

LAND USE IMPACTS ON STREAMWATER NITROGEN AND PHOSPHORUS

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ABSTRACT

Nitrogen and phosphorus data were obtained monthly for 14 years for streams draining three adjacent catchments of different land use. Comparisons of concentrations between catchments showed a land-use effect for total phosphorus and dissolved reactive phosphorus in the order pasture > pine > native but this order was reversed for nitrate. No effect of land use was detected for ammonium. The catchment converted from pasture to pine near the start of the study period began to show consistent streamwater chemistry differences relative to the pasture catchment after 4 to 5 years of tree growth. The results of trend testing were difficult to interpret solely in terms of changes in land use because significant trends were found to occur in data collected from catchments with stable land use.

We conclude that long-term monitoring alone is of limited value in understanding the influence of land use on water quality and that research efforts are better directed when complementary studies on catchment processes are also conducted.

Keywords: land use; water quality; nitrogen; phosphorus; afforestation; podocarp/hardwood forest; *Pinus radiata*.

INTRODUCTION

It is generally believed that streams draining pastures have higher concentrations of the eutrophying elements nitrogen and phosphorus than streams draining undisturbed exotic and indigenous forests. There is some supportive evidence for this belief in the reviews of New Zealand data carried out by Cooke (1980) and Wilcock (1986). However, both authors acknowledged the difficulties in ascribing differences to land use alone when other factors also varied between catchments (e.g., slope, rainfall, geology). More convincing data for examining the influence of land use on streamwater chemistry can be provided from studies on neighbouring catchments in which the differences are restricted to land use. Although the Purukohukohu experimental basin was initially established to examine the hydrological consequences of land-use change (Dons 1987), advantage has been taken of the nested catchment experimental design to determine any land-use/streamwater-chemistry relationships. In this paper we report on 14 years of monthly nitrogen and phosphorus data gathered from three catchments within the Purukohukohu basin that differ in their land use.

SITE DESCRIPTION

The three study catchments (Puruwai, Purutaka, and Puruki) are within the Purukohukohu experimental basin, central North Island, New Zealand (176° 13'E, 38° 26'S). All three catchments have moderately steep topography (average slopes of 17°), possess porous soils developed from volcanic ash (Typic Vitrandepts) which overlie impermeable ignimbrite, and have annual rainfalls of about 1550 mm. The Puruwai catchment (28 ha) consists of native podocarp/mixed hardwood forest, whereas in both of the other catchments this vegetation was cleared in the 1920s and replaced with pasture grasses. The Puruki catchment (34 ha) was afforested with *Pinus radiata* D. Don in 1973 at 2000 stems/ha and progressively thinned to 550 stems/ha over the period 1979 to 1981. By 1980 the trees had reached a mean height of 11.5 m and canopy closure had occurred. Further thinning to 275 stems/ha was carried out in 26 ha of the catchment during 1983 and 1984. The Purutaka catchment is in pasture (Yorkshire fog, perennial ryegrass, and white clover) and is used year-round for grazing by cattle and sheep. This pasture catchment has a topographical area of 23 ha but it possesses a dry valley which loses water to deep seepage, making the effective catchment area 10 ha (Dons 1987). In March, the pasture catchment receives an annual topdressing of 15% potassic superphosphate at an application rate equivalent to 30 kg P/ha. The pine catchment has not received any fertiliser since afforestation occurred.

The streams in these catchments arise as clearly defined springs and are fed by further springs along their length. A dense mat of vegetation, principally floating sweet grass (*Glyceria fluitans* (L.) R. Br.), covers the stream channels in the pasture catchment and the upper reaches of the pine catchment. Vegetation is sparse in the stream channels of the lower pine catchment and the native catchment. Both the pasture catchment and pine catchment streams can cease flowing for periods during late summer whereas flow from the native catchment is perennial.

METHODS

Sampling

Streamwater samples were collected at the flow-measuring structures at the catchment outlets. Sampling began in mid-1972 and was conducted initially at 2-weekly intervals. In 1980 the sampling interval was changed to monthly. Immediately after collection, a portion of the sample was filtered (0.45 μm cellulose acetate). Both filtered and unfiltered fractions were then frozen prior to analysis.

Chemical Analysis

Frozen samples were thawed at room temperature, with the unfiltered fraction being analysed for total phosphorus (TP) and the filtered fraction being analysed for dissolved reactive phosphorus (DRP), ammonium nitrogen ($\text{NH}_4\text{-N}$), and nitrate nitrogen ($\text{NO}_3\text{-N}$). Total phosphorus was determined after persulphate digestion (Gales *et al.* 1966) to a detection limit of 4 mg/m³. Dissolved nutrients were analysed by manual methods until 1979 (APHA-AWWA-WPCF 1971) with detection limits of 4 mg DRP/m³, 5 mg $\text{NH}_4\text{-N}$ /m³, and 2 mg $\text{NO}_3\text{-N}$ /m³. Since the beginning of 1979, dissolved nutrients have been analysed by automated methods (Downes 1978a, b; Technicon Corporation 1973) with detection limits of 1 mg DRP/m³, 5 mg $\text{NH}_4\text{-N}$ /m³, and 1 mg $\text{NO}_3\text{-N}$ /m³.

Data Analysis

To avoid biasing the datasets towards the early years of collection, pre-1980 data were reduced to the same monthly intervals as post-1980 data. Results recorded as below the detection limit were assigned values of half the detection limit. The proportion of samples in any one dataset that were below the detection limits never exceeded 1%. Statistical analysis was made using SAS (1985) computer packages. Significance testing was performed to the 95% level of significance.

RESULTS

Summary of Data

Time plots of flow and streamwater chemistry are presented in Fig. 1 to 5. Several gaps in the data record occur and these resulted either from the absence of water to sample (i.e., late summer drying up of the streams in the pasture and pine catchments) or from technical failures (e.g., lost samples, analysis methods failing).

Normality testing using a modified Kolmogorov D-statistic (Stephens 1974) showed all untransformed datasets to have non-normal probability density functions and only two logarithmically transformed datasets (pasture dissolved reactive phosphorus and pasture total phosphorus) to have normal probability density functions. Summary statistics were therefore restricted to distribution-free descriptors (medians and ranges)

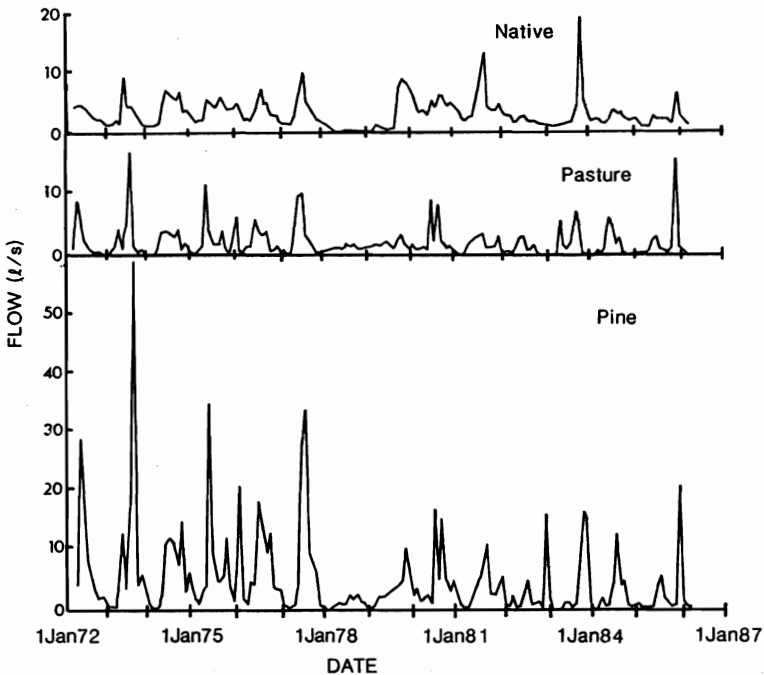


FIG. 1—Instantaneous flows recorded for the three study catchments at the time of monthly sampling.

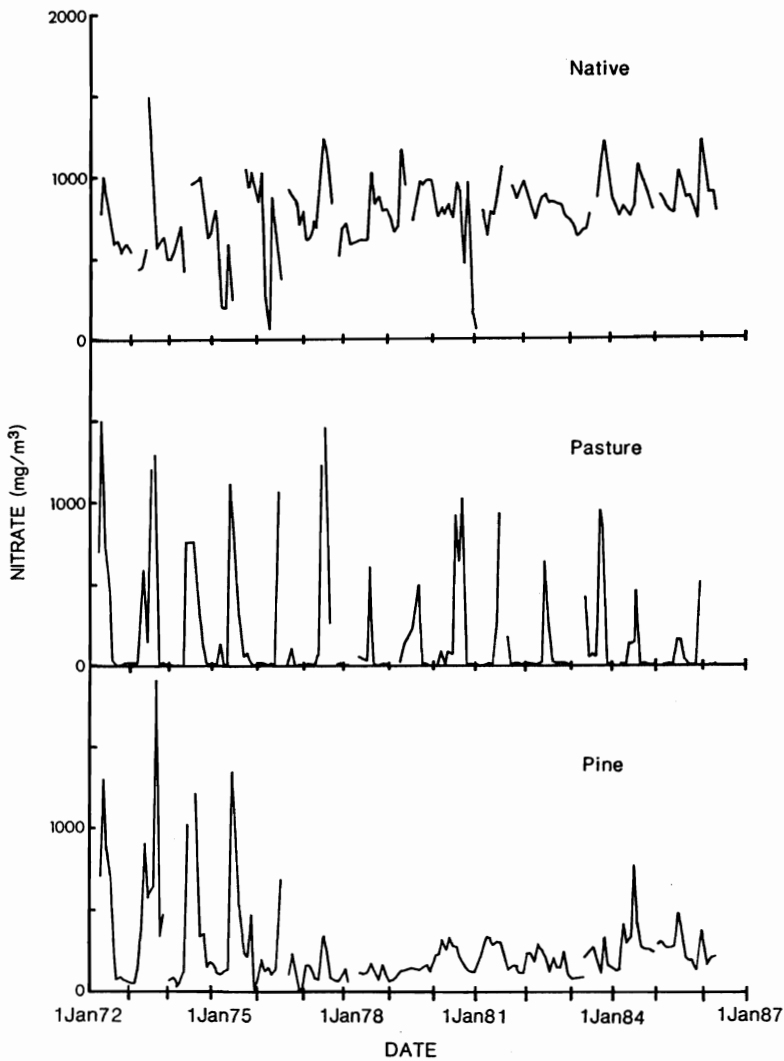


FIG. 2—Time plots of the nitrate-nitrogen concentrations found in the monthly streamwater samples collected from the three study catchments.

and comparisons between catchments were restricted to distribution-free rank methods (Table 1). Despite datasets showing the wide ranges typical of streamwater nitrogen and phosphorus data (*see* Cooke 1980), statistical testing showed significant differences between catchments for three of the four determinands. Concentrations of both total phosphorus and dissolved reactive phosphorus showed a land-use effect in the order pasture > pine > native, whereas the land-use effect was reversed for nitrate.

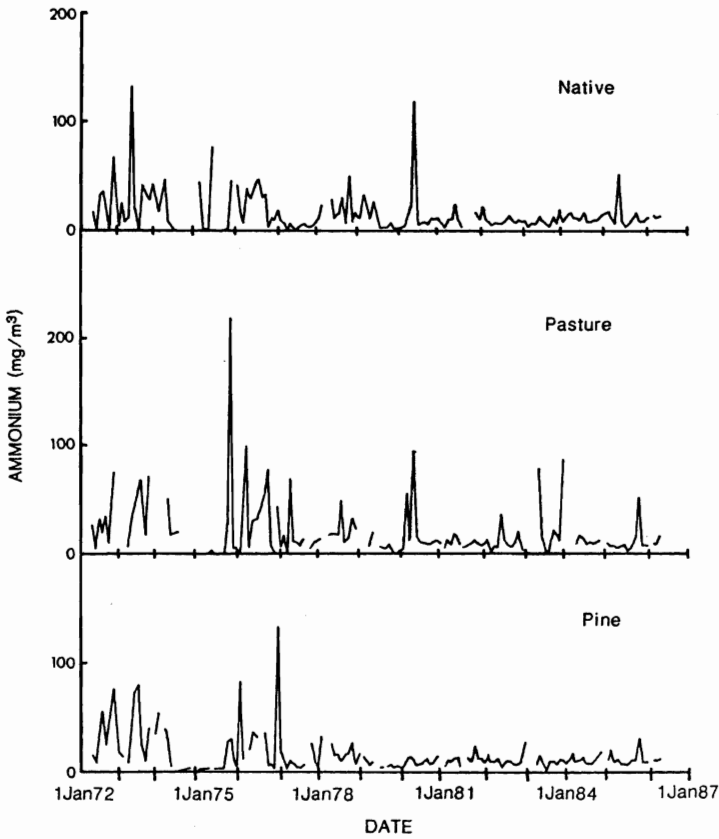


FIG. 3—Time plots of the ammonium-nitrogen concentrations found in the monthly stream-water samples collected from the three study catchments.

Flow Dependence

Streamwater chemistry often shows a dependence on flow rate (e.g., Bond 1979; Webb & Walling 1985) and therefore regressions between concentration and flow rate can be used to reduce the unexplained variance in datasets (Hirsch *et al.* 1982). Concentration-flow relations were initially tested using distribution-free Spearman rank correlations. Significant relationships between concentration and flow were found for five of the 12 datasets and their Spearman correlation coefficients are presented in Table 2. Flow-adjusted concentrations for these five datasets were derived from the log-log regressions (Table 2) by use of Equation (1),

$$\text{Flow-adjusted concentration} = C_i \times \left(\frac{\bar{Q}}{Q_i} \right)^b \quad \text{----- (1)}$$

- where C_i = measured concentration of sample i
- Q_i = flow at sampling time i
- \bar{Q} = geometric mean of all sampled flows
- and b = exponent of the regression equation.

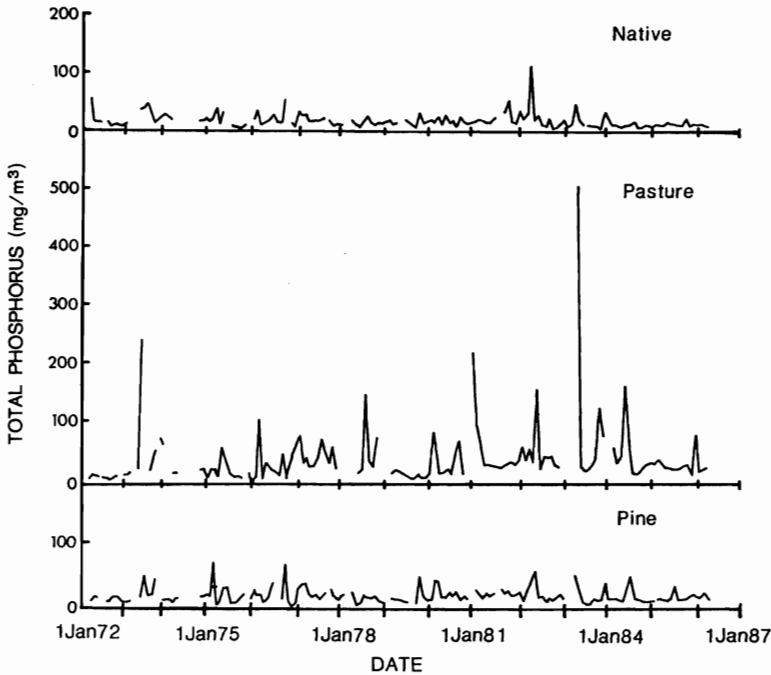


FIG. 4—Time plots of the total phosphorus concentrations found in the monthly streamwater samples collected from the three study catchments.

TABLE 1—Summary and comparison of total phosphorus (TP), dissolved reactive phosphorus (DRP), ammonium-nitrogen ($\text{NH}_4\text{-N}$), and nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentration data (mg/m^3) collected monthly from the three study catchments over the period 1972 to 1986

Determinand	Pasture	Pine	Native	Comparison*
TP median	31	18	13	PA>PI>NA
TP range	2-516	3-75	2-112	
TP n	128	143	140	
DRP median	12	8	3	PA>PI>NA
DRP range	0.5-216	0.5-28	0.5-21	
DRP n	128	144	142	
$\text{NH}_4\text{-N}$ median	12	11	10	PA≈PI≈NA
$\text{NH}_4\text{-N}$ range	2.5-217	2.5-821	2.5-133	
$\text{NH}_4\text{-N}$ n	131	143	141	
$\text{NO}_3\text{-N}$ median	13	176	805	NA>PI>PA
$\text{NO}_3\text{-N}$ range	1-1500	4-1900	69-1500	
$\text{NO}_3\text{-N}$ n	140	153	148	

* Kruskal-Wallis k-sample test on ranks to determine if differences existed followed by a comparison of mean ranks using both Duncan's Multiple Range test and Scheffe's test to determine where the differences lay ($p<0.05$).

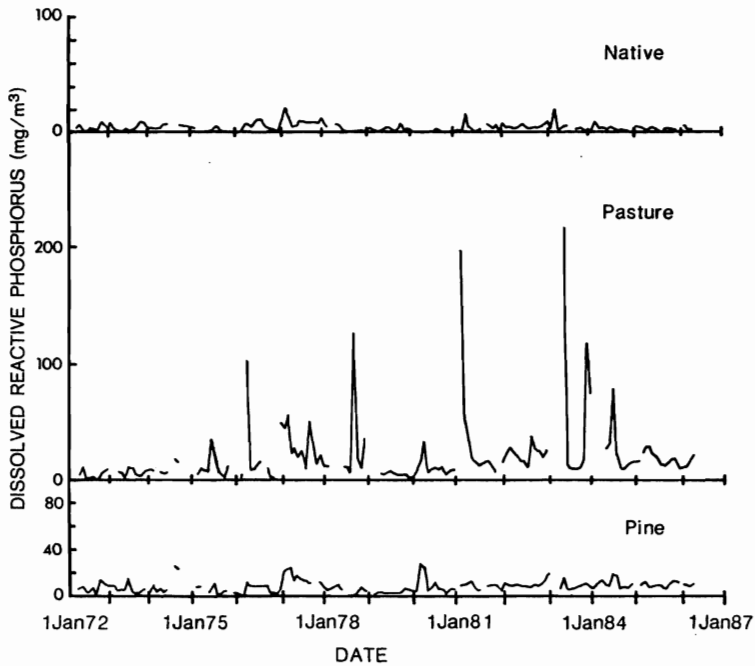


FIG. 5—Time plots of the dissolved reactive phosphorus concentrations found in the monthly streamwater samples collected from the three study catchments.

TABLE 2—Spearman rank correlation coefficients (ρ) for datasets showing a significant relationship ($p < 0.05$) between concentration and flow and the logarithmic regression equations used to derive flow-adjusted concentrations

Catchment	Determinand	Spearman's ρ	Regression equation*
Pasture	$\text{NO}_3\text{-N}$	0.624	$C = 18 Q^{1.26}$
Pasture	DRP	-0.271	$C = 15 Q^{-0.22}$
Pine	$\text{NO}_3\text{-N}$	0.321	$C = 145 Q^{0.24}$
Pine	TP	0.183	$C = 17 Q^{0.06}$
Native	$\text{NO}_3\text{-N}$	0.431	$C = 700 Q^{0.05}$

* C = concentration (mg/m^3)
Q = flow (l/s)

Although these regressions are not strictly valid because residuals were not normally distributed, the violations appeared minor. The exponents in the regression equations for pine total phosphorus and native nitrate were small and therefore flow-adjusted concentrations were little different from unadjusted concentrations. By comparison, the other three datasets showed a marked influence of flow adjustment, particularly the nitrate in both the pasture catchment and pine catchment (early years) where the extreme high values (*see* Fig. 2) were reduced by adjustment for flow effects.

Seasonality

Of the 12 datasets, the pasture nitrate and pine nitrate (particularly early years) were the only two that demonstrated seasonal effects, with winter nitrate values being highest (*see* Fig. 2). These seasonal effects were largely removed from the datasets when flow-adjusted concentrations were calculated. The dominant influence of flow (rather than season *per se*) is further evidenced by observations of high nitrate concentrations when summer flows were high (e.g., pasture nitrate of 839 mg N/m³ on November 1983 sampling) and low nitrate concentrations when winter flows were low (e.g., in both the pasture and pine catchments during the dry winter of 1978, Fig. 2).

Trends

Time series analysis was performed on the datasets (including flow-adjusted datasets) using two non-parametric trend detection methods – an extended Kendall tau test (Hirsch *et al.* 1982) and Spearman's rho test (Conover 1980). Both tests can cope with missing values and can be modified to take into account serial dependence (Lettenmaier 1976; Hirsch & Slack 1984). Serial dependence was found for datasets from both the pine catchment (nitrate, flow-adjusted nitrate, dissolved reactive phosphorus) and the native catchment (nitrate, flow-adjusted nitrate, dissolved reactive phosphorus), with each datum point being significantly related to the previous datum point (lag 1 autocorrelation coefficients (ρ) in the range 0.4 to 0.5), therefore reducing the effective sample size to about half the total sample size.

Each catchment had at least one dataset that demonstrated a significant trend with time (Table 3). The observed trends in pasture dissolved reactive phosphorus, pasture nitrate, and native nitrate occurred despite stable land-use in these catchments. This finding prevents simply relating trends in pine dissolved reactive phosphorus and nitrate to the pasture-to-pine land-use change that occurred during the study period. The decreasing trend in flow remains as the only trend that can be ascribed to afforestation.

TABLE 3—Catchment datasets that show a significant trend with time as determined by two non-parametric trend tests (modified Kendall test and a Spearman's ρ test)

Catchment	Dataset*	Trend direction†	Trend magnitude‡
Pasture	(F) DRP	+	7.0
	(F) NO ₃ -N	-	6.1
	TP	+	3.8
Pine	Flow	-	5.8
	DRP	+	3.1
	(F) NO ₃ -N	+	4.5
Native	(F) NO ₃ -N	+	2.3

* Datasets prefixed with (F) indicate flow-adjusted data.

† + = increasing trend with time, - = decreasing with time.

‡ Trend magnitude obtained from modified Kendall tau test (Hirsch *et al.* 1982) and expressed as percentage change per year compared to the median value. This does not imply a linear trend.

tion, with this trend having been more rigorously determined using the complete hydrological record (Dons 1981, 1987).

Because of the equivocal results of the trend testing, we examined the total phosphorus, dissolved reactive phosphorus, and nitrate datasets from the pasture and pine catchments more closely for effects of afforestation on water chemistry. Rank comparisons of pasture and pine datasets for each year show that the water chemistry of the catchments was not significantly different in the early years of the study but that differences began to appear after about 4 to 5 years of tree growth (Table 4). After 7 years of tree growth, water chemistry differences between the catchments were apparent every year.

TABLE 4—Rank comparisons of total phosphorus (TP), dissolved reactive phosphorus (DRP), and nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations in the pasture (PA) and pine (PI) catchments for each year of the study period

Year*	Comparison†		
	TP	DRP	$\text{NO}_3\text{-N}$
1972	PA=PI	PA=PI	PI=PA
1973	PA>PI	PA=PI	PI=PA
1974	PA=PI	PA=PI	PI=PA
1975	PA=PI	PA=PI	PI>PA
1976	PA=PI	PA=PI	PI>PA
1977	PA>PI	PA>PI	PI=PA
1978	PA>PI	PA>PI	PI>PA
1979	PA=PI	PA=PI	PI>PA
1980	PA>PI	PA>PI	PI>PA
1981	PA>PI	PA>PI	PI>PA
1982	PA>PI	PA>PI	PI>PA
1983	PA>PI	PA>PI	PI>PA
1984	PA>PI	PA>PI	PI>PA
1985	PA>PI	PA>PI	PI>PA

* Pine catchment was afforested from pasture in August 1973 and canopy closure occurred in 1979.

† Wilcoxon test at 95% level of significance.

The influence of afforestation on streamwater nitrate was of particular interest. The results of comparing whole datasets (Table 1), datasets year-by-year (Table 4), and of trend testing (Table 3) all indicate that nitrate concentrations may be expected to increase upon afforestation of pasture. This somewhat surprising result led to further data analysis. The residuals from the pine catchment's nitrate *versus* time regression show a significant decreasing trend with time (Spearman rho test), viz, the variability in nitrate concentrations decreased upon afforestation. This decrease in variability can be seen in the time plot (Fig. 2) and is a result of both significant decreases in annual maxima and increases in annual minima (Spearman rho tests). The residuals from the pine catchment's log nitrate *versus* log flow regression show a significant increasing

trend with time (Spearman rho test), viz, there has been a change through time in the relationship between concentration and flow indicating a change in the underlying processes supplying nitrate to the sampling site. Although this change in the concentration/flow relationship is likely to have occurred gradually, in line with the growth of pine trees, it is informative to examine separate nitrate/flow relationships for pre- and post-canopy closure (Equations 2 and 3);

$$\text{pre-closure nitrate} = 86Q^{0.51} \quad (r^2 = 0.53, n = 72) \quad \text{-----} \quad (2)$$

$$\text{post-closure nitrate} = 196Q^{0.04} \quad (r^2 = 0.15, n = 81) \quad \text{-----} \quad (3)$$

where nitrate is in mg $\text{NO}_3\text{-N}/\text{m}^3$ and Q is in l/s. Comparison of the exponents of Equations (2) and (3) shows that pre-closure nitrate concentrations are strongly influenced by flow whereas post-closure nitrate concentrations are only weakly influenced by flow. The regressions were significantly different from each other. By simple mathematical rearrangement of Equations (2) and (3) it can be shown that at flows less than 5.8 l/s post-closure nitrate concentrations were likely to be higher than pre-closure concentrations, whereas the reverse is true at flows greater than 5.8 l/s. Because the median flow at times of sampling was 3.3 l/s, the post-closure nitrate concentrations were, on average, higher than pre-closure concentrations.

DISCUSSION

This study has shown differences in streamwater nitrogen and phosphorus concentrations between three neighbouring catchments with different land-uses. Because of the nested catchment experimental design, we have confidence in ascribing such differences to the influence of land use. Further confidence in making such a conclusion is provided by the early years of data from the pasture and pine catchments, when both catchments were essentially in pasture and their streamwater nitrogen and phosphorus chemistry was indistinguishable (Table 4). This experimental design, incorporating both spatial and temporal controls, provides optimal power for detecting differences (Green 1979) but is rarely accomplished in catchment water-quality studies. The importance of both spatial and temporal controls can be seen from the data generated in this study. For example, if only the pine catchment data was available (i.e., no spatial control) then it may have been falsely concluded that the impact of afforestation of pasture is to increase streamwater dissolved reactive phosphorus concentrations (positive trend of Table 3). However, the existence of data from the neighbouring pasture catchment shows that there was a greater increasing trend in dissolved reactive phosphorus concentrations in the spatial control (Table 3), with the implication being that the pasture-to-pine land-use change has attenuated this rise in dissolved reactive phosphorus. The net effect has been that in later years streamwater dissolved reactive phosphorus concentrations were greater in the pasture catchment than the pine catchment (Table 4).

Although the long-term monitoring of streamwater chemistry has proved capable of detecting differences between catchments and trends through time, such data represent only a small part of the information required to form a sound understanding of the impacts of land use on water quality. Reviews by Cooke (1980) and McColl & Hughes (1981) stressed the need for research aimed at understanding the processes operating within catchments that influence the fate of nutrients and regulate their release to

receiving waters. Such an understanding is crucial because water managers are required to interpret streamwater chemistry data and to develop management strategies aimed at minimising the water-quality impacts of land-based activities.

The need for information on catchment processes is often overlooked when streamwater data confirm reasonable *a priori* hypotheses. For example, in this study streamwater dissolved reactive phosphorus and total phosphorus concentrations were higher in the pasture catchment than in the forested catchments (Table 1) and this is consistent with the input of phosphorus fertiliser to the pasture catchment. By comparison, the results presented for nitrate (Table 1) that show lowest concentrations in streamwaters draining the pasture catchment are contrary to any reasoned *a priori* hypothesis that could be proposed. Forest ecosystems are regarded as efficient nitrogen-cyclers whereas pastoral ecosystems lose nitrate via leaching from dung and urine spots (Clark & Rosswall 1981; Gandar 1982; Keeney 1986). Explaining the somewhat surprising streamwater nitrate data reported in this paper requires the use of information gathered from process studies we have conducted in the catchments (Cooper & Cooke 1984; Cooper 1986; Cooper & Thomsen 1988), the findings from which are summarised in Table 5. These studies have shown that although the leaching of nitrate to spring waters is highest in the pasture catchment, this is not reflected in the data at the catchment outlets because nitrate removal processes are most rapid in the pasture catchment's stream channel. Because the major nitrate removal process is that of plant uptake rather than denitrification (Cooper & Cooke 1984) there is only temporary removal of nitrogen, with much of this nitrogen being exported from the catchment in particulate form (as decaying plant material) during stormflows (Cooper & Thomsen 1988). The other surprising finding is the high nitrate concentrations we measured in the streamwaters draining the native forest. These concentrations are high compared to those reported for streams draining other native forests in New Zealand (Cooke 1980; Wilcock 1986) but, in the absence of detailed comparative nitrogen cycling studies within the forests, we are unable to provide an explanation.

TABLE 5—Summary of processes influencing nitrate in the Purukohukohu catchments and their consequences for streamwater nitrate

Process or consequence	Catchment			Reference
	Pasture	Pine	Native	
Process – soil nitrification	high	low	medium	Cooper (1986)
Consequence – soil NO ₃ -N	high	low	medium	Cooper (1986)
Consequence – spring NO ₃ -N	high (2500 mg/m ³)	low (600 mg/m ³)	medium (890 mg/m ³)	Cooper (1986); Cooper & Thomsen (1988)
Process – NO ₃ -N uptake in stream	extremely high	medium	low	Cooper & Cooke (1984); Cooper & Thomsen (1988)
Consequence – NO ₃ -N at catchment outlet	low (13 mg/m ³)	medium (176 mg/m ³)	high (805 mg/m ³)	This paper

The information on catchment nitrogen processes also allows us to interpret the influences of flow on nitrate concentrations that we observed in this study. At higher flows the stream channel removal processes are less able to modify nitrate levels because of shorter residence times and lower channel surface area to water volume ratios (Hoare 1979; Cooper & Cooke 1984). The consequence is that nitrate levels at the catchment outlets show a positive relationship with flow (Table 2).

The changing nitrate dynamics observed upon afforestation of Puruki can also be explained by the information gathered on catchment processes. Hoare (1979) reported that in 1973–74 nitrate concentrations in the springs of Puruki catchment averaged 2600 mg N/m³, probably reflecting the recent pastoral land use (cf. 2500 mg N/m³ found in springs of the pasture catchment by Cooper 1986). By 1982 these spring nitrate concentrations had declined to 600 mg N/m³, a result of nitrification suppression beneath the growing pine trees (Cooper 1986). This decline in incoming nitrate concentration has been offset by an apparent decrease in stream channel nitrate removal rates. Hoare (1979) estimated from 1972 data an average stream channel nitrate removal rate in Puruki of 0.38 g N/m² daily whereas it can be calculated from Cooper & Thomsen (1988) that in 1983 this removal rate averaged about 0.02 g N/m² daily. This decrease in nitrate removal rate is possibly a consequence of the increased shading that has occurred with tree growth which would decrease stream channel plant activity. Because at high flows the stream channel processes are unable to greatly alter incoming nitrate concentrations there has been a decreasing trend in annual nitrate maxima measured at the catchment outlet, reflecting the declining spring concentrations. Conversely, because stream channel processing rates have declined there has been an increasing trend in annual nitrate minima. Furthermore, because stream channel nitrate removal rates have declined, the relationship between flow and nitrate concentration at the catchment outlet has changed from being quite strong to being quite weak (Equations 2 and 3).

The long-term data presented in this paper have revealed an influence of land use on streamwater nitrogen and phosphorus. However, we also note that correct interpretation of data gathered at the catchment outlets requires an understanding of processes operating within the catchments. With the benefit of hindsight, we now question the value of using only monitoring of streamwater chemistry as a strategy for furthering our understanding of the impacts of land use on water quality. Our experiences with the Purukohukohu catchments have convinced us that long-term monitoring at catchment outlets needs to be combined with intensive studies on catchment processes if the information is to be of value to the water manager.

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