THE DISTRIBUTION AND MOVEMENT OF 'REACTIVE' PHOSPHORUS THROUGH CATCHMENTS UNDER VARIED LAND USE

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SUMMARY: Four small catchments of the Taita Experimental Basin are being studied. The soils, geology, meteorological and hydrological characteristics and vegetation are well documented. The flux of reactive phosphorus through the system is examined in detail. Reactive phosphorous run-off from a grassed catchment was about twice as much as from forested catchments.

INTRODUCTION

The study of chemical run-off from land under different kinds of use and management is a high priority with the Freshwater Section of the Ecology Division of D.S.I.R. The reason for this is simple. Chemical run-off must be a major contribution to the eutrophication of lakes by providing additional nutrients. Of course, chemical run-off occurs naturally, just as eutrophication of lakes proceeds naturally. The problem is to distinguish between natural chemical run-off and additional run-off promoted by man's activities, and to determine the extent to which this additional run-off stimulates 'accelerated' eutrophication. Further, if it were possible to apportion responsibility among man's various activities, there would be some prospect of management to retard eutrophication.

Very little sufficiently comprehensive evidence is available to apportion responsibility for eutrophication between natural processes on the one hand, and man's activities on the other. To apportion blame among the many and varied aspects of man's activities is complete guesswork at the present time.

Phosphorus, added to natural waters by way of fertilisers, detergents and human and other animal wastes, is regarded as being of prime importance in promoting 'accelerated' eutrophication. The work described here is limited to a study of dissolved 'reactive' phosphorus, which for the most part means the orthophosphate ion (but which also includes inorganic phosphorus associated with filterable clay colloids and phosphorus held in organic combination in solution, if these readily hydrolyse in contact with acidified molybdate). These forms are the ones most readily available as plant nutrients.

THE EXPERIMENTAL CATCHMENTS

Four small catchments comprise the Taita International Hydrological Decade Experimental Basin. They are situated on the hills on the eastern side of the Hutt Valley at the Soil Bureau. The catchments were selected for study because of their convenience and for their well-known history, vegetation, soils, stream flow characteristics and local climate (Atkinson in press, Druce

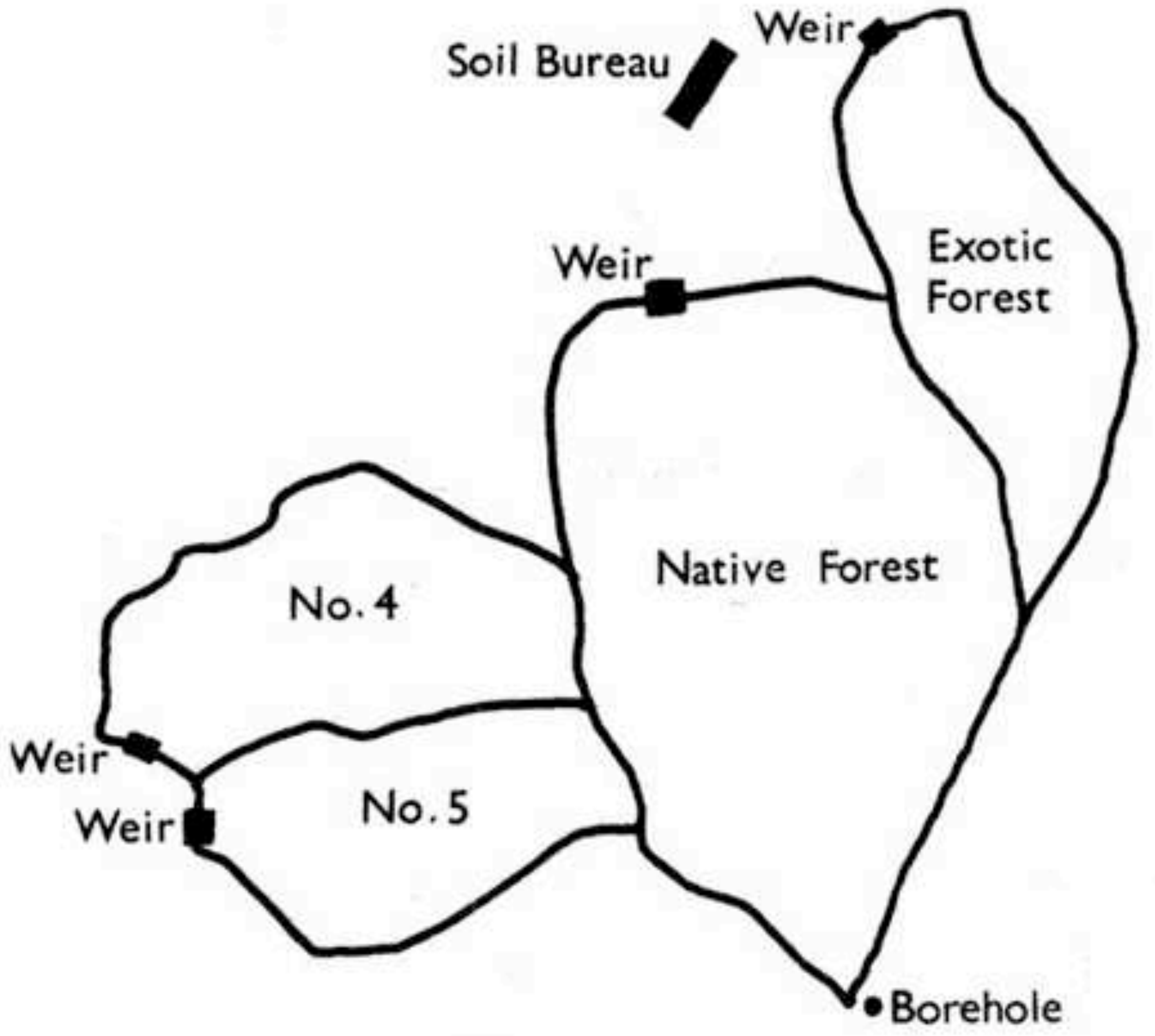


FIGURE 1. *The position of the Taita catchments relative to each other*

1957, Jackson, Aldridge and Thompson 1968, Pohlen 1960). Figure 1 shows the position of each catchment relative to the others.

The *Native Forest Catchment* studied is 10.93ha in extent and has been set aside for the study of the regeneration of native vegetation and associated soil changes. The original vegetation was almost entirely beech forest (*Nothofagus* spp.), but as a result of fires the present vegetation is all secondary, ranging in age from 20 to 105 years. At present 85 percent of the area is covered with scrub and exotic pines, the remainder with native forest. The development is towards kamahi (*Weinmannia racemosa*) and hard beech (*N. truncata*) forest. Stream flow from the catchment has been measured continuously since 1955. Management of the area is restricted to pine eradication and maintenance of tracks, fences and the grass firebreak which surrounds the catchment.

The *Exotic Forest Catchment* is 3.97ha in extent, and it adjacent to the northern edge of the native forest catchment. Before development its vegetation resembled that of the native forest catchment. In the mid-fifties a grass firebreak was established around it, and during 1958 and 1959 the vegetation was cut and burned. Planting with western red cedar (*Thuja plicata*) Douglas fir (*Pseudotsuga taxifolia*) and Corsican pine (*Pinus nigra*) was started in 1959. From time to time during the 1960s, release cutting and planting to replace dead trees has taken place. Stream flow has been recorded since 1961.

Catchment Number Four is 4.69ha in extent, and backs on to the native forest catchment's southern edge. It is covered in secondary vegetation similar to that found in the native forest catchment. A wide grassed firebreak has been established along the top of the area to separate it from the native forest catchment. Stream flow has been measured since 1968.

Catchment Number Five is 3.60ha in extent. It is adjacent to catchment Number Four and backs on to the native forest catchment. Until 1958 it was clothed in secondary vegetation similar to that of the native forest catchment. Between 1958 and 1960 most of the catchment was burned and sown to pasture. Trees were retained along the stream channels to maintain stability. The areas cleared for pasture were initially treated with lime at the rate of 10 cwt/acre (1255 kg/ha), and with molybdic superphosphate at 6 cwt/acre (753kg/ha). Since then dressings of lime at 5 cwt/acre (628 kg/ha) and superphosphate at 3 cwt/acre (377 kg/ha) have been applied, with molybdic superphosphate being used in alternate years. Spraying with 2,4,5-T is carried out to control gorse. Grazing has usually been at the rate of six sheep/acre (15 sheep/ha). Records of grazing, spraying and topdressing are kept. Stream flow has been measured continuously since 1968.

The soils of all four catchments are mainly central yellow-brown earths and related steepland soils derived from greywacke. The underlying basement rock is described by Kingma (1967) as alternating argillite and greywacke sandstone of Jurassic Age. Their petrology has been described by Reed (1957). A borehole sunk on the main ridge at the apex of the native forest catchment reached a depth of 160 feet (48m) without encountering unweathered rock, but beds of hard, grey, relatively unweathered greywacke outcrop in some of the valleys. Occasional quartz veins cut across the beds of sandstone.

Table 1 has been extracted from the soil map of Atkinson (in press), and shows the relative importance of major soil types in the four catchments on a map area basis. The commonest soils are the Taita clay loams and hill soils, which, together with the Tawai steepland soils, are derived from greywacke. The Wingate hill soils and older Bucks clay loam are both derived from loess. Other recognisable soils such as Pinehaven silt loam and Pomare silt loam occur in negligible quantities within the catchments. General similarity of distribution of soils is apparent among the catchments. The exotic forest catchment diverges most from the general pattern, with Wingate hill soils being more common there.

Climatological records have been kept systematically since 1957, and at various times extensive studies of rainfall variation over the experimental

TABLE 1. *The relative importance of several soil types in the catchments of the Taita experimental basin*

Catchment	Taita hill soils and clay loams	Tawai steepland soils	Wingate hill soils	Bucks clay loam	Others
Native forest	75%	13%	10%	2%	0%
Exotic forest	50%	25%	22%	1%	3%
Number four	71%	11%	16%	0%	2%
Number five	73%	16%	10%	0%	1%
Parent material	Greywacke			Loess	

station have been carried out. Relationships between rainfall and streamflow in the four catchments are well known.

METHODS

Two stream water samples were taken at intervals of two minutes at the outlets to each catchment on every sampling occasion. The samples were stored in pyrex glass. Filtration through 0.45 micron Millipore filters was completed within an hour of collection in most instances. Analysis for reactive phosphorus followed the method of Murphy and Riley (1962) using 10cm cells in an Hitachi Perkin Elmer spectrophotometer.

Rainfall was collected variously from aluminium sheets, polythene, stainless steel and glass funnels and stored in pyrex glass. Filtration and analysis for reactive phosphorus was the same as for stream water.

Where reactive phosphorus was extracted from surface soils the following procedure was adopted. A soil core 5cm deep and 2.5cm in diameter was air-dried for several days. It was loosely broken up and sieved through a 1mm mesh. A measure, weighing approximately 0.25gm, of the sieved material was mixed with 100ml of distilled water and allowed to stand overnight (*ca.* 18 hours). It was then filtered and analysed as for stream water.

OBSERVATIONS AND EXPERIMENTAL RESULTS

Figure 2 is a diagrammatic representation of the distribution and movement of phosphorus within a catchment. The concentrations of reactive phosphorus which were found in various aqueous components are shown in microgrammes per litre.

Rainfall may make significant contributions of phosphorus to the catchments. At Taita, Miller (1961) estimated the input of total phosphorus at 18.9, 21.4 and 24.5 mg/m^2 in the years 1956 to 1958. The work was repeated in 1965 and in this year the input was 65 mg/m^2. These quantities are equivalent to average concentrations of 12, 14, 22 and 41 μg/1 of phosphorus in rainwater respectively. These figures, like most estimates of chemical inputs with rainfall, are likely to be erroneous because they represent measurements of what ends up in solution in rain-collecting apparatus rather than what is in rainfall. Dust and salt particles impacted on funnels often make major contributions to chemicals found in rainfall collections (White, Starkey and Saunders 1971). Where clean apparatus is put out specially to collect a particular shower, reactive phosphorus concentrations between 0-10 μg/l are found. A mean value of 3 μg/l or even less is likely to be typical for the actual rain in the Hutt Valley. Most of the phosphorus found in "normal" rainfall collections could more properly be regarded as part of the recycling phosphorus system associated with the ground surface, litter and vegetation layer through wind carried dust, pollen and the like. Relatively high concentrations of reactive phosphorus can be found in leaf drip and trunk flow, but it is difficult to determine what part of this is caused by aerial contamination, and what is attributable to recretion by vegetation. Evaporation and possibly evapotranspiration draw phosphorus to the surface and make it available for solution by rain when it next falls.

Classical ideas tell us that phosphorus is rapidly taken out of solution as water passes through

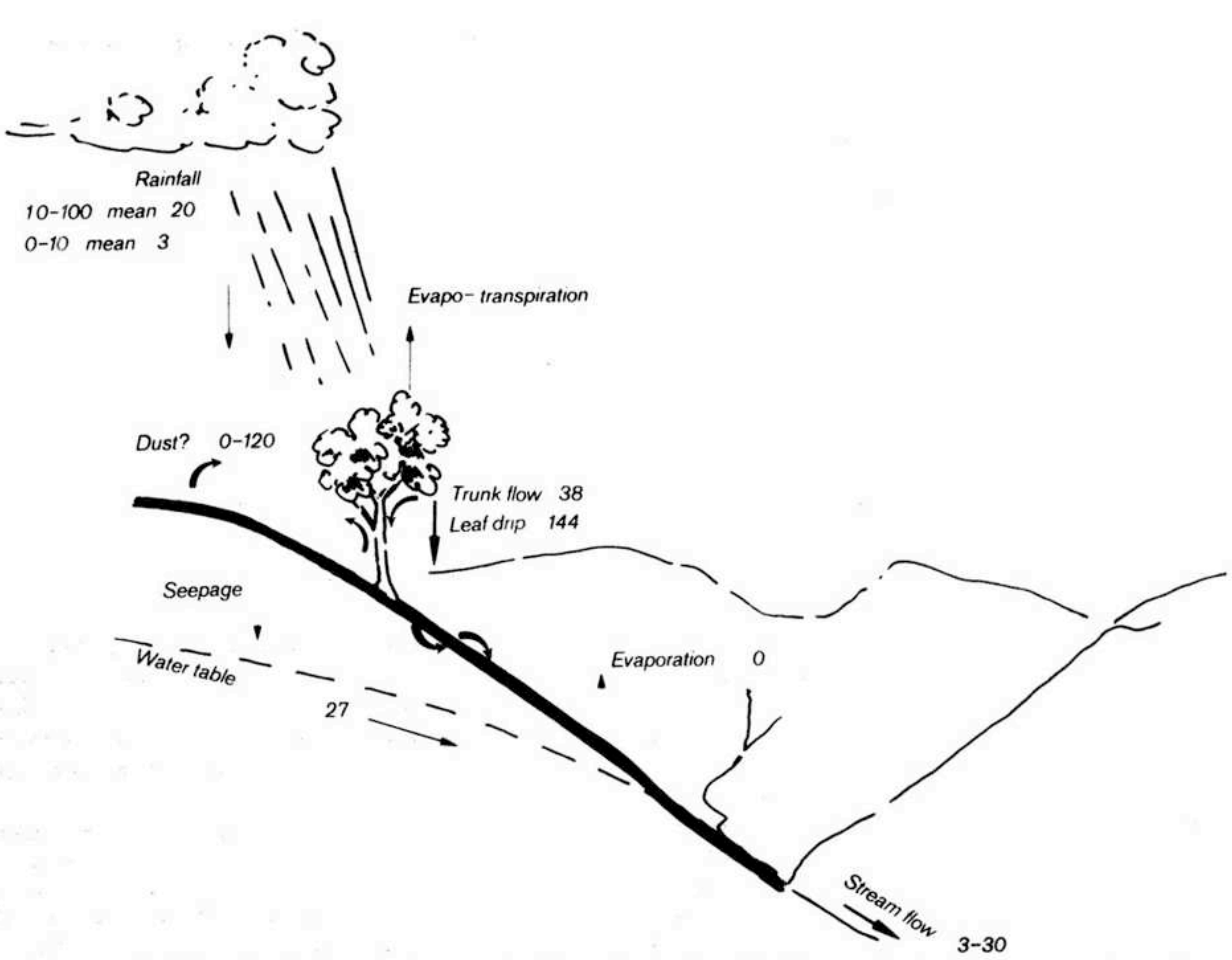


FIGURE 2. *The distribution and concentration of reactive phosphorus in the various aqueous components on a catchment* (μg/l)

soil and subsoil. It was therefore with some surprise that water taken from below the water table of these catchments was found to have concentrations of reactive phosphorus ranging from 27-29 μg/l. Waters with these concentrations of reactive phosphorus were found at all depths in a borehole at the head of the native forest catchment. As similar concentrations (i.e. 26-29 μg/l) were found in the local tap-water which is drawn largely from artesian sources, it seemed that this level of phosphorus concentration might be general.

The concentration of reactive phosphorus in stream run-off was found to vary from 3-33 μg/l, each of the streams having a characteristic range (Table 2). No doubt a great many factors influence the concentration of stream run-off, but at this time only a few can be guessed at.

Over the duration of two floods in October 1971, the quantity of reactive phosphorus lost to each catchment was calculated by integrating flow rates and phosphorus concentrations. The phosphorus lost is listed in Table 2 as mg/ha during each flood, the first lasting two days and the second five days. On the basis of comparable areas the number five catchment lost 3.5, 2.1 and 1.9 times as much reactive phosphorus as the exotic forest, native forest and number

TABLE 2. *The reactive phosphorus content of the stream water at the outlets of four catchments*

	Native forest	Exotic forest	Number four	Number five
Observed ranges of P concentration ($\mu g/l$)	7.3-20.2	3.5-27.0	8.9-26.8	12.2-33.2
Mean P concentration of 34 estimates ($\mu g/l$)	10.9	11.1	16.5	18.2
P leaving catchment over 2 days (mg/ha)	721	360	910	1714
P leaving catchment over 5 days (mg/ha)	2831	1772	2977	5741
100 x (stream flow in 7 days)/rainfall volume	48	28	40	54
P leaving catchments when run-off is adjusted to be 50% of rainfall volume (mg/ha)	3694	3808	4859	6903

four catchment respectively. Part of these differences was caused by the fact that different proportions of the rain input left the catchments by the streams (Table 2), but a proportional adjustment to bring all of the run-off to 50 percent of the input shows that much of the difference persists, so that the disparities are both qualitative and quantitative.

Table 3 shows that well established differences in reactive phosphorus concentrations in streamflow exist between catchments. In addition, highly significant differences occur between sampling occasions and only a small part of these differences can be attributed to variations in flow rate (Table 4). Examination of individual floods reveals that patterns exist which influence all four catchments simultaneously. A relatively small flood showed significant positive relationships between flow rate and reactive phosphorus concentration. A flood which followed two days later was large (with a frequency of about two per year) and negligible changes in phosphorus concentration occurred with changing flow rate.

Complex interactions of many environmental processes seem to affect the reactive phosphorus concentrations in streams, but these operate on all catchments irrespective of their vegetation or use. Some of the more obvious of these factors may be: 1) concentration of reactive phosphorus in rain; (2) the time since it last rained, which in turn affects availability of phosphorus from aerial contamination, recretion sources and decomposition; and (3) the ratio of seepage water to surface run-off.

TABLE 3. *The variation of reactive phosphorus concentration attributable to differences between catchments and between sampling occasions*

	Sums of Squares	Degrees of Freedom	Mean Squares	F	P
Catchments	111679	3	37226	310	h.s.
Sampling times	216282	13	16637	139	h.s.
Interaction	44179	39	1133	9	h.s.
Error	6698	56	120		
Total	378838	111			

TABLE 4. *The variation of reactive phosphorus concentration attributable to differences between catchments and between stream flow rates*

	Sums of Squares	Degrees of Freedom	Mean Squares	F	P
Catchments	74254	3	24751	12.9	h.s.
Flow rates	16138	2	8069	4.2	<.05
Interaction	15783	6	2631	1.4	n.s.
Error	107033	56	1911		
Total	213208	67			

At low flow rates when stream water was derived very largely from ground water, reactive phosphorus concentrations were always lower than those found in the borehole. This prompted examination of the phosphorus concentrations at stream sources. Table 5 shows that many of these sources had higher phosphorus concentrations than the water at the outlets of the catchments, and several of them had concentrations which approached those of the borehole. Surprisingly, the most obvious source in the number five catchment had concentrations far in excess of the borehole water. This particular source appeared to emerge from a fault in a greywacke exposure. The possibility that greywacke might be the origin of these high phosphorus concentrations seemed unlikely but warranted further examination. Opposite Taita, on the other side of the Hutt Valley, quarrying activities have exposed greywacke in both weathered and unweathered condition. A number of springs emerge from the quarry face. Five of these were sampled and found to contain between 4 and 9 $\mu g/l$ of reactive phosphorus. Solution of phosphorus from greywacke offers no explanation for the high concentrations found in the borehole water or in the springs of the number five catchment.

TABLE 5. *Reactive phosphorus concentrations at stream sources and at catchments outlets* ($\mu g/l$)

Catchment	Date	Outlet	Sources
Native forest	18 Oct. 71	13.9	23.2
	4 Nov. 71	9.8	10.7
		9.8	8.6
			10.0
			24.3
			13.2
Native forest (west side)	4 Nov. 71	17.0	31.2
		17.0	
Number five	3 Nov. 71	18.9	110.0
		19.8	68.5
	5 Nov. 71	17.2	89.1
		16.8	44.8
Number four	5 Nov. 71	16.5	23.2
		17.3	14.5

These springs are in the centre of a catchment which is regularly topdressed. If there was some mechanism by which phosphorus from superphosphate fertiliser could reach the groundwater, this would provide an explanation for the high concentrations. Once in the groundwater the concentrations in the waters of adjacent catchments could be influenced. Figure 3 shows evidence of decreasing phosphorus concentrations as distance from the number five catchment increases. To suggest that phosphorus can remain in solution in high concentrations while passing through soil and subsoil of this type goes against all the evidence, but the only alternative suggestion that can be offered at this time is to postulate the existence of a very deep water source rich in phosphorus. On the basis of the number and distribution of sources examined in this study, the probability of a phosphorus-rich, deep water source emerging where it does is about one in 10.

While it is possible that the phosphorus in the stream sources controls concentrations leaving each catchment at low flow rates, this cannot be so at high flows, for although they might increase five hundredfold, the concentration differences between the catchments persist.

Under conditions of heavy, persistent rainfall, surface run-off of water into streams becomes an increasingly important component of the stream flow, and the concentration of reactive phosphorus

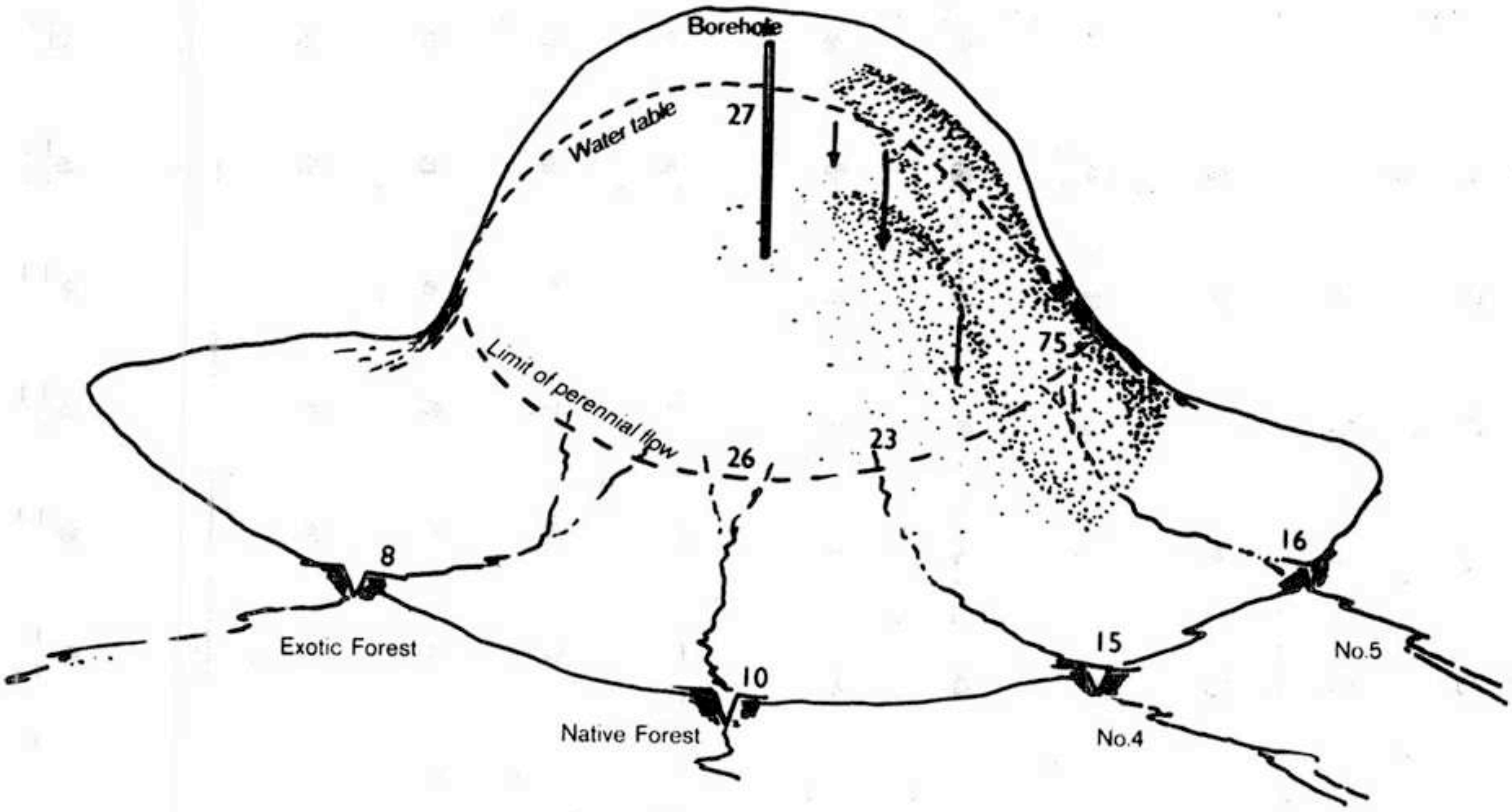
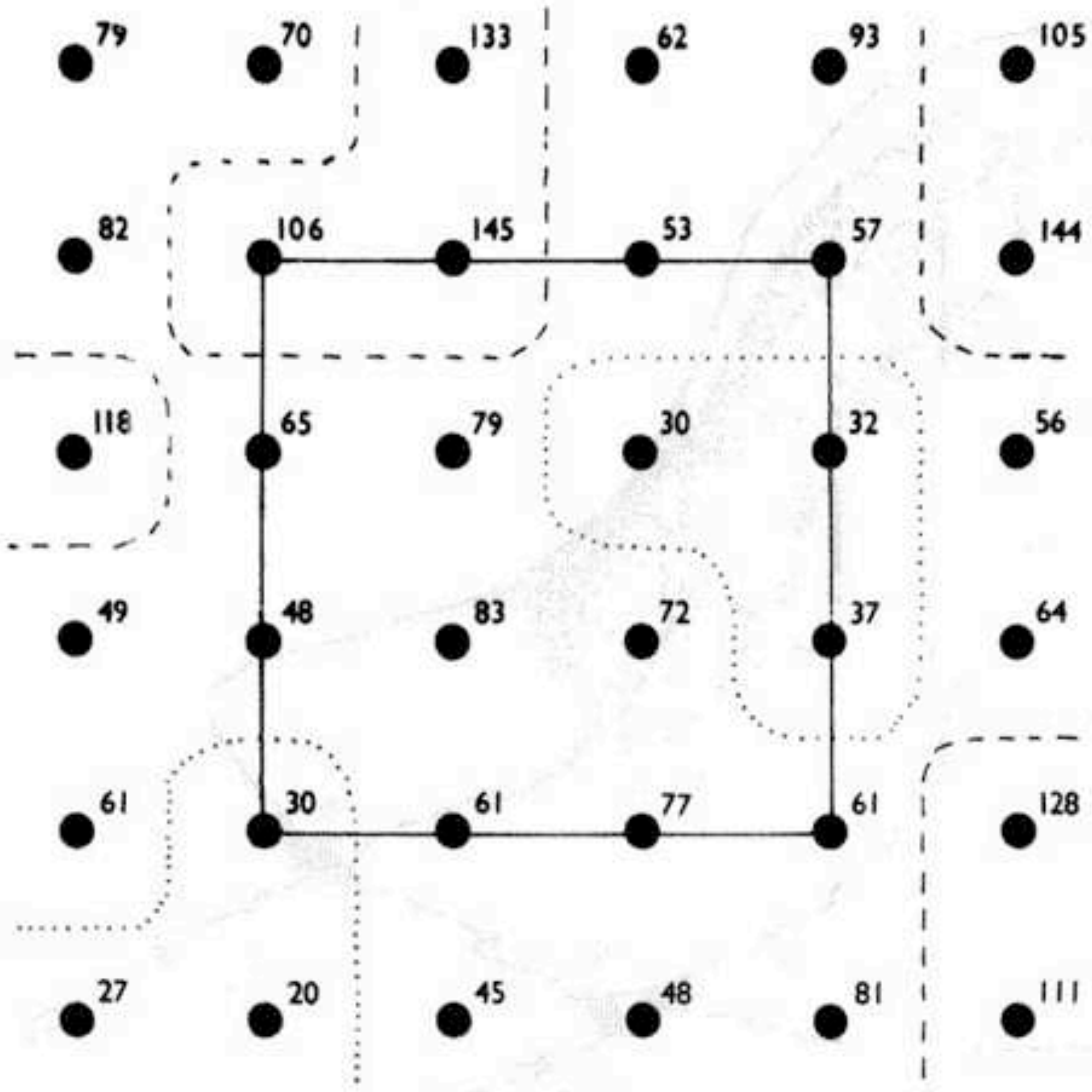


FIGURE 3. *Reactive phosphorus concentrations of sources and outlets of the four Taita catchments* $(\mu g/l)$

in water leaving the catchment must be determined largely by the concentration in rainfall and the amount which can be dissolved at the surface of vegetation, litter and soil. As it is impossible for the differences between catchments to be caused by differences in rainfall composition, the differences must be the result of differences among the catchments themselves.

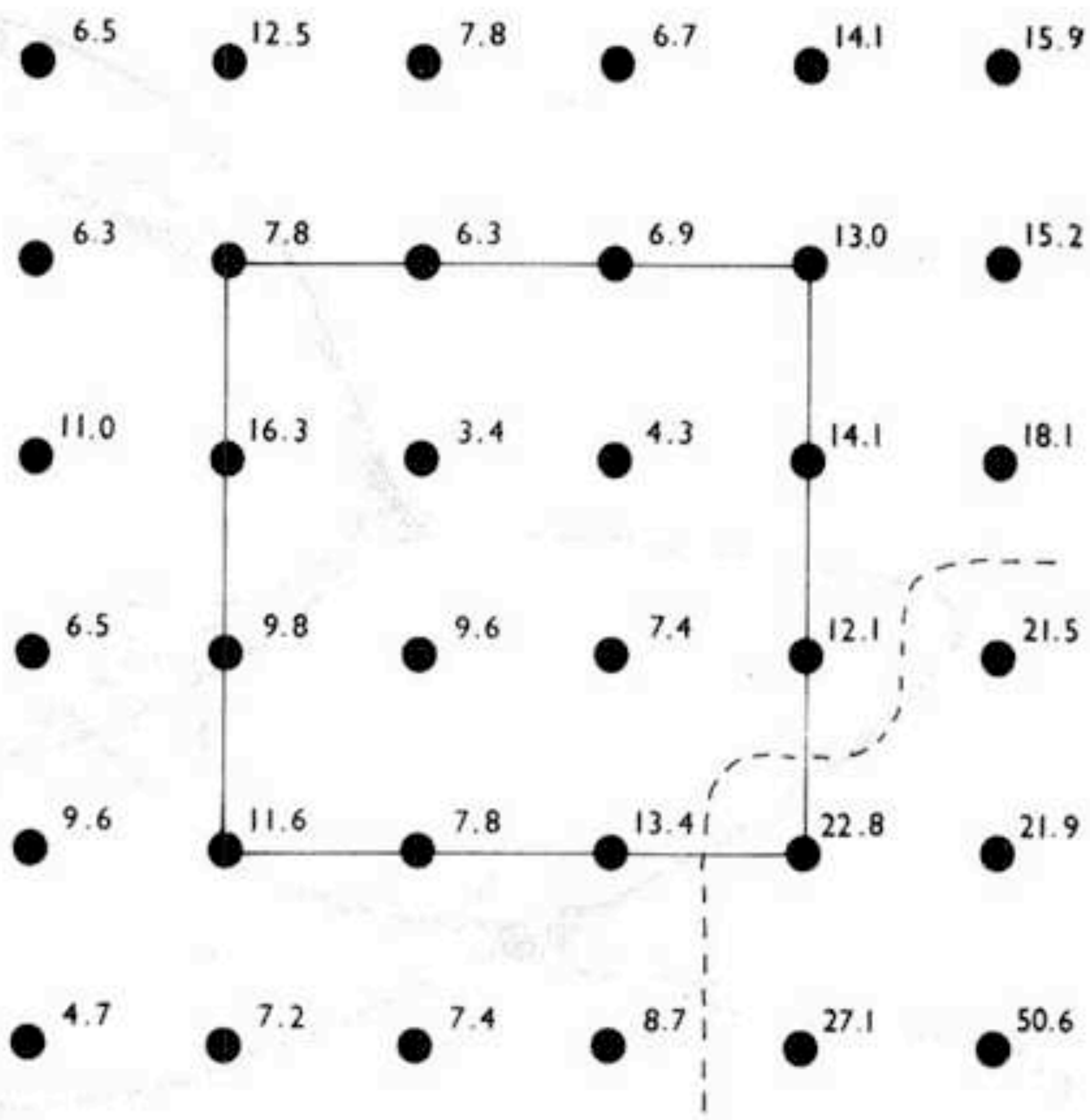
The distribution of readily available reactive phosphorus at the soil surface was examined at two situations in the number five catchment. Thirty-six soil cores were taken at 15cm intervals from each of two areas measuring 75cm by 75cm. Figures 4 and 5 show the distribution of reactive phosphorus concentrations extracted from these cores. Replicate extractions and analyses from the innermost 16 cores of each area show that the patchy distribution of readily available reactive phosphorus is real. From these results it was certain that sampling over the whole catchment to establish some indication of the ready availability of reactive phosphorus for solution would give a non-random distribution with very great variability.

This was shown to be so. A large proportion of cores taken from positions scattered all over the catchment gave up little reactive phosphorus, while a few contributed large concentrations (Fig. 6). The mean for 46 samples was 16.6 $\mu g/l$. If the three cores giving the highest concentrations are ignored then the mean value becomes $9.4 \mu g/l$. There is little reason to suppose that the extraction procedure for reactive phosphorus bears any close relationship to solution processes occurring during surface run-off, but the fact remains that the mean concentration for the 46 samples corresponds with concentrations leaving number five catchment at times of high flow. When the cores giving high concentrations are ignored the mean concentration corresponds to that leaving the forested catchments at high flows. This led to the hypothesis that collection and extraction of reactive phosphorus from 46 cores taken from a forested catchment would give



	s. of s.	dfs	ms	F	P
Position	23143	14	1653	22.6	h.s.
Error	1095	15	73		
Total	24238	29			

FIGURE 4. *The distribution of readily available reactive phosphorus from soil cores taken from* $0.5m^2$ *of the number five catchment* ($\mu g/l$)



	s. of s.	dfs	ms	F	P
Position	584	15	38.9	14.3	h.s.
Error	44	16	2.7		
Total	627	31			

FIGURE 5. *The distribution of readily available reactive phosphorus from soil cores taken from* $0.5m^2$ *of the number five catchment* ($\mu g/l$)

a similar distribution to that of number five catchment except that cores with high concentrations would be missing. This proved to be so, and the mean reactive phosphorus concentration of 9.4 $\mu g/l$ corresponds to the concentration leaving the native forest catchment at high flows. The absence of high concentration cores among the native forest catchment samples was not statistically significant. For this reason additional samples were taken from the native forest catchment. Absence of cores yielding reactive phosphorus in excess of 55 $\mu g/l$ became statistically significantly ($P<0.01$) on taking a further 46 samples.

The cores taken from number five catchment were collected a few days after sheep had been removed and the pasture was closely cropped. A fortnight later, in the absence of sheep and following a little rain, grass growth resumed in a conspicuously patchy manner. Cores were taken from patches where growth had resumed and were paired with cores from adjacent areas where growth was not conspicuous. The reactive phosphorus extracted from the cores of the two groups was different (Table 6). Much greater phosphorus concentrations were given up by the soils supporting renewed grass growth. The patches of good growth were usually between 0.3 and $1.5m^2$ in extent, sometimes situated in hollows but often on convex slopes. The patchiness could be due to patchy application of fertiliser—the topography of the catchment would prevent even

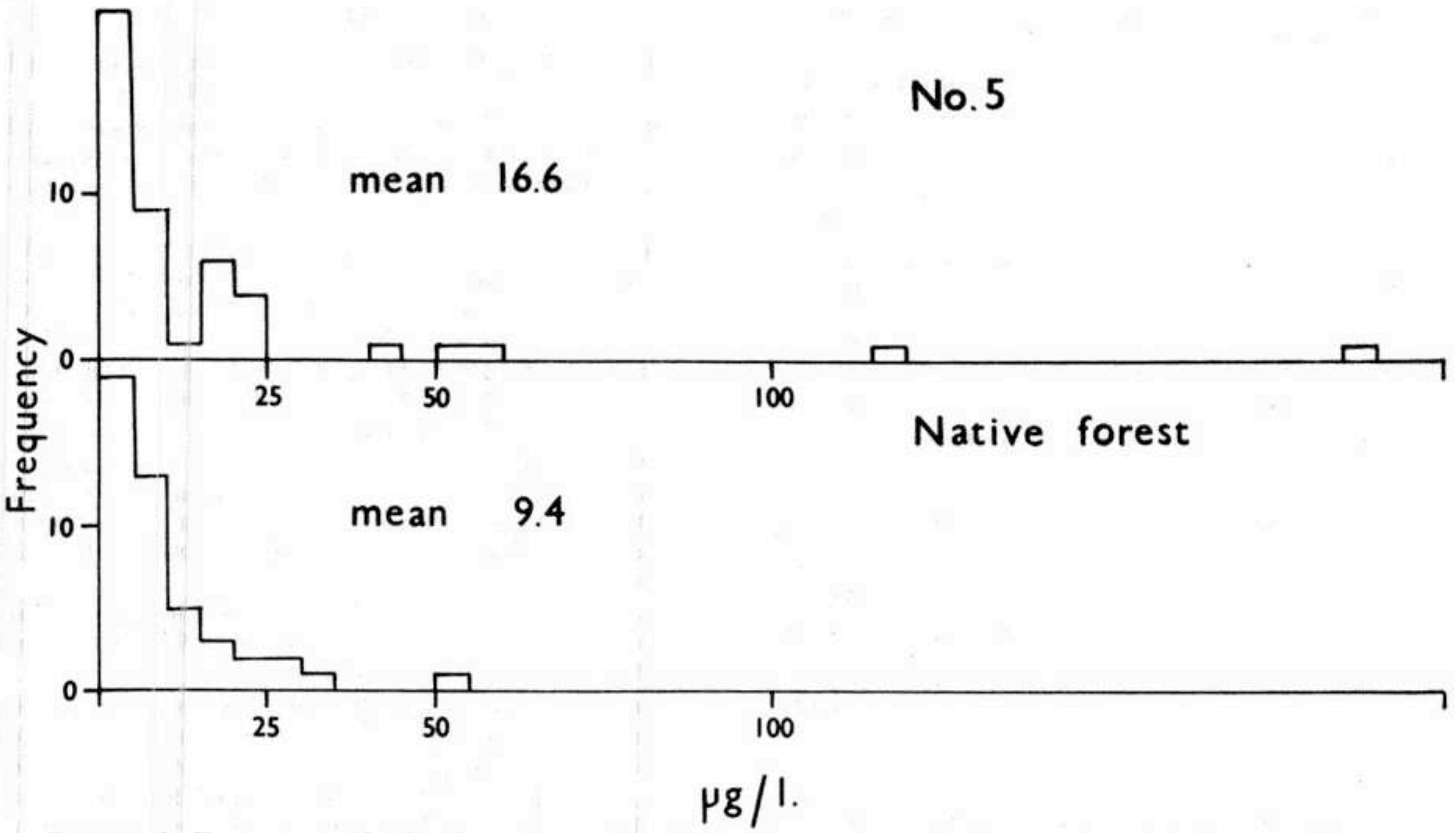


FIGURE 6. *Frequency distribution of reactive phosphorus concentrations extracted from soil cores taken from the number five and native forest catchments (µg/l)*

application. Alternatively, it could be caused by dung or urine patches. For the most part the net effect of grazing and resting behaviour of sheep is likely to result in further aggregation of nutrient phosphorus by way of urination and defæcation.

TABLE 6. *Readily available reactive phosphorus concentrations obtained from soils which had produced 'good' grass growth and 'poor' grass growth in the absence of grazing*

'Good' grass growth reactive P in extract (µg/1)	'Poor' grass growth reactive P in extract (µg/1)
225.2	53.5
222.2	73.5
95.7	46.0
260.1	18.3
44.4	18.5
74.1	26.3
28.8	14.4

Phosphorus added as superphosphate fertiliser at the rate of 3 cwt/acre/year approximates to 35-40 kg/ha/annum. Martin and Mulloy (1971) estimate that land carrying five sheep to the acre (*ca.* 12.5 sheep/ha) has returned to it in dung 35 kg/ha/annum of inorganic phosphorus together with 6 kg/ha/annum of organic phosphorus. The annual contribution of phosphorus from the urine of five sheep on an acre is negligible, amounting perhaps to one thousandth of the contribution from dung, but it, like the inorganic phosphorus in dung, will be readily available as a plant nutrient or for solution in run-off with heavy rain.

CONCLUSIONS

The conclusions which can be drawn from this work are limited and a number of loose ends remain. Nevertheless reactive phosphorus leaves the number five catchment at between 2 and 3.5 times the rate at which reactive phosphorus leaves the forested catchments. The reasons for these differences must be associated largely with catchment factors rather than with variations in meteorology, pedology and geology. Obvious features which separate number five from the forested catchments are:— (1) it is partially under grass; (2) it is topdressed regularly; and (3) it carries sheep. It has not been possible to proportion responsibility for the additional phosphorus loss among these three factors as yet, but the situation seems amenable to resolution by experiment. The second phase of this work will start soon and will involve a repeat of what has been done so far, following further application of fertiliser to the number five catchment.

The most important of the loose ends requiring attention is to establish the reason for the high phosphorus concentration stream source in the number five catchment. Although it makes a negligible contribution to phosphorus losses at high flow rates, on the annual scale it is important, for about half of the stream output from these catchments takes place as low flows (Dr R. J. Jackson pers.comm.).

All of this leaves unanswered the question, "— is the additional loss of reactive phosphorus significant in speeding up the process of eutrophication?" This is another question altogether, which cannot be answered adequately by work in the Taita catchments. In a way it describes precisely the other half of the responsibilities of the Freshwater Section.

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