Water quality and sediment and nutrient export from New Zealand hill-land catchments of contrasting land use

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Abstract   Measurements were made of suspended sediment (SS), volatile suspended solids, dissolved organic carbon (DOC), nitrogen (N) and phosphorus (P) concentrations, turbidity, black disk visibility, pH, alkalinity, and temperature, at monthly intervals for 2–5 years on nine streams draining catchments with pasture, pine plantation, and native forest land uses. Stream flow and flow-weighted concentrations of SS, N, and P were also measured for up to 2 years from pasture, native forest, and mixed land-use catchments enabling calculation of export (kg ha^{-1} yr^{-1}). During 1996–97, export from the pasture stream was 2.5- to 7-fold higher for SS (988), total P (1.50), total Kjeldahl N (5.65), nitrate N (4.37), and ammoniacal N (0.34) than from the stream draining native forest. In contrast, export of DOC (25.5) and dissolved reactive P (DRP) (0.25) from the pasture stream were within 20% of the native stream's values. Export of SS and nutrients (except DRP) from the pasture catchment was 4- to 15-fold higher during the winters of 1995 and 1996 than winter 1997 when rainfall was half the normal level. Streams draining native forest had lower temperature, sediment, and nutrient concentrations (except DRP), and higher water clarity, than those draining pine forest and pasture. A pine/scrub stream had the highest SS and turbidity and lowest DRP, pH, and alkalinity. Pasture streams had the highest concentrations of all N species (geometric means 2- to 4-fold > native), total P, and DOC, and also showed the greatest variation in water quality attributes in relation to season and flow. The influences of land use were attributable to differences in both source materials of sediment and nutrients available for transport and changes in rates of in-stream processing.

Keywords   agriculture; plantation forestry; native forest; phosphorus; nitrate; nitrogen; dissolved organic carbon; pH; alkalinity; erosion; sediment; stream flow; temperature

INTRODUCTION

Diffuse sources of pollution from agricultural land have been identified as a major source of sediment and nutrients in surface waters in New Zealand (Smith et al. 1993a; Vant 1999) and elsewhere (Howarth et al. 1996; Jordan et al. 1997; Carpenter et al. 1998; Russell et al. 1998; Larsen et al. 1999). Increased concentrations of sediment can degrade stream habitats (Ryan 1991; Waters 1995; Wood & Armitage 1999), infill estuaries and impoundments (Jowett 1984), and reduce the aesthetic appeal of surface waters (Davies-Colley et al. 1993). Excessive nutrient concentrations may result in undesirable levels of aquatic plant growth (MFE 1992; Biggs 2000) and high nitrate concentrations can restrict use of water for drinking (Heathwaite et al. 1996). Land-use change can also alter soil water chemistry with flow-on effects for aquatic ecosystems. For example, in Denmark conifer afforestation of soils with poor buffering capacity was associated with an increased acidification of surface waters and an impoverished aquatic fauna (Friberg et al. 1998). Afforestation and deforestation have resulted in variable responses in stream carbon (C) fluxes, but little information is available on C fluxes from agricultural catchments (Hope et al. 1994). Organic C has important influences in stream energy flow (Findlay et al. 2001), contaminant binding (Haitzer et al. 1998), and optical properties (Davies-Colley et al. 1993), and its transport to the

ocean in streams is an important link in the global C cycle (Hope et al. 1994). Because of these effects, there is a need to understand the impacts of changing land use on the amounts, forms, and timing of inputs of sediment, C, and nutrients, and on influences on surface water acidity, so that appropriate management strategies can be developed to control these changes within acceptable levels.

In addition to land use, other catchment characteristics, including geology, soils, and climate, have strong influences on water yield, water quality, and nutrient and sediment exports (e.g., Close & Davies-Colley 1990; Hicks & Griffiths 1992). Therefore, these factors need to be similar for comparisons between streams in different land uses to be valid. This requirement can be met by long-term study of a catchment during land-use change or, more rapidly, by comparison with neighbouring catchments in which land use is the major difference. The latter approach has been adopted in this study, with comparison of water quality and export of sediment, dissolved organic C, nitrogen (N), and phosphorus (P) from adjacent catchments in pasture, native forest, and mixed land use. The study is part of a long-term research programme on the sustainability of agricultural practices in which the response of stream water quality and exports to changes in land use and management practices will be measured (Quinn & Cooper 1997; Quinn et al. 2001). Previous studies on water quality and sediment issues in these catchments have described historical erosion patterns (DeRose 1998), land-use effects on soil physical properties and contaminant run-off (Nguyen et al. 1998), stream water quality at baseflows in spring (Quinn et al. 1997a), water temperature in relation to shade (Rutherford et al. 1997), channel morphology (Davies-Colley 1997), hyporheic ecology (Boulton et al. 1997), response of stream microbes to variation in dissolved organic C among land uses (Findlay et al. 1997; Findlay 2001), and the role of riparian wetlands in controlling sediment and nutrient inputs to streams (Nguyen & Downes 1997a,b; Nguyen et al. 1999).

The present study was initiated to provide more detailed information on the effects of land use on biogeochemical linkages between terrestrial source areas and aquatic receptors. Specific objectives of the investigations were: (1) to determine the spatial and temporal variations in key water quality attributes in streams draining different land cover types at Whatawhata; and (2) to quantify the influence of land use and seasonal and annual hydrologic variations on the export of suspended sediment, dissolved
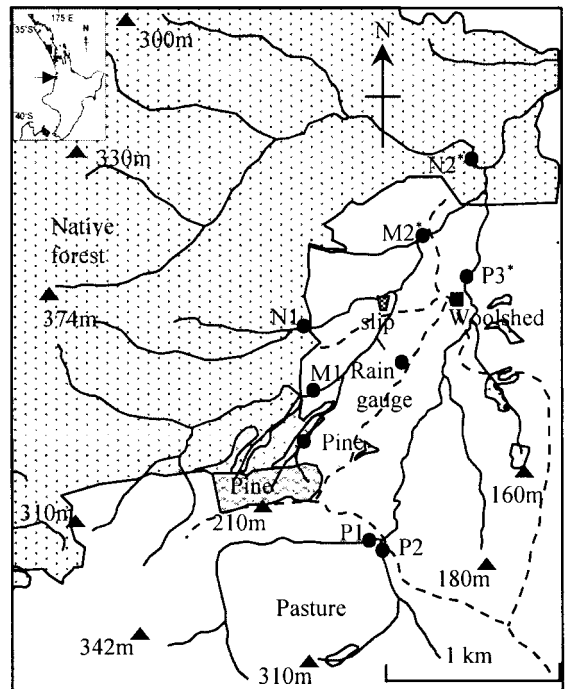
Fig. 1 Location map of sampling sites at Whatawhata Research Centre, New Zealand showing the main streams. Material export was measured using continuous sampling at three sites indicated by an asterisk. Highest points of elevation in subcatchments are shown by triangles and farm roads are shown as dashed lines.

organic C, N, and P. We hypothesised that conversion from forest to pasture will result in more pronounced seasonal trends in water quality because removal of forest cover increases the exposure of the land to erosive forces and increases seasonal growth of in-stream plants, with resulting greater in-stream uptake of nutrients. Pine afforestation of land that was formerly in pasture was predicted to reduce streamwater dissolved-nutrient concentrations, as a result of absence of fertiliser application and less mobilisation by grazing animals, and to reduce pH and alkalinity because of acid leachate from pine litter.

METHODS

Study site

All streams in this study are tributaries of Mangaotama Stream. They are within 3.5 km of each other at the Whatawhata Research Centre and the adjacent native (podocarp-hardwood) forest reserve,

along the Hakarimata Range, west of Hamilton (175°15′E, 37°47′S) on the North Island of New Zealand (Fig. 1; Table 1). Annual rainfall of 1600 mm is reasonably distributed throughout the year, but tends to be lower in summer and early autumn (January–March) than winter months (June–August) (Smith et al. 1993b). Mean air temperature is 13.7°C, and mean solar radiation is 11.2 MJ m^{-2} day^{-1} (Smith et al. 1993b). The area is dominated by steep (>30°) to hilly (17–20°) topography, with parent rocks of sedimentary sandstones and siltstones (greywacke and argillite) laid down in the Mesozoic upon which have developed yellow brown earth soils (Kaawa hill soil, an Ochreptic Hapludult, and the Waingaro steepland soil, an Umbric Dystrochrept). Patches of overlying volcanic ash remain in less steep parts of the catchments and these have formed yellow brown loam soils (Dunmore silt loam, a Typic Hapludand). The valleys are mainly "v"-shaped, but narrow floodplains occur in the valley bottoms along the mainstem reaches. Headwater streams in pasture often start as small valley bottom wetlands, unless the slope is too steep to allow wetland soils to persist or the valley bottoms are shaded by riparian vegetation.

The pasture area was converted from native forest c. 75 years ago and is intensively stocked (13 stock units ha^{-1}) with sheep and cattle (2.3:1 ratio as stock units) (Peter Moore, AgResearch pers. comm.), and vegetated with clover and pasture grasses. The catchment of the "Pine" site was also converted from native forest to pasture c. 75 years ago, and planted with *Pinus radiata* in 1971. The sampling site was located in a downstream area of regenerating native forest below the confluence of two tributaries with pine plantation headwaters that comprise 55% of the upstream catchment area. The lower part of the Pine stream catchment was pasture, grazed intensively by

cattle during winter, before being fenced off and retired from grazing for native forest to regenerate naturally within 2 years of the pine forest planting (Peter Moore, AgResearch pers. comm.). The upper, pine-afforested parts of this catchment were grazed as an agroforestry system by sheep from Years 2–7 after pine planting and then by sheep and cattle (Peter Moore, AgResearch pers. comm.). This maintained low pasture cover beneath the pines. The native forest catchments of sites N1 and N2 have podocarp-hardwood forest cover dominated by tawa (*Beilschmiedia tawa*), rewarewa (*Knightia excelsa*), and rimu (*Dacrydium cupressinum*), with tanekaha (*Phyllocladus trichomanoides*) and kahikatea (*Dacrycarpus dacrydioides*) also common canopy trees. The native forest cover has persisted since before human settlement but the areas were used for "over-winter grazing" by cattle until the early 1980s (Peter Moore, AgResearch pers. comm.).

The lower mixed catchment site (M2) was 400 m down stream of a large (c. 0.41 ha) landslide (Fig. 1) that formed in July 1995 and has continued to expand and erode since then. A woolshed and stockyards drain into the pasture catchment just above P3 (Fig. 1).

The roads through the study area are unsealed gravel and probably carry more traffic than normal farm roads, because of the research function of the site, particularly the main access road that runs along the eastern ridge of the pasture catchment to the woolshed and crosses culverts over a tributary and the mainstem upstream of the lower pasture site (P3, Fig. 1). A less used road crosses a culvert over the Kiripaka above M2. No roads are located where they are likely to result in run-off above the remaining sites (Fig. 1). The most frequent traffic is two and four-wheeled motorbikes used by farm staff, with less frequent car and light utility vehicle traffic.

Table 1 Summary of site information.

Land use	Site code	Synonyms	Map ref. S14	Catchment area (km^2)
Native forest	N1	NKL	919776	0.52
Native forest	N2	NW5	926785	3.00
Pasture	P1	PW2	923764	0.95
Pasture	P2	PW3	924763	0.49
Pasture	P3	PW5	928777	2.59
Pine/scrub[*]	Pine	Pine	921772	0.11
Mixed[†]	M1	NKR	920772	1.31
Mixed[‡]	M2	DB4	926780	2.66

[*]55% pine + 45% regenerating scrub/forest. [†]69% native forest + 28% pasture + 3% pine. [‡]55% native forest + 41% pasture + 4% pine.

Phosphorus fertiliser application to pasture occurs as an 80/20 mix of reactive phosphatic rock and sulphur (S) super 30 giving 20.7 kg P ha^{-1} yr^{-1} and 12.6 kg S ha^{-1} yr^{-1}. This was applied, by fixed-wing aircraft, during March in 1995 and 1996, May–June in 1997, and May in 1999, with no fertiliser applied in 1998 (Bill Carlson, AgResearch pers. comm.). Studies at a site 50 km east of the study area indicate that atmospheric deposition is likely to contribute c. 0.8 kg P ha^{-1} yr^{-1} (Cooke 1988) and 6 kg N ha^{-1} yr^{-1} (Cooke & Cooper 1988). No artificial N fertiliser is applied but symbiotic N fixation by forage legumes, is expected to be up to 55–85 kg N ha^{-1} yr^{-1} (Ledgard et al. 1987). The pine plantation has not received any fertiliser for at least the last 20 years and probably not since pines were planted in 1971 (Bill Carlson, AgResearch pers. comm.).

Stream flows were monitored continuously at three of the lower catchment sites (P3, M2, and N2, Fig. 1) as part of the National Hydrometric Network (http://www.niwa.cri.nz/rc/prog/database/). Float operated systems recorded water levels at 15-min intervals on Campbell CR10 data-loggers. Downstream control of water levels was provided by a crump weir at M2 and natural bedrock ledges above waterfalls at P3 and M2. A box flume was installed at P3 to increase the sensitivity of low-flow measurements. There were no gaps in the flow records for P3 during the study period, nor for N2 or M2 during the exports calculation period (August 1995–August 1997). Gaps at other times in 1995–99 (3% of period at M2 and 8% at N2) were patched using a spatial interpolation approach based on the P3 flow duration curve (Hughes & Smakhtin 1996). The specific flows (l km^{-2} s^{-1}) measured at the three weirs at the times of water sampling were used to estimate flows at the upstream sampling sites without weirs (P1, P2, Pine, M1, and N1) to investigate the effects of state of flow on water quality during the monthly and storm samplings.

Sample collection and analysis

Land-use effects on water quality were investigated by collecting grab water samples in acid-washed polyethylene bottles and measuring horizontal black disk visibility (Davies-Colley 1993) at one pine site, three pasture sites, two native forest sites, and two mixed catchment sites (Table 1; Fig. 1) at monthly intervals from April 1995 until August 1999. Samples were stored on ice and refrigerated overnight before analysis for turbidity (Hach 2100A meter), suspended solids (SS) (GF/C filtration and 24 h at 105°C, APHA 1998), volatile SS (VSS) (GF/

C filtration, drying 24 h at 105°C and combustion 6 h at 400°C), alkalinity (as CaCO$_3$), pH (Radiometer 26 meter), and conductivity (Radiometer CDM83 meter). A fraction was filtered through a 0.45 μm membrane before analysis for: dissolved organic C (DOC) (Shimadzu 5000A TOC analyser), dissolved reactive P (DRP) (automated molybdenum blue/ascorbic acid (APHA 1998)), total P (TP) (acid persulphate digestion followed by molybdenum blue colorimetry (APHA 1998)), ammonium N (NH$_4$-N) (automated phenol/hypochlorite colorimetry method), nitrate N (NO$_3$-N) (cadmium column reduction of NO$_3$ to NO$_2$, then diazotization with sulphanilamide and NEDDE and NO$_2$-N subtracted from NO$_3$-N (APHA 1998)), and total Kjeldahl N (TKN) (acid digestion followed by indophenol blue colorimetry (APHA 1998)). Total N (TN) was estimated as the sum of NO$_3$-N and TKN.

Export calculations

Sediment, C, and nutrient exports were measured using automatic samplers (Manning Model 4901) at three adjacent c. 3 km^2 catchments draining pasture (Mangaotama = P3, July 1995–July 1997), native forest (Whakakai = N2, September 1995–July 1997), and a mixed land use (Kiripaka = M2, July 1995–July 1997) (Fig. 1). Automatic samplers collected stream water at 4.5-h intervals into acid-washed polyethylene bottles containing mercuric chloride preservative, with eight samples combined in each bottle. The bottles were collected at monthly intervals and combined in proportion to the flow recorded at the site during the filling of each bottle to make a single sample for the month. These samples were analysed for SS, DOC, TP, DRP, TKN, NH$_4$-N, and NO$_3$-N, using the methods described above except that DOC was analysed by the Institute of Environmental Science and Research, Gracefield, using the method of APHA (1998). The flow record at each sampling site was processed using the TIDEDA program (Thompson & Wrigley 1976) and rating current at July 1999. The concentration of each composite sample was multiplied by the volume of water that passed the site over the sample collection period. The resulting exports were summed and averaged to give seasonal and annual exports. For times when no samples were taken, because of equipment failure, exports were estimated from least squares regression relationships between the logarithm of average flow for the sampling interval (litres s^{-1}) and the logarithm of nutrient or sediment mass per unit time (data log transformed to satisfy

normality requirements of regression analysis). A correction factor was applied (Ferguson 1987) to eliminate the underestimation bias resulting from using geometric mean prediction rather than arithmetic mean prediction. The variances (adjusted r^2 values) explained by these relationships between flows and exports for N2, M2, and P3, respectively, were: 45, 68, and 86% for SS; 51, 79, and 64% for DOC; 82, 70, and 89% for TP; 82, 48, and 69% for DRP; 56, 91, and 84% for TKN; 90, 93, and 94% for NO_3-N; and 63, 58, and 62% for NH_4-N.

Seasonal trend analysis was carried out on flow-adjusted data in a two-step process (after Smith et al. 1996) to avoid the effects of flow masking underlying seasonal influences. First, for each determinant and site, raw data from monthly grab samples were plotted against specific flow and LOWESS (locally weighted regression scatterplot smoothing (Cleveland 1979)) smoothed using Data Desk™ (Velleman 1992) with a 30% span. The seasonal trends were then investigated by regressing the adjusted residuals (raw datum–smoothed datum for the flow on that occasion at the sample site (for weirs) or the downstream weir) against the number of days from mid winter (15 July, being the middle day of the coolest month from long-term air temperature data at Whatawhata (Smith et al. 1993b)) to the sampling date. Seasonal effects were inferred if the regression coefficient of these flow-adjusted residuals against time since mid winter was statistically significant ($P < 0.05$).

RESULTS

## Correlations between water quality variables

The correlations between the water quality variables measured during the regular monthly samplings at all the stream sites combined are shown in Table 2. As expected, very strong relationships occurred between the optical/sediment variables (i.e., SS, black disk, and turbidity), and between volatile and total SS ($r > 0.73$ for individual data and $r > 0.88$ for site means). The measures of TKN and DOC were also strongly correlated.

Alkalinity, conductivity, and pH were strongly correlated with each other ($r = 0.50$ to 0.83 for individual data) and with stream flow ($r = -0.56$ to -0.82 for individual data). Flow was also correlated to the optical variables and nitrate for all individual observations.

Increasing conductivity is sometimes used as an indicator of increasing nutrient enrichment of waters, but in this data set conductivity gave mixed signals being negatively correlated with N species and positively correlated with DRP.

Table 2 Interrelationships between water quality variables at eight Whatawhata, New Zealand, stream sites. Specific flow and water quality attributes were log-transformed except for dissolved reactive phosphorus (square root transformed), alkalinity, and pH (not transformed). Relationships between individual data points and mean site values (excluding storm samples) are shown in the bottom and top sectors of the table respectively. Values in bold and italics are statistically significant at $P < 0.0001$, and those in italics only are statistically significant at $P < 0.05$ ($n = 266$–526 for individual pairs and $n = 8$ for site means). (Turb. = turbidity; BD = black disk, SS = suspended solids, VSS = volatile SS, TKN = total Kjeldahl nitrogen; TP = total phosphorus; DRP = dissolved reactive phosphorus; DOC = dissolved organic carbon; EC = electrical conductivity; Alk. = alkalinity; SQ = specific flow (litres s^{-1} km^{-2}).)

|	Turb.	BD	SS	VSS	TKN	NO_3-N	NH_4-N	TP	DRP	DOC	pH	EC	Alk.
Turb.		*−0.92*	*0.89*	*0.76*	0.42	0.29	0.41	−0.19	−0.62	0.32	−0.68	−0.40	*−0.84*
BD	***−0.86***		*−0.97*	*−0.90*	*−0.70*	*−0.59*	*−0.67*	−0.02	0.53	−0.49	0.50	0.63	*0.85*
SS	***0.88***	***−0.74***		*0.95*	*0.78*	*0.60*	*0.76*	0.10	−0.56	0.62	−0.48	−0.70	*−0.85*
VSS	***0.61***	***−0.56***	***0.79***		*0.83*	*0.73*	*0.84*	0.24	−0.41	0.65	−0.45	−0.70	*−0.79*
TKN	***0.65***	***−0.54***	***0.65***	***0.49***		*0.81*	*0.99*	0.32	−0.37	*0.86*	−0.08	*−0.91*	*−0.62*
NO_3-N	***0.26***	***−0.32***	***0.38***	***0.27***	***0.27***		*0.77*	0.58	0.07	0.52	0.07	−0.53	−0.32
NH_4-N	***0.21***	***−0.30***	***0.35***	***0.24***	***0.40***	***0.37***		0.29	−0.40	*0.90*	−0.15	*−0.92*	−0.64
TP	***0.58***	***−0.43***	***0.54***	***0.43***	***0.60***	*0.14*	***0.20***		*0.71*	−0.03	0.64	0.00	0.39
DRP	***−0.22***	***0.20***	***−0.25***	*−0.17*	−0.06	−0.07	*−0.10*	***0.45***		−0.63	0.73	0.63	0.86
DOC	***0.33***	***−0.33***	***0.21***	0.04	***0.50***	***−0.21***	0.06	***0.37***	−0.10		−0.27	*−0.93*	−0.67
pH	***−0.63***	***0.48***	***−0.53***	***−0.37***	***−0.25***	***−0.32***	***−0.20***	−0.03	***0.42***	0.02		0.20	*0.78*
EC	***−0.42***	***0.49***	***−0.51***	***−0.39***	***−0.42***	***−0.51***	***−0.28***	0.01	−0.05	***0.50***	***0.50***		*0.72*
Alk.	***−0.64***	***0.52***	***−0.60***	***−0.47***	*−0.16*	***−0.52***	***−0.37***	*−0.12*	***0.44***	0.10	***0.72***	***0.83***	
SQ	***0.67***	***−0.48***	***0.62***	***0.28***	***0.27***	***0.51***	***0.21***	0.10	***−0.28***	−0.06	***−0.56***	***−0.74***	***−0.82***
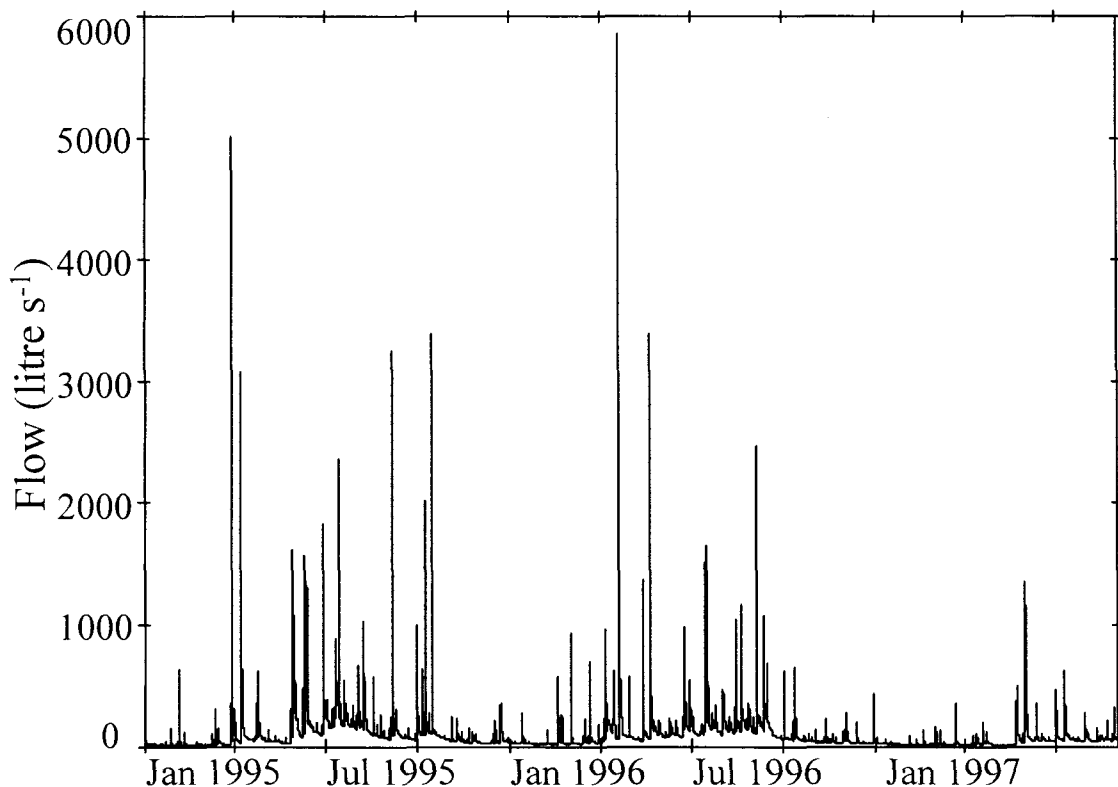
Fig. 2 Hydrograph at P3 sampling site from January 1995 to August 1997 showing the lower winter flows in 1997 than the two previous years.

Land-use effects on water yield and sediment and nutrient exports

Average annual run-off for the period 1995–99 inclusive was 1026, 978, and 962 mm for the pasture, mixed, and native forest catchments, respectively, compared with mean annual rainfall of 1720 mm (range = 1385 in 1997 to 2021 in 1996) on a mid-catchment ridge between the pasture and mixed catchments (Fig. 1). Run-off was considerably higher from all land uses in winter 1995 to spring 1996 than in summer 1996/97 to winter 1997, reflecting the lower rainfall during the latter period (Fig. 2 and 3A). As expected, water yield as a proportion of rainfall was highest in winter and spring, least in summer, and intermediate in autumn (Fig. 3A). For example, run-off at the pasture stream (P3) weir averaged 78% of rainfall in winter, 76% in spring, 47% in autumn, and 37% in summer (Fig 3A). The 7-day moving average low flows for 1995–99 were 4.82, 4.39, and 5.66 $l\ s^{-1}\ km^{-2}$ for the pasture, mixed, and native forest catchments, respectively.

Annual average sediment and nutrient exports from the pasture catchment at P3 are summarised in Table 3 for a wet year, from 23 August 1995 to 23 August 1996 (rainfall = 1891 mm yr^{-1} cf. 1995–99 mean of 1720 mm yr^{-1}), and a dry year, from 23 August 1996 to 23 August 1997 (rainfall = 1380 mm yr^{-1}). These may be underestimates of actual exports, because collection of samples at 4.5-h intervals probably under-sampled peak flows and we could not account for flow variations during the 36 h taken to fill each bottle. Exports from the mixed land use (Site M2) and native forest (Site N2) catchments during the dry period are also presented and compared with those from the Toenepi dairy pasture catchment in the Waikato lowlands 45 km east of Whatawhata, pasture and native forest hill-land at Purukohukohu 120 km south-east of Whatawhata, and a range of other New Zealand catchments.

During the wet year the pasture catchment exported 2.2- to 3.2-fold more SS, TP, NH_4-N, NO_3-N, TKN, and TN than during the dry year, and
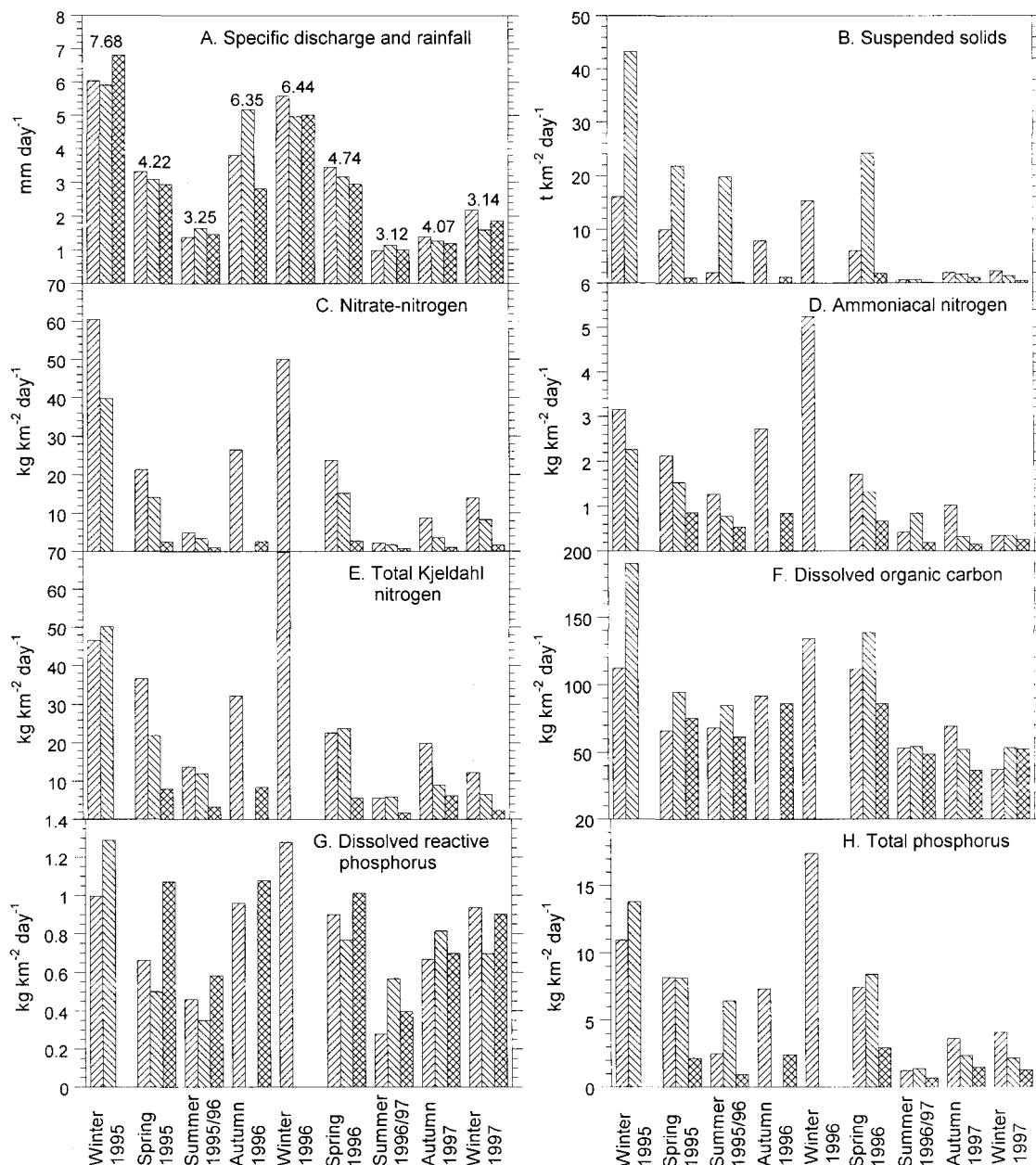
Fig. 3 Comparison of seasonal average loads of water, sediment, and nutrients from catchments with pasture (Site P3, upward sloping hatched bars), mixed (Site M2, pasture, pine, and native forest, downward sloping hatched bars), and native forest (Site N2, cross-hatched bars) land uses at Whatawhata Research Centre from winter 1995 to winter 1997. Seasons defined as: winter, June–August; spring, September–November; summer, December–February; and autumn, March–May. Note a later start time and equipment failures resulted in no data (other than discharge) from mixed site (M2) in autumn and winter 1996 and the native forest stream (N2) in winter 1995 and winter 1996. Average seasonal rainfall (mm day^{-1}) at a mid-catchment rain gauge (Fig. 1) is shown as numerals in Fig. 3A.

dissolved reactive P and DOC were 24 and 31% higher during the wet year (Table 3).

Exports of total P and all forms of N in 1996–97 were 2.5- to 7.7-fold higher from the wholly pasture catchment than the native catchment, with the mixed catchment intermediate. Sediment export was greatest in the mixed catchment that received ongoing erosion from a large (area c. 0.41 ha) landslide that formed in July 1995 and has continued to expand and erode during the study period. The mean SS also increased 6- to 9-fold between the sites upstream (N1 and M1) and Site M2 downstream of the slip input to Kiripaka Stream (Table 3). Sediment yields from the wholly pasture catchment were 3-fold higher than from the native forest catchment, but dissolved organic carbon export was only 20% higher and DRP export was similar from all catchments.

Seasonal patterns of average specific yield of water, sediment, dissolved organic carbon, and N and P species for the period from winter 1995 to winter 1997 are shown for the pasture, native forest, and mixed land-use catchments in Fig. 3. There was considerable variation, between seasons, and years, in average seasonal discharge and exports of suspended sediment and nutrients. The variations in relative exports of sediment and nutrients between land uses reflected the annual patterns discussed above. Specific discharge and exports were typically greatest in winter and least in summer, but exports were consistently lower in autumn and winter of 1997 than in winter of 1995 and autumn and winter of 1996, reflecting the lower rainfall in 1997 (Fig. 3A). The difference in exports between the dry winter of 1997, when rainfall was about half of normal, and the more typical winters of 1995 and 1996 were greatest for ammoniacal N (15-fold higher at P3 in winter 1996; Fig. 3D), followed by suspended sediment (7-fold higher at P3 in winter 1996; Fig. 3B), and total Kjeldahl N (6-fold higher at P3 in winter 1996; Fig. 3E). Exports of nitrate, TP, and DOC were c. 4-fold higher in the wetter winters of 1995 and 1996 than in 1997 (Fig. 3C,H,F, respectively). DRP export was c. 4-fold higher in winter than summer but differences in flow between different winters had little influence (Fig. 3G).

## Influences of land use, flow, and season on water quality

The effects of land use (pasture, pine, and native forest), season, and flow on water quality attributes are illustrated for a pasture, a pine, and a native forest site in Fig. 4. Land-use effects were investigated by comparing the monthly monitoring results from the two upstream pasture sites (P1 and P2), the pine site, and the two native forest sites (N1 and N2). Alkalinity, pH, and VSS comparisons used data from 30 occasions between April 1995 and September 1997. DOC, turbidity, and conductivity comparisons used data from 45 occasions between April 1995 and August 1999 (gap between August 1997 and August

Fig. 4 Time-series of dissolved organic carbon (DOC), suspended sediment (SS); dissolved reactive phosphorus (DRP); total phosphorus (TP); total Kjeldahl nitrogen (TKN); nitrate nitrogen (NO_3-N); total ammoniacal nitrogen (NH_4-N); and pH at pasture (P3, squares); pine (triangles); and native forest (N2, diamonds) streams at Whatawhata, Waikato, New Zealand, April 1995–July 1997.

Table 3 Land-use effects on exports (kg ha^{-1} yr^{-1}) of sediment and nutrient from adjacent catchments at Whatawhata Research Centre, Waikato, New Zealand, averaged for the periods 23 August 1995–23 August 1996 (a wet year) and 23 August 1996–23 August 1997 (a dry year), compared with data for other mixed-grazing pasture catchments. (SS = suspended solids; DRP = dissolved reactive phosphorus; TP = total phosphorus; NH_4-N = total ammoniacal nitrogen; NO_3-N = nitrate nitrogen; TKN = total Kjeldahl nitrogen; TN = total nitrogen; DOC = dissolved organic carbon.)

Land use (site code)	SS	DRP	TP	NH_4-N	NO_3-N	TKN	TN	DOC
Pasture (P3) 1995–96	3212	0.31	3.24	1.04	9.40	13.94	23.24	33.4
Pasture (P3) 1996–97	988	0.25	1.50	0.34	4.37	5.65	10.02	25.5
Mixed (M2) 1996–97	2632	0.26	1.33	0.26	2.55	4.21	6.76	27.4
Native (N2) 1996–97	320	0.27	0.58	0.12	0.55	1.52	2.07	20.2
New Zealand pasture*	600–2000	0.04–0.3	0.3–1.7	0–0.30	1–5	–	4–19	–
Toenepi dairy pasture†	142	0.54	1.16	1.08	29.3	5.55	35.3	–
Purukohukohu pasture‡§	22	0.37	1.67	0.48	1.19	10.76	11.95	–
Purukohukohu native forest‡§	27	0.017	0.12	0.056	2.84	0.83	3.67	–

*Wilcock (1986) and Vant (1999). †Wilcock et al. (1999). ‡Dons (1987). §Cooper & Thomsen (1988).
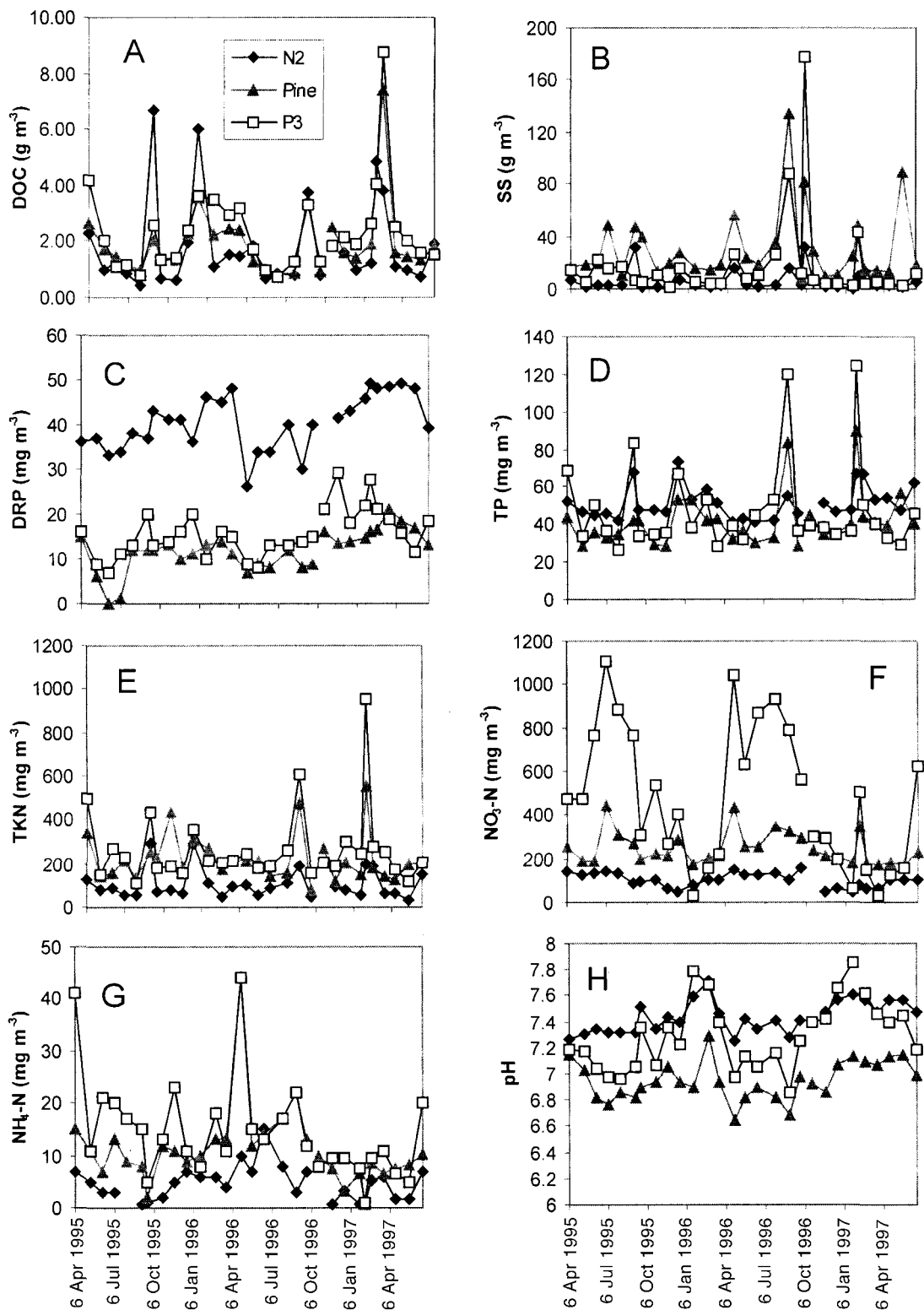
Table 4 Summary of water quality results for seven sites of contrasting land use at Whatawhata Research Centre, New Zealand, April 1995–August 1999. (AM = arithmetic mean; SS = suspended solids; VSS = volatile SS; Turb. = turbidity; BD = black disk; DRP = dissolved reactive phosphorus; TP = total phosphorus; NH_4-N = total ammoniacal nitrogen; NO_3-N = nitrate nitrogen; TKN = total Kjeldahl nitrogen; TN = total nitrogen; Alk. = alkalinity; EC = electrical conductivity; DOC = dissolved organic carbon.)

Parameter and land use	Site	AM	Median	Min.	Max.	N	Parameter	AM	Median	Min.	Max.	N
VSS (g m⁻³)							**SS (g m⁻³)**					
Native	N1	1.2	0.9	0.2	4.3	33		8.8	5.0	2.0	64.5	54
Native	N2	0.9	0.6	0.2	4.2	32		6.9	2.9	0.4	24.0	54
Pasture	P1	2.2	1.2	0.2	11.2	33		40.3	9.6	2.7	1270.0	54
Pasture	P2	2.3	2.1	0.2	8.4	33		20.6	9.3	2.3	365.0	54
Pasture	P3	1.8	1.1	0.2	8.8	33		26.9	6.2	2.0	722.0	54
Pine	Pine	2.9	1.9	0.2	9.0	33		29.6	18.2	5.7	191.0	54
Mixed	M1	1.5	0.9	0.2	10.0	33		13.2	7.1	2.1	147.0	54
Mixed	M2	4.7	1.1	0.2	57.0	33		82.4	7.6	2.5	1392.0	54
Turb. (NTU)							**BD (m)**					
Native	N1	12.4	10.2	5.5	55.1	45		0.66	0.67	0.16	1.08	53
Native	N2	8.4	6.2	2.6	28.0	44		1.01	0.97	0.27	2.21	50
Pasture	P1	17.5	10.9	3.0	80.9	45		0.50	0.47	0.17	1.08	53
Pasture	P2	12.7	8.8	2.3	39.1	45		0.56	0.53	0.17	1.00	53
Pasture	P3	13.8	9.5	4.0	95.5	45		0.66	0.67	0.10	1.56	53
Pine	Pine	28.9	23.6	8.6	116.0	45		0.40	0.38	0.08	0.75	32
Mixed	M1	15.0	10.6	6.0	116.0	45		0.57	0.57	0.11	1.15	53
Mixed	M2	50.4	10.5	3.8	756.0	45		0.59	0.56	0.02	1.35	53
DRP (mg m⁻³)							**TP (mg m⁻³)**					
Native	N1	17.6	16.0	4.4	45.0	54		33.7	31.0	17.0	67.5	54
Native	N2	38.3	40.0	7.6	54.0	53		53.5	49.0	32.0	116.0	53
Pasture	P1	20.4	20.0	4.2	43.1	54		58.6	46.5	26.0	388.0	54
Pasture	P2	29.5	29.0	5.7	45.2	54		67.0	62.0	33.0	224.0	54
Pasture	P3	13.7	13.0	2.1	29.0	53		45.7	38.0	21.0	136.0	53
Pine	Pine	11.0	11.2	0.0	21.0	54		42.8	39.5	16.0	151.0	54
Mixed	M1	38.2	40.2	11.8	71.0	54		58.6	56.0	34.0	127.0	54
Mixed	M2	26.3	26.7	3.0	54.7	54		76.5	46.0	26.0	629.0	54
NO₃-N (mg m⁻³)							**NH₄-N (mg m⁻³)**					
Native	N1	121	117	71	193	50		6.2	4.7	0.5	36.5	54
Native	N2	99	101	46	158	53		5.0	3.1	0.5	51.4	52
Pasture	P1	507	450	2	1239	54		14.7	11.0	0.5	52.1	54
Pasture	P2	858	774	21	1950	54		23.7	16.6	0.5	97.0	54
Pasture	P3	455	364	22	1200	54		14.5	11.0	0.5	64.9	53
Pine	Pine	253	214	166	825	54		11.8	9.0	0.5	51.9	54
Mixed	M1	582	579	53	1174	54		6.9	6.0	0.5	29.0	54
Mixed	M2	362	338	1	903	54		10.9	7.5	0.5	94.0	54
TKN (mg m⁻³)							**TN (mg m⁻³)**					
Native	N1	128	108	47	442	54		249	229	159	528.5	54
Native	N2	97	81	5	293	52		196	190	80	376	52
Pasture	P1	260	200	50	1519	53		765	659	181	2758	53
Pasture	P2	295	243	126	1038	53		1144	1146	216	2176	53
Pasture	P3	235	207	100	609	53		679	541	205	1500	53
Pine	Pine	196	179	50	584	54		449	409	279	1186	54
Mixed	M1	151	133	50	584	53		730	732	213	1347	53
Mixed	M2	219	154	50	2056	54		581	499	108	2480	54
EC (μS cm⁻¹)							**Alk. (g CaCO₃ m⁻³)**					
Native	N1	107	109	81	132	45		19	18	10	26	30
Native	N2	115	118	85	135	44		21	20	11	32	30
Pasture	P1	96	97	77	119	45		18	17	8	29	30
Pasture	P2	98	95	82	141	45		18	17	9	30	30
Pasture	P3	98	95	77	119	45		18	17	9	30	29

Parameter and land use	Site	AM	Median	Min.	Max.	N	Parameter	AM	Median	Min.	Max.	N
Pine	Pine	101	102	85	113	45		14	14	6	20	30
Mixed	M1	113	111	86	138	45		21	20	11	32	30
Mixed	M2	106	107	73	128	45		19	19	3	31	30
DOC (g m^{-3})							pH					
Native	N1	1.68	1.32	0.20	7.97	42		7.17	7.15	6.87	7.60	32
Native	N2	1.56	1.10	0.10	6.70	41		7.44	7.46	7.25	7.71	31
Pasture	P1	1.89	1.60	0.42	7.74	42		7.43	7.44	7.11	7.85	32
Pasture	P2	2.10	1.92	0.71	7.62	42		7.31	7.29	7.00	7.77	32
Pasture	P3	2.28	2.01	0.73	8.80	42		7.29	7.26	6.86	7.86	32
Pine	Pine	1.84	1.62	0.83	7.42	41		6.98	6.96	6.65	7.32	32
Mixed	M1	1.50	1.26	0.54	5.61	42		7.35	7.33	6.89	8.09	32
Mixed	M2	1.64	1.45	0.52	5.54	42		7.33	7.29	6.10	8.51	32

Table 5 Land-use effects on average water quality at two native forest streams (N1 and N2), a predominantly pine stream (Pine), and two pasture streams (P1 and P2) at Whatawhata, Waikato, New Zealand (geometric means, except for pH, and temperature (arithmetic means)). Results of post-hoc Scheffe tests for statistically significant differences ($P < 0.05$) are also shown. See Table 4 for number of samples.

Parameter	Native	Pine	Pasture	Scheffe tests
Suspended solids (g m^{-3})	4.5	20.9	11.6	N<Pa<Pi
Turbidity (NTU)	8.7	24.7	11.3	N<Pa<Pi
Black disk (m)	0.75	0.37	0.48	Pi<Pa<N
Volatile suspended solids (g m^{-3})	0.7	2.0	1.6	N<Pa=Pi
Dissolved organic carbon (g m^{-3})	1.26	1.65	1.84	N<Pi=Pa
Total nitrogen (mg m^{-3})	220	428	816	N<Pi<Pa
Total Kjeldahl nitrogen (mg m^{-3})	96	174	225	N<Pi<Pa
Nitrate nitrogen (mg m^{-3})	111	237	446	N<Pi<Pa
Ammoniacal nitrogen (mg m^{-3})	4.2	9.4	13.4	N<Pi<Pa
Total phosphorus (mg m^{-3})	41	40	56	N=Pi<Pa
Dissolved reactive phosphorus (mg m^{-3})	24	10	23	Pi<Pa=N
pH	7.3	7.0	7.4	Pi<N=Pa
Temperature (°C)	12.4	13.6	15.0	N<Pi<Pa
Conductivity (µS cm^{-1})	110.6	100.9	96.4	Pa<Pi<N
Alkalinity (g CaCO$_3$ m^{-3})	21.1	14.3	18.1	Pi<Pa<N

1998). Nutrient comparisons used data from 54 sampling occasions between April 1995 and August 1999. The results are summarised for individual streams in Table 4 and are compared among the pine, native, and pasture land uses in Table 5. Native forest streams had the lowest geometric means for temperature, SS, VSS, turbidity, DOC, and nutrient concentrations (except DRP), and the highest visual water clarity (Table 5). The pine stream had 3- to 4-fold higher geometric mean values of SS, VSS, and turbidity than native forest streams (pastures were intermediate), and its visual water clarity was half that of the native forest streams. The pine stream also had lower DRP, pH, and alkalinity than the pasture and native forest streams. Pasture streams had the highest concentrations of NO_3-N, NH_4-N, TKN (2- to 4-fold higher than the native sites), TP, and DOC.

Stream flow effects on water quality attributes were compared among the sites by examining correlations with the specific flow at the site (or downstream weir) (Table 6). Flow had the strongest influence at the pasture sites, followed by the mixed pasture/native sites and then the native and pine forest sites. Alkalinity, conductivity, turbidity, and pH all had strong negative correlations with flow (mean r values of –0.91 to –0.67). Temperature, DRP, and black disk had weaker, negative relationships with flow (mean r values of –0.43 to –0.49). DOC was also weakly negatively related to flow at the pasture sites, but relationships with flow

were weaker and inconsistent at sites in other land uses. In contrast, flow had strong, positive, relationships with NO_3-N, SS, and turbidity (mean r values 0.59–0.71) and weak positive relationships with TKN and VSS (mean r values 0.28 and 0.27,

respectively). Notably, TP and NH_4-N showed no consistent relationship with flow.

Seasonal influences on water quality determinants, after accounting for the influence of flow, are summarised in Table 7. As expected, temperature

Table 6 Pearson correlation coefficients (r) between water quality attributes and specific flow. Flow and water quality attributes were log-transformed except for dissolved reactive phosphorus (DRP) (square root transformed), temperature, alkalinity, and pH (not transformed). Values in bold and italics are statistically significant at $P < 0.0001$, and those in italics only are statistically significant at $P < 0.05$. See Table 1 for site codes and Table 4 for number of samples. (VSS = volatile suspended solids; DOC = dissolved organic carbon.)

| | Land use | | | | | | | | |
| | Pasture | | | Native | | | Mixed | | |
Attribute	P1	P2	P3	N1	N2	Pine	M1	M2	Mean r
Alkalinity	*−0.95*	*−0.94*	*−0.95*	*−0.82*	*−0.92*	*−0.92*	*−0.89*	*−0.91*	−0.91
Conductivity	*−0.91*	*−0.84*	*−0.90*	*−0.73*	*−0.77*	*−0.76*	*−0.76*	*−0.85*	−0.81
Turbidity	*0.75*	*0.77*	*0.83*	*0.63*	*0.77*	*0.42*	*0.77*	*0.75*	0.71
pH	*−0.75*	*−0.76*	*−0.85*	−0.09	*−0.71*	*−0.74*	*−0.73*	*−0.76*	−0.67
Suspended solids	*0.72*	*0.75*	*0.82*	*0.50*	*0.62*	*0.53*	*0.71*	*0.72*	0.67
Nitrate	*0.67*	*0.72*	*0.81*	0.17	0.27	*0.77*	*0.68*	*0.66*	0.59
Black disk	*−0.57*	−0.48	*−0.58*	−0.27	−0.45	−0.43	−0.44	*−0.67*	−0.49
Temperature	−0.44	−0.45	*−0.51*	−0.41	−0.37	−0.41	−0.45	−0.48	−0.44
DRP	−0.43	−0.45	−0.39	*−0.57*	−0.47	−0.45	−0.48	−0.21	−0.43
Total Kjeldahl N	0.23	0.24	0.21	*0.31*	*0.31*	0.11	0.37	0.49	0.28
VSS	*0.34*	*0.42*	*0.44*	0.19	−0.14	0.04	0.30	*0.59*	0.27
NH_4-N	0.26	0.06	0.40	0.15	0.00	*0.32*	0.14	*0.31*	0.20
DOC	−0.39	−0.38	−0.32	0.18	0.22	−0.11	−0.01	0.05	−0.09
Total phosphorus	0.11	0.14	0.14	−0.12	−0.15	−0.16	0.01	*0.47*	0.05
Mean absolute r	0.54	0.53	0.58	0.37	0.44	0.44	0.48	0.56	

Table 7 Seasonal trends on water quality. Results are the regression coefficients of attribute values, after allowing for flow effects, against days from mid winter (see Methods for details). Positive trends indicate higher values in summer than winter. Values in bold and italics are statistically significant at $P < 0.001$, those in italics only are statistically significant at $P < 0.05$, and dashes indicate no statistically significant trend. See Table 1 for site codes and Table 4 for number of samples. (DRP = dissolved reactive phosphorus; VSS = volatile suspended solids; DOC = dissolved organic carbon.)

| | Land use | | | | | | | |
| | Pasture | | | Native | | | Mixed | |
Attribute	P1	P2	P3	N1	N2	Pine	M1	M2
Alkalinity	−	−	*0.013*	−	−	−	−	−
Conductivity	*−0.027*	−	−	−	−	−	−	−
Turbidity	−	−	−	−	−	−	−	−
pH	*0.0012*	*0.0008*	*0.0011*	−	−	−	−	−
Suspended solids	−	−	−	−	−	−	−	−
Nitrate	*−1.77*	*−1.55*	*−1.63*	−0.16	*−0.26*	−0.48	*−1.97*	*−1.38*
Black disk	−	−	−	−	−	−	−	*−0.001*
Temperature	*0.038*	*0.027*	*0.030*	*0.016*	*0.028*	*0.017*	*0.020*	*0.027*
DRP	−	−	*0.030*	−	−	−	−	−
Total Kjeldahl N	0.345	*0.821*	*0.824*	−	−	*0.657*	−	−
VSS	−	−	−	−	−	−	−	−
NH_4-N	−	−	−	−	−	*−0.0035*	−	−
DOC	*0.0084*	*0.0076*	*0.0118*	−	−	*0.0067*	−	−
Total phosphorus	−	−	−	*0.057*	−	−	−	−

varied with season at all sites, with the weakest influence occurring at the small pine forest and native forest streams and the strongest influence at a small pasture stream. Nitrate decreased towards summer at all sites. Total Kjeldahl N and DOC at the pasture and pine sites showed the opposite seasonal trend to nitrate, with higher values in summer. The pasture sites also showed trends of higher pH towards summer. Notably, few or no statistically significant seasonal trends were detected for flow-adjusted values of alkalinity, electrical conductivity, TP, DRP, NH_4-N, VSS, SS, turbidity, or black disk visibility.

DISCUSSION

This comparison of streams draining adjacent catchments provides clear evidence that land use exerts strong influences on stream water quality and sediment and nutrient exports, and also influences the seasonal variability of water quality. This data set also provides a basis for evaluating the effects on water quality and water resources of changes in land management currently being implemented to improve the sustainability of land use in the Mangaotama catchment (Quinn et al. 2001).

Hydrology

The conversion from forest to pasture land use appears to have had relatively minor effects on the hydrology of the catchments at Whatawhata. Native forest catchments are expected to yield less water than pasture, because of higher interception, evaporation, and transpiration losses, but may sustain higher base flows (Fahey & Rowe 1992; Rowe et al. 1997). Our findings support these expectations, with 7% higher average annual run-off from pasture and 17% higher 7-day low-flow from the native forest. However, the effect of pastoral development on water yield was much lower than the 60% increase reported for a paired, small catchment comparison of pasture and native forest at Purukohukohu in the central North Island (Dons 1987). It is possible that the pasture catchment in our study (above P3) received less rainfall than the native and mixed land-use catchments (above N2, and M2, respectively), because of its slightly lower average elevation (Fig. 1) (Griffiths & McSaveney 1983). Rainfall varied by up to 13% among sites for September 1994 to November 1997 in eight storage rain gauges, spread throughout the pasture catchment and the low-mid elevation parts of the mixed catchment (authors'

unpubl. data). However, contrary to the finding of Griffiths & McSaveney (1983) that rainfall increased with elevation over spatial scales from the coast to the main divide of New Zealand, rainfall was weakly, and negatively, correlated with elevation ($r = -0.53$, $P = 0.22$) over the much more local spatial scale (a few kilometres) of our study area. These findings highlight the need for a network of rainfall gauges throughout catchments, even when they are adjacent as in this study, to be able to evaluate the effects of land use on water yield confidently.

Nutrients

Previous studies have demonstrated the important influence of land use on N and P concentrations in New Zealand rivers at local (Cooper et al. 1987; Cooper & Thomsen 1988), regional (Vant 1999), and national scales (Close & Davies-Colley 1990; Smith et al. 1993a; Maasdam & Smith 1994). Our comparison of multiple sites in adjacent catchments, in steep to rolling hill-country, has helped to quantify the influences of pastoral development and subsequent pine afforestation of land that was previously in pasture. We have also demonstrated strong influences on nutrient concentrations and exports resulting from variations in flow, seasonal factors, and year-to-year differences in rainfall.

Total N export from the wholly pasture catchment is at the high end of the reported range for New Zealand pasture catchments (Table 3) (Wilcock 1986; Cooper et al. 1987; Vant 1999; Wilcock et al. 1999), and similar to that from cropland in the Chesapeake Bay catchment in the eastern United States (18 kg N ha^{-1} yr^{-1} (Jordan et al. 1997)). Median TN concentrations at the pasture and mixed land-use sites (499–1146 mg m^{-3}) exceeded the 90 percentile value for the New Zealand rivers in the National Rivers Monitoring Network, but were similar to the value reported for the Waipa River to which the catchment drains (Smith & Maasdam 1994). This indicates that TN values are very high by New Zealand standards, but similar to other streams in the Waipa catchment. TKN comprised c. 60–70% of the TN export from the pasture, native, and mixed land-use catchments at Whatawhata, compared with only 16% at the lowland pasture site at Toenepi located 45 km east. TKN includes particulate N (derived mainly from soil erosion), dissolved organic N (derived from autochothonous production and soil leaching), and ammonium N (Meybeck 1993). The high contribution of TKN to the TN export indicates that surface run-off/erosion processes play an important role in N loss at the steep

hill site at Whatawhata, but only a minor role in the flatter, artificially-drained landscape at Toenepi, where nitrate leaching is the main N loss process. This indicates that effective land management strategies to control N loss in steep to strongly rolling hill-land such as Whatawhata will need to target both nitrate control (e.g., by enhancing denitrification in riparian wetlands) and particulate N control (e.g., by pasture management, provision of grassy filter strips, and protecting stream banks from erosion).

TP export was also at the high end of the range reported for New Zealand pasture catchments in the dry year (1996–97), and in the wet year (1995–96) was almost twice as high as the maximum previously reported for New Zealand pasture (Table 3) and near the top of the range reported for catchments draining to Chesapeake Bay in the eastern United States (0.07–4 kg P ha^{-1} yr^{-1} (Jordan et al. 1997)). This suggests pastoral hill country is likely to be an important source of nutrients to the Waikato River.

DRP made a minor contribution (9–19%) to the TP export from the pasture and mixed land-use catchments at Whatawhata, which was strongly dominated by particulate P (Table 2). In contrast DRP comprised 63% of the TP export in the lowland Toenepi pasture catchment, with this being attributed to the importance of point source inputs from dairy-shed treatment systems and the low erosion rates (Wilcock et al. 1999). The predominance of particulates in the TP emphasises the dominant role of erosion-driven processes in nutrient exporting at the steep, hill-land, Whatawhata site. This implies that P control measures need to focus on land management activities that control erosion (e.g., tree planting to stabilise slips), pasture management to maintain grass cover, and riparian zone management to enhance filtration of sediment in overland flow and reduce stream bank erosion (e.g., by providing grass filter strips and reducing access to streams by cattle that can enhance erosion of stream banks (Trimble & Mendel 1995)).

The ratios of nutrient exports from the Whatawhata pasture and native catchments in 1996–97 were similar to corresponding ratios in the Purukohukohu catchments in the central North Island of New Zealand for TN (4.8 cf. 3.3), but lower for TP (2.6 cf. 14), DRP (0.9 cf. 22), NH$_4$-N (2.8 cf. 8.6), and TKN (3.7 cf. 13), and greater for NO$_3$-N (7.9 cf. 0.4). This highlights the potential for erroneous conclusions if findings on the effects of land use on nutrient exports are transferred between regions with different geology, soils, and rainfall, and

indicates that region-specific studies are required to support predictions of land-use effects.

The differences in nutrient concentrations and exports from the pasture sites between the wet and dry year, and between seasons demonstrate the dynamic nature of land-use influences at a site, and the difficulties of using short-term studies to make generalisations about catchment budgets. These results, and the strong correlation between nitrate and flow at most sites (Table 6) support the view that flow plays a key role in regulating nutrient concentrations and exports, but also indicate that seasonal factors unrelated to flow also play a role in regulating nitrate. Although the pasture site exported 7.9-fold more nitrate than native forest, under summer low-flow conditions nitrate was sometimes lower in pasture than native forest streams (Fig. 3). Several processes probably contribute to the flow and season-dependent fluctuations in nitrate concentrations and exports. Nitrate accumulates in topsoil during dry periods as a result of mineralisation of soil organic matter, and the input of dung and urine from stock in pasture. During dry periods, particularly in summer, evapo-transpiration often exceeds rainfall and there is little downward movement of nitrate into groundwater and streams. The water that does reach the streams under summer low-flow conditions probably arrives mainly as groundwater that passes through riparian wetlands, where denitrification removes much of the available nitrate before it enters the stream (Cooper 1990; Nguyen & Downes 1997a; Nguyen et al. 1999). In-stream plant growth is also maximal under stable flow conditions in summer (J. Quinn unpubl. data), with the resulting high uptake of N (Cooper 1990; Quinn et al. 1997b). As soil moisture increases during winter, nitrate is flushed from the soil at a time when in-stream plant growth is low, and N concentrations and exports reach their maximum level of c. 800–1200 mg m^{-3} (Fig. 3 and 4). Nitrate concentrations in groundwater upslope of riparian wetlands are typically in this range in pasture at Whatawhata (Findlay et al. 2001), indicating that under wet, winter conditions riparian and in-stream removal processes are much less effective in controlling nitrate concentrations in pasture streams than under drier conditions in summer. Notably, the highest in-stream nitrate concentration (1900 mg NO$_3$-N m^{-3}) was recorded at P3 in June 1998 shortly after a 20-year return period storm that occurred after an extended dry period in early 1998 and scoured out much of the wetland vegetation from headwater channels in the pasture catchment. Native forest streams also show annual patterns of higher nitrate

export and concentrations in winter and minimum values in summer, but the seasonal fluctuations are less marked (Fig. 2 and 3). This probably reflects the lower N input to the forest (lower N-fixation by plants), the absence of N mobilisation by grazing animals, and less in-stream N uptake by plants that were 13-fold less productive in native forest than pasture streams under spring conditions (Quinn et al. 1997a).

The median concentrations of NO_3-N in the native forest streams were typical of New Zealand rivers in the National Rivers Water Quality Network (Smith & Maasdam 1994), and at about the level at which periphyton growth is expected to start to be N limited (c. 100 mg dissolved inorganic N m^{-3} (MFE 1992)). Corresponding median values exceeded this level at the pine (2.5-fold), mixed land use (3.5- to 6-fold) and pasture streams (4.5- to 8.5-fold). However, NO_3-N concentration at the pasture sites dropped to well below periphyton growth limitation thresholds under summer low-flow conditions (minima = 2–22 mg NO_3-N m^{-3}, Table 3) when periphyton C:N ratios indicated N-deficiency during growth experiments at P3 (Quinn et al. 1997b). The typical maximum NO_3-N concentrations at the pasture sites (c. 1200 mg NO_3-N m^{-3}, Table 4) were an order of magnitude below the guidelines for water consumption by humans (11 300 mg NO_3-N m^{-3}) and stock (30 000 mg NO_3-N m^{-3}) (ANZEEC 1992; MoH 1995).

Although NH_4-N concentrations were higher in pasture than the pine and native forest streams (Table 5), they were consistently low (maximum = 97 mg NH_4-N m^{-3} at P2, Table 4) relative to the chronic effect concentrations (EC_{20}) at pH 8 of the New Zealand mayfly *Deleatidium* sp. (1000 mg m^{-3} total ammonia N) and fingernail clam *Sphaerium novaezelandiae* (420 mg m^{-3} total ammonia N) (Hickey et al. 1999) and the EPA (1999) chronic criterion for fish early life stages (1710 mg m^{-3} total ammonia N). This indicates that the direct inputs of animal faecal material by stock with uncontrolled access to the pasture stream at Whatawhata does not result in general toxicity problems for aquatic life resulting from ammonia, although localised impacts may occur (e.g., around cow pats).

Land use had much less influence on TP and DRP exports and concentrations than on NO_3-N and TKN in our study. Although TP export was 2.6-fold higher from the pasture than the native forest stream, both DRP exports and concentrations were similar from both land uses (Tables 3, 4, and 5). This is consistent with the findings of preliminary studies on land-use

effects on water quality in the study area (Quinn et al. 1997a) and the high DRP concentrations from the native forest streams indicate an unusual geological source that masks any land-use influence. The median DRP and TP concentrations at the eight Whatawhata sites (Table 4) were equivalent to the 75–95 percentile and 70–85 percentile values, respectively, of rivers in the National Rivers Water Quality Network (Smith & Maasdam 1994) and were generally above the level at which periphyton growth is expected to be P limited (c. 15–30 mg DRP m^{-3} (MFE 1992)).

TP and DRP exports from all land uses differed less between seasons and between the wet and dry years than NO_3-N exports (Table 3; Fig. 3). DRP concentrations in the monthly monitoring data set were less strongly correlated than NO_3-N concentrations with flow, and TP was only significantly correlated with flow at one site (M2, Table 6). However, the TP and DRP exports followed the same pattern as NO_3-N export of maximum values in the wet year and during winters of 1995 and 1996, minimum values in summer and low values in the dry winter of 1997 (Fig. 3). Contrary to some previous studies (e.g., Wilcock et al. 1999), our monthly samples did not show up any peaks in TP or DRP concentration around periods of aerial top-dressing with P fertiliser.

The ratio of SS to TP export from the mixed catchment below the large earthflow slip was 2- to 3-fold higher than from the wholly pasture and native forest catchments (Table 3). This reflects the lower P content of the deep sub-soils eroding from the slip than the surface soils that are usually eroded from catchments.

Sediment

Geology, rainfall, and topography are the main controls on sediment export of New Zealand catchments (Hicks & Griffiths 1992). Reported exports range over three orders of magnitude, from 14 t km^{-2} yr^{-1} from a lowland Waikato catchment (Wilcock et al. 1999) to 19 970 t km^{-2} yr^{-1} from Waiapu catchment on the East Coast of the North Island and 29 600 t km^{-2} yr^{-1} from the Cropp River on the West Coast of the South Island (Hicks & Griffiths 1992). However, within a regional setting, land use can exert an important influence. The pasture catchment lacking major earthflow slips (Mangaotama, P3) in our study exported 3-fold more sediment than the adjacent native forest catchment (Table 3). Furthermore, the mixed pasture and forest catchment (M2) exported 8-fold more than the forest

catchment during 1996–97 (Table 3), 1–2 years after a major, deep earthflow slip occurred in its pasture section. The sediment export was much higher when the slip first occurred. Analysis of the surface topography at the slip site indicated that 11 000 t of sediment were eroded between July 1995 and April 1996 (Megan Balks, University of Waikato pers. comm.). This is equivalent to 41 300 kg^{-1} ha^{-1} at Site M2, equivalent to 42 and 129 times the annual exports from the wholly pasture and native forest catchment during 1996–97, and demonstrates how local landslides can dominate the long-term sediment export from small catchments. The influence of pasture land use on the occurrence of this large slip is debatable. The slip occurred on a very steep, north-facing, hillslope in a v-shaped valley, where the stream was eroding the slope toe, and the deep-seated nature of the slip suggests a geological cause. However, surface soil cracking was observed on many north-facing pasture slopes during the dry summer of early 1995 and it is possible that the cracking enabled entry of water deep into the soil to the impermeable sublayer and helped initiate the slip by building up pore water pressure and contributing to gravity-failure of the hillslope. This cracking would not be expected to occur under forest, where shade reduces surface soil temperatures. Notably, four much shallower slips have occurred in the pasture section of the valley above the large slip, whereas the SS monitoring at the native forest edge (N1, Fig. 1) has not indicated any significant slips in the forested part of the catchment upstream.

Unsealed roads are often an important source of sediment in streams, particularly in forestry where heavy trucks are used (Coker et al. 1993; Jones et al. 2000). However, in this study, the mean SS and turbidity were greater at P1 above road influences than at P3, down stream of road run-off inputs (Table 4). This indicates minimal roading impact on average conditions, but it is possible that road run-off becomes a more important source of sediment exported from the pasture catchment during storms and may contribute to the higher sediment export from the pasture than the road-less native catchment.

In two other paired catchment comparisons in New Zealand, Fahey (2000) found that a pasture catchment exported 2.4 times more sediment (83 t km^{-2} yr^{-1}) than an adjacent mature pine forested catchment in coastal hill-country of Hawke's Bay, whereas pasture and native forest exported similar low amounts of sediment (22 and 27 t km^{-2} yr^{-1}, respectively) in adjacent hill-country catchments in the central North Island (Dons 1987).

The sediment export from the pasture catchment at Whatawhata was 7-fold higher during 1996–97 than from a Waikato, lowland, dairy pasture catchment at Toenepi with a higher stocking rate (Wilcock et al. 1999). Wilcock et al. (1999) considered that, because of the flat-undulating topography of the Toenepi catchment, most of the SS was derived from in-stream plant material and redistribution of sediments eroded within the stream channel. In contrast, the steep hillslopes and slip scars indicate that hillslope sediment sources actively contribute sediment in the steep-rolling pasture catchments at Whatawhata, although erosion of sediments stored in stream banks is also an important source (DeRose 1998). Hillslopes are particularly important down stream of the large earthflow slip in the Kiripaka catchment where continued slumping and surface erosion of the bare slip face contribute sediment directly to the stream channel. The much higher sediment export from Whatawhata than Toenepi emphasises the importance of topography in controlling sediment export and the greater need for erosion control strategies to manage sediment exports in uplands than lowlands.

Optical properties

Land use also appeared to influence the optical properties of stream waters, with pasture streams having, on average, 30% higher turbidity than native forest streams and 36% lower visual clarity as measured by black disk (Table 5). However, the pine stream had the lowest visual clarity, and turbidity and SS were typically 2- to 4-fold higher than the pasture and native streams (Table 5). These patterns are consistent with those from earlier comparisons of other pine forest streams, with pasture and native forest in the study area (Quinn et al. 1997a). The high turbidity of the pine stream is probably the result of erosion of sediment deposits built up within the channel during the pasture phase after the pines and regenerating native forest shaded the channel. The grass that protected the stream bank sediments and enabled the stream channel to narrow under the high light conditions in pasture become shaded out under forest lighting, leading to channel erosion as the stream channel doubles to a natural forest stream width (Davies-Colley 1997; Trimble 1997). The finding that this stream still has high SS and turbidity c. 23–28 years after pine afforestation and release from grazing indicates that the channel widening phenomenon described by Davies-Colley (1997) can degrade the optical quality of small streams for an extended period.

Dissolved organic carbon

DOC exports from streams in our study (20.2–27.4 kg ha^{-1} yr^{-1}, Table 3) were close to the median value of 18.6 kg ha^{-1} yr^{-1} (range = 1.6–484 kg ha^{-1} yr^{-1}) for 67 temperate and boreal catchments in North America, Russia, and New Zealand (Hope et al. 1994). Higher DOC exports have been reported for New Zealand catchments in Westland draining undisturbed native forest catchments (88 and 89 kg DOC ha^{-1} yr^{-1} from Maimai catchments M6 and M15, respectively) (Moore 1989) and undisturbed pakihi wetlands (378 and 417 kg DOC ha^{-1} yr^{-1} from Larry River catchment L2 (Collier et al. 1989; Moore & Jackson 1989), respectively). Two factors that are likely to be important in the 4.4-fold higher DOC export from the native forest catchments in Westland than in our Waikato study are the 50% higher rainfall at the Westland site and differences in forest type. Higher rainfall could produce greater leaching of DOC from soils and vegetation (Hope et al. 1994). The beeches (*Nothofagus* spp.), that dominate the Westland forest, produce very high DOC in stemflow that appears to be related to the presence of scale insects which exude honey dew and allow development of sooty mould fungi (Moore 1989). The very high DOC export from the pakihi wetland catchment in Westland was attributed to the inability of the subsoils to absorb DOC and the saturated conditions for much of the year enabling water to move across the surface soil or through the organic surface horizons (Moore & Jackson 1989).

The change from native forest to pasture land use appears to have led to a small increase in stream DOC concentrations and exports at our study site. DOC exports from the pasture and mixed (pasture, pine, and native) catchments were 20–25% higher than the native forest catchment (Table 3), although this pattern was not consistent in all seasons (Fig. 3), and the overall geometric mean DOC concentration in pasture streams was 50% higher than native forest streams (Table 5). Higher DOC in pasture streams supports the findings of a preliminary comparison in the study area during spring 1992 (Quinn et al. 1997a). Recent studies indicate that groundwater in the pasture, pine, and native forest catchments contains uniformly low concentrations of DOC (<1 g m^{-3}) and the extracellular enzyme activity "signatures" of microbial communities exposed to these groundwaters indicates that the character of DOC is also similar across these land uses (Findlay et al. 2001). However, DOC is added and changes in DOC character occur as groundwater passes through riparian wetlands to streams and these changes may be associated with increases in growth rate of epilithic bacteria exposed to the water (Findlay et al. 2001). Wetlands are more common in riparian areas and within headwater stream channels in pasture catchments, probably resulting from the lack of riparian trees and high light enabling vegetation to encroach on stream channels (Davies-Colley 1997). This may account for the higher DOC concentrations in pasture than native forest streams, although the release of DOC by in-stream plants that are more productive in the pasture streams (Quinn et al. 1997a), may also play a role in increasing pasture stream DOC concentrations. The 32% higher DOC in the pine than native forest streams (Table 5) is consistent with preliminary comparisons between pasture and other pine forest streams in the study area (Quinn et al. 1997a) and the finding by Findlay et al. (2001) that DOC increased more along riparian wetland flowpaths in pine than native forest at the study site. Minimal in-stream vegetation was present in the well-shaded Pine catchment, so this can be discounted as a source of the higher DOC in the Pine than the native catchment streams. These findings indicate that land use does influence DOC in streams and suggest that wetlands play an important role in determining this effect.

Alkalinity and acidification

Conifer afforestation has been associated with acidification of streams in Britian and Europe (Ormerod 1989; Friberg et al. 1998), but has not been demonstrated previously in New Zealand (Maclaren 1996). Our comparison showed that 23–25 years after 55% of the Pine stream's catchment was planted with *Pinus radiata* and the remainder was left fallow for native forest to regenerate, average pH (7.0) is 0.3 and 0.4 units lower, and alkalinity (14.3 g CaCO$_3$ m^{-3}) was 32 and 21% lower, than in adjacent native forest and pasture streams, respectively (Table 5). The reduction in pH is not expected to be ecologically important for benthic invertebrates or fish (Collier et al. 1990). However, alkalinity was low at the native forest and pasture sites, with median values of 17–20 g CaCO$_3$ m^{-3} (Table 4) exceeded in 83–90% of samples from the National Rivers Monitoring Network (Smith & Maasdam 1994), and the further drop at the Pine stream (median 14 g CaCO$_3$ m^{-3}) may restrict aquatic snails that have been observed to be absent from lakes and streams with alkalinity of less than 10–20 g CaCO$_3$ m^{-3} (Lodge et al. 1987; Huryn et al. 1995). This suggests that acidification associated with pine afforestation has the potential to have ecological effects on

invertebrate communities in these poorly buffered streams.

In conclusion, this study has demonstrated that land use has strong influences on stream water quality and sediment and nutrient exports from Waikato hill-land catchments. Pasture streams had higher exports of sediment, nutrients, and DOC, higher stream temperatures, and lower visual clarity than native forest streams. Pine afforestation was associated with high down stream suspended sediment concentrations and slight acidification. Pastoral development has also increased the seasonal variations in many attributes, particularly temperature and nitrate concentrations. A variety of factors contribute to these differences, including changes in the sources of sediment and nutrients arising from animal grazing activity, removal of forest cover, and changes in riparian and in-stream processes associated with removal of riparian shade. Control of these "off-site" effects of land management on water resources and aquatic ecosystems is an important aspect of sustainable land management. This study has helped to determine the magnitude of land-use effects on hill-land streams and provided a baseline for assessing future actions to reduce these effects by adopting more sustainable land management practices in the Mangaotama catchment.

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