operation of this model does not validate the use of the Langmuir equation in P sorption isotherm resolution, it does extend its usefulness. It would be of interest to examine how closely the predicted amounts of P in each sorption region correspond to those found in field soils with time following P addition.

Using correlation and regression analysis, Ryden et al. (1976) suggested that an amount of P corresponding to that which was more-physically sorbed was removed during two extractions with distilled water, each of 1 hour duration. This approach did not define the actual source of P extracted or its distribution in the soil before extraction. The model developed and used in the present study suggests that P present in the soil solution and that which is chemisorbed, as well as more-physically sorbed P, may contribute to the amount of P removed by water extraction.

Despite these limitations, and the need for further evaluation, it is apparent that the P sorption mechanisms proposed by Ryden et al. (1977a) can be developed to describe experimental data using a kinetic model. It is possible that further evaluation of this model may lead to an increased ability to predict the fate of fertilizer P added to soil.

SUMMARY AND CONCLUSIONS

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The work presented in this thesis may be summarised as follows:

1. The results obtained in this study support those of other workers in indicating that some New Zealand surface waters contain P concentrations close to or within the range of 0.01 to 0.05mg l^{-1} regarded as critical for algal bloom development, and are therefore sensitive to increases in P concentrations.
2. Before land clearing, low and stable concentrations of P forms and sediment were obtained in stream flow from two small, adjacent, scrub-covered, and minimally-disturbed catchments. The variations in the concentrations of P forms and sediment, both within and between storm flows, after land clearing emphasised the need for intensive stream sampling as well as complete hydrograph data to calculate P and sediment loadings.
3. High and irregular concentrations of P forms and sediment were obtained in storm flow from two catchments following land clearing and fertilizer P application. This was partly due to the technique of land clearing which did not include conservation measures or channel protection from debris.
4. Although the concentrations of P forms and sediment in storm flow were high relative to background levels following clearing and fertilizer application, it is possible that grazed and regularly fertilized pasture will continue to yield similarly high concentrations.
5. The aerial application of fertilizer P had a substantial effect on the loss of P from the catchment in stream flow. Although the losses obtained (approximately 1% of fertilizer P added) are rather

insignificant from an agronomic standpoint, they may contribute significantly to the P enrichment of waters.

6. Although the amounts of water-extractable P in surface soils decreased after storm events, apparently due to the leaching of DIP from soil in surface runoff, the values were usually re-established within 7 to 10 days. Experimental data suggested that the mineralization of particulate OP may contribute to the relatively stable levels of water-extractable P in soils.
7. Following the aerial application of fertilizer P, the high levels of water-extractable P initially present in soils of the catchment declined rapidly to more stable, lower levels which tended towards an equilibrium value. The use of a series of small pots established in the field (pot soils) and containing mixed soil from the catchment and added fertilizer P, demonstrated that it was possible to replicate the field situation reliably without taking the large number of samples required to characterise the whole catchment.
8. Data obtained for the two catchments during two years following fertilizer P addition indicated that mean DIP concentrations in the surface runoff component of stream flow and water-extractable P levels in soil followed a similar pattern of decline in each year. The close correlations obtained between mean DIP concentrations in surface runoff and water-extractable P values for both field and pot soils suggest that the pattern of declining water-extractable P in soil following P addition in the laboratory, obtained in the present study and reported in the literature, may be applicable to field soils and the movement of P in surface water.
9. Evidence from pots in the field containing fertilized soils suggested that water-extractable P, following fertilizer P addition, is

essentially confined to the upper 1cm of soil, there being no detectable movement of fertilizer P below 1cm. Close linear relationships between mean DIP concentrations in the surface runoff component of stream flow and water-extractable soil P in the upper 1cm of soil were obtained.

10. In a glasshouse trial conducted with two contrasting soils, the decrease in water-extractable P following fertilizer P application closely paralleled the changes in plant-available P, as evaluated by growing ryegrass plants.
11. For a given soil studied, the rate of decline in water-extractable P was directly proportional to both the amount of P added and that initially extractable immediately following P addition. This implies that the rate and extent of P sorption in a soil is directly related to the initial soil solution P concentration. Differences were obtained, however, between three contrasting soils in the rate and extent of P sorption and these were reflected in the curves for the proportional decline in water-extractable P.
12. A kinetic model based on the Langmuir equation was developed to simulate the decline in water-extractability of P added to three soils. Three populations of sites were assumed and the appropriate sorption maxima and binding energy constants were derived from sorption isotherm studies. The model provided a satisfactory prediction of the fate of different fertilizer P additions to each of three contrasting soils. It is probable that development of this model could provide a useful basis for predicting the fate of fertilizer P added to soils and the potential movement of that added P in surface runoff waters.

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APPENDICES

Appendix 1.

Data Relating to Two Soils in the Study Catchments

(1) Shannon silt loam

Reference number : 14a on N.Z. Soil Bureau Map 102

Soil name : Shannon silt loam, rolling phase

Parent material : Loess (Ohakean)

Topography : Flat to gently undulating and rolling; dissected terraces

Altitude : 60 - 600 m

Mean annual rainfall : 1020 - 1270 mm

Brief description of representative soil profile:

A_1 : 0 - 20 cm dark brown (10 YR 3/3) silt loam; nut structure

B_{1g} : 20 - 30 cm light olive brown (2.5 Y 5/4) to light yellowish brown (2.5 Y 6/4) silt loam; few brown mottles and few concretions; nut structure

B_{21g} : 30 - 48 cm light olive brown (2.5 Y 5/4) heavy silt loam; many brown mottles; very thin clay coatings; weak blocky structure

B_{22g} : 48 - 63 cm pale olive (5 Y 6/3) heavy silt loam; abundant brown mottles; thin clay coatings; weak blocky structure

$C_{1}x$: 63 - on cm yellowish brown (10 YR 5/8) silt loam; few vertical veins; compact

Distinguishing features of soil and environment:

On intermediate and high terraces, from silty loess, under moderate rainfall (1020 - 1270 mm) with short summer dry seasons. Imperfectly drained with dark brown A horizon overlying light yellowish brown to light olive brown B horizon with brown mottles and thin clay coatings in the lower part. A weakly-developed fragipan occurs at about 76 cm with some vertical grey veining. Occurs under a higher rainfall than Tokomaru silt loam and has browner A horizon, browner B horizon with higher chromas, lighter textures, less development of clay coatings, and less well developed fragipan

Overall drainage : Imperfectly drained

Internal drainage : Medium to slow

Natural nutient status : Moderate: low P, medium Ca, high K

Present land use : Fattening and dairying

Potential land use : Fattening, dairying, and cropping

Limitations for intensive soil use: Imperfect drainage

Pasture response to topdressing : Phosphate, potash, lime

Soil erosion : Nil. Slight sheet if cultivated

(2) Raumai hill soils

Reference number : 17 H on N.Z. Soil Bureau Map 102

Soil name : Raumai hill soils

Parent material : Sandstone, and loess

Topography : Moderately steep and moderately steep to steep; valley sides

Altitude : 60 - 270 m

Mean annual rainfall : 1020 - 1270 mm

Brief description of representative soil profile:

A_1 : 0 - 15 cm dark greyish brown (10 YR 4/2) sandy loam; nut structure

B_{2g} : 15 - 48 cm pale olive (5 Y 6/3) heavy sandy loam to sandy clay loam; many brown mottles; weak blocky structure

B_{3g} : 48 - 63 cm pale olive (5 Y 6/3) and yellowish brown (10 YR 5/8) mottled sandy loam; massive

C_1 : 63 - on cm light olive brown (2.5 Y 5/6) and grey sand with iron-staining; firm

Distinguishing features of soil and environment:

On hill slopes of dissected terrace lands, mainly from weakly consolidated sandstone with some loess, under low to moderate rainfall (1020 - 1270 mm) with short summer dry seasons. Moderately well and well drained with sandy loam A horizon overlying pale olive, light olive brown, or light yellowish brown hues of (5 Y or 2.5 Y) firm massive sandy loam to sandy clay loam with brown mottles. Differs from Halcombe hill soils (15 H) in being sandier in texture

Overall drainage : Moderately well and well drained

Internal drainage : Medium to slow

Natural nutrient status : Moderate; low P and Ca, high K

Present land use : Fattening, store stock, and some dairying

Potential land use : Fattening, store, and breeding sheep

Limitations for intensive soil use : Hilly slope, pastures revert readily to scrub

Pasture responses to topdressing : Phosphate, potash, lime

Soil erosion : Moderate slips

Appendix 2.

Monthly rainfall recorded in the two catchments during the winter periods of three successive years

Month	Rainfall (mm) in		
	1974	1975	1976
Jan	-	-	-
Feb	-	-	-
Mar	-	-	30
April	n.a.*	94	98
May	n.a.	77	132
June	n.a.	90	340
July	284	119	128
Aug	93	206	152
Sept	121	64	87
Oct	133	80	68
Nov	78	72	44
Dec	-	-	-
Total	n.a.	802	1,079

[*] n.a. = not available.

```
* CSMP73 INPUT LIST *  25.003.000

    *     LANGMUIR SORPTION MODEL FOR THE PAHIATUA SOIL
    *
    *
    *     CONSTANTS USED IN MODEL
    *
    *     SOLN = SOIL SOLUTION CONCENTRATION
    *
    *        A = AMOUNT OF P IN REGION 1
    *        C = AMOUNT OF P IN REGION 2
    *        E = AMOUNT OF P IN REGION 3
    *
    *     VAC1 = NUMBER OF VACANT SITES IN REGION 1
    *     VAC2 = NUMBER OF VACANT SITES IN REGION 2
    *     VAC3 = NUMBER OF VACANT SITES IN REGION 3
    *
    *       I1 = INCREMENT OF P SORBED ONTO REGION 1
    *       I2 = INCREMENT OF P DESORBED FROM REGION 1
    *       I3 = INCREMENT OF P SORBED ONTO REGION 2
    *       I4 = INCREMENT OF P DESORBED FROM REGION 2
    *       I5 = INCREMENT OF P SORBED ONTO REGION 3
    *       I6 = INCREMENT OF P DESORBED FROM REGION 3
    *
    *      MEANINGS FOR KF1,KR1,KF2,KR2,KF3,KR3, ARE EXPLAINED IN THE TEXT
    *
      TIMER FINTIM=300,PRDEL=10,DELT=.005
      PARAM SOLN=187.5,A=67.2,C=11.1,E=1.6,KF1=.014,KR1=.00027,KF2=.031,...
      KR2=.04,KF3=.002,KR3=1.05
      SOLND=SOLN
      AD=A
      CD=C
      ED=E
      VAC1=89-A
      I1=KF1*SOLN*DELT*VAC1/10
      I2=KR1*DELT*A/10
      VAC2=286-C
      I3=KF2*SOLN*DELT*VAC2/10
      I4=KR2*DELT*C/10
      VAC3=520-E
      I5=KF3*SOLN*DELT*VAC3/10
      I6=KR3*DELT*E/10
      A=AD+I1-I2
      C=CD+I3-I4
      E=ED+I5-I6
      SOLN=SOLND+(I2+I4+I6-I1-I3-I5)/0.4
      PRINT SOLN,A,C,E
      ENDJOB
```

```
TIME                SOLN         A            C            E
0.00             1.7790E 02   6.7229E 01   1.1899E 01   4.6124E 00
1.0000E 01       1.4085E 00   6.8211E 01   3.7748E 01   4.8378E 01
2.0000E 01       1.1738E 00   6.8563E 01   4.5796E 01   4.0071E 01
3.0000E 01       1.0002E 00   6.8852E 01   5.1799E 01   3.3848E 01
4.0000E 01       8.6960E-01   6.9095E 01   5.6331E 01   2.9126E 01
5.0000E 01       7.7018E-01   6.9303E 01   5.9783E 01   2.5506E 01
6.0000E 01       6.9378E-01   6.9485E 01   6.2428E 01   2.2710E 01
7.0000E 01       6.3465E-01   6.9646E 01   6.4462E 01   2.0538E 01
8.0000E 01       5.8862E-01   6.9792E 01   6.6029E 01   1.8843E 01
9.0000E 01       5.5262E-01   6.9926E 01   6.7238E 01   1.7515E 01
1.0000E 02       5.2436E-01   7.0050E 01   6.8169E 01   1.6471E 01
1.1000E 02       5.0210E-01   7.0167E 01   6.8884E 01   1.5648E 01
1.2000E 02       4.8451E-01   7.0278E 01   6.9431E 01   1.4997E 01
1.3000E 02       4.7056E-01   7.0383E 01   6.9846E 01   1.4482E 01
1.4000E 02       4.5947E-01   7.0485E 01   7.0158E 01   1.4073E 01
1.5000E 02       4.5063E-01   7.0584E 01   7.0389E 01   1.3747E 01
1.6000E 02       4.4355E-01   7.0680E 01   7.0556E 01   1.3487E 01
1.7000E 02       4.3786E-01   7.0773E 01   7.0673E 01   1.3279E 01
1.8000E 02       4.3326E-01   7.0865E 01   7.0751E 01   1.3111E 01
1.9000E 02       4.2953E-01   7.0955E 01   7.0798E 01   1.2976E 01
2.0000E 02       4.2649E-01   7.1044E 01   7.0820E 01   1.2866E 01
2.1000E 02       4.2398E-01   7.1131E 01   7.0823E 01   1.2776E 01
2.2000E 02       4.2191E-01   7.1218E 01   7.0812E 01   1.2702E 01
2.3000E 02       4.2017E-01   7.1303E 01   7.0788E 01   1.2641E 01
2.4000E 02       4.1870E-01   7.1387E 01   7.0756E 01   1.2589E 01
2.5000E 02       4.1744E-01   7.1471E 01   7.0716E 01   1.2546E 01
2.6000E 02       4.1635E-01   7.1554E 01   7.0671E 01   1.2509E 01
2.7000E 02       4.1539E-01   7.1636E 01   7.0621E 01   1.2477E 01
2.8000E 02       4.1455E-01   7.1717E 01   7.0568E 01   1.2449E 01
2.9000E 02       4.1378E-01   7.1797E 01   7.0513E 01   1.2424E 01
3.0000E 02       4.1309E-01   7.1677E 01   7.0456E 01   1.2402E 01
```

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* CSMP73 INPUT LIST *  25.003.000

          *     LANGMUIR SURPTION MODEL FOR THE DANNEVIRKE SOIL
          *
          *
          *     CONSTANTS USED IN MODEL
          *
          *     SOLN = SOIL SOLUTION CONCENTRATION
          *
          *        A = AMOUNT OF P IN REGION 1
          *        C = AMOUNT OF P IN REGION 2
          *        E = AMOUNT OF P IN REGION 3
          *
          *     VAC1 = NUMBER OF VACANT SITES IN REGION 1
          *     VAC2 = NUMBER OF VACANT SITES IN REGION 2
          *     VAC3 = NUMBER OF VACANT SITES IN REGION 3
          *
          *       I1 = INCREMENT OF F SORBED ONTO REGION 1
          *       I2 = INCREMENT OF P DESORBED FROM REGION 1
          *       I3 = INCREMENT OF P SORBED ONTO REGION 2
          *       I4 = INCREMENT OF P DESORBED FROM REGION 2
          *       I5 = INCREMENT OF P SORBED ONTO REGION 3
          *       I6 = INCREMENT OF P DESORBED FROM REGION 3
          *
          *      MEANINGS FOR KF1,KR1,KF2,KR2,KF3,KR3, ARE EXPLAINED IN THE TEXT
          *
         TIMER FINTIM=300,PRDEL=10,DELT=.005
         PARAM SOLN=168.8,A=94.7,C=5.9,E=.43,KF1=.031,KR1=.00027,KF2=.044,...
         KR2=.04,KF3=.043,KR3=1.05
         SOLND=SOLN
         AD=A
         CD=C
         ED=E
         VAC1=154-A
         I1=KF1*SOLN*DELT*VAC1/10
         I2=KR1*DELT*A/10
         VAC2=372-C
         I3=KF2*SOLN*DELT*VAC2/10
         I4=KR2*DELT*C/10
         VAC3=785-E
         I5=KF3*SOLN*DELT*VAC3/10
         I6=KR3*DELT*E/10
         A=AD+I1-I2
         C=CD+I3-I4
         E=ED+I5-I6
         SOLN=SOLND+(I2+I4+I6-I1-I3-I5)/0.45
         PRINT SOLN,A,C,E
         ENDJOB
```

```
TIME              SOLN           A              C              E
0.00              1.5911E 02     9.4855E 01     7.2594E 00     3.2771E 00
1.0000E 01        8.1189E-01     9.9007E 01     4.1879E 01     3.5739E 01
2.0000E 01        6.1507E-01     1.0017E 02     5.0165E 01     2.6376E 01
3.0000E 01        4.8196E-01     1.0105E 02     5.5681E 01     2.0046E 01
4.0000E 01        3.9082E-01     1.0173E 02     5.9373E 01     1.5715E 01
5.0000E 01        3.2785E-01     1.0227E 02     6.1642E 01     1.2726E 01
6.0000E 01        2.8405E-01     1.0273E 02     6.3479E 01     1.0050E 01
7.0000E 01        2.5341E-01     1.0313E 02     6.4546E 01     9.2001E 00
8.0000E 01        2.3166E-01     1.0348E 02     6.5220E 01     8.1636E 00
9.0000E 01        2.1662E-01     1.0380E 02     6.5621E 01     7.4677E 00
1.0000E 02        2.0578E-01     1.0410E 02     6.5834E 01     6.9612E 00
1.1000E 02        1.9600E-01     1.0439E 02     6.5915E 01     6.6006E 00
1.2000E 02        1.9237E-01     1.0466E 02     6.5905E 01     6.3422E 00
1.3000E 02        1.8823E-01     1.0492E 02     6.5832E 01     6.1552E 00
1.4000E 02        1.8515E-01     1.0517E 02     6.5715E 01     6.0183E 00
1.5000E 02        1.8281E-01     1.0542E 02     6.5569E 01     5.9165E 00
1.6000E 02        1.8099E-01     1.0567E 02     6.5402E 01     5.8394E 00
1.7000E 02        1.7953E-01     1.0591E 02     6.5222E 01     5.7796E 00
1.8000E 02        1.7834E-01     1.0615E 02     6.5033E 01     5.7320E 00
1.9000E 02        1.7732E-01     1.0638E 02     6.4838E 01     5.6930E 00
2.0000E 02        1.7643E-01     1.0661E 02     6.4639E 01     5.6600E 00
2.1000E 02        1.7564E-01     1.0684E 02     6.4439E 01     5.6314E 00
2.2000E 02        1.7491E-01     1.0707E 02     6.4238E 01     5.6059E 00
2.3000E 02        1.7423E-01     1.0729E 02     6.4037E 01     5.5826E 00
2.4000E 02        1.7359E-01     1.0751E 02     6.3837E 01     5.5609E 00
2.5000E 02        1.7297E-01     1.0773E 02     6.3638E 01     5.5404E 00
2.6000E 02        1.7237E-01     1.0795E 02     6.3440E 01     5.5207E 00
2.7000E 02        1.7179E-01     1.0817E 02     6.3243E 01     5.5018E 00
2.8000E 02        1.7122E-01     1.0838E 02     6.3048E 01     5.4833E 00
2.9000E 02        1.7066E-01     1.0859E 02     6.2854E 01     5.4652E 00
3.0000E 02        1.7011E-01     1.0880E 02     6.2662E 01     5.4475E 00
```

```
* CSMP73 INPUT LIST *  25.003.000

       *     LANGMUIR SORPTION MODEL FOR THE EGMONT SOIL
       *
       *
       *     CONSTANTS USED IN MODEL
       *
       *     SOLN = SOIL SOLUTION CONCENTRATION
       *
       *        A = AMOUNT OF P IN REGION 1
       *        C = AMOUNT OF P IN REGION 2
       *        E = AMOUNT OF P IN REGION 3
       *
       *     VAC1 = NUMBER OF VACANT SITES IN REGION 1
       *     VAC2 = NUMBER OF VACANT SITES IN REGION 2
       *     VAC3 = NUMBER OF VACANT SITES IN REGION 3
       *
       *       I1 = INCREMENT OF P SORBED ONTO REGION 1
       *       I2 = INCREMENT OF P DESORBED FROM REGION 1
       *       I3 = INCREMENT OF P SORBED ONTO REGION 2
       *       I4 = INCREMENT OF P DESORBED FROM REGION 2
       *       I5 = INCREMENT OF P SORBED ONTO REGION 3
       *       I6 = INCREMENT OF P DESORBED FROM REGION 3
       *
       *      MEANINGS FOR KF1,KR1,KF2,KR2,KF3,KR3, ARE EXPLAINED IN THE TEXT
       *
      TIMER FINTIM=300,PRDEL=10,DELT=.005
      PARAM SOLN=150,A=639,C=57,E=4,KF1=.035,KR1=.00027,KF2=.042,...
      KR2=.04,KF3=.057,KR3=1.05
      SOLND=SOLN
      AD=A
      CD=C
      ED=E
      VAC1=870-A
      I1=KF1*SOLN*DELT*VAC1/10
      I2=KR1*DELT*A/10
      VAC2=1515-C
      I3=KF2*SOLN*DELT*VAC2/10
      I4=KR2*DELT*C/10
      VAC3=2220-E
      I5=KF3*SOLN*DELT*VAC3/10
      I6=KR3*DELT*E/10
      A=AD+I1-I2
      C=CD+I3-I4
      E=ED+I5-I6
      SOLN=SOLND+(I2+I4+I6-I1-I3-I5)/0.5
      PRINT SOLN,A,C,E
      ENDJOB
```

```
TIME              SOLN         A            C            E
0.00              1.2066E 02   6.3961E 02   6.1592E 01   1.3471E 01
1.0000E 01        2.2863E-01   6.4402E 02   9.2786E 01   3.8080E 01
2.0000E 01        1.7809E-01   6.4544E 02   1.0091E 02   2.8562E 01
3.0000E 01        1.4413E-01   6.4652E 02   1.0625E 02   2.2165E 01
4.0000E 01        1.2122E-01   6.4737E 02   1.0972E 02   1.7849E 01
5.0000E 01        1.0569E-01   6.4808E 02   1.1194E 02   1.4928E 01
6.0000E 01        9.5134E-02   6.4868E 02   1.1333E 02   1.2946E 01
7.0000E 01        8.7922E-02   6.4921E 02   1.1415E 02   1.1596E 01
8.0000E 01        8.2971E-02   6.4969E 02   1.1459E 02   1.0674E 01
9.0000E 01        7.9549E-02   6.5014E 02   1.1478E 02   1.0041E 01
1.0000E 02        7.7162E-02   6.5057E 02   1.1479E 02   9.6038E 00
1.1000E 02        7.5476E-02   6.5098E 02   1.1469E 02   9.2994E 00
1.2000E 02        7.4265E-02   6.5137E 02   1.1450E 02   9.0849E 00
1.3000E 02        7.3377E-02   6.5176E 02   1.1427E 02   8.9314E 00
1.4000E 02        7.2706E-02   6.5214E 02   1.1400E 02   8.8192E 00
1.5000E 02        7.2188E-02   6.5252E 02   1.1371E 02   8.7352E 00
1.6000E 02        7.1769E-02   6.5289E 02   1.1340E 02   8.6703E 00
1.7000E 02        7.1420E-02   6.5326E 02   1.1309E 02   8.6184E 00
1.8000E 02        7.1117E-02   6.5362E 02   1.1277E 02   8.5753E 00
1.9000E 02        7.0848E-02   6.5398E 02   1.1244E 02   8.5383E 00
2.0000E 02        7.0601E-02   6.5434E 02   1.1212E 02   8.5055E 00
2.1000E 02        7.0369E-02   6.5469E 02   1.1179E 02   8.4756E 00
2.2000E 02        7.0149E-02   6.5505E 02   1.1147E 02   8.4477E 00
2.3000E 02        6.9937E-02   6.5540E 02   1.1115E 02   8.4211E 00
2.4000E 02        6.9731E-02   6.5574E 02   1.1083E 02   8.3956E 00
2.5000E 02        6.9529E-02   6.5609E 02   1.1051E 02   8.3709E 00
2.6000E 02        6.9330E-02   6.5643E 02   1.1019E 02   8.3467E 00
2.7000E 02        6.9134E-02   6.5677E 02   1.0987E 02   8.3229E 00
2.8000E 02        6.8941E-02   6.5711E 02   1.0956E 02   8.2994E 00
2.9000E 02        6.8749E-02   6.5744E 02   1.0925E 02   8.2763E 00
3.0000E 02        6.8559E-02   6.5778E 02   1.0894E 02   8.2534E 00
```