

Nutrient Dynamics in Manure Amended Grasslands

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Thesis submitted for the degree of Doctor of Philosophy

Date of submission: February 1994

Date of acceptance: March 1994

Summary

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Following the surface application of different fertiliser treatments (cattle slurry, cattle manure, and inorganic fertiliser) to grassed hillslopes, the transport of nitrogen (N) and phosphorus (P) was monitored on controlled plots. The plots measured 30 m by 5 m, the lower 10 m acting as an untreated buffer zone, in order to examine the effect of following current codes of practice when applying fertilisers (MAFF and WOAD, 1991). Surface and sub-surface nutrient flow pathways were monitored, by sampling water from the saturated and unsaturated zones of the soil profile, and from surface runoff.

Sub-surface flow was dominated by NO_3^- -N. However, concentrations of this N species were relatively low (3-6 mg l^{-1}), and differences between treatments and the control were not significant. Generally, this indicated immobilisation of N species and P fractions, outputs in plant uptake and possibly to atmosphere (denitrification).

For surface runoff, concentrations of N and P from treated plots were significantly higher than those from the control. N was largely present as organic-N and NH_4^+ -N for the slurry and manure (15 mg l^{-1} and 5 mg l^{-1} respectively), and as NH_4^+ -N and NO_3^- -N for the inorganic fertiliser (20 mg l^{-1} in both cases). P was largely present as PO_4^- -P (0.5 mg l^{-1} for manure and slurry, 10 mg l^{-1} for inorganic fertiliser), except for the manure treatment, where some 75 % of the total was organic-P. The 10 m buffer was effective in reducing the delivery of N and P in surface runoff, differences between the treatments and the control being rendered insignificant. This result was qualified in terms of the ratio of the buffer area to the treated area and the relatively low surface loads of N and P observed.

N and P transport was then examined under less controlled conditions at the field to headwater catchment scale (4-18 ha). Sub-surface throughflow was associated with similar concentrations of NO_3^- -N (3-8 mg l^{-1}) and very low concentrations of PO_4^- -P

(0.03-0.1 mg l⁻¹). These concentrations appeared to vary more in relation to seasonal changes in the level of discharge from the catchment than to changes in land-use, which implied that N and P in sub-surface throughflow was transport rather than supply limited. This was in broad agreement with observations made at the plot scale.

At this larger scale, fluctuations in the concentrations of NH₄⁺-N and PO₄⁻-P occurred during rainfall events in response to what was probably the short-term occurrence of surface runoff from partial source areas of reduced infiltration capacity or variable source areas of saturation. These short-term fluctuations implied variations in topography and the distribution of surface derived N and P at the catchment scale. There was evidence of the occurrence of preferential flow during field experiments at both scales, which had important implications for the timing and magnitude of N and P transport.

Finally, a functional and semi-distributed mathematical model was constructed to operate at the headwater catchment scale, and the effect of spatial variability in the interaction between land-use and topography on the transport of N and P was considered further.

Acknowledgements

This study was funded by a NERC studentship GT4/90/AAPS/52. All the fieldwork was carried out at two separate sites in South Devon; Seale-Hayne Faculty Farm, University of Plymouth, and the Merrifield catchment near Slapton. At Seale-Hayne, thanks are extended to the agriculture technicians Peter Russell, Patrick Bugg and Andrew, for never once questioning the sanity of what I was trying to do on my controlled plots, at least within my earshot. Thanks are also offered to Frances Vickery and Anne Kraus in the laboratories, for patiently explaining the various analytical techniques, frequently reminding me of the locations of reagents, putting up with fridges full of samples, and the crisis management course for breakdowns on ageing autoanalysers.

During the work in the Merrifield catchment, the support of the staff of the Slapton Ley Field Centre (Field Studies Council) was much appreciated, particularly the continued weekly monitoring at Merrifield carried out by the placement students despite limited resources. Thanks are also extended to Mr N. J. Eastley for free access to his farmland.

Carrying out several months of fieldwork over 200 miles away from home was made so much easier by the support and friendship of the postgraduate community at Seale-Hayne. Due to their ready acceptance of a brash and frequently muddy Northerner, Devon proved to be an enjoyable place to live as well as a place of work. Equally, I would like to thank the postgraduates and staff of Sheffield University for remembering who I was each time I returned.

This study was jointly supervised by Louise Heathwaite of Sheffield University and Rob Parkinson of Seale-Hayne. Both are thanked for their contrasting styles of supervision which combined to my benefit. Louise is thanked in particular for tempering my minimalist tendencies in certain aspects of field and analytical work, and in writing up. Rob and his wife Anne Gellatly are thanked for support, shelter, and Guinness by the log fire during the fieldwork phases. Rob's frequent reminder that the PhD is not the definitive statement on life was eventually reflected in the way I handled certain setbacks. In addition to the supervision of Louise and Rob, I benefited from the

contribution of my second supervisor at Sheffield, Rob Ferguson. Despite his commitments as Head of Department, Rob was of considerable assistance in developing the basic structure of the mathematical model, and in commenting upon the chapters in the thesis relating to the model.

Much of the fieldwork would have been extremely difficult to carry out without the donation of an Austin Maestro from my parents-in-law, Muriel and David Stonehewer. Perforated with rust though it was, the Maestro never failed on frequent trips up and down the M5.

Finally, I would like to thank Yvonne for her patience, support, encouragement, and love, particularly during the times when I was away on fieldwork. This thesis is not dedicated to her, I've moaned about it too much to make that an appropriate gesture.

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Glossary of terms used in the thesis

NO₃⁻-N: Nitrate nitrogen

NH₄⁺-N: Ammonium nitrogen

PO₄⁻-P: Orthophosphate or molybdate reactive phosphate phosphorus

Organic-N: Dissolved and particulate organic nitrogen and particulate soil bound nitrogen

Organic-P: Dissolved and particulate organic phosphorus and particulate soil bound phosphorus

Chapter 1

Placing the Research in Context, Defining Aim and Objectives

1.1. Introduction

The purpose of this research was to examine one aspect of the transport of nutrients from the terrestrial ecosystem to the aquatic ecosystem, in this particular case the transport of nitrogen (N) and phosphorus (P) from grassed hillslopes to receiving freshwater courses. There are two reasons why this kind of study is of importance.

1. The transport of nutrients from the terrestrial ecosystem represents a loss to the components of that ecosystem. In the case of agriculture, this might entail a reduction in the efficiency of the production of a crop.
2. Addition of nutrients to the aquatic ecosystem above that which occurs naturally may result in deleterious effects to that ecosystem.

This chapter seeks to place the research in context by working backwards from the aquatic to the terrestrial ecosystem. Firstly, the effect of increased input of nutrients to freshwaters is considered in terms of different definitions of freshwater quality, for example, the impact on suitability for drinking water supply. Then, the sources from which increased nutrient input to freshwaters may emanate are considered, and one particular source is identified as warranting further research, not only to increase the understanding of how nutrients are transported from this source, but also to facilitate improved estimations of the contribution of this source in relation to others when nutrient transport is considered at the catchment scale. This leads logically to a definition of the overall aim and detailed objectives of the research in the final part of the chapter.

1.2. The effect of nutrient input on the quality of freshwaters

The quality of freshwaters can be defined in numerous ways, depending on the purpose of the definition. The definition may be broad, such as the grading of river water quality from 1 - 4, depending upon its potential as a drinking supply, its ability to support aquatic life, and its amenity value. Class 1 is defined as water of high quality, suitable for drinking and capable of sustaining high class fisheries, whereas Class 4 is defined as water which is grossly polluted and likely to cause a nuisance (NRA, 1989). Alternatively, the definition of water quality may be narrow, such as the maximum permissible concentration of $11.3 \text{ mg l}^{-1} \text{ NO}_3^- \text{-N}$ in a drinking water supply as set by European Commission Directive (CEC, 1980). Whatever the definition, the input of nutrients into, and the transport of nutrients along water courses often has important implications for freshwater quality in both rivers and lakes.

The input of nutrients to freshwaters is a natural process and one that the productivity of the aquatic ecosystem depends upon. In rivers, for example, nutrients are often supplied in organic matter such as leaf litter. However, water quality may be affected if the input of nutrients increases above that which occurs naturally, one extreme example being the discharge of organic matter from an intensive livestock rearing unit to a nearby water course. In this case, bacteria would immediately colonise the discharge, and utilise so much oxygen in the decomposition of the organic matter within it that a stretch of water may rapidly become deoxygenated. This in turn would lead to the loss of most invertebrates and fish, with a remaining aquatic community dominated by filamentous bacteria such as sewage fungus (Moss, 1988).

In lakes, the quality of water is often related to the productivity and growth of plants, and as the energy contained in suspended material is generally less than in rivers, the primary producers (phytoplankton and algae) in lakes depend more upon the supply of dissolved nutrients. The most important nutrients, in terms of limitation to the productivity and the growth of algae and higher plants, are considered to be nitrogen (N) and phosphorus (P) respectively (Moss, 1988; Heathwaite, 1993). This forms the basis of the limiting nutrient concept, which argues that both the absolute and relative

quantities of nutrients regulate primary productivity in lakes, and that the ratio in which nutrients are taken up by primary producers is reflected in their cellular material. A ratio of 106C:16N:1P is often cited as the standard for determining which is the limiting nutrient in a body of water, and P is considered to be the limiting nutrient in most temperate lakes (Ryding and Rast, 1989). There are restrictions to the application of this concept, the most notable being that it relies on steady state conditions. Therefore, fluctuations in temperature and light availability, or seasonal changes in nutrient supply might cause the concept to fail (Ryding and Rast, 1989; Heathwaite, 1993). However, accepting the general validity of the concept, the relevant question in respect of water quality in lakes is what happens when an increase in the input of nutrients, notably N and P, alters the limitation on the productivity and growth of plants.

Artificial increases in the input of nutrients to lakes can facilitate a change in the trophic status of those lakes from oligotrophic (nutrient poor) to eutrophic (nutrient rich), a process defined as artificial or cultural eutrophication by Ryding and Rast (1989), who also quoted the OECD definition of eutrophication as follows.

"The nutrient enrichment of waters which results in the stimulation of an array of symptomatic changes, among which increased production of algae and macrophytes, deterioration of water quality and other symptomatic changes, are found to be undesirable and to interfere with water uses".

Some of these symptomatic changes are described by Moss (1988). In extreme cases the symptoms may be similar to those described in the example of organic pollution in rivers given on page 2. Dense suspended algal growth can increase to a point where there is depletion of light and oxygen, leading to complete loss of submerged aquatic plants. Spawning and living habitat for fish is then lost, which in turn has a negative effect on the population of fish eating birds. In short, the whole conservation value of the habitat is diminished. Before this extreme is reached there may still be negative impacts on the overall quality of the waterbody. The loss of open water leads to a reduced amenity value, and if the water is to be used for domestic supply, an increase in algal growth can lead to increases in filtration and purification costs.

Increased amounts of the nutrients N and P in freshwaters can have negative impacts on water quality by other definitions. For example, O'Riordan and Bentham (1993) considered the medical evidence of a link between increased concentration of nitrate in drinking water and the clinical condition of methaemoglobinaemia in infants, popularly described as "blue baby syndrome" because the primary symptom is oxygen starvation. They noted that while the risk to infants suffering from this condition is high, the incidence is low, the last recorded case in the UK being in 1972. On balance it was concluded that methaemoglobinaemia was not a serious health risk that warranted the reduction of current nitrate concentrations in water on its own, but that this conclusion should be treated with a little caution as methaemoglobinaemia is not a notifiable disease, and therefore the true incidence is not known.

Medical research has also identified a potential link between nitrate and stomach cancer in humans through the reduction of nitrate to nitrite, which then reacts with the products of digestion in the stomach to form carcinogenic N-nitroso compounds. However, the certainty of this link is very difficult to establish because of the complicating factor of the role of diet in the inhibition of carcinogen formation, with the quality of diet being related to social class. The long latency period involved in the development of this cancer also makes it difficult to relate any particular incidence to the quality of diet and nitrate content in water consumed at the time the cancer began (Forman *et. al.*, 1985; O'Riordan and Bentham, 1993). Both Keeney (1986) and Wild (1993) also discussed the issue of methaemoglobinaemia, and in addition, both noted that elevated concentrations of nitrate can be a particular hazard to cattle and sheep because the rumen of these animals facilitates the reduction of nitrate to the more poisonous nitrite. The intake of nitrate from drinking water has apparently caused nitrite poisoning of livestock in the USA for many years.

1.3. Defining the sources of nutrient input to freshwaters

Having established that the increased input of the nutrients N and P to freshwaters can be detrimental to the quality of that water by numerous definitions, it is important to identify the sources of input. There are a number of sources, and these sources differ both in terms of the mechanism of nutrient transport and in the chemical composition of the nutrients input. For example, the source could be a single discrete point, such as a leaking slurry tank on an intensive livestock rearing unit. This source would yield N and P both in organic matter and as soluble inorganic ions. Alternatively, the source could be much more diffuse, such as a lowland arable catchment subject to large inputs of inorganic fertiliser. This source would yield N and P largely as inorganic ions.

Therefore, if one wishes to control the input of N and P to freshwaters in order to protect water quality, it is not sufficient only to be aware of all the sources of increased nutrient supply. For reasons that will be explained more fully during the course of this chapter, one must seek to understand as fully as possible both the pathways by which N and P are transported from source to water, and the processes which determine all the species of N and fractions of P that are transported, along with their relative magnitudes.

This philosophy is not new, and while seldom being stated explicitly, it usually finds its expression in a number of different contexts. For example, Koeman (1984), in a review of the environmental problems caused by the use of inorganic fertilisers, acknowledged that the problem cannot be examined in isolation. The author made the following statement, including reference to three different sources of nutrient input.

"It is at present extremely difficult to assess the exclusive role of fertilisers in connection with changes in environmental quality as the same nutrients as well as organic compounds enter into the same environment through domestic effluents and the use or disposal of animal manures."

In another context, it may often be relatively simple to identify P as the limiting nutrient in a eutrophication problem, and to identify the main source of P as sewage treatment effluent. However, it is much more difficult to predict the effectiveness of reducing

inputs of P from this one source if the input of P from diffuse agricultural sources is not also adequately quantified (Vighi and Chiaudani, 1984). Osborne and Wiley (1988) stated that despite initial extensive efforts to control point source inputs in the US, established water quality standards could not be achieved in many regions because of the impacts of non-point sources which were not addressed. Finally, Johnes and Heathwaite (1992) stressed the need to quantify the contributions made by all the different N species and P fractions to total nutrient loading in water, this being in the context of an introduction to a new laboratory procedure for the determination of total N and P in fresh water samples.

The degree of understanding of the pathways and processes involved in the transport of N and P to freshwaters varies depending upon the source. In developed countries at least, it can be argued that the process of organic pollution from sewage is well understood. This is so much the case that the same biological processes are used to treat sewage as would be used naturally in a river, except that the processes are concentrated and controlled in a sewage treatment works (Moss, 1988). However, such an example is used to demonstrate that in general point sources are easier to deal with than diffuse sources. The pathways leading to a point discharge into fresh waters are usually well defined and are often controlled. This makes it that much easier to define and control the processes which determine the amounts and forms of N and P at the point of discharge. Diffuse sources are by their very nature harder to define and control (Heathwaite, 1993), and it is evident from the examples cited thus far that agricultural operations contribute to diffuse sources of N and P input to freshwaters.

1.4. Agriculture and diffuse sources of nutrient input to freshwaters

Agriculture is the major land-use in the UK, accounting for approximately 75 % of the nation's land area (Royal Society, 1983). Moss (1988) has noted that agricultural operations often involve the removal of natural land covers which tend to conserve N and P within the terrestrial ecosystem, for example, woodland. Following the removal of natural land cover, the magnitude of the increase in N and P transport depends upon

a number of factors. In cropping systems these factors could include the duration for which ground is left without crop cover, the amounts of fertiliser used, and whether or not a drainage system is employed. In livestock systems possible factors include methods of animal housing, methods of dung and urine storage and disposal, stocking density in grazed fields, and the amount of fertiliser used to improve and maintain pasture. Table 1.1 shows how changes in land-use can increase the amounts of N and P transported from catchments to receiving water courses.

Table 1.1 Effects of land-use on the concentration of N and P in stream waters, and their annual rates of loss, for a range of catchments in the east and central states of the USA. Values given are means (from Moss, 1988).

Type of catchment	Number of catchments	<u>Concentrations in stream waters</u>			
		Total-P ($\mu\text{g l}^{-1}$)	Ortho-phosphate-P ($\mu\text{g l}^{-1}$)	Total-N (mg l^{-1})	Inorganic-N (mg l^{-1})
Forest	53	14	6	0.85	0.23
Mostly forest	170	35	14	0.89	0.35
Mostly agric.	96	66	27	1.8	1.05
Agriculture	91	135	58	4.2	3.2

Table 1.1 continued

Type of catchment	Number of catchments	<u>Gross amounts lost from catchments ($\text{kg ha}^{-1}\text{year}^{-1}$)</u>			
		Total-P	Ortho-phosphate-P	Total-N	Inorganic-N
Forest	53	0.08	0.04	4.4	1.3
Mostly forest	170	0.17	0.07	4.5	1.8
Mostly agric.	96	0.23	0.09	6.3	3.7
Agriculture	91	0.31	0.13	9.8	7.4

The nature of a diffuse agricultural source of nutrient input is such that a series of processes takes place between the agricultural operation on the land surface and the input of nutrients into the receiving freshwater. These processes will be subject to spatial and temporal variability due to factors such as weather, topography, and variations in soil structure. Therefore, there is a need to define the pathways of N and P transport from source to water, and a need to define the processes that modify N speciation and P fractionation within those pathways. If these pathways and processes can be defined, it then becomes possible to relate nutrient input to agricultural operation more closely. This in turn facilitates a more accurate prediction of changes in nutrient input to freshwaters that would result from changes in agricultural operation. The need to define pathways and processes is reflected in the body of research on this subject carried out to date.

Traditionally, research into nutrient transport has focused on the transport of N and P as soluble inorganic ions (usually NO_3^- -N and PO_4^- -P), and the agricultural systems studied are usually cropping systems involving the use of inorganic fertilisers (Troake and Walling, 1974; Duxbury and Peverly, 1978; Vinten *et. al.*, 1991; Goss *et. al.*, 1993). Such a focus is quite justifiable, in view of earlier consideration of the following two subjects. Firstly, the role of soluble forms of N and P in eutrophication, where increased transport of N and P from intensively managed arable catchments is often regarded as a key contributory factor. Secondly, the possible links between nitrate in drinking water and certain medical conditions. However, Koeman's (1984) argument still stands. Even if inorganic N species and P fractions from inorganic sources constitute the majority of increased levels of N and P input to freshwaters, their effect cannot be quantified unless the pathways and processes involved in the delivery of N species and P fractions from organic sources (including organic matter in arable soils as well as organic manures) are also defined and quantified. This is particularly the case in catchments with mixed agricultural operations, and it leads to a closer consideration of the role played by livestock manures as sources of N and P input to freshwaters.

1.5. Livestock agriculture and organic sources of nutrient input to freshwaters

Since the Second World War, and particularly in the 1960s and 1970s, the agricultural industry in the UK has undergone a process of intensification and specialisation. One consequence of this process has been the decline of the traditional mixed arable and livestock farm (Spedding, 1983). Arable operations tend to be concentrated in the east of the UK, where the factors of flatter landscape and drier than average climate combine to make favourable conditions for the intensive production of crops such as barley, wheat and potatoes. Conversely, the factors of poorer soils, undulating landscapes, and a wetter than average climate combine to make conditions in the west of the country more suited to dairy, beef cattle, and sheep production operations. This distribution in land-use is reflected in the proportion of agricultural land under grass in different parts of England and Wales (see Fig. 1.1). The areas in the west with the darkest shading in Fig. 1.1. contain around 66 % of the grass in England and Wales, with grassland over five years old and rough grazing accounting for more than 40 % of this total. The central areas contain approximately 25 % of the total grass in England and Wales, where as the lightly shaded areas of the east contain less than 20 % (figures from Royal Society, 1983).

Whilst it is overly simplistic to portray an east-west split in agricultural operations and to imply that mixed farming is in terminal decline, for the purposes of examining the transport of nutrients it is useful to consider two contrasting agricultural scenarios. Firstly, there is the intensive arable operation. This operation is highly mechanised, relying on high yielding crop varieties that require high inputs of inorganic fertiliser. In addition, the use of pesticides allows annual cropping without rotation. Thus, the soil is left without crop cover for a portion of every year, increasing the likelihood of nutrient losses due to the processes of leaching and soil erosion (Seymour and Girardet, 1986). N is lost largely as soluble NO_3^- -N in drainage waters, and P is lost largely as PO_4^- -P bound to eroded soil particles, although these losses can be much reduced if fertiliser application is avoided in the autumn in particular and matched to crop requirement at other times (Wild, 1993). Although ground is at times left without crop cover in organic

rotation based systems, there is evidence that organic systems can reduce the risk of erosion by maintaining the structure and organic matter content of soils (Reganold, 1988), and there is also evidence that careful management of an organic rotation increases the efficiency with which nutrients are utilised, which in turn reduces the amount of nutrient loss from the system (Seymour and Girardet, 1986; Elm Farm Research Centre, 1988).

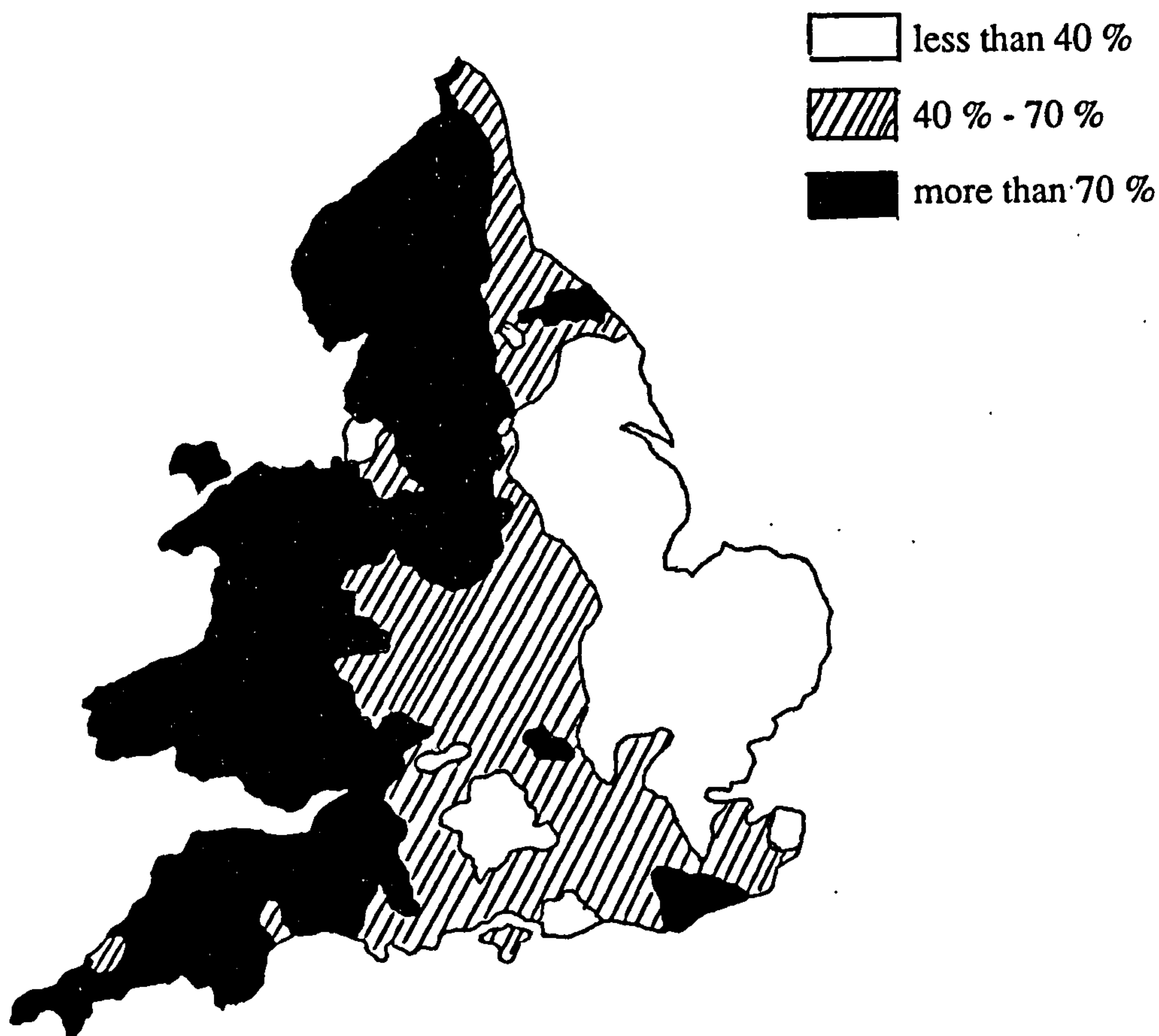


Fig. 1.1. The proportion of agricultural land under grass in England and Wales (from Royal Society, 1983).

Secondly, there is the intensive livestock operation. Again this operation is highly mechanised, and it has relied on increasing the productivity of the livestock enterprise. Spedding (1983), cited the case of the dairy industry. In 1948, a dairy unit yielding 4500 l of milk per cow at a stocking density of 1.7 cows per hectare was regarded as

exceptionally productive. In the early 1970s, figures of 5500 l per cow and a stocking density of 2.4 cows per hectare were regarded as the norm. Figures from the Royal Society (1983) indicated that as well as increases in productivity, the actual number of animals in the UK was increasing. For example, the total number of cattle in the UK in 1950 was estimated at 10.6 million, compared with 13.5 million in 1979.

Intensification of livestock operations inevitably leads to production of more animal manure for a given area of land. In addition, livestock are frequently housed indoors during the winter, leading to the accumulation of manures and increased pressure on storage facilities, with the development of these facilities often failing to keep pace with the intensification of the operation. The combination of increased stocking density and indoor housing can lead to excessive land applications of manures to avoid the overloading of storage facilities. This is most likely to happen in late winter when land is wet and susceptible to traffic damage, which if it occurs will facilitate the increased runoff of water and transport of nutrients (Parkinson, 1993). To avoid the overloading of storage facilities livestock may also be turned out to grazing earlier than planned. However, if the land is still relatively wet from winter rain it will in this case be susceptible to damage from intensive animal trampling (poaching) rather than wheeled traffic. Furthermore, there will still be applications of nutrients to the land in the form of animal excreta, so the potential for the increased transport of nutrients remains. It could be argued that with careful storage and application, the nutrients within livestock manures could be utilised to increase yields of herbage for the livestock to consume. However, the relative cheapness and ease of use of inorganic fertilisers reinforces the view of livestock manure as a waste with an attendant disposal problem, rather than a valuable nutrient resource (Dam Kofoed, 1984; Tunney, 1984; Edwards, 1990). Given this situation, an increase in the transport of N and P to receiving freshwaters would be expected, both from the diffuse source of heavy applications of manure to the land surface, and also from the point source of over-burdened storage facilities.

Recently published figures support this expectation in that recorded incidents of pollution of water courses due to agricultural runoff increased in number throughout the 1980s (NRA and MAFF, 1990). The increase in recorded runoff pollution incidents due

to cattle farming in particular is depicted in Fig. 1.2. Even if some of the increase was due to the increased reporting of incidents in accordance with increased environmental awareness, it is evident that a considerable number of pollution incidents were occurring. And even if the number of recorded incidents is seen to decrease throughout the 1990s, the need to quantify the impact of these incidents in terms of the amounts of N and P transported remains.

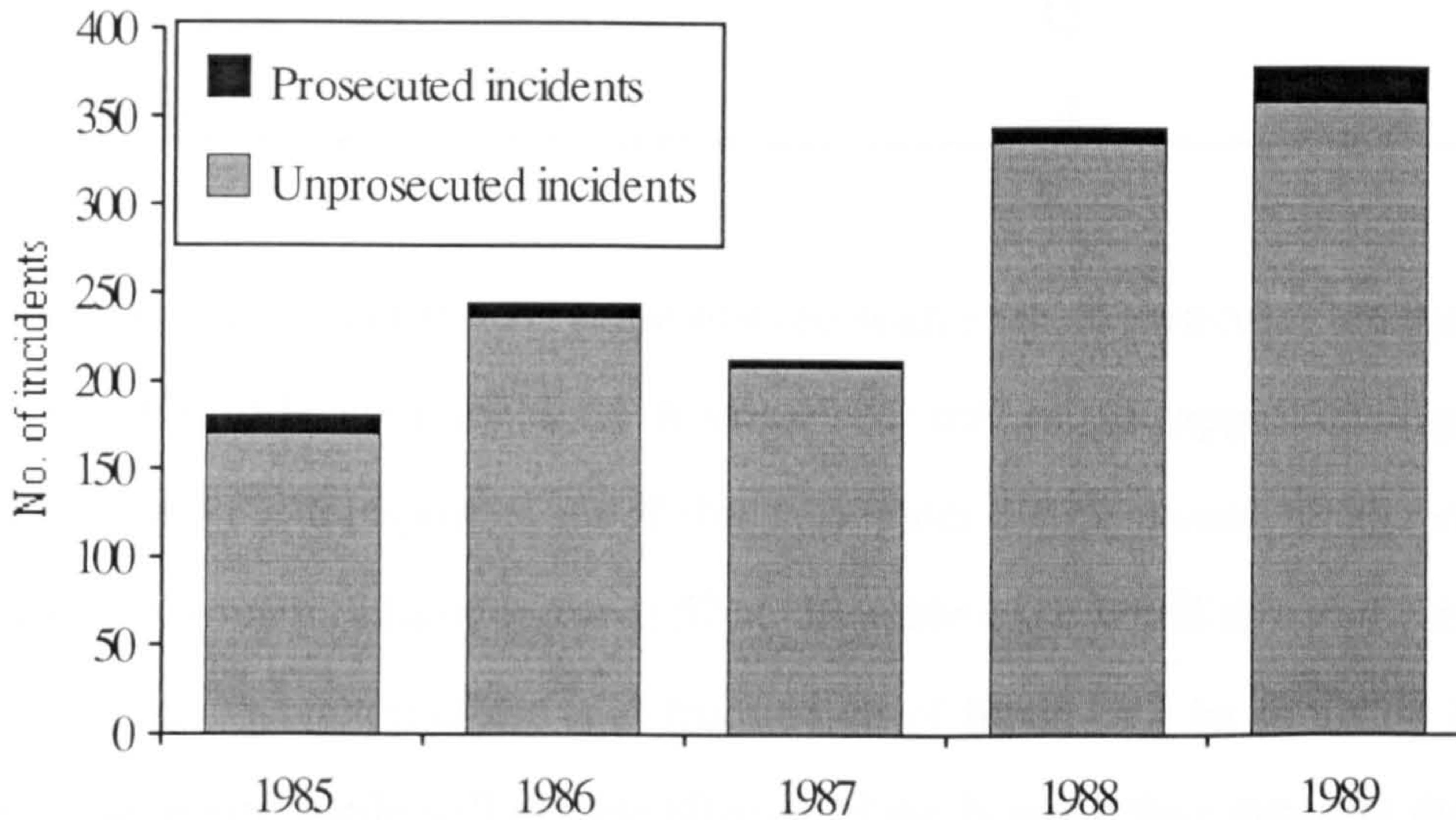


Fig. 1.2. Land runoff pollution attributed to cattle farming, incidents and prosecutions, 1985-1989 (figures from NRA and MAFF, 1990).

Fig. 1.2 summarises temporal increases in pollution incidents. As one example of spatial variability in the incidence of pollution, Table 1.2 compares runoff pollution incidents due to cattle in NRA South West Region with the total number of incidents for England and Wales. It can be seen that South West Region accounted for a considerably higher proportion of the total number of pollution incidents than its area would suggest. This is perhaps one indication of the consequences of concentrating intensive livestock farming operations in certain areas of the country, particularly those areas such as South West England which are characterised in parts by undulating landscape and higher than average annual rainfall totals.

Table 1.2. Land runoff pollution incidents due to cattle, 1989 (figures from NRA and MAFF, 1990).

	South West Region	Total England and Wales
Reported incidents	128	380
Serious incidents	32	68
Prosecutions	4	20

The transport of N and P from cattle manure sources is of particular interest in light of the quantities of N and P involved. A single cow will excrete approximately 18 kg of P per year, and the transport of all of this to a water course would be equivalent to the typical load from 212 ha of forest or 57 ha of arable land. It will also excrete 58 kg of N per year, the equivalent of the load from 68 ha of forest or 6 ha of arable land (Moss, 1988). Generally, cattle will excrete 80-90% of the N and P they ingest in plant material (De La Lande Cramer, 1985), which has important implications for the transport of N and P when one considers that until relatively recently, grassland still accounted for approximately 38 % of agricultural land-use in the UK (Royal Society, 1983), and in the European Union as a whole, grazing accounted for 50 % of grassland use (Tunney, 1984).

In lowland catchments with mixed land-use, grazing may often be restricted to the more steeply sloping land between plateaux and water courses, allowing the more suitable flatter lands to be used for highly mechanised intensive arable production (Heathwaite *et. al.*, 1990b). Such a system of land use inevitably increases the likelihood of increases in N and P transport, as quantities of nutrients are being voided in areas close to water courses, where the transport energy of water flowing downhill is maximised by the gradient of the slope. Grazing of livestock also results in the high spatial variability of nutrient application, with most of the nutrients being concentrated within small patches of voided manure (Cooke, 1984). This reduces the efficiency with which the

surrounding vegetation can take up the applied nutrients, which in turn leaves more N and P available for transport to receiving freshwaters.

Understandably, there has been a response to the increase in the number of incidents of freshwater pollution attributed to livestock manures. There is now a *Code of Good Agricultural Practice for the Protection of Water* (MAFF and WOAD, 1991). The guidelines concerning livestock manures contained within this code are summarised thus.

1. Land-surface applications of manures and slurries should not exceed $250 \text{ kg ha}^{-1} \text{ a}^{-1}$ of total N equivalent.
2. In high risk areas (for example, steep slopes, land with poor drainage), such applications should be limited to $50 \text{ m}^3 \text{ ha}^{-1}$ with at least three weeks between applications.
3. There should be no applications within 10 m of a water course.
4. A reduction in the intensity of grazing in the autumn is to be encouraged, in order to reduce the risks of nutrient transport as soils become wetter and rates of plant uptake decrease.

While clearly being based on experience and sound reasoning, the more quantitative scientific basis for these guidelines is less apparent. If one is to be effective in controlling the quality of freshwater, there remains the particular need to quantify the contribution to increased transport of N and P attributable to livestock manure sources. As explained earlier, for diffuse sources, this need involves defining the pathways of nutrient transport, and defining the processes of nutrient transformation, thus allowing a quantification of the absolute and relative amounts of N species and P fractions that are delivered along the defined pathways. Cooke (1984) indirectly supported this assessment in the context of the efficient use of N:

"Because nitrogen losses from livestock wastes constitute a major loss of nitrogen from UK agriculture, we recommend that work aimed at quantifying the main pathways of loss, devising practical ways of minimising them, and improving the conversion of nitrogen in livestock feed to protein for human food be accorded high priority."

In response to the need outlined above, a programme of research was developed.

1.6. Research - Aim and objectives

The programme of research was designed to fulfil the following basic aim.

Aim: To further the understanding of the pathways and processes involved in the transport of N and P following applications of cattle manure to sloping grassland.

Fulfilment of this aim involved achieving a set of six specific objectives, and these objectives were defined and arranged in order to address the problems of scale that arise when seeking to understand more about the pathways and processes of N and P transport from a diffuse source. Firstly, a detailed knowledge of pathways and processes was sought through the construction of a conceptual model, followed by examination of the components of this model by means of controlled plot-scale field experiments (objectives 1 and 2). Heathwaite *et. al.* (1993) have noted the importance of linking the findings of detailed one-dimensional profile or two-dimensional plot studies to what happens in the three-dimensional reality of a drainage basin, and in this case that link was made through experimentation as defined in objective 3. While it is true that processes are most accurately described at the smallest scale, the complexity of the system under examination often makes it impractical to aggregate many small scale descriptions in order to fully describe processes at the large scale without some form of generalisation (Armstrong and Burt, 1993). In response to this problem, objectives 4

and 5 were defined as the construction of a catchment-scale mathematical model of the concepts under examination. This was followed by the identification of the generalisation and loss of detail in the model that could be sustained before it failed in the purpose defined by the final objective. Having described the approach to the definition and ordering of the six objectives, they can now be listed in detail as follows.

1. Produce a conceptual model of N and P transport from the defined source. The model is to be based on current understanding as derived from literature, and includes the following components.

(a) Hillslope hydrology - pathways of water movement.

(b) Processes of transformation of N from one species to another, and the relative proportions of each species that are transported within each pathway of water movement.

(c) Processes of transformation of P from one fraction to another, and the relative proportions of each fraction that are transported within each pathway of water movement.

2. Conduct a programme of plot scale field experiments in order to examine pathways and processes in detail under controlled conditions.

3. Examine N and P transport by experimentation at the field to headwater catchment scale, in less detail and under less controlled conditions than at the plot scale, in order to evaluate the general timing and magnitude of N and P transport at a more realistic spatial scale.

4. Use the results of experiments at both scales to select and calibrate an appropriate mathematical structure for modelling the defined concepts at the headwater catchment scale.

5. Using data available from previous monitoring programmes at the headwater catchment scale, test the simulation capabilities of the model at this scale.

6. Use the model to predict the effect of different manure application practices on the transport of N and P, thus enabling the identification of particular circumstances where further experimental work would be beneficial.

These objectives are portrayed as components of a research programme in Fig. 1.3, and the following chapters deal with each of these components in turn, beginning with the conceptual model and ending with the application of the mathematical model.

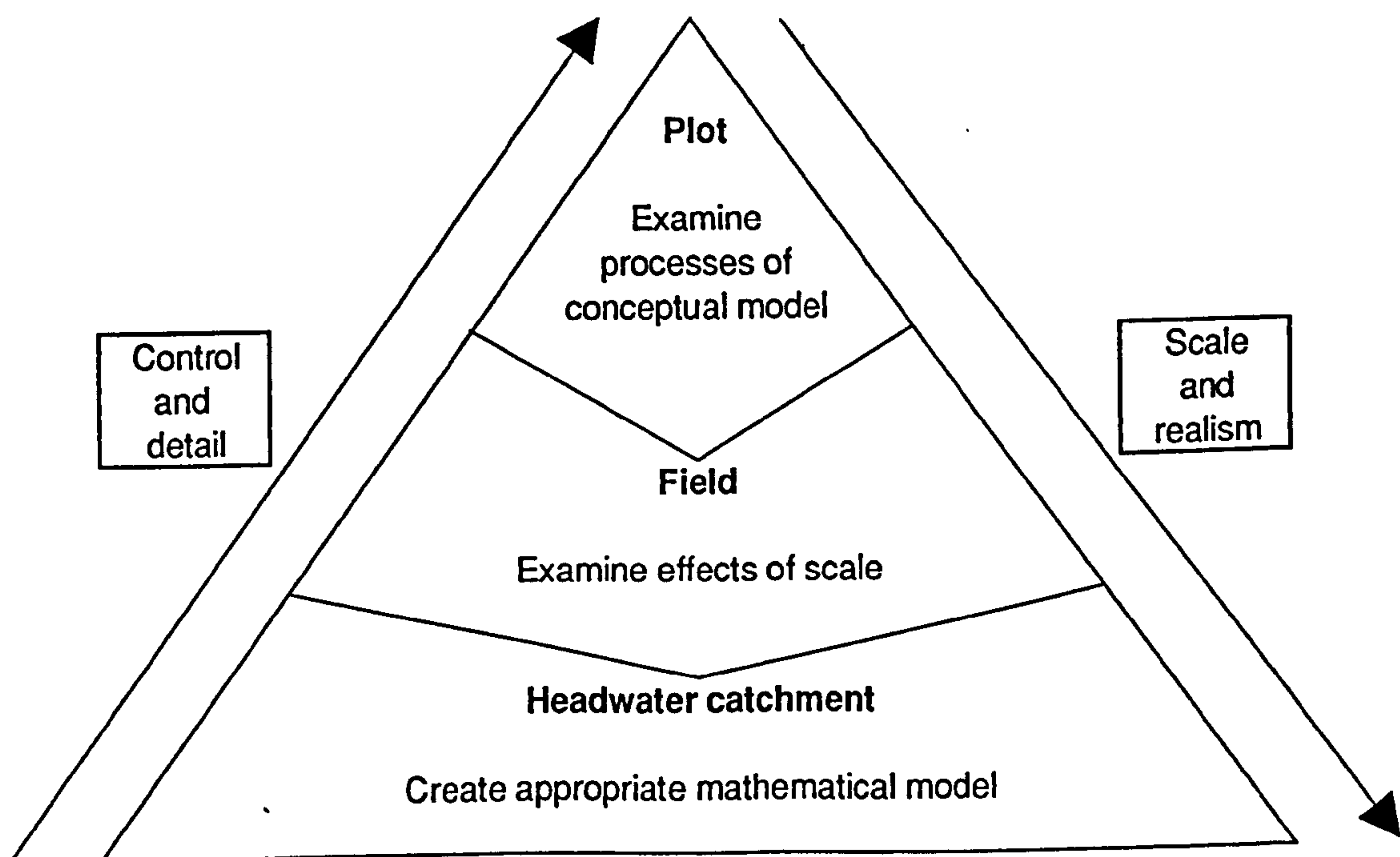


Fig. 1.3. Components of the research programme

1.7. Chapter summary

1. The quality of freshwaters can be defined in numerous ways.
2. Increased input of nutrients, in particular N and P, can have negative impacts on water quality by several definitions. These negative impacts include.
 - (a) Eutrophication, which can reduce the wildlife habitat and amenity value of freshwaters, and can increase filtration costs where water is supplied for domestic use.
 - (b) Possible risks to health associated with increased concentrations of nitrate in drinking water, in particular the condition of methaemoglobinaemia in infants, the occurrence of stomach cancer in humans, and the poisoning of ruminatory animals such as cattle and sheep.
3. Increased input of N and P can be attributed to a number of sources. These sources may be a discrete point, such as the outlet pipe from a sewage treatment works. Alternatively, they may be diffuse, such as an intensively farmed arable catchment subject to large applications of inorganic fertiliser.
4. In order to control water quality, one must not only be aware of all the sources of increased input of N and P. One must also define the pathways along which transport takes place, and the processes that determine and quantify which species of N and fractions of P are delivered along each pathway.
5. A number of sources of increased transport of N and P can be attributed to agriculture.
6. Traditionally, research on agricultural sources has focused on the transport of inorganic ions of N and P, often from intensive arable operations. However, even if these are the major sources of increased transport in many catchments, increased

transport from organic sources (manure) of both organic and inorganic forms of N and P must also be quantified. Then the effects of each source can be accurately assessed, both independently, and in conjunction with other sources.

7. The processes of intensification and specialisation in agriculture may have created the situation where livestock manure (in particular that from cattle) is a major source of increased transport of N and P in certain areas of the UK.

8. In view of the above points, a programme of research was proposed with the following general aim: to further the understanding of the pathways and processes involved in the transport of N and P following applications of cattle manure to sloping grassland.

Chapter 2

A Conceptual Model

2.1. Model Components

The transport of N and P from grassed hillslopes to receiving waters is determined by the interaction of a series of hydrological and biochemical processes. The processes of hillslope hydrology define the pathways of N and P transport, and biochemical processes define N speciation and P fractionation within each pathway. Both these sets of processes are affected, and to some extent controlled, by agricultural operations and topography. This combination of processes and controls forms the structure of the conceptual model outlined below. Different approaches to the problem of mathematically describing this conceptual model structure are discussed later in Chapter 5.

2.2. Hillslope Hydrology

The processes of hillslope hydrology (for an idealised convex slope) are detailed in Fig. 2.1. Here, the main concern is with mechanisms of water flow from slopes both during and immediately following rainfall, since it is usually the input of rainfall that triggers the most significant outputs of water, N, and P from a hillslope. Other hydrological processes will be considered in the context of how they affect soil-water conditions preceding rainfall events.

At the onset of precipitation, the infiltration rate of the soil is usually high, especially if the soil near the surface is well structured and antecedent water content is low. This infiltration rate is progressively reduced as rain splash causes the surface structure of the soil to collapse, and wetting causes soil swelling and the closure of fissures (Romkens *et. al.*, 1990; Wild, 1993). Eventually a steady rate of infiltration is reached. If at any time the rate of rainfall exceeds the rate of infiltration, then infiltration excess,

or Hortonian, overland flow will occur (after Horton, 1933; overland flow may also be called surface runoff). This model of overland flow is more accurately described as delayed Hortonian overland flow, because there is likely to be a delay following the onset of rainfall before the infiltration rate becomes less than the rate of rainfall.

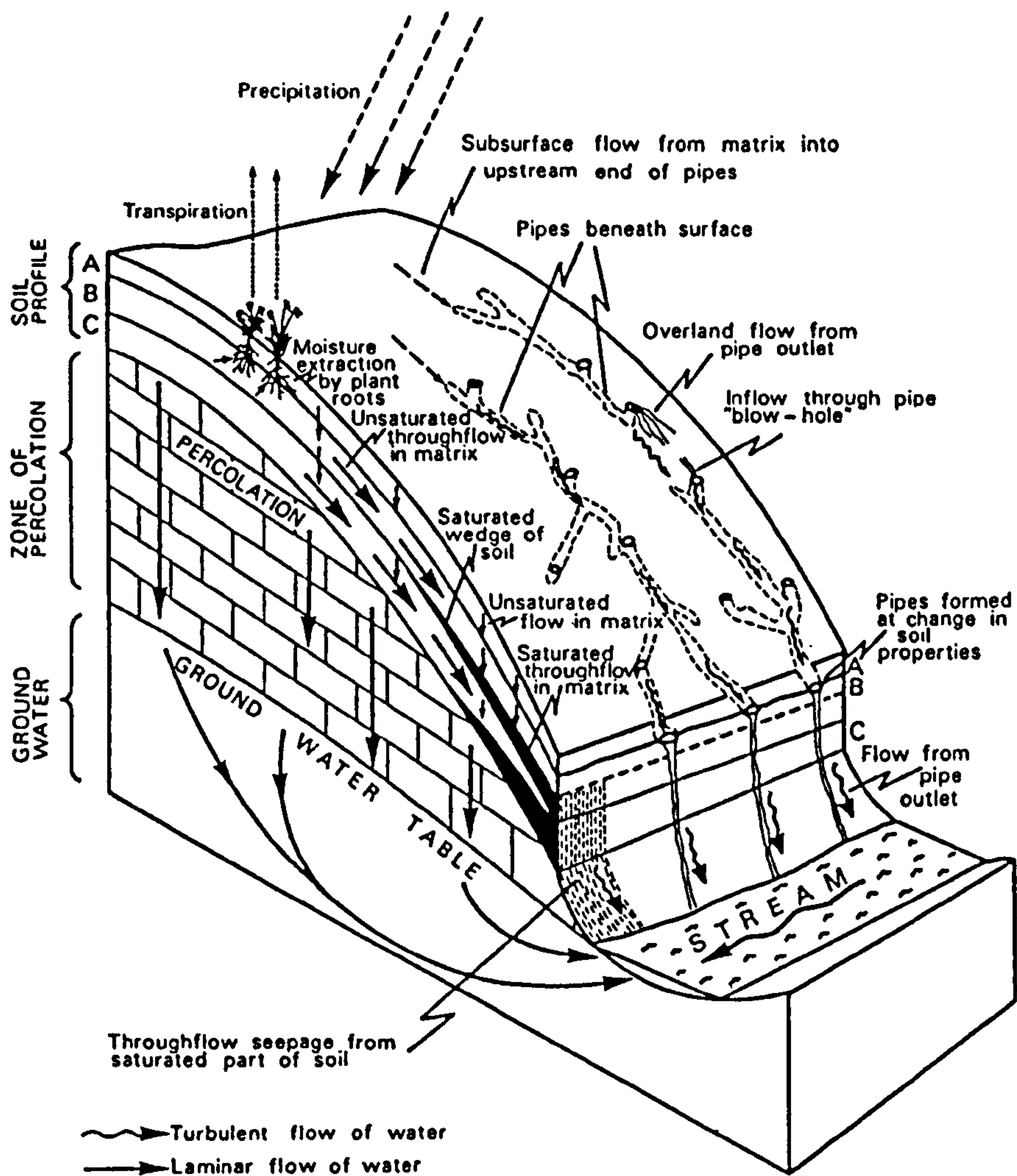


Fig. 2.1. The processes of hillslope hydrology (from Atkinson, 1978)

The concept of infiltration excess overland flow occurring uniformly over an entire hillslope surface is now generally regarded as false (Anderson and Burt, 1990). More often, rapid Hortonian overland flow will occur in restricted areas where the initial infiltration capacity of the soil has been reduced by human or animal activity (Gerits *et al.*, 1990). For example, heavy grazing on grass slopes can cause compaction and poaching on parts of the slope surface, significantly reducing infiltration capacity, and

the likelihood of infiltration excess overland flow is thus increased (Heathwaite *et. al.*, 1990b). Repeated applications of cattle slurry on wet soils, using heavy machinery, may cause structural damage similar to that caused by livestock, with similar consequent effects (Lea, 1979; Pollock, 1979). The concept of the localised occurrence of infiltration excess overland flow, caused by spatial variation in land-use effects, is the basis of what is often termed the "Partial Area Model" for this particular flow mechanism (after Betson, 1964).

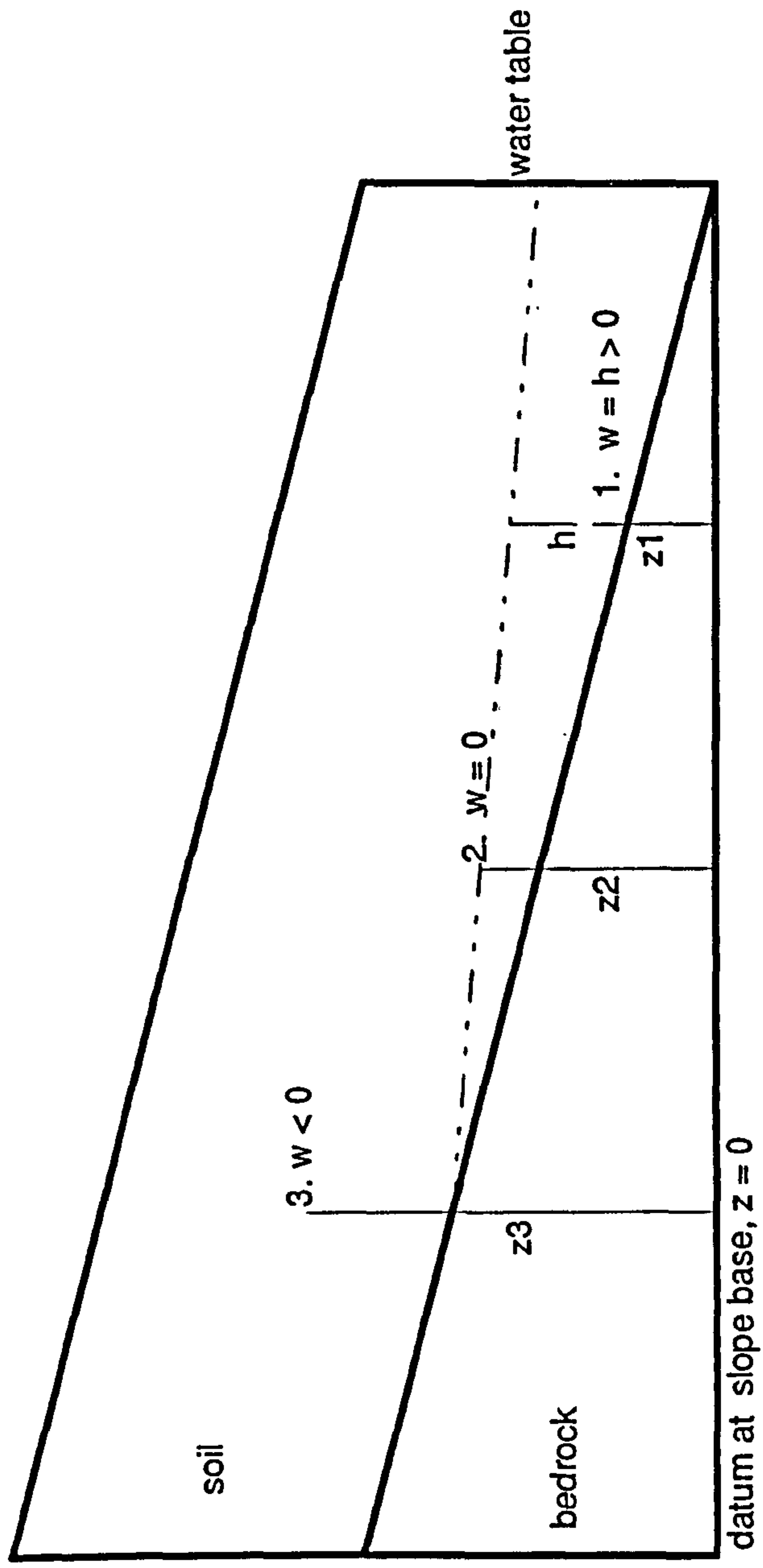
Water infiltrating the soil will begin to percolate both vertically through the profile and laterally downslope. Rates of sub-surface water movement are quite variable, depending on the size of the pores in the soil structure through which transmission of water is taking place. Hydrologists use numerous interchangeable definitions of soil pore size, so before describing sub-surface flow mechanisms it is useful to attempt some kind of standardisation. Bache (1990) has offered the following definitions of pore size in relation to their function in the transmission of water.

- 1) Residual pores ($< 0.5 \mu\text{m}$) - no transmission of water.
- 2) Storage pores ($0.5 - 50 \mu\text{m}$) - retain water against drainage under gravity, involved in matrix flow, also termed micropores.
- 3) Transmission pores ($50 - 500 \mu\text{m}$) - allow free drainage under gravity, sometimes termed macropores, also involved in matrix flow.
- 4) Fissures ($> 500 \mu\text{m}$) - allow turbulent flow as in pipes, involved in preferential flow, also termed macropores, or pipes where large and continuous.

Upon infiltrating the soil, some water may be conducted rapidly through fissures, root channels, or macropores (Germann, 1990; Armstrong and Burt, 1993; Wild, 1993). Flow through these discrete channels has been referred to as pipe flow or preferential flow, the size of the channel required to support this type of flow having been defined as that which causes the water flow regime to be turbulent, and therefore non-Darcian (Atkinson, 1978; Massey, 1983). Soil compaction due to grazing or heavy machinery may cause the collapse of these channels near the surface, therefore reducing the amount of water that initially flows through this pathway.

Water also flows through the smaller soil pores that constitute the soil matrix. The flow regime here is usually laminar, thus conforming to Darcy's Law (Atkinson, 1978; Massey, 1983). The rate of this matrix flow is dependent on the difference in hydraulic potential between two given points. Hydraulic potential basically consists of two components, gravitational potential and matric potential (or suction). Gravitational potential relative to the base of a slope increases as one moves up the slope. Matric potential depends on the capillary tension between the water and surface of the soil pores, and is defined as the difference between the pore water pressure and atmospheric pressure. It can be regarded as the head of water required to overcome the pore water suction and thus set the water in motion, and as such it is often expressed as a negative number in unsaturated conditions (Berryman *et. al.*, 1976; Atkinson, 1978). In saturated conditions, matric potential becomes positive to a degree which is determined by the depth below the water table of a given point in the soil profile (see Fig. 2.2). Water in the soil matrix flows from regions of high hydraulic potential to regions where the hydraulic potential is lower, and the rate of flow depends on the potential gradient between two given points. Matrix flow occurs in both saturated or unsaturated conditions, and while these two flow regimes are similar in that water flows in response to a potential gradient, the rate of movement in unsaturated conditions is also affected by the difference in water content and hydraulic conductivity between any two points. These additional factors are incorporated in the Richards equation, which is normally used to describe matrix flow in unsaturated conditions (Armstrong and Burt, 1993).

The nature of a stream hydrograph both during and following rainfall is affected by the degree of interaction between preferential and matrix flow processes. Preferential flow may account for a rapid rise in stream discharge following rain (Coles and Trudgill, 1985), especially if preferential flow paths lead to an artificial drainage network (Wild, 1993). The water that follows this pathway can be described as "new" water, and it will have a different chemical composition to the "old" water already resident in the soil matrix. Alternatively, preferential flow could be responsible for rapid recharge of a saturated zone at the base of the soil profile. This facilitates a translatory or "piston" flow process, whereby old water is pushed out at the slope base by means of saturated



- Point 1. Hydraulic potential = gz_1 (Gravitational potential) + h (Matric potential)
- Point 2. Hydraulic potential = gz_2 (Gravitational potential) + 0 (Matric potential)
- Point 3. Hydraulic potential = gz_3 (Gravitational potential) + w (Matric potential)

Fig. 2.2. Definition of hydraulic potential for soil moisture on a hillslope (reproduced from Atkinson, 1978)

matrix flow, even though preferential flow is responsible for recharge further upslope (Burt and Butcher, 1985a; Burt, 1987; Anderson and Burt, 1990). During their hydrological studies in South Devon, Troake and Walling (1973) noted two peaks in stream storm hydrographs. The first "quick flow" peak only accounted for 0.2 % - 3 % of total runoff, and was attributed to localised overland flow. A larger "delayed flow" peak was attributed to sub-surface throughflow from wetter areas of the soil matrix. The same observations were made later by Burt *et. al.* (1983), and interpreted similarly. Quick flow was attributed to both overland flow and preferential flow. Delayed flow, occurring up to two days after the quick flow peak, was attributed to translatory sub-surface throughflow. Although a double peak storm hydrograph may not be representative of the response of streams to rainfall in general, it is evident that the nature of the interaction between surface and sub-surface flow mechanisms has important implications for both the timing and chemical composition of stormflow from hillslopes. These implications will be discussed further below.

Hillslope hydrological processes are affected by topographic factors as well as agricultural operations. Hollows, for example, provide a focus for water drainage, thus increasing the likelihood of saturation of one particular area which varies in size, depending on rainfall intensity and duration. This generates what is termed a "Variable Source Area" of saturation excess overland flow, the saturation excess consisting of a mixture of rainfall on the saturated area and sub-surface water that has flowed downslope before being forced to return to the soil surface (Anderson and Burt, 1990). Even if surface saturation does not occur, hollows are likely to contribute as Variable Source Areas to increased rates of sub-surface flow (Burt and Arkell, 1986; Burt, 1987; Anderson and Burt, 1990). The delayed stormflow peaks observed by Troake and Walling (1973), and Burt *et. al.* (1983) are attributed to Variable Source Areas of increased surface and sub-surface flow. Topographic factors can therefore contribute to the generation of surface and sub-surface stormflow at rainfall intensities much lower than those required to generate infiltration excess overland flow.

The permeability of the bedrock beneath the soil profile is important in determining the significance of certain hillslope hydrology processes. Where soil overlies impermeable

bedrock and there is no flat floodplain to separate a steep slope from the stream, subsurface lateral throughflow becomes a major run-off mechanism (Burt and Arkell, 1986). In other cases, more water will percolate vertically through rock to groundwater, perhaps re-emerging at the foot of a slope after some time as the groundwater level fluctuates in a damped response to rainfall inputs.

Finally, the processes of evaporation and transpiration can significantly slow the movement of water both down the soil profile and downslope, depending upon the season. They may also have a marked effect on soil structure, for example, causing cracking in exceptionally dry periods. This cracking would initially induce preferential flow when rainfall occurs subsequently, until the cracks are closed by soil swelling and surface sealing (Romkens *et. al.*, 1990).

Three mechanisms of water flow from hillslopes have been described, and these are summarised in Fig 2.3. It is important to note that hillslope hydrological processes are subject to a high degree of spatial and temporal variability, as a consequence of both topographic controls and agricultural operations. Fig 2.4 illustrates the interaction between storm flow mechanisms, topography, and human activity.

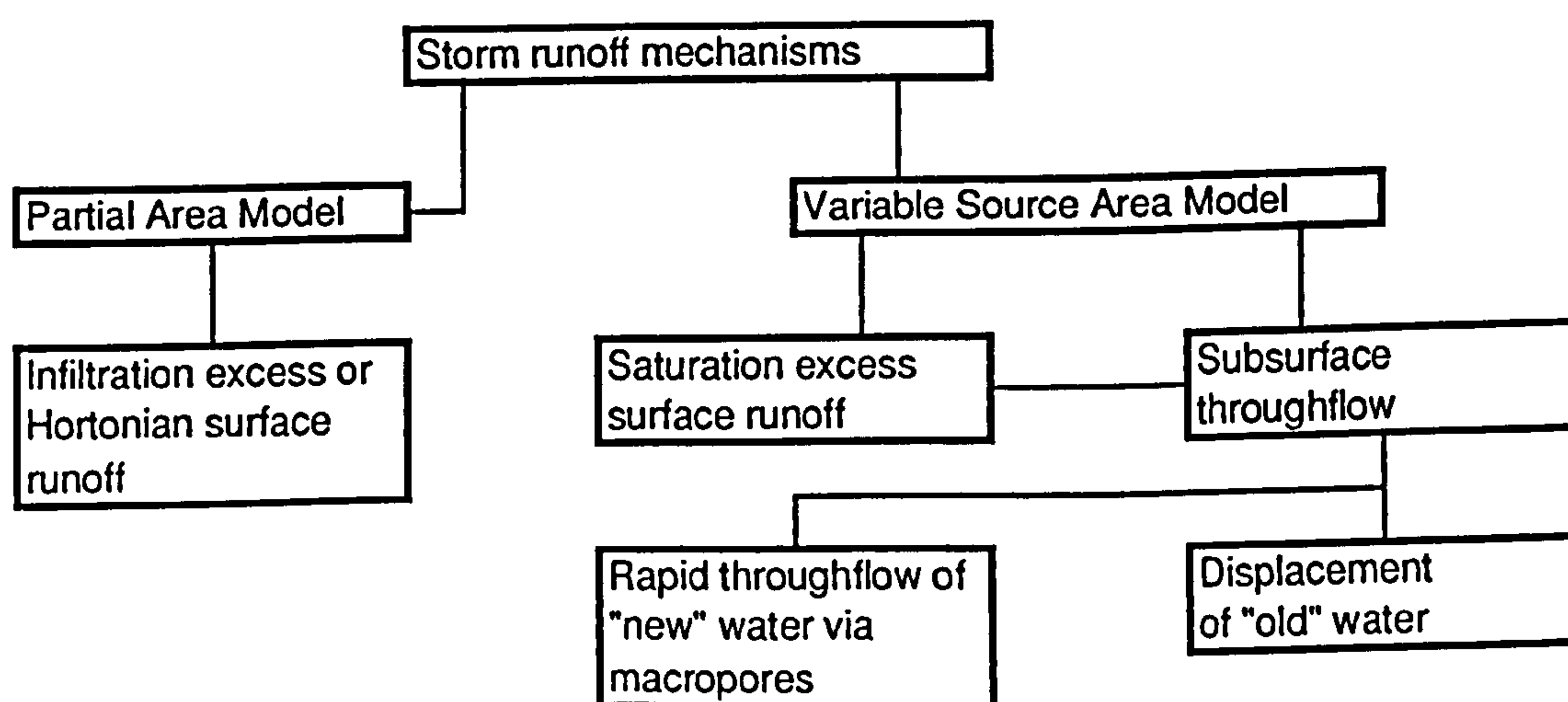


Fig. 2.3. Mechanisms of storm runoff from hillslopes (from Burt, 1987)

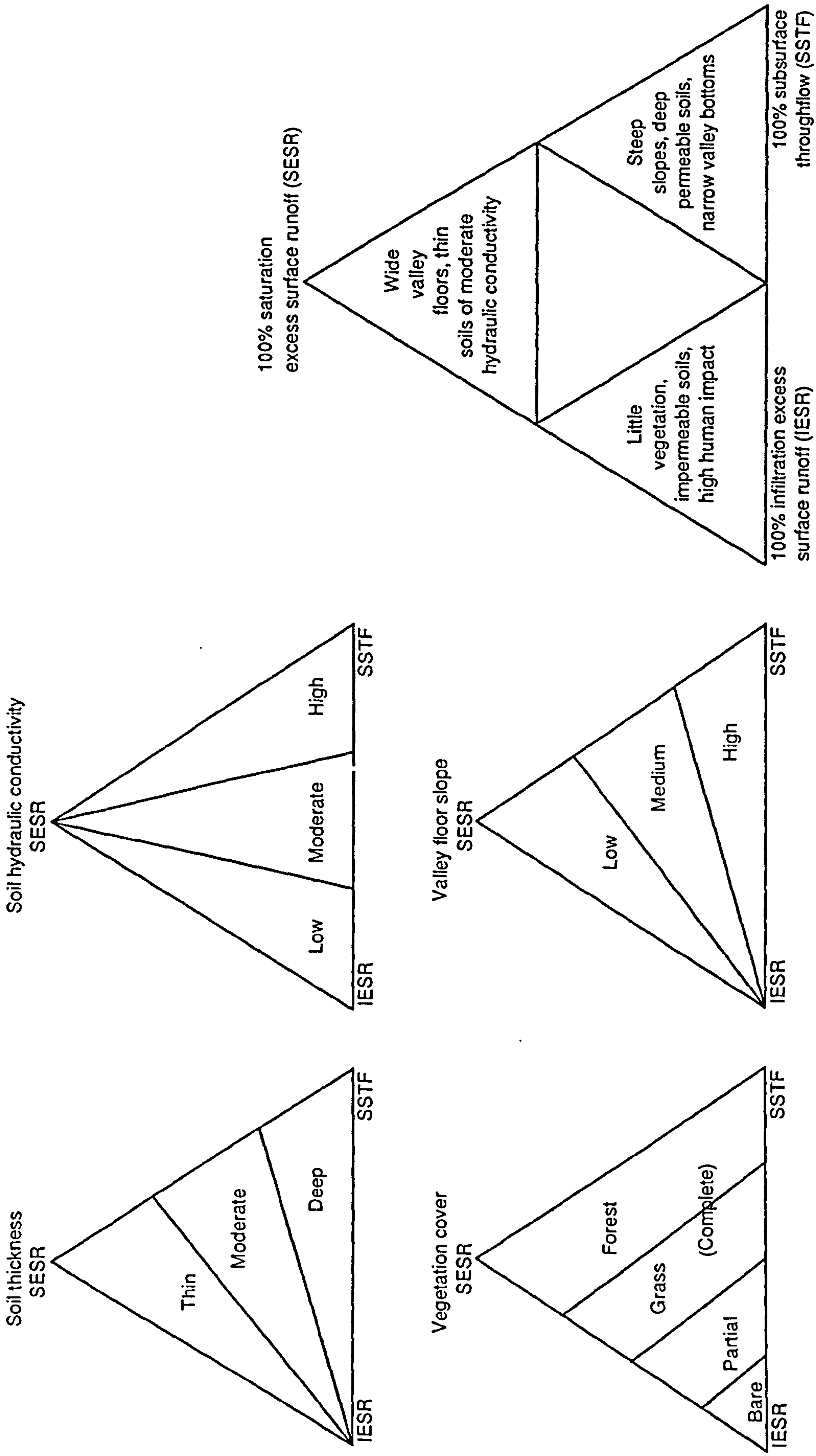


Fig. 2.4. The origin of stormflow in relation to catchment characteristics. The large triangle summarises the other four and shows how the percentage of flow for each runoff type is scaled along the appropriate axis. The four small triangles show storm runoff production with respect to specific catchment properties. (From Anderson and Burt, 1990)

2.3. Nitrogen biochemistry

For the purposes of this study, the main sources of N available for transport were considered to be, inputs in applications of cattle manure, storage and release from the soil-water structure, and to a lesser extent, inputs from the atmosphere. Each of these sources and the interaction between them is discussed in turn.

Cattle manures can be placed into one of three groups, manure, slurry, or dirty water, each group being characterised by the amount of dry matter present in the manure and the methods required to handle it. In the early 1980s it was estimated that in England and Wales some 70% of collected cattle droppings were collected as slurry, with most of the rest being collected as farmyard manure (Royal Society, 1983). Current advice within the *Code of Good Agricultural Practice for the Protection of Water* (MAFF and WOAD, 1991) allows for the surface application of dirty water from livestock units at any time of the year provided conditions are suitable, whereas the guidelines governing the application of manure and slurry are more strict. Increasingly, farms with a limited liquid waste storage capacity are separating slurry into dirty water and a solid for handling separately in the spring as a solution to winter storage problems. However, since the above classifications of manure take no account of N content and speciation, which for dirty water can be quite variable (see Table 2.1), the implications of changes in manure handling practices in terms of the transport of N have yet to be evaluated (see Parkinson, 1993).

Table 2.1. Typical analyses of N in cattle manures (fresh weight basis)

	Dry matter (%)	Total N (%)
Cattle manure ¹	25	0.5-0.6
Cattle manure ²	25	0.6
Cattle slurry ¹	10	0.5
Cattle slurry ²	10	0.5
Dairy dirty water ²	0.1-1	0.002-0.2

¹ Reproduced from Wild (1993)

² Reproduced from Archer (1991)

The speciation of N within cattle manures is important in determining the pathways of N loss. Manures generally do not have a high concentration of nitrate, but they do have a high ammonium concentration, which is readily volatilised as ammonia if manures are applied to the land surface (Loehr, 1977; Archer, 1991; Powlson, 1992). Dam Kofoed (1984) notes that 30-35% of the total N in farmyard manure is in the ammonium form, the figure for slurry being 60-65%. The rest of the N is classified as organic. De La Lande Cramer (1985) divides slurries into two fractions, mineral and organic, and states that in general 80% of the mineral fraction will be ammonium, and it is possible for all of this ammonium to be volatilised. Figures relating to ammonia volatilisation during experimental applications of cattle slurry to grassland are given by Wild (1993). In the experiments, 42% of the N in the slurry was present as ammonium. For winter surface application, 31% of the total N application was volatilised as ammonia, for spring surface application, the figure was 20%. Smith (1992) quotes the same experiment and gives the loads. These are, 248 kg ha⁻¹ total N applied in winter and 262 kg ha⁻¹ in spring, resulting in 77 kg ha⁻¹ ammonia volatilised in winter and 53 kg ha⁻¹ in spring. Vinten and Smith (1993) note that ammonia volatilisation from dung and urine patches on grazed grassland can be particularly high, but where the N is applied in slurry, volatilisation losses can be reduced considerably if the slurry is injected beneath the surface. They also note that the volatilisation process is very temperature dependent, with higher temperatures facilitating the conversion of NH₄OH to NH₃ gas and water. Both ammonium and organic N can be transported within water leaving hillslopes as overland flow. Whilst organic N may not be regarded as being available for conversion to more soluble forms such as nitrate in the short term, as ammonium is (Archer, 1991), this does not make it immobile. Surface waters can carry manure just as they carry soil particles downslope during erosive processes. Heathwaite *et. al.* (1990b), when recording surface runoff from land heavily grazed by cattle, noted that 40% of total N delivery was as organic N, and 60% was as ammonium.

The occurrence of overland flow from any area depends on either an infiltration excess or saturation of the profile. It has already been acknowledged that heavy grazing by cattle reduces the infiltration capacity of areas by compaction, and increases

susceptibility to erosive forces by removal of vegetation (Heathwaite *et. al.*, 1990b). Therefore, the areas most susceptible to infiltration excess overland flow are also the areas with the highest amounts of surface deposited N in dung and urine. Such areas are key sources of surface delivered organic and ammonium N. Surface application of organic manure can have similar results, which Pollock (1979) summarises as follows. Firstly, ammonium ion concentration may cause damage to plant foliage, and heavy applications may smother plant growth, thus increasing the susceptibility to erosion. Secondly, use of heavy machinery on wet soils may cause damage similar to livestock poaching. This effect is compounded if the farmer repeats applications on the same area in order to limit the area of damage. Finally, high application rates lead to the accumulation of a surface mat of organic matter, which reduces permeability to air and water, resulting in poor rooting conditions for grass. If the land is subsequently grazed, the shallow rooted grass is more susceptible to poaching, with the attendant effects described above.

Much of the rain falling onto a surface application of manure will eventually percolate into the soil profile, carrying with it quantities of soluble organic and ammonium N, which then become subject to a number of reactions. These reactions are summarised by Bache (1990) for solutes in general.

- 1) Precipitation and dissolution
- 2) Cation exchange on negatively charged surfaces
- 3) Ligand exchange on variably charged surfaces
- 4) Oxidation and reduction processes

The direction and rate of these reactions is dependent on temperature, pH, and soil water and oxygen content, and since these properties are rarely in equilibrium in soil, it follows that the dynamics of N speciation within soils is complex.

N speciation in the soil is principally affected by a series of oxidation and reduction reactions that constitute the soil N cycle (Fig. 2.5). Of the incoming organic and ammonium N, soil micro-organisms will retain parts in their cellular structure, eventually incorporating some into humus, thus building up soil organic matter. This retention of N in organic form is known as immobilisation. The reverse process,

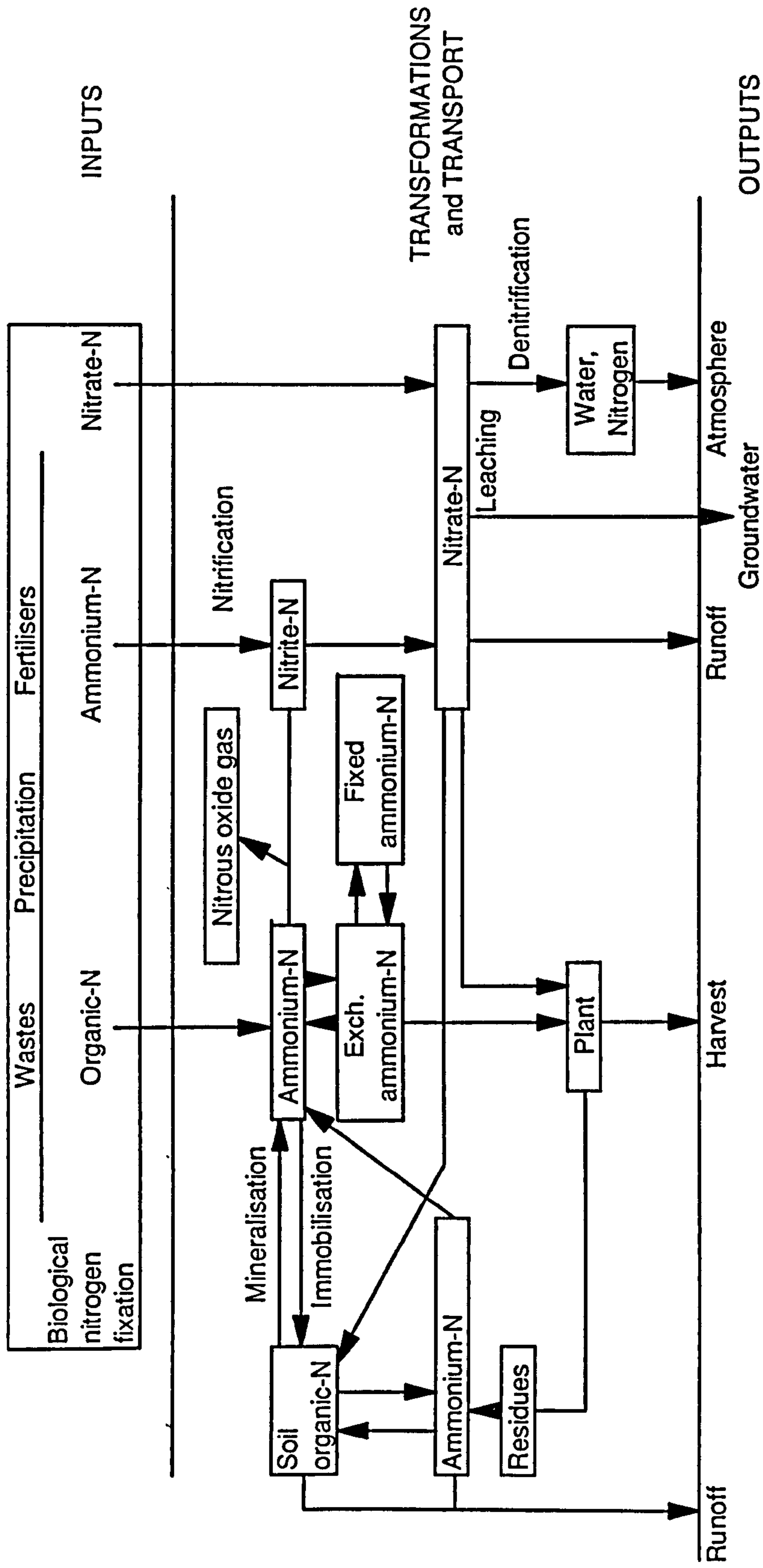


Fig. 2.5. The soil N cycle (from Keeney, 1986)

conversion of organic nitrogen to ammonium, is known as mineralisation. Both processes can occur simultaneously (Keeney, 1986; Powlson, 1992). The balance between immobilisation and mineralisation depends on a number of factors and consequently is hard to define. Perhaps the most important factor in the balance is the C:N ratio, with low ratios favouring mineralisation and high ratios favouring immobilisation (Vinten and Smith, 1993). Therefore in the short term, incorporation of fresh organic material rich in N and poorer in C (for example, cattle slurry), will promote mineralisation, whereas those poorer in N and rich in C (for example, cereal straw) will promote immobilisation (Powlson, 1992; Vinten and Smith, 1993). However, it is not just the absolute C:N ratio of the incorporated material which may determine whether mineralisation or immobilisation is promoted, the C:N ratio of the material in relation to the ratio in the soil organic matter is also of importance. As a very general guide, De La Lande Cramer (1985) states that 50% of the organic fraction of a slurry will be mineralised in the year of application, and the remaining 50% will be mineralised more slowly in subsequent years.

Ammonium is readily adsorbed within the soil as an exchangeable cation or taken up by growing plants, and therefore it is rarely transported sub-surface in significant quantities. Duxbury and Peverly (1978) did record significant quantities of ammonium in drainage from organic soils in particular, and attributed this in part to transport along preferential flow pathways. While ammonium might be adsorbed in general, in the right conditions it is rapidly oxidised by specialist bacteria to nitrite and then nitrate, a process known as nitrification (Loehr, 1977; Keeney, 1986; Powlson, 1992; Wild, 1993). Organisms use the nitrification reaction to provide energy for growth, rather than the incorporation or release of N that takes place in immobilisation or mineralisation reactions (Sprent, 1990).

Soil water content is an important factor in determining the rate of nitrification. Jarvis (1992) notes that drainage increases aeration and enhances nitrification. Following heavy applications of slurry to land in March, Thijeel and Burford (1975) observed the opposite effect. The heavy surface covering restricted evaporation over the summer and autumn, reducing soil aeration and delaying nitrification. For grassland soils, it has been

argued that the rate of nitrification increases with moisture content until field capacity is reached (presumably the point where aeration begins to be reduced markedly as transmission pores begin to fill with water), and that the nitrification rate also increases with an increase in soil pH (Royal Society, 1983). As one indication of the rate of nitrification, Wild (1993) stated that following the application of fertiliser, nitrification of the ammonium within the fertiliser can be completed in 1-4 weeks under good growing conditions.

Nitrate is soluble and mobile in soil water, rendering it susceptible to transport and leaching in sub-surface throughflow (Burt *et al.*, 1983; Powlson, 1992; Wild, 1993). Keeney (1986) has examined the movement of nitrate in soil water in detail, and concluded that rates of nitrate movement are much influenced by the interaction between preferential and matrix flow processes, just as storm hydrographs are affected by the same interaction. For example, if significant N is dissolved in water occupying larger pores, then increases in preferential flow rates through these pores will result in increased delivery of nitrate. This is probable if the larger pores are well aerated, thus stimulating the nitrification process. Alternatively, it may be that more nitrate is present in finer pores due to the processes of anion sorption or entrapment if the pores are so small as to be stagnant. In this situation, nitrate delivery will only increase with a significant increase in matrix flow, and nitrate movement will therefore be retarded if preferential flow is the dominant storm transport pathway. The problem of describing the interaction between sub-surface flow processes and nitrate transport is seen as being of increasing importance in the task of quantifying overall losses of nitrate (Addiscott, 1993). Nitrate leaching losses from grassland are generally regarded to be much lower than those from arable soils, because grasses can absorb large amounts of nitrate through a well distributed fibrous root system, and because perennial grasses can absorb nutrients throughout the year if the soil temperature and water content are at suitable levels. For annual fertiliser N additions of 250-500 kg N ha⁻¹ to grasslands in South-East England, observed leaching losses of nitrate have ranged from 2-5% of the N applied (see Royal Society, 1983). In addition to sub-surface transport, the surface transport of nitrate also occurs in connection with variable source areas of saturation

excess overland flow. Here, the nitrate dissolved in water re-emerging from the soil profile will mix with nitrate dissolved in rainfall (Burt and Arkell, 1986; Burt, 1987).

Nitrate in soil water can be reduced to gaseous NO, N₂O and N₂ which are then emitted to the atmosphere, this reduction process being known as denitrification. As with nitrification, the denitrification reaction is used by organisms to provide energy for growth (Sprent, 1990). The process occurs when soils are wet (but not necessarily waterlogged) and the temperature is high enough to support microbial activity (Vinten and Smith, 1993). The rate and extent of denitrification is also determined by carbon supply, and in general, there is little evidence of denitrification taking place below the rooting zone (Loehr, 1977; Keeney, 1986; Powlson, 1992; Wild, 1993). The experimental applications of cattle slurry previously referred to in relation to ammonia volatilisation (Wild, 1993), also contained quantification of denitrification losses. Denitrification from surface applications was low, ranging from 12% of total N applied in the winter to 2% in spring. When the slurry was injected, however, the losses were 21% and 7% respectively. Again, Smith (1992) gives the loads for the same experiment. These are, 30 kg ha⁻¹ and 4.5 kg ha⁻¹ for surface application in winter and spring respectively, and 52 kg ha⁻¹ and 18 kg ha⁻¹ for injection. The process of injection supplies a high volume of water to the soil, containing energy-rich organic substances, thus creating favourable conditions for nitrate reduction (Loehr, 1977; Vinten and Smith, 1993). Denitrification could be regarded as useful in reducing the delivery of nitrate in sub-surface waters, particularly following application of manures rich in degradable matter (Keeney, 1986), but in global terms, the process may be far from environmentally benign. N₂O is implicated in global warming, being 150 times more effective as a greenhouse gas than CO₂. Therefore, it is important that the reduction process in denitrification proceeds all the way to N₂, and the need for more information on the soil conditions that lead to a production of N₂O rather than N₂ has been noted (Powlson, 1992).

N may also enter the hillslope system from the atmosphere, both as wet deposition in rainfall (usually soluble ammonium nitrate), and as dry deposition (gases and particulates). Amounts can be significant. Goulding (1990) recorded 35-40 kg N ha⁻¹

total annual deposition for arable land in the south and east of England, stating that the amount for grassland would be a little lower. More recent estimates for Rothamsted are 50-60 kg N ha⁻¹ (Powlson, 1992). Bache (1990) quotes figures of 3-11 kg N ha⁻¹ as ammonium nitrate in wet deposition alone, this for Northern Britain in 1981.

The timing of manure applications is important in determining the potential transport of N, particularly if the manure has a high content of readily available N (that is mineralised or ammonium N). Autumn through to early winter is a critical period, when plant uptake ceases and before the soil becomes cold enough to inhibit nitrification. For grassland this period is probably from early September to early December (Archer, 1991). This is also the period when transport will increase due to increased soil water content and rates of water movement (Powlson, 1992). Smith (1992) gives figures for the transport of nitrate-N following applications of slurry to grassland at different times of the year. They vary between 10 kg ha⁻¹ for a June application, and 90 kg ha⁻¹ for a November application. Parkinson (1993) cites the case of an experiment where the careful injection of slurry in spring did not lead to increased sub-surface transport of N in the following months, because the additional N input was taken up in enhanced crop growth.

2.4. Phosphorus biochemistry

In biological systems, the reactive processes affecting P are much more limited than those affecting N. Whether in organic or inorganic compounds or complexes, P is always transferred as ionic phosphate (Kirby, 1978; Williams, 1978). For the purposes of this study, the main sources of P available for transport were considered to be, inputs in applications of cattle manures (see table 2.2), and storage and release from the soil-water structure.

Table 2.2. Typical analyses of P in cattle manures (fresh weight basis)

	Dry matter (%)	Total P (%)
Cattle manure ¹	25	0.15
Farmyard manure ²	27	0.20
Cattle slurry ¹	10	0.10
Cattle slurry ²	8	0.10
Cattle slurry ³	7	0.15

(Figures for dirty water were not available from these sources)

¹ Reproduced from Wild (1993).

² Reproduced from Dam Kofoed (1984).

³ Reproduced from Smith (1992).

Organic P in cattle manures is present as phosphate in compounds such as phospholipids, proteins, and sugar-phosphates. The solubility of these compounds often depends on the strength of the hydrogen bond between the phosphate ion and water molecule (Williams, 1978). Whether dissolved or not, organic P is a major fraction transported within overland flow. Heathwaite *et. al.* (1990b), when recording increased overland flow and soil erosion from heavily grazed grassland plots, also recorded 80% of the total P transported as either organic or particulate P. As well as undissolved organic P, particulate P can contain phosphate bound as a complex to mineral soil cations (this complexing process is discussed further below), so for mineral soils at least, there is an established link between soil erosion induced by the overland flow of water and the increased transport of particulate P. Dam Kofoed (1984) cites two experiments where cattle slurry and manure were applied to sloping arable soils. In both experiments, incorporation of the manure significantly reduced surface transport of sediment and total P, compared to direct surface applications.

Unlike N, P within the soil profile undergoes no oxidation or reduction processes. The major reactive process is that of ligand exchange. Here, a surface complex forms between the phosphate anion and a metal cation, usually iron or aluminium. This

complex is particularly strong, so that the concentration of soluble phosphate in mineral soils is low (Kirby, 1978; Williams, 1978; Wild, 1993). It therefore follows that the sub-surface delivery of P is also low, both as soluble organic phosphorus (also called soluble unreactive phosphate), and as the free soluble phosphate ion (also called orthophosphate or soluble reactive phosphate). Wild (1993) gives the average concentration of phosphate-P in drainage water from three arable sites in Southern and Eastern England as 0.06 mg l^{-1} . In one of two experiments cited by Dam Kofoed (1984), the concentration was 0.03 mg l^{-1} , regardless of the amount of manure applied to the surface. Vetter and Steffens (1981) found that under slurry applications of $90 \text{ m}^3 \text{ ha}^{-1} \text{ a}^{-1}$, considerable amounts of P could be displaced to deeper soil layers where plant uptake would not be possible. However, despite this accumulation at depth, transport of P to ground and drainage waters was no higher than from areas receiving no application of slurry, at least for mineral soils.

Considerable quantities of P can be transported from organic soils, where there are few mineral ions with which the phosphate ion can form complexes. Duxbury and Peverly (1978) compared P transport in drainage water from adjacent mineral and organic soils under similar management practices. They observed an average annual load of 0.6 kg ha^{-1} phosphate-P from mineral soil, compared with 30.7 kg ha^{-1} from organic soil. The maximum concentration of phosphate-P in water draining from organic soil was some 10 mg l^{-1} . Scheffer and Kuntze (1989) note that in acid high moor soils, poor in iron and aluminium, phosphates are very mobile. They give average values for the amount of P leached from these soils annually as $3\text{-}10 \text{ kg P ha}^{-1}$ for grassland and $10\text{-}36 \text{ kg P ha}^{-1}$ for arable land, depending on land management practices and rates of fertiliser usage. Vetter and Steffens (1981) give figures from an experiment where 160 kg ha^{-1} of phosphate in fertiliser was applied to raised bog peat. Concentrations of P in drainage water ranged from $6\text{-}12 \text{ mg l}^{-1}$, and the average annual load of phosphorus was 11 kg ha^{-1} . They argue that the iron and aluminium in acid peat soils are fixed by organic compounds to form chelates, thus preventing the complexing of P. Even in mineral soils, some P can be transported in preferential flow, the quantity and fraction being dependent on the size and position of the flow channel. For example,

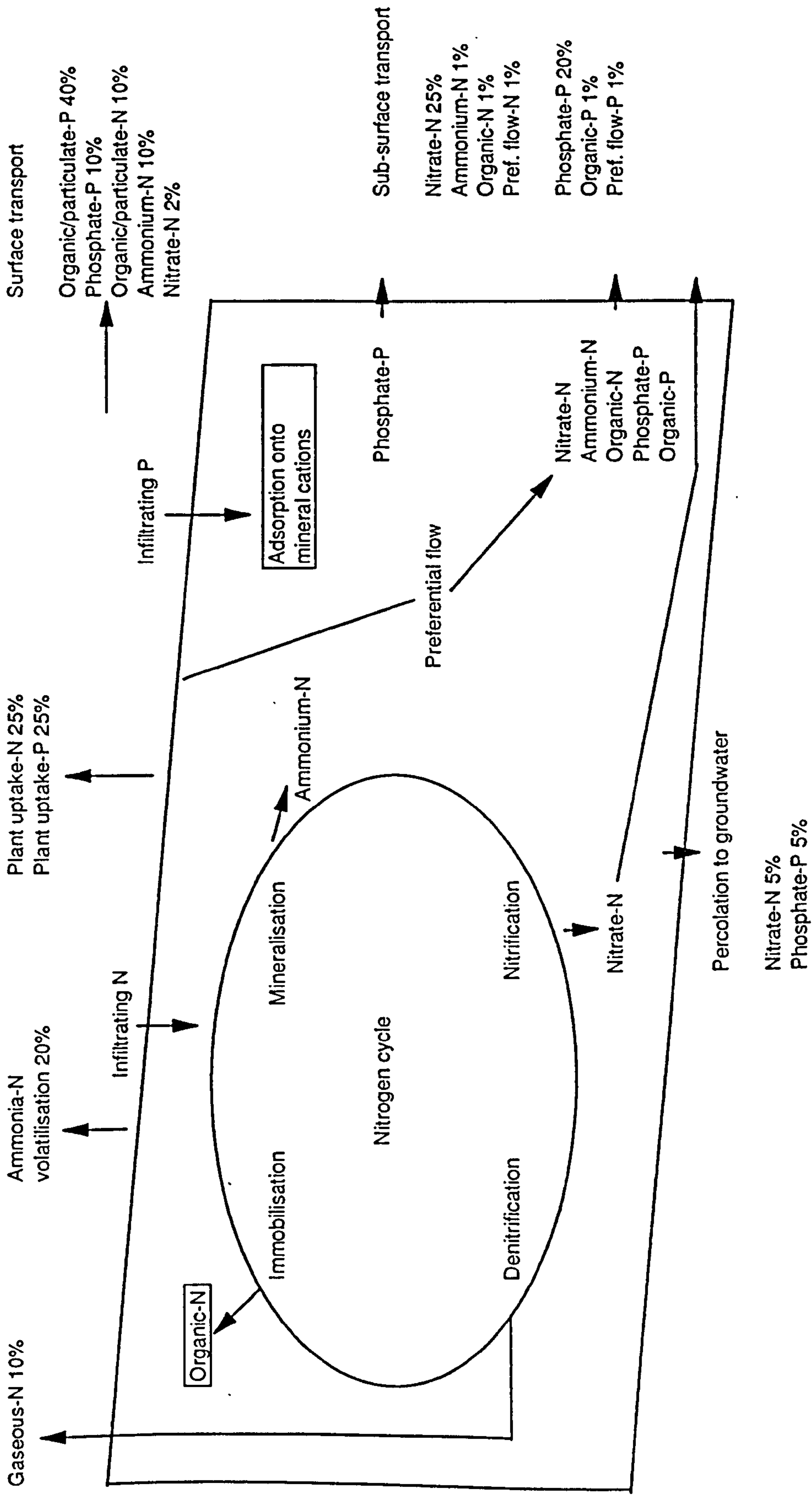
Gower (1980) observed much higher transport of particulate P when slurry was applied to land containing shallow drains back-filled with stones, compared with a similar application to land where the drains were deeper and back-filled with soil. Keeney (1986) notes that preferential movement of water through larger pores can cause rapid transport of phosphate, presumably because the turbulent flow regime is not conducive to the ligand exchange process.

Finally, there is the consideration of saturation excess overland flow. For mineral soils, transport of P within saturation excess overland flow will be similar to that for infiltration excess overland flow. For organic soils, some extra transport of soluble phosphate can be expected, depending on the concentration in water re-emerging from the soil profile.

As a simple illustration of the biochemical processes described in this and the previous section, Fig. 2.6 presents relative quantities of N species and P fractions transported within different hydrological pathways, following a hypothetical application of cattle manure.

2.5. Chapter summary

1. The processes of hillslope hydrology define the pathways of N and P delivery. Biochemical processes define N speciation and P fractionation within each pathway.
2. Both hydrological and biochemical processes are affected by topography and agricultural operations. Therefore, the interaction of hydrological and biochemical processes, topography, and land-use determines the overall magnitude and timing of N and P transport from grassed hillslopes to receiving water courses.



Note. The percentages given for N species and P fractions are for the purposes of illustration, and assume that no N or P is permanently immobilised. These percentages will vary in response to factors such as water input and soil water content, slope, timing of application.

Fig. 2.6. Pathways of N and P transport following a hypothetical application of cattle manure to a grassed hillslope

3. Hillslope hydrology pathways can be summarised as.

- (a) Infiltration excess overland flow (a "Partial Source Area" model can be applied).
- (b) Saturation excess overland flow (a "Variable Source Area" model can be applied).
- (c) Sub-surface preferential flow.
- (d) Sub-surface matrix flow.
- (e) Percolation to groundwater.

4. N speciation can be summarised as.

- (a) Organic (particulate and dissolved) and ammonium N in infiltration excess overland flow, with some additional nitrate N in saturation excess overland flow.
- (b) Nitrate and possibly ammonium N in preferential flow.
- (c) Nitrate N in matrix flow and percolation to groundwater.

5. P fractionation can be summarised as.

- (a) Organic (particulate and dissolved) and soil-bound particulate phosphate P in overland flow, possibly with additional dissolved phosphate P in saturation excess overland flow from organic soils.
- (b) Some particulate and dissolved phosphate P in preferential flow.
- (c) Very little dissolved phosphate P in matrix flow from mineral soils, more from organic soils, the same applying for percolation to groundwater.

Chapter 3

Plot-scale Field Experiments

3.1. Site selection and description

Plot-based experiments were chosen as a means of examining in detail the processes described in the conceptual model, under conditions that were controlled but still representative of current agricultural practice (objective 3, Chapter 1, section 1.6). Any success in quantifying the processes under examination depended first on the care taken in selection of an experimental site, the following selection criteria being used.

- 1) Sloping permanent pasture, with a known recent land-use history.
- 2) Readily accessible, and in close proximity to laboratory and other technical facilities.
- 3) Chosen in conjunction with a separate headwater catchment site, so that the effects of scaling up observations could be made on sites that were similar in terms of land-use, slope and soil type (refer back to introduction to objectives and objective 4, section 1.6. The headwater catchment site is described in detail at the start of Chapter 4, which covers the experimental programme at the field to headwater catchment scale).

The site eventually chosen was within a 2 ha field of permanent pasture known as Sidney Meadow, part of the Seale-Hayne Faculty farm, University of Plymouth (OS grid reference SX828721). Average annual rainfall for the site is 980 mm, elevation is approximately 50 m above sea level, and slope angle changes from 10° over the lower 10 m of the site to 15° over the upper 20 m (see Fig 3.1, and topographic survey details in Appendix 1). The soil of Sidney Meadow is a weakly structured brown earth of the Denbigh Association, silty clay loam in texture with poorly defined horizons (Fig 3.2), and a pH of approximately 5.5. Underlying the soil is a layer of shattered Devonian slate, bedded at various angles from horizontal to approximately 30° , and at depths ranging from 0.3 m at the top of the site to 2 m at the bottom.



Fig. 3.1. The plots at Sidney Meadow in March 1992. The light squares are the covers of surface runoff collection troughs.



Fig. 3.2. The soil profile at Sidney Meadow. Stripes on the metre rule are 5 cm wide.

The presence of this semi-permeable layer facilitates relatively rapid sub-surface lateral throughflow of water during rainfall events, an important pathway of N and P transport as described in the conceptual model in Chapter 2 (Burt *et. al.*, 1983; Burt and Butcher, 1985a). When wet, the Munsell colour of the soil ranges from 7.5 YR 4/2 at the surface to 7.5-10 YR 3/2 near the slate. Over the last five years, the field has been subject to short periods of light grazing by cattle and sheep, such that there are few signs of poaching. Further details of Sidney Meadow, including recent fertiliser applications and the results of a topographic survey, are given in Appendix 1.

Some mean values of soil bulk density and extractable soil N and P for Sidney Meadow are given below in Table 3.1. Due to the constraint of time, it did not prove possible to make repeated measurements of bulk density throughout the field experimentation period, so the values given here are simply to provide an impression, and to allow comparison with values obtained at the headwater catchment site which are given later in Chapter 4. For the same reason, measurements of extractable soil N and P were not made until towards the end of the experimentation period, and then only at one depth. Again, these values were obtained simply to give an impression, and to allow comparison between the two field sites.

Table 3.1. Soil bulk density and extractable N and P at Sidney Meadow

Depth (cm)	Mean		Mean		Mean soil N ² (mg g ⁻¹)	S.E. of mean (mg g ⁻¹)	Mean soil P ² (mg g ⁻¹)	S.E. of mean (mg g ⁻¹)
	water content ¹ (%)	S.E. of mean (%)	bulk density ¹ (g cm ⁻³)	S.E. of mean (g cm ⁻³)				
0-5	49.8	3.57	0.91	0.04	-	-	-	-
10-15	37.5	2.82	1.32	0.05	-	-	-	-
25-30	35.8	2.18	1.28	0.02	0.0021	0.0004	0.0109	0.0027
45-50 (slate)	28.3	1.41	1.59	0.06	-	-	-	-

Notes relating to Table 3.1.

¹ Number of samples = 5, taken in March 1991. Sample volume = 225 cm³. Water content is volumetric, and bulk density is expressed on a dry basis.

² Number of samples = 4, taken in January 1993. Sample weight = 250 g. N and P contents are expressed on a dry basis also. N was extracted using potassium chloride, P was extracted using sodium bicarbonate (methods from MAFF and ADAS, 1981).

3.2. Experimental design

Three treatments were chosen for this study. Full details of the timing and rates of application for these treatments are given later in section 3.3, but for now it is sufficient simply to state that the treatments chosen were as follows.

- 1) Surface application of liquid cattle slurry.
- 2) Surface application of solid cattle manure containing bedding material.
- 3) Surface application of granular inorganic fertiliser.

Treatments of slurry and manure provided a contrast in terms of water content and texture, thus allowing identification of possible differences in the processes of N and P transport as discussed in the conceptual model. The inclusion of inorganic fertiliser as a treatment allowed comparison between applications of N and P which were largely in organic form with those where N and P were wholly in inorganic form. This comparison is of particular relevance when inorganic fertiliser is considered as a more convenient alternative to the use of organic manures (Dam Kofoed, 1984; Tunney, 1984; Edwards, 1990). Grazing by livestock was considered as a treatment but was not chosen, primarily because of the difficulties of incorporating such a treatment in a detailed and comparative study of hydrological and chemical processes at the plot scale. The spatial variability of N and P applications under grazing, with the additional factors of localised compaction and poaching, merits the detailed study of this treatment in isolation (for example, see Heathwaite *et. al.*, 1990a and b).

The site was divided into twelve plots, each measuring 30 m downslope by 5 m across, with a 1 m discard strip between each plot. The plots were split into three blocks of

four, each block containing randomly arranged replicates of the three treatments and a control plot (see Fig 3.3). In order to examine the effect of following current guidelines on good agricultural practice (MAFF and WOAD, 1991), treatments were applied to the top 20 m of each plot, the bottom 10 m being left as a buffer zone. Therefore, the extent to which N and P from applied treatments penetrated this buffer zone could be assessed. The top of the site was hydrologically isolated from the rest of Sidney Meadow and the field above by digging a trench well into the slate layer, inserting a polythene membrane to a depth of over 1 m and backfilling. This would prevent water entering from above the site, conceptually treating the top of the site as the top of a slope, and thus facilitating the calculation of the quantity of water, N, and P entering and leaving the plots (Vinten *et. al.*, 1991; Armstrong and Burt, 1993). It was assumed that the direction of water flow on the site would be predominantly vertical or parallel to the main slope, since slope angles perpendicular to the main slope were very small, and there were no significant humps or hollows in the site. Therefore, adjacent plots were not isolated from each other, but as a precaution all sub-surface monitoring on the plots took place close to the centre of the 5 m width.

3.2.1. Instrumentation

For the purposes of instrumentation, each plot was marked out into three 10 m zones, the upper two zones receiving treatments and the lower zone acting as a buffer. Splitting the plots in this way facilitated measurement of the movement of water, N, and P at regular intervals on the site slope. An instrumentation plan is shown in Fig 3.4. It was assumed that hydrological processes would not vary significantly across the plots, as even an application of slurry would only be equivalent to an extra 5 mm of water input compared to an average monthly rainfall total of 70-80 mm at the time of application. Therefore, hydrological instrumentation was largely confined to the three control plots. This instrumentation will be described first, followed by a description of instrumentation used to obtain water samples for analysis of N and P content.

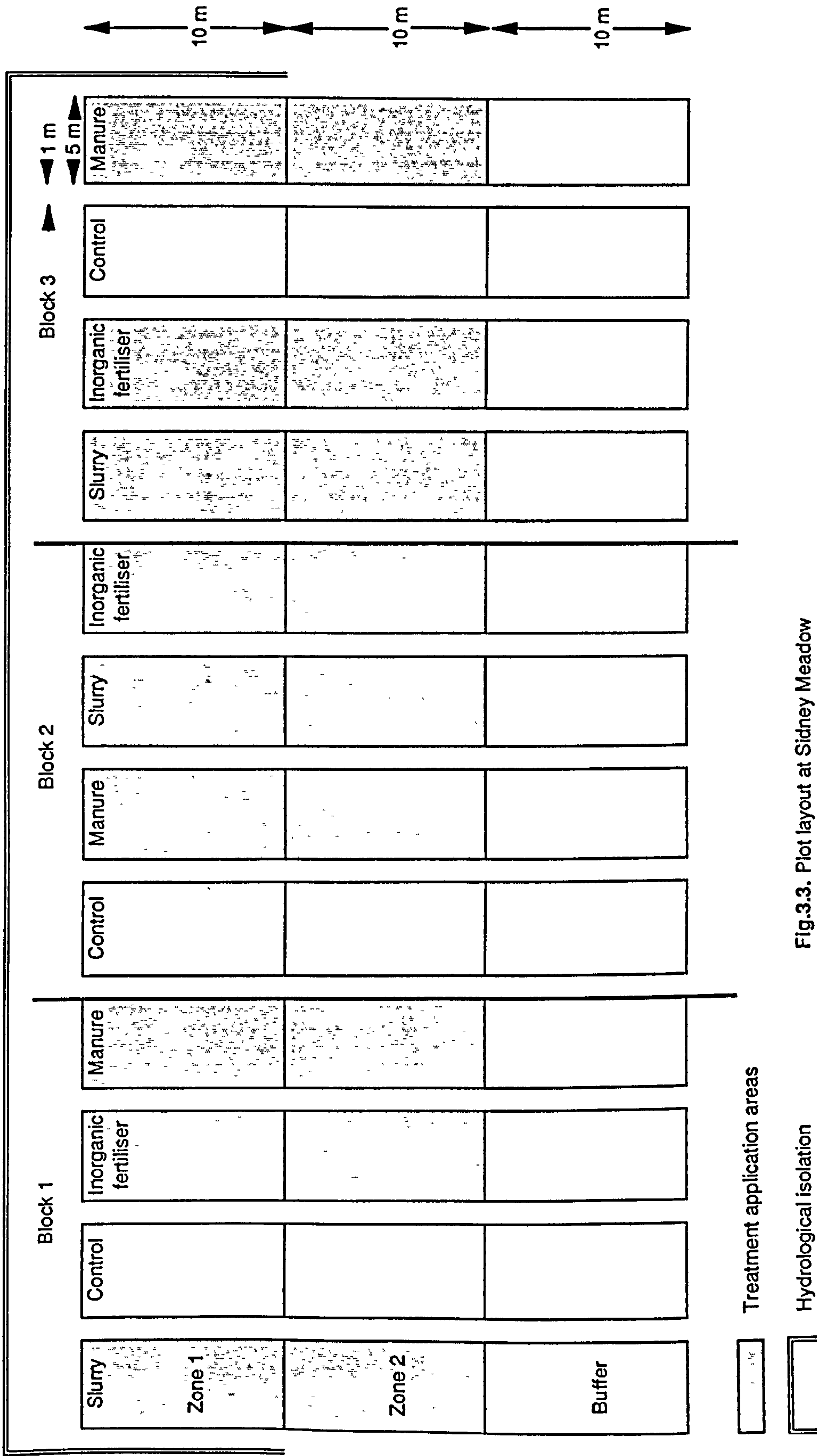


Fig.3.3. Plot layout at Sidney Meadow

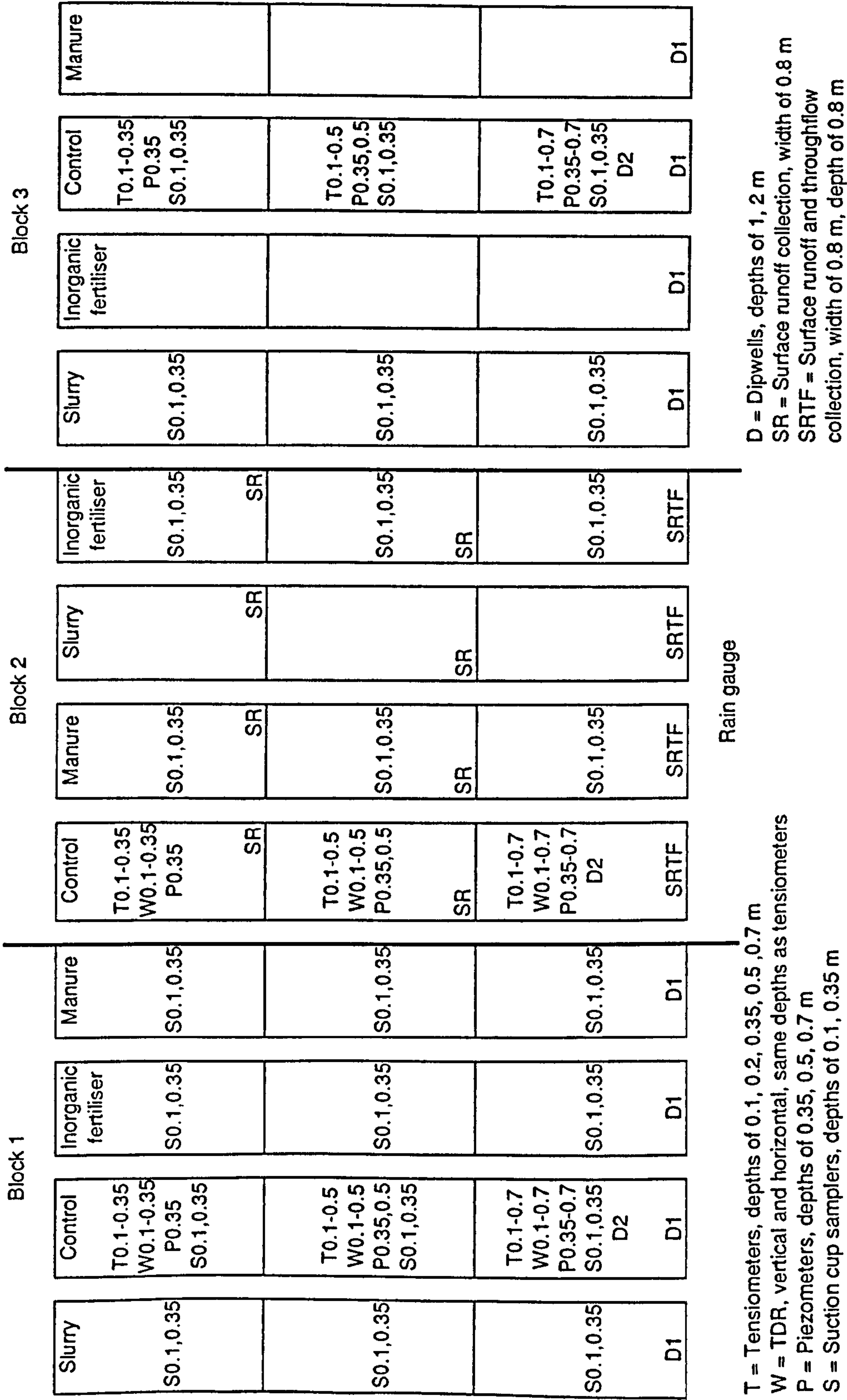


Fig. 3.4. Instrument location at Sidney Meadow

(a) Tensiometers

Mercury manometer tensiometers, built to a design by Burt and Beasant (1984, see Fig. 3.5), were placed in each zone of each of the three control plots, at depths ranging from 0.1 m to 0.7 m. These instruments were capable of measuring negative or positive matric potentials to an accuracy of ± 1 mm Hg (negative potential here being used to denote suction). By calculating the height of each instrument relative to a datum at the bottom of the plot, gravitational potential could be added to matric potential to give the total hydraulic potential for each instrument. In conjunction with measurements of soil water content and hydraulic conductivity, these hydraulic potentials could be used to give estimates of rates of unsaturated sub-surface flow both down the soil profile and downslope, these estimates being based on Darcy's Law or the similar Richards equation for unsaturated flow (Berryman *et. al.*, 1976; Atkinson, 1978; Armstrong and Burt, 1993). The tensiometers were monitored daily, at the same time each day in order to minimise diurnal temperature effects.

(b) Time Domain Reflectometry (TDR)

Originally developed for testing cables (Fellner-Feldegg, 1969), the TDR technique has been successfully adapted to measure water content in the soil (Ledieu *et. al.*, 1986; Whalley, 1989). Essentially, the two wires of a coaxial line are used to make two parts of a probe which is inserted into the soil. An electromagnetic pulse is sent down one wire, it travels through the soil and returns through the other wire to a monitor. The travel time of the pulse is directly proportional to the water content of the soil. It has been argued that TDR calibration is independent of soil type because the relative permittivity of soil over the frequency range utilised by commercial instruments is independent of the relative proportions of bound and free water in the soil (Whalley, 1989). Accepting this, a universal calibration equation can be used to convert the obtained reading into a volumetric water content. In this study, a polynomial equation derived by Topp *et. al.* (1980) was used.

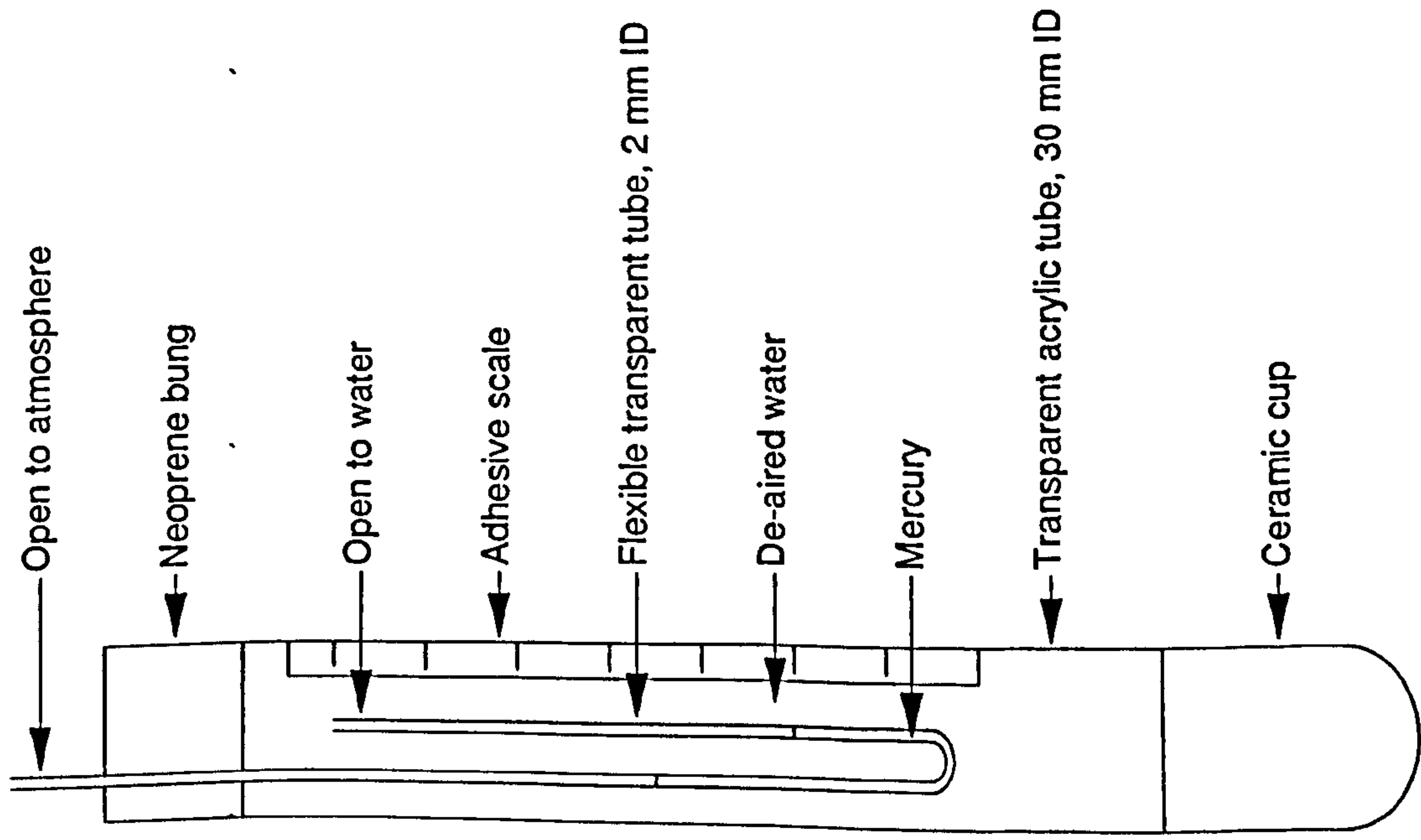


Fig. 3.5. Mercury manometer tensiometer

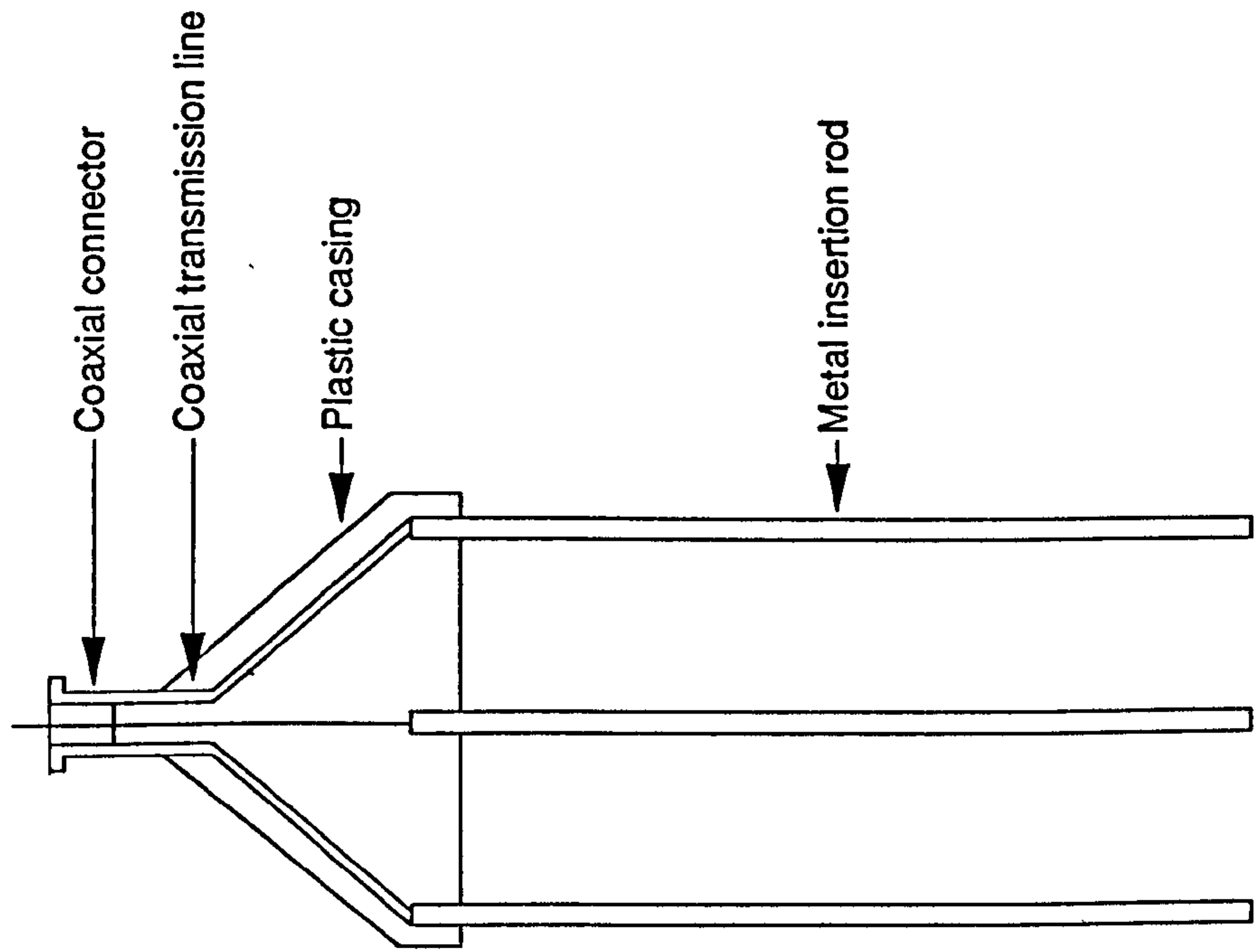


Fig. 3.6. TDR probe

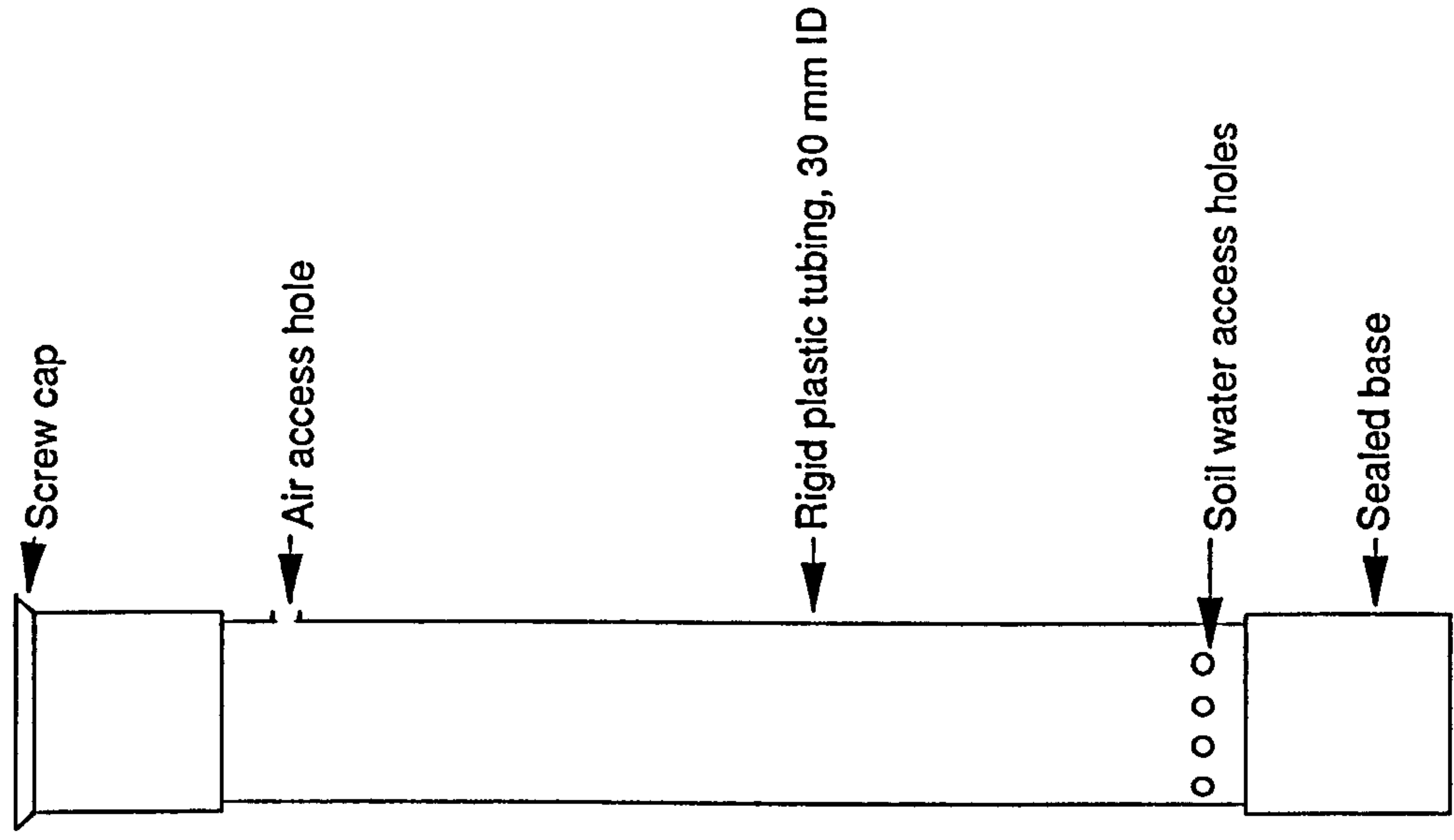


Fig. 3.7. Piezometer

Accuracies of better than $\pm 1\%$ have been claimed for the TDR technique (Ledieu *et al.*, 1986). However, accuracy varies with the volume of soil affecting the measurement and the spatial sensitivity within that volume, both of these factors depending on the configuration of the probe used (Baker and Lascano, 1989; Zegelin and White, 1989). A three wire probe was used in this study, with configuration as shown in Fig 3.6. The band of influence in the plane perpendicular to the wires is narrow (approximately 30 mm), so the probes give very good resolution when placed horizontally. Also, there is little variation in sensitivity over the length of the wires, allowing long probes to be placed vertically in the soil for the purpose of obtaining average water contents over the depth of the soil profile sampled (again see Baker and Lascano, 1989). Probes with the configuration shown in Fig. 3.6 were installed horizontally, adjacent to the tensiometer networks and at the same depths. Additionally, probes with wires of lengths from 0.1 m to 0.7 m were installed vertically in the same locality as the horizontal probes, primarily for the purpose of comparing the two sets of readings obtained. Both sets of probes were monitored weekly.

(c) Piezometers

Built to a simple design shown in Fig 3.7, manually read piezometers were used to detect the presence of positive potentials of water in the soil profile due to the build up of a saturated zone. They were installed in the same locality as the tensiometers and TDR probes, at depths of 0.35, 0.5, and 0.7 m. The height of the head of water in the piezometer tube was measured with a dipwell probe, to an accuracy of ± 2.5 mm. After measurement, if required the water in the piezometer could be sampled and retained for chemical analysis. Piezometers were monitored daily.

(d) Dipwells

These were used to monitor changes in the depth of the permanently saturated zone at the foot of the slope. Three dipwells were installed to a depth of 2 m in the bottom zone

of each of the control plots. In addition, dipwells were installed to a depth of 1 m at the base of all the plots to allow replicated sampling of water from the saturated zone for each of the treatments and the control. All these instruments were monitored daily using the dipwell probe. Once per week, 100 ml samples were extracted from the 1 m dipwells and retained for chemical analysis. This sampling frequency increased to daily in the event of significant rainfall.

(e) Throughflow collection pits

Throughflow pits were sited at the bottom of each of the four plots in the central block of the site (see Fig. 3.4). They were installed to a depth of 0.8 m (the approximate depth at which slate began to appear in the slope profile), over a width of 0.8 m, and lined with polythene to retain water draining from the upslope profile (Fig. 3.8). Water was pumped out of the pits each day, the volume being recorded. 100 ml samples were retained for chemical analysis at the same times as those taken from the 1 m dipwells.

Throughflow collection pits provide a direct and simple means of estimating the rate of sub-surface flow from the soil profile to the prescribed depth. However, because the continuity of the soil matrix is broken, distortions in the flow pattern will occur, inevitably leading to errors. Notably, a saturated wedge has to build up at the pit face before flow into the pit can occur (Atkinson, 1978). This can lead to restriction of water movement and under-estimation of flow rates during drier periods.

(f) Surface runoff collection troughs

These were located in all three zones of each of the four plots in the central block, their layout being staggered to allow the free flow of water down the length of the slope (see Fig. 3.4). Surface runoff over a width of 0.8 m was channelled into a covered container (see Fig. 3.9) which was emptied daily. Total daily volumes were recorded, and when possible, 100 ml samples were retained for analysis. Daily volumes of less than 50 ml were not retained.

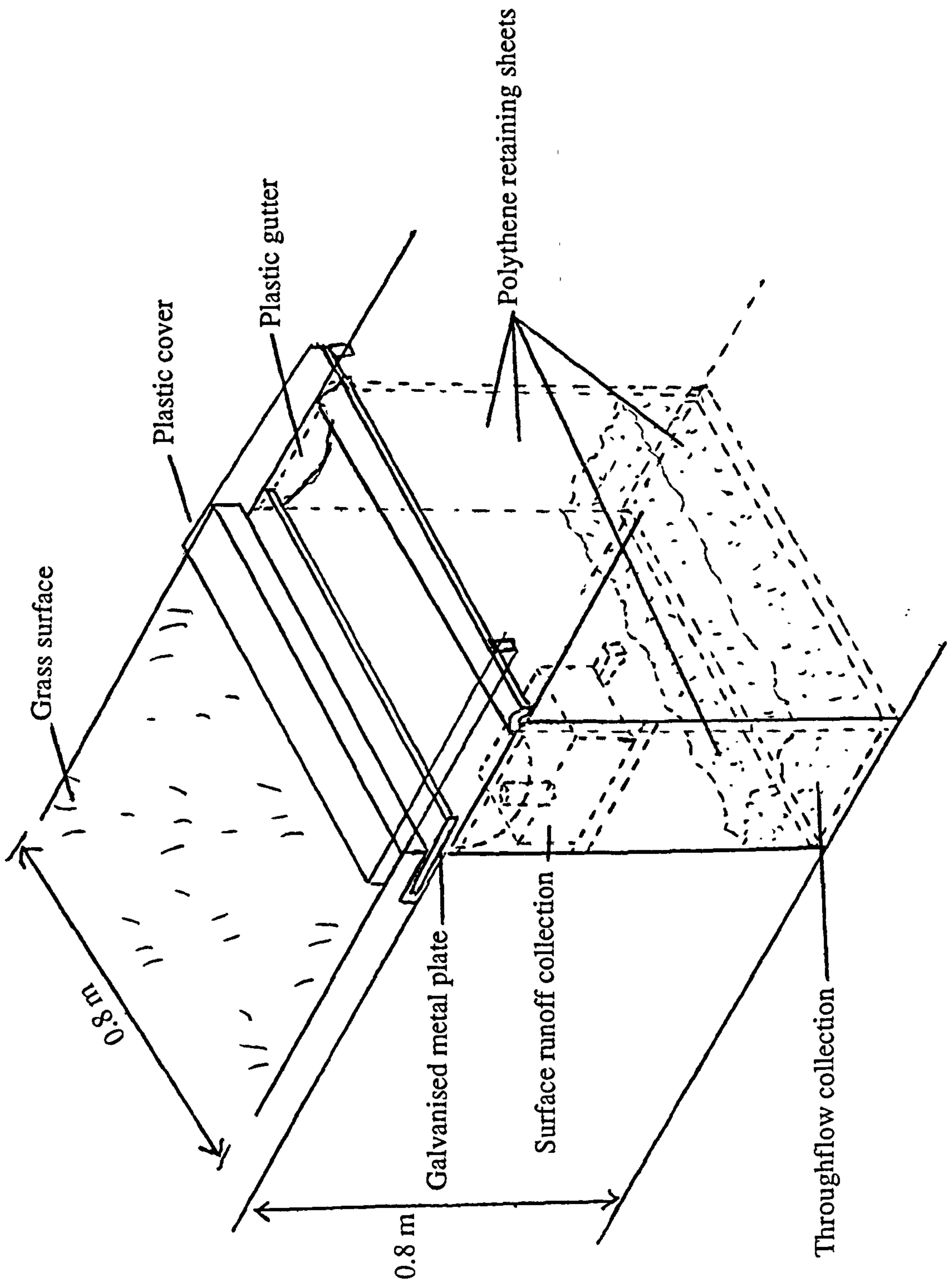


Fig. 3.8. Combined surface runoff and throughflow collection

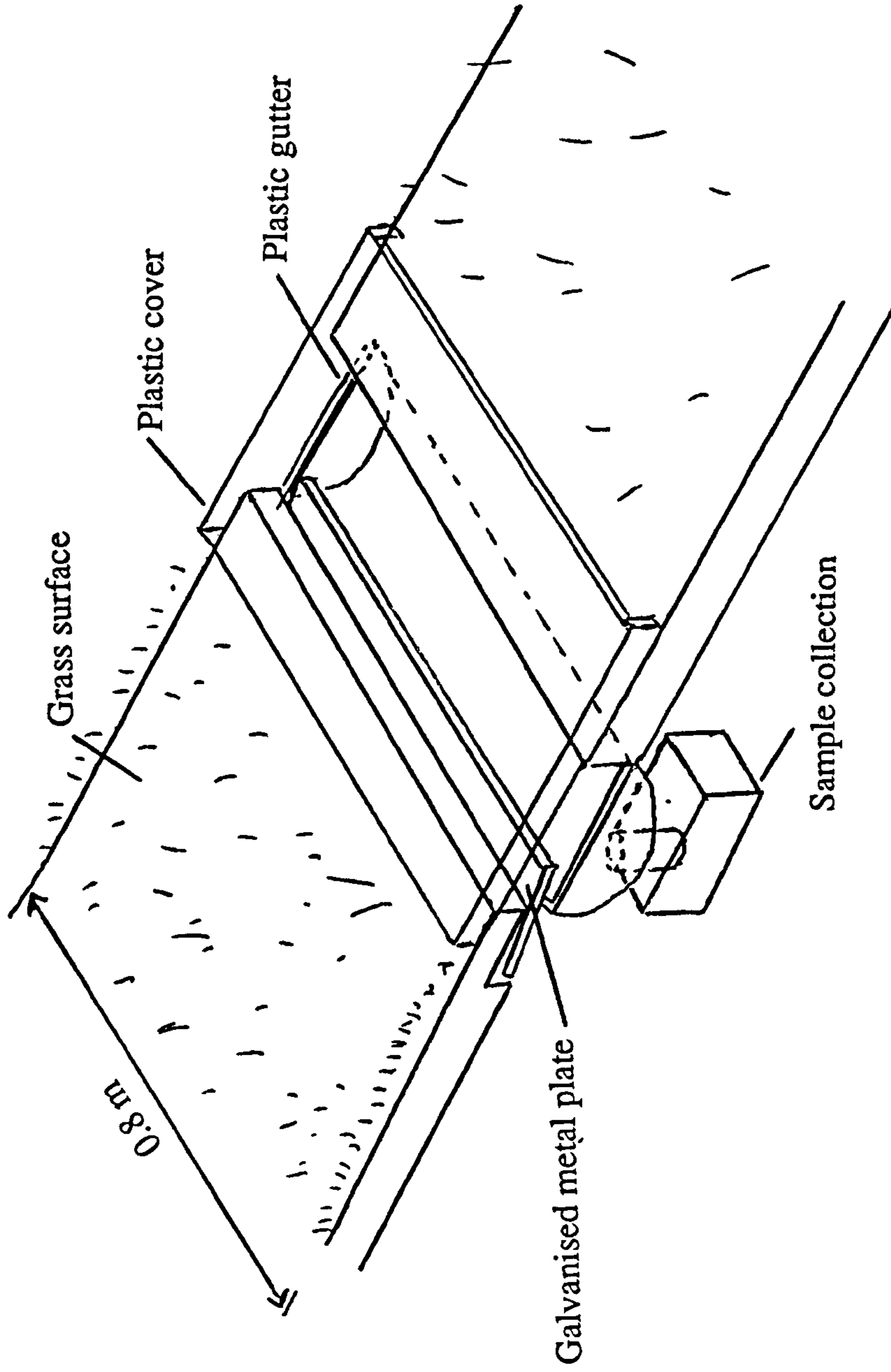


Fig. 3.9. Surface runoff collection trough

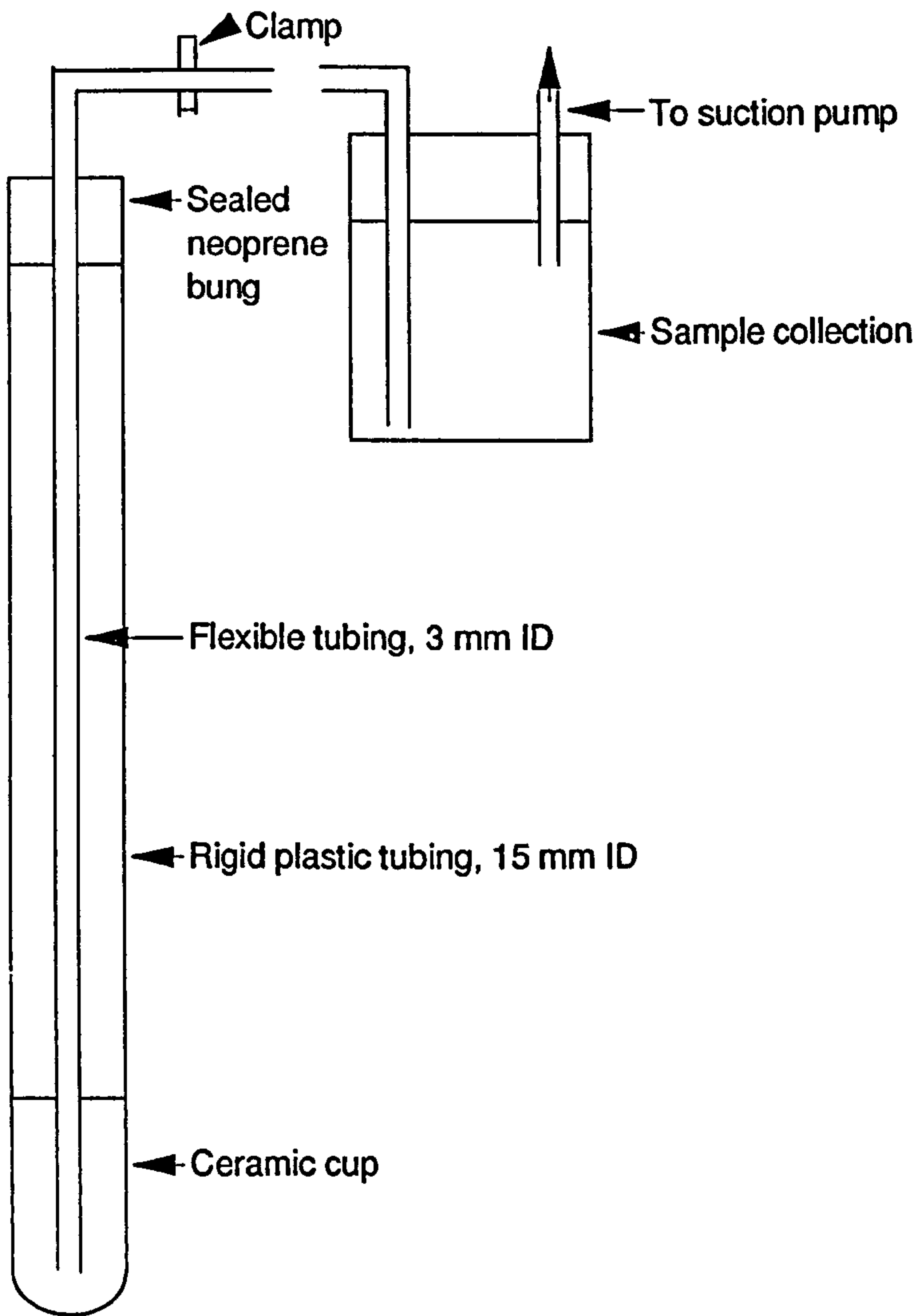


Fig. 3.10. Ceramic suction cup sampler

(g) Ceramic suction cup samplers

Built to a design shown in Fig. 3.10, suction samplers were installed at depths of 0.1 m and 0.35 m in all three zones of eight of the twelve plots, in effect giving duplicate samples for each treatment and zone. The depths of installation were chosen to cover that part of the soil profile which it was thought would remain unsaturated for the majority of the experimental period. Samples of 50-100 ml were extracted once per week by applying a suction of approximately 80 mm Hg over a period of 24 hours.

There is always difficulty in determining the origins of a sample obtained by applying a suction to the soil matrix, firstly because the potential field of the water around the sampler is distorted, and secondly because in the field situation it is almost impossible to determine the proportion of the sample obtained from soil pores where the water is largely mobile, as opposed to those pores where the water is largely retained (Grossmann and Udluft, 1991). This problem is exacerbated in soils with a structure that facilitates preferential flow (for example see Magid *et. al.*, 1992). Therefore, in this experiment suction cup samples were used simply to detect broad changes in the concentrations of N species and P fractions under the applied treatments, and to see if these changes were more notable than those taking place in the buffer zone. Rates of transport of N and P were not inferred from these samples.

There are other problems with the use of ceramic suction cup samplers, most notably the selective sorption of cations such as Mg^{+} and Ca^{+} , and the adsorption of P. It is possible for the cups to reach chemical equilibrium with the soil solution after a certain period of time, but each time soil solution chemistry changes a new equilibrium has to be reached, so the cups in effect damp out sudden changes in soil solution chemistry (Abbott, 1990).

3.2.2. Chemical analysis procedures

The chemical analysis procedure for water samples is shown in Fig. 3.11. Firstly, subsamples of all samples except those from the suction cup samplers were filtered through

Whatman GF/C papers within an hour of collection and refrigerated at approximately 4° C. Within 48 hours of collection, these filtered samples were analysed for nitrate nitrogen (NO_3^- -N), ammonium nitrogen (NH_4^+ -N), and orthophosphate phosphorus (PO_4^- -P), using standard colourimetric techniques on a Technicon AA2 autoanalyser. NO_3^- -N was actually measured as TON (NO_3^- -N + NO_2^- -N), using sodium hydroxide, copper-hydrazine, and sulphanilamide reagents, and a stock standard solution of potassium nitrate (after Henriksen and Selmer Olsen, 1970). Nitrite (NO_2^- -N) is an intermediate product of nitrification or denitrification, and since as such it is in an unstable oxidation state it is quickly oxidised or reduced (Keeney, 1986). Therefore, TON usually consists largely of NO_3^- -N, and for the purposes of this study results are referred to as concentrations or loads of NO_3^- -N. NH_4^+ -N was measured using salicylate and dichloroisocyanuric acid - sodium salt reagents, a citrate buffer, and a stock standard solution of ammonium chloride (Chemlab, 1981). PO_4^- -P was measured as orthophosphate, using ascorbic acid and ammonium molybdate reagents, and a stock standard solution of potassium dihydrogen orthophosphate (Murphy and Riley, 1962). All reagents and stock standard solutions were refrigerated and kept for no more than two weeks. The range of standards needed for each batch of samples to be analysed were made up fresh on the day of analysis. Autoanalyser flow diagrams for the three techniques are shown in Appendix 2.

Unfiltered portions of each sample were refrigerated and analysed within two weeks for total N and total P, using a simultaneous persulphate digestion technique based on autoclaving (Hosomi and Sudo, 1986), followed by NO_3^- -N and PO_4^- -P analysis by autoanalyser as before. The combined amounts of dissolved organic plus particulate bound N and P within each sample could then be calculated by difference. Although the relative proportions of dissolved organic and particulate N and P within the total could not be calculated in this instance (this would have required digestion and analysis of a filtered sub-sample to yield dissolved organic N and P, which the constraints of time and laboratory capacity did not allow), for the sake of brevity the combined amounts are referred to in the results simply as organic-N and organic-P respectively. In the case of the suction cup samples, the difference calculation would yield only dissolved

organic-N and organic-P, as the samples were effectively filtered by the cup in the field and would therefore contain no particulate matter.

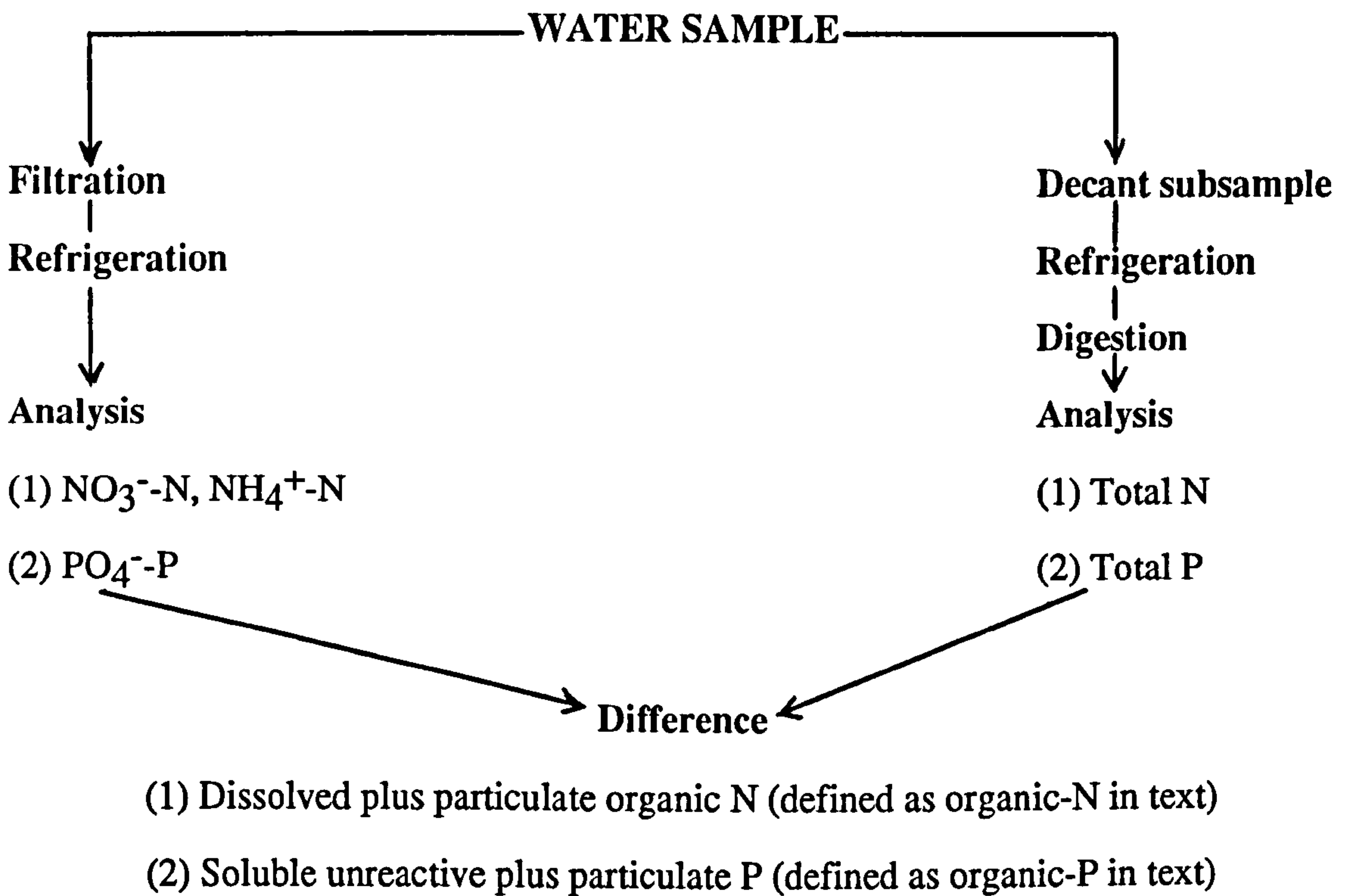


Fig. 3.11. Analysis procedure for water samples

Immediately following application of treatments to the plots, samples of the cattle manure and slurry were retained for total N and total P analysis, using the Kjeldahl and ash solution methods respectively (MAFF and ADAS, 1981). It would have been desirable to use the same digestion and analysis techniques as used on the water samples, thus allowing the N and P composition of the manure and slurry to be determined in more detail. However, due to the nature of the material, the coloration of samples, and the high concentrations of N and P involved, the digestion and autoanalysis techniques did not prove to be suitable.

3.2.3. Analysis of soil hydrophysical properties

Soil cores of length 12.7 cm and volume 1038 cm³ were extracted vertically from depths of 0.2 m and 0.5 m and taken to the laboratory for determination of saturated hydraulic conductivity (Klute and Dirksen, 1986). These values would later be used in conjunction with water content and tension readings in order to estimate sub-surface rates of water flow. As with the soil bulk density and extractable N and P determinations, they would also allow comparison with values obtained from the headwater catchment site.

Infiltration rates on the site were estimated using the double ring infiltrometer method, the inner ring having an area of 255 cm². The head of water in both rings was kept constant at approximately 30 cm during the 5 hours over which measurements took place. Initially, measurements of infiltration were made every 15 minutes, this frequency decreasing to hourly after the first hour. At the levels of treatment application used during the experiment, it was assumed that infiltration rates would vary little across the site. The sole purpose of the measurements was therefore to ascertain the intensity of rainfall at which infiltration excess surface runoff would be likely to occur.

3.2.4. Meteorological information

Daily rainfall totals were recorded on site using a Bradford rain gauge. Rainwater caught in the gauge was sampled and analysed in the same manner as other water samples, in order to ascertain the input of N and P through wet deposition. In addition to this on-site rain gauge, a similar gauge and an autographic gauge, both located at the Seale-Hayne weather station approximately 1 km to the north of the site, provided weekly and hourly rainfall totals respectively.

Readings of soil temperature were also available from the Seale-Hayne weather station, taken on a weekly basis at depths of 0.1 m and 0.2 m. These were useful as indicators of changes in the rate of soil micro-organism and plant growth activity.

3.3. Experimental programme

The first application of treatments took place in mid-February 1992. This time was chosen as an important one for the application of manure and slurry for two reasons. Firstly, it is approaching the time when storage facilities for manures from animals housed indoors over winter may be reaching capacity. This is particularly the case where slurry separation facilities, which facilitate the separation and spreading of the dirty water component of slurry at any time of year in accordance with published guidelines (MAFF and WOAD, 1991), are not available (Parkinson, 1993). Secondly, it is a time when soil water content will still be at winter mean (or field capacity), and consequently rates of water movement may be high.

In accordance with the *Code of Good Agricultural Practice*, slurry and manure were applied at rates of 50 m³ ha⁻¹ and 49 t ha⁻¹ respectively (MAFF and WOAD, 1991). These rates are given as equivalent to 250 kg total N ha⁻¹ and 100 kg total P ha⁻¹. However, analysis of the slurry and manure used revealed that total N and P contents were quite variable (see Table 3.2 below). No inorganic fertiliser was applied at this stage, in line with likely agricultural practice for permanent pasture (see Appendix 1 for past fertiliser application dates for Sidney Meadow).

Table 3.2. Composition of slurry and manure applied in February 1992

	Mean water content (%) (wet basis)	Standard error	Total N (kg ha ⁻¹)	Standard error	Total P (kg ha ⁻¹)	Standard error
Slurry	97.2	0.283	138	8.31	69	17.10
Manure	69.6	4.660	364	8.08	118	7.35

No. of samples = 5.

The instrumentation on the site was monitored until mid-March 1992, at the intervals set out in section 3.2.1 above. In mid-March, slurry was re-applied at the same rate, but

manure was not re-applied, due to both physical remnants from the previous application and the higher N and P content of the manure relative to the slurry (see Table. 3.2). Inorganic fertiliser was now applied as a mixture of ammonium nitrate at the rate of 250 kg N ha⁻¹, and calcium phosphate at the rate of 100 kg P ha⁻¹. Monitoring continued until mid-April 1992.

During the period mid-February to mid-April, the maximum daily rainfall total was 11 mm, and the maximum rainfall intensity was 3 mm h⁻¹. Furthermore, the total rainfall for December 1991 to April 1992 inclusive was only 50% of the long term mean for that period. Consequently, no surface runoff was generated, either by means of saturation or infiltration excess. Because surface run-off is regarded as an important pathway for the transport and delivery of N and P, particularly in organic form (again, see Heathwaite *et. al.*, 1990b), a rainfall simulation experiment was designed to generate infiltration excess surface runoff.

In early May 1992, the grass on the site was cut to reflect likely conditions under conservation or grazing. The three treatments were re-applied to the plots in mid-May 1992, at the rates given previously. In the week immediately following application, four intense storms were simulated on consecutive days using a single rain-gun irrigator placed at the bottom of the plots. Water was sprayed into the air over the plots through an arc of 180°, the rain-gun being moved to several positions at the bottom of the plots to ensure as even a coverage of water as possible. In each storm, 15 mm of water was applied to the plots over a period of 35 minutes, equivalent to a rate of 24 mm h⁻¹. This intensity was required in order to generate collectable quantities of infiltration excess surface run-off, given that water had to be supplied by tanker, thus limiting the duration over which it was feasible to run each simulation. The distribution of the water applied to the plots was checked by placing 2 litre plastic containers in each zone of every plot. Total volumes of water in these containers after each storm were recorded, and samples of the water were retained for chemical analysis. The same applied for water in the surface run-off collection troughs.

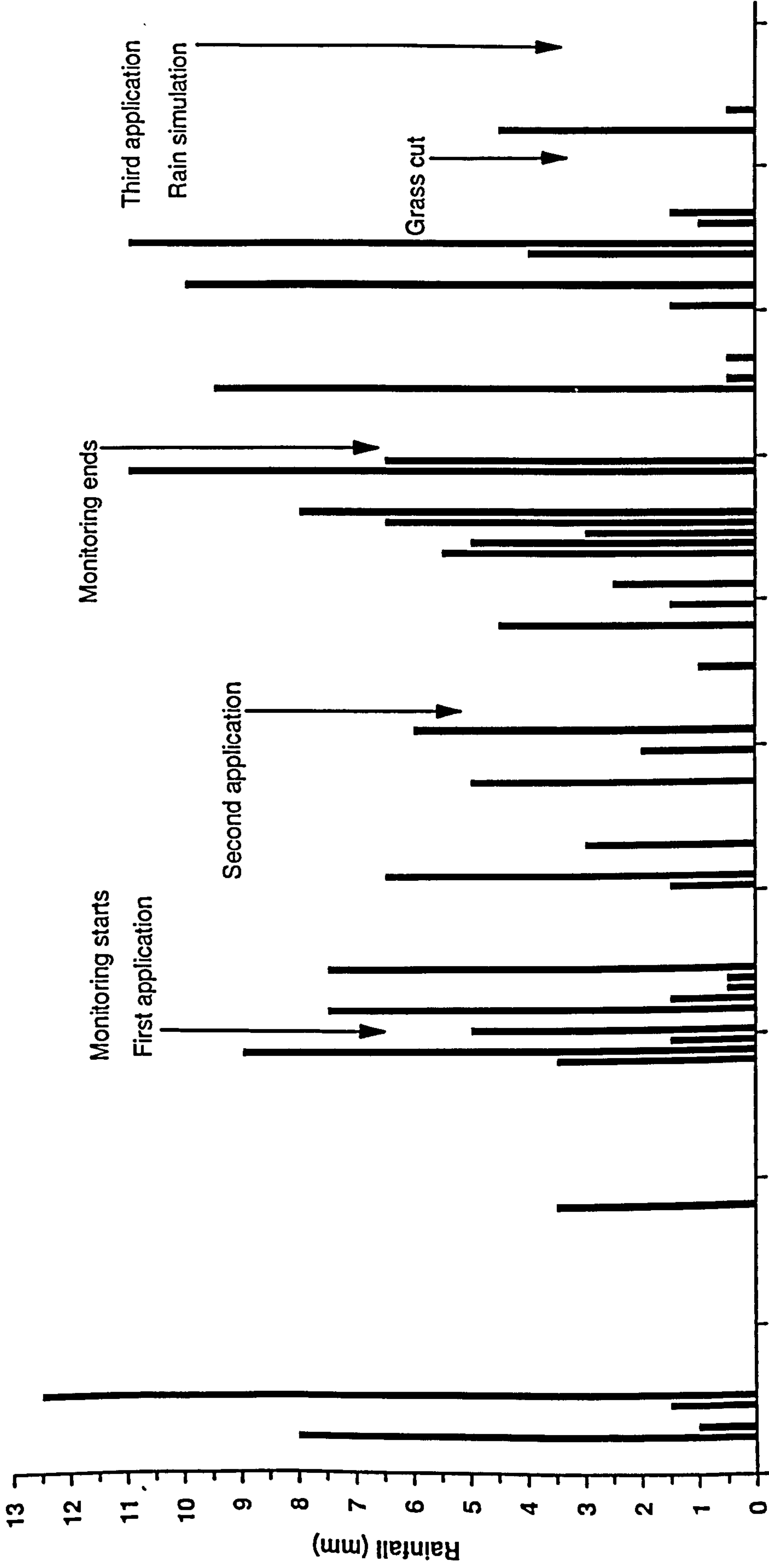
Table 3.3. Summary of treatment applications during the experimental programme at Sidney Meadow

Date	Treatment Application	Notes
mid-February 1992	49 t ha ⁻¹ manure 50 m ³ ha ⁻¹ slurry	Too early for inorganic fertiliser on pasture
mid-March 1992	50m ³ ha ⁻¹ slurry 250 kg N ha ⁻¹ , 100 kg P ha ⁻¹ of inorganic fertiliser	manure residues so no application
mid-May 1992	49 t ha ⁻¹ manure 50 m ³ ha ⁻¹ slurry 250 kg N ha ⁻¹ , 100 kg P ha ⁻¹ of inorganic fertiliser	rainfall simulation to generate surface runoff data

3.4. Results and Discussion

3.4.1. Rainfall and infiltration

Both immediately prior to and during the experimental period at Sidney Meadow, rainfall was low (Fig 3.12). Only April saw a monthly total above average at 122% of the long-term mean. January was exceptionally dry, only 27% of the long-term mean total being recorded, with over half of this falling on one day. The maximum daily total recorded during the experimental period was 11 mm, and the maximum hourly intensity recorded on the autographic gauge at Seale-Hayne was 3 mm h⁻¹. In all, the total rainfall for the period January to April 1992 inclusive was approximately 50% of the long-term mean (1961-1991). All three gauges used in the experiment recorded daily totals within 3 mm of each other. N and P concentrations within rain water were found to be negligible throughout this period. NH₄⁺-N and PO₄⁻-P were below the limits of detection by autoanalysis, while NO₃⁻-N was always below 0.5 mg l⁻¹.



01-Jan-92 15-Jan-92 29-Jan-92 12-Feb-92 26-Feb-92 11-Mar-92 25-Mar-92 08-Apr-92 22-Apr-92 06-May-92 20-May-92
 Fig. 3.12. Daily rainfall during the experimental programme at Sidney Meadow

The results of three infiltration tests carried out on 27th, 28th February 1992, and 29th March 1992 are shown combined in Fig. 3.13. Initial infiltration capacity varied widely between 13 mm h⁻¹ and 28 mm h⁻¹, depending on antecedent conditions. In all three cases, a final infiltration capacity of 5-8 mm h⁻¹ was reached after around one hour. While only being approximate, these measurements of infiltration capacity clearly show that the rainfall during the experimental period before rainfall simulation took place was never of sufficient intensity to generate infiltration excess surface run-off.

3.4.2. Soil water content

There was little fluctuation in soil water content during the main monitoring period from mid February to mid-April 1992, reflecting the relatively low amount of rainfall (see Fig. 3.14a-c). Water contents in all three zones of the control plots were broadly similar according to the horizontally oriented TDR probes (if required, refer once more to Figs. 3.3 and 3.4 for the location of plots, zones and instrumentation). In particular, there appeared to be very little difference in water content between zones 1 and 2, an indication that the hydrological effect of isolating the top of the site had not been too significant in this instance. Water content in the buffer zone was slightly higher than in the upper two zones, probably because the slope angle at the bottom of the site was some 5° less than further up.

Generally, a decrease in water content with increasing depth of soil profile was observed in all three zones, a pattern also noted in soil cores extracted for bulk density analysis (see Table 3.1). Under equilibrium conditions when rain was not falling, this distribution in soil water content was probably a reflection of soil structure in that the lower bulk densities measured near to the surface (see Table 3.1) indicated the presence of more water storage pores than at depth. This observation would be consistent with the greater content of organic matter that is generally found in soils under grass than in cultivated soils, the presence of organic matter promoting a soil structure with a greater water retention capacity (Spedding, 1983; Wild, 1993).

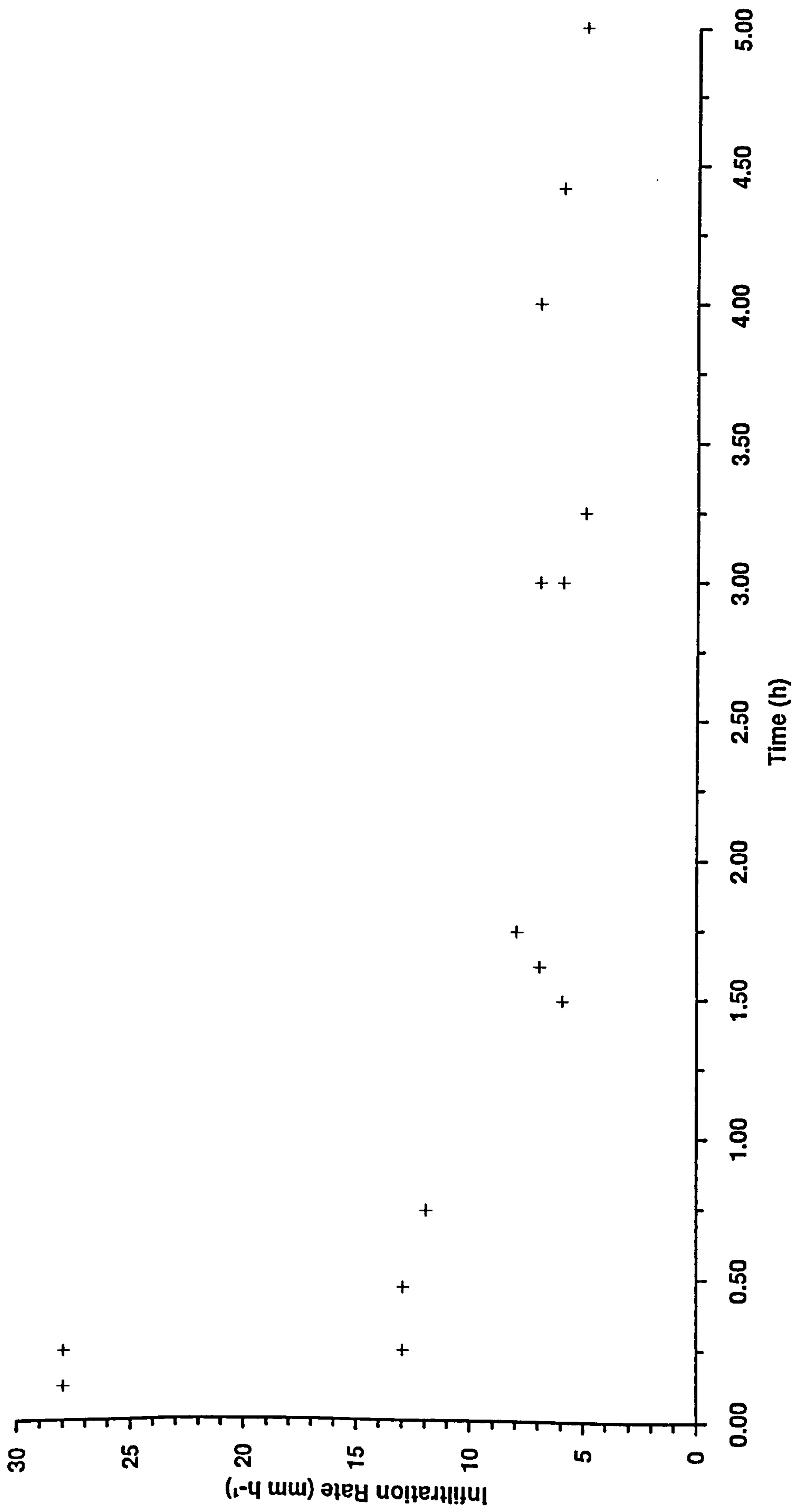


Fig. 3.13. Infiltration capacity at Sidney Meadow, February - March 1992

(Error bars in this and all subsequent figs. indicate ± 1 standard error from the mean)

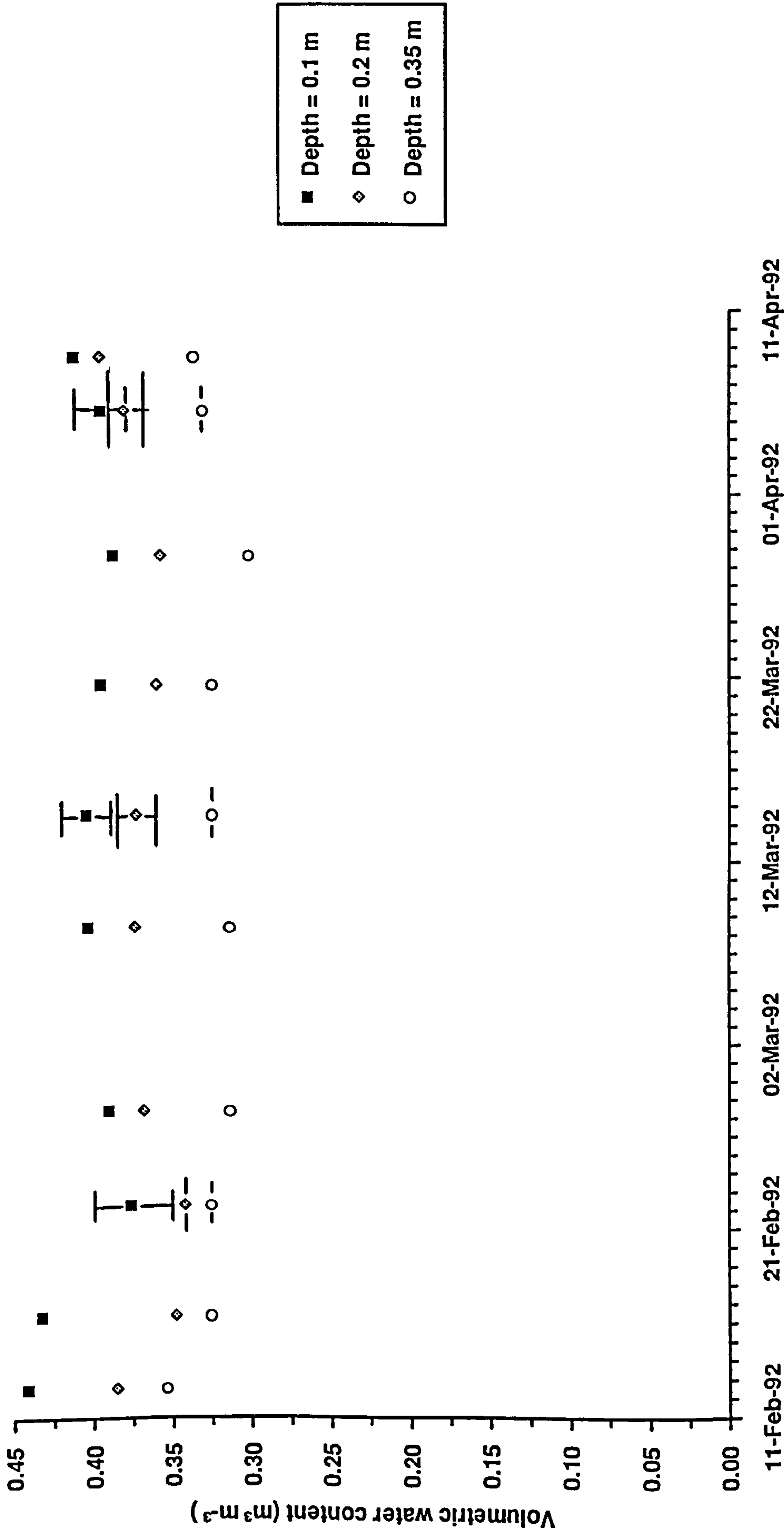


Fig. 3.14a. Mean water content in zone 1 (horizontal TDR)

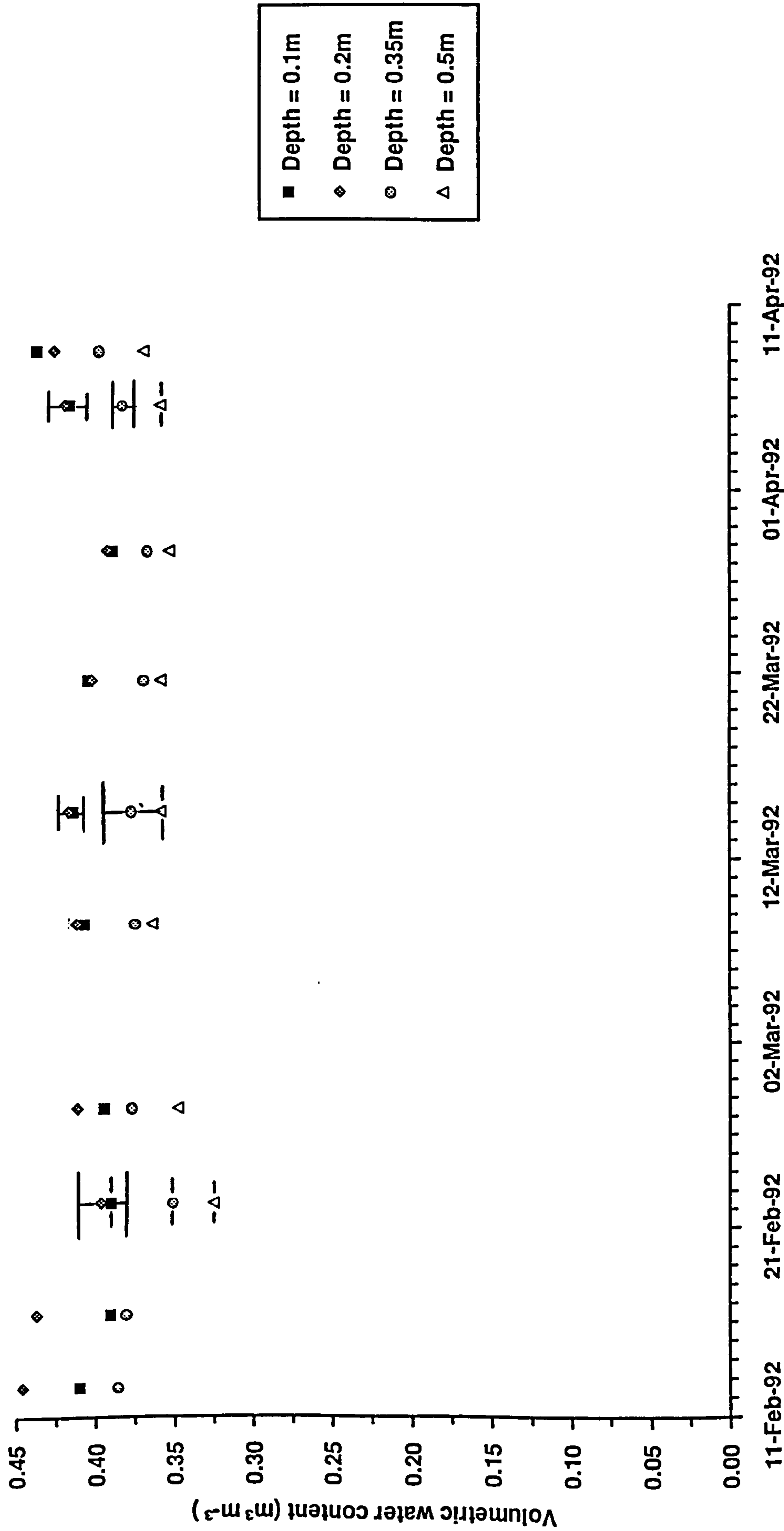


Fig. 3.14b. Mean water content in zone 2 (horizontal TDR)

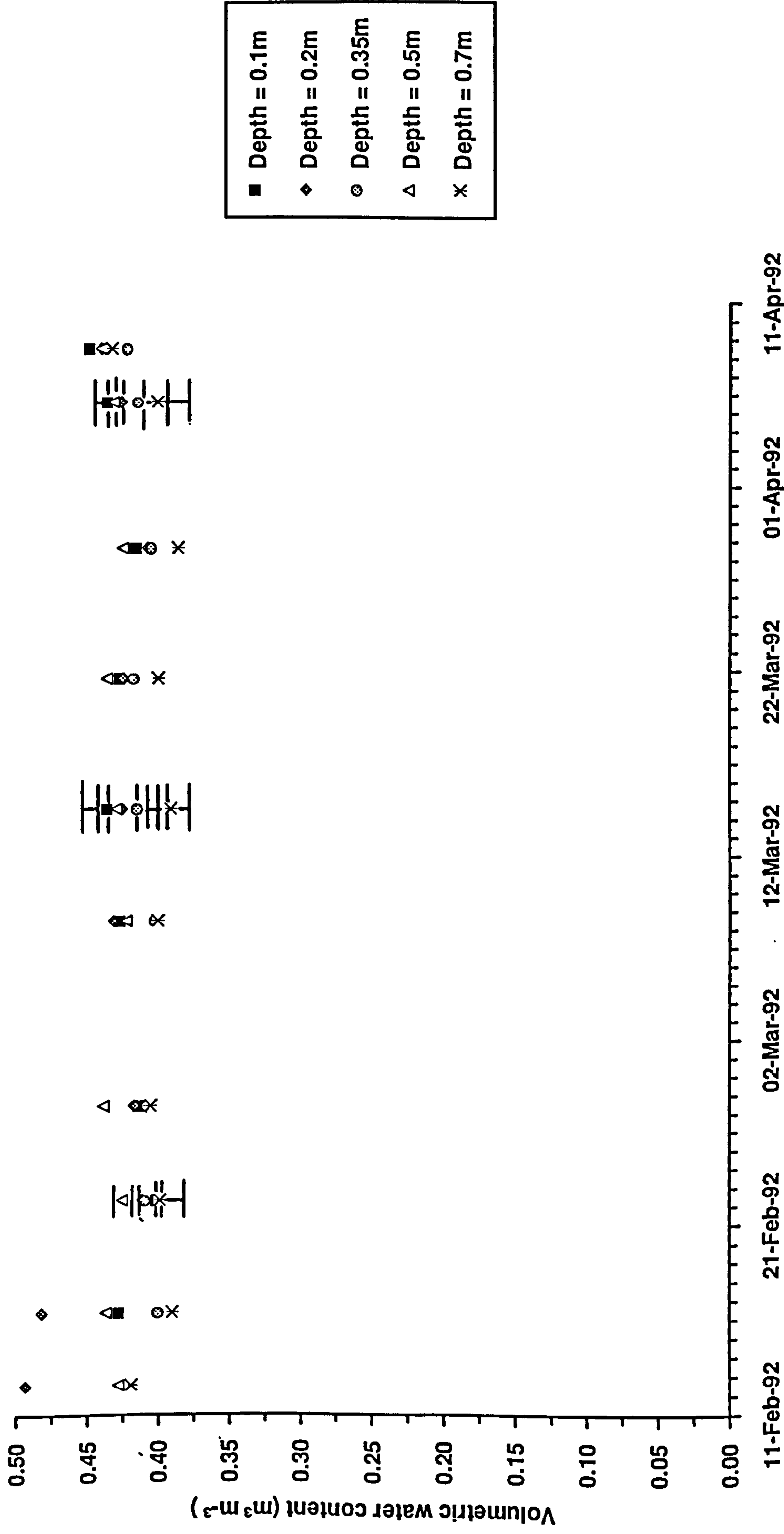


Fig. 3.14c. Mean water content in the buffer zone (horizontal TDR)

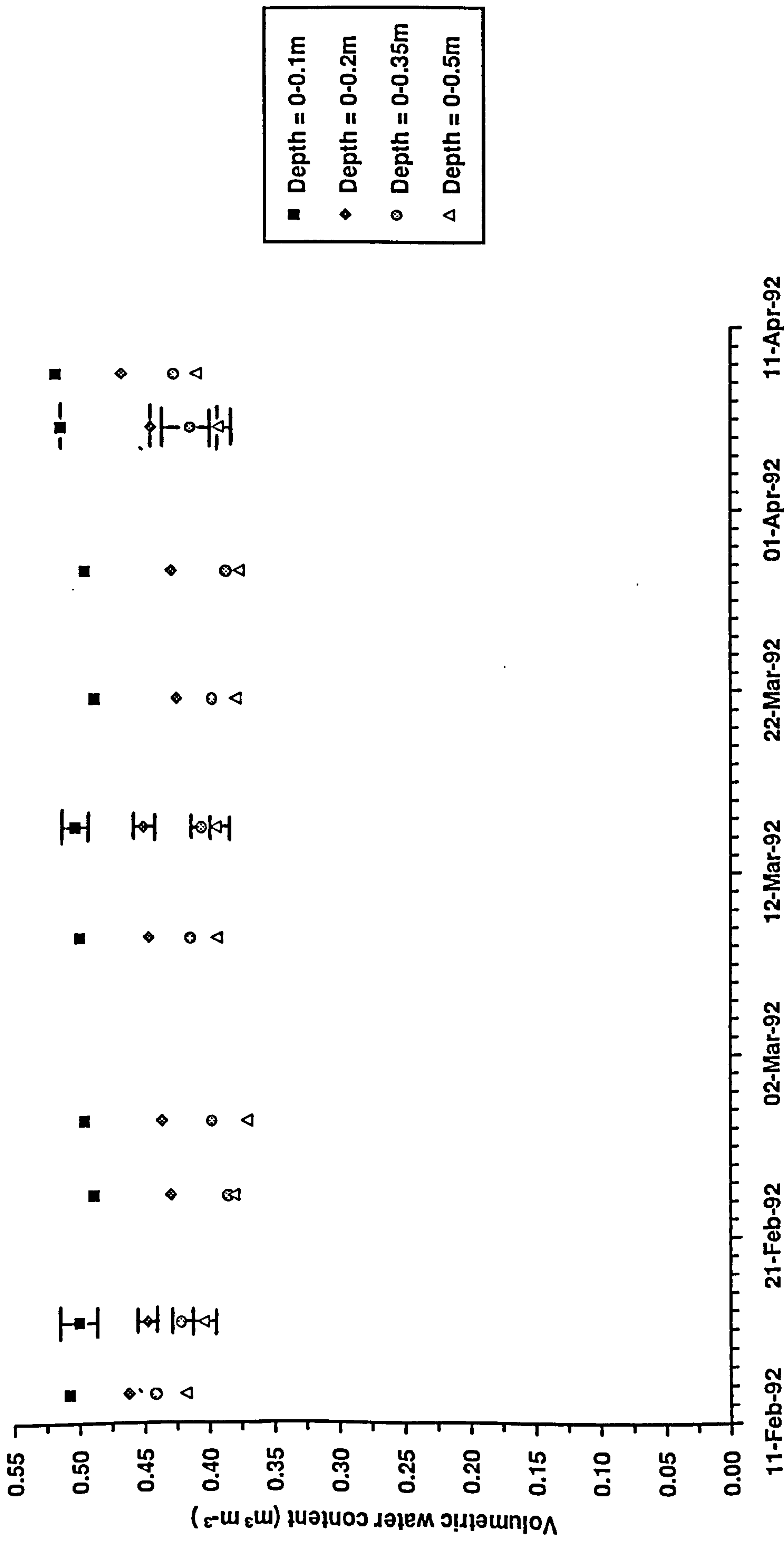


Fig. 3.15. Mean water content in zone 2 (vertical TDR)

When working on similar soils in a field adjacent to Sidney Meadow, Twomlow *et. al.* (1990) observed a 1986 / 1987 winter mean water content over the top 80 cm of the soil profile of $0.4 \text{ m}^3 \text{ m}^{-3}$. This winter mean, which is defined simply as the maximum water content which is maintained with little fluctuation during the winter months (see Reid and Parkinson, 1987), is comparable with that observed at Sidney Meadow (see Fig. 3.14a-c once more). The magnitude of winter mean and the duration for which it is maintained are dependent on the prevailing weather conditions. For Sidney Meadow, there appeared to be no significant variation in water content for the period mid-February to mid-April 1992, which indicated that water content was at winter mean level and therefore that the background rate of water flow through the soil was at its highest. It also indicated that rates of evapotranspiration were relatively low.

Because Twomlow *et. al.* were studying cultivated soil, they were able to examine the effect on the drainage properties of the soil of changes in soil structure due to different cultivation practices. They observed the presence of an impermeable zone at the base of the plough layer 0.2 m down which restricted the vertical movement of water through the soil profile. During rainfall, this caused a rapid increase in the matric potential of the surface layer, and the hydraulic gradient that resulted caused a rapid flow of water to drains via macropores above the plough sole, indicating that preferential flow could be triggered in this weakly structured soil given the right conditions (see also Coles and Trudgill, 1985). Loosening of the plough layer led to a shift in pore size distribution that gave rise to greater retention of water to a depth of 0.4 m. Consequently, a greater proportion of rainfall was diverted into the subsoil, transmission to the drains via macropore flow was reduced, and drainage was therefore delayed. This has implications for water flow in Sidney Meadow in that if the number of water storage pores and hence water content decreases with increasing profile depth, the hydraulic gradient that forms during rainfall may be sufficient in certain cases to trigger preferential flow via soil macropores. The effect of this in terms of water flow and N and P transport will be discussed later in this chapter.

The decrease in water content with profile depth was less marked in the buffer zone than in the upper two zones (Fig. 3.14c), perhaps indicating an influx from upslope.

This view was reinforced by observing an increase in water content deeper in the profile of the buffer zone in response to the rainfall in early April. This kind of response, where the water content at 0.5-0.7 m appeared to exceed that at 0.2-0.35 m, was certainly not observed in zones 1 and 2. The exact pathway of this influx of water was not clear. It may either have been lateral flow through the soil matrix or the upwelling of a water table perched on the slate layer. These pathways will also be discussed further during the course of this chapter.

Water content as recorded over sections of the soil profile by the vertically oriented TDR probes showed a similar pattern to that recorded by the horizontal probes (for an example see Fig. 3.15). The values appear higher than those for the horizontal probes, but the installation of vertical probes is such that they include the water in the top 0.1 m of the profile in the measurement, this part of the profile generally being the wettest at this time of year.

3.4.3. Soil hydraulic potential and rates of sub-surface throughflow

If measurements of soil water content give an indication of the absolute status of the soil matrix at any particular time, then measurements of soil hydraulic potential provide further indications of the direction and rate of water movement. Hydraulic potential consists mainly of matric and gravitational components, and it is first useful to consider these separately to see which, if either, is the dominant component affecting the flow of water.

During the main monitoring period at Sidney Meadow, matric potential at all depths of measurement was nearly always negative, indicating that the soil water content was below saturation point and that the water was held under some degree of suction (Fig. 3.16a-c shows mean values for each depth). Notable exceptions were in the buffer zone, where a zone of saturation rose to within 0.7 m of the surface both in mid-February and early April, and where there also appeared to be a brief occurrence of surface saturation on 12th March following 6 mm of rain (Fig. 3.16a).

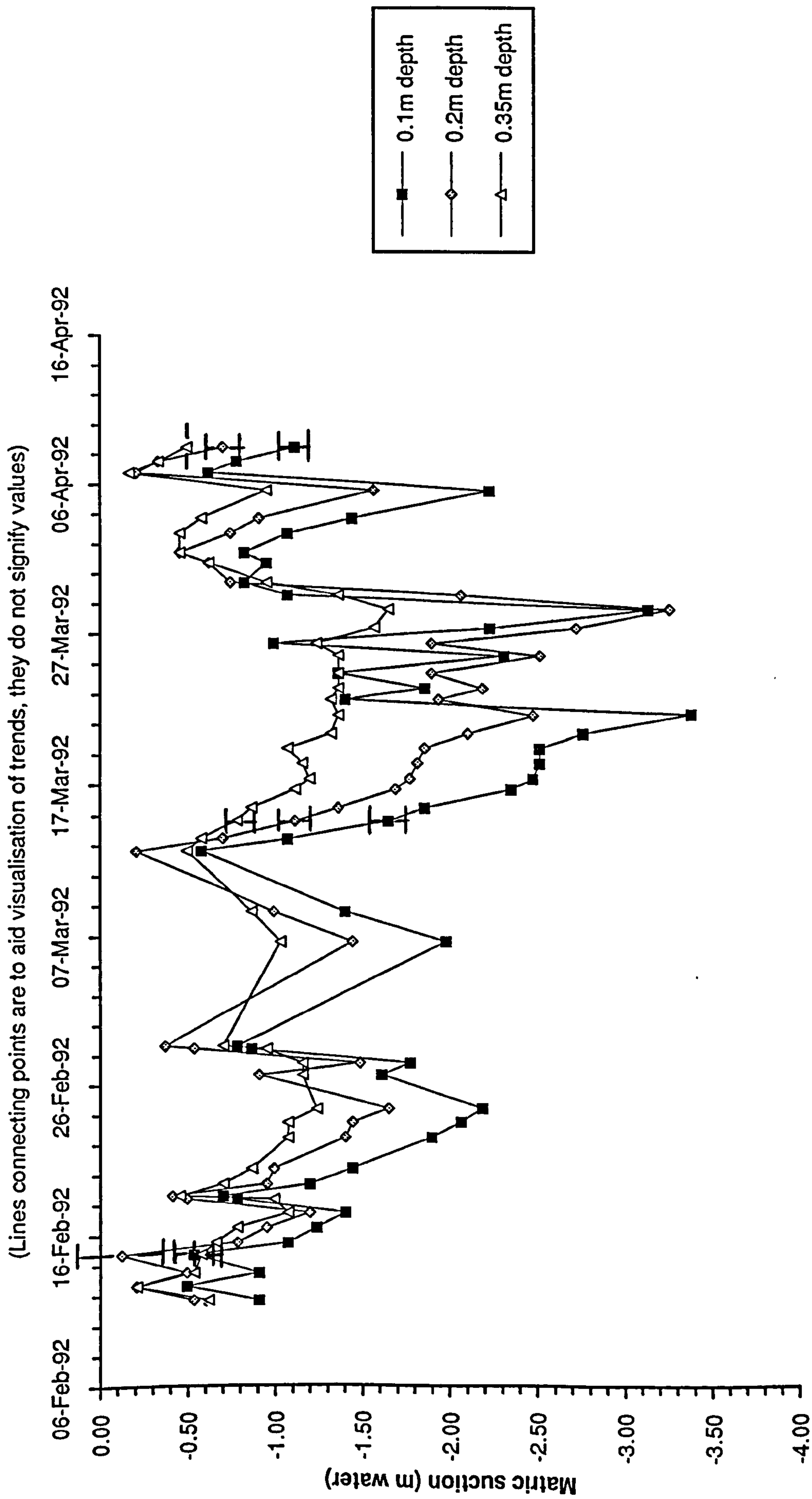


Fig. 3.16a. Mean matric suction in zone 1

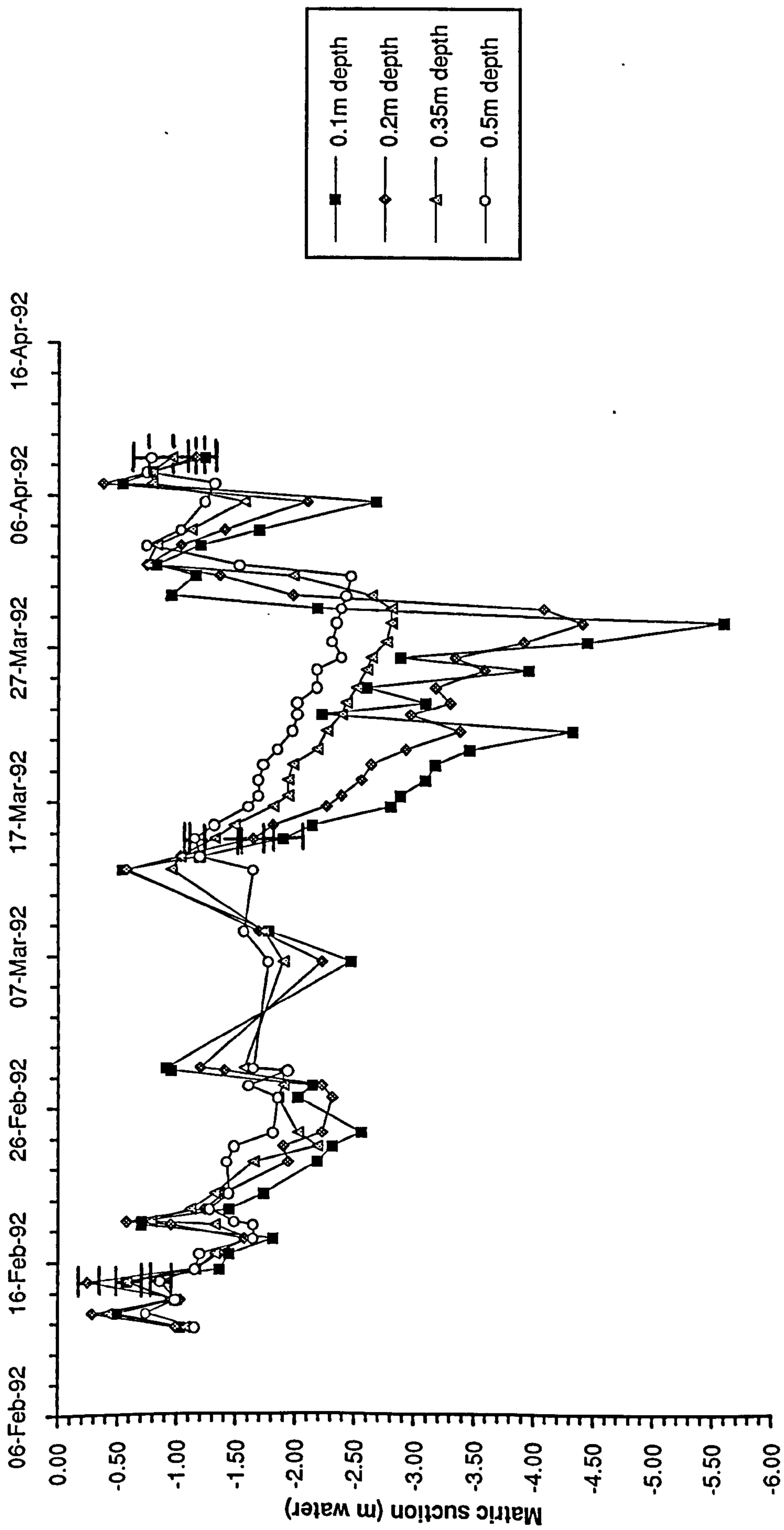


Fig. 3.16b. Mean matric suction in zone 2

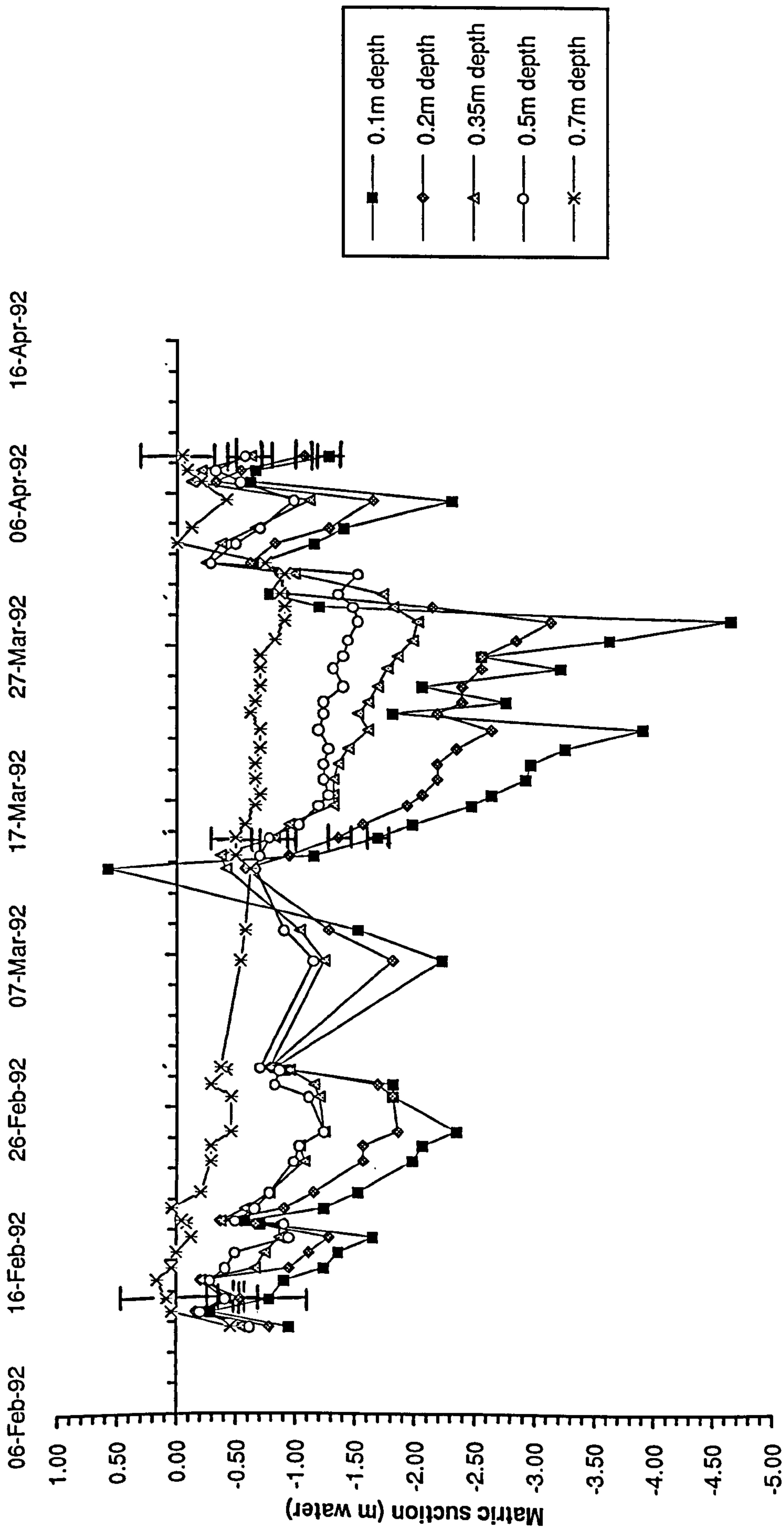


Fig. 3.16c. Mean matric suction in the buffer zone

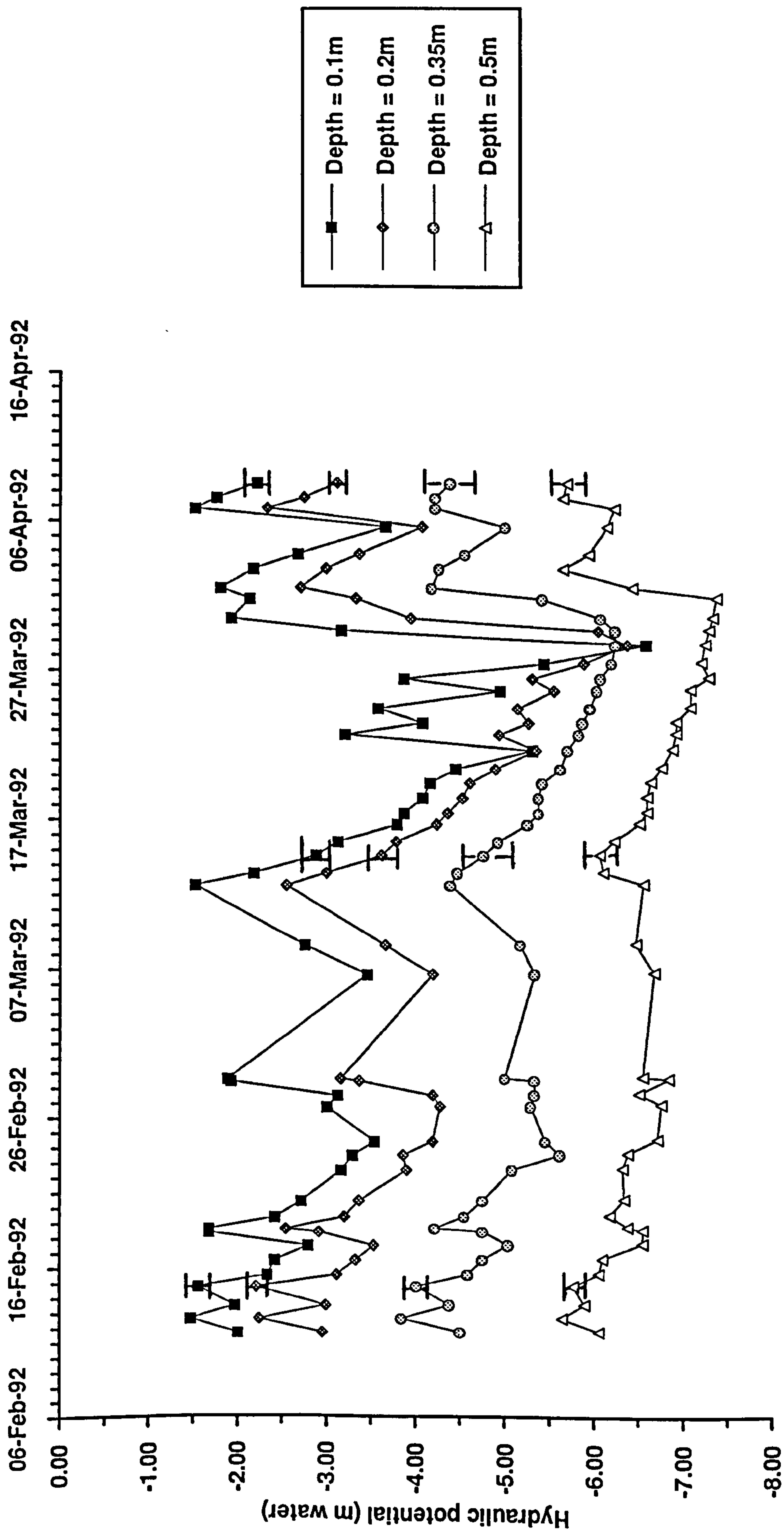


Fig. 3.17. Mean hydraulic potential in zone 2, relative to the soil surface

Matric potentials varied little with depth through the soil profile, the only real difference being in the degree of fluctuation. This tended to decrease with increasing depth, as the effects of infiltration and any evapotranspiration became more damped.

The similarity in matric potentials at different depths indicated that the flow of water would largely be determined by differences in gravitational potential between points. This is illustrated over the profile for zone 2 in Fig. 3.17, where plots of hydraulic potential show that water flow is virtually always down-profile. Rates of water flow are determined by the hydraulic gradient between two points, some example values being given in Table 3.4 below.

Table 3.4. Examples of hydraulic gradients between certain measuring points

	Down profile gradient, zone 2			Down slope gradient, zone 2 to buffer zone				
	Z 2 0.1 m to 0.2 m	Z 2 0.2 m to 0.35 m	Z 2 0.35 m to 0.5 m	Z 2 0.1 m to Buf 0.1 m	Z 2 0.2 m to Buf 0.2 m	Z 2 0.35 m to Buf 0.35 m	Z 2 0.5 m to Buf 0.5 m	Z 2 0.1 m to Buf 0.5 m
20 th Feb	6.6	9.2	10.7	1.5	1.5	1.4	1.4	1.8
20 th Mar	4.5	4.9	7.6	1.5	1.4	1.4	1.4	1.7

Z2 = Zone 2. Buf = Buffer zone. 0.1 m - 0.5 m indicate depths in the profile for the zone in question. Gradients are dimensionless.

The values in Table 3.4 show that hydraulic gradients in the vertical plane down the soil profile were considerably steeper than those in the lateral plane down-slope. This was the case for all three zones throughout the monitoring period of mid-February to mid-April. The last column in Table 3.4 illustrates that gradients between any two depths in different zones are similar to gradients between the same depths in different zones. It is clear that during this monitoring period at least, most water in the soil matrix was flowing vertically downwards as opposed to laterally. The eventual fate of this water was not so clear. It may simply have been percolating through the slate layer to a water table, a proportion of it perhaps re-emerging at the base of the slope, or, much of it may

have been retained directly above the slate layer, from where it would flow laterally downslope in the upper layers of slate or the lower parts of the soil profile.

Despite uncertainty over exact pathways, it was assumed that some water would have moved laterally downslope and in part through the soil structure, mainly because of the apparent influx of water into the lower parts of the buffer zone profile, as discussed in section 3.4.2 above. It is this component of flow that is of particular interest when considering the sub-surface transport of N and P on hillslopes. Therefore, what follows is a summary of an attempt to estimate the rate of lateral sub-surface throughflow from the available data on soil water content, hydraulic potential, and hydraulic conductivity. By comparing these estimates with the observed quantities of water draining into the throughflow collection pits, one could at least test the quality of the interpretation of the hydrological data obtained.

Determination of hydraulic conductivity for at least one value of soil water content is important when making even the crudest estimate of the rate of soil water movement. Results of laboratory determinations of saturated hydraulic conductivity using extracted soil cores are shown in Table 3.5.

Table 3.5. Saturated hydraulic conductivity as determined in the laboratory

Core number	Bulk density (dry basis) (g cm ⁻³)	Saturated volumetric water content (%)	Saturated hydraulic conductivity (ksat) (mm h ⁻¹)
2/2/20	1.16	55	86
5/1/20	1.30	60	28
5/2/20	1.30	45	80
11/2/20	1.37	46	8
Mean	1.28	52	50
Standard error	0.04	4	19
2/3/50	1.68	45	4
5/3/50	1.35	44	150
11/3/50	1.37	37	150
Mean	1.43	42	101
Standard error	0.11	3	49

Notes relating to Table 3.5.

Core number = plot/zone/extraction depth, cm. Core dimensions = 127 mm long x 102 mm diameter.

Cores were extracted in January 1993.

Even the small number of cores analysed indicated that saturated hydraulic conductivity was spatially highly variable. Errors can occur with this technique, particularly due to leakages down the sides of the core if extraction from the soil profile is not carried out with care (Klute and Dirksen, 1986). However, such errors would not account for the high conductivities observed in some of the cores. These conductivities were probably indicative of the presence of cracks or fissures in the soil, and therefore what was being observed was effectively preferential flow under saturated conditions. The lower conductivities of 4-8 mm h⁻¹ probably represented rates of saturated flow through a soil matrix that did not contain cracks or fissures, and where the largest pores were transmission pores (from Bache, 1990, see Chapter 2, section 2.2 for pore definitions).

In making this estimate of the rate of water movement, it was assumed that given the soil water conditions in Sidney Meadow from February to April 1992 and the low rainfall, most of the sub-surface throughflow would occur as matrix flow. Therefore, the maximum hydraulic conductivity was taken as 8 mm h⁻¹, or 0.19 m day⁻¹. As soil water content decreases from saturation, hydraulic conductivity decreases quite rapidly as the water has to be transmitted through smaller pores. Here, the relationship between hydraulic conductivity and water content was described by a simple exponential equation of the form,

$$y = (e^{bx}) - 1$$

which generated the curve shown in Fig 3.18, when saturated volumetric water content was set at 50% and saturated hydraulic conductivity was taken as 8 mm h⁻¹.

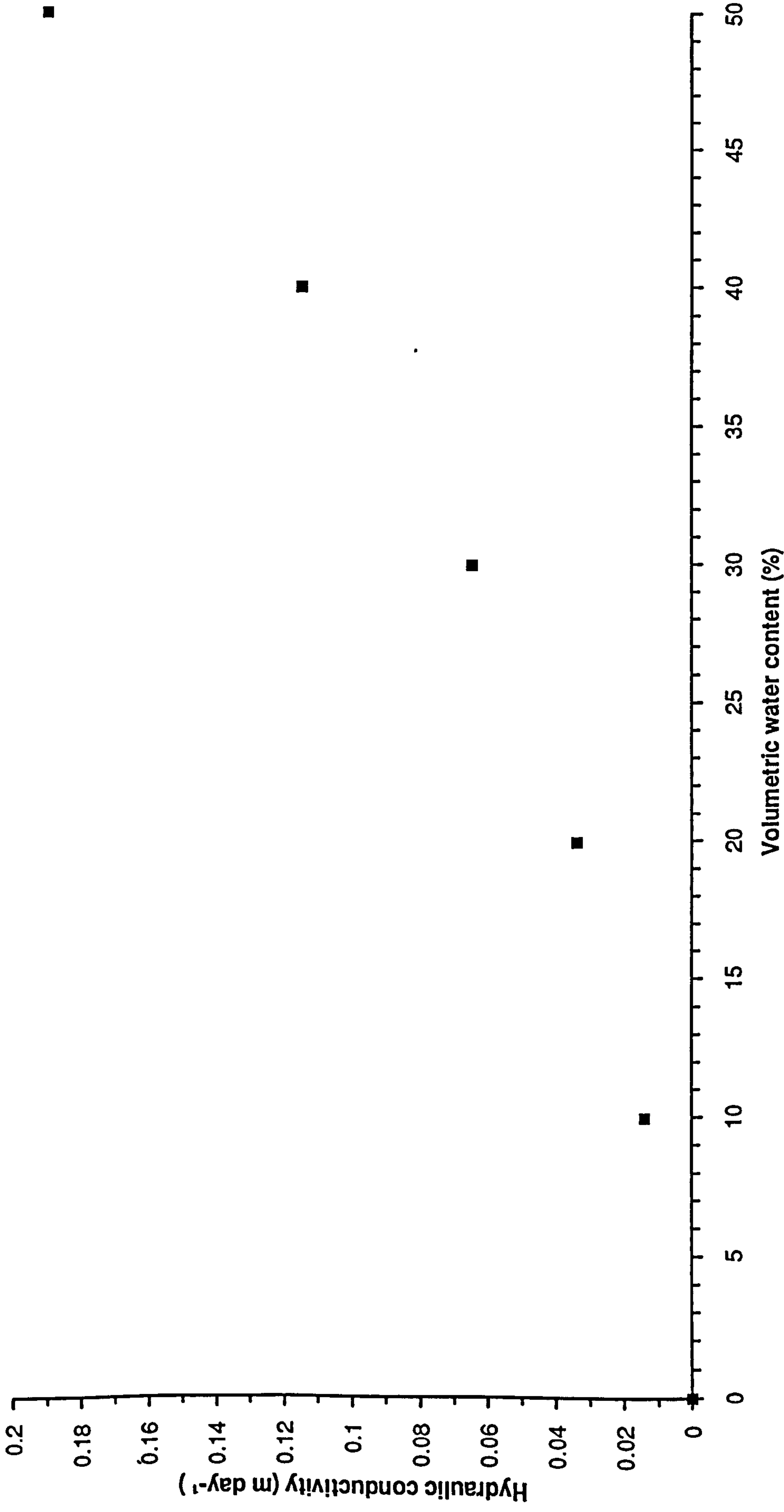


Fig. 3.18. Soil water content and estimated hydraulic conductivity

Despite the changes in soil water content and hydraulic potential observed through the soil profile, it has been shown that these differences are of little significance when comparing movement of water from one zone to another, particularly in the case of hydraulic potential gradient (again see Table 3.4). Consequently, for the purpose of this estimate, each zone was treated mathematically as a uniform storage block, with one mean water content and hydraulic potential. Working only on the centre replicate where the throughflow collection pits were sited (see Fig. 3.4), values of water content and corresponding hydraulic conductivity were calculated for the dates for which data were available (see Table 3.6).

Table 3.6. Mean soil water content and calculated hydraulic conductivity

Date	Volumetric water content zone 1 (%)	Volumetric water content zone 2 (%)	Volumetric water content buf zn (%)	Hydraulic cond. zone 1 (m day ⁻¹)	Hydraulic cond. zone 2 (m day ⁻¹)	Hydraulic cond. buf zone (m day ⁻¹)
22 Feb 92	35	37	41	0.09	0.10	0.12
27 Feb 92	37	39	42	0.10	0.11	0.13
8 Mar 92	37	39	42	0.10	0.11	0.13
14 Mar 92	38	40	42	0.10	0.11	0.13
21 Mar 92	37	39	42	0.10	0.11	0.13
28 Mar 92	36	38	41	0.09	0.10	0.12
5 Apr 92	38	40	42	0.10	0.12	0.13
8 Apr 92	39	41	44	0.11	0.12	0.14

Data from the tensiometers were used to calculate mean hydraulic gradients between zone 2 and the buffer zone for the same dates. Assuming laminar flow in the matrix, Darcy's Law was applied, and the following equation was used to obtain crude estimates of the rate of flow of water into the throughflow collection pits,

$$Q = k A \frac{d\phi}{dL}, \text{ where,}$$

$$Q = \text{flow, m}^3 \text{ day}^{-1}.$$

k = hydraulic conductivity at the water content in the buffer zone, m day^{-1} .

A = area of the collection pit face, m^2 .

$\frac{d\phi}{dL}$ = hydraulic potential gradient between zone 2 and buffer zone, unitless.

Accepting the assumptions made and the inevitable errors, there was some degree of agreement between the volumes of flow estimated and the volumes observed in the throughflow collection pits (see Fig. 3.19). Of more significance was the difference between estimation and observation regarding the response to rainfall. During the drier period of mid to late March, it can be seen that rates of flow were grossly over-estimated. However, even following rainfall of relatively low intensity occurring in February and early April, rates of flow appeared to be under-estimated. Adopting the principles of matrix flow apparently led to a smoothing of the sub-surface throughflow patterns. There are (at least) two possible explanations of this smoothing effect. Firstly, it could be that the presence of the throughflow collection pits themselves was preventing the matrix flow of water during the drier periods, causing a saturated wedge to build up at the pit face, which then drained rapidly following rainfall (again see section 3.2.1 and Atkinson, 1978). Secondly, it may be that the water content and hydraulic conductivity of the whole soil structure was at a critical boundary during much of the monitoring period, such that during even low intensity rainfall, substantial preferential flow occurred through the larger transmission pores and fissures. Coles and Trudgill (1985) observed this effect when working on similar soils in South Devon, and Twomlow *et. al.* (1990) observed a similar effect due to build up of water above a plough pan on cultivated soils in a field adjacent to Sidney Meadow. In between rainfall events, it is argued that only slow matrix flow takes place.

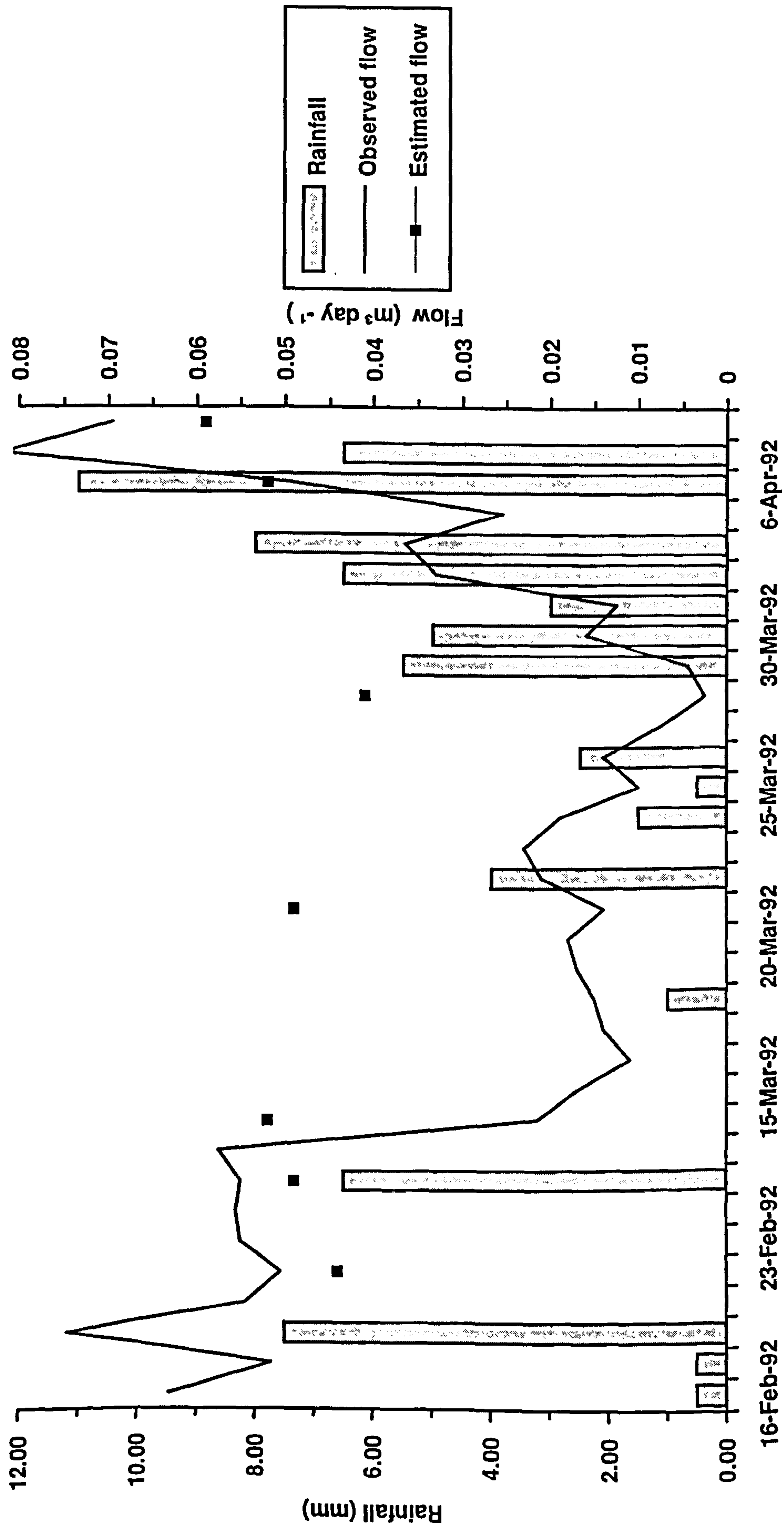


Fig. 3.19. Flow into throughflow collection pits compared with estimates from other field data

This issue of throughflow mechanisms can be explored further by examining the influence of saturated flow in Sidney Meadow during the monitoring period. None of the installed piezometers recorded any occurrence of saturated flow above a depth of 0.5 m, and the instruments at 0.7 m in the buffer zone only recorded sporadic instances of saturated flow lasting no more than 24 hours.

From readings of the dipwells in the control plots (see Fig. 3.4 for locations), it was apparent that the influence of saturated flow was largely confined to the lower soil profile toward the bottom of the buffer zone (Fig. 3.20). Readings from plot 5 in the central block indicated that during mid-February and early April, the level of the saturated zone rose above the bottom of the throughflow collection pits. These were the times when rates of throughflow tended to be under-estimated by assuming unsaturated matrix flow. Therefore, it would appear that a general rise in the level of the saturated zone may have been responsible for the fluctuation in rates of throughflow, rather than the distorting influence of the collection pits. The cause of the rise in the level of the saturated zone cannot be clearly identified from the data available. Rapid fluctuation in the depth of the saturated zone following relatively low rainfall is perhaps an indication of charging by means of preferential flow from the surface, but the pathway is not certain. For example, water may have been forced upward out of the slate layer due to the pressure of inputs from the slope above the experimental site, or water may have flowed through the profile and perched on the slate layer at the foot of the slope. The spatial variation in the absolute depth of the saturated zone in Sidney Meadow (relative to point 1 on the topographic survey, details in Appendix 1), was of some interest in this respect (see Figs. 3.20 and 3.21). Clearly, the saturated zone was not a horizontal water table, indicating that water may have been perched on layers of slate bedded at different depths and angles. This may also imply sideways movement of water in the saturated zone.

16-Feb-92 21-Feb-92 26-Feb-92 2-Mar-92 7-Mar-92 12-Mar-92 17-Mar-92 22-Mar-92 27-Mar-92 1-Apr-92 6-Apr-92 11-Apr-92

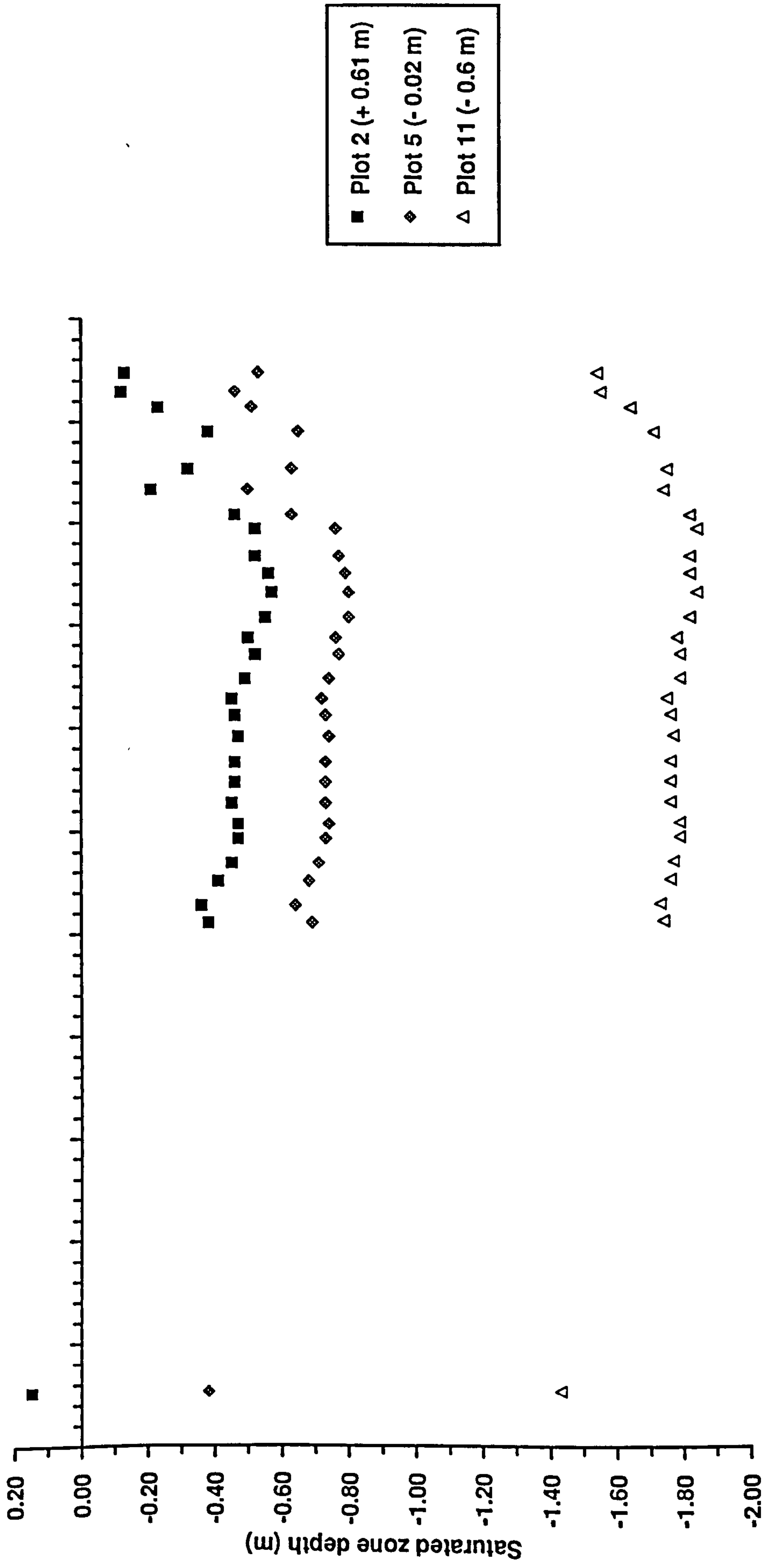


Fig. 3.20. Depth of saturated zone in buffer zone of control plots (relative to point 1 on the topographic survey, see Appendix 1)

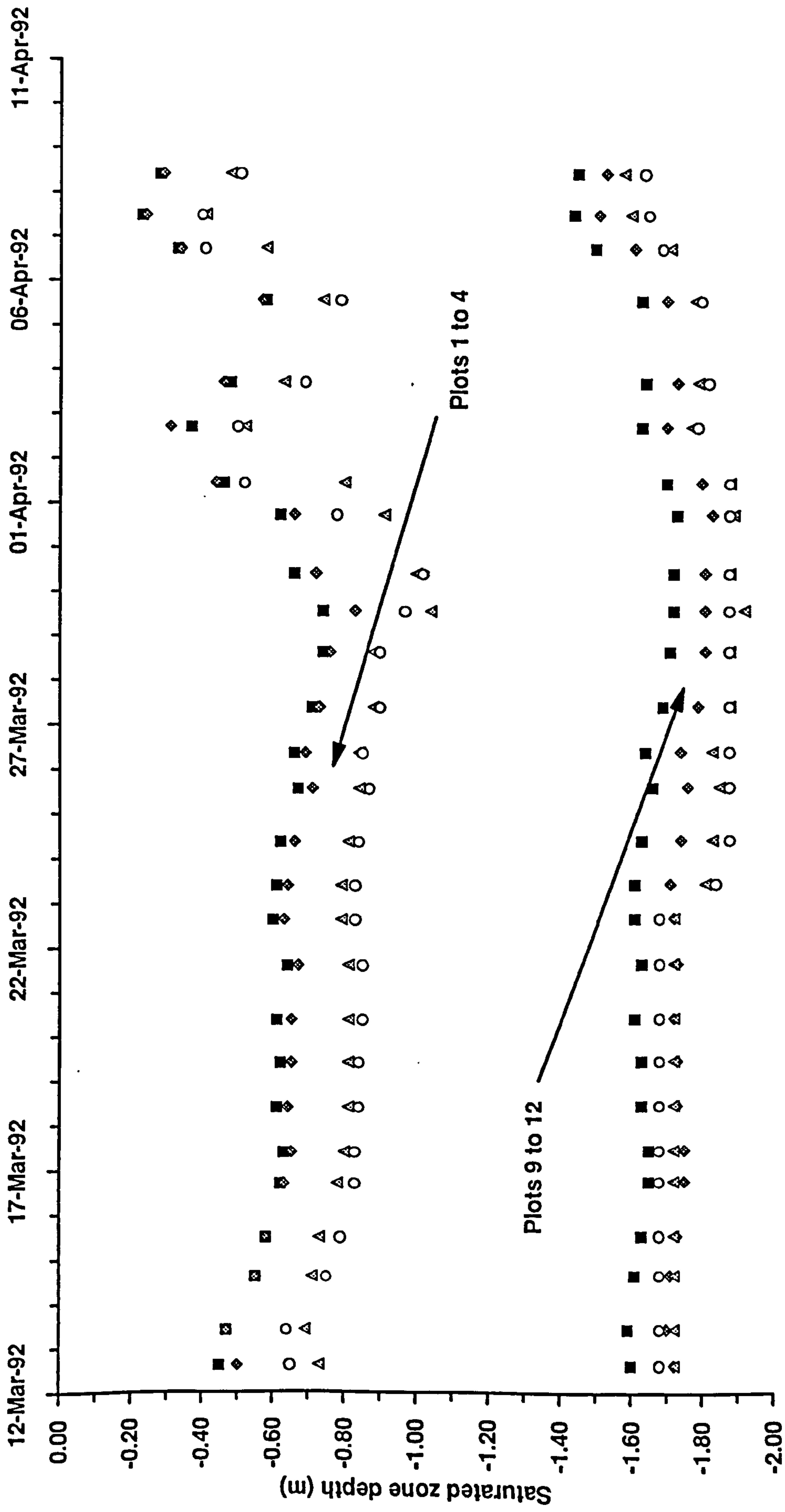


Fig. 3.21. Depth of the saturated zone at the bottom of the plots (relative to point 1 on the topographic survey, see Appendix 1)

A number of workers have employed tracing techniques to identify pathways of sub-surface flow on hillslopes during rainfall events. For example, Leaney *et. al.* (1993) compared the signatures in rainfall of the conservative tracer chloride and the stable isotope deuterium with signatures in soil water and throughflow for a mid-slope podzolic soil under unfertilised pasture. They concluded that for all rainfall events at all times of the year, 80-90% of throughflow was due to preferential flow of rainwater through macropores. They also noted that a perched water table was established soon after the onset of rainfall, and mixing of rainwater in this water table tended to damp the short-term variations in chloride and deuterium concentrations that were observed in rainfall. Although the weakly structured soil of Sidney Meadow is not directly comparable with a podzol, the response to rainfall and the rise in the level of what appeared to be a perched water table at Sidney Meadow is not inconsistent with the observations made by Leaney *et. al.* If this is a correct interpretation of the throughflow mechanisms at Sidney Meadow, it has implications for the transport of N and P that have been discussed in the conceptual model of Chapter 2 and are discussed further in later parts of this chapter.

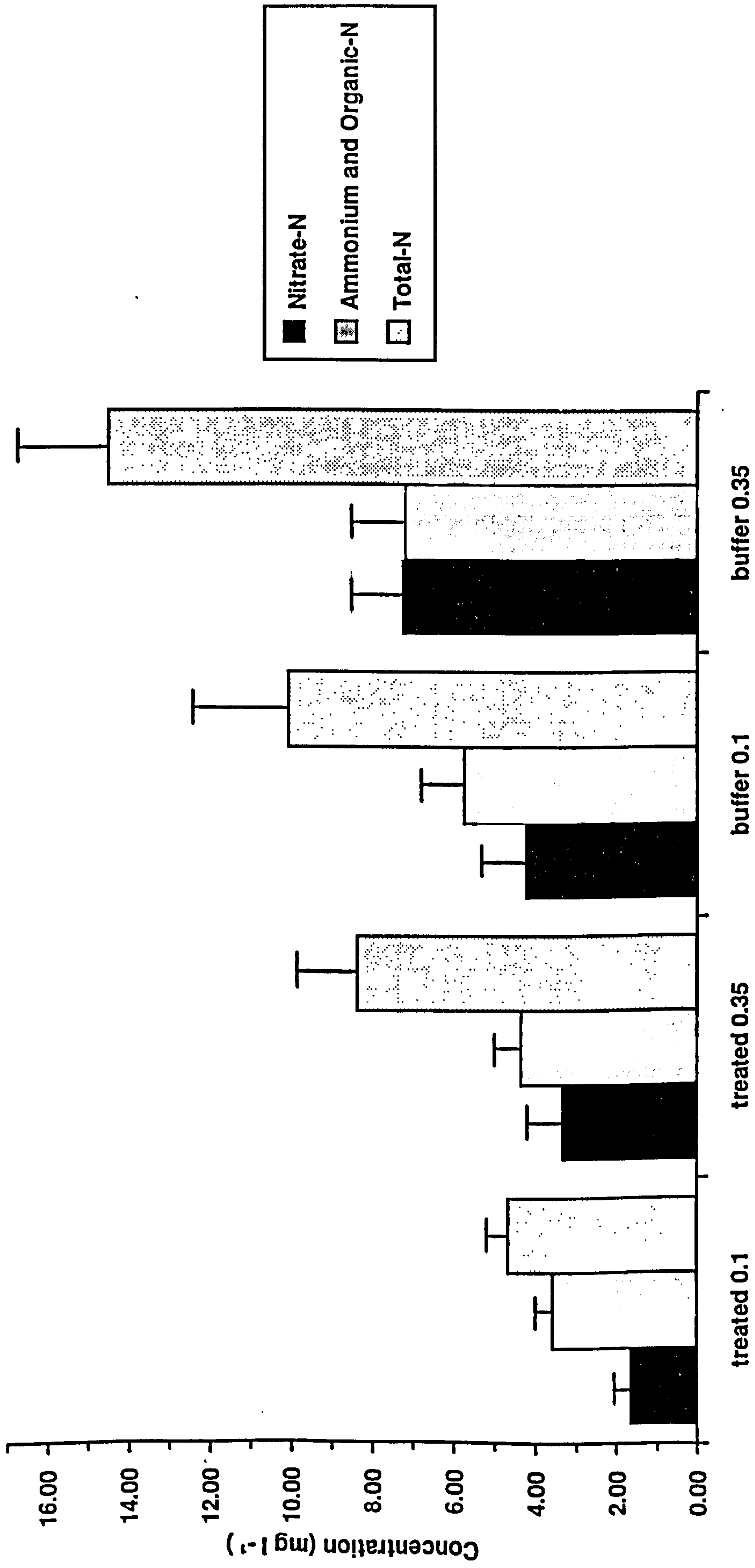
Wilson *et. al.* (1993) used bromide from buried line sources to investigate sub-surface flow during storm events on a forested hillslope. Rapid preferential flow in macropores was observed, with bromide breakthrough occurring in a collection pit 65 m from the line source just 3 hours after release on one occasion. Micropores were identified as a sink for bromide during storm events, with some 47% of the tracer being immobilised in these pores. In subsequent events, initial sub-surface flow showed a dilution of bromide due to 'new' water flowing preferentially, followed by a flushing of bromide from micropores and a delayed increase in concentration (this is an indication of what could happen to NO_3^- -N in similar flow pathways as discussed in Chapter 2 and later parts of this chapter). It was also noted that the interaction between stormflow in the upper 2 m of the soil profile and groundwater was not significant, although there was evidence of significant lateral stormflow below 2 m.

The interaction between throughflow in the upper soil horizons and groundwater flow was examined by O'Brien and Hendershot (1993). They used a range of conservative

and reactive tracers to separate streamflow in a small forested catchment into components of throughflow, groundwater flow, and upwelling flow, where water rises from the groundwater and into the upper soil horizons before flowing into the stream. It was found that conservative tracers allowed identification of the mix of water sources, since their composition was unaffected by the soil matrix, whereas the reactive tracers interacted with the soil matrix such that their final chemical composition reflected the pathway they had taken between source and stream. Such an approach might have been usefully employed at Sidney Meadow to ascertain whether groundwater was upwelling into the throughflow collection pits, or if the saturated zone consisted entirely of a perched water table with no groundwater input. The application of a conservative tracer above the line of hydrological isolation could also have been used to see if water from the slope above the site was flowing beneath the plots and re-emerging in the throughflow pits at the base of the slope. Trudgill (1987), has examined the suitability of three fluorescent dyes for similar soil water tracing applications, both in the laboratory and the field.

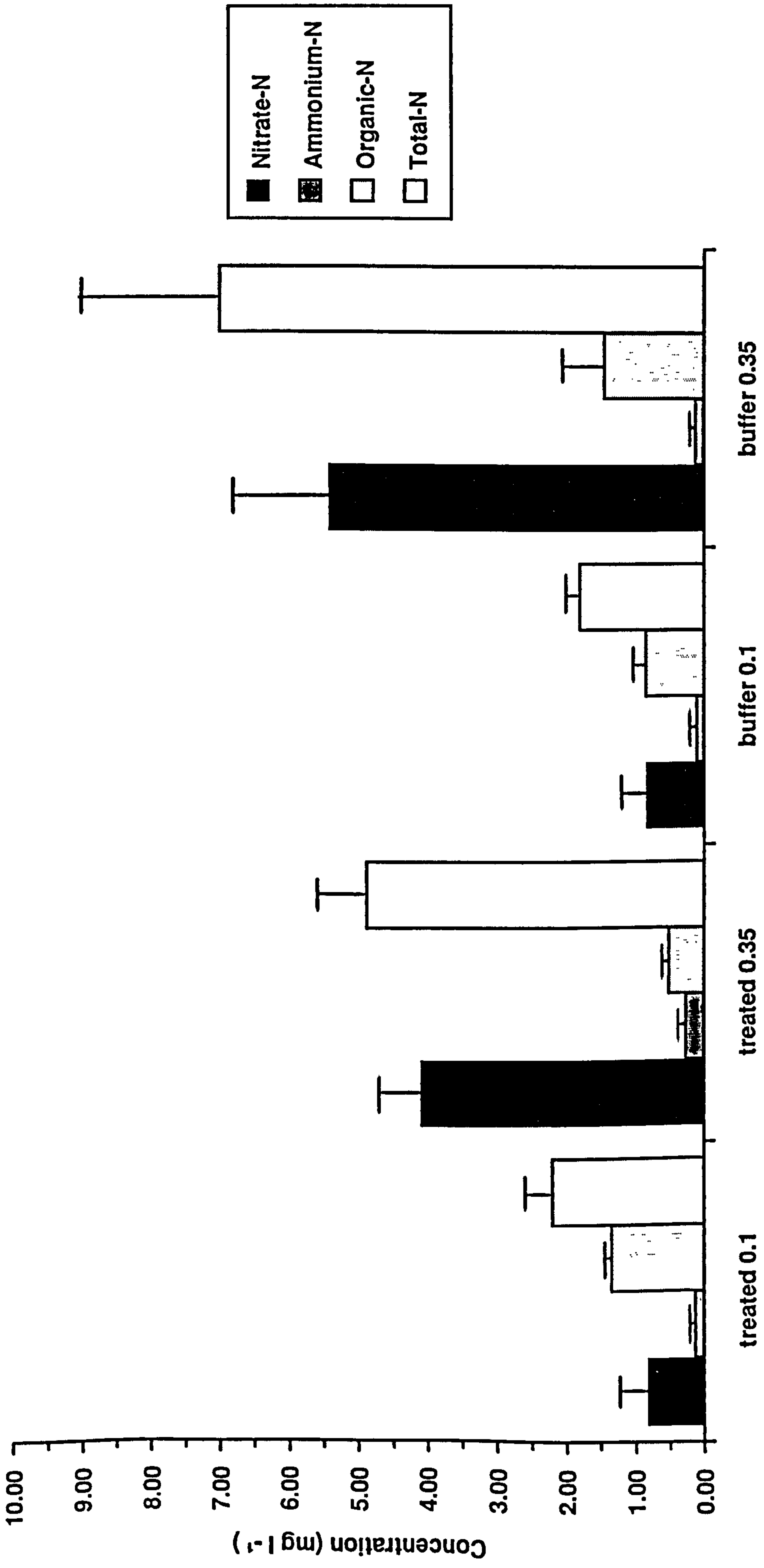
3.4.4. Nitrogen and phosphorus in the soil water

For water obtained from suction samplers, the differences in N concentration between the control and the treatments were not significant at any point in time or space on the site ($p > 0.05$, using both analysis of variance and non-parametric techniques suited to low numbers of observations and non-uniform distributions). Furthermore, concentrations of P were always below the detectable limit of 0.1 mg l^{-1} for the autoanalysis technique used (see section 3.2.2). Magid *et. al.* (1992) have noted that teflon suction cup samplers are better suited for the study of P in soil water solution, because ceramic suction cups can adsorb considerable quantities of P. For the purpose of observing general patterns of N speciation within suction samples over space and time, the results for each point on the slope and depth of sampling were combined (see Figs. 3.22-3.24). The emerging patterns were of some interest.



Slope position and depth (m)

Fig. 3.22. N speciation in suction cup samples, 13 Feb 1992



Slope position and depth (m)

Fig. 3.23. N speciation in suction cup samples, 19 March 1992

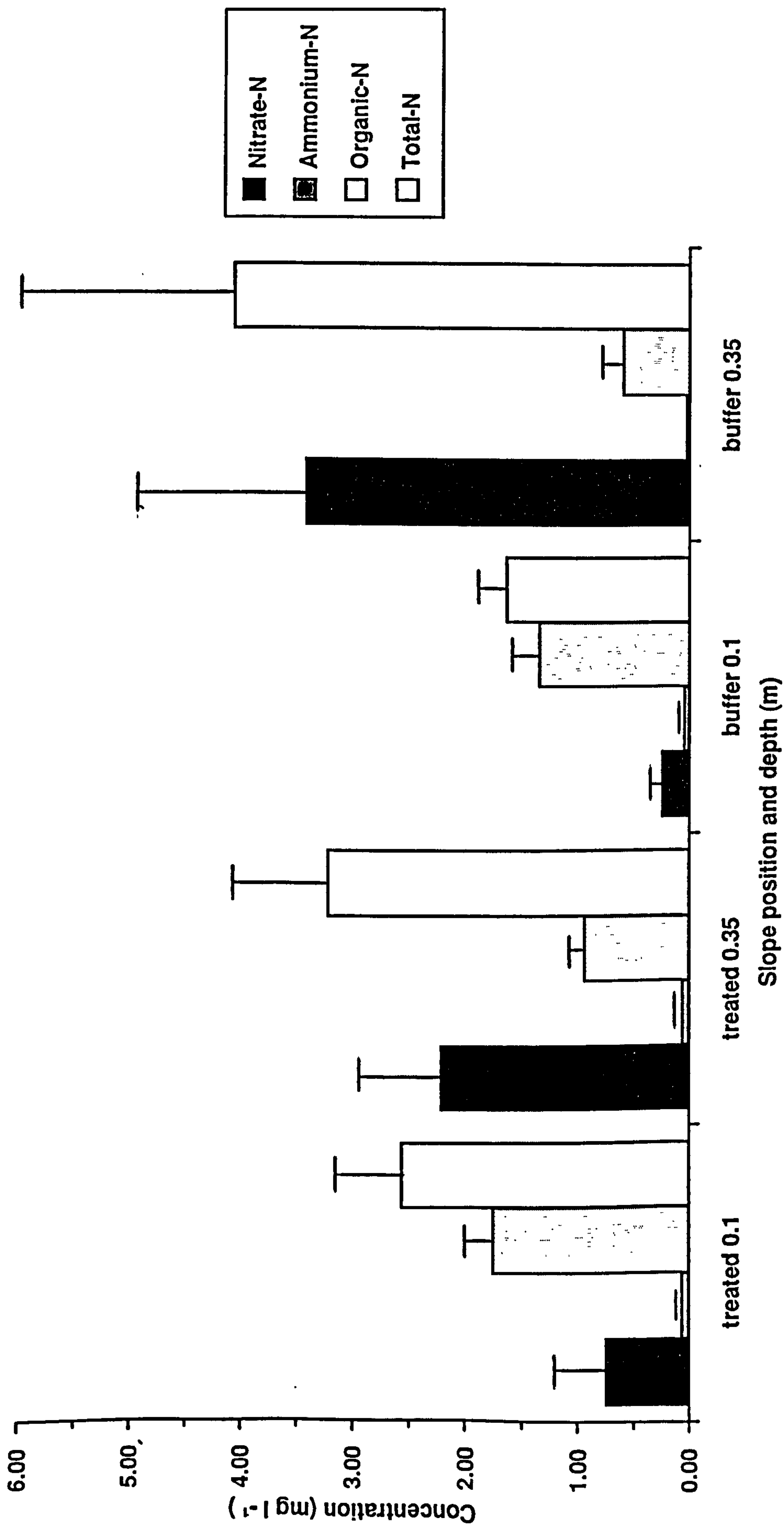


Fig. 3.24. N speciation in suction cup samples, 26 March 1992

Firstly, despite the application of treatments in mid-February and mid-March (Table 3.3), a general reduction in the concentration of N in solution was observed from mid-February to the end of March. This was attributed to the increased activity of soil micro-organisms and to favourable conditions for plant uptake, in that low rainfall was contributing to a low rate of N flushing through the soil structure. Data from the Seale-Hayne meteorological station indicated that soil temperature conditions for micro-organism activity and plant uptake were becoming more favourable from late February onwards (Fig. 3.25). There was certainly clear visual evidence of increased rates of grass growth from early March onwards, particularly on the treated plots.

Secondly, significant increases in NO_3^- -N were recorded both down-profile and down-slope ($p < 0.05$, using analysis of variance), such that concentrations at 0.35 m in the buffer zone were higher than anywhere in the treated zones. If this NO_3^- -N had been accumulating in soil micropores beneath the rooting zone, such that it may have been flushed into transmission pores had rainfall and rates of sub-surface flow been higher, some doubt would be raised about the effectiveness of the buffer in this particular situation.

It has been demonstrated in other experiments that riparian buffer strips can be quite effective in reducing sub-surface NO_3^- -N loads to water courses (Moorby and Cook, 1992; Haycock and Burt, 1993; Haycock and Pinay, 1993). The effectiveness of these buffer strips depends generally on a zone of saturation to within a few centimetres of the soil surface and a rich supply of organic carbon in the soil, thus creating suitable conditions for the reduction of NO_3^- -N to gaseous forms of N by denitrification (see Chapter 2, section 2.3). For grass vegetated buffer zones, Haycock and Pinay have observed an 84% retention of NO_3^- -N within the first 5 m of the buffer, independent of the NO_3^- -N load entering the buffer. This rate of retention rises to 99% for buffers vegetated with poplar, because of an increase in the amount of carbon in soil under tree cover. It is argued that this process is particularly effective in winter, when plant uptake of NO_3^- -N is at a minimum and load in throughflow is at a maximum. However, it is important that the buffer vegetation remains undisturbed and that the buffer is not underdrained.

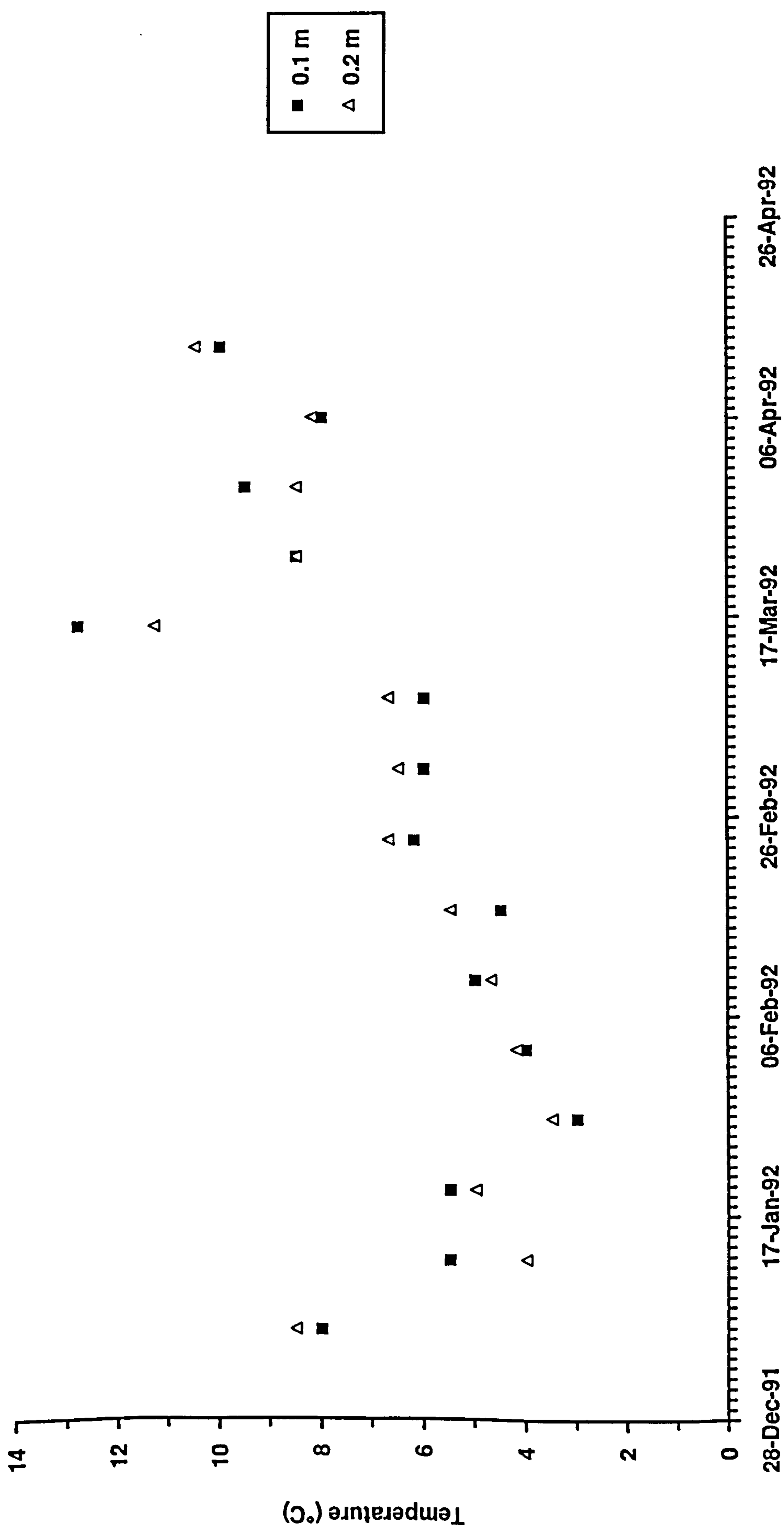


Fig. 3.25. Soil temperature at the Seale-Hayne meteorological station

For sites such as Sidney Meadow, where steep slopes end rather abruptly at water courses, the widespread occurrence of conditions favourable for riparian zone denitrification is not guaranteed. This might be even more the case if the pasture was underdrained. Garwood *et. al.* (1985) noted that when 400 kg N ha⁻¹ was applied to drained and undrained sections of permanent grassland, sub-surface loss of NO₃⁻-N was 216 kg ha⁻¹ from the drained section compared with 69 kg ha⁻¹ from the undrained section, and denitrification losses were 46 kg ha⁻¹ and 64 kg ha⁻¹ respectively. However, when Barraclough *et. al.* (1992) examined the transport of NO₃⁻-N from grazed swards following applications of fertiliser N, they could not support the hypothesis that drainage increased rates of NO₃⁻-N leaching and reduced denitrification. Other factors were found to be of importance, such as the age of the grass sward. They concluded that predicting NO₃⁻-N leaching from a grazed sward following fertiliser application was extremely difficult.

Assuming that widespread denitrification does not take place, the transport of NO₃⁻-N then depends on rates of sub-surface throughflow and on the pore size in which most of the NO₃⁻-N is being held, which in the case of Sidney Meadow was not determined. It may be that much of the recorded NO₃⁻-N had accumulated in residual pores by means of anion attraction to soil cations. Therefore, an increase in the rate of sub-surface flow would only cause a significant increase in the transport of NO₃⁻-N if there was a degree of mixing between "old" and "new" water. Magid *et. al.* (1992) compared suction cups with zero tension lysimeters when measuring the sub-surface transport of P. They observed much higher concentrations of P in the lysimeters than in the suction cup samples. Dye tracing revealed substantial preferential flow. The suction samples were therefore reflecting the concentration of P in stagnant pores, which was low due to soil adsorption, and the lysimeters were reflecting the concentration of P in preferential flow. Although P behaves differently to N in soil water, the need to identify transport pathways applies to both nutrients.

Patterns in NH₄⁺-N and dissolved organic-N concentrations in suction samples were harder to define. An increase in organic-N between March 19th and March 26th was observed, perhaps due to the effects of infiltration following treatment application.

Concentrations of $\text{NH}_4^+\text{-N}$ were very low, particularly in late March (see Fig. 3.24), which indicated a combination of immobilisation, plant uptake, and nitrification. Weier and MacRae (1993) used incubated soil cores to study net rates of mineralisation and nitrification under permanent pasture. The organic-N content of these soils had been traditionally high due to a previous vegetative cover dominated by legumes. They observed no net mineralisation in the cores after some 12 weeks, concluding that near the surface high C:N ratios promoted immobilisation, while further down the soil profile the dense root mass of the grass ensured efficient uptake of any mineralised or nitrified N. This may have been essentially similar to what was occurring at Sidney Meadow from late February onwards in 1992.

Water sampled from the throughflow collection pits and the dipwells gave an indication of the concentrations of N and P actually flowing from the bottom of the plots. As with the suction samples, P concentrations from these sources were below the detectable limit of 0.1 mg l^{-1} . Due to the low rainfall, low numbers of samples were collected, and therefore the results shown here for N speciation are the combined results from both collection troughs and dipwells for the period mid-March to mid-April 1992 (Fig. 3.26). Such results should be treated with caution, as they disguise the temporal reductions in N concentration that were observed here as well as in the suction samples. The N in these throughflow samples was almost entirely the $\text{NO}_3^-\text{-N}$ species, concentrations being similar to those in the suction samples, and relatively low compared to the EC directive limit of 11.3 mg l^{-1} . Differences between the control and the treatments were apparent but not quite significant ($p > 0.05$, using analysis of variance). Concentrations of $\text{NH}_4^+\text{-N}$ and organic-N were similar to those observed in the suction samples. The UK maximum admissible concentration (MAC) for $\text{NH}_4^+\text{-N}$ in public water supply is 0.5 mg l^{-1} of the ion, and the MAC relating to organic-N is $1 \text{ mg Kjeldahl-N l}^{-1}$ (figures from Heathwaite *et. al.*, 1993). Therefore, on the basis of these MACs it would seem that the transport of N in sub-surface flow from Sidney Meadow during the monitoring period was not significantly high. Generally, the patterns observed in the suction samples were repeated in the throughflow collection pits and dipwells. $\text{NH}_4^+\text{-N}$ and organic-N appeared to be largely immobilised in the soil, while any increase in the rate

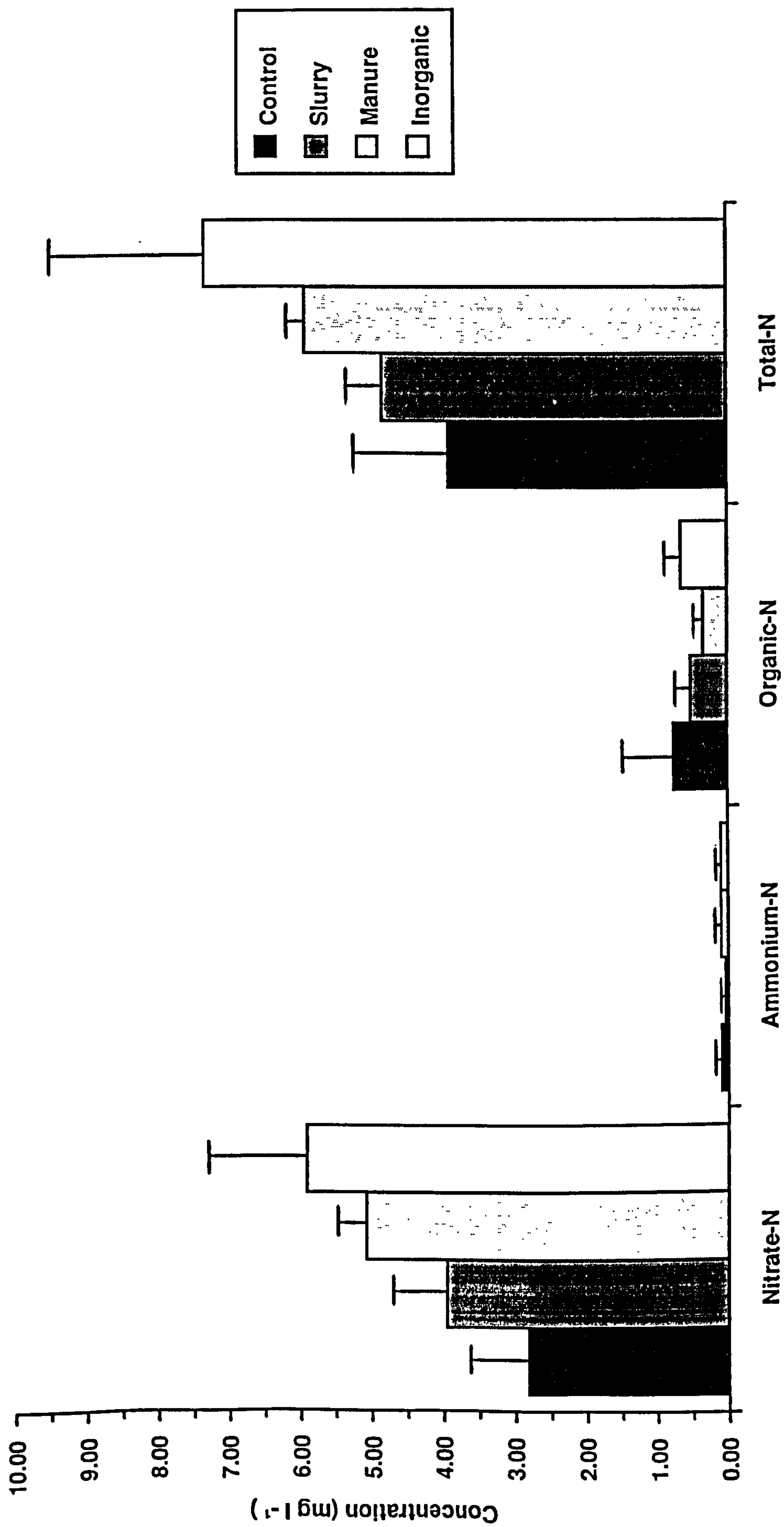


Fig. 3.26. N speciation in throughflow collection pits and dipwells, March - April 1992

of mineralisation and nitrification was more than offset by the processes of plant uptake and perhaps denitrification, thus rendering differences between treatments insignificant.

Regarding the undetectable concentrations of P in soil water, it has been observed by He *et. al.* (1991), that for a range of soils, once P is adsorbed onto soil surfaces then its subsequent desorbability is negligible. Approximately 10-50% of the adsorbed P remains isotopically exchangeable in the short-term, which would account for P available for uptake by plants or for available P as determined by some commonly used chemical methods, for example Olsen's extract. This is not to imply that the transport of P in sub-surface flow from Sidney Meadow was insignificant as far as water quality is concerned. For instance, a P concentration of 20-30 $\mu\text{g P l}^{-1}$ is quoted as the eutrophic boundary for lakes in temperate regions (Ryding and Rast, 1989). Therefore, it is important that more sensitive techniques for collecting and analysing samples than were used in this instance should be employed when examining the transport of P in sub-surface throughflow.

3.4.5. Nitrogen and phosphorus in surface runoff from the simulated storms

Perhaps not surprisingly, there was a degree of spatial variation in both the intensity of rainfall and the amounts of runoff resulting from the four rainfall simulations carried out in May 1992, mean values being shown in Table 3.7.

Due to the siting of the irrigation gun at the bottom of the plots, the buffer zone received less water than the treated zones. This would have had implications for the chemistry of surface runoff in that less clean water would have been available for mixing with the water running off the treated zones, but on the other hand, under the less intense rainfall in the buffer, more infiltration would have occurred and less runoff, as was indeed observed.

Table 3.7. Mean rainfall intensity and surface runoff collected during the four simulations.

	Rainfall (mm h ⁻¹)	Standard error (mm h ⁻¹)	Surface runoff (ml)	Standard error (ml)
Zone 1	25	3.36	374	146
Zone 2	26	2.09	335	137
Buffer	16	2.33	248	119

For rainfall no. of samples = 10 per zone. For surface runoff no. of samples = 16 per zone.

N concentrations in the water used during the simulations were below 0.5 mg l⁻¹, and P concentrations were below the limit of detection. Concentrations of N and P in surface runoff did not differ significantly from simulation to simulation, except for the inorganic fertiliser treatment, where reductions in NO₃⁻-N and NH₄⁺-N were noted after the third simulation.

N speciation in surface runoff flowing from the treated zones was markedly different to that observed in sub-surface waters (Fig. 3.27a). NO₃⁻-N concentrations were low for the control, slurry, and manure, but very high for the inorganic fertiliser, differences between the control and the treatments being significant (p<0.05, using analysis of variance). Concentrations of NH₄⁺-N in runoff from slurry, manure, and inorganic fertiliser were significantly higher than from the control (p<0.05), and concentrations of organic-N in runoff from slurry and manure were significantly higher than those from the control and inorganic fertiliser (p<0.05). All species of N from manure were observed at higher concentrations than from slurry, perhaps reflecting the higher proportion of solid matter and total N within the manure (see Table 3.2). Concentrations of NO₃⁻-N and NH₄⁺-N in runoff from inorganic fertiliser were significantly higher than for slurry and manure, but surface applications of fertiliser would have rapidly dissolved, whereas residues of slurry and manure would have remained on the surface

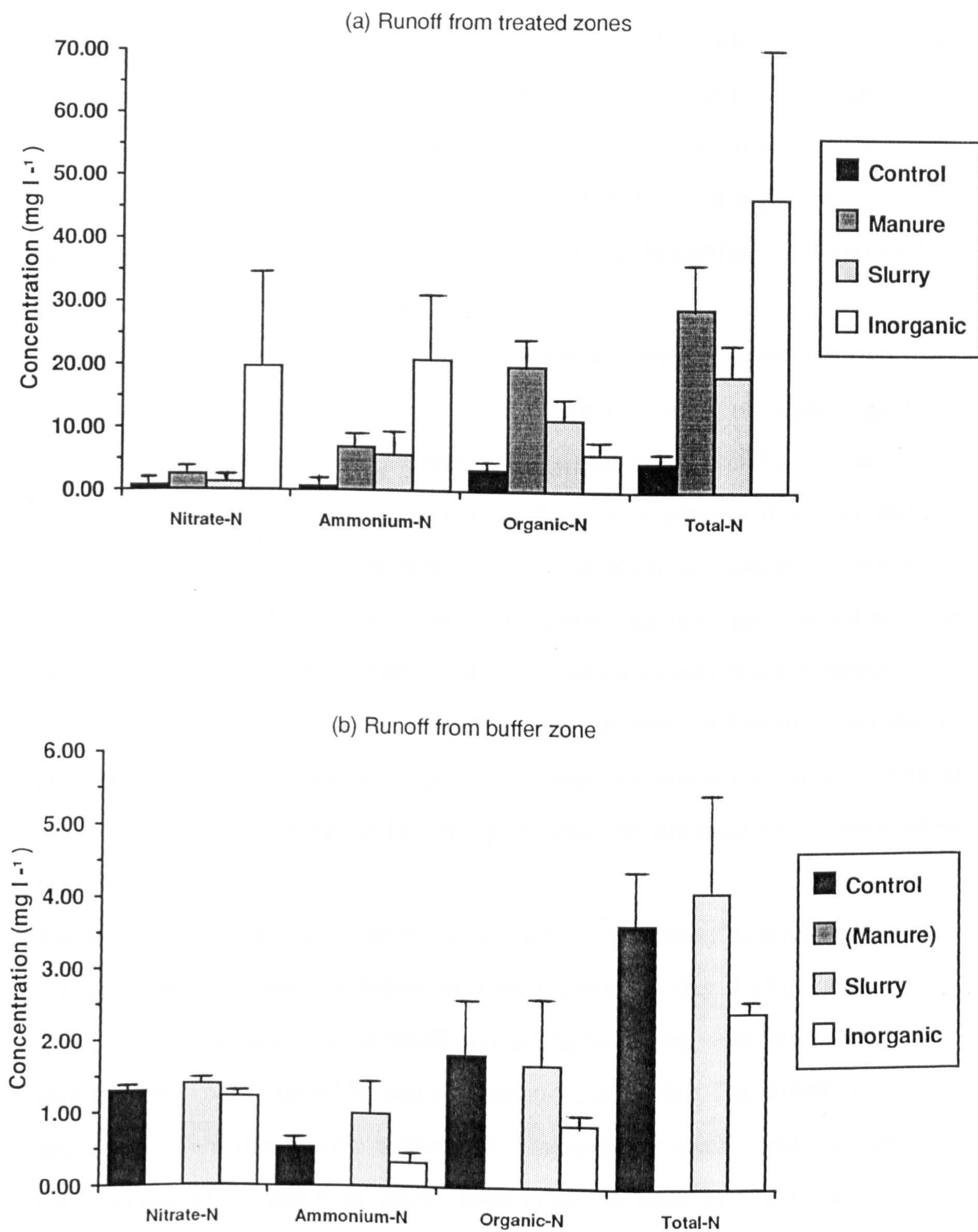


Fig. 3.27. N speciation in surface runoff

for longer periods. Therefore, total surface transport from each treatment was dependent on the amount and intensity of rainfall over a longer duration than was simulated.

Under the conditions of the simulation, the effect of the buffer was immediately apparent (Fig. 3.27b). Concentrations of all N species in runoff from the buffer were much reduced, and differences between the control and the treatments were not significant ($p > 0.05$). However, concentrations of NH_4^+ -N and organic-N were still considerably higher than those observed in sub-surface throughflow, and also slightly above the UK MACs for public water supply.

It should be noted at this point that although analysis of surface runoff only took place within the central block of the experimental site, implying in this particular respect that treatments were not replicated, throughout the whole experimental period at Sidney Meadow there were no observed significant differences between blocks of plots in terms of, N and P in applied treatments, soil and vegetation type, soil water content and matric potential, and N and P as measured in suction cup and dipwell samples. These factors, together with the lack of observed significant differences between samples from the two treated zones within each plot and generally between all four simulated storms, promoted confidence in the assumption that observed differences in the chemical characteristics of surface runoff between plots could be attributed to treatment rather than site.

The simulation of surface runoff provided the first opportunity to measure detectable concentrations of P during the Sidney Meadow experiments (Fig. 3.28a). For the treated zones, PO_4^- -P concentrations in runoff from all the treatments were significantly higher than from the control ($p < 0.05$), and concentrations of organic-P in runoff from slurry and manure were significantly higher than those from the control ($p < 0.05$). The high concentration of organic-P in runoff from inorganic fertiliser can be attributed to undissolved granules, remembering that samples for PO_4^- -P analysis were filtered immediately, but samples retained for total-P analysis were unfiltered (see section 3.2.2). The concentration of total-P in runoff from manure was higher than for slurry, again reflecting the higher amount present in the manure. As with N, the effect of the buffer was clear (Fig. 3.28b). Concentrations of all P fractions were much reduced, and

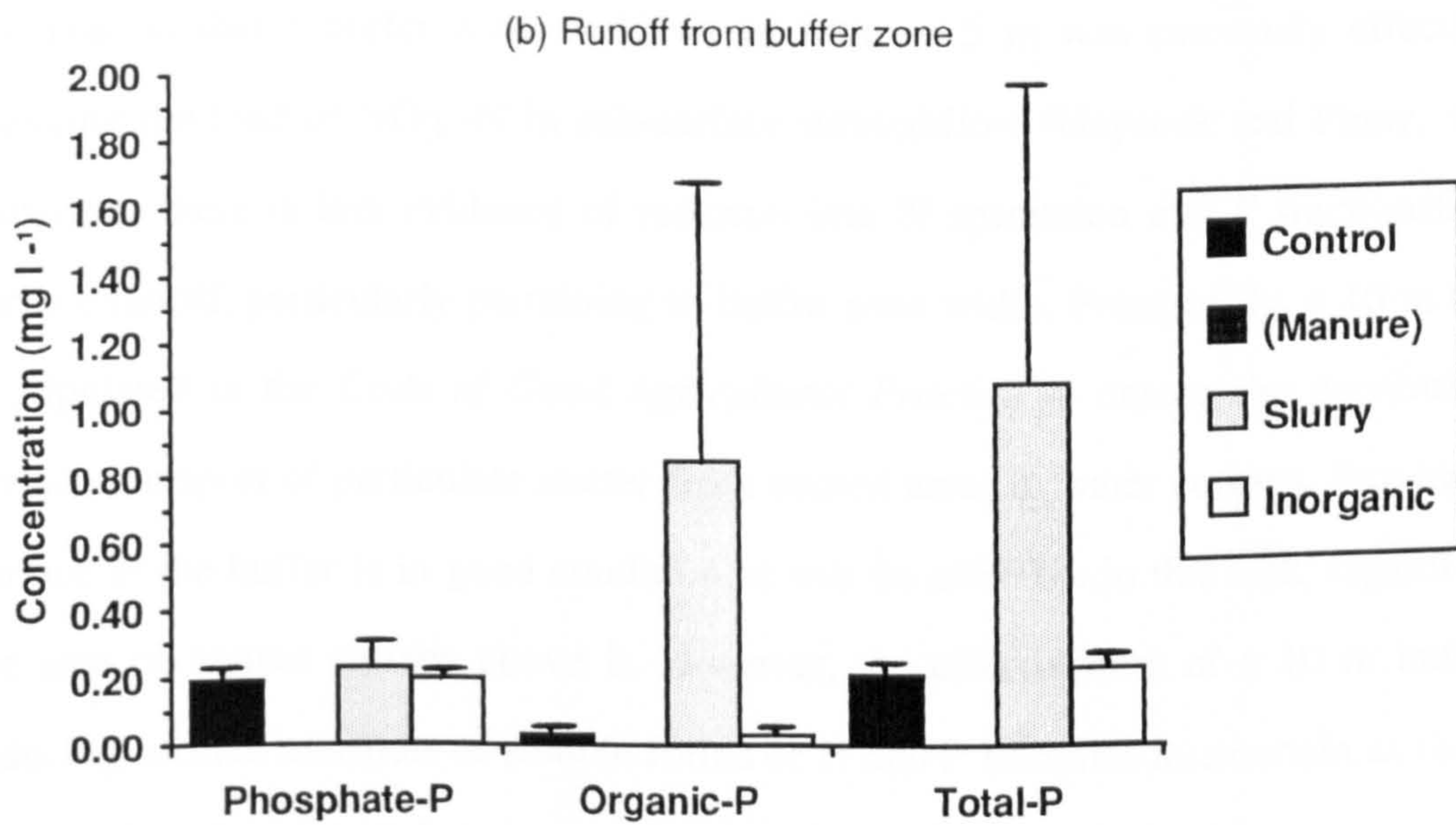
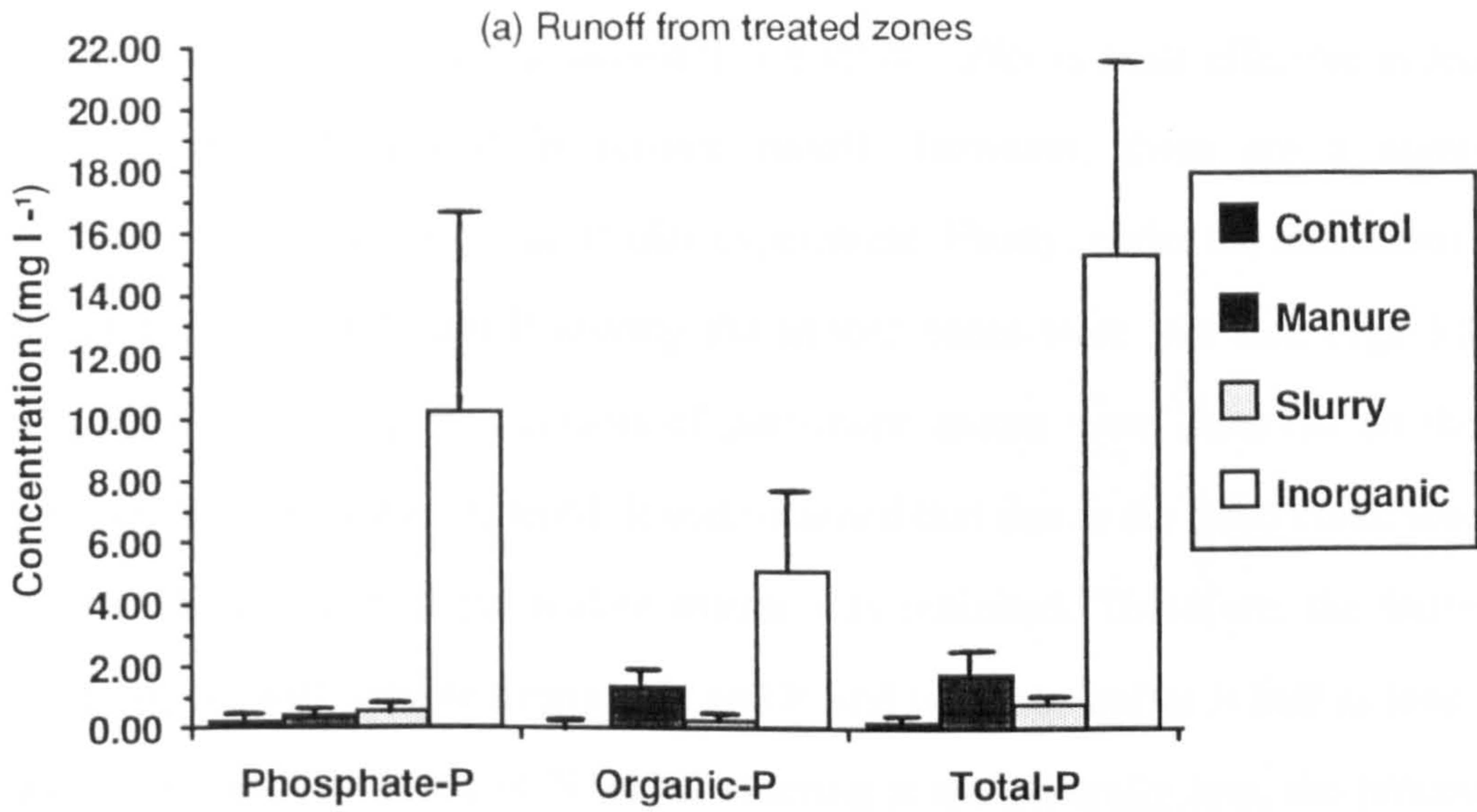


Fig. 3.28. P fractionation in surface runoff

the differences between the control and the treatments were not significant ($p>0.05$). However, the observed concentrations were still high in relation to those values discussed in respect of lake eutrophication, for example.

At first, it might be tempting to accept that a 10 m buffer is most effective in reducing the transport of N and P in surface runoff. However, there are a number of qualifications attached to this particular experiment. Firstly, under the conditions of the simulations, loads of N and P leaving the treated zones were low (see Figs 3.29 and 3.30). Secondly, negligible amounts of particulate matter were observed on the filter papers when samples were filtered. It was assumed that due to the good condition of the grass sward, transport of particulate matter was inhibited. Therefore, the buffer was dealing largely with soluble forms of N and P, and when the buffer is half as long as the treated zones and the loads of N and P entering it are generally low, the processes of mixing and dilution will not surprisingly deliver the results observed.

The discussion in section 3.4.4 has highlighted the amount of research into quantifying transport of N and P via sub-surface pathways. Of particular interest was the observation that a buffer zone width of as little as 5 m was extremely effective in reducing the load of NO_3^- -N in sub-surface throughflow (Haycock and Pinay, 1993). However, there is less evidence of research into N speciation and P fractionation in surface runoff, particularly pertaining to buffer zone width. Presumably, a 10 m buffer is stipulated in the *Code of Good Agricultural Practice* to ensure the prevention of surface transport of particulate matter from treated areas to water courses. Provided the surface of the buffer is in good condition, it will be effective in this task, regardless of the area of treated surface above it. However, the effectiveness of a 10 m buffer in reducing surface transport of soluble forms of N and P becomes less certain as the area of treated surface above it increases, because it will have to deal with greater volumes of surface runoff, and increasing N and P loads, with a fixed mixing, dilution and infiltration capacity.

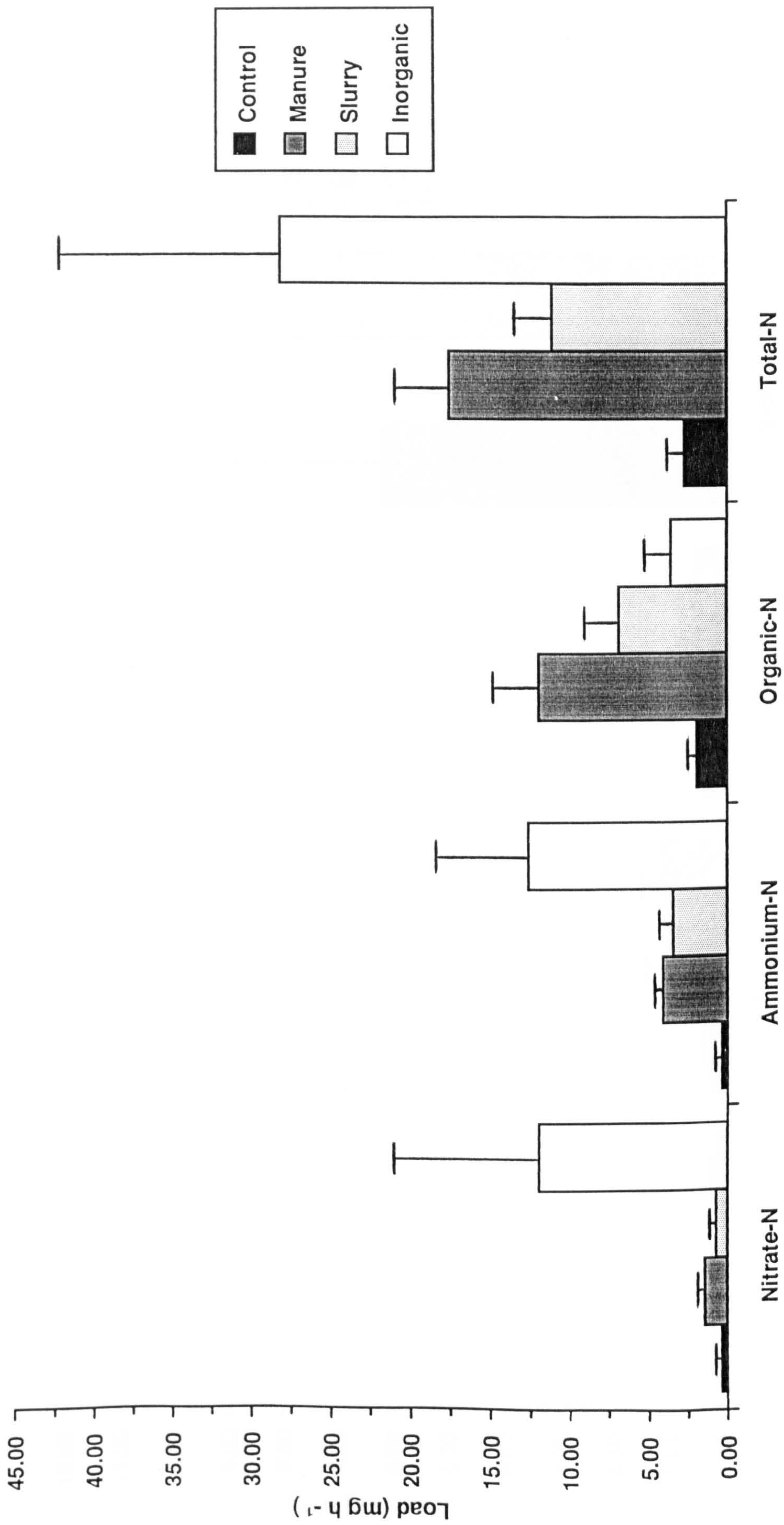


Fig. 3.29. N loads in surface runoff from treated zones

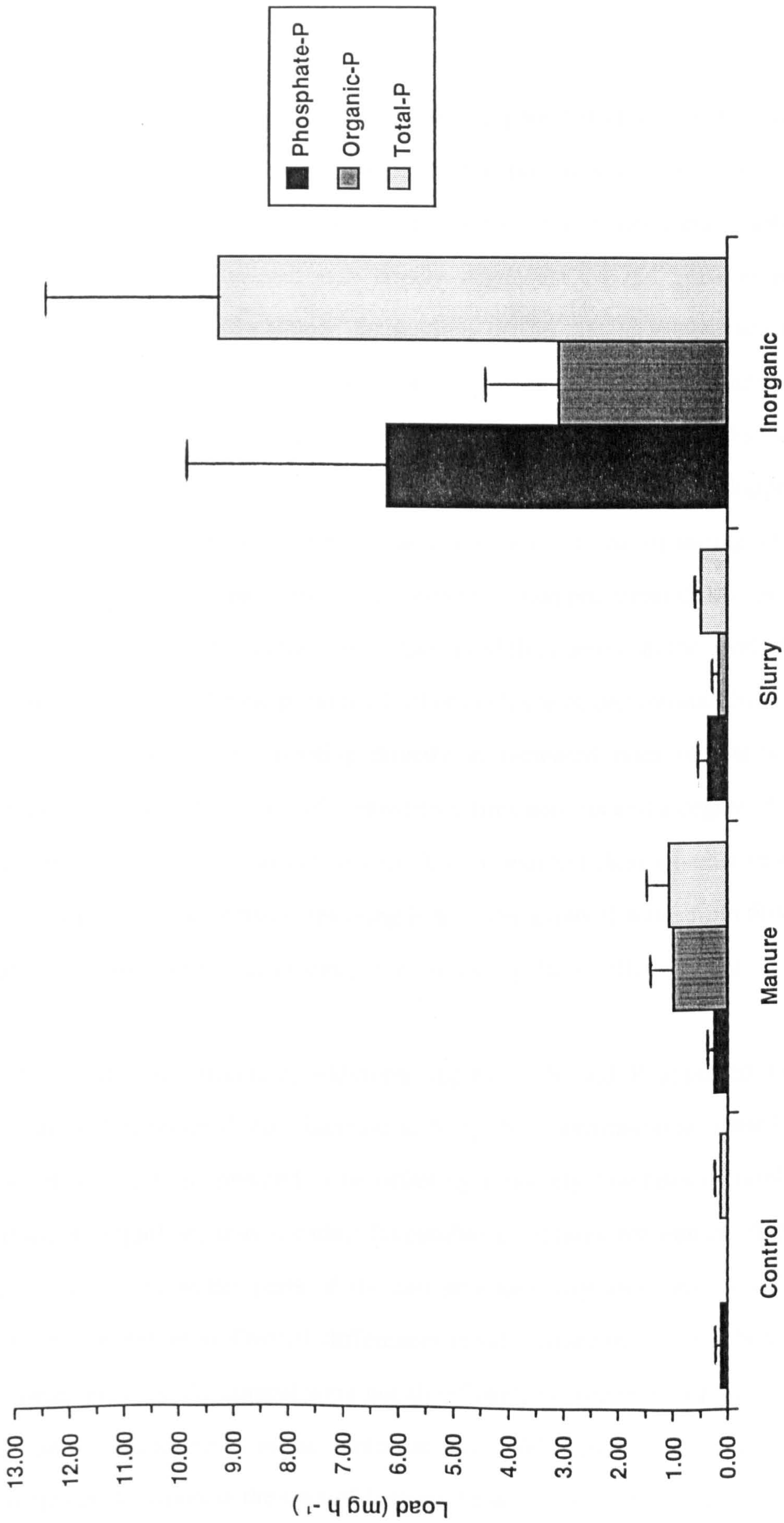


Fig. 3.30. P loads in surface runoff from treated zones

3.5. Chapter summary

1. Observations of soil water content and matric potential at Sidney Meadow indicated that for most of the experimental period, the direction of water flow was predominantly vertically downward, and that despite some reduction in water content with increasing depth, the rate of movement was largely dependent on the gravitational potential gradient between any two points. Estimations of the rate of sub-surface throughflow based on water content, hydraulic potential and saturated hydraulic conductivity values were generally in reasonable agreement with observations of rates of discharge into the throughflow collection pits. However, the estimated pattern of discharge was much smoother than the observed pattern, and allowing for the distorting effects of the throughflow collection pits, this was an indication that preferential flow processes were occurring in response to rainfall inputs. Observed fluctuations in the level of what could be a perched saturated zone provided further evidence of preferential flow, but whether preferential flow was contributing directly to increased rates of discharge into the throughflow pits, or by means of a translatory flow process and a degree of mixing with water in the soil matrix was not certain. Also, it was not clear whether upwelling from groundwater was taking place, resulting in the interaction of water from this source with water in the soil profile before entry into the throughflow collection pits.

2. Within the soil structure, additional inputs of N and P appeared to be largely immobilised or retained. Any increase in NO_3^- -N concentration attributed to increased rates of nitrification appeared to be offset by relatively low rates of rainfall and sub-surface throughflow, thus creating favourable conditions for enhanced plant uptake. Denitrification in wetter parts of the soil structure may also have offset increases in NO_3^- -N concentration. Overall, differences in sub-surface transport of N and P between the treatments and the control were not significant. Measurement of NO_3^- -N in suction cup samples indicated an accumulation at depth. Whether this would have contributed to increased transport in the case of increased rates of water flow would have depended on the water flow pathways and the pore size in which the NO_3^- -N was accumulated,

which would determine the degree of mixing between "old and "new" water. It may also have depended on whether the distribution of water would have created areas of saturation with conditions more favourable for denitrification.

3. Immediately following the application of slurry, manure and inorganic fertiliser, considerable quantities of N and P were transported in simulated runoff. In this experiment, N was largely present as organic-N and NH_4^+ -N for the slurry and manure, and as NH_4^+ -N and NO_3^- -N for the inorganic fertiliser. P was largely present as PO_4^- -P, except for the manure treatment, where some 75 % of the total was organic-P. Concentrations from inorganic fertiliser appeared to be significantly higher than for slurry and manure, but surface applications of fertiliser would have rapidly dissolved, whereas residues of slurry and manure would have remained on the surface for longer periods. Therefore, total surface transport from each treatment was dependent on the amount and intensity of rainfall over a longer duration than was simulated. The effectiveness of a 10 m buffer in reducing surface concentration and transport of N and P was clear, but this effectiveness has to be viewed in relation to the amounts of runoff observed, and in the case of N and P in solution, the area of buffer in comparison to the area of treated land above it, since the buffer has a fixed dilution and infiltration capacity.

Chapter 4

Experiments at the Field to Headwater Catchment Scale

It was stressed in Chapter 1 (section 1.6) that the objectives of this study were arranged in order to address the issue of scale. The plot scale experiments described in Chapter 3 provided a means of examining processes in detail under controlled conditions. The experiments at the field to headwater catchment scale described in this chapter allowed observation of both the timing and magnitude of the same processes under less controlled and more realistic conditions. Thus, a link between two dimensional plot studies and the three dimensional reality of a drainage basin could be made (Heathwaite *et. al.*, 1993), and the feasibility of scaling up the interpretations made of mechanisms operating at the plot-scale could be assessed. Moreover, the examination of processes at the larger scale enabled consideration of the effect of variations in topography as well as land-use, something which was not possible at the plot scale. Finally, experiments at the field to headwater catchment scale provided data for testing the mathematical model, the process of model construction and testing being described in Chapters 5 and 6.

4.1. Site selection and description

This larger scale site was selected at the same time as the plot site, the primary criteria for selection being that it should be as similar to Sidney Meadow as possible in terms of land-use, slope, soil type and climate. On these criteria and others that will be discussed below, the site chosen for field-scale experiments was a field of semi-permanent pasture within the Merrifield catchment, near Slapton, South Devon (Ordnance Survey grid reference. SX817475). This field comprises one part of the headwater catchment for the Merrifield stream, itself one small part of the Slapton Ley catchment (Fig. 4.1). Merrifield stream provided the basis for observations of N and P transport from the whole headwater catchment.

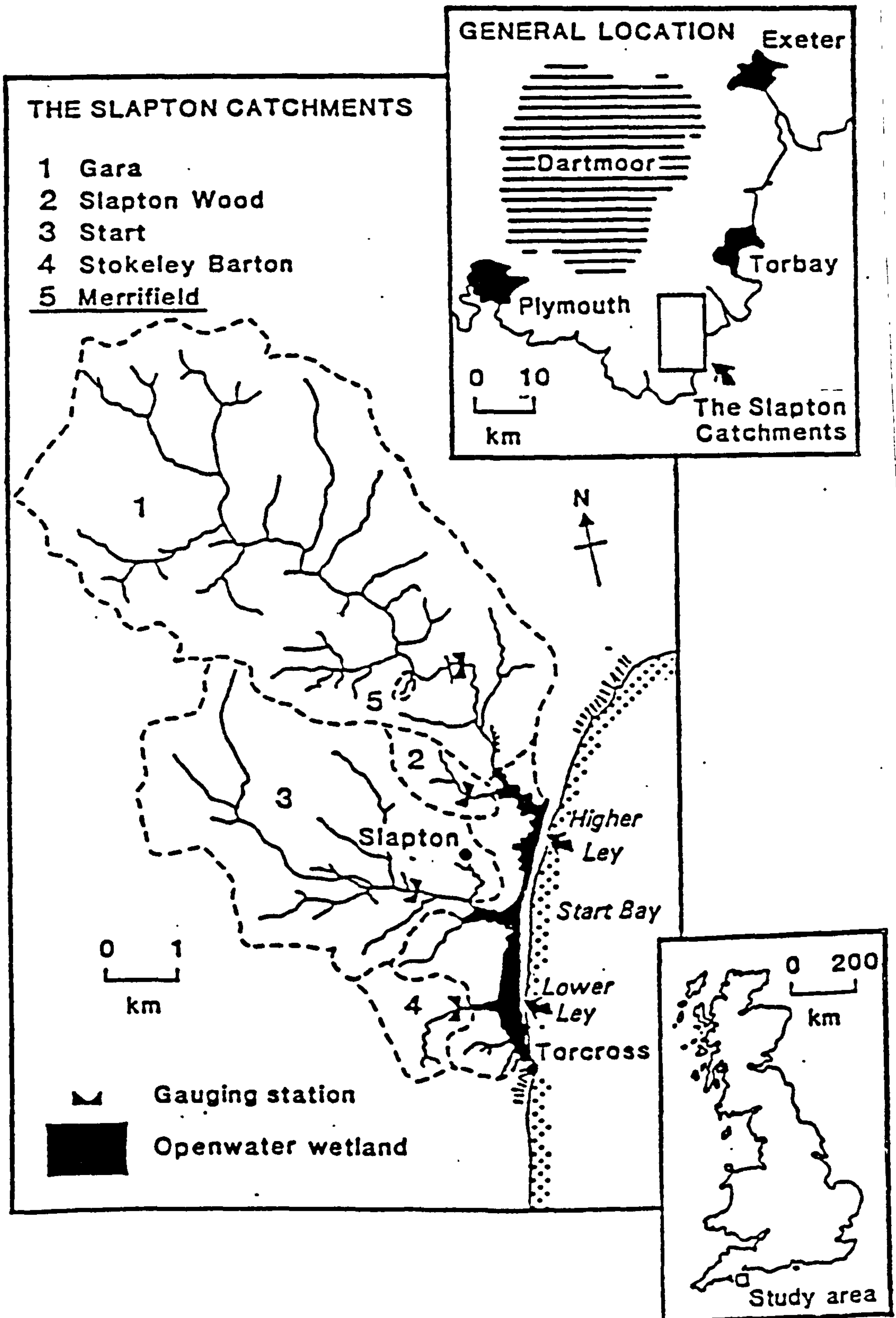


Fig. 4.1. The location of the Merrifield catchment (from Heathwaite *et. al*, 1990b)



Fig. 4.2. The slopes of the Merrifield catchment.

The Merrifield catchment is characterised by flat plateaux breaking sharply to steep slopes of approximately 20° which end abruptly at the stream banks, especially in the upper parts of the catchment (Fig. 4.2). Land-use over the whole catchment is predominantly permanent pasture, almost exclusively so on the steeply sloping parts of the catchment. The field used as the experimental site comprised a mixture of temporary and permanent pasture from 1989 - spring 1993 inclusive. During this period, the field received inorganic fertiliser applications of approximately 300 kg ha⁻¹ of 20:10:10 N:P₂O₅:K₂O in March of each year, a regime similar to that employed at Sidney Meadow (see Appendix 1). The field was subject to intermittent light grazing by cattle or sheep, with very little grazing taking place during the winter months. This appeared to be the pattern for most of the catchment slopes. Before 1989 and after spring 1993, land-use for the field has tended to comprise a mixture of arable on the plateau and pasture on the slope (for example, see Fig. 4.3 for land-use in 1987-1988). Mean annual rainfall in the area is approximately 1000 mm.

Like Sidney Meadow, the soil of Merrifield is a weakly structured brown earth of the Denbigh series, silty clay loam in texture, with poorly defined horizons overlying layers of shattered Devonian slate. Profile depths range from 40 cm on the plateau to over 1 m at the foot of the slope. Oxidation of iron in the slate bedrock has given a strong red-brown colour to the soil (Munsell Code 5 YR 4/8). Soil pH is approximately 4-5, bulk densities and extractable N and P were as given in table 4.1 below. Trudgill (1983) gives a detailed description of soils under natural woodland close to Slapton.

As with Sidney Meadow, the constraint of time made it impossible to make repeated measurements of soil bulk density throughout the field experimentation period, so the values given in Table 4.1 are simply to provide an impression, and to allow comparison with values obtained at Sidney Meadow. For the same reason, measurements of extractable soil N and P were not made until towards the end of the experimentation period, and then only at one depth. Again, these values were obtained simply to give an impression, and to allow comparison between the two field sites.

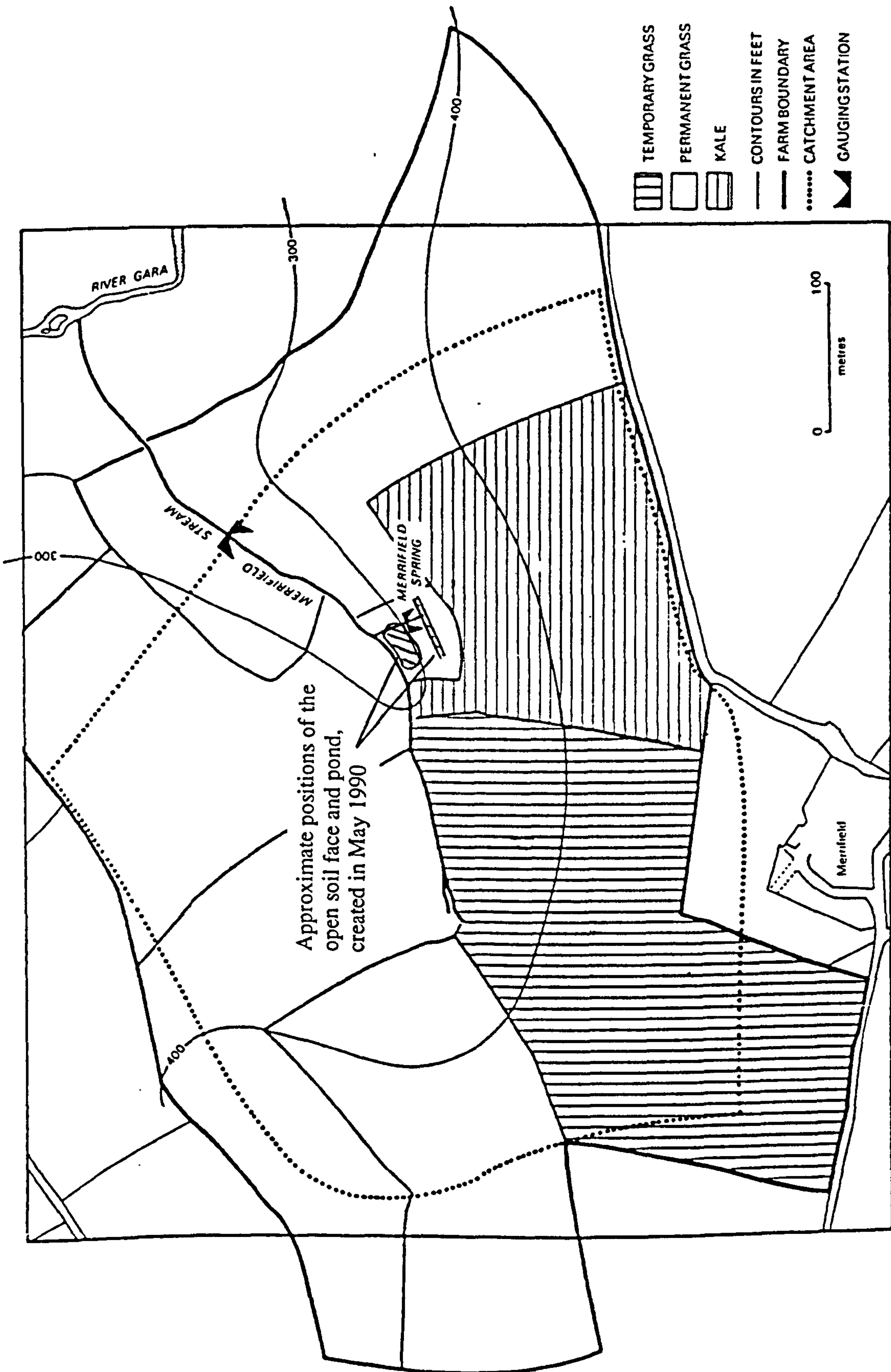


Fig. 4.3. The Merrifield catchment, 1987-1988 (from Heathwaite *et. al.*, 1990b)

Table 4.1. Soil bulk density and extractable N and P Merrifield

Depth (cm)	Mean	S.E. of mean	Mean	S.E. of mean	Mean	S.E. of mean	Mean	S.E. of mean
	water content ¹ (%)		bulk density ¹ (g cm ⁻³)		soil N ² (mg g ⁻¹)		soil P ² (mg g ⁻¹)	
10-15	40.9	1.73	1.28	0.03	-	-	-	-
20-25	41.4	0.87	1.27	0.02	0.0007	0.0003	0.0043	0.0037
35-40	35.2	1.07	1.39	0.03	-	-	-	-
50-55	36.0	1.34	1.36	0.05	-	-	-	-

¹ Number of samples = 6, taken in October 1992. Sample volume = 225 cm³. Water content is volumetric, and bulk density is expressed on a dry basis.

² Number of samples = 4, taken in January 1993. Sample weight = 250 g. N and P contents are expressed on a dry basis also. N was extracted using potassium chloride, P was extracted using sodium bicarbonate (methods from MAFF and ADAS, 1981).

Soil bulk density at Merrifield was comparable with that at Sidney Meadow (see Table 3.1), showing a general increase with increasing depth in the soil profile. Extractable soil N and P contents were lower and spatially more variable than at Sidney Meadow, but two factors regarding this should be noted, firstly that samples were taken from Sidney Meadow eight months after experimental treatments had been applied three times, and secondly that Merrifield had been subjected to changes in land-use within the previous five years.

As well as the similarities with Sidney Meadow, a further reason for choosing the Merrifield catchment was the availability of past experimental records. Hydrological research in the area commenced in 1969, much of it associated with the Slapton Ley Field Centre, run by the Field Studies Council. As part of a two-year NERC funded project under the "Agriculture and the Environment" programme (project no. GST /02 / 198), monitoring of N and P in stream discharge commenced at Merrifield in 1987. Two V-notch weirs were installed in the catchment, one on the stream and one on

a spring issuing from the lower part of the chosen field site (see Fig. 4.3 once more). Weekly observations of discharge, NO_3^- -N, NH_4^+ -N, and PO_4^- -P were made from the weir on the stream, virtually without interruption during the period autumn 1987 to autumn 1990, and more intermittently from autumn 1990 until monitoring ceased in the early spring of 1993. The record for the spring was less comprehensive, covering only the hydrological year 1987-1988, and autumn 1992-spring 1993. In the hydrological year 1987-1988, detailed studies were carried out within the catchment, including plot scale work and intensive monitoring of several storm events. Many of the results of this project have been published (for example, Heathwaite *et. al.*, 1990a and b), but a considerable quantity of data remain to be examined.

4.2. Methodology

4.2.1. Experimental design

Prior to the Autumn of 1992, the two V-notch weirs at Merrifield were removed, repaired, re-installed, and calibrated in accordance with B.S. 3680: Part 4A (British Standards Institute, 1965). Due to the activities of the landowner, the siting of the 90° V-notch weir on the spring had to be altered. Soil had been cut by the landowner from the point in the slope where the spring emerged, producing a vertical open face some 70-80 m long by 2-3 m deep. Beneath this face, soil and slate had been hollowed and piled into a retaining bank in order to create a pond. Water seeping from the open face collected in a ditch which was channelled to fill the pond (Fig. 4.3. shows the locations of the soil face and the pond). The V-notch weir was sited on this channel, the spring in effect now being a large throughflow and surface runoff collection trough, draining some 4 ha of the field above. Fig. 4.4 shows the siting of the weir, with the pond and retaining bank shown in the background, and the siting of the weir in relation to part of the vertical face is shown in Fig. 4.5. The 120° V-notch weir on the stream was re-installed within a few metres of its original location, its catchment area being 18 ha.



Fig.4.4. The V-notch weir on Merrifield spring, showing the stage height recorder and automatic water sampler. The pond and retaining bank is in the background.



Fig.4.5. The V-notch weir on Merrifield spring, with part of the open soil face in the background.

Daily rainfall totals were measured with a Bradford rain gauge installed approximately 5 m from the weir sited on the spring. Water collecting in this gauge was retained and analysed for N and P content at Seale-Hayne when appropriate, using the analytical procedure described in Chapter 3, section 3.2.2. Records of hourly rainfall intensity were available from the Slapton Ley Field Centre meteorological station, located in Slapton village approximately 2 km from Merrifield.

Rock and Taylor interval water samplers were installed by each of the weirs, water being sampled immediately upstream of the weir control sections (again see Fig. 4.4). These were used to obtain 250-300 ml samples at hourly intervals over a 24-36 hour period, either during or immediately after significant storm events in the winter of 1992-1993. Samples were analysed at Seale-Hayne for N and P content, again using the procedure described in Chapter 3, section 3.2.2 (see Fig 3.11).

During the autumn and winter period of 1992-1993, water content in the slope above the spring was measured at irregular time intervals using vertical TDR probes (see Chapter 3, section 3.2.1 for a description of the TDR technique). Measurements were taken at nine points, three each at the bottom, middle, and top of the slope respectively, and over profile depths of 0.1 m and 0.2 m. The purpose of these measurements was simply to enable a broad comparison with water content as observed at Sidney Meadow. Adopting the same approach as for soil water content, matric suction was measured at depths of 0.2 m and 0.4 m using "Quickdraw" soil moisture probes (ELE International, 1991). Again, the measurements were taken purely for comparative purposes, not as part of any detailed measuring programme designed to evaluate rates of sub-surface flow at Merrifield.

The final part of this comparative process was to measure infiltration capacity and extract cores for laboratory determination of saturated hydraulic conductivity. Infiltration capacity was measured at random locations using the same double ring infiltrometer as used at Sidney Meadow. Cores for hydraulic conductivity determination were taken from random locations at a depth of 0.2 m, and subject to the analytical procedure described in Chapter 3, section 3.2.3.

No attempt was made to control land-use at Merrifield during this monitoring period, firstly because the objectives of larger scale experimentation as detailed at the start of this chapter did not necessitate control of land-use, and secondly because it would have proved difficult to impose such controls. Generally, the slopes of the catchment were subject to intermittent light grazing by cattle or sheep, and there was no arable cultivation on the plateaux until early spring 1993 when monitoring had ceased.

4.2.2. Past experimental records

Data from two sources were examined, the record of weekly observations of N and P in spring and stream discharge from Merrifield, spanning from 1987-1993, and the intensive monitoring of storm events at Merrifield in the year 1987-1988. The first data set would give a general indication of the levels of discharge and N and P transport in a predominantly grassland system. The second data set would provide information on the levels of N and P transport in particular circumstances, for example when surface runoff occurred. The same chemical analytical methods were used to obtain these data as were used at Seale-Hayne, which would facilitate comparison of different data sets.

Although surface applications of N and P were not the same at Merrifield in 1987-1988 (or 1992-1993) as they were at Sidney Meadow in 1992, the predominance of grazing in the catchment (see Fig. 4.3 once more) would ensure the presence of the same species of N and fractions of P on the surface, and it was of interest to see how this was reflected in the chemical composition of the water during storm events.

4.3. Results and discussion

4.3.1. Infiltration capacity

Practical difficulties in the use of the double ring infiltrometer method, involving rapid drainage and the consequent problem of adequate water supply, combined to restrict the number of meaningful data sets to two (see Fig. 4.6). On the limited basis of these

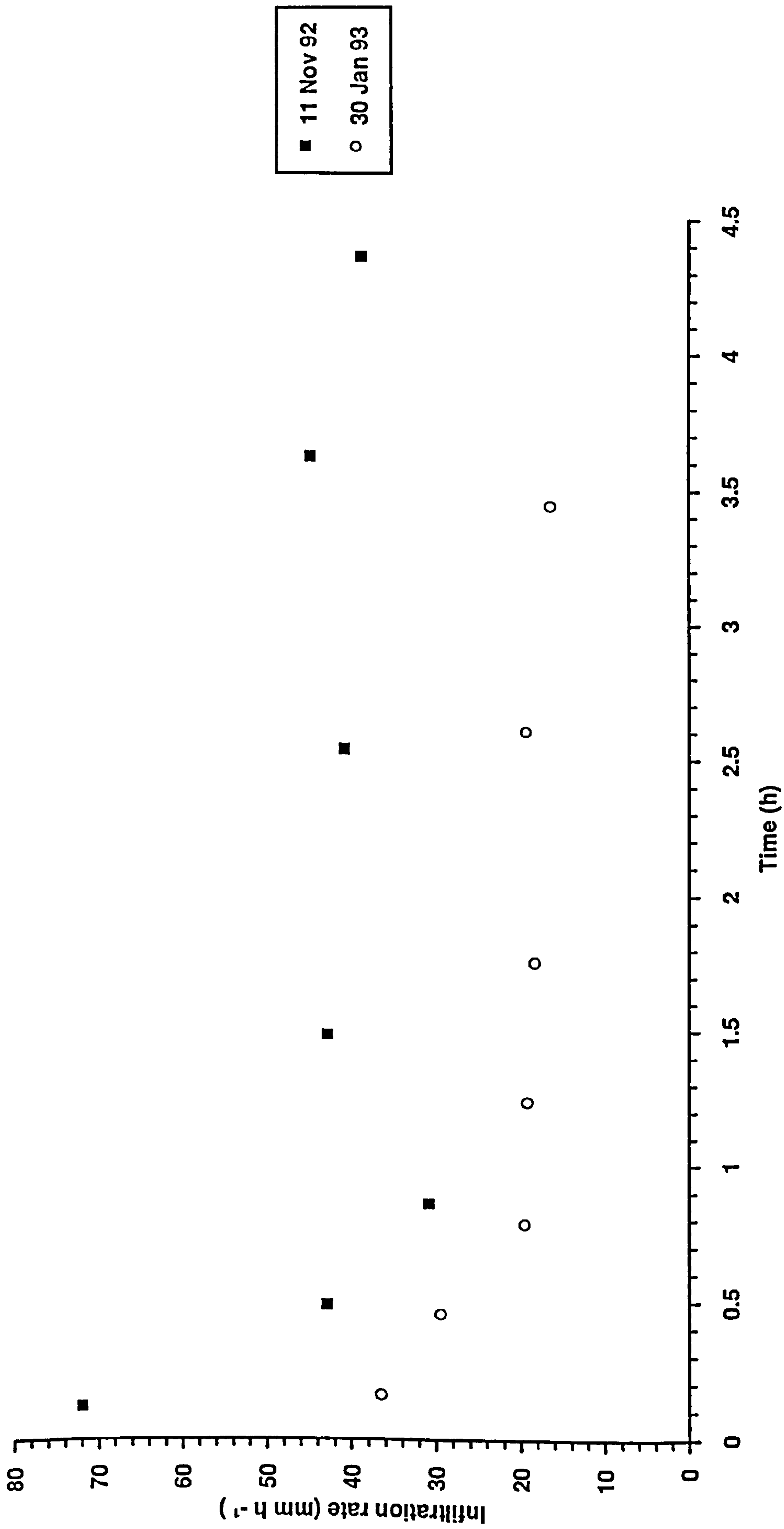


Fig. 4.6. Infiltration capacity at Merrifield, Nov 1992 and Jan 1993

results, it would seem that infiltration capacity at Merrifield was higher than at Sidney Meadow (see Fig. 3.13), although taking into account factors such as timing of the measurements, soil water content and bulk density, the importance of this difference cannot be established. It is clear from the measurements at both sites that under current land-uses and stocking rates that cause little compaction or poaching, the occurrence of infiltration excess surface runoff on this type of site will be limited. The importance of the effect of more intensive land-use on infiltration capacity was noted during monitoring at Merrifield in 1987-1988 (Heathwaite *et. al.*, 1990b). Infiltration capacity was reduced to less than 1 mm h^{-1} on parts of the kale area following heavy grazing by sheep, and to around 3 mm h^{-1} on parts of the permanent pasture following heavy grazing by cattle. Therefore, there was a high probability of infiltration excess surface runoff occurring from these partial areas where infiltration capacity was greatly reduced by compaction and poaching.

4.3.2. Soil water content, matric suction, and saturated hydraulic conductivity

Winter water contents near the surface of the soil profile were similar to those at Sidney Meadow (see Fig 4.7, and compare with Fig. 3.14), although they were more variable over time, perhaps a reflection of the greater variability in the amounts and intensity of rainfall encountered at Merrifield. There was evidence from the middle of the slope of a decrease in water content with depth, the water content over 0.2 m of profile being consistently lower than over the top 0.1 m. As with Sidney Meadow, this was probably a reflection of soil structure in that the lower bulk densities measured near to the surface (see Table 4.1) indicated the presence of more water storage pores than at depth.

Matric suction was found to be comparable with that observed at Sidney Meadow during the wetter periods of mid-February and early April 1992 (see Fig. 4.8, and compare with Fig. 3.16). More importantly, there was no significant difference between suction at 0.2 m and 0.4 m. This indicated that the flow of water would largely be influenced by gravity, and along with the water content data it provided limited

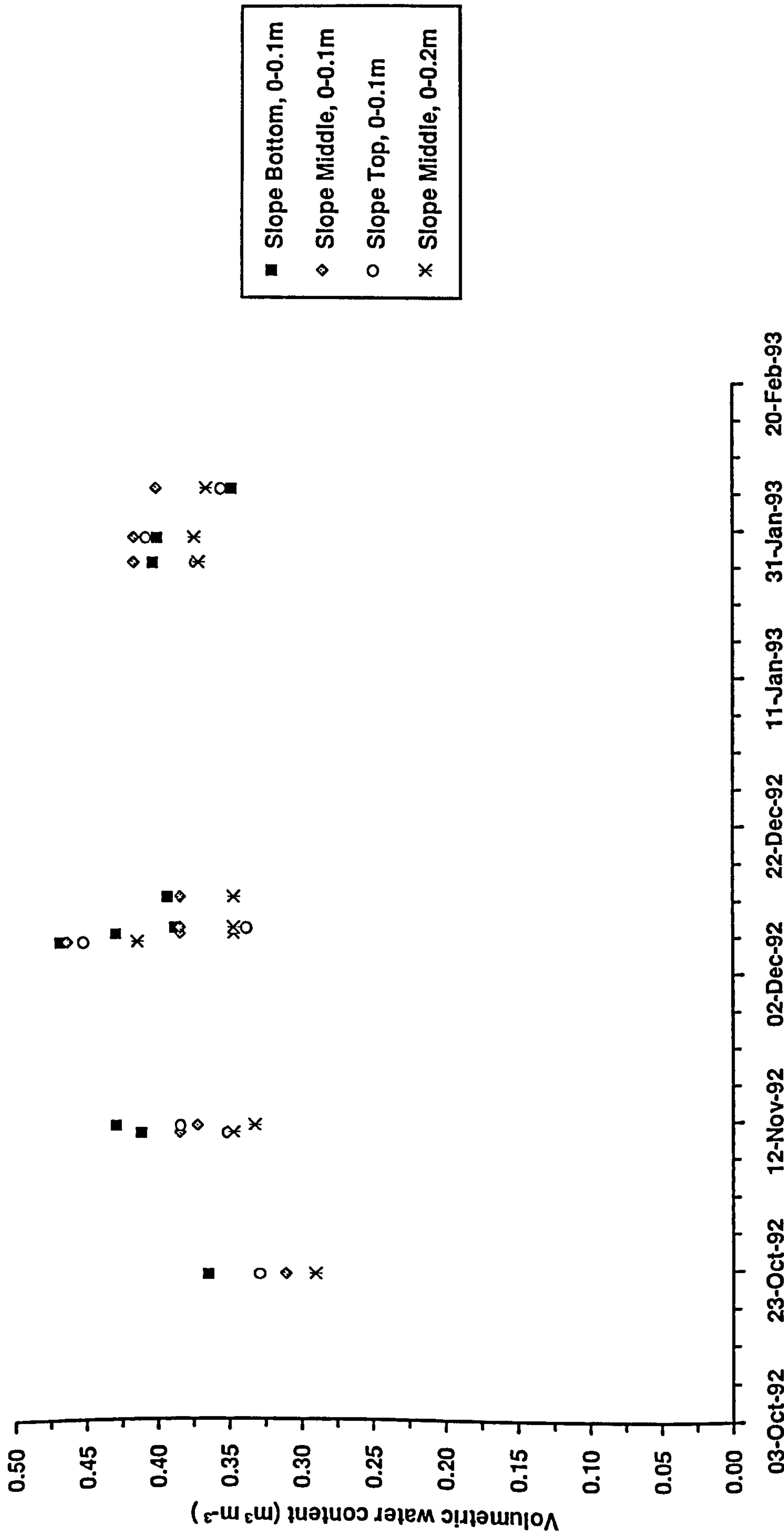


Fig. 4.7. Mean soil water content at Merrifield (vertical TDR)

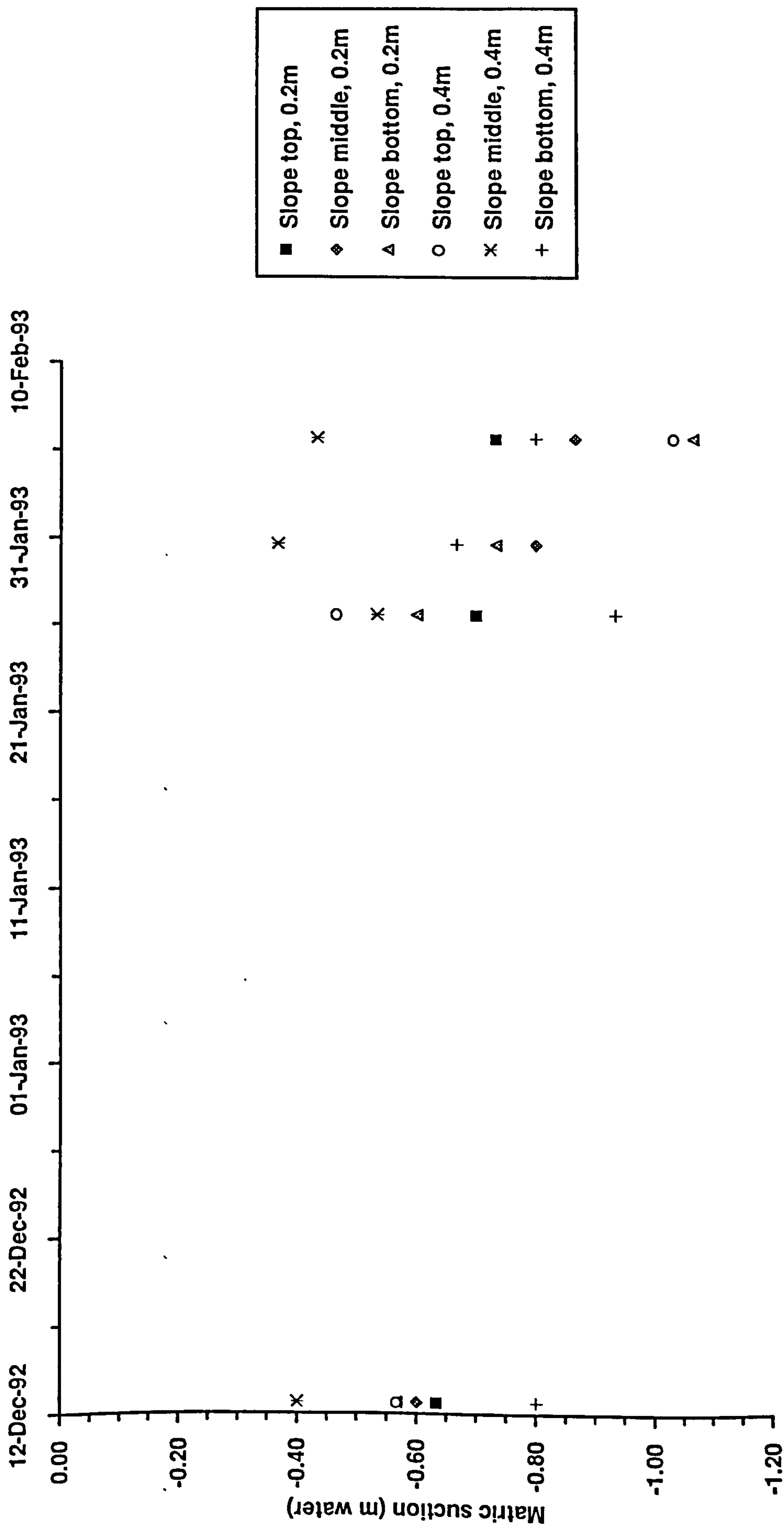


Fig. 4.8. Mean matric suction at Merrifield

evidence that as at Sidney Meadow, the direction of flow would be predominantly vertically downwards.

Saturated hydraulic conductivities as determined from the cores taken from Merrifield are shown below in Table 4.2.

Table 4.2. Saturated hydraulic conductivity as determined in the laboratory

Core	Bulk density (dry basis) (g cm ⁻³)	Saturated volumetric water content (%)	Saturated hydraulic conductivity (k _{sat}) (mm h ⁻¹)
1/T/20	1.16	60	53
1/M/20	1.28	54	41
2/M/20	1.22	57	25
3/M/20	1.23	55	31
Mean	1.22	57	38
Standard error	0.02	1	6

Core code: T = Slope top, M = Slope middle, 20 = extraction depth in cm. Core dimensions = 127 mm long x 102 mm diameter. Cores were extracted in January 1993.

Rates of saturated hydraulic conductivity were of the same magnitude as those taken from the same depth at Sidney Meadow (see Table 3.5), but there appeared to be a lower degree of spatial variation. This might be attributed to past arable cultivation at Merrifield, resulting in a more mixed and uniform structure in the upper soil profile than would occur under the permanent grass of Sidney Meadow.

4.3.3. N and P in stream and spring discharge, 1987-1993

The record of weekly observations at Merrifield provided a useful insight into the water and N and P dynamics of the catchment. Perhaps of most interest was the record for NO₃⁻-N in both the stream and spring water (see Figs. 4.9 and 4.10). Concentrations of

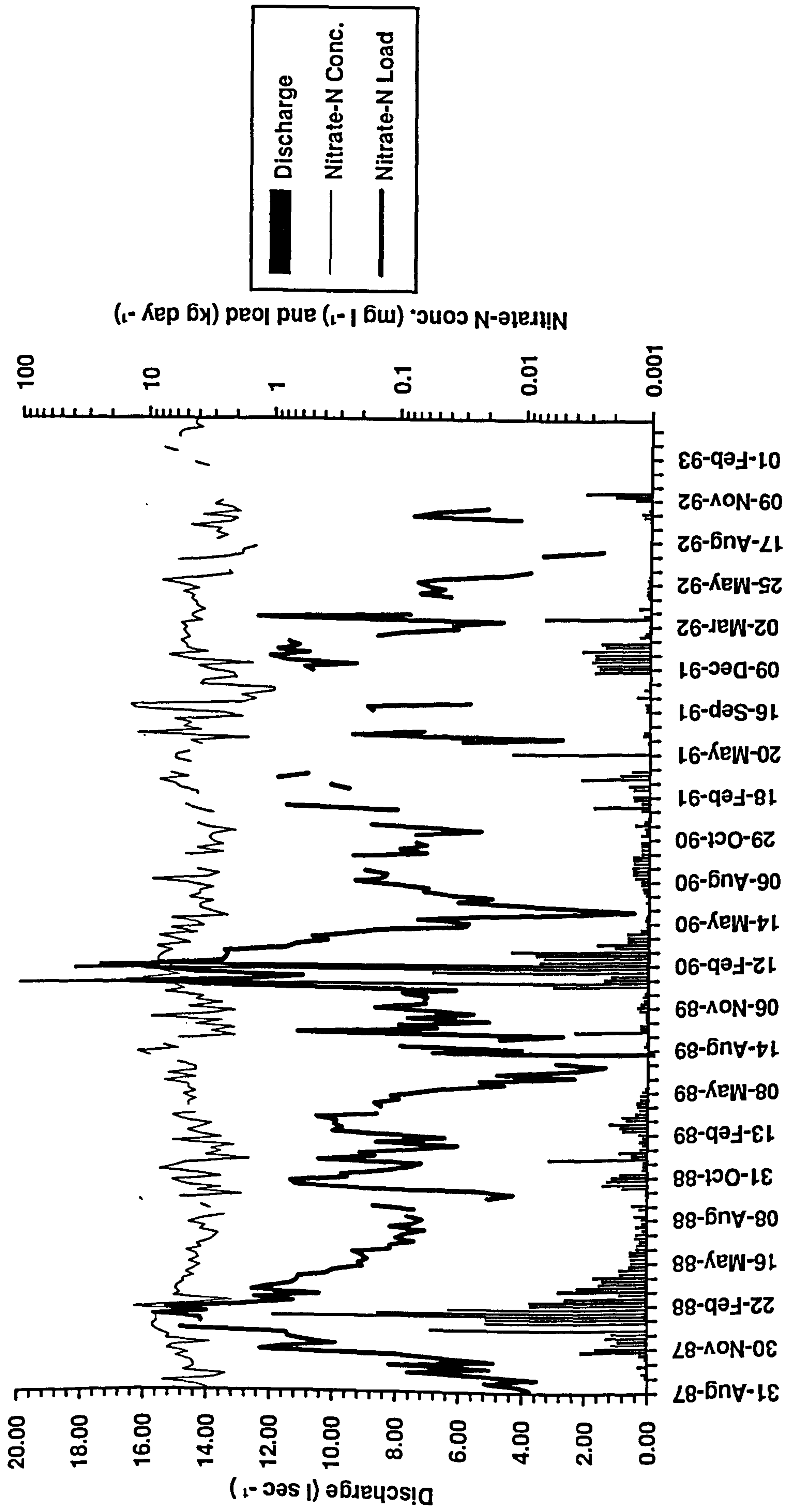


Fig. 4.9. Nitrate-N in Merrifield stream, 1987 - 1993

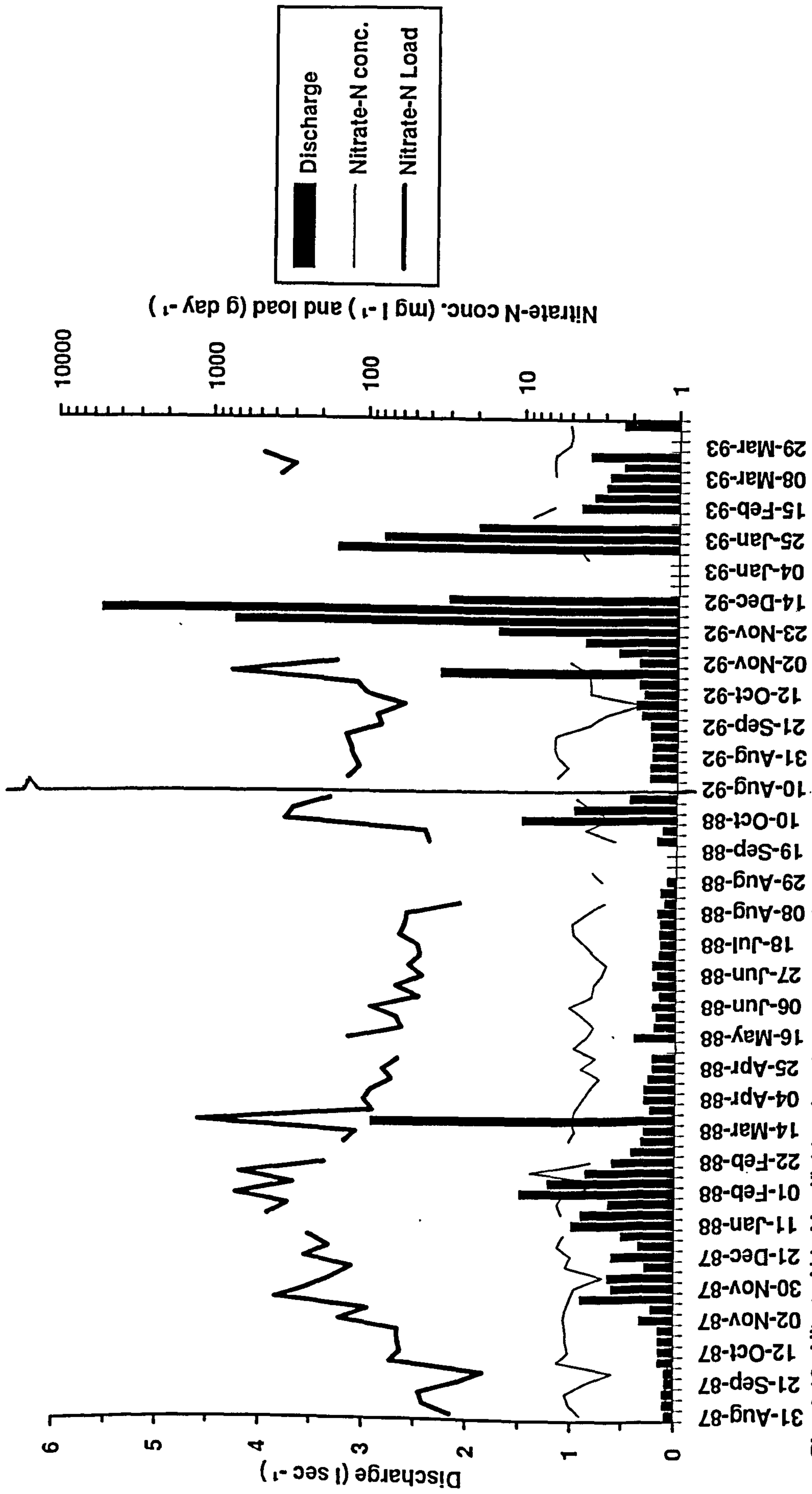


Fig. 4.10. Nitrate-N in Merrifield spring, 1987 - 1988 and 1992 - 1993

NO_3^- -N from both sources were usually in the range 2-6 mg l^{-1} , and rarely exceeded 10 mg l^{-1} . This was comparable to concentrations observed in sub-surface throughflow at Sidney Meadow (see Fig. 3.26). The switches from arable to pasture on the plateaux that occurred in 1989 appeared to have no effect on NO_3^- -N concentration, indicating that the levels observed were probably typical of NO_3^- -N in sub-surface flow occurring predominantly under pasture on this type of soil. However, when Trudgill *et al.* (1991) examined soil NO_3^- -N concentration under arable land, grassland, and woodland in the nearby Slapton Wood catchment from autumn 1983 to spring 1985, they concluded that there was no significant relationship between land-use and soil NO_3^- -N concentration, and that spatial variations in soil NO_3^- -N were in part related to variations in topography. This may explain why land-use changes at Merrifield did not significantly affect NO_3^- -N concentration in spring and stream water, and it highlights the importance of conducting catchment scale studies of nutrient transport.

Although no detailed analysis of the time-series was carried out, there appeared to be evidence of an increase in NO_3^- -N concentration during the winter months, especially in the stream water (see Fig. 4.9). This effect was also noted at Sidney Meadow, and although the increase corresponds to increasing rates of discharge, the cause is most likely to be an accumulation in soil water following the cessation of plant uptake in the autumn and before the soil becomes cold enough to inhibit nitrification. For grassland this critical period is probably from early September to early December (Archer, 1991). Smith (1992) gives figures for the transport of nitrate-N following applications of slurry to grassland at different times of the year. They vary between 10 kg ha^{-1} for a June application, and 90 kg ha^{-1} for a November application.

The combination of increasing concentration and discharge is certainly reflected in the increased load of NO_3^- -N from the catchment in the winter months (see Fig. 4.9), and it may be that the increasing rate of water transport is more important than the increased supply of NO_3^- -N. For example, in the above mentioned experiment, Trudgill *et al.* (1991) were unable to show a significant relationship between soil NO_3^- -N concentration and concentration in stream discharge through time, despite the fact that for each land-use there was an increase in soil NO_3^- -N concentration through the

autumn and winter months. Taking into account spatial variations in land-use and topography, and temporal variations in weather, they concluded that NO_3^- -N delivery to the stream was probably limited by rates of water transport rather than NO_3^- -N supply.

Concentrations of NH_4^+ -N in both the stream and spring water were generally less than 0.1 mg l^{-1} , and rarely exceeded 0.2 mg l^{-1} (Figs. 4.11 and 4.12). Again, this was comparable with concentrations observed in sub-surface throughflow at Sidney Meadow (Fig. 3.26). Analyses of storm events in 1987-1988, which will be discussed in more detail later in this chapter, showed that rainfall intensity did on occasions exceed 5 mm h^{-1} , the maximum recorded being 9 mm h^{-1} . Given the low infiltration capacity of certain parts of the catchment due to compaction and poaching (see section 4.3.1 above), it is therefore probable that infiltration excess surface runoff took place from these partial areas at certain times. There may also have been surface runoff caused by variable source areas of saturation excess (see Chapter 2, section 2.2). If there were instances of surface runoff at times of high rainfall and discharge, either infiltration or saturation excess, they were not marked by any notable increase in NH_4^+ -N concentration. This could mean that either the sources of surface runoff did not contain significant amounts of NH_4^+ -N, such as is found in manure, or that the quantities of surface runoff compared to sub-surface throughflow were so low that dilution of the surface derived NH_4^+ -N took place. The second of these explanations is more plausible, firstly because the areas of surface runoff were likely to be limited, and secondly because the duration of surface runoff would be limited to a time-scale of hours during storm events, which means that it is unlikely that a weekly sampling regime would coincide with the occurrence of surface runoff. Concentration of NH_4^+ -N did not appear to fluctuate in response to fluctuations in discharge, so overall, the NH_4^+ -N load from the catchment was related to the level of discharge.

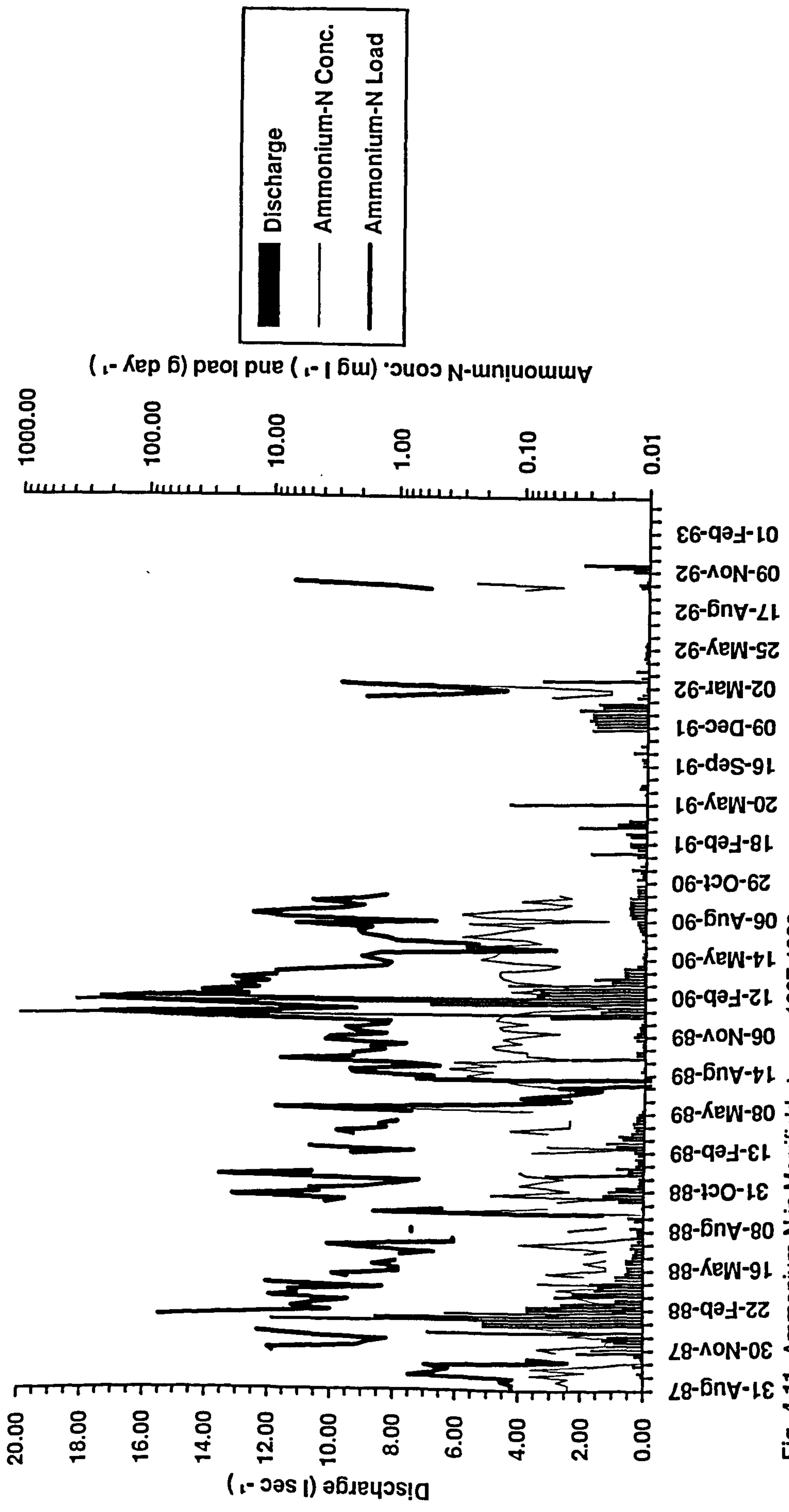


Fig. 4.11. Ammonium-N in Merrifield stream, 1987-1993

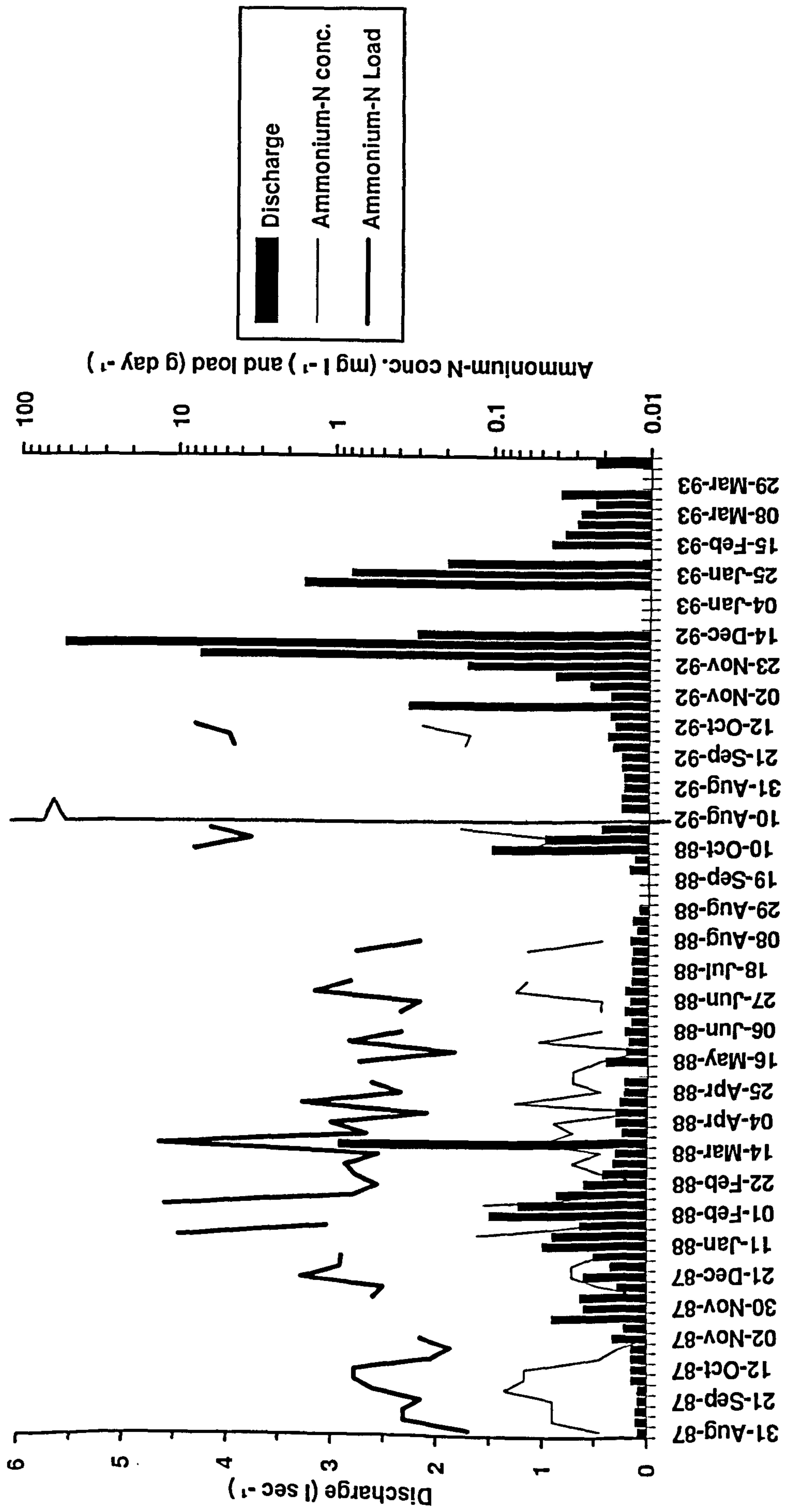


Fig. 4.12. Ammonium-N in Merrifield spring, 1987 - 1988 and 1992 - 1993

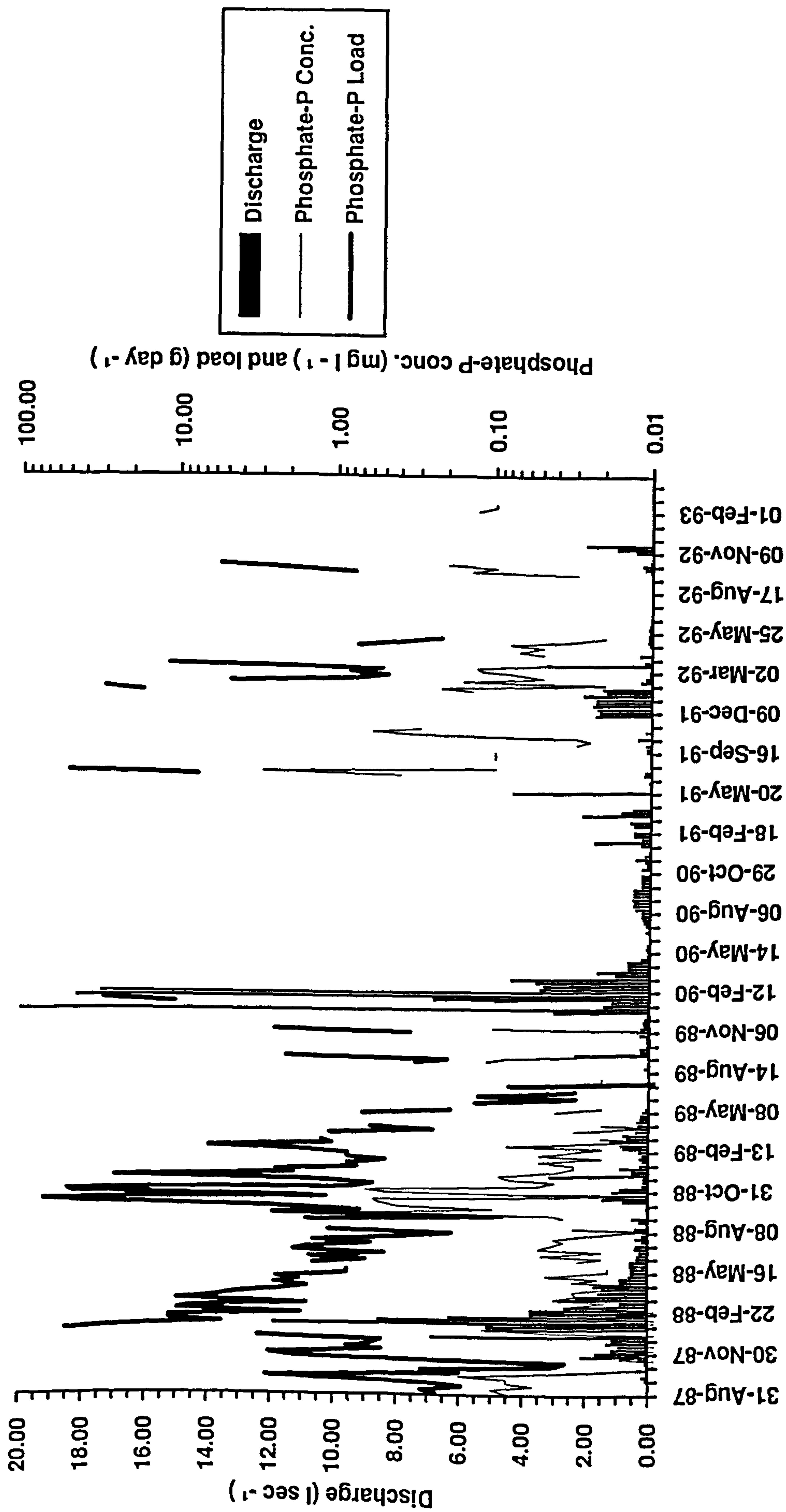


Fig. 4.13. Phosphate-P in Merrifield stream, 1987 - 1993

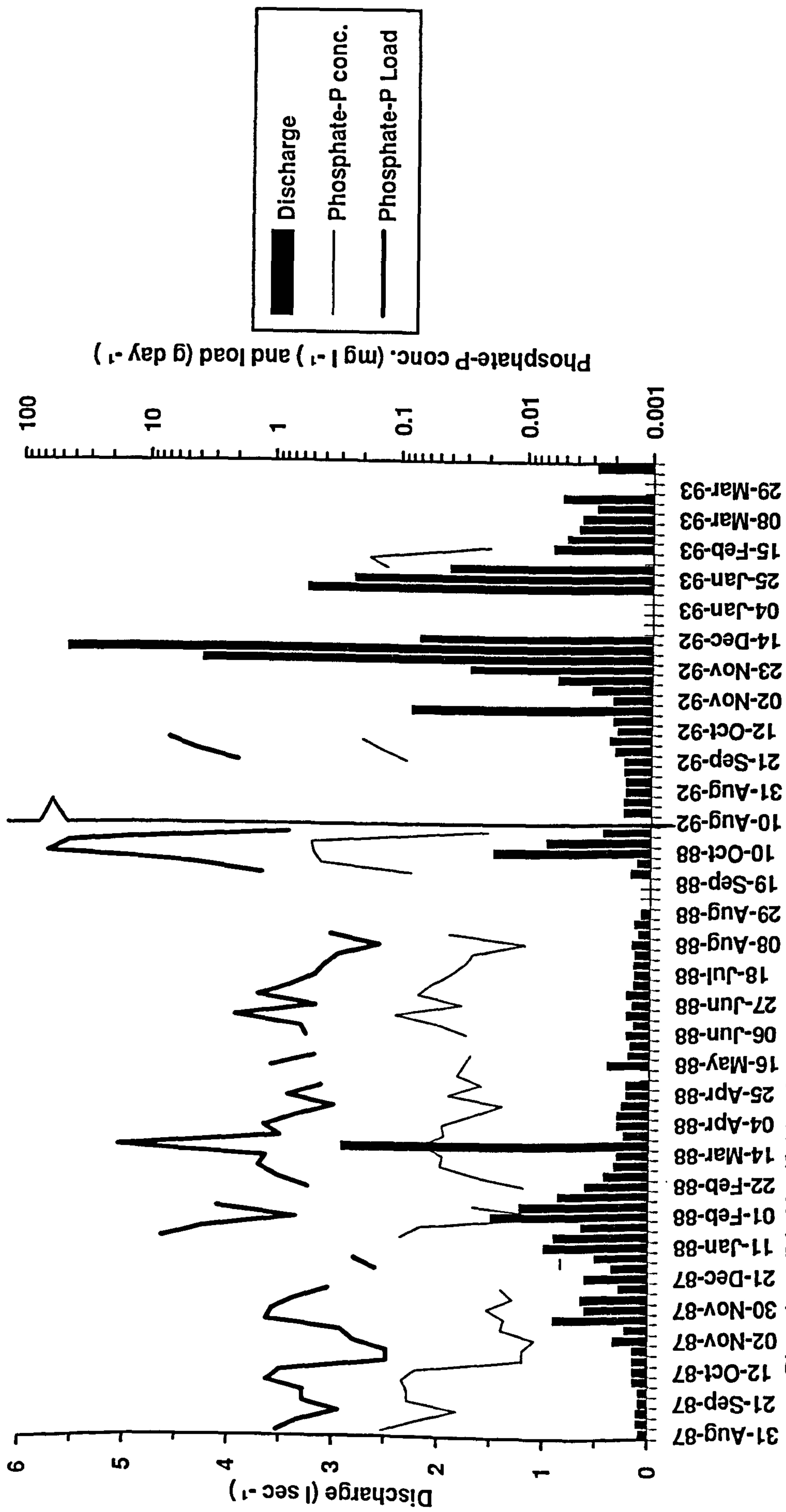


Fig. 4.14. Phosphate-P in Merrifield spring, 1987 - 1988 and 1992 - 1993

Although the method of autoanalysis used for measuring PO_4^- -P concentration for the weekly record at Merrifield was the same as the one used at Seale-Hayne, in the period 1987-1990 chemical analysis actually took place on a different machine at Slapton Ley Field Centre, and this may account for the lower limits of detection which were achieved before the analytical operation was transferred to Seale-Hayne. During the year 1987-1988 in particular, detectable concentrations in the range 0.01-0.05 mg l^{-1} PO_4^- -P were recorded in both the stream and spring water. Overall, concentrations rarely exceeded the 0.1 mg l^{-1} which often proved to be the limit of detection at Seale-Hayne (Figs. 4.13 and 4.14). As with NH_4^+ -N, there appeared to be no marked increase in PO_4^- -P concentration that could be associated with the occurrence of surface runoff during times of high discharge. Again, this would imply that the spatial and temporal extent of surface runoff was too limited to show significantly on the weekly record. If anything, significant increases in concentration upto 1 mg l^{-1} PO_4^- -P seemed to occur in late summer / early autumn, notable examples in the stream record being 1987, 1988, and 1991. The reason for these increases is not known, but if combined with relatively high levels of discharge they can result in considerable increases in the PO_4^- -P load from the catchment. This effect was noted in both stream and spring water in October 1988 (again, see Figs. 4.13 and 4.14). As with NO_3^- -N and NH_4^+ -N, the PO_4^- -P load from the catchment was generally related to the level of discharge.

4.3.4. The response of the Merrifield catchment to a storm event, March 1988

This particular storm event was relatively intense, some 36.5 mm of rain falling over a nine hour period on the 21st March 1988. The response of the spring and stream discharge to this rainfall is illustrated in Fig. 4.15. The rapid and high peaking of spring and stream discharge following the peak rainfall intensity of 9 mm h^{-1} was a clear indication that some degree of surface runoff was taking place, if only from limited partial or variable source areas and for a short period of time, and perhaps in conjunction with rapid preferential throughflow. The smaller peak in stream discharge immediately preceding the main peak might be attributed to the onset of preferential

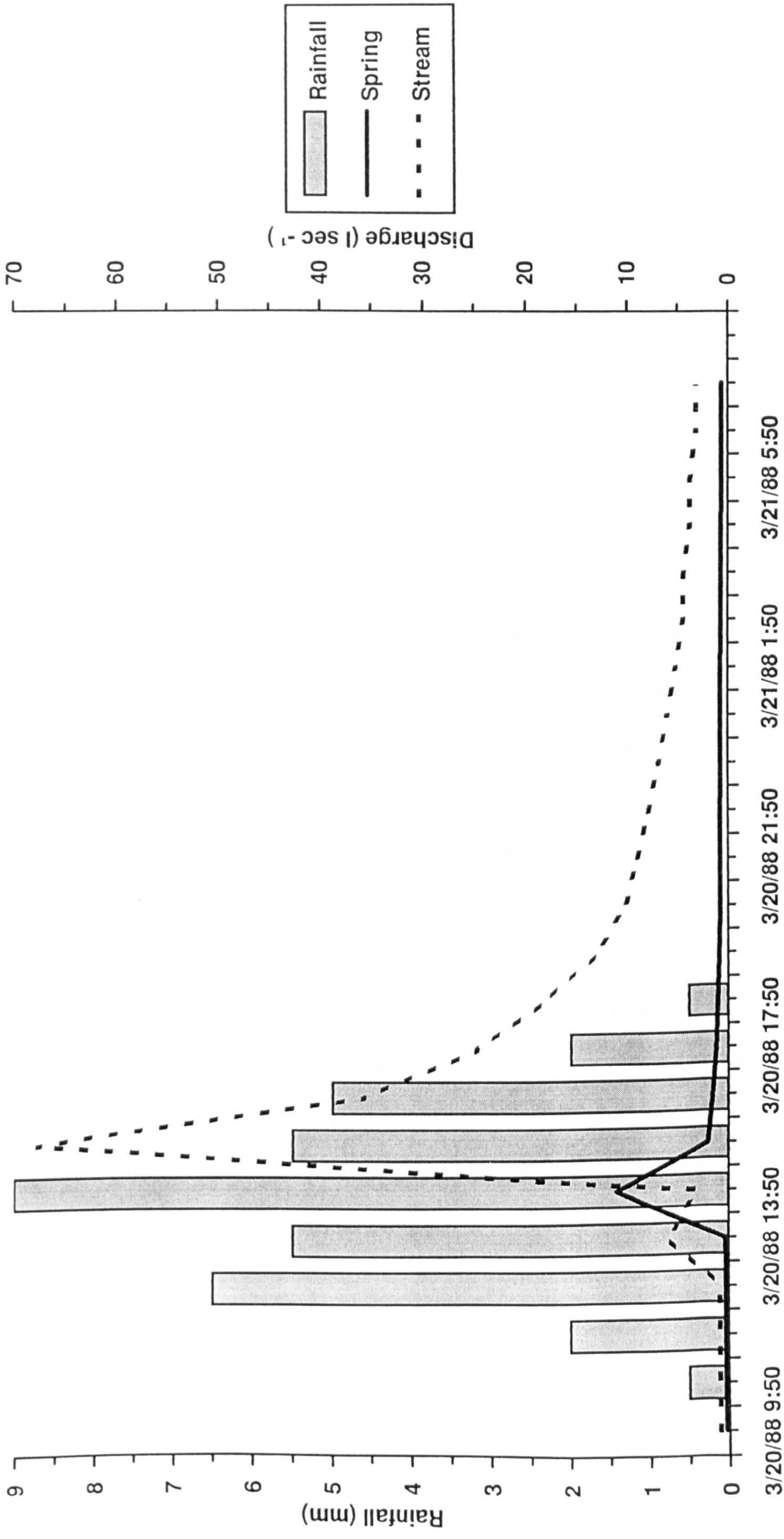


Fig. 4.15. Rainfall and discharge at Merrifield, March 1988 storm event

throughflow and a smaller amount of surface runoff, although this interpretation is not certain.

In the case of this storm at least, it would seem that the timing of the discharge response across the whole catchment was almost as rapid as for the section of field draining to the spring, for although the X-axis on Fig. 4.15 is slightly distorted to accommodate the rainfall columns, the actual chart recordings showed that peak discharge on the stream occurred within thirty minutes of peak discharge on the spring. This would indicate that the timing of hydrological processes does not alter significantly with the observed increases in scale, which facilitates the application of mechanisms interpreted at the plot scale in order to interpret observations at the headwater catchment scale.

The transport of NO_3^- -N in spring and stream water during this storm event is shown in Figs. 4.16 and 4.17 respectively. Unfortunately, sampling only commenced at the spring immediately after peak discharge had occurred. However, there is some evidence from the stream at least of dilution in NO_3^- -N concentration both immediately prior to and during peak discharge, and the first concentration recorded at the spring was also the lowest. This dilution effect could be attributed to a mixing of water low in NO_3^- -N, flowing from the surface or preferentially, with water richer in NO_3^- -N flowing through the soil matrix (Keeney, 1986; Armstrong and Burt, 1993). Certainly, an observation of this kind is not in conflict with the concentrations of NO_3^- -N in surface and sub-surface flow as recorded at Sidney Meadow (see Figs. 3.27 and 3.26 respectively). The steady concentration of $5\text{-}6 \text{ mg l}^{-1}$ observed in the spring and stream in the hours following the storm event is comparable with the concentration observed in sub-surface throughflow in Sidney Meadow at this time of year, and with concentrations observed in the weekly record.

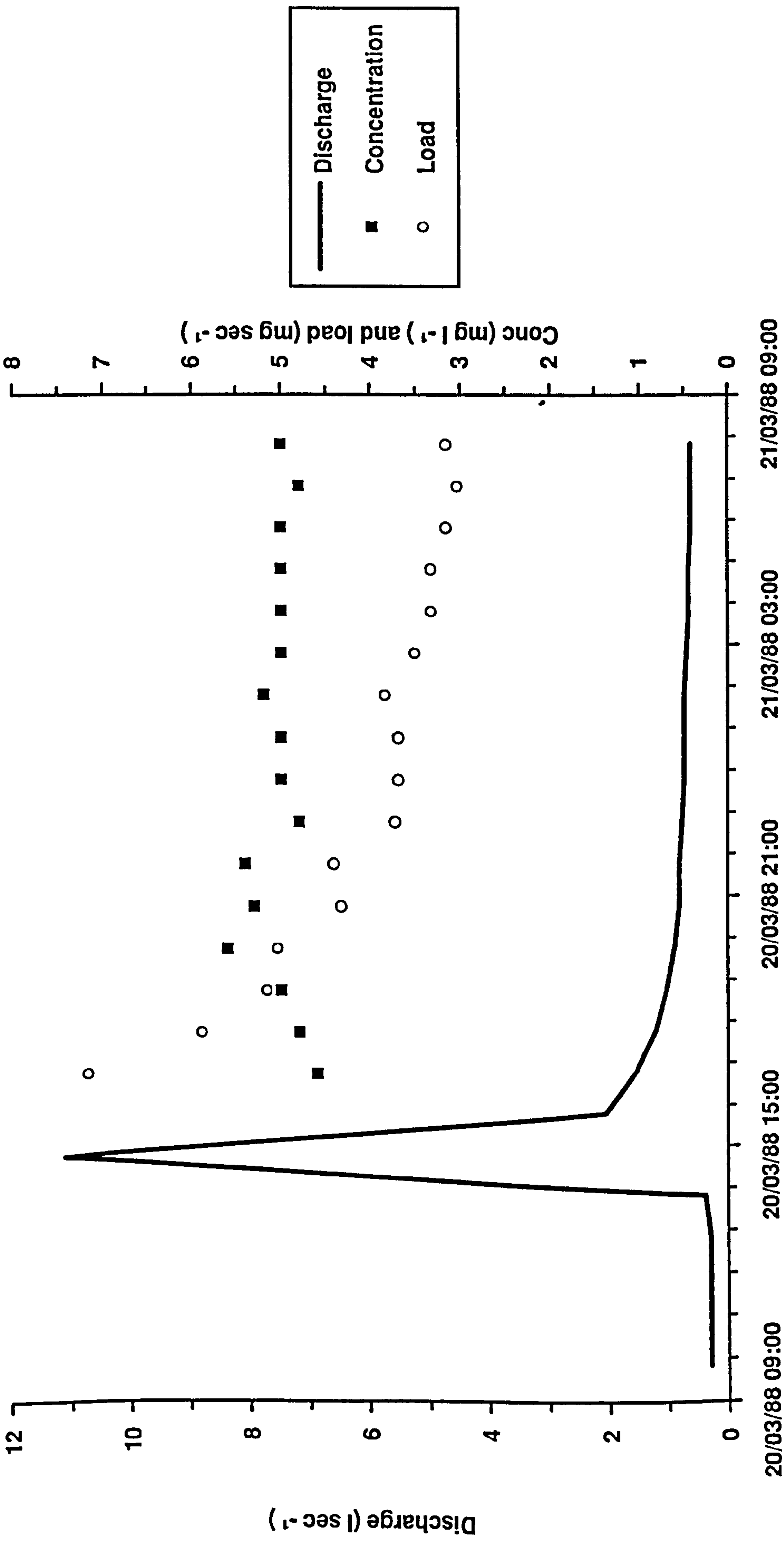


Fig. 4.16. Nitrate-N in Merrifield spring, March 1988 storm event

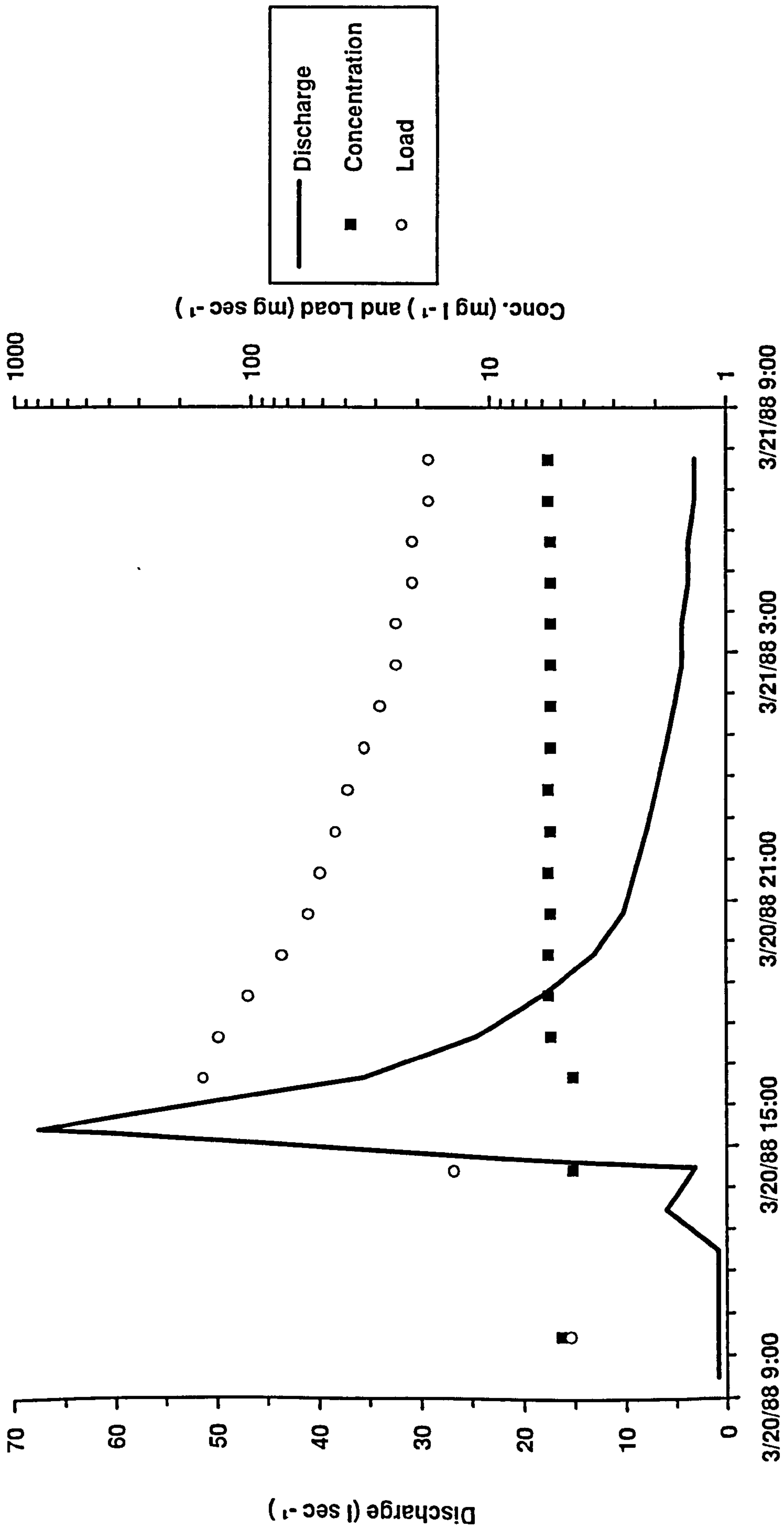


Fig. 4.17. Nitrate-N in Merrifield stream, March 1988 storm event

Lines drawn between points are to aid visualisation of fluctuations

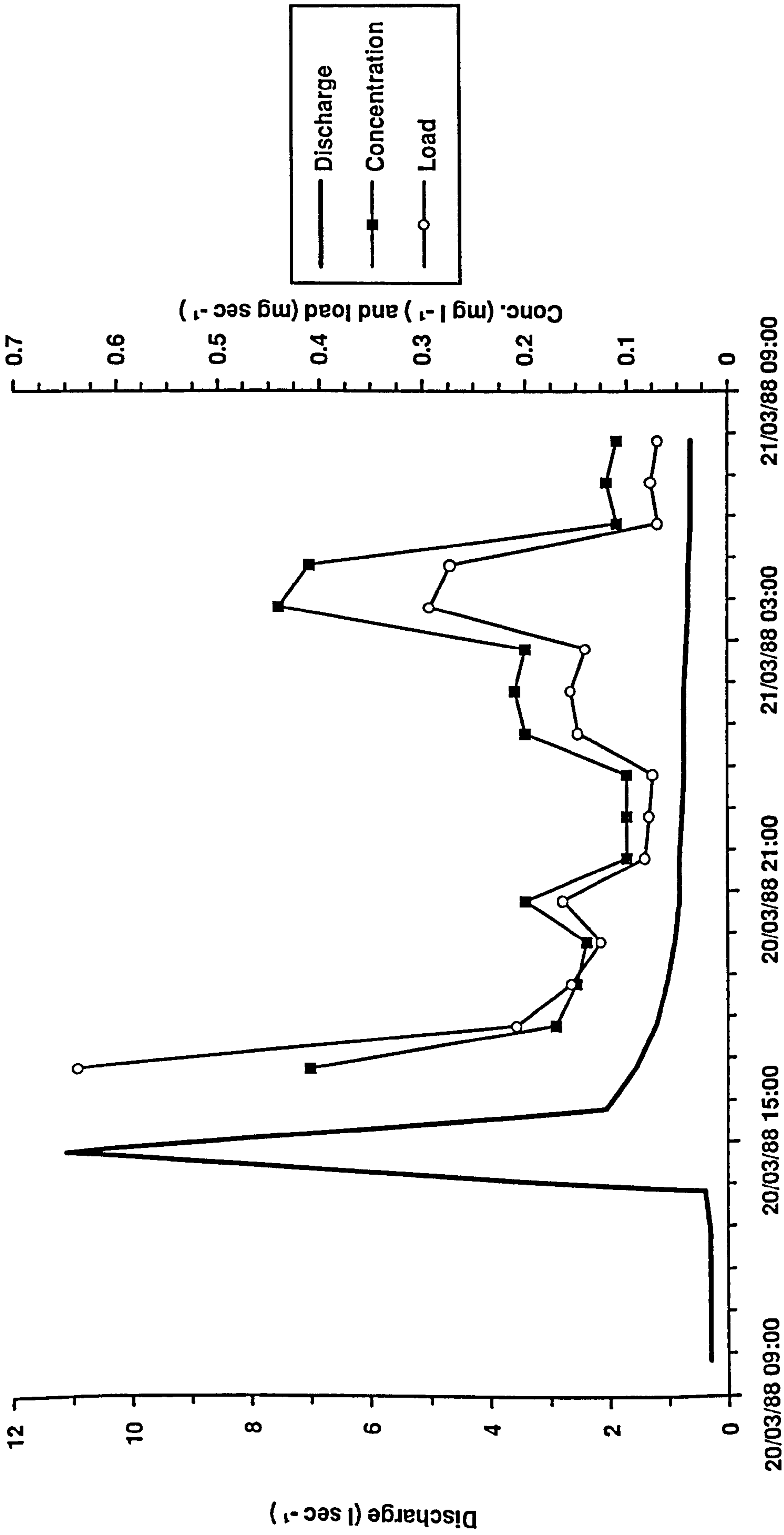


Fig. 4.18. Ammonium-N in Merrifield spring, March 1988 storm event

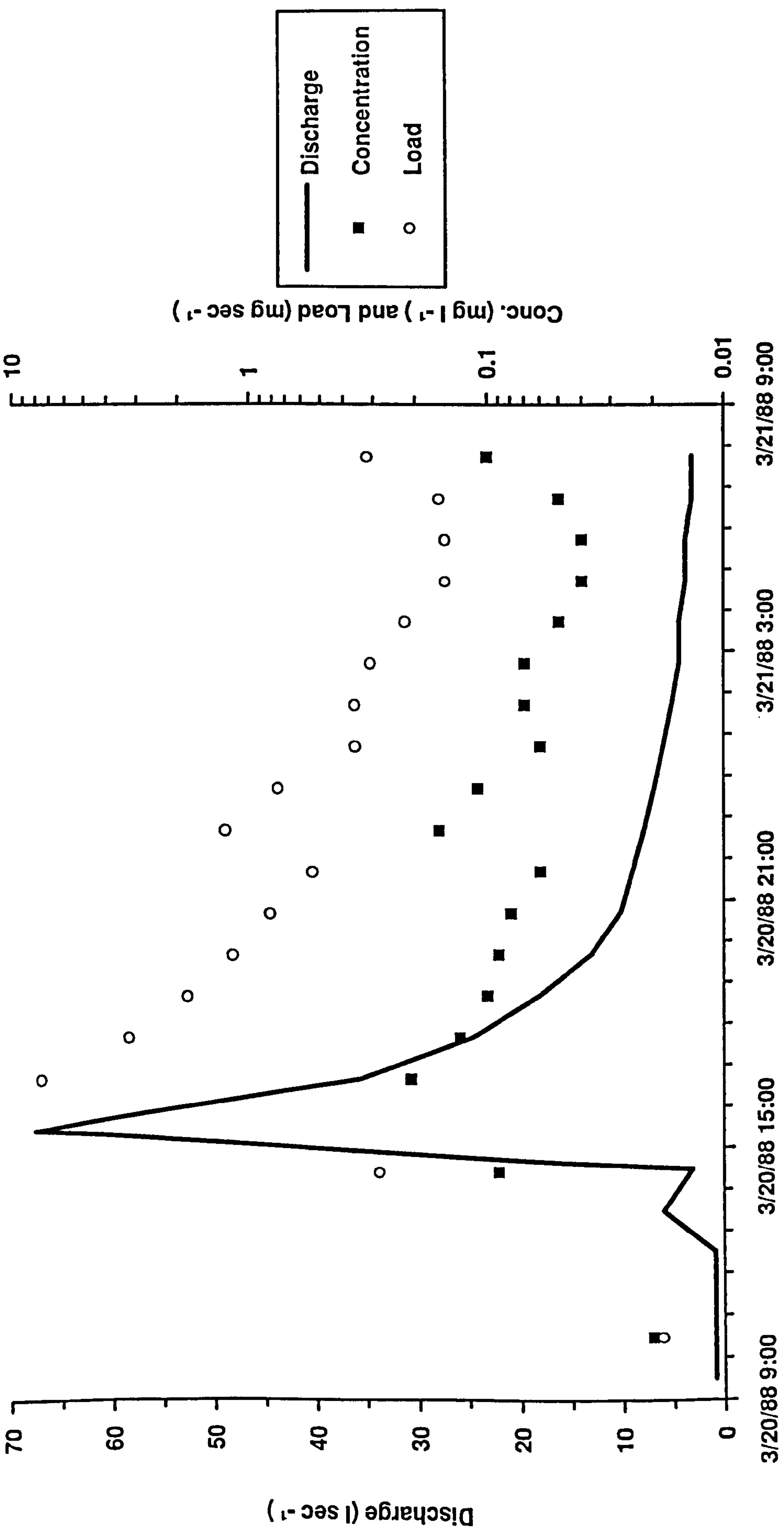


Fig. 4.19. Ammonium-N in Merrifield stream, March 1988 storm event

Under the land-use predominating at Merrifield at the time of this storm event, which included areas of relatively intense grazing, it would be expected that an occurrence of surface runoff would result in changes in the level of $\text{NH}_4^+\text{-N}$ in spring and stream water, due mainly to the presence of dung and urine on the slope surfaces. The actual response of $\text{NH}_4^+\text{-N}$ in spring and stream water is shown in Figs. 4.18 and 4.19 respectively. While there was evidence of an increase in $\text{NH}_4^+\text{-N}$ concentration during peak discharge, there were also considerable fluctuations in concentration in the hours following the storm event. These fluctuations could be attributed to pulses of preferential flow containing surface derived $\text{NH}_4^+\text{-N}$ and travelling at different rates, although transport of $\text{NH}_4^+\text{-N}$ along this pathway without significant adsorption is associated with organic rather than mineral soils (Duxbury and Peverly, 1978). Or, it may be that increased sub-surface flow following the storm event was creating small areas of saturation from which saturation excess surface runoff was then taking place. Whatever the exact mechanisms of $\text{NH}_4^+\text{-N}$ transport, there is evidence from the chemographs that the response of the catchment to the storm event may not have been as uniform as the hydrographs alone imply.

The response of $\text{PO}_4^-\text{-P}$ further complicates interpretation of this storm event (see Figs. 4.20 and 4.21). Concentration in the stream showed no response to the storm event, remaining at a level of 0.03 mg l^{-1} , typical for sub-surface throughflow in this kind of system (Dam Kofoed, 1984). Concentration in the spring showed similar fluctuations to those occurring with $\text{NH}_4^+\text{-N}$, with concentrations generally being almost double those observed in the stream. This would imply some kind of surface input to the spring at least, perhaps by the mechanisms described for $\text{NH}_4^+\text{-N}$ above. Why there should be fluctuations in $\text{PO}_4^-\text{-P}$ concentration in the spring and not in the stream is not clear, especially when fluctuations in $\text{NH}_4^+\text{-N}$ concentration were observed in both the spring and stream. Increased levels of both $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^-\text{-P}$ would be expected from the same surface sources in a predominantly grassland system. Therefore, these observations imply a degree of spatial variability in the transport of N and P at the headwater catchment scale during intense storm events. Set in the context of total loads of N and P delivered from the catchment during this particular storm, it is prudent not

Lines drawn between points are to aid visualisation of fluctuations

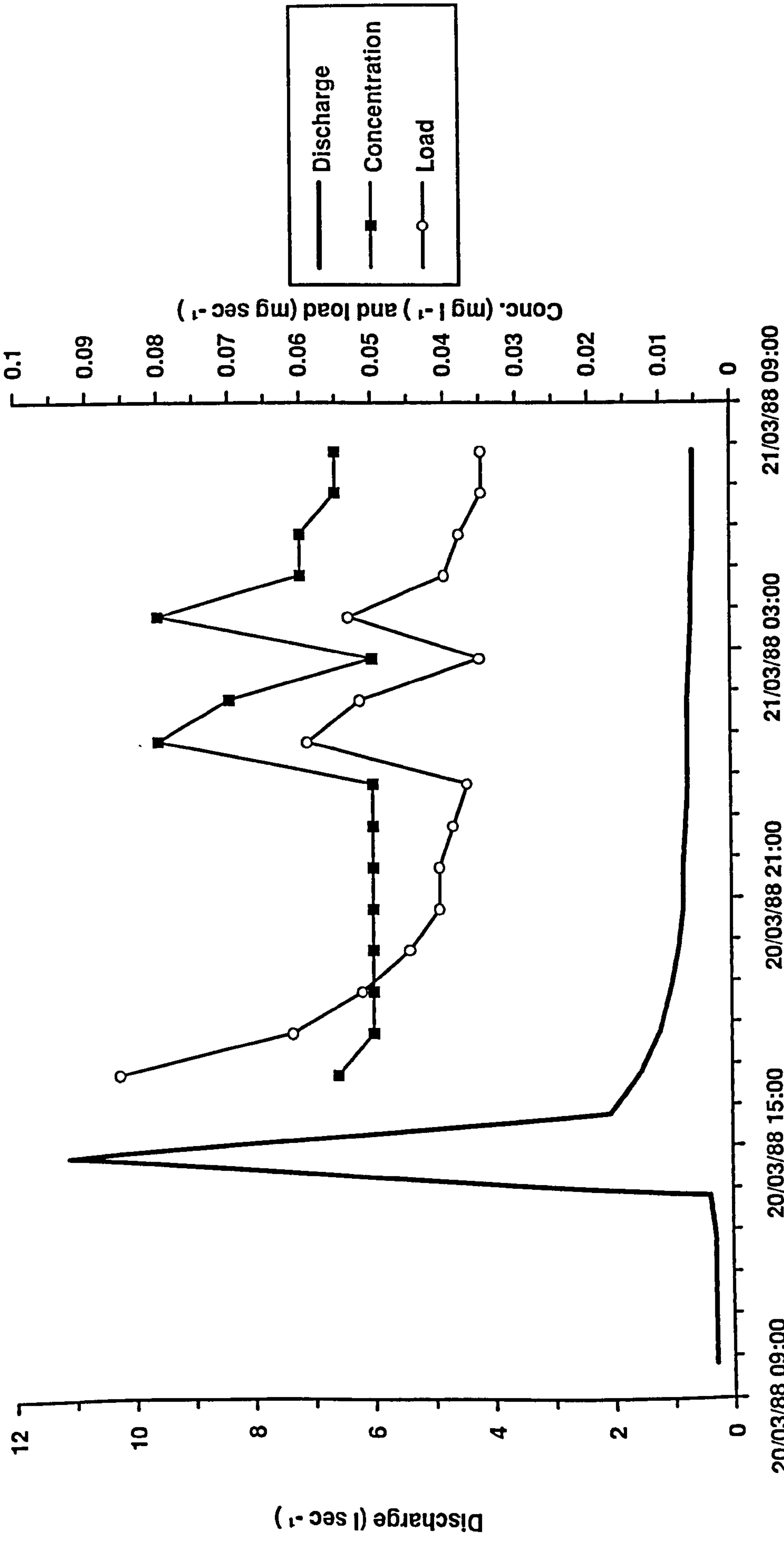


Fig. 4.20. Phosphate-P in Merrifield spring, March 1988 storm event

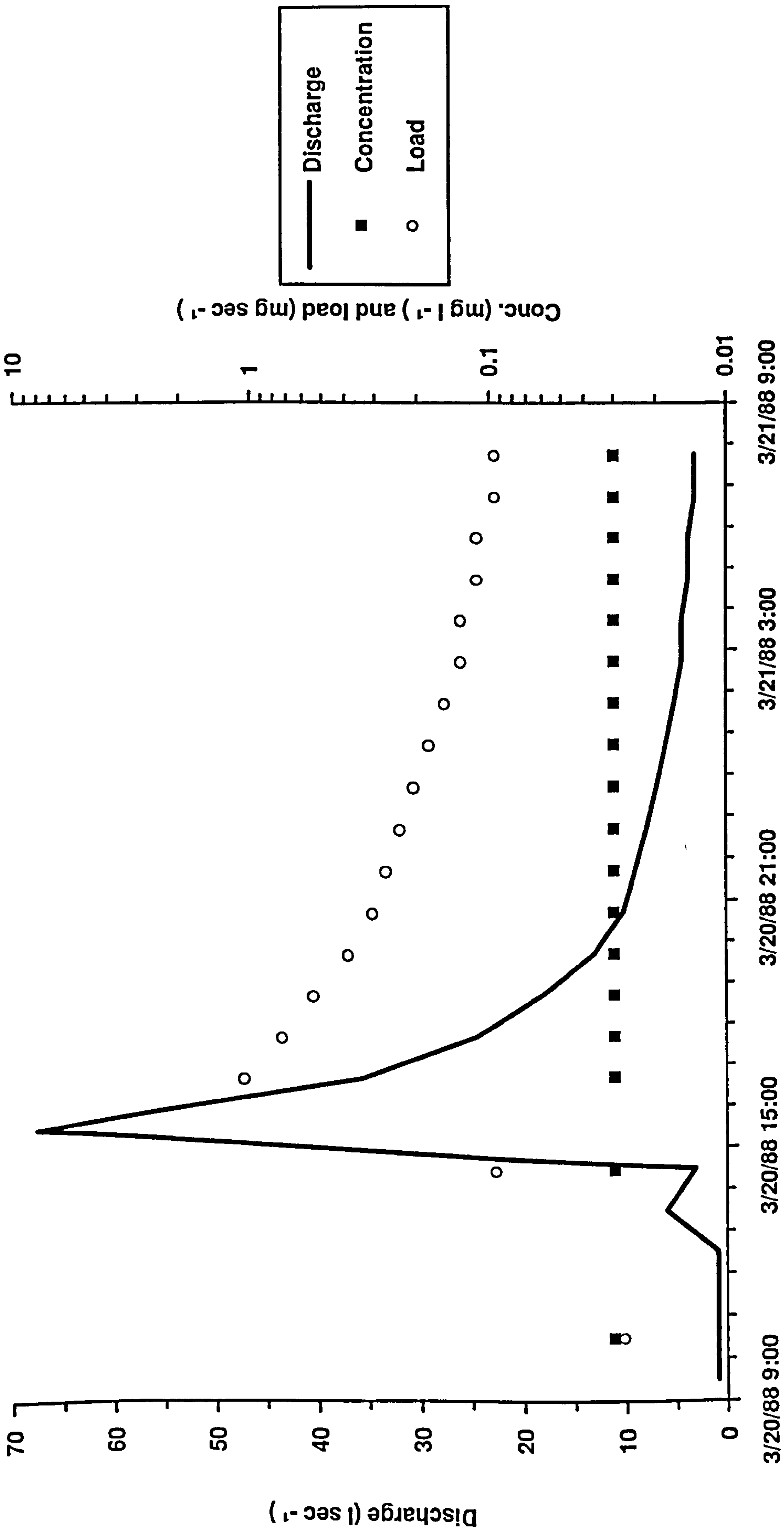


Fig. 4.21. Phosphate-P in Merrifield stream, March 1988 storm event

to overstress the importance of these short-term fluctuations in $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^-\text{-P}$ concentration. Nevertheless, they do serve as important indicators of the interactions between land-use and topography that require examination if one is to accurately describe and quantify N and P transport at this scale.

4.3.5. Storm event monitoring at Merrifield, winter 1992-1993

Unfortunately, this part of the experimental programme was fraught with difficulty, and few useful results were obtained. The problems began in November 1992, when exceptionally heavy rain (approximately 220 mm fell between 10th November and 10th December) caused the retaining bank of the pond to collapse (see Fig. 4.22). Large quantities of soil and slate were washed from the bank into the stream, almost completely submerging the V-notch weir (see Fig. 4.23). Therefore, the measurement of discharge on the stream proved to be impossible. Further problems with the timing of weather forecasts and transport to the site meant that the peaks of the winter's two main storm events, in December 1992 and January 1993, were missed. On both occasions, sampling at the spring and stream took place over the 48 hours following peak discharge, and these proved to be the only samples obtained. None of these samples contained detectable quantities of $\text{NH}_4^+\text{-N}$, $\text{PO}_4^-\text{-P}$, organic-N, or organic-P, a reflection of the light grazing taking place within the catchment, and the fact that during monitoring it was clear that surface runoff was not taking place. N and P concentrations in rainwater retained in the rain gauge were found to be negligible on both occasions.

Levels of $\text{NO}_3^-\text{-N}$ in spring and stream water in December 1992 and January 1993 are shown in Figs. 4.24 and 4.25 respectively. The observed concentrations of 4-7 mg l⁻¹ were comparable with previous years at the site and with concentrations observed at Sidney Meadow, a further indication that $\text{NO}_3^-\text{-N}$ levels in sub-surface throughflow varied little in response to changes in surface applications of N and P from different animal sources on this type of site. Interestingly, $\text{NO}_3^-\text{-N}$ concentration in December was considerably lower than in January, this presumably being due to the diluting effect of the high discharge occurring in December following heavy and prolonged rain.



Fig. 4.22. Collapse of the pond retaining bank at Merrifield.



Fig.4.23. Submersion of the V-notch weir on Merrifield stream with spoil from the pond retaining bank.

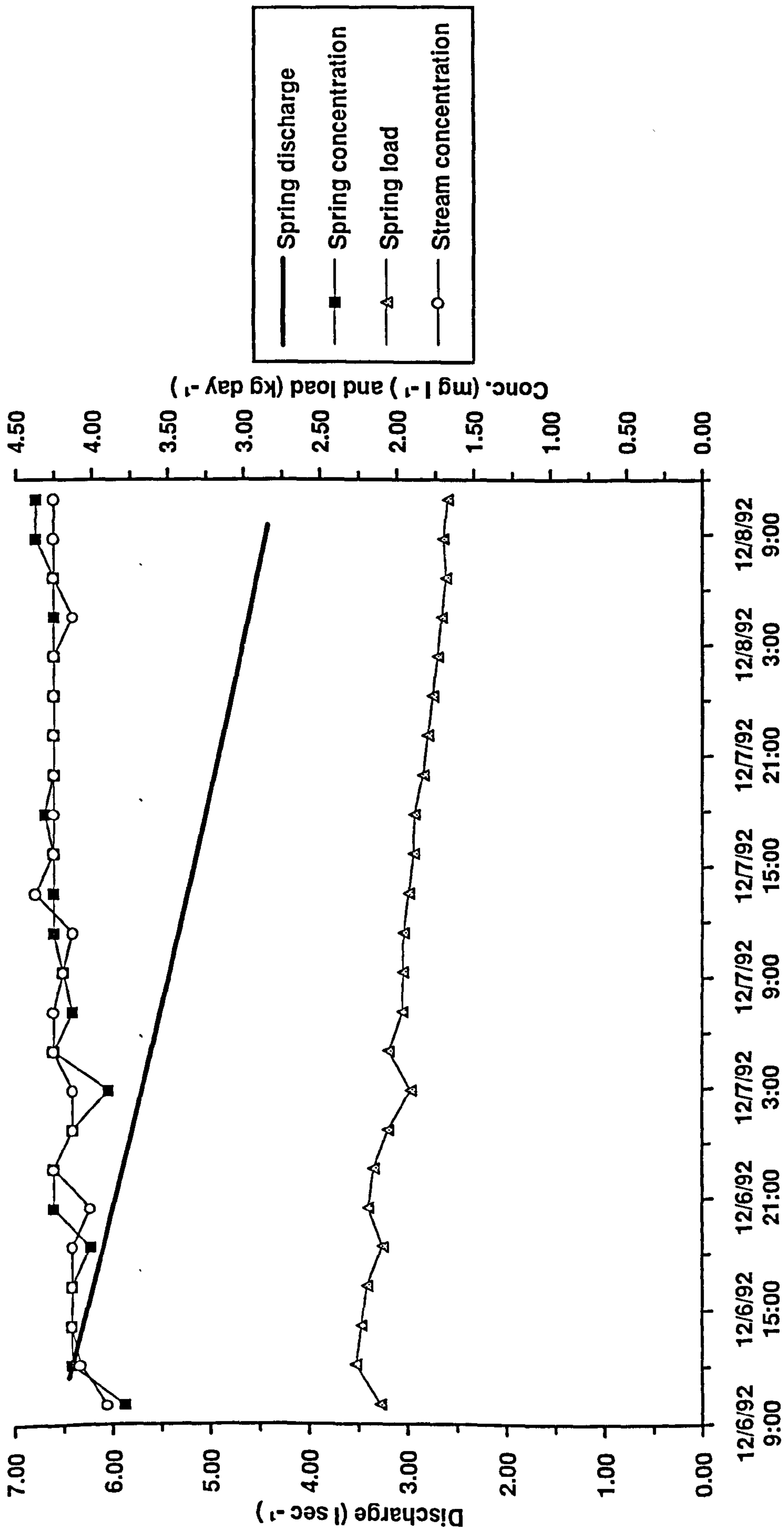


Fig. 4.24. Nitrate-N in Merrifield spring and stream, December 1992

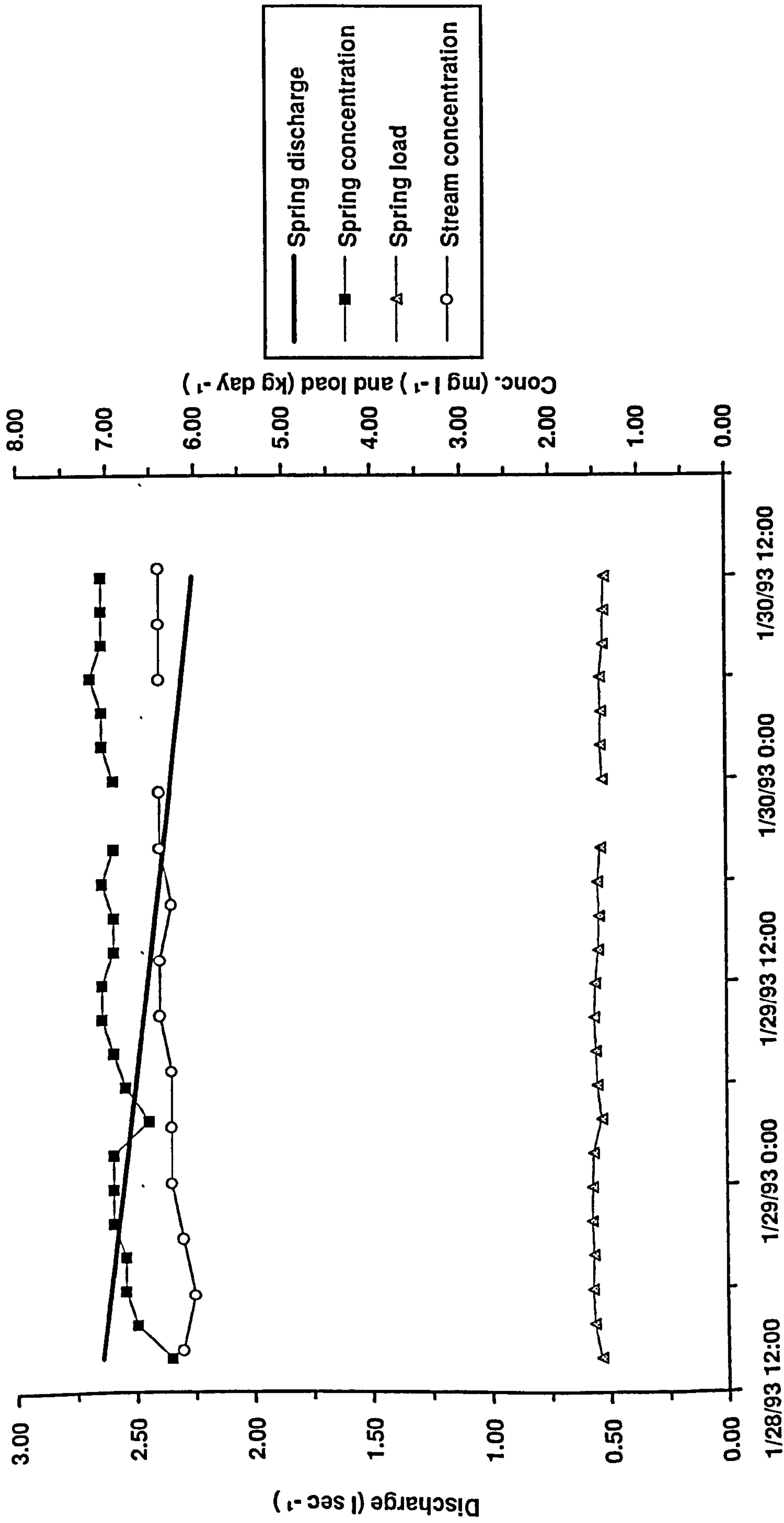


Fig. 4.25. Nitrate-N in Merrifield spring and stream, January 1993

4.4. Chapter summary

1. The Merrifield catchment possessed similar properties to Sidney Meadow in terms of, soil type and bulk density, winter water content and matric potential, saturated hydraulic conductivity.

2. Records of weekly observations showed that NO_3^- -N concentration in both spring and stream water was very similar, usually in the range 2-6 mg l^{-1} , and rarely exceeding 10 mg l^{-1} . This range was comparable with that observed in sub-surface throughflow at Sidney Meadow.

Concentration of NH_4^+ -N was largely the same in both spring and stream water, usually less than 0.1 mg l^{-1} , and rarely exceeding 0.2 mg l^{-1} . Again, this was comparable with concentration observed in sub-surface throughflow at Sidney Meadow. If surface runoff was occurring at the time that any of the weekly samples were taken, this wasn't reflected in fluctuations in NH_4^+ -N concentration.

PO_4^- -P concentration in both spring and stream water was also largely the same, the range of 0.01-0.05 mg l^{-1} being that expected in sub-surface throughflow on this type of site. As with NH_4^+ -N, any occurrence of surface runoff was not reflected in fluctuations in PO_4^- -P concentration.

3. During a storm event at Merrifield, there was evidence of NO_3^- -N dilution at peak discharge. This may have been due to mixing of sub-surface matrix flow with surface runoff or preferential flow, both lower in NO_3^- -N concentration. Such an observation was consistent with experimental records from Sidney Meadow, where surface runoff under manure and slurry applications was shown to contain NO_3^- -N in the range 1-2 mg l^{-1} , and where there was also evidence of preferential flow taking place during rainfall of relatively low intensity.

NH_4^+ -N concentration appeared to increase at peak discharge, implying an input from surface runoff and / or preferential flow. There were also considerable fluctuations in NH_4^+ -N concentration following peak discharge, which could be attributed to differing

rates of preferential flow containing surface derived NH_4^+ -N, or to the build up of variable source areas of saturation from which surface runoff would occur. Similar patterns were observed for PO_4^- -P, implying similar transport mechanisms.

4. In general, it would appear that water flow and N and P transport mechanisms similar to those studied at Sidney Meadow also operate at Merrifield, and over a comparable time period for this scale of catchment at least.

With sub-surface throughflow in particular, the ranges of concentration for NO_3^- -N, NH_4^+ -N, and PO_4^- -P at Merrifield were comparable to those at Sidney Meadow. Observations over a number of years showed little change in concentration in response to changes in surface applications resulting from varying grazing intensities and fertilising regimes. This may imply that the levels observed are typical for sub-surface throughflow under most management regimes for pasture on this type of soil. In other words, quantities of N and P in mobile sub-surface water are largely held constant by the processes of immobilisation, adsorption, plant uptake, and denitrification, the rate of these processes being able to vary sufficiently in most cases to accommodate changes in the surface application of N and P. The possible exception to this interpretation is NO_3^- -N, which is also the most significant species in terms of sub-surface loading of N and P. From the monitoring at Sidney Meadow and Merrifield there was evidence of an increase in NO_3^- -N concentration in winter, following the cessation of plant uptake and before the slowing of the nitrification process. Therefore, a significant surface application in late autumn could increase the sub-surface loading of NO_3^- -N during winter, above that normally expected for the system. The danger of this is already noted in the literature (eg. MAFF and WOAD, 1991).

For surface runoff, interpretation of how mechanisms operate at the catchment scale is more difficult than for the plot scale, the main problem being one of short-term spatial variation during intense storm events. Certainly when surface runoff probably occurred, the response of the Merrifield catchment was rapid, peak discharge on the spring occurring immediately in response to maximum rainfall intensity, and the peak discharge on the stream occurring only thirty minutes later. And, despite the obvious

differences in surface applications, the immediate response of NH_4^+ -N and PO_4^- -P concentration to peak discharge at Merrifield was evidence of surface transport mechanisms similar to those that occurred at Sidney Meadow. Therefore more specifically, the problem at Merrifield is the determination of the magnitude of surface flow of water and N and P transport, given the likely spatial variability in partial areas contributing to infiltration excess surface runoff, variable source areas contributing to saturation excess surface runoff, and the role of preferential flow in contributing to variable source areas. This highlights the importance of the interaction between land-use and topography at the headwater catchment scale.

5. In conclusion, it would seem possible to apply the interpretation of mechanisms at the plot scale to the headwater catchment scale simply by scaling up. The key question is the degree of spatial sensitivity required at the catchment scale in order to accurately determine water flows and N and P transport. This question applies not only to intense storm events, but also to variations in rates of sub-surface flow in response to low intensity rainfall, as was experienced when attempting to estimate rates of sub-surface throughflow at Sidney Meadow in Chapter 3. The use of a mathematical model as described in the following two chapters is partially an attempt to answer this question, as well as a means of exploring the possible effects of different grassland management practices.

Chapter 5

Modelling Approach and Model Construction

Essentially, the modelling procedure was an attempt to produce an appropriate mathematical description of the processes in the conceptual model of Chapter 2, as examined by the field experiments described in Chapters 3 and 4. Taking into account the level of understanding achieved for each of the processes discussed in the conceptual model, and the theoretical and practical constraints on model complexity, the mathematical model was designed to operate at the headwater catchment scale. The steps in the modelling procedure can be summarised thus (see also the objectives of mathematical modelling contained in Chapter 1, section 1.6).

1. An examination of different modelling approaches.
2. Selection of the most suitable modelling approach.
3. Model construction and preliminary testing.
4. Model calibration.
5. Testing of the model's accuracy and sensitivity against observations at Sidney Meadow in the first half of 1992, and in the Merrifield catchment in the hydrological year 1987-1988 (a process of 'hind'casting rather than forecasting).
6. Using the model to explore the possible implications for N and P transport of different land-use practices. For example, varying the width of an untreated buffer strip.

Steps 1-3 are discussed in this chapter, while the remaining steps are covered in Chapter 6.

5.1. Approaches to modelling water flow and nutrient transport

Modelling approaches can largely be distinguished by the amount of detail in which processes are described, which generally determines the model's complexity and the extent to which spatial and temporal variability can be accommodated. Here, modelling approaches have been divided into three groups.

1. Input / Output or 'Black Box' models

This type of model relates the output of water and nutrients from a system directly to the input, with no examination of the processes taking place in-between, hence the term 'black box'. One example of this approach is the Export Coefficient model, where surveys of land-use and stream water chemistry are carried out in a catchment, and from this information each particular land-use is given a coefficient that determines the quantity of nutrients exported from land under that use (for example see Rast and Lee, 1983; Johnes and O'Sullivan, 1989). These coefficients can then be used to predict the changes in stream water chemistry that will result from changing patterns of land-use. The spatial and temporal scales of operation for this type of model are usually catchment and annual respectively. Whilst accurate predictions of nutrient loadings on freshwater bodies such as lakes can be made, the relatively low sensitivity and lack of process detail in this approach restrict its application. For example, it would not be possible to predict the daily transport of nitrate from an arable crop on the basis of fertiliser inputs to the crop and residual nitrate already in the soil system.

2. Functional or simplified mechanistic models

These models usually incorporate inputs, storage elements and outputs, with simplified equations being used to describe the main processes that determine the rate of movement of water and nutrients between storage elements, for example drainage and evapotranspiration. Because no attempt is made to fully describe all the processes taking

place within the system, the functional approach is sometimes defined as 'grey box' modelling.

An example of the functional approach in hillslope hydrology is the model developed by Burt and Butcher (1984) to simulate the processes of hillslope runoff. In this model, the hillslope is represented by ten elemental water stores, each with its own water content. Simulated rainfall is allowed to infiltrate the stores at a set rate, and if rainfall intensity exceeds this rate then the excess water is transferred to the surface of the adjacent downslope store as infiltration excess surface runoff. Sub-surface throughflow is simulated using a simplified version of Darcy's Law, which determines the rate at which water is transferred from one store to the next on the basis of store water content and slope gradient. If a store should become full, the excess water is transported to the surface of the adjacent downslope store as saturation excess surface runoff. Because the model deals with storm events, the time step is hourly, and although it was developed for teaching purposes and therefore wasn't calibrated for a particular field situation, the model output accurately represents the likely pattern of discharge from a hillslope during a storm event.

As Armstrong and Burt (1993) point out, the functional approach is often used to predict nutrient budgets, especially for nitrogen. A good example is the 'SLIM' model developed by Addiscott to predict the daily nitrogen balance in the soil during winter (Addiscott, 1977; Addiscott and Whitmore, 1991). Here, storage and rate parameters for transport processes are derived from easily obtained information such as soil particle size distribution and water content. These parameters can be incorporated in simple mathematical equations which best describe each storage and transport process. The soil profile is divided into a series of layers, and the soil water is divided into mobile and immobile phases. Following a rainfall input, vertical movement of water is determined from rates of drainage and evapotranspiration. Infiltrating rain displaces water and nitrate in the mobile phase, followed by nitrate movement between the mobile and immobile phases to represent the process of equilibration. Although 'SLIM' is primarily a leaching model, nitrogen mineralisation and crop uptake routines have also been added.

The advantages of using the functional approach include the ease of obtaining input parameters, simplicity and clarity of operation, and the relatively rapid calculation of outputs. However, problems occur in predicting outputs in certain circumstances, including high rainfall intensity and water movement, spatial variability in soil properties such as hydraulic conductivity, and operation of the model at different sites with markedly different soil structures. Cameron and Wild (1982) noted some of these problems when examining an early version of Addiscott's model alongside a similar model by Burns (1974).

3. Process-based or fully mechanistic models

This detailed approach to modelling requires complex mathematical descriptions of virtually every process in the system under examination. In the case of sub-surface throughflow for example, this may include numerical solutions to both the Richards equation for unsaturated flow and to Darcy's Law for saturated flow. Rates of surface runoff might be determined by slope gradient and coefficients of surface roughness. For nutrient transport, numerical solutions to convection-dispersion equations might be required (see Jarvis *et. al.*, 1991), and for nitrogen the modelling of species transformation is required, including mineralisation, immobilisation, nitrification, denitrification, and plant uptake. Given the detail and complexity of the calculations involved, it might be appropriate to call this approach 'Pandora's box' modelling.

Theoretically, because this approach to modelling seeks to understand processes, it will ultimately lead to the most accurate prediction of the way a system behaves. In practical terms at present however, models adopting this approach are complicated, expensive to construct and operate, require considerable parameterisation, and are difficult to verify (Burt and Butcher, 1986). Despite these problems a number of models have been developed. An example for hillslope hydrology is a physically based model described by Abbot *et. al.* (1986). Models of solute transport and transformation include those developed by Hutson and Wagenet (1991), Bergstrom and Jarvis (1991), and Wallach and van Genuchten (1990).

In Chapter 3, the extent to which spatial variability within the soil structure was considered proved to be quite important when mathematically describing the rate of sub-surface throughflow on the hillslope, and the above three approaches to modelling can be distinguished by the extent to which they take account of spatial variability within a system such as a catchment. Burt and Butcher (1986) refer to models which treat a catchment as spatially homogeneous as 'lumped' models. These models, including export coefficient models, do not consider the internal mechanisms of the catchment. At the other extreme, models which fully consider the spatial variability of the catchment are referred to as 'distributed' models. Fully distributed models, which are process based, are defined as those which are based on theoretically acceptable continuum equations (Beven and O'Connell, 1982). In between lumped and fully distributed models come 'semi-distributed' models. These models usually divide a catchment into homogeneous sub-areas which are treated as lumped units.

The definition of 'semi-distributed' may overlap other methods of defining modelling approaches. For example, the Burt and Butcher (1984) hillslope runoff model can be described as semi-distributed, functional, physically based and essentially two-dimensional. As another example, the Beven and Kirkby (1979) basin hydrology model can be described as semi-distributed, functional, perhaps less physically based than Burt and Butcher's model, but much more able to predict the spatial variability in flow processes across the three dimensions of a catchment that occurs due to variations in topography. However a model is defined, Burt and Butcher (1986) note the particular advantages of using the semi-distributed approach as follows.

- 1) Semi-distributed models maintain both the physical basis of model parameters and the spatial context of process operation.
- 2) Semi-distributed models are much more flexible than lumped models, but much less costly to operate than fully distributed models.

The problem of dealing with spatial variability in soils has led to the development of models that predict the movement of water and solutes by using a stochastic approach (Armstrong and Burt, 1993). This somewhat different approach to modelling may prove to be of considerable use in predicting the flow of water through spatially random soil

structures where the preferential flow process dominates. Addiscott and Wagenet (1985) have indeed noted that stochastic models have already proved useful in assessing the impact of variability in the hydraulic properties of soils, and that simpler models of this type will lend themselves to management as well as research uses.

5.2. Selection of a suitable modelling approach

The following criteria were used when selecting a suitable modelling approach for the purposes of this study.

1. The understanding of process mechanisms attained from development of the conceptual model and experimental work carried out.
2. Data available for calibration and testing.
3. Computational power readily available.
4. Models already available.

On the basis of these criteria it was decided that a functional semi-distributed approach would be most appropriate. A lumped model would lack the flexibility to describe the different water flow pathways, N and P transport and transformation, and the spatial variability inferred from experimental results. The limited understanding of N and P transport and transformation, particularly within the soil structure, the limited amount of data available for manure amended grasslands, and the computational power available all precluded the development of a process-based and fully distributed model at this stage.

There are numerous models of hillslope and catchment hydrology, and numerous models of solute transport within soil structures. Models combining these processes are not so common, however, and it is possible that none have been applied specifically to manure amendments on grassed hillslopes. Therefore, it was decided that the principles of the Burt and Butcher (1984) hillslope runoff model would be modified and adapted to produce a semi-distributed functional headwater catchment hydrology model. This model would then be expanded by the inclusion of functional equations to describe the movement of N species and P fractions from surface applications, along the pathways

defined by the hydrological processes. As far as the author is aware, the semi-distributed and functional approach to describing total N and P transport from catchments has not been widely employed.

5.3. Model construction

5.3.1. Basic model structure

As with the Burt and Butcher model, the structure of this model comprises a series of cascading storage elements that represent the hillslope (see Fig. 5.1). At present, the number of stores is three, originally corresponding to the zoning of the plots at Sidney Meadow for instrumentation purposes (see Figs. 3.3 and 3.4), but this number can be increased if required. The length, width, volume and slope angle of each store can be set independently, and the depth of each store can be derived from the other dimensions as and when required. Usually, the store dimensions are set to represent increasing soil depth as one progresses down the slope, after the observations at Sidney Meadow and Merrifield. Fig. 5.2 shows how the three converging slopes of a simple headwater catchment can be 'unfolded' to be represented by three stores of decreasing width.

Following the setting of the initial parameters, the model operates on three nested loops. The outermost loop is a daily time step for the number of days specified in the simulation, the middle loop is an hourly time step which only runs on days when there is rainfall, and the innermost loop calculates the inputs and outputs of water, N, and P for each store over whichever of the two time steps is in operation. The hourly time step was selected as the most appropriate unit for the modelling of rainfall intensity and surface runoff during rainfall events. However, since experiments conducted in this study and those included in the conceptual model of Chapter 2 have indicated that the transport of N and P from surface applications of manure may take several weeks, it was regarded that for days when no rainfall occurred the hourly time step was unnecessarily short, and so a daily time-step was included to increase the speed of model operation and reduce model output.

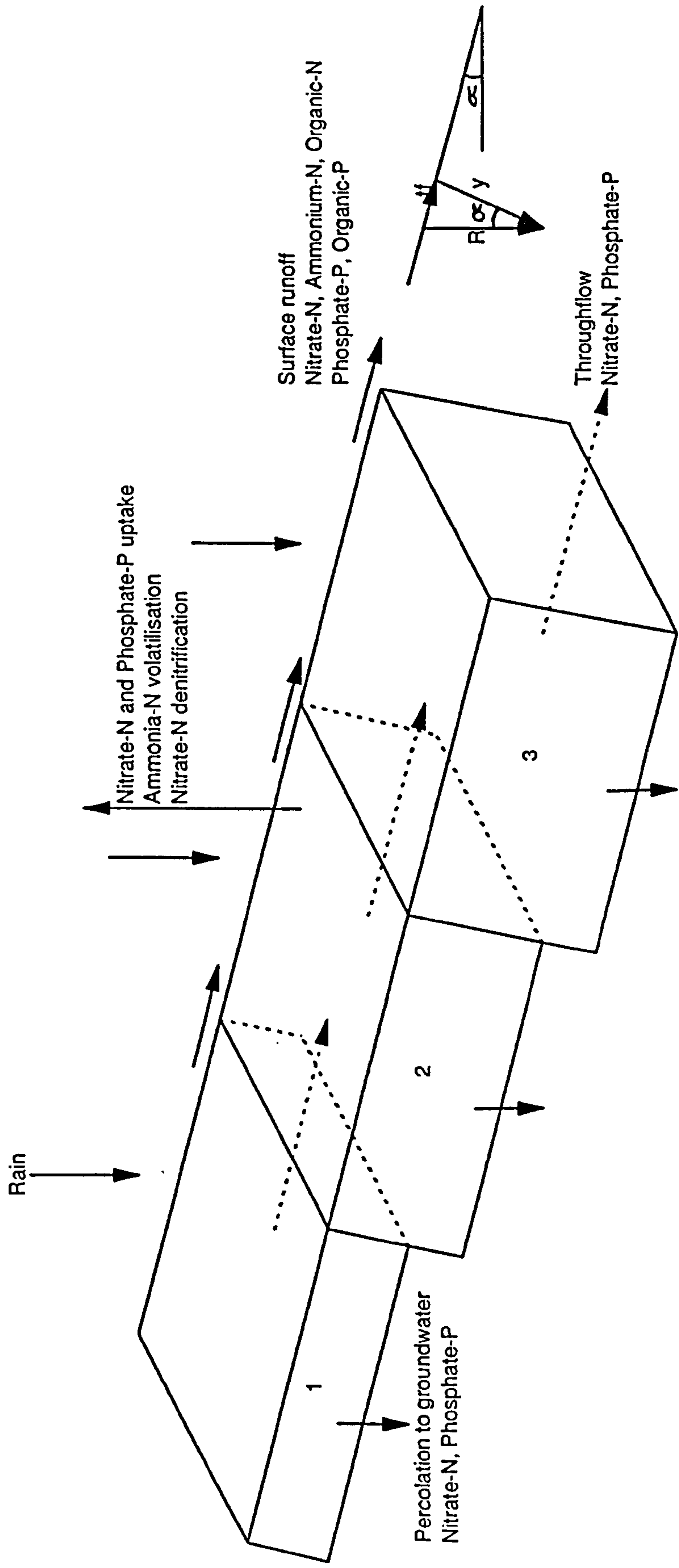


Fig.5.1. Model structure

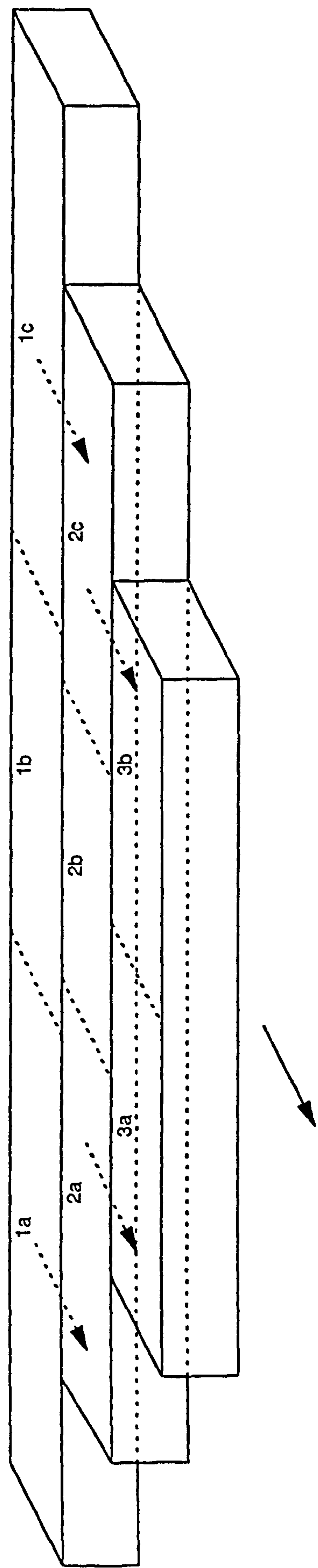
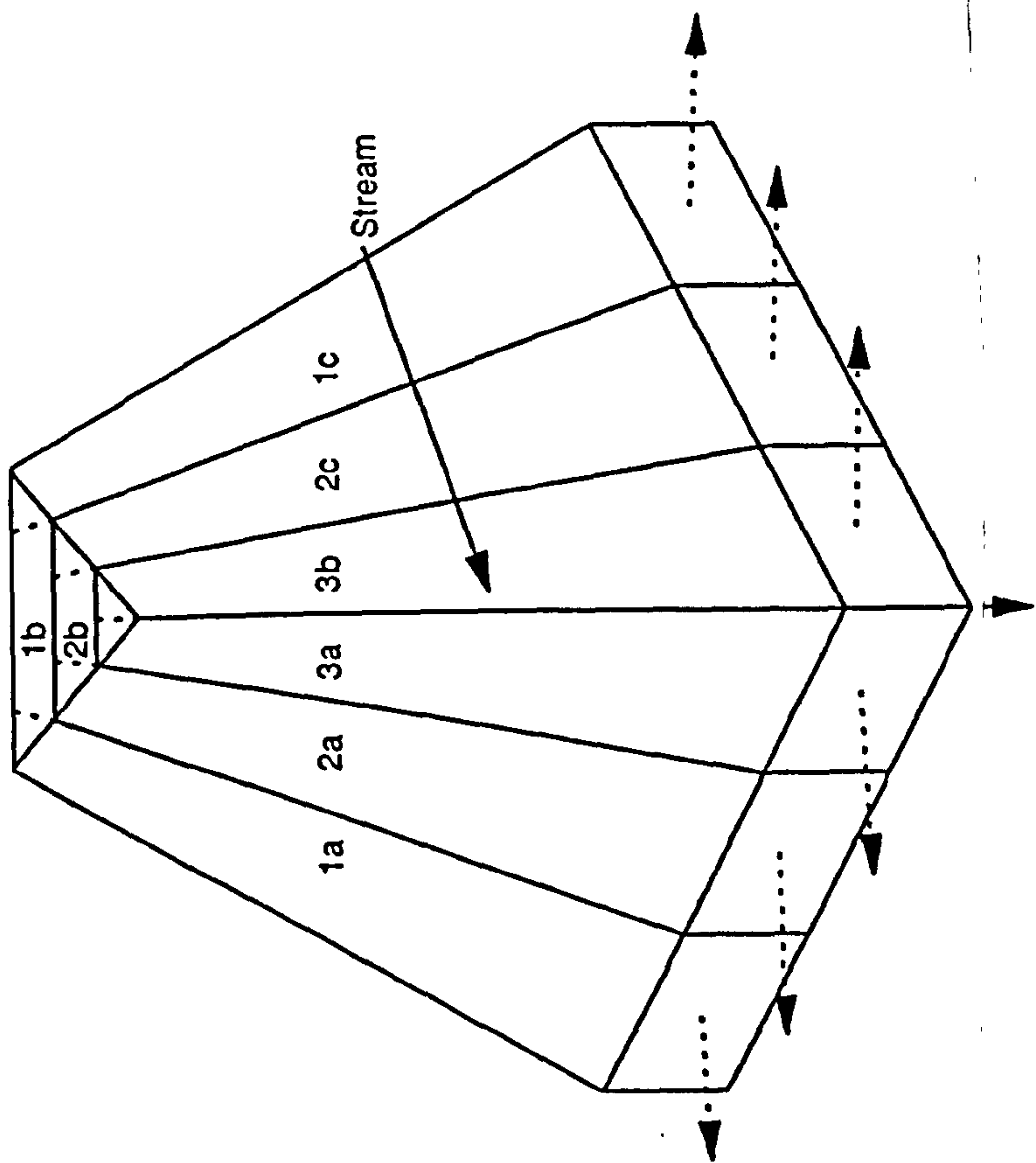


Fig. 5.2. Unfolding of a headwater catchment to be represented by 3 storage elements

Appendix 3 contains a full listing of the model programme (which is written in QBasic), together with a glossary of the variable names used.

5.3.2. Modelling of water movement

Firstly, the number of days for which the model is to run is set. At the start of each day, the model asks if any rain falls on that particular day. If the answer is no, the model moves to a daily time step and calculates the movement of water, N and P for that day. If the answer is yes, the model moves to an hourly time step and with each step asks for the amount of rain that falls within that particular hour.

All three stores have a high initial infiltration capacity, ic_0 . Once 5 mm of rain has fallen in any one day, this capacity is reduced to a low final value, ic_f . If the hourly rainfall exceeds the infiltration capacity of the store, the excess volume of water is sent to the surface of the next store downslope. If the store happens to be at the slope bottom, then the excess water is treated as infiltration excess surface runoff.

Each store has its own initial volumetric water content, S , which is allowed to vary between a minimum value, S_{min} , and a maximum value, S_{max} . The hydraulic conductivity, K , of each store at any particular time is derived from a value of saturated hydraulic conductivity, K_{sat} , using the following equation:

$$K = K_{sat} \frac{(S - S_{min})}{(S_{max} - S_{min})}$$

Initial values of S , S_{min} , S_{max} , and K_{sat} can all be set independently for each store.

Throughflow from each store is calculated from the hydraulic conductivity, K , the slope angle of the store, α , and the effective area from which water can flow from the lower vertical face of the store, which is given by $S / \text{store length}$, L . Under winter conditions, it is assumed that most water flows vertically downwards under the influence of gravity. If this flow is represented by the resultant, R , in the triangle in Fig. 5.1, then the rate of throughflow, tf , can be represented by:

$$tf = R \sin\alpha.$$

Therefore, substituting K for R, the volume of throughflow from the store can be calculated as:

$$tf = K \sin\alpha \frac{S}{L}.$$

For slope angles between 10° and 20°, the values of sin and tan are very similar, so it is acceptable to use K multiplied by either of these definitions of slope gradient. This might aid visualisation of a gravity dominated system where hydraulic gradient largely corresponds to the physical slope gradient.

In addition to throughflow, a low rate of percolation, dp , through the base of each store is calculated using a percolation hydraulic conductivity, K_p . The equation which determines the volume of percolation from each store is as follows:

$$dp = K_p L w, \text{ where } w \text{ denotes store width.}$$

This percolation is treated as an addition to groundwater. At present, there is no facility to simulate the upwelling of groundwater at the base of the slope as a contribution to throughflow during periods of high rainfall. When the hydrological data from Sidney Meadow were examined, the possibility of a contribution to throughflow from upwelling water was considered (see Chapter 3, sections 3.4.2-3). Little understanding of this pathway was gained from the experiments carried out, so its significance in terms of water flow and N and P transport remains to be established.

A low rate of evapotranspiration, $evapr$, is also included for days when there is no rainfall. The amount of evapotranspiration, $evap$, from each store on these dry days is given by:

$$evap = evapr L w.$$

Although measurement of rates of evapotranspiration did not take place at either Sidney Meadow or Merrifield, it was assumed that sufficient meteorological information would be available to allow an adequate estimation, particularly for the winter and early spring periods when rates are likely to be low. There is at present no facility to vary the value of evapr in response to changes in temperature or plant activity, so operation of the model is currently restricted to the winter and early spring period. This is in line with experimental observations made in the field.

For each time step, the input of water to each store as rainfall and throughflow, and the output as throughflow, percolation and evapotranspiration, are combined to give a new store water content. If the new water content exceeds S_{max} , the excess water is output to the surface of the next store downslope. If the store happens to be at the slope base, then the excess water is treated as saturation excess runoff or return flow, **rtf**.

At the end of each time step, the model produces a summary of the water status of each store, including the store water content and hydraulic conductivity, and the volumes of infiltration, throughflow, and surface runoff occurring during the time step. Examples of model output for hourly and daily time steps, and a daily summary, can be seen in Table 5.1.

Table 5.1. Examples of printed output from the model

(a) Hourly time step

Day no. 1 Hour no. 1 Rates are per hour

Rainfall in mm/h? 4

store	inf	of	tf	rtf	k	S
1	347.20	0.00	5.10	0.00	30.00	78460.29
2	272.80	0.00	6.68	0.00	30.00	76994.80
3	100.00	0.00	7.29	0.00	30.00	33848.87

store	naof	natf	nartf	nsurf	nasub	nbof	ncof	ncsub
1	0.00	0.03	0.00	2160.85	468.09	0.00	0.00	7.29
2	0.00	0.04	0.00	1697.81	459.68	0.00	0.00	5.73
3	0.00	0.04	0.00	0.00	202.09	0.00	0.00	0.00

Table 5.1. continued

store	paof	patf	partf	psurf	pasub	pbof	pbsub
1	0.000	0.000	0.000	867.238	2.337	0.000	0.521
2	0.000	0.000	0.000	681.401	2.298	0.000	0.409
3	0.000	0.000	0.000	0.000	1.009	0.000	0.000

Total Water Delivery (m³) = 7.2900

Total N Delivery (kg) = 0.0437

Total P Delivery (kg) = 0.00022

(b) Daily time step

Day no. 2 Is there any rain today? n

Rates are per day

store	inf	of	tf	rtf	k	S
1	0.00	0.00	136.90	0.00	782.29	80105.55
2	0.00	0.00	176.01	0.00	771.71	78420.41
3	0.00	0.00	189.15	0.00	763.14	34373.47

store	naof	natf	nartf	nsurf	nasub	nbof	ncof	ncsub
1	0.00	0.77	0.00	2042.29	428.44	0.00	0.00	48.07
2	0.00	0.99	0.00	1602.74	420.90	0.00	0.00	37.77
3	0.00	1.06	0.00	0.00	183.63	0.00	0.00	1.62

store	paof	patf	partf	psurf	pasub	pbof	pbsub
1	0.000	0.004	0.000	852.651	2.428	0.000	3.434
2	0.000	0.005	0.000	669.810	2.351	0.000	2.698
3	0.000	0.005	0.000	0.000	0.968	0.000	0.115

Total Water Delivery (m³) = 189.1476

Total N Delivery (kg) = 1.0603

Total P Delivery (kg) = 0.00543

(c) Daily summary

Up to the end of day 2

Total Rainfall (mm) = 29

Total Overland Flow (m³) = 180.00

Total Throughflow (m³) = 375.59

Total Deep Percolation (m³) = 180.00

Total Evaporation (m³) = 180.00

Table 5.1. continued

Total Nitrate-N in Overland Flow (kg) = 0.07

Total Ammonium-N in Overland Flow (kg) = 0.44

Total Organic-N in Overland Flow (kg) = 1.10

Total Nitrate-N in Throughflow (kg) = 2.14

Total Nitrate-N in Deep Percolation (kg) = 1.02

Total Ammonium-N Volatilised (kg) = 64.58

Total N in Plant Uptake (kg) = 104.30

Total N Denitrified (kg) = 65.55

Total Phosphate-P in Overland Flow (kg) = 0.037

Total Organic-P in Overland Flow (kg) = 0.073

Total Phosphate-P in Throughflow (kg) = 0.011

Total Phosphate-P in Deep Percolation (kg) = 0.005

Total P in Plant Uptake (kg) = 20.94

5.3.3. Modelling of N transport and transformation

The surface of each store is allocated a quantity of total N, $nsuf$, which is not divided into species. The value of $nsuf$ depends on the application rate of surface applied manure that is to be simulated, and may be zero if the store is to act as a buffer zone. When rainfall occurs, the incoming rainwater picks up predetermined concentrations of NO_3^- -N, NH_4^+ -N, and organic-N, according to the values of $nasufc$, $nbsufc$, and $ncsufc$ respectively. The quantity of these N species is subtracted from the total N pool, $nsuf$. Once $nsuf$ becomes zero, the values of $nasufc$, $nbsufc$, and $ncsufc$ also become zero.

If infiltration excess overland flow occurs, the excess water that moves to the surface of the next store downslope is mixed with the incoming rainwater for that second store, and the quantities of the N species within each body of water are also mixed to give new concentrations before the water is split into runoff and infiltration. Water moving from one store to the next as surface runoff does not pick up further quantities of N species as it goes along, instead it is treated as being fully loaded with N from the surface of the first store it comes into contact with. This approach was based on observations made during the storm simulations at Sidney Meadow

(Chapter 3, section 3.4.5), when there was found to be no significant increase in loads from the second treated zone when compared to loads from the first treated zone upslope. However, it should be noted that volumes of surface runoff and loads of nutrients during these simulations were relatively low, so the realism of adopting this approach to nutrient loading when volumes of surface runoff are much higher needs to be established.

Within the sub-surface volume of each store, there are two pre-determined pools of N. The first of these is the mobile pool for NO_3^- -N, **nasub**, which is treated as fully soluble with a concentration, **nasubc**. The second is classified as an immobile pool, **ncsub**. Consequently, only NO_3^- -N can move in sub-surface flow, with the concentration **nasubc** determining the quantities in throughflow, **natf**, and percolation, **nadp**, for each time step. Infiltrating NO_3^- -N is added to the mobile pool, **nasub**, but infiltrating NH_4^+ -N is added to the immobile pool, **ncsub**. In effect, this treats all infiltrating NH_4^+ -N as being initially immobilised, which is a simplification of what might happen in reality, where a proportion of NH_4^+ -N may be immediately nitrified and added to the mobile pool or temporarily held within the soil structure as an exchangeable ion (see Chapter 2, section 2.3, and Fig. 2.5). The implication of adopting this approach is that slightly less NO_3^- -N becomes immediately available for transport, denitrification or uptake than perhaps would be the case in reality.

Infiltrating organic-N is added to the immobile pool **ncsub**. During each time step, a small and fixed proportion of the immobile pool, **ncsub**, is transferred to the mobile pool, **nasub**, the rate of transfer being determined by the value of **nccr**. This is a simple representation of the mineralisation and nitrification processes, more NO_3^- -N being produced in response to inputs to the immobile pool. At the same time, two small and fixed proportions of the mobile pool are removed from the system altogether to represent the processes of plant uptake and denitrification, the rates of removal being determined by the values of **naupr** and **nadnitr** respectively. Despite these N cycle processes being conceptually well understood (Chapter 2, section 2.3), because they were not measured directly in the field further data are required to facilitate model calibration and testing. This will be discussed further in Chapter 6.

At the end of each time step, the inputs to and outputs from each N pool are combined to give new pool totals, and a new NO_3^- -N concentration, nasubc , is calculated. If saturation excess occurs, the excess water which flows on the surface not only carries with it the sub-surface concentration of NO_3^- -N, but also picks up quantities of surface NO_3^- -N, NH_4^+ -N, and organic-N, according to the concentration values of nasufc , nbsufc , and ncsufc for the next store downslope. As with infiltration excess, saturation excess water is mixed with incoming rainwater for the downslope store in question.

In addition to the inputs, transfers, stores and outputs detailed above, N is also removed directly from the surface pool, nsuf , to simulate the processes of ammonia volatilisation, increased plant uptake, and denitrification. Fixed proportions of the surface pool are allocated for these processes according to the values of nvol , nup , and ndnit , and the rates of removal are determined by the values of nvotr , nupr , and ndnitr . Again, these are processes that are conceptually well understood but where further experimental data are required to facilitate model calibration and testing.

All of the proportions and rates of conversion for the processes of transformation, volatilisation, uptake, and denitrification are fixed at the start of the simulation, and none can be varied in response to changes in water content or temperature. In this respect, as with the simulation of evapotranspiration, the model is at present restricted to simulation of events within the winter or early spring period, but it is technically straightforward to alter these parameters if simulations of other seasonal time periods are required.

5.3.4. Modelling of P transport and transformation

As with N modelling, the surface of each store is allocated a quantity of total P, psuf , which is not split into fractions. When rainfall occurs, the incoming rainwater picks up predetermined concentrations of PO_4^- -P and organic-P, according to the values of pasufc and pbsufc respectively. The quantity of these P species is subtracted from the total P pool, psuf . Once psuf becomes zero, the values of pasufc and pbsufc also become zero. The transport and mixing of P fractions in infiltration excess surface

runoff with those in incoming rainwater further downslope is treated in the same manner as the transport and mixing of N species.

Within each store, there are also mobile and immobile pools for P. The mobile pool, **pasub**, is soluble PO_4^- -P, with a concentration value, **pasubc**, that determines the amounts of PO_4^- -P transported in throughflow, **patf**, and percolation, **padp**. Infiltrating PO_4^- -P and organic-P are both added to the immobile pool, **pbsub**, as a simplified simulation of the process of complexation with soil mineral cations (Chapter 2, section 2.4). During each time step, a small and fixed proportion of the immobile pool is transferred to the mobile pool, **pasub**, the rate of transfer being determined by the value of **pbc**. This represents what He *et. al.* (1991) would refer to as isotopically exchangeable PO_4^- -P, with very small increases in the amounts of PO_4^- -P being released in response to increasing P inputs to the store. At the same time, a small and fixed proportion of the mobile pool is removed from the system altogether to represent the process of plant uptake, the rate of removal being determined by the value of **paupr**. These chosen functions for the sub-surface transformation and transport of P are, as with N, based more on concepts derived from literature than experimental observations at Sidney Meadow or Merrifield, and the conditions that apply to N regarding the further acquisition of data also apply to P. At the end of each time step, the inputs to and outputs from each P pool are combined to give new pool totals, and a new PO_4^- -P concentration, **pasubc**, is calculated. Any saturation excess is treated in the same manner as described for N species.

As with N, P is also removed directly from the surface pool, **psuf**, to simulate the process of increased plant uptake. A fixed proportion of the surface pool is allocated for this process according to the value of **pup**, and the rate of removal is determined by the value of **pupr**. Once more, the proportions and rates of conversion for the processes of transformation and plant uptake are fixed at the start of the simulation, and none can be varied in response to changes in water content or temperature.

5.4. Preliminary model testing

The purpose of preliminary testing was simply to check that the model was responding in a generally realistic manner to certain hypothetical situations. Fig. 5.3 summarises the output of the model in response to a storm event of 33.5 mm occurring over 7 hours. In this event, the top two stores had surface applications of total N and P as cattle manure at the rate of 250 kg N ha⁻¹ and 100 kg P ha⁻¹ respectively, whilst the bottom store had no surface application. Some of the parameter values used in the test are given in Table 5.2, while others were largely the same as those given in the model programme listing in Appendix 3. Concentrations of N and P in surface runoff and sub-surface throughflow were derived from observations at Sidney Meadow and Merrifield. Values for rates of N and P transformation were derived from sources in the conceptual model of Chapter 2, for example the experiments quantifying plant uptake, volatilisation, and denitrification following slurry application to grassland, as quoted by Smith (1992) and Wild (1993).

Table 5.2. Some parameter values for preliminary model testing

Store no.*	Length (m)	Width (m)	Depth (m)	Slope angle (°)	Initial water content (m ³ m ⁻³)	Final water content (m ³ m ⁻³)
1	10	10	0.50	15	0.40	0.44
2	10	10	0.75	15	0.40	0.43
3	10	10	1.00	10	0.42	0.45

* See Fig. 5.1 for store arrangement.

In terms of both hydrology and chemistry, the modelled response to a storm event of this magnitude was in general agreement with the conceptual model and the experimental observations at Sidney Meadow and Merrifield (see Fig. 5.3). The maximum rainfall intensity was such that infiltration excess surface runoff occurred,

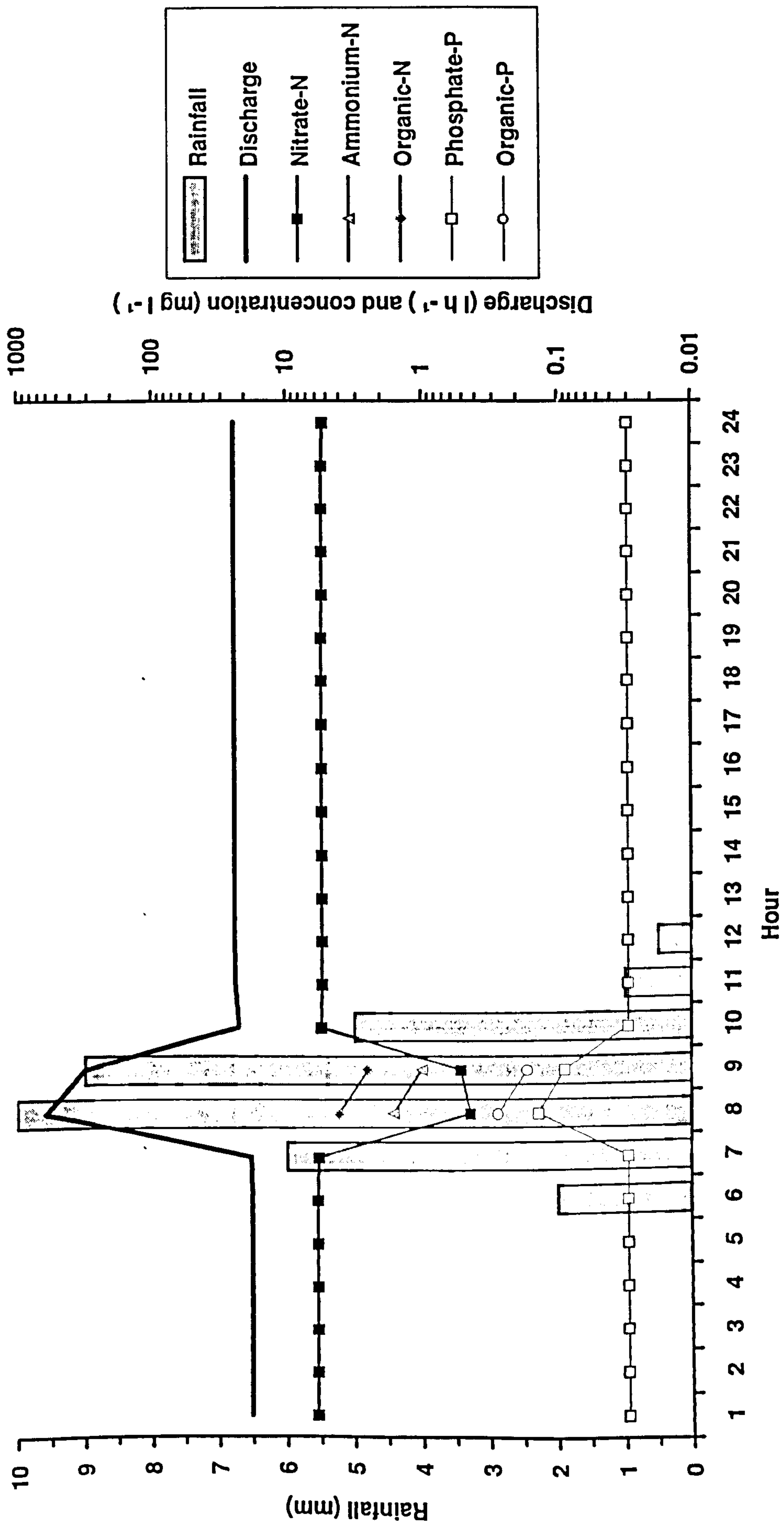


Fig. 5.3. An example of model output for a hypothetical storm event

leading to a rapid and high peaking of discharge. Although it is not easily visualised on the logarithmic scale used in Fig. 5.3, discharge following rainfall was some 30% higher than before the storm, and there was a slight increase after the main peak followed by a slow recession, this being a reflection of increased sub-surface throughflow following the storm event. Concentration of NO_3^- -N was reduced by 2 mg l^{-1} at peak discharge, due to the low concentration of NO_3^- -N in surface runoff from animal manures diluting NO_3^- -N in sub-surface throughflow. The opposite effect was observed for PO_4^- -P, because concentration of this ion is higher in surface runoff than in sub-surface throughflow, at least for mineral soils.

According to the philosophy of the model construction, the transport of NH_4^+ -N, organic-N, and organic-P only occurred when surface runoff was taking place. The dilution of these species and fractions from hours 8-9 was realistic, because during this time period the quantity of surface runoff was decreasing and sub-surface throughflow was increasing. This change in the pattern of discharge was also inferred from the increase in NO_3^- -N concentration and decrease in PO_4^- -P concentration.

Further tests were carried out to check the operation of other processes included in the model, for example, saturation excess surface runoff, percolation, evaporation, plant uptake, volatilisation, and denitrification. The general pattern of operation of all these processes was realistic in terms of the volumes of water flow and the quantities of N and P being transported.

5.5. Chapter summary

1. Modelling approaches can be placed into one of three categories as follows.

- 1) Input / output or 'black box' models
- 2) Functional or simplified mechanistic models
- 3) Process-based or fully mechanistic models

Theoretically, the flexibility and accuracy of modelling increases as one moves from category 1 to category 3, but in practice, models in category 3 are usually very complex, demanding of a large number of parameters, and hard to verify.

2. Models can be described as 'lumped' or 'distributed', depending on the extent to which they take into account spatial variability in a system. Lumped models treat a system as spatially homogeneous, distributed models use continuum equations to fully describe spatial variations in a system. In-between these two extremes come semi-distributed models, which divide a system into homogeneous sub-areas which are then treated as lumped units. There are two main advantages to using semi-distributed models.

1) Semi-distributed models maintain both the physical basis of model parameters and the spatial context of process operation.

2) Semi-distributed models are much more flexible than lumped models, but much less costly to operate than fully distributed models.

3. For the purposes of this study, a functional and semi-distributed approach to modelling was adopted. It was decided that a lumped model would lack the flexibility to describe the different water flow pathways, N and P transport and transformation, and the spatial variability inferred from experimental results. On the other hand, the limited understanding of N and P transport and transformation, particularly within the soil structure, the amount of data available for manure amended grasslands, and the computational power available all precluded the development of a process-based and fully distributed model at this stage.

4. The structure of the model comprises a series of cascading storage elements that represent the hillslope. The length, width, volume and slope angle of each store can be set independently, and the depth of each store can be derived from the other dimensions as and when required. Usually, the store dimensions are set to represent increasing soil depth as one progresses down the slope. A simple headwater catchment can be 'unfolded' to be represented by cascading stores of decreasing width. Following the setting of the initial parameters, the model operates on three nested loops. The outermost loop is a daily time step for the number of days specified in the simulation, the middle loop is an hourly time step which only runs on days when there is rainfall,

and the innermost loop calculates the inputs and outputs of water, N, and P for each store over whichever of the two time steps is in operation. The model calculates quantities of surface runoff and sub-surface throughflow in response to rainfall inputs, and the quantities of N species and P fractions transported along these pathways.

5. Preliminary testing of the model demonstrated that the simulation of the processes included was in general accordance with the conceptual model and experimental observations made at Sidney Meadow and Merrifield.

Chapter 6

Model Calibration, Testing, and Application

6.1. Model calibration

Having established that the mathematical model operated in a generally realistic manner in terms of the conceptual model and observations made in the field, it was then necessary to calibrate the model to simulate processes on the type of site used for the field experiments. In line with the functional approach, values for parameters were selected that were representative of values observed in the field, so that the mathematical structure of the model could easily be related to physical reality despite a lack of complete detail and accuracy. For example, consider the chosen values of the major hydrological parameters for a plot at Sidney Meadow (Table 6.1; refer to the glossary in Appendix 3 for definitions of variable names used in this table and elsewhere in this chapter).

Table 6.1. Typical hydrological parameters for a Sidney Meadow plot

Store no.	Length (m)	Width (m)	Depth (m)	Slope		Smin (m ³ m ⁻³)	Smax (m ³ m ⁻³)	Ksat (mm h ⁻¹)	ic0 (mm h ⁻¹)	icf (mm h ⁻¹)
				angle (°)						
1	10	5	0.35	15		0.30	0.50	40	30	6
2	10	5	0.50	15		0.30	0.50	40	30	6
3	10	5	0.70	10		0.30	0.50	40	30	6

For stores 1 and 2, the chosen store depth corresponded approximately to the depth of soil above the slate layer in zones 1 and 2 of the experimental plots respectively, and for store 3, the chosen depth was an estimate of the depth of profile contributing to flow into the throughflow pits at the bottom of zone 3, since in this case modelled

throughflow was compared with that observed in the throughflow pits (see Figs. 3.3 and 3.4 for locations of zones and throughflow pits if required). The values of slope angle and infiltration rates given were based on measurements made at the site in 1992. Minimum water content was selected as an approximation of the point where the rate of throughflow becomes insignificant, and maximum water content was based on measured values of soil saturation (see Table 3.5). It may be remembered that measurements of saturated hydraulic conductivity on soil cores extracted from Sidney Meadow varied quite widely (see Table 3.5 once more), perhaps indicating the presence of fissures within the soil structure and differing pathways of throughflow. For functional modelling purposes, the simplified approach of adopting one averaged rate of sub-surface throughflow was taken, and so one value of Ksat towards the centre of the observed range was chosen.

A similar overall approach was adopted when selecting values for the major chemical parameters (Table 6.2).

Table 6.2. Typical chemical parameters for a Sidney Meadow plot

	Surface	Surface	Surface	Surface	Surface	Surface	Surface	Sub-surf	Sub-surf
Store	N	P	NO ₃ ⁻ -N	NH ₄ ⁺ -N	org-N	PO ₄ ⁻ -P	org-P	NO ₃ ⁻ -N	PO ₄ ⁻ -P
no.	(kg ha ⁻¹)	(kg ha ⁻¹)	(mg l ⁻¹)	(mg l ⁻¹)	(mg l ⁻¹)	(mg l ⁻¹)	(mg l ⁻¹)	(mg l ⁻¹)	(mg l ⁻¹)
1	250	100	1	6	15	0.5	1	6	0.03
2	250	100	1	6	15	0.5	1	6	0.03
3	0	0	0	0	0	0.0	0	6	0.03

The quantities of total surface N and P depend on the treatment being applied, the values given in this case corresponding to a surface application of cattle manure in accordance with the *Code of Good Agricultural Practice*. The concentration values for N species and P fractions to be carried in surface flow were based on measurements from the storm simulation experiments at Sidney Meadow (see Chapter 3, section 3.4.5). Zero concentrations were assigned to store 3 in order for this store to act as a

buffer zone, but this could be changed easily if one wished to examine the implications of applying treatments right up to the stream bank.

Sub-surface NO_3^- -N and PO_4^- -P concentrations were based both on measurements at Sidney Meadow and observations from the Merrifield long term record. In this example, the NO_3^- -N concentration was chosen as representative of that occurring in late winter on this kind of site, an important period for manure spreading operations (see Chapter 1, section 1.5) and therefore the selected period of operation for the model. In every model simulation, the initial values for the immobile sub-surface N and P pools were set to zero. This was clearly not representative of reality, but the primary function of the model in this respect was to simulate increases in the amounts of sub-surface mobile N and P due to increased rates of conversion from the immobile pool. Therefore, zero was selected as a system background or datum value to which additions could be made in response to infiltration of N and P from the surface.

Other hydrological and chemical parameters, including rates of evapotranspiration, percolation to groundwater, ammonia volatilisation, N and P transformation in the soil, and plant uptake of N and P, could not be calibrated from data available from either Sidney Meadow or Merrifield. These processes become increasingly significant in terms of N and P transport as the duration of a modelling run increases, so for the purposes of this study modelling runs were restricted to periods of a few days, and estimates of the rates of the above processes were obtained from other sources. For example, after studying the figures quoted by Smith (1992) and Wild (1993), it was estimated that 25% of the N in a surface application of manure would be volatilised as ammonia over a period of 30 days, and rates of volatilisation were set accordingly (see Chapter 2, section 2.3). In the same way, it was estimated that over the same time period, 20% of the applied N would be taken up by plants and 5% would be denitrified. If in the future the model is required to operate over time periods of several weeks rather than days, it is important that other data sources be consulted and that these process parameters be calibrated more accurately.

6.2. Model testing

The model was not tested in the strictest sense in that a prediction is made and then observations are made in the field to ascertain the accuracy of the prediction. Nor was it tested against observations from other field sites. At this stage, testing was still quite closely linked to calibration in that the model parameters were set using the approach detailed in section 6.1, then rainfall figures recorded at both the Sidney Meadow and Merrifield sites were used to generate simulated water flows, and these simulations were compared with the recorded observations at both field sites. Thus, it could be argued that a process of 'hind'casting rather than forecasting was employed.

In addition to this, it was not possible to test the chemical output of the model, this being for two reasons. Firstly, the problems with low rainfall at Sidney Meadow meant that most of the data were involved in the initial calibration of the model. It was not possible to collect sufficient data for half to be used for process interpretation and model calibration, with the other half being retained for model testing. Besides this, the processes of surface runoff had to be simulated and therefore did not coincide with the records of throughflow. Secondly, there was no accurate record of the quantities of surface applications of N and P at Merrifield, particularly for periods of grazing.

Therefore, it is important to stress that the model is not being presented as fully tested, but equally important to stress that the objectives of this research programme, as detailed in Chapter 1, section 1.6, did not require the production of a fully tested model in order to be fulfilled. An integral part of the modelling process was to examine the concept of scale, in particular how the interpretation of processes made at the plot or field scale could be generalised and applied to the headwater catchment scale, and the extent to which spatial variations in the interaction between land-use and topography at the catchment scale could also be generalised without seriously limiting the ability to simulate or predict the flow of water and transport of N and P. The limited testing carried out has given much insight into the functional adequacy of the constructed model, the importance of considering scale, and how the model can be applied to

predict the effect of different manure application practices on N and P transport from grassed hillslopes.

6.2.1. Modelling throughflow at Sidney Meadow

Using the recorded hourly and daily rainfall totals, the model was used to simulate rates of throughflow into the collection pits for the period 14th March to 8th April 1992. Using TDR water content records, the initial water contents for the three stores were set at 0.38, 0.40, and 0.42 m³ m⁻³ respectively. Overall, the simulation of throughflow agreed well with observed levels, the simulated total for the period being 482 l compared to an observed total of 487 l (Fig. 6.1). However, the simulated pattern of throughflow was considerably smoother than the observed pattern. Given that the modelling of throughflow is based on a simplified description of matrix flow and that experimental evidence indicated the occurrence of preferential flow, this was not surprising. Indeed, this phenomenon has already been discussed at length in Chapter 3, section 3.4.3 in relation to estimating throughflow from soil water measurements. What is of particular importance is the implications in terms of the transport of N and P. For sub-surface throughflow, which is the only type of flow that occurred during the period in question, it is likely that over the whole period the simulated totals for N and P transport would have agreed well with observed totals, since the sub-surface concentrations of N and P used to calibrate the model were derived from experimental observations at Sidney Meadow and Merrifield. There may have been short term errors associated with dilution at times of high flow or accumulation and concentration at times of low flow, but these would have tended to cancel each other out.

More serious errors in simulating N and P transport could occur in cases where preferential flow leads to variable source areas of saturation and surface runoff, depending on how far up the slope the area of saturation extends. If saturation and surface runoff was restricted to a buffer zone for example, then it would not matter greatly if the model simulation counted this saturation excess surface runoff as sub-surface throughflow over a longer period, since the water in both cases would have

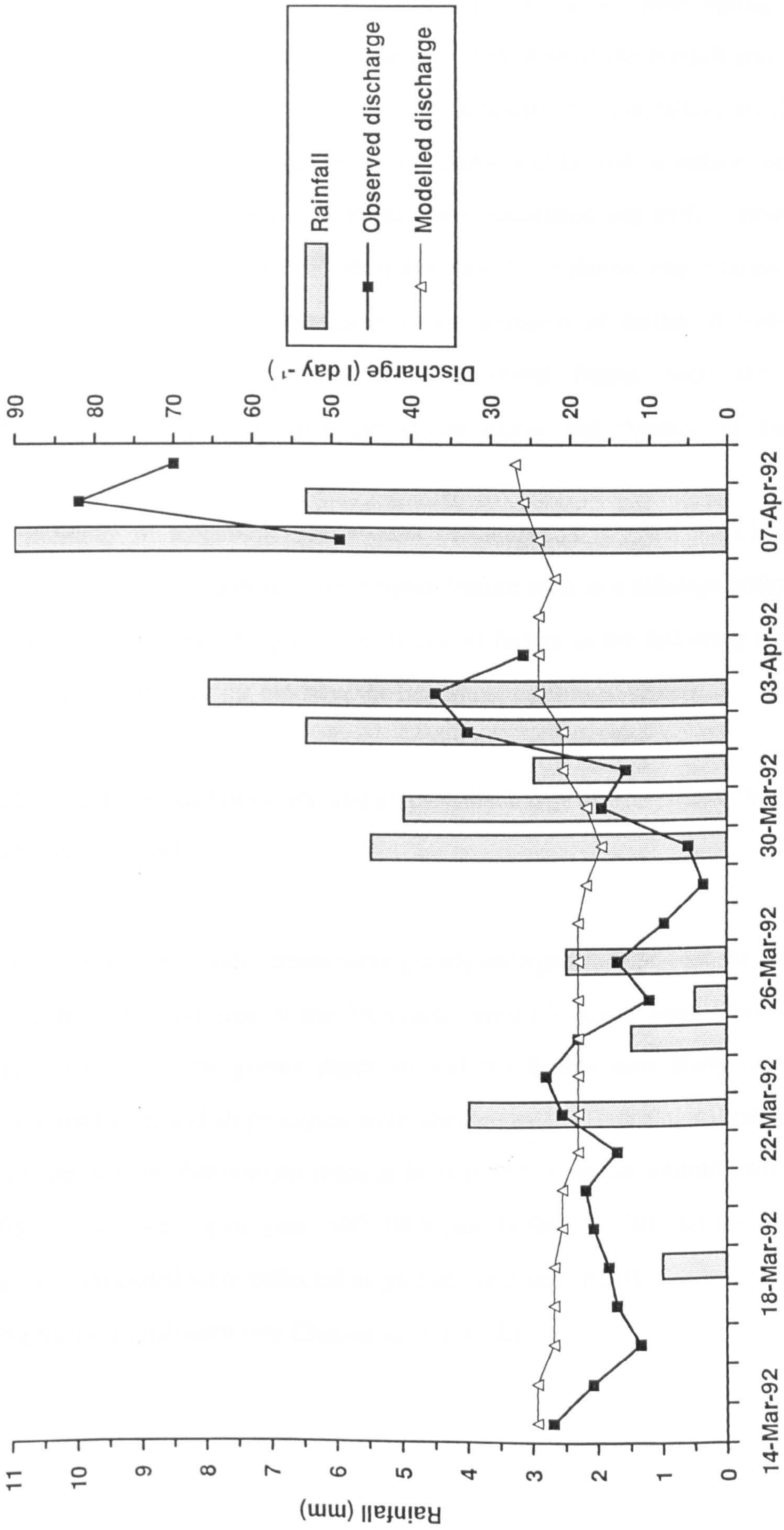


Fig. 6.1. Modelling of throughflow at Sidney Meadow

similar chemical characteristics. There would only be an error during the rainfall period, since the model would simulate the infiltration of the rainfall and transport of sub-surface NO_3^- -N and PO_4^- -P, where as in reality the rain falling on the saturated area would have mixed with the saturation excess and flowed as surface runoff without transporting sub-surface N and P. If, however, saturation and surface runoff occurred within any part of a treated zone, then any model simulation which failed to generate this surface runoff would underestimate the transport of surface derived N and P, particularly in organic, particulate and mineral forms, with the degree of underestimation depending upon the spatial extent and duration of the saturation occurrence.

The build up of a variable source area of saturation is often associated with the concentration of soil water in a topographic feature such as a hillslope hollow (see Burt and Arkell, 1986), and this process is discussed further in the following section, which describes the testing of the model at the headwater catchment scale.

6.2.2. Modelling rainfall events and stream discharge at Merrifield, November 1987 - March 1988

In this instance, the model stores were greatly enlarged to represent the 18 ha of land within the catchment area of the Merrifield stream V-notch weir. Store depths were increased to reflect the greater depths of soil profile that were likely to contribute to stream discharge, and slope angles were also increased. Hydrological parameters were set on the basis of observations made at Merrifield both in the autumn / winter of 1992-1993 and the hydrological year 1987-1988 (see Table 6.3). Data for the rainfall events that were simulated were collected as part of the 2-year NERC funded research project in the Slapton catchment (see Chapter 4, section 4.1).

Table 6.3. Hydrological parameters for modelling at Merrifield

Store no.	Length (m)	Width (m)	Depth (m)	Slope		Smin (m ³ m ⁻³)	Smax (m ³ m ⁻³)	Ksat (mm h ⁻¹)	ic0 (mm h ⁻¹)	icf (mm h ⁻¹)
				angle (°)						
1	140	700	2.0	15		0.30	0.50	40	30	8
2	140	550	2.5	20		0.30	0.50	40	30	8
3	10	450	3.0	20		0.30	0.50	40	30	8

(a) Intense storm event, 20th - 21st March 1988

Being the most intense of the recorded rainfall events at Merrifield, this storm was chosen as a starting point for modelling stream discharge in the catchment. No records of antecedent soil water content were available, so the initial store water contents were all set at 0.40 m³ m⁻³, this value being within the range of water contents observed at Sidney Meadow in March 1992 (see Fig. 3.14). Using the recorded hourly rainfall totals, the results of the model simulation in comparison to observed stream discharge can be seen in Fig. 6.2. The initial simulated discharge agreed very well with observed discharge, but the final simulated discharge was approximately half of that observed. After peak discharge, the recession in simulated discharge was much more rapid than that observed, the overall implication being that the model was storing water and releasing it more slowly after the storm than would seem to be the case in reality.

In this intense storm, the large peak discharge was simulated by means of widespread infiltration excess surface runoff and increased sub-surface throughflow, but from Fig. 6.2 it can be seen that peak discharge was underestimated by some 25%. Here, the implication is that in reality there was an additional contribution of smaller areas of saturation excess surface runoff and saturated throughflow to peak discharge, perhaps fed by preferential flow pathways. The model may have overestimated the spatial extent of infiltration excess surface runoff, but in reality, the same volume of water may have contributed to peak discharge by this pathway, with the source being several compacted

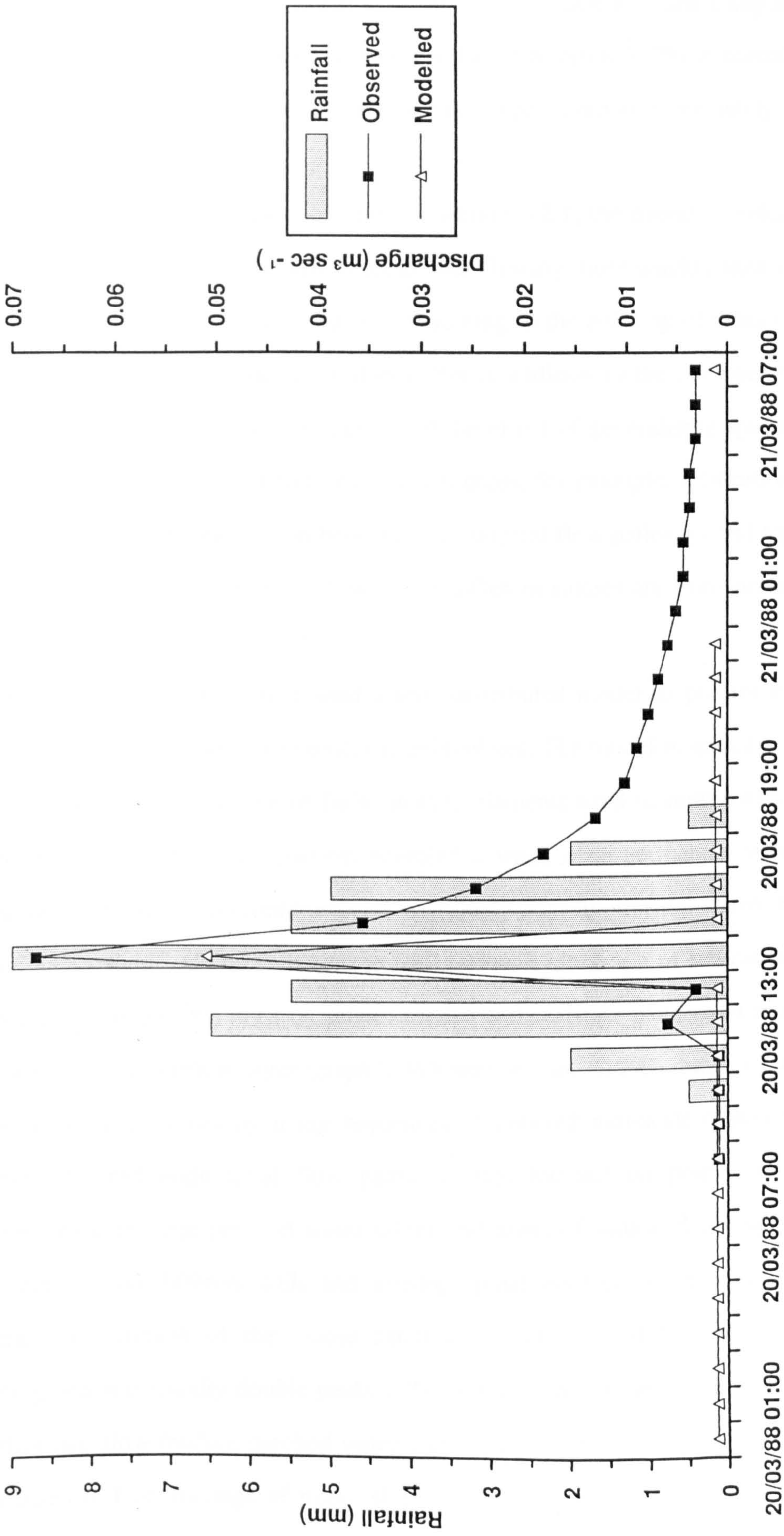


Fig. 6.2. Modelling of stream discharge at Merrifield, March 1988 storm (uniform soil water content)

partial areas where final infiltration capacity was $1\text{-}3\text{ mm h}^{-1}$ (see Chapter 4, section 4.3.1), compared to the generalised model value of 8 mm h^{-1} . These partial areas may also have accounted for the small peak in discharge recorded immediately prior to the main peak.

As with the Sidney Meadow simulation in section 6.2.1, the overall implication is that some of the water within the soil structure was flowing more quickly than indicated by the model simulation, with that water contributing to the build up of areas of saturation towards the base of the catchment slopes. But in addition to the interpretation of flow pathways and rates, there is the question of the effect of generalising spatial variations in the contribution of water from different sources, for example, infiltration excess. In order to illustrate the interaction between hydrological flow pathways and topography at the catchment scale, the results of two quite different studies are summarised briefly as follows.

Quinn and Beven (1993) have used a semi-distributed model to predict soil moisture dynamics in the Plynlimon catchment in mid-Wales. The model is spatially sensitive on account of the large number of finite storage elements used to represent a catchment. Prediction of soil moisture patterns revealed a small semi-permanent variable source area of saturation that could expand extremely rapidly during storm events, thus providing a significant contribution to the outflow hydrograph of the catchment. They concluded that "models must be able to predict soil moisture patterns in time and space as well as the outflow hydrograph". Wheater *et. al.* (1993) have examined flow processes on hillslopes by using sequences of detailed plot-scale observations. They identified rapid preferential flow pathways that focused on points of topographic convergence to form perched water tables and areas of saturated throughflow. These observations on different soils and hillslope positions were eventually linked to the outflow hydrograph of the whole catchment. During rainfall events, this outflow hydrograph was usually double peaked. The initial hydrograph 'spike' was attributed to preferential flow feeding perched water tables, and the delayed hydrograph 'hump' was attributed to free drainage of upper slope alpine podzols to depth, which was in turn

contributing to the slow drainage of a C horizon water table further downslope and below the perched water tables.

Within the limits of spatial sensitivity set by the three store configuration of the model, it was decided to attempt a representation of saturation excess surface runoff by increasing the water content of stores 1 and 2 to $0.45 \text{ m}^3 \text{ m}^{-3}$ and setting the water content of store 3 to the maximum value of $0.50 \text{ m}^3 \text{ m}^{-3}$. The resulting simulation of stream discharge was of some interest (see Fig. 6.3). Simulated peak discharge was much closer to the observed value, the recession in simulated discharge following the peak was much less abrupt, and the final simulated discharge was in good agreement with the observed discharge. The simulated discharge also included a small increase prior to the main peak, although it was not exactly of the same nature as the small peak observed.

The only penalty came in the overestimation of initial stream discharge. Again, this was an indication of the tendency of the model structure to store water over longer periods than would occur in reality, such that the increase in store water contents required to generate a saturation excess also led to an increase in sub-surface throughflow over the longer term. This would seem to be an inevitable error when the only means of simulating sub-surface throughflow is as a function of a matrix flow process. The questions to be considered are therefore:

- 1) the extent to which the magnitude and significance of such an error can be reduced by refining the existing model structure without abandoning the functional and semi-distributed approach in favour of something more complex, and
- 2) whether the purposes for which the model is to be used demand the reduction of such an error in the first place.

These questions will be considered during the remainder of this chapter, and particularly in the last two sections.

The implications for N and P transport arising from the modelling of this storm event are largely the same as those discussed for Sidney Meadow in section 6.2.1 above. In the latter simulation of this storm, the model was set to generate saturation excess surface runoff in a uniform manner over the whole of the bottom 10 m of the catchment

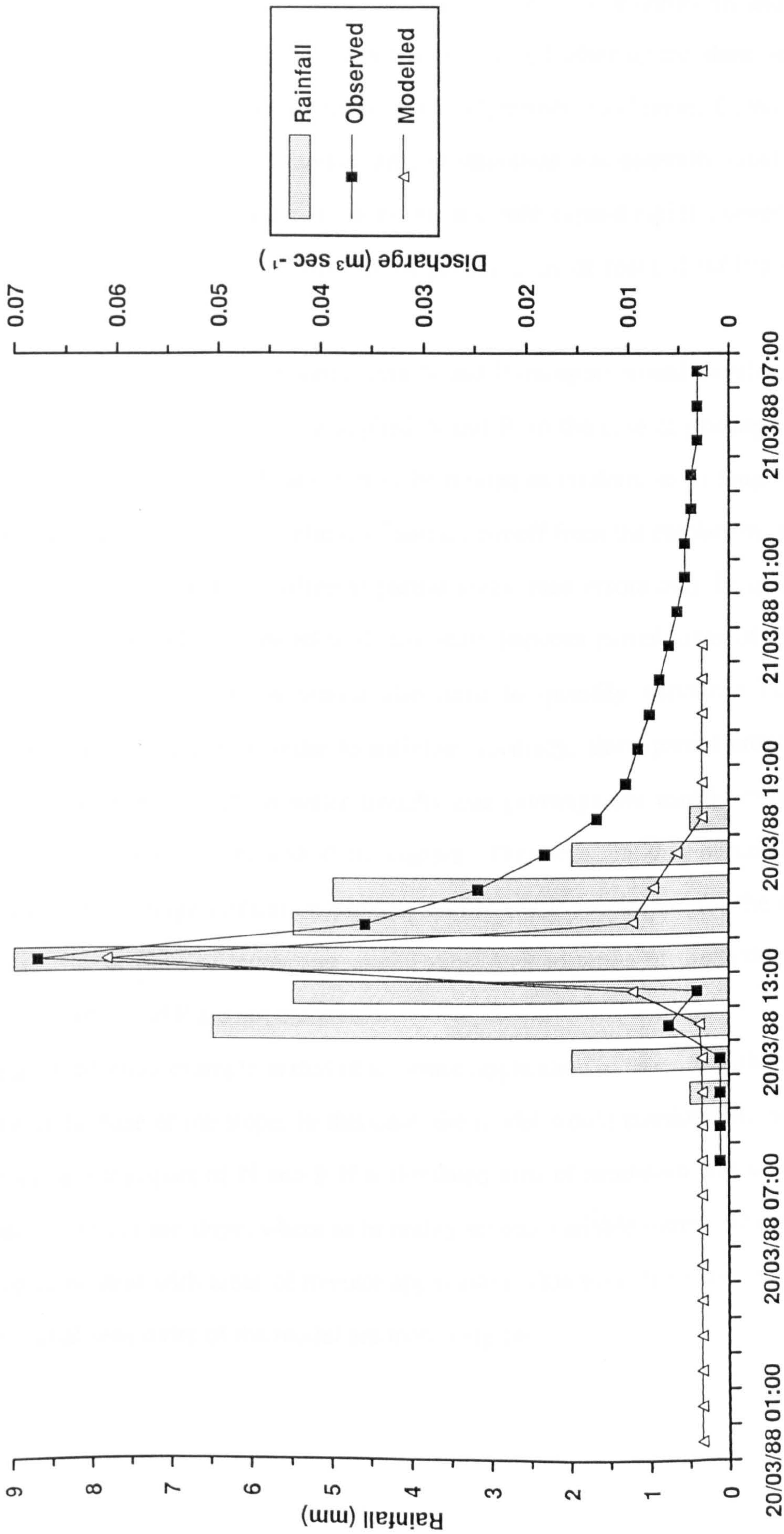


Fig. 6.3. Modelling of stream discharge at Merrifield, March 1988 storm (bottom 10 m of slope saturated)

slopes. In reality, the areas of saturation may have been more numerous and discrete, in effect covering less of the slope width but extending further up the slope length. When modelling soil moisture distributions in the Plynlimon catchment, Quinn and Beven (1993) noted that the variable source area of saturation was generally small and limited to the riparian area, but during storm events it would expand rapidly, covering more of the catchment slope. The contribution of partial areas of reduced infiltration capacity has to be considered also.

The accuracy of the model in simulating N and P transport would therefore depend on the spatial distribution of surface applied N and P. In the case of grazing for example, the distribution of surface N and P may be treated as random, so as long as the model simulates the correct overall volume of surface runoff from the catchment, regardless of varying contributions from different partial areas, then errors may be quite small. If, however, the model was altered to differentiate between partial areas of high and low infiltration capacity, then it would also have to quantify variations in the spatial distribution in N and P in order to maintain accuracy, since partial areas of reduced infiltration capacity such as water troughs and gateways are usually coincident with higher applications of N and P in manure. Therefore, in this particular example, provided the average infiltration capacity and N and P application for the catchment is known, the benefits of increasing spatial sensitivity in terms of predicting the surface transport of N and P are not automatic.

A rather different example is that of a surface application of manure with a 10 m buffer zone at the base of the slope. In this case, the model would considerably underestimate the surface transport of N and P if a simulated area of saturation was confined to the bottom 10 m of the slope, where as in reality several variable source areas of saturation were coincident with areas of manure application. This time, the benefits of increasing the spatial sensitivity of the model are more tangible.

(b) Rainfall event, 1st - 8th February 1988

In this instance, a series of less intense rainfall events occurring over the period of a week was chosen for modelling. Initial water contents were set at $0.47 \text{ m}^3 \text{ m}^{-3}$ for stores 1 and 2, and $0.50 \text{ m}^3 \text{ m}^{-3}$ for store 3. These water contents were chosen as a reflection of the higher soil water contents likely to occur in early February as compared with late March. The recorded hourly rainfall totals for the entire week were lumped together on a compressed x-axis, together with observed and simulated levels of stream discharge (Fig. 6.4). Clearly, the model was significantly underestimating levels of stream discharge for this period, by as much as a factor of four at certain times. It is unlikely that even setting all initial store water contents at their maximum value would have simulated the levels of discharge observed, and besides, it is most unlikely that the entire area of the catchment was saturated.

Given that all other parameters except initial water content were the same as for the March storm, the marked underestimation of discharge in this case is not easily explained. The V-notch weir on the stream was cleaned out and checked in mid-January 1988, so it is unlikely that errors were made in recording stage height. It is true, however, that the observed pattern of discharge was quite unusual. There appears to have been a brief response to the most intense rainfall of 7 mm h^{-1} , but after this stream discharge was seen to steadily decrease despite rainfall continuing throughout the week, such that discharge at the end of the week was lower than at the start. Whether the relatively small changes in the level of discharge were within the bounds of observational error is not certain, for example, there were rather abrupt but small changes in the height of the chart recording line which indicate that the mechanism may have been sticking at times.

Whatever the flow pathway, there was almost certainly some other contribution to stream discharge during this period that was not present in March. It is possible that there was an additional contribution from upwelling ground water occurring over a longer time period than was considered here, this water being channelled in large fissures to form intermittently flowing springs. Leaving aside the short-term

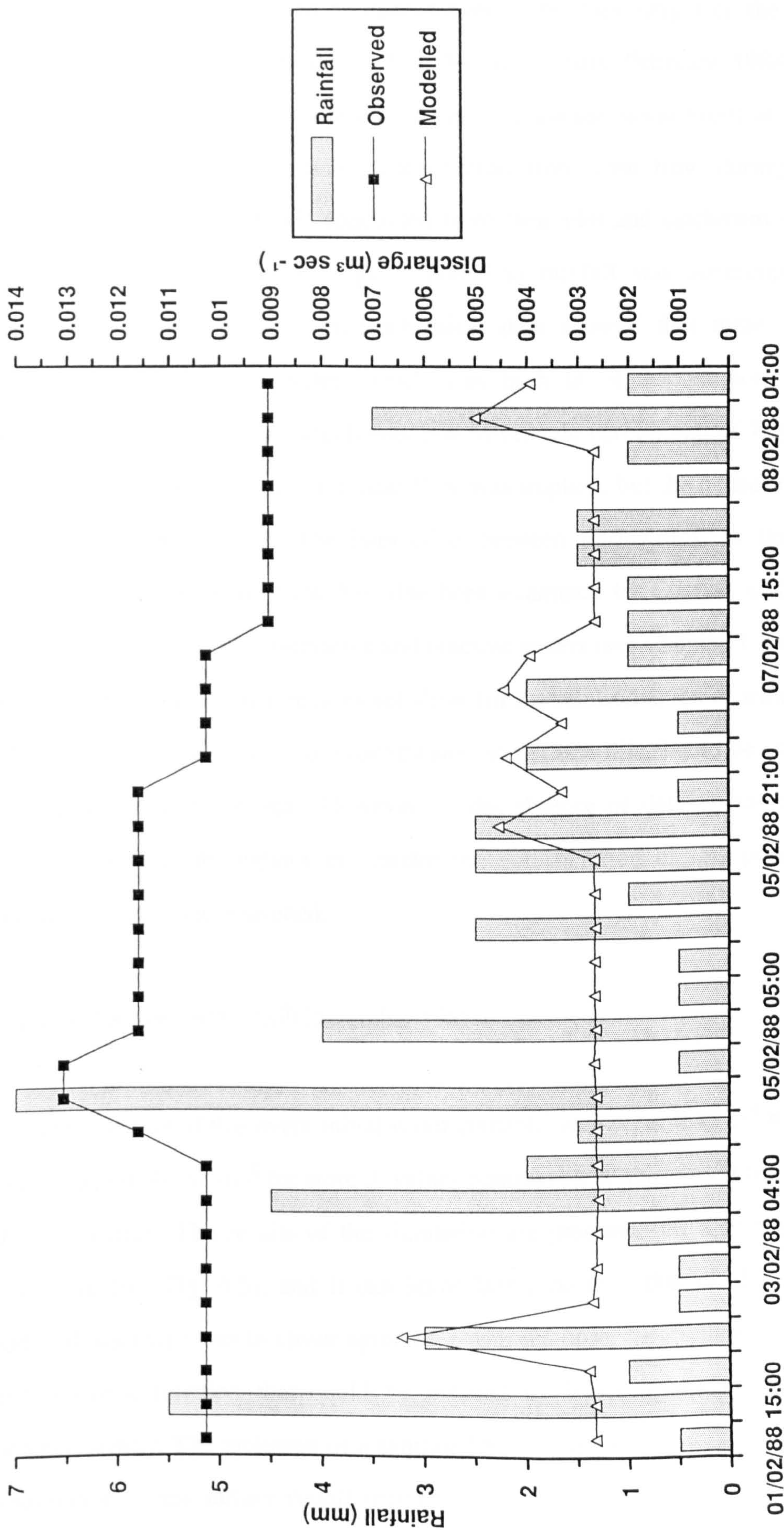


Fig. 6.4. Modelling of stream discharge at Merrifield, February 1988

fluctuations in discharge caused by rainfall events, the stage height on the stream weir rose from 3 cm in mid-October 1987 to 14 cm in early February 1988, but it had receded to 10 cm even immediately following the intense storm event of 21st March. This would indicate an increasing contribution from base flow during the winter months. Wheater *et. al.* (1993) concluded from their plot and catchment scale studies that the double peaked hydrograph response to rainfall was superimposed on an underlying baseflow process. Hydrochemical data showed that there was a clear distinction between event water, which was high in organic carbon and of low alkalinity, and the baseflow, which was low in organic carbon and of high alkalinity. Therefore, a distinct flow path for base flow was implied, but the hydrological origins of this flow were obscure. The interaction between throughflow in the upper soil horizons and groundwater flow has also been examined by O'Brien and Hendershot (1993), using a range of conservative and reactive tracers (see Chapter 3, section 3.4.3). At present, the model structure does not allow for the reintroduction of water that is lost from the stores as percolation to groundwater, so perhaps this should be considered for the wettest times of the year. However, in the absence of data on the depth of the groundwater table throughout the catchment, consideration of this process remains speculative rather than reasoned.

(c) Rainfall event, 15th - 18th December 1987

For the modelling of this event initial water contents were set at $0.45 \text{ m}^3 \text{ m}^{-3}$ for stores 1 and 2, and $0.50 \text{ m}^3 \text{ m}^{-3}$ for store 3, values comparable to those used for the February 1988 simulation. The results of the simulation are presented on a compressed x-axis once more (see Fig. 6.5), and it can immediately be seen that on this occasion the modelled discharge was in closer agreement with the observed discharge, there being a general over-estimation that could be reduced by lowering the initial store water contents slightly. The inclusion of a saturated bottom store to generate peaks attributed to saturation excess surface runoff seemed to work quite well once more, although the timing of the simulated peaks was slightly ahead of the observed peaks. Initial and final

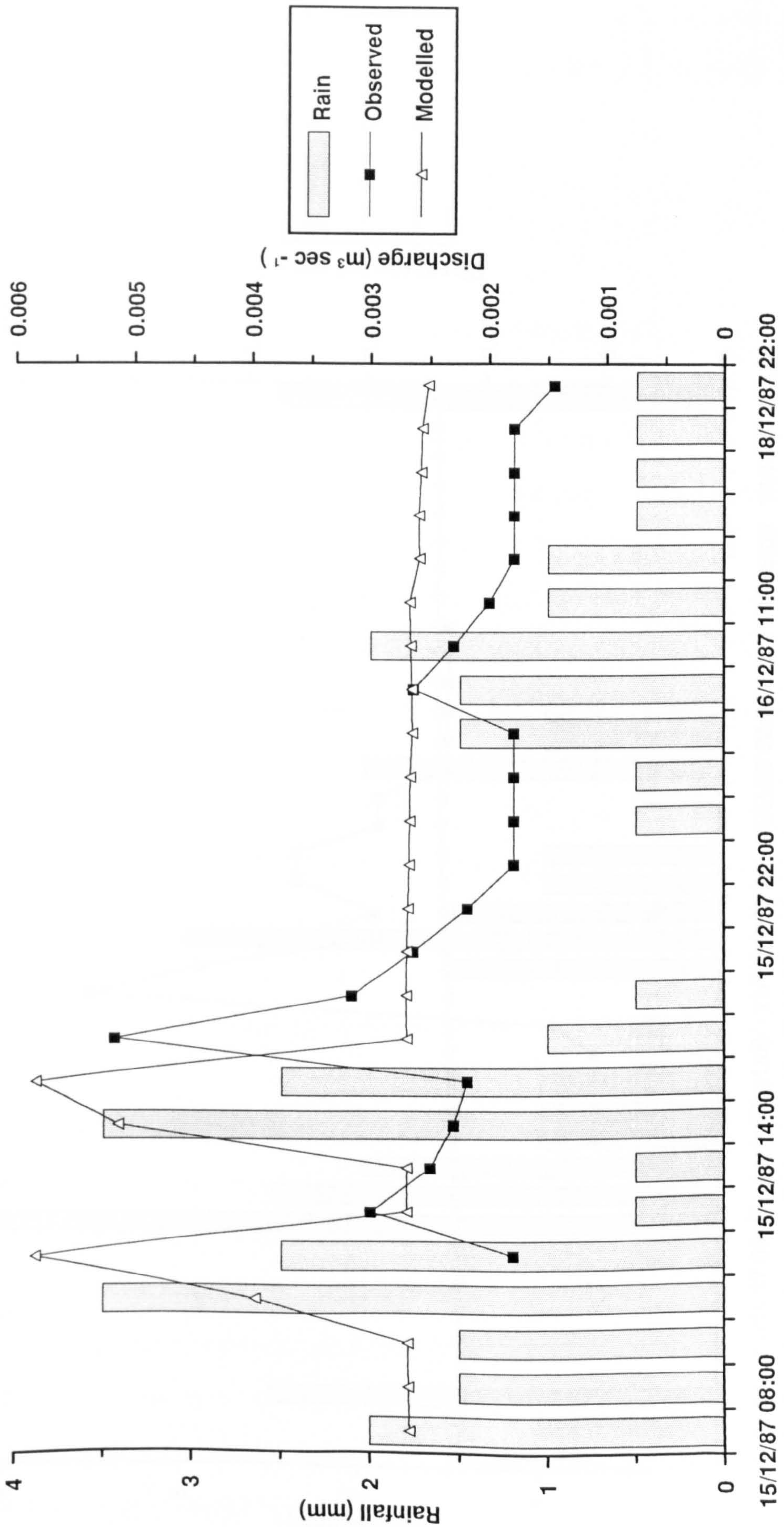
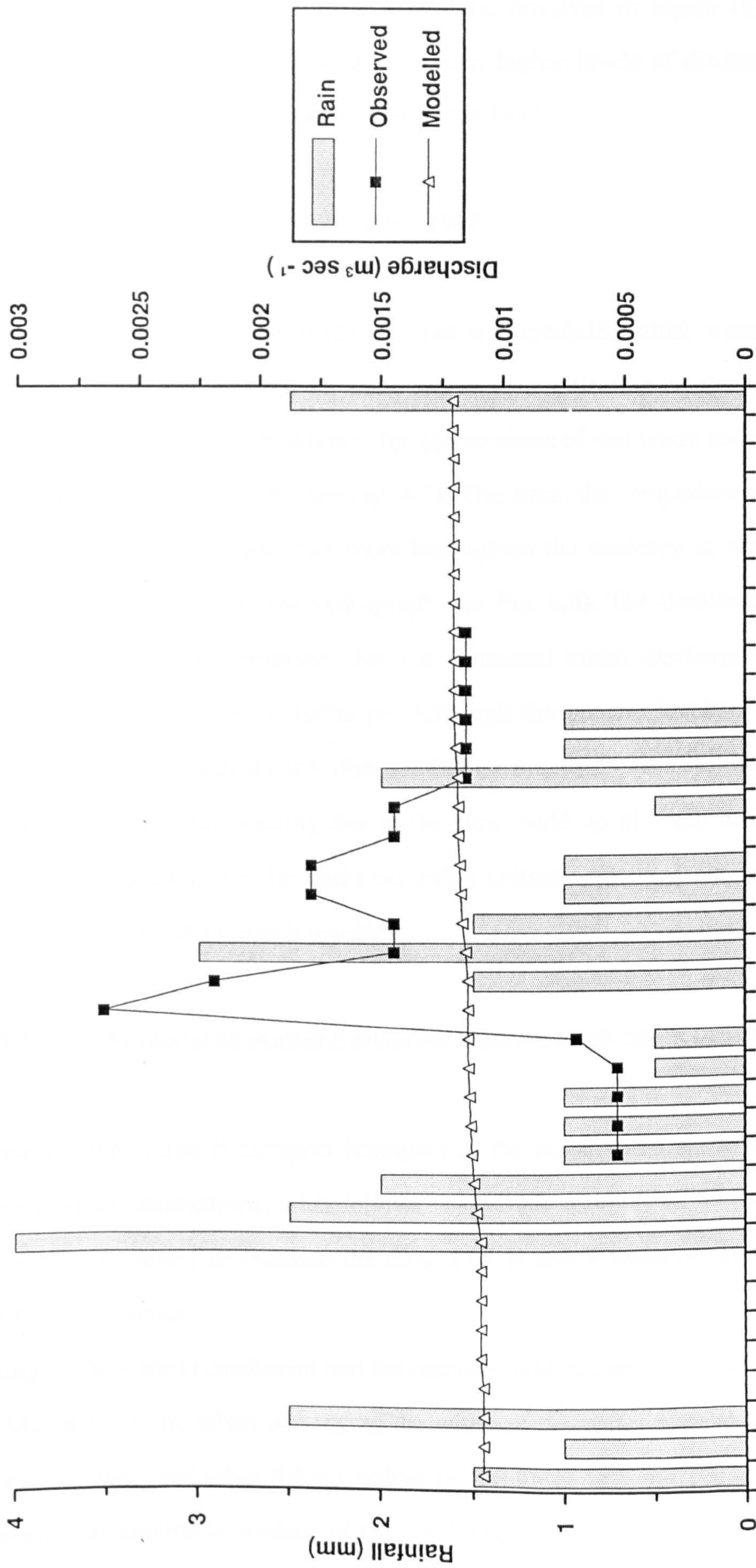


Fig. 6.5. Modelling of stream discharge at Merrifield, December 1987



10/11/87 23:00 11/11/87 05:00 11/11/87 11:00 11/11/87 17:00 11/11/87 23:00 12/11/87 05:00 12/11/87 11:00

Fig. 6.6. Modelling of stream discharge at Merrifield, November 1987

levels of discharge were comparable with those observed in March 1988, so whatever the process was that contributed to the much higher levels of discharge in February 1988, it was clearly not operating in December 1987.

(d) Rainfall event, 10th - 12th November 1987

For this final simulation of rainfall events at Merrifield, initial water contents were reduced to $0.40 \text{ m}^3 \text{ m}^{-3}$ for all three stores as a reflection of the lower soil water content that is likely in mid-autumn (for observations of soil water content at Merrifield in autumn / winter 1992-1993 see Fig. 4.7). This time, the comparison of simulated and observed stream discharges once more highlighted the tendency of the model to store water and smooth the outflow hydrograph (see Fig. 6.6). The simulated final discharge agreed well with that observed, but the simulated initial discharge was more than double the observed initial discharge. Although the general levels of discharge were considerably lower than for the other rainfall events, there were still notable short term fluctuations. This was possibly due to the slow build up of small areas of saturation, which would account for the peaks occurring neither coincident nor immediately after the highest recorded rainfall intensities.

6.3. Using the model to examine different manure application practices

Although the N and P transport functions of the model have yet to be tested against experimental observations, what follows is a simple example of how the model might be applied in future to examine the effects on N and P transport of different manure application practices.

Using the Merrifield catchment and the recorded hourly rainfall intensities for the storm in March 1988, the effect of varying the width of the buffer zone at the bottom of the slope was examined when the equivalent of 250 kg N ha^{-1} and 100 kg P ha^{-1} in cattle manure was applied to surface of the catchment slopes. N and P transport parameters were set using the approach described in section 6.1 and as listed in Table 6.2 in

particular. Buffer zone widths of 0, 2, 5, 10, 20, 30, and 50 m were simulated, and in each case the initial water content was set at $0.45 \text{ m}^3 \text{ m}^{-3}$ for all three stores. For an intense storm such as this, the most significant transport of N and P occurred at the time of peak discharge in response to the occurrence of surface runoff. Fig. 6.7 shows the model simulation of total N and P loading to the stream, in both surface and sub-surface water at the time of peak discharge, and for the different widths of buffer zone considered.

Not surprisingly, an increase in the width of the buffer zone led to a decrease in the loading of N and P to the stream. The main point of interest was the nature of the curves that were generated in these model simulations, in that there was no clear cut off point where loads were considerably reduced in response to a slight increase in buffer width. Here, the modelling of surface transport was based on N and P carried in water and largely in solution. The reduction of N and P load was thus proportional to the amount of clean rainwater falling on the buffer zone that was able to dilute surface runoff from the treated parts of the slope, hence the wider the buffer the greater the dilution, resulting in the form of curves observed in Fig. 6.7.

Presumably, a primary reason for specifying a minimum 10 m buffer in the *Code of Good Agricultural Practice* (MAFF and WOAD, 1991) is to ensure that particulate matter from manure or slurry does not fall directly into a water course. Given the quantities of N and P associated with such particulate matter this is perfectly sensible. However, the samples of surface runoff collected during the storm simulations at Sidney Meadow were found to contain very little particulate matter because the good condition of the grass sward largely prevented the transport of particulate matter (see Chapter 3, section 3.4.5). Relatively high concentrations of N species and P fractions were still recorded, so the presumption was that much of this N and P was carried in solution, and that was the basis on which the model functions were derived.

It is right to question the absolute accuracy of observations from a few small-scale simulations, but the concept of surface derived N and P in solution remains as discussed in Chapter 3, section 3.4.5, namely that if a buffer zone is required to significantly dilute concentrations of N and P in surface runoff as well as sub-surface throughflow

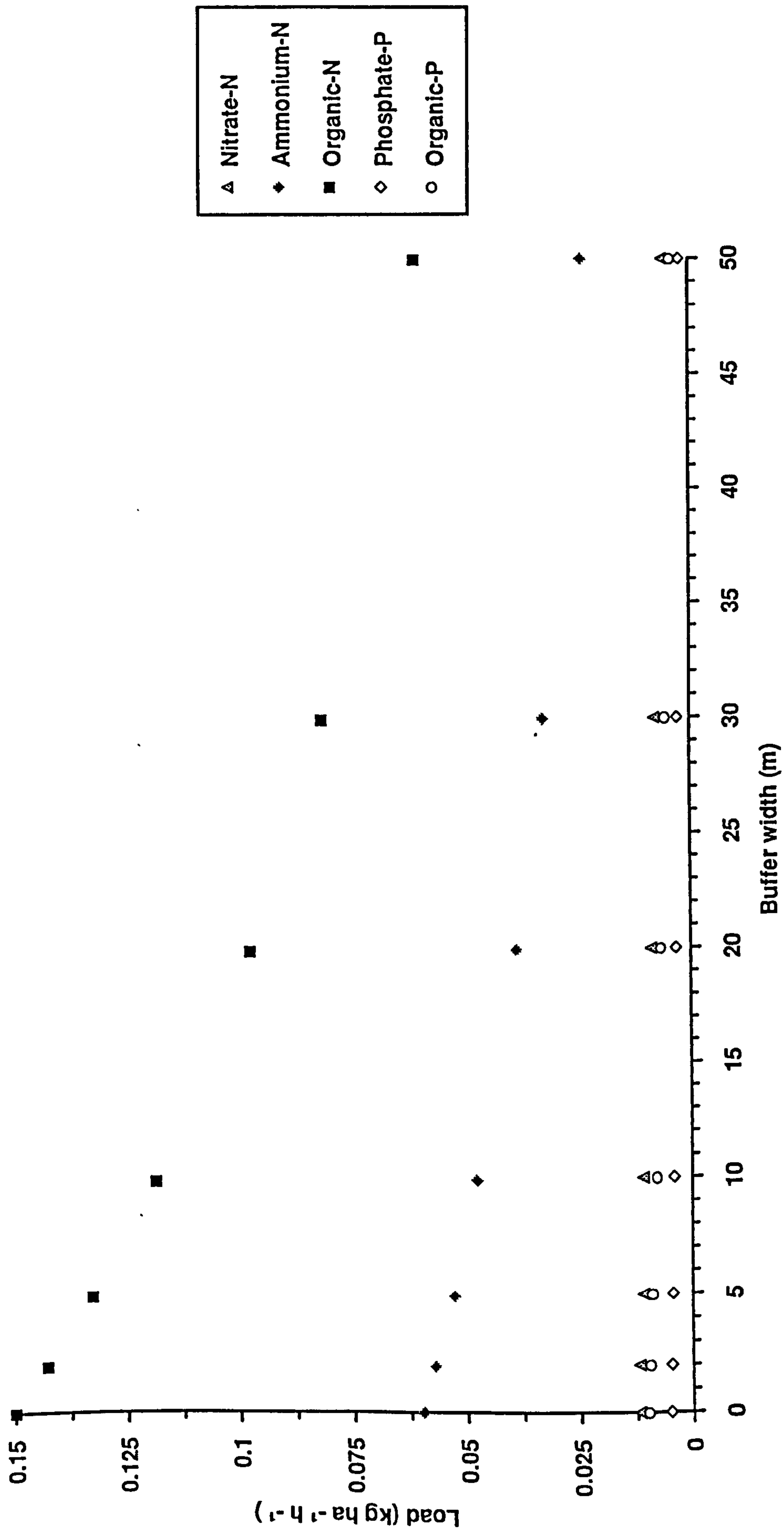


Fig. 6.7. Modelling of peak N and P loads in surface runoff and throughflow combined

then the area of that buffer should be related to the area of treated land above it, and not necessarily set at some arbitrary value. At Sidney Meadow a 10 m buffer was extremely effective, but the length of treated zone above it was only 20 m. At Merrifield the slope length approaches 300 m in places. Therefore, if an application of manure or slurry was made at Merrifield, a 10 m buffer might fail to significantly reduce transport of N and P during intense storm events when widespread infiltration excess or saturation excess surface runoff takes place.

The above argument would clearly need to be substantiated by adequate testing of the model functions and further observations in the field, but nevertheless it serves as an example of how the model can be applied to ask questions about the effects of different manure application practices, thus focusing on areas that warrant further experimental investigation.

6.4. Chapter summary

1. A limited amount of testing has demonstrated that in general the model is able to simulate water flow processes on hillslopes with some degree of accuracy, both at the plot and headwater catchment scales. The N and P transport functions within the model remain to be tested against experimental observations. Further testing is then required to establish the ease with which the model can be made to operate on differing soil types. In the longer term it is important that the model is tested against criteria that enable its usefulness to be compared with other models (Addiscott and Wagenet, 1985)
2. The model function for sub-surface throughflow is such that it tends to produce smoother patterns of discharge than are observed experimentally. The implication is that the adoption of a simplified form of Darcian matrix flow leads to longer storage and slower release of water than occurs in reality. This can lead to an underestimation of flow at times of high rainfall, probably because the model is failing to simulate a process of preferential flow that leads to the occurrence of variable source areas of

saturation. These areas of saturation contribute to increased flow both by means of increased sub-surface throughflow and saturation excess surface runoff.

The implication of such short term errors in terms of N and P transport would depend on the spatial distribution of N and P on the surface. In the case of grazing for example, the distribution of surface N and P may be random, so as long as the model simulates the correct overall volume of surface runoff then errors may be quite small. However, in the case of a surface application of manure with a 10 m buffer zone, the model would considerably underestimate the surface transport of N and P if a simulated area of saturation was confined to the bottom 10 m of the slope, where as in reality several variable source areas of saturation were coincident with areas of manure application.

The occurrence of the above mentioned errors raises questions about the adequacy of the functions the model uses to describe flow processes, the spatial sensitivity of the model, and the extent to which these errors can be minimised without sacrificing a functional and semi-distributed approach. The problem of modelling sub-surface flow more accurately may be alleviated by the inclusion of a function that immediately transfers a proportion of water infiltrating a store to the next store downslope, thus crudely modelling a preferential flow process. Such a function may only be allowed to operate above a certain threshold store water content, so that preferential flow is not modelled during drier periods. The difficulties of modelling preferential flow are highlighted by Di Pietro and Lafolie (1991), who employed a complex but what could be described as functional kinematic wave approach to model macropore flow in an artificially created double porosity soil column. At high water input intensities the model performed satisfactorily, but at low intensities it proved difficult to model the diffusion of the preferential flow into soil micropores. Therefore, the problem in functional terms is to define the soil water content at which preferential flow is not attenuated by diffusion into micropores, and consequently is able to contribute to rapid increases in sub-surface throughflow and areas of saturation.

The spatial sensitivity of the model could be improved simply by using more stores. This would increase the complexity of the model and the data required to calibrate and test it, but it would also enhance the modelling process. For example, topographical

features such as hillslope hollows could be incorporated, which would facilitate the modelling of water convergence in hollows and the build up of variable source areas of saturation. This in turn would increase the accuracy with which the transport of N and P is modelled, particularly via surface pathways.

3. It has been demonstrated that the model can be used to examine the effects on N and P transport of different manure application practices, varying widths of buffer zone being considered in this particular instance. Examples of other subjects worthy of consideration might be, the effect of variations in the rate of treatment application, and a comparison between short periods of intense rainfall and longer periods of more diffuse rainfall.

4. Despite certain limits in process interpretation and spatial sensitivity, it would appear that the model can be used to ask questions about the effects of different manure application practices, enabling a focus on areas that warrant further experimental investigation. It would also appear possible to improve the performance and accuracy of the model without abandoning the functional and semi-distributed approach, thus increasing the potential range of applications to which the model may be suited.

Of equal importance is the fact that the development of the model has facilitated consideration of the interaction between land-use and topography at the headwater catchment scale, and how this affects spatial and temporal patterns in the transport of N and P from grassed hillslopes. The effect of generalising processes interpreted at the plot scale has been examined, and particular instances where generalisation might lead to significant reduction in the accuracy with which N and P transport is modelled at the headwater catchment scale have been identified.

Chapter 7

Conclusions

The first section of this chapter forms an analysis of the extent to which the aim and objectives of the research, as stated in Chapter 1, were fulfilled. The second section examines appropriate ways of developing the research in light of the criticisms levelled in the first section, which then leads on to a summary of the overall contribution the research has made in the final section of the chapter.

7.1. Fulfilment of the research aim and objectives

The general aim of the research was stated in Chapter 1, section 1.6, as follows.

Aim: To further the understanding of the pathways and processes involved in the transport of N and P following applications of cattle manure to sloping grassland.

The way in which such a general aim was achieved, and the extent to which it was achieved, was determined by the degree of fulfilment of the specific objectives stated in Chapter 1, section 1.6. Rather than list each of these objectives in isolation and discuss how well each was fulfilled, it was decided that it would be more useful to pose a series of questions that link different objectives together, thus facilitating a more coherent and structured criticism of the research as a whole. The series of questions posed is listed below, each question being followed by a discussion.

(1) Did any observations made during field experiments lead to a questioning of any of the ideas contained in the conceptual model as summarised in Chapter 2, section 2.5 ?

Bearing in mind the limitations of the experimental work, which are discussed mainly in answer to the next question, the answer to this question is largely no.

During the plot experiments at Sidney Meadow, the hydrological pathways observed were lateral sub-surface throughflow and infiltration excess surface runoff, the widespread occurrence of the latter only being in response to simulated rainfall of high intensity.

Sub-surface throughflow was almost completely associated with NO_3^- -N, with concentrations generally being in the range of 3-6 mg l^{-1} , which is well below the EC Directive limit of 11.3 mg l^{-1} for drinking water supply. Concentrations of NH_4^+ -N and organic-N in throughflow were always less than half the UK Maximum Admissible Concentrations of 0.5 mg l^{-1} and 1 mg l^{-1} (Kjeldahl-N) respectively, while PO_4^- -P concentrations were always below the autoanalyser's detectable limit of 0.1 mg l^{-1} . Under the conditions and for the duration of this experiment at least, it would seem that treatment derived NH_4^+ -N, organic-N and PO_4^- -P were largely immobilised in the soil structure, while any increase in the rate of mineralisation and nitrification leading to NO_3^- -N production was more than offset by the processes of plant uptake and perhaps denitrification, thus rendering differences between treatments and control insignificant. There was evidence of preferential flow acting as part of the throughflow process, but this did not lead to the transport of significant quantities of surface derived NH_4^+ -N and PO_4^- -P as suggested in the conceptual model. However, given the weakly structured nature of the soil, it is unlikely that large enough fissures would have existed to allow the transport of NH_4^+ -N and PO_4^- -P without them being largely immobilised before emerging at the base of the slope.

For surface runoff, concentrations of N and P from treated plots were significantly higher than those from the control. N was largely present as NH_4^+ -N and organic-N for the slurry and manure, with mean concentrations in the order of 5 mg l^{-1} and 15 mg l^{-1} respectively. For the inorganic fertiliser, concentrations approaching 20 mg l^{-1} were observed for both NO_3^- -N and NH_4^+ -N. PO_4^- -P concentrations from both the manure and slurry were 0.5 mg l^{-1} , but more organic-P was present within runoff from manure than slurry, the concentrations being 1 mg l^{-1} and 0.3 mg l^{-1} respectively. This may have been due to the greater quantity of organic matter in the manure as compared with the slurry. Concentrations of PO_4^- -P and organic-P from inorganic fertiliser were

10 mg l⁻¹ and 5 mg l⁻¹ respectively. As with N, these concentrations were significantly higher than those from manure and slurry, but this was probably an indication of the higher solubility of N and P in the inorganic fertiliser in the short-term immediately following application, which is when observations were made.

The 10 m buffer zone was most effective in reducing the transport of N and P in surface runoff from the treatments, such that differences between the treatments and the control became insignificant. Average concentrations for NO₃⁻-N, NH₄⁺-N and organic-N were approximately 1 mg l⁻¹, 0.5 mg l⁻¹ and 1.5 mg l⁻¹ respectively, while those for PO₄⁻-P and organic-P were 0.2 mg l⁻¹ and 0.3 mg l⁻¹. However, it was noted that N and P loads in surface runoff were low, that most N and P was dissolved, and that the buffer zone was half as long as the treated zones. Since the 10 m buffer zone as stipulated in *The Code of Good Agricultural Practice* has a fixed dilution and infiltration capacity, the implication is that in a field situation where the treated area is that much greater in relation to the buffer area, the buffer may not be as effective as it was at Sidney Meadow.

The observations made at Merrifield did not contradict any of those made at Sidney Meadow. Sub-surface throughflow was associated with similar concentrations of NO₃⁻-N (3-8 mg l⁻¹) and very low concentrations of PO₄⁻-P (0.03-0.1 mg l⁻¹). These concentrations appeared to vary more in relation to seasonal changes in the level of discharge from the catchment than to changes in land-use, which implied that N and P in sub-surface throughflow was transport rather than supply limited. This is in broad agreement with observations made at Sidney Meadow and for a combination of land-uses in the nearby Slapton Wood catchment (see Trudgill *et. al.*, 1991).

While surface treatments at Merrifield were not the same as those at Sidney Meadow, fluctuations in the concentrations of NH₄⁺-N and PO₄⁻-P only occurred in response to what was probably the short-term occurrence of surface runoff from partial source areas of reduced infiltration or variable source areas of saturation. These short-term fluctuations in NH₄⁺-N and PO₄⁻-P during rainfall events implied variations in topography and the distribution of surface derived N and P at the catchment scale.

(2) How thoroughly were the ideas of the conceptual model examined by the field experiments ?

It was inevitable that the whole research approach, with a progression from concepts to a mathematical model operating at the headwater catchment scale, would lead to limitations on the detail and replication of the field experimental work. These limitations are considered both in answer to this question, and in answer to the next question in respect of the effect that such limitations had on the construction of the model.

Perhaps the major limit on the effectiveness of the experiments at Sidney Meadow was outwith the powers of design and control in that total rainfall was only half the average for the time of year. Ideally, one would wish to take account of such occurrences by running plot experiments over two or three years at least. Simulation of surface runoff proved successful, but at best it only provided short-term observations of runoff processes immediately following treatment application. Given the time it takes for N and P to be released from organic manures (for example see De La Lande Cramer, 1985; Wild, 1993), it would have been desirable to observe surface runoff processes at intervals over a period of at least a month following treatment application.

Low rainfall also meant low rates of sub-surface throughflow, with observations of grass sward length under treatments suggesting that conditions were favourable for increased rates of plant uptake. It would have been useful to observe the effects of higher rates of throughflow on the transport of N and P, and to observe the effects of the establishment of variable source areas of saturation. The combination of these two effects is of particular interest, because while higher rates of throughflow may increase transport of N and P, areas of saturation purely within the buffer may facilitate the removal of NO_3^- -N by denitrification (see Haycock and Pinay, 1993).

Even allowing for the low rainfall at Sidney Meadow, there was evidence of preferential flow occurring, which had important implications for the distribution of water on the hillslope and the transport of N and P. The design of the experiment was adequate for the determination of rates of subsurface throughflow in general, but it

lacked the sensitivity to identify the cause of short term increases in throughflow following rainfall. In this instance, tracers may have been applied usefully to determine the pathways rain water took following infiltration of the soil, and how long it took for this water to reach the base of the slope (for example, see Atkinson, 1978; Leaney *et. al*, 1993; Wilson *et. al*, 1993).

Tracers might also have been applied to check that water from above the experimental site was not finding its way into the throughflow pits and dipwells at the bottom of the plots, for example via increases in the level of the groundwater table (O'Brien and Hendershot, 1993; Wheater *et. al*, 1993). Although hydrological isolation was installed to prevent this, the nature of the weathered slate beneath the soil profile is such that one would have to insert an impermeable layer several metres into the slate to ensure perfect isolation. Given that data from the dipwells at the base of the slope suggested that the detected water table was perched (see Figs. 3.20 and 3.21), it would have been of use to insert deep dipwells (upto 5 m) at points further up the slope to monitor the movement of this water table throughout the experimental site.

Neither Sidney Meadow nor Merrifield were artificially drained, and although the use of drainage may not be common on these types of permanently grassed hillslopes, there is still the general question of what the effect of drainage might be on the transport of N and P. For example, as already mentioned in Chapter 3, section 3.4.4, Garwood *et. al*. (1985) observed that when permanent grass receiving 400 kg N ha^{-1} was drained, the amount of NO_3^- -N leached increased from 69 kg N ha^{-1} to 216 kg N ha^{-1} , and the amount of N denitrified decreased from 64 kg N ha^{-1} to 46 kg N ha^{-1} .

This second mention of denitrification prompts a consideration of how thoroughly the field experiments examined the processes of N and P transformation. While the emphasis of the research was on the transport of N and P downslope toward water courses, and a detailed examination of transformation processes at the laboratory profile or plot scale was not therefore feasible within the constraints of time and physical resources, it would certainly have been of use to produce basic N and P balances for the experiments. In the case of N transformation for example, field techniques can be employed to estimate the quantities of N associated with plant uptake, denitrification,

ammonia volatilisation and soil storage (again see Garwood *et. al*, 1985). Similarly, it would have been useful to estimate the quantities of P associated with plant uptake and soil storage.

Finally, there is the consideration of topography and land-use effects that were not thoroughly examined as part of the field experiments. Sidney Meadow was topographically uniform, which meant that it was not possible to observe the effects of factors such as hillslope hollows on the distribution and movement of water on the slope. The Merrifield catchment certainly contained a number of hillslope hollows, and it is at the field scale that the contribution of these hollows to the generation of variable source areas of saturation is best examined (see Burt and Butcher, 1985b; Burt and Arkell, 1986), particularly in relation to how this affects spatial and temporal variations in the transport of N and P.

At Sidney Meadow, it was also not possible to examine the land-use effect of localised compaction, due either to traffic or grazing, which can cause partial source areas of increased infiltration excess surface runoff. The effect of compaction and poaching due to grazing has been examined in the past at Merrifield, using small plots and rainfall simulation (Heathwaite *et. al.*, 1990a and b). Given the significance of the results of these experiments in terms of the surface transport of N and P, it would be of use to continue this type of experiment, using larger plots and natural rainfall where possible.

(3) Given that not all the ideas contained in the conceptual model were thoroughly examined by the field experiments, did the limitations of the experimental work cause difficulties in constructing a working mathematical model?

The adoption of a functional and semi-distributed approach to modelling largely ensured that the difficulties arising from the limitations of the experimental work were minimised, the data from Sidney Meadow and Merrifield being sufficient for the initial calibration and preliminary testing of the model. Clearly, it would have been extremely difficult to both construct and in any way calibrate a fully mechanistic and distributed model on the basis of the experimental data available.

Errors and omissions within the model structure were apparent. For example, there was no function to model preferential flow, and the use of only three soil water stores made it difficult to adequately model variable source areas of saturation and partial source areas of reduced infiltration capacity.

The calibration and testing of the model was also limited. Hydrology functions were calibrated with data from Sidney Meadow and Merrifield, but their testing was confined to simulation of past rainfall events at Merrifield. Most N and P transport functions were calibrated with data from Sidney Meadow, but none were tested, and while functions for denitrification, ammonia volatilisation, plant uptake, and N and P in soil storage were included in the model, none were calibrated by the experimental work, preliminary values being derived from literature (for example Wild, 1993).

Despite these limitations to process interpretation and spatial sensitivity, it would appear that the model can be used to ask questions about the effects of different manure application practices, such as varying the width of a treatment free buffer strip, thus enabling a focus on areas that warrant further experimental investigation. It would also appear possible to improve the performance and accuracy of the model without abandoning the functional and semi-distributed approach, thus increasing the potential range of applications to which the model may be suited. For example, the number of stores can be increased to incorporate the effects of topography and the spatial variability in soil physical conditions arising from land-uses such as grazing.

Of equal importance in relation to the research objectives is the fact that the development of the model facilitated consideration of the interaction between land-use and topography at the headwater catchment scale, and how this affects spatial and temporal patterns in the transport of N and P from grassed hillslopes. The effect of generalising processes interpreted at the plot scale was examined, and particular instances where generalisation might lead to significant reduction in the accuracy with which N and P transport is modelled at the headwater catchment scale were identified.

7.2. Developing the research

7.2.1. Experimental work

Identification and quantification of the preferential flow process is of considerable importance, since the effect that this process has on the rate of movement and distribution of water in subsurface throughflow, including contributions to perched water tables and variable source areas of saturation, can have considerable implications for the transport of N and P in both subsurface throughflow and surface runoff. Following this, the effects attributable to variations in topography and land-use on a site should be examined, particularly in relation to variable source areas of saturation and partial source areas of reduced infiltration capacity. Together, these two areas of experimentation should enable examination of the primary causes of surface runoff, which is a particularly significant pathway of N and P transport from surface applied organic manures.

The collection of data that facilitate the construction of N and P balances is probably next in order of importance, which involves quantification of the processes of ammonia volatilisation, denitrification, plant uptake and animal intake, and immobilisation of N and P in the soil. Collection of these data may necessitate the running of experiments of longer duration than previously, which in itself would provide useful information on the downslope transport of N and P over the longer term.

At the field or headwater catchment scale, it would be useful to monitor the level of the groundwater table at points covering the entire slope section, together with concentrations of N and P. Thus it may be possible determine if at any time water that is percolating to groundwater reappears at the base of the slope, and the contribution that this water makes to the sub-surface transport of N and P. However, such a system of monitoring may be complicated if perched zones of saturation are established above the groundwater table.

Eventually, one might wish to consider the transport of N and P from surface applied organic manures on sites with markedly different soil types and structures, which would

be followed by consideration of the spatial and temporal operation of processes in larger catchments which contain a mixture of soil types, topography and land-use.

7.2.2. Modelling

The current model can be improved both by the addition of new functions and the refinement of the existing structure. Experimental observation would suggest the inclusion of two new functions, the first and most important of these being a function to model the preferential flow process, and the second being a function to model flow both to and from the groundwater table. These functions could be incorporated within the existing model programme with relative ease, and later calibrated and tested as further experimental data become available.

Refinement of the existing structure can be achieved in two ways. Firstly, the number of stores used to represent a catchment could be increased in order to increase the model's sensitivity to spatial variations due to topography and land-use effects. In addition to the extra calibration requirements, the inclusion of more stores would increase the model's complexity in that the representation of flow processes becomes truly three dimensional. For example, water is allowed to flow across the slope between adjacent stores as well as downslope to the store below. The results of initial testing would suggest that this increase in sensitivity and complexity is required even at the scale of the Merrifield catchment. Eventually, if larger catchments are to be considered, then this sort of refinement is also required to maintain the temporal accuracy of the response of water distribution on hillslopes to rainfall events (see Quinn and Beven, 1993).

Secondly, the existing functions can be thoroughly calibrated and tested as further experimental data become available. Refinement of certain functions may become necessary in light of this. For example, the functions that describe ammonia volatilisation, denitrification, and plant uptake are at present very simple, and it may prove impossible for these functions to provide accurate descriptions without an increase in their mathematical complexity.

7.3. The overall contribution of the research

Although few workers may have examined the transport of several N species and P fractions in both surface runoff and sub-surface throughflow from grassed hillslopes under controlled conditions, it is nevertheless true that most of the processes examined in this study have been examined in considerably more detail elsewhere, either in isolation or in another context. Therefore, perhaps the main contribution of this research project has been to adapt and integrate the existing knowledge of processes with specific reference to the question of scale, in order to apply that knowledge to a particular environmental problem in a more co-ordinated, if sometimes less detailed, manner than before.

In the case of organic manures and their application to grassland hillslopes, it quickly became apparent during the course of this study that much valuable work had already been carried out. The processes of hillslope hydrology are well understood (Chapter 2, section 2.2), and are already being modelled in considerable detail and at large catchment scales (Chapter 5, section 5.1). Likewise, the processes of N and P chemistry within the soil-water environment are also well understood, and while the emphasis in applying this understanding may have been on arable systems, inorganic fertilisers, and NO_3^- -N, the body of knowledge concerning livestock systems and other forms of N and P would seem to be considerable (Chapter 1, sections 1.4 and 1.5; Chapter 2, sections 2.3 and 2.4). Unfortunately, these different strands of research often seem to have remained separate and disjointed, and the emphasis of this project (whether fully intended at the outset or not) was to bring some of these strands together in a structure which could be used to address a problem at an appropriate scale and level of detail. Construction of such a structure then enabled the identification of weak points where further knowledge was required.

Inevitably, this approach was confronted squarely by the problems of considering scale. Detailed knowledge of processes can be acquired at the laboratory or plot scale, the problems come in accounting for the spatial and temporal variability in the operation of these processes at the catchment scale. Given that resources are limited, the issue

becomes one of how much loss of detail can be tolerated before a structure fails to support itself under the weight of the difficulty of the questions it is required to answer. It is felt that this research went a little way toward addressing the problem of scale by linking observations from plot scale experiments with less detailed observations from a headwater catchment, then producing a working mathematical model structure, the complexity of which did not go beyond the understanding gained from the rest of the research. While weak points in the model structure have been identified, it would seem that the model is capable of examining the environmental implications (in terms of N and P transport) of different land management practices.

Finally, it remains to summarise the research project's contribution to addressing the environmental implications of the application of organic manures to grassed hillslopes. The basic justification for the programme of research, as stated in Chapter 1, is that one has to consider all sources of N and P found in freshwaters, and that to date rather more emphasis has been placed on arable systems and inorganic forms of N and P. It is hoped that the approach of the research has encouraged a view of organic manure as a potentially significant source of N and P, that the transport of N and P from this source in water is subject to a high degree of spatial and temporal variability in steeply sloping catchments, and that in certain areas the application of organic manure to grassed hillslopes should be treated with the same rigour as is accorded to inorganic fertiliser in other areas. Whether the manure drops out of the back of a slurry spreader or out of the back of a cow, it is not sufficient merely to physically prevent that manure dropping further into a water course.

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Appendix 1

Sidney Meadow Site Details

Permanent pasture

Area = 2 ha

pH = 5.5

Denbigh soil series, silty clay loam texture

Sampling date	P mg l ⁻¹ /ADAS index	K mg l ⁻¹ /ADAS index	Mg mg l ⁻¹ /ADAS index	Organic matter*
July 1990	20/2	238/2	135/3	13.0
July 1987	18/2	173/2	-	12.7

*Calculated by loss on ignition.

Recent fertiliser record

Year	Date	Fertiliser	Rate (kg ha ⁻¹)
1990/1991	Figures not available	Figures not available	Figures not available
1989/1990	29/6/90	34.5% N ¹	170
	12/3/90	24:13:0 N:P:K ²	160
	9/3/90	24:13:0 N:P:K	345
1988/1989	23/3/89	25:5:5 N:P:K	250
1987/1988	9/5/88	25:5:5 N:P:K	250
	19/4/88	25:5:5 N:P:K	275
	25/2/88	25:5:5 N:P:K	245

¹ Form of fertiliser = NH₄NO₃. ² Form of fertiliser = (NH₄)₂PO₄.

Block	Treatment	Survey location number	Distance from point 1	Vertical height from point 1	
Block 1	Slurry	39	28.2,6.3	8.4,1.4	
		29	18.3,3.7		
		19		0,0	
	Control	35	24.3,5	15	9,0.6
		25			
		15			
	Inorganic fertiliser				
	Manure	40	35,5.8	5	19.4,-0.3
Block 2	Control	36	34.3,4.7	16	25.6,0
		26			
		16			
	Manure				
	Slurry				
	Inorganic fertiliser				
		9			44.5,-1
Block 3	Slurry	41	52.9,4.8		
	Inorganic fertiliser				
	Control	38	66.1,3.1	18	62,-0.6
		28			
	Manure	42	75.1,4	24	71.8,-0.4
		34			

1 = Survey location number

0,0 = distance along ground from point 1, vertical height from point 1.

Fig.1. Sidney Meadow topographic site survey

Appendix 2

Technicon AAII Autoanalyser Flow Diagrams

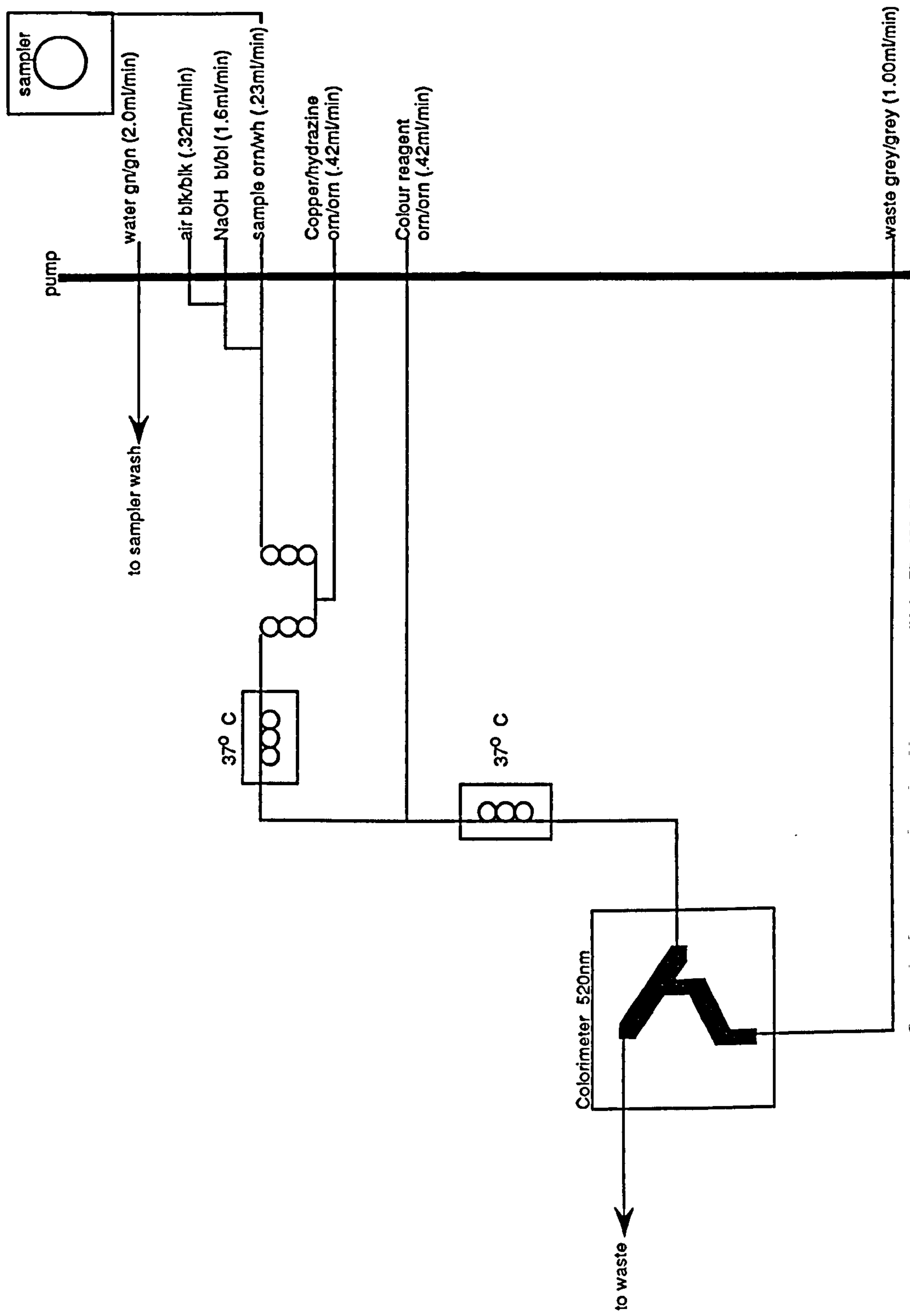


Fig.1. Nitrate and nitrite (TON, Range: 0-50 mg l⁻¹ of the ion)

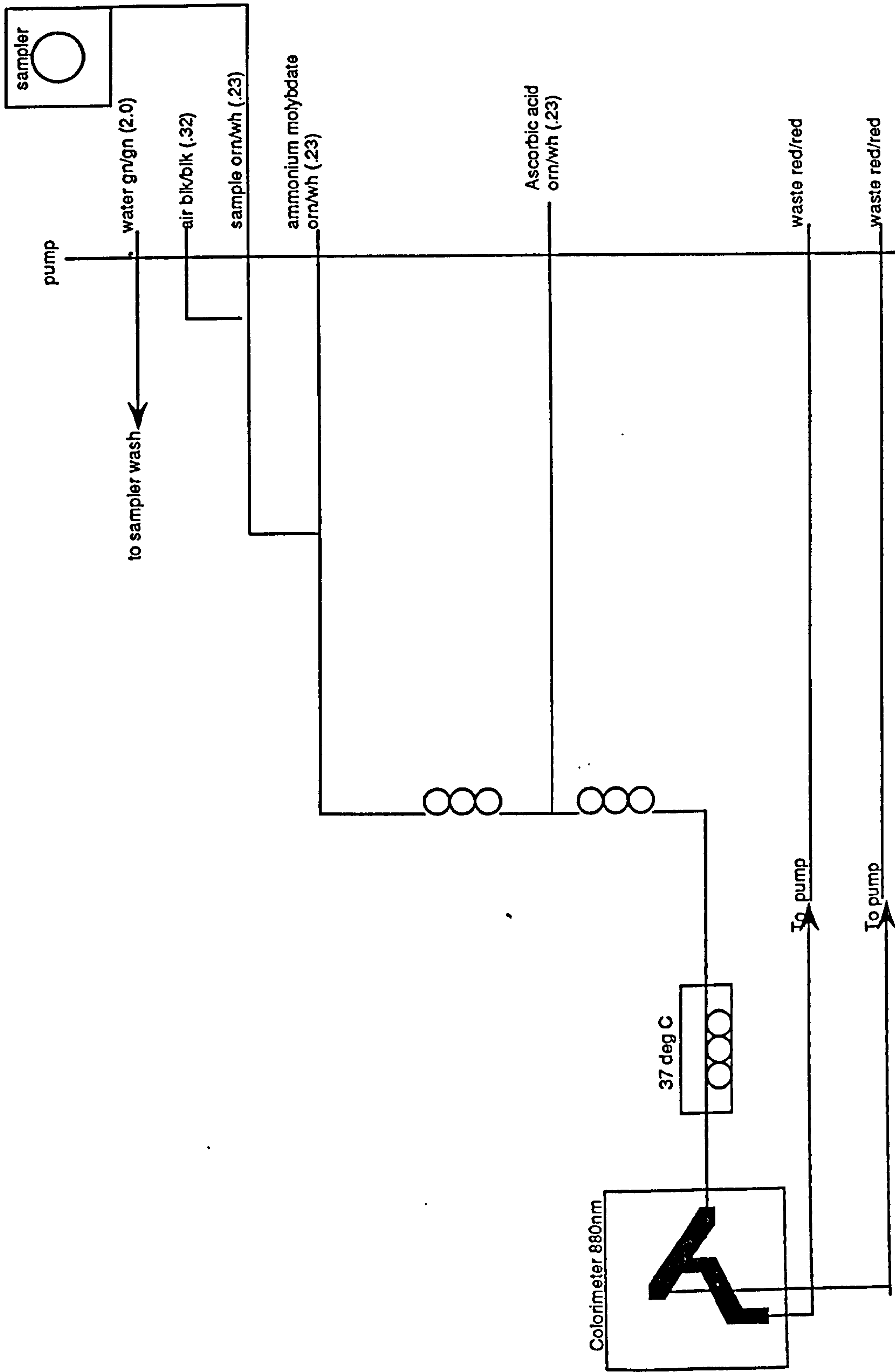


Fig.2. Orthophosphate (Range: 0.2-10 mg l⁻¹ of the ion)

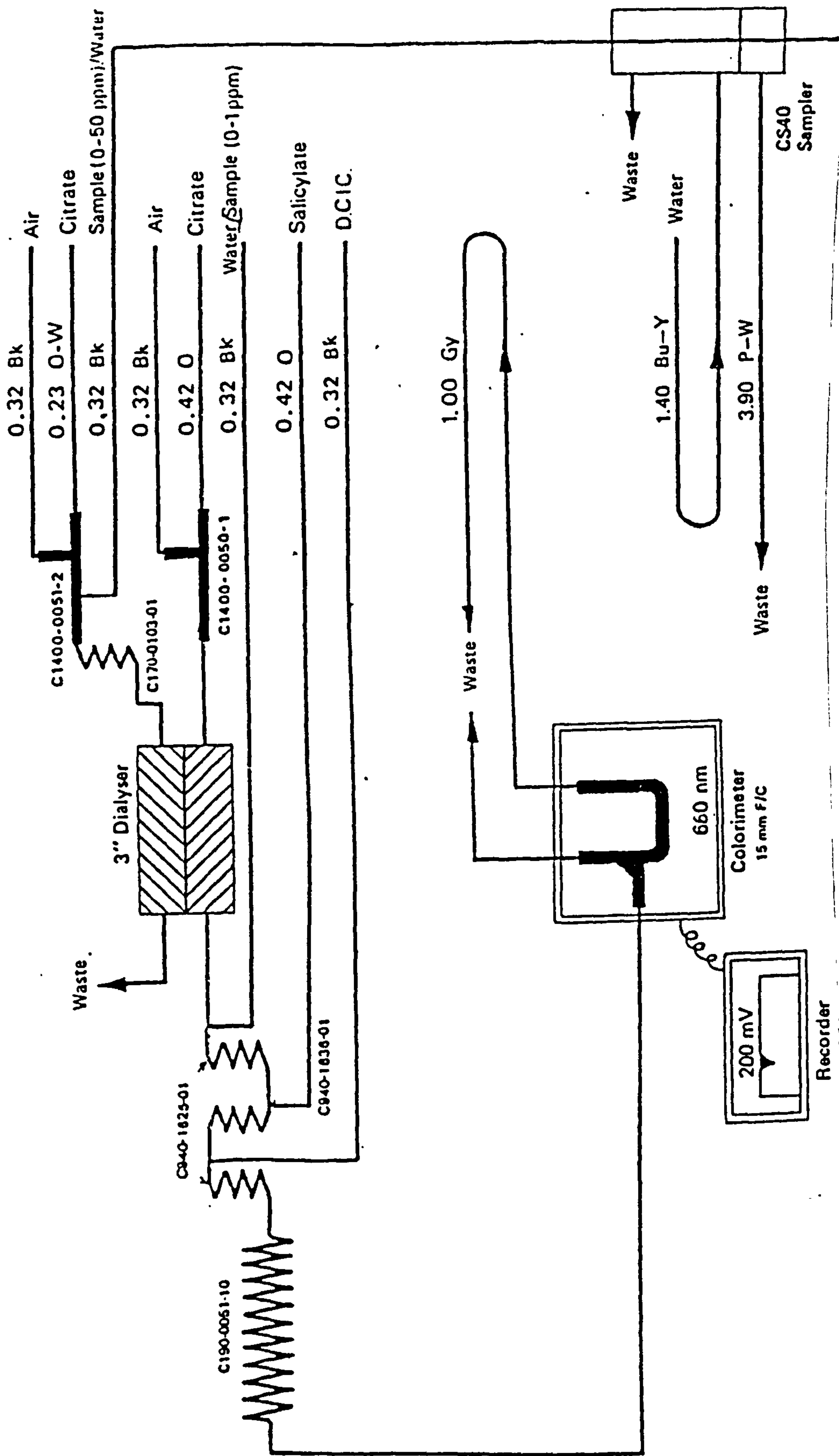


Fig.3. Ammonium (Ranges: 0-1 and 0-50 mg l⁻¹ NH₄⁺-N)

Appendix 3

Model Programme Listing and Glossary

1. Model programme listing (Qbasic version 4.5)

```
'program slopehy 7
'version 7, 160993, PG / RIF
CLS
nstore = 3: dmax = 5
ic0 = 30: icf = 8
rftot = 0: qtot = 0
oftot = 0: tftot = 0: dptot = 0: evaptot = 0: prevppt = 0
naoftot = 0: natftot = 0: nadptot = 0: nboftot = 0: ncoftot = 0
nvoltot = 0: nuptot = 0: ndnittot = 0
paoftot = 0: patftot = 0: padptot = 0: pboftot = 0: puptot = 0
OPTION BASE 1
DIM L(nstore), w(nstore), smin(nstore), s(nstore), smax(nstore), grad(nstore),
ksat(nstore)
L(1) = 124: L(2) = 124: L(3) = 50
w(1) = 700: w(2) = 550: w(3) = 500
smin(1) = 52080: smin(2) = 51150: smin(3) = 22500
s(1) = 78120: s(2) = 76725: s(3) = 33750
smax(1) = 86800: smax(2) = 85250: smax(3) = 37500
grad(1) = .27: grad(2) = .36: grad(3) = .36
DIM nsuf(nstore), nasufc(nstore), nasub(nstore), nasubc(nstore), nbsufc(nstore)
nsuf(1) = 2170: nsuf(2) = 1705: nsuf(3) = 0
nasufc(1) = .001: nasufc(2) = .001: nasufc(3) = 0
nasub(1) = 468.72: nasub(2) = 460.35: nasub(3) = 202.5
nasubc(1) = .006: nasubc(2) = .006: nasubc(3) = .006
nbsufc(1) = .006: nbsufc(2) = .006: nbsufc(3) = 0
DIM ncsufc(nstore), ncsufc(nstore), nvol(nstore), nvolr(nstore), nup(nstore),
nupr(nstore), ndinit(nstore), ndnitr(nstore)
ncsufc(1) = .015: ncsufc(2) = .015: ncsufc(3) = 0
ncsub(1) = 0: ncsufc(2) = 0: ncsufc(3) = 0
FOR a = 1 TO nstore
nvol(a) = .25 * nsuf(a)
nup(a) = .2 * nsuf(a)
```

```

ndnit(a) = .05 * nsuf(a)
NEXT a
DIM psuf(nstore), pasufc(nstore), pasub(nstore), pasubc(nstore), pbsufc(nstore),
pbsub(nstore), pup(nstore), pupr(nstore)
psuf(1) = 868: psuf(2) = 682: psuf(3) = 0
pasufc(1) = .0005: pasufc(2) = .0005: pasufc(3) = 0
pasub(1) = 2.34: pasub(2) = 2.3: pasub(3) = 1.01
pasubc(1) = .00003: pasubc(2) = .00003: pasubc(3) = .00003
pbsufc(1) = .001: pasufc(2) = .001: pbsufc(3) = 0
pbsub(1) = 0: pbsub(2) = 0: pbsub(3) = 0
FOR a = 1 TO nstore
pup(a) = .2 * psuf(a)
NEXT a
FOR d = 1 TO dmax
    prevppt = 0
    PRINT "Day no. "; d;
    INPUT "Is there any rain today"; rf$
FOR t = 1 TO 24
    IF LCASE$(rf$) = "y" THEN
        CLS
        ksat(1) = 40: ksat(2) = 40: ksat(3) = 40
        kp = 1 / 48: evapr = 0: nccr = .033 / 24: pbcr = .033 / 24:
        naupr = .001: paupr = .001: nadnitr = .001
        FOR a = 1 TO nstore
            nvolr(a) = nvol(a) / 30 / 24
            nupr(a) = nup(a) / 30 / 24
            ndnitr(a) = ndnit(a) / 30 / 24
            pupr(a) = pup(a) / 30 / 24
        NEXT a
        PRINT "Day no. "; d; "Hour no. "; t; "Rates are per hour"
        INPUT "Rainfall in mm/h"; ppt
    ELSE
        ksat(1) = 960: ksat(2) = 960: ksat(3) = 960
        t = 24: ppt = 0: kp = .5: evapr = 1: prevppt = 0
        nccr = .033: pbcr = .033
        naupr = .024: paupr = .024: nadnitr = .024
        FOR a = 1 TO nstore
            nvolr(a) = nvol(a) / 30
            nupr(a) = nup(a) / 30
            ndnitr(a) = ndnit(a) / 30

```



```

    pupr(a) = pup(a) / 30
    NEXT a
    PRINT "Rates are per day"
END IF
PRINT : PRINT "store  inf  of  tf  rtf  k  S"
LOCATE 9, 1
PRINT "store  naof  natf  nartf  nsurf  nasub  nbof  ncof  ncsub"
LOCATE 14, 1
PRINT "store  paof  patf  partf  psurf  pasub  pbof  pbsub"
tfin = 0: ofin = 0
natfin = 0: naofin = 0: nbofin = 0: ncofin = 0
patfin = 0: paofin = 0: pbofin = 0
FOR n = 1 TO nstore
    IF prevppt < 5 THEN
        ic = ic0 * L(n) * w(n) / 1000
    ELSE
        ic = icf * L(n) * w(n) / 1000
    END IF
    rain = ppt * L(n) * w(n) / 1000
    IF rain + ofin = 0 THEN
        nasurfc = 0: nbsurfc = 0: ncsurfc = 0
        pasurfc = 0: pbsurfc = 0
    ELSE
        nasurfc = ((rain * nasufc(n)) + naofin) / (rain + ofin)
        nbsurfc = ((rain * nbsufc(n)) + nbofin) / (rain + ofin)
        ncsurfc = ((rain * ncsufc(n)) + ncofin) / (rain + ofin)
        pasurfc = ((rain * pasufc(n)) + paofin) / (rain + ofin)
        pbsurfc = ((rain * pbsufc(n)) + pbofin) / (rain + ofin)
    END IF
    IF s(n) = smax(n) THEN ic = 0
    IF ic < rain + ofin THEN
        inf = ic
        of = rain + ofin - inf
        nainf = inf * nasurfc
        naof = (rain * nasufc(n)) + naofin - nainf
        nbinf = inf * nbsurfc
        nbof = (rain * nbsufc(n)) + nbofin - nbinf
        ncinf = inf * ncsurfc
        ncof = (rain * ncsufc(n)) + ncofin - ncinf
        painf = inf * pasurfc

```

```

    paof = (rain * pasufc(n)) + paofin - painf
    pbinf = inf * pbsufc
    pbof = (rain * pbsufc(n)) + pbofin - pbinf
ELSE
    inf = rain + ofin
    of = 0
    nainf = (rain * nasufc(n)) + naofin
    naof = 0
    nbinf = (rain * nbsufc(n)) + nbofin
    nbof = 0
    ncinf = (rain * ncsufc(n)) + ncofin
    ncof = 0
    painf = (rain * pasufc(n)) + paofin
    paof = 0
    pbinf = (rain * pbsufc(n)) + pbofin
    pbof = 0
END IF
nsuf(n) = nsuf(n) - nainf - naof - nbinf - nbof - ncinf - ncof - nvolr(n) -
nupr(n) - ndnitr(n)
IF nsuf(n) < 0 THEN nsuf(n) = 0
IF nsuf(n) = 0 THEN nasufc(n) = 0
IF nsuf(n) = 0 THEN nbsufc(n) = 0
IF nsuf(n) = 0 THEN ncsufc(n) = 0
psuf(n) = psuf(n) - painf - paof - pbinf - pbof - pupr(n)
IF psuf(n) < 0 THEN psuf(n) = 0
IF psuf(n) = 0 THEN pasufc(n) = 0
IF psuf(n) = 0 THEN pbsufc(n) = 0
k = ksaf(n) * (s(n) - smin(n)) / (smax(n) - smin(n))
IF k < 0 THEN k = 0
tf = (k / 1000) * grad(n) * s(n) / L(n)
IF s(n) <= smin(n) THEN kp = 0
dp = kp * L(n) * w(n) / 1000
IF s(n) <= smin(n) THEN evapr = 0
evap = evapr * L(n) * w(n) / 1000
natf = tf * nasubc(n)
nadp = dp * nasubc(n)
patf = tf * pasubc(n)
padp = dp * pasubc(n)
naup = naupr * nasub(n)
nadnit = nadnitr * nasub(n)

```

```

paup = paupr * pasub(n)
s(n) = s(n) + inf + tfin - tf - dp - evap
IF s(n) < smin(n) THEN s(n) = smin(n)
nasub(n) = nasub(n) + nainf + natfin + (nccr * ncsub(n)) - natf - nadp -
naup - nadnit
IF nasub(n) < 0 THEN nasub(n) = 0
nasubc(n) = nasub(n) / s(n)
ncsub(n) = ncsub(n) + nbinf + ncinf - (nccr * ncsub(n))
IF ncsub(n) < 0 THEN ncsub(n) = 0
pasub(n) = pasub(n) + patfin + (pbcr * pbsub(n)) - patf - padp - paup
IF pasub(n) < 0 THEN pasub(n) = 0
pbsub(n) = pbsub(n) + painf + pbinf - (pbcr * pbsub(n))
IF pbsub(n) < 0 THEN pbsub(n) = 0
IF s(n) > smax(n) THEN
    rtf = s(n) - smax(n)
    of = of + rtf
    s(n) = smax(n)
    nartf = rtf * (nasubc(n) + nasufc(n))
    naof = naof + nartf
    nasub(n) = nasub(n) - (rtf * nasubc(n))
    nbrtf = rtf * nbsufc(n)
    nbof = nbof + nbrtf
    ncrtf = rtf * ncsufc(n)
    ncof = ncof + ncrtf
    nsuf(n) = nsuf(n) - (rtf * nasufc(n)) - nbrtf - ncrtf
    partf = rtf * (pasubc(n) + pasufc(n))
    paof = paof + partf
    pasub(n) = pasub(n) - (rtf * pasubc(n))
    pbrtf = rtf * pbsufc(n)
    pbof = pbof + pbrtf
    psuf(n) = psuf(n) - (rtf * pasufc(n)) - pbrtf
ELSE
    rtf = 0
    nartf = 0: nbrtf = 0: ncrtf = 0
    partf = 0: pbrtf = 0
END IF
row = n + 4
LOCATE row, 1
PRINT n;
PRINT USING "#####.##"; inf; of; tf; rtf; k; s(n)

```

```

row = n + 9
LOCATE row, 1
PRINT n;
PRINT USING "#####.###"; naof; natf; nartf; nsuf(n); nasub(n); nbof;
ncof; ncsub(n)
row = n + 14
LOCATE row, 1
PRINT n;
PRINT USING "#####.###"; paof; patf; partf; psuf(n); pasub(n); pbof;
pbsub(n)
tfin = tf: ofin = of
natfin = natf: naofin = naof: nbofin = nbof: ncofin = ncof
patfin = patf: paofin = paof: pbofin = pbof
dptot = dptot + dp: evaptot = evaptot + evap
nadptot = nadptot + nadp
padptot = padptot + padp
nvoltot = nvoltot + nvolr(n)
nuptot = nuptot + nupr(n) + naup
ndnittot = ndnittot + ndnitr(n) + nadnit
puptot = puptot + pupr(n) + paup
NEXT n
q = tf + of
PRINT : PRINT "Total Water Delivery (m3) =";
PRINT USING "#####.#####"; q
totn = naof + natf + nbof + ncof
PRINT USING "#####.#####"; totn
totp = paof + patf + pbof
PRINT USING "#####.#####"; totp
PRINT : PRINT "Press 'c' key to continue when ready"
DO
ans$ = INKEY$
LOOP UNTIL (LCASE$(ans$) = "c")
CLS
prevppt = prevppt + ppt
rftot = rftot + ppt: qtot = qtot + q
oftot = oftot + of: tftot = tftot + tf
naoftot = naoftot + naof: natftot = natftot + natf
nboftot = nboftot + nbof: ncoftot = ncoftot + ncof
paoftot = paoftot + paof: patftot = patftot + patf
pboftot = pboftot + pbof

```

```

NEXT t
PRINT "Up to the end of day "; d
PRINT : PRINT "Total Rainfall (mm) =";
PRINT rftot
PRINT "Total Overland Flow (m3) =";
PRINT USING "####.##"; oftot
PRINT "Total Throughflow (m3) =";
PRINT USING "####.##"; tftot
PRINT "Total Deep Percolation (m3) =";
PRINT USING "####.##"; dptot
PRINT "Total Evapotranspiration (m3) =";
PRINT USING "####.##"; evaptot
PRINT : PRINT "Total Nitrate-N in Overland Flow (kg) =";
PRINT USING "####.##"; naoftot
PRINT "Total Ammonium-N in Overland Flow (kg) =";
PRINT USING "####.##"; nboftot
PRINT "Total Organic-N in Overland Flow (kg) =";
PRINT USING "####.##"; ncoftot
PRINT "Total Nitrate-N in Throughflow (kg) =";
PRINT USING "####.##"; natftot
PRINT "Total Nitrate-N in Deep Percolation (kg) =";
PRINT USING "####.##"; nadptot
PRINT "Total Ammonium-N Volatilised (kg) =";
PRINT USING "####.##"; nvoltot
PRINT "Total N in plant uptake (kg) =";
PRINT USING "####.##"; nuptot
PRINT "Total N Denitrified (kg) =";
PRINT USING "####.##"; ndnittot
PRINT "Total Phosphate-P in Overland Flow (kg) =";
PRINT USING "####.###"; paoftot
PRINT "Total Organic-P in Overland Flow (kg) =";
PRINT USING "####.###"; pboftot
PRINT "Total Phosphate-P in Throughflow (kg) =";
PRINT USING "####.###"; patftot
PRINT "Total Phosphate-P in Deep Percolation (kg) =";
PRINT USING "####.###"; nadptot
PRINT "Total P in plant uptake (kg) =";
PRINT USING "####.##"; puptot
PRINT : PRINT "Press 'c' key to continue when ready"
DO

```

```
ans$ = INKEY$  
LOOP UNTIL (LCASE$(ans$) = "c")  
CLS  
NEXT d  
END
```

Glossary of variable names

nstore: no. of stores.

dmax: no. of days in the run.

ico: initial infiltration capacity (mm h^{-1}).

icf: infiltration capacity after 5 mm of rain in any day (mm h^{-1}).

rftot: rainfall counter (mm).

qtot: combined flow counter (not including deep percolation) (m^3).

oftot: overland flow counter (m^3).

tftot: throughflow counter (m^3).

dptot: deep percolation counter (m^3).

evaptot: evapotranspiration counter (m^3)

prevppt: total rainfall in the previous hours of the day (mm).

naoftot: Nitrate in overland flow counter (kg).

natftot: Nitrate in throughflow counter (kg).

nadptot: Nitrate in deep percolation counter (kg).

nboftot: Ammonium in overland flow counter (kg).

ncoftot: Dissolved and particulate Organic N in overland flow counter (kg).

nvoltot: Ammonia volatilisation counter (kg)

nuptot: Nitrate in plant uptake counter (kg)

ndnittot: Nitrate in denitrification counter (kg)

paoftot: Phosphate in overland flow counter (kg).

patftot: Phosphate in Throughflow counter (kg).

padptot: Phosphate in deep percolation counter (kg).

pboftot: Dissolved organic and particulate P in overland flow counter (kg).

puptot: Phosphate in plant uptake counter (kg).

Arrays

L: surface length (m).

w: surface width (m).

smin: minimum water content (m^3).

s: initial water content (m^3).

smax: maximum water content (m^3).

grad: store slope gradient (sine of slope angle to horizontal).

ksat: saturated hydraulic conductivity ($mm\ h^{-1}$ or $mm\ day^{-1}$)

nsuf: total surface nitrogen store (kg).

nasufc: surface nitrate concentration ($kg\ m^{-3}$).

nasub: subsurface nitrate store (kg).

nasubc: subsurface nitrate concentration ($kg\ m^{-3}$).

nbsufc: surface ammonium concentration ($kg\ m^{-3}$).

ncsufc: surface organic N concentration ($kg\ m^{-3}$).

ncsub: subsurface organic N store (kg).

nvol: quantity of surface N store allocated for volatilisation (kg)

nvolr: rate of volatilisation ($kg\ h^{-1}$ or $kg\ day^{-1}$).

nup: quantity of surface N store allocated for plant uptake (kg).

nupr: rate of plant uptake ($kg\ h^{-1}$ or $kg\ day^{-1}$).

ndnit: quantity of surface N store allocated for denitrification (kg).

ndnitr: rate of denitrification ($kg\ h^{-1}$ or $kg\ day^{-1}$).

psuf: total surface phosphorus store (kg).

pasufc: surface phosphate concentration ($kg\ m^{-3}$).

pasub: subsurface phosphate store (kg).

pasubc: subsurface phosphate concentration ($kg\ m^{-3}$).

pbsufc: surface organic P concentration ($kg\ m^{-3}$).

pbsub: subsurface organic P store (kg).

pup: quantity of surface P store allocated for plant uptake (kg).

pupr: (rate of plant uptake (kg h^{-1} or kg m^{-3})).

rf\$: rainfall indicator (Y/N).

kp: deep percolation saturated hydraulic conductivity (mm h^{-1} or mm day^{-1}).

evapr: evaporation rate (mm h^{-1} or mm day^{-1}).

nccr: conversion rate for immobile N to dissolved nitrate (proportion of store per hr or day).

pbcr: conversion rate for immobile P to phosphate (proportion of store per hr or day).

naupr: rate of nitrate uptake from subsurface store (proportion of store per hr or day).

paupr: rate of phosphate uptake from subsurface store (proportion of store per hr or day).

nadnitr: rate of nitrate denitrification from subsurface store (proportion of store per hr or day).

ppt: rainfall input (mm h^{-1}).

tfin: throughflow input from upslope store (m^3).

ofin: overland flow input from upslope store (m^3).

natfin: nitrate in throughflow input (kg).

naofin: nitrate in overland flow input (kg).

nbofin: ammonium in overland flow input (kg).

ncofin: organic N in overland flow input (kg).

patfin: phosphate in throughflow input (kg).

paofin: phosphate in overland flow input (kg).

pbofin: organic P in overland flow input (kg).

ic: infiltration capacity (m^3).

rain: rainfall input (m^3).

nasurfc: mixed surface nitrate concentration (kg m^{-3}).

nbsurfc: mixed surface ammonium concentration (kg m^{-3}).

ncsurfc: mixed surface organic N concentration (kg m^{-3}).

pasurfc: mixed surface phosphate concentration (kg m^{-3}).

pbsurfc: mixed surface organic P concentration (kg m^{-3}).
 inf: infiltration input to store (m^3).
 of: overland flow output to downslope store (m^3).
 nainf: nitrate in infiltration input (kg).
 naof: nitrate in overland flow output (kg).
 nbinf: ammonium in infiltration input (kg).
 nbof: ammonium in overland flow output (kg).
 ncinf: organic N in infiltration input (kg).
 ncof: organic N in overland flow output (kg).
 painf: phosphate in onfiltration input (kg).
 paof: phosphate in overland flow output (kg).
 pbinf: organic P infiltration input (kg).
 pbof: organic P overland flow output (kg).
 k: hydraulic conductivity (mm h^{-1} or mm day^{-1}).
 tf: throughflow output to downslope store (m^3).
 dp: deep percolation to groundwater (m^3).
 natf: nitrate in throughflow output to downslope store (kg).
 nadp: nitrate in deep percolation to groundwater (kg).
 patf: phosphate in throughflow output to downslope store (kg).
 padp: phosphate in deep percolation to groundwater (kg).
 naup: nitrate in plant uptake (kg).
 nadnit: nitrate in denitrification (kg).
 paup: phosphate in plant uptake (kg).
 rtf: saturation excess overland flow output to downslope store (m^3).
 nartf: nitrate in stauration excess overland flow output (kg).
 nbrtf: ammonium in saturation excess overland flow output (kg).
 ncrtf: organic N in saturation excess overland flow output (kg).
 partf: phosphate in saturation excess overland flow output (kg).
 pbrtf: organic P in saturation excess overland flow output (kg).
 row: row no. on screen at which model output is to be printed (1-25).

q: combined flow for each hour or day in the run (not including deep percolation) (m³).

totn: total nitrogen in combined flow for each hour or day in the run (kg).

totp: total phosphorus in combined flow for each hour or day in the run (kg).