N AND P CONCENTRATION-DISCHARGE RELATIONSHIPS ACROSS A RANGE OF WAIKATO CATCHMENTS

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Abstract

Waikato Regional Council operates a river water quality monitoring programme where samples are taken monthly at 114 sites and analysed for concentrations (C) of a range of water quality parameters. Water flow (or discharge, D) is measured at or nearby 26 of these sites, which allows *nutrient concentration–river discharge relationships* (C-D relationships) to be established.

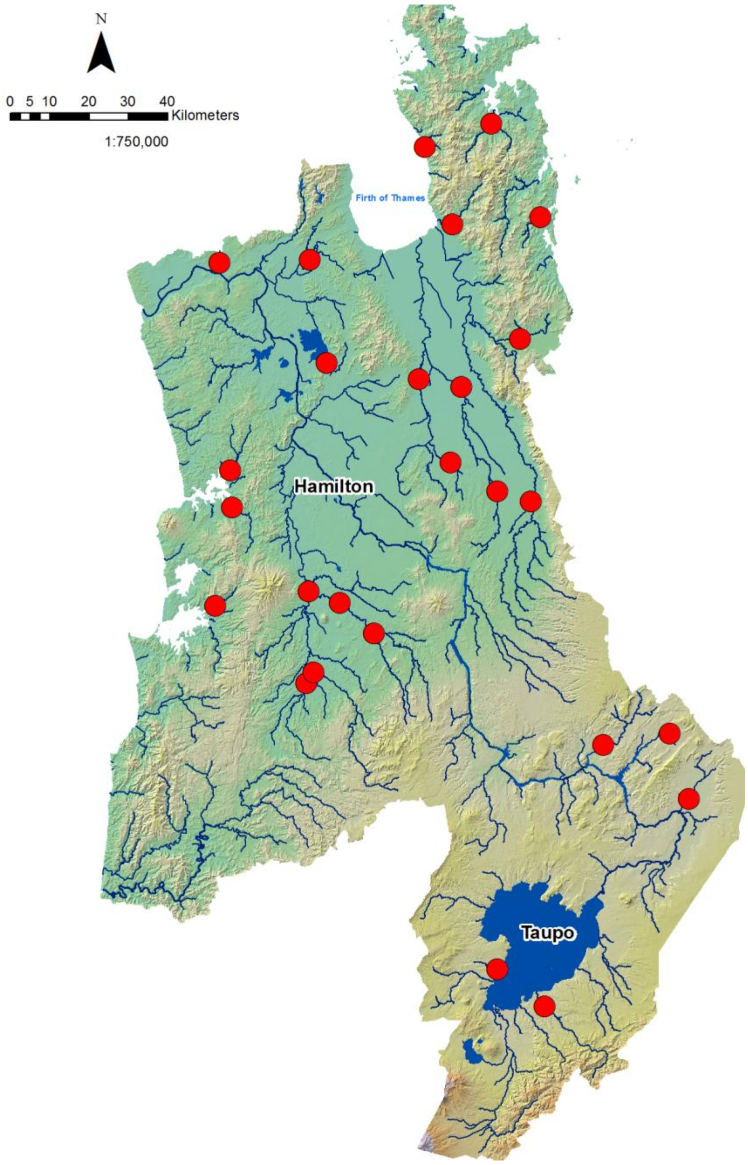
The patterns of the C-D relationships were surprisingly similar across the region in spite of substantial differences in natural conditions, land use and the potential effect of point source discharges. Statistically highly significant ($p \leq 0.005$) C-D relationships were found at nearly all sites (n=24–26) for total nitrogen (TN), nitrate nitrogen (NO_3-N) and total phosphorus (TP); all but two of which were positive. Ammonium nitrogen (NH_4-N) and dissolved reactive phosphorus (DRP) were less frequently correlated to discharge. While all significant correlations (n=18) were positive in the case of NH_4-N, 9 of the 14 significant correlations for DRP were negative. In spite of many C-D relationships being statistically highly significant, there is typically a wide spread in the data, resulting in substantial uncertainty if the equations are used for predictions.

To evaluate to what extent these relationships provide information on the transfer pathways from the land surface to river monitoring sites, we stratified all concentration data into those from sampling dates when baseflow (BF) dominated discharge versus those when quickflow (QF) was dominant. As the positive C-D relationships imply, average baseflow concentrations of TN, NO_3-N and NH_4-N were lower than quickflow concentrations at the same site, whereas negative C-D relationships for TP or DRP were associated with higher concentrations of these solutes in baseflow compared with quickflow.

As BF is largely due to discharge of (older) groundwater, while quickflow is predominantly due to (younger) near-surface flows, trends in these data reflect land management changes at different time scales. Deteriorating NO_3-N concentrations were predominantly the combined effect of BF and QF deteriorations, while TP trends, both positive and negative, were largely due to trends in BF. The prominent role of baseflow in determining these river concentration trends highlights the importance of understanding a nutrient’s mean residence time in the groundwater system of a particular catchment when trying to link a concentration change to a land management change.

Introduction

Waikato Regional Council (WRC) operates a water quality monitoring programme where 'grab' samples are taken monthly at 114 stream and river sites and analysed for concentrations (C) of a range of water quality parameters (Vant, 2013). Water flow (or discharge, D) is measured at or nearby 26 of these sites, which are shown in Fig. 1.



Having concentration and discharge data available allows investigation of whether measured concentrations show a systematic relationship with the discharge occurring at the time of sampling.

Ideally, there was data for the 20-year period from 1993 to 2012 available for this analysis, but time series for several sites were shorter (minimum of 5 years).

This paper focuses on the *nutrient concentration – river discharge relationships* (C-D relationships) established for nitrate nitrogen (NO_3-N), ammoniacal nitrogen (NH_4-N), total nitrogen (TN), total phosphorus (TP), and dissolved reactive phosphorus (DRP).

It forms part of an ongoing study on what the combined analysis of concentration and discharge data can reveal about nutrient transfers from the land into surface water bodies.

Fig. 1: Location of the 26 stream/river monitoring sites in the Waikato region for which C-D relationships were established.

Establishment of concentration-discharge relationships (C-D relationships)

Strong seasonal patterns of nutrient concentrations measured in rivers are evident in the time series data from many monitoring sites. NO_3-N concentrations in Piako River (at Kiwitahi), for example, often approach the detection limit (0.02 mg L^{-1}) in summer, but can reach up to 5 mg L^{-1} in winter (Fig. 2). The corresponding discharge data suggest that low NO_3-N concentrations coincide with low discharge, while high nitrate concentrations often coincide with high discharge.

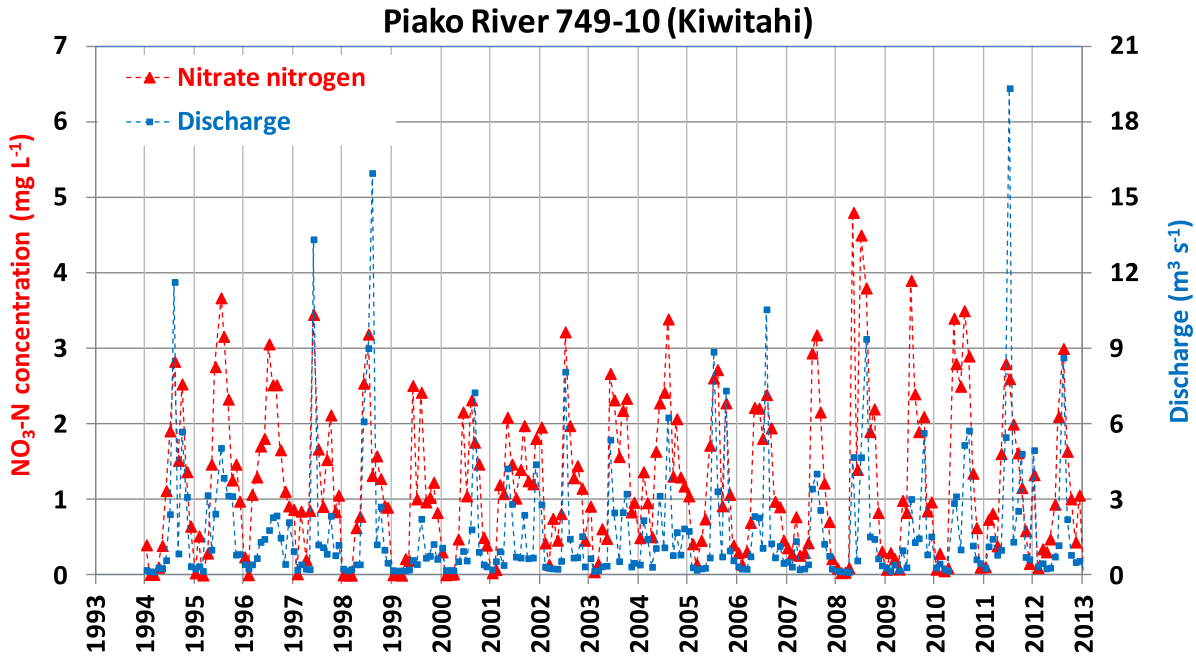
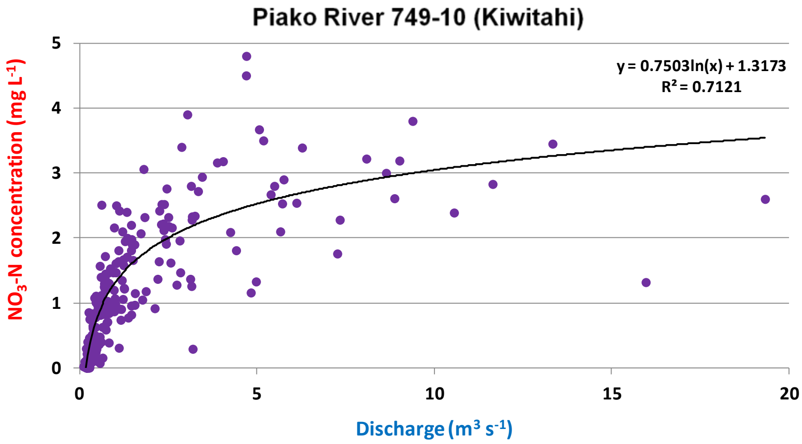
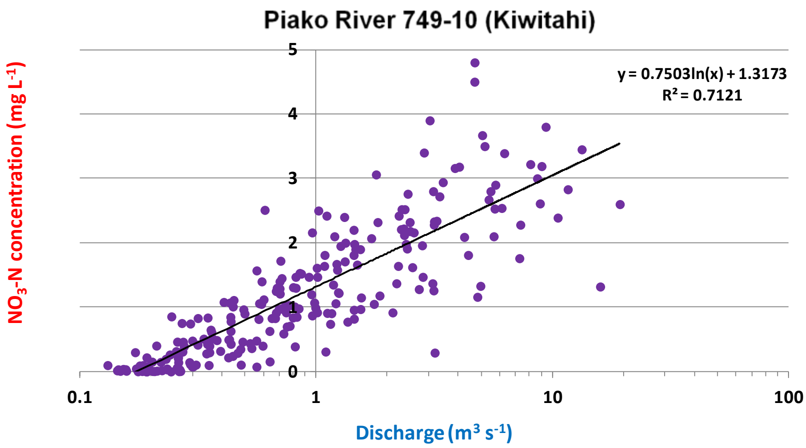


Fig. 2: NO_3-N and discharge time series for Piako River (at Kiwitahi).



Graphing nitrate concentrations directly against discharge confirms the suspected positive C-D relationship, as nitrate concentrations increase with increasing discharge (Fig. 3a).



Given that discharge often varies across several orders of magnitude, a log axis is conventionally used to plot these concentration-discharge relationships (Fig. 3b).

Fig. 3: C-D relationship for NO_3-N at Piako River using a) non-transformed x-axis, b) log-transformed x-axis.

C-D relationships for nitrogen and phosphorus forms

Table 1 provides an overview of all relationships established for measured N and P forms. A stringent significance level ($\alpha = 0.005$) was chosen for this analysis, i.e. all accepted C-D relationships can be categorized as 'highly significant'.

Table 1: Overview of C-D relationships for N and P forms.

	Positive	Not significant	Negative
Total Nitrogen (TN)	26	0	0
Nitrate Nitrogen (NO_3-N)	25	1	0
Ammoniacal Nitrogen (NH_4-N)	18	8	0
Total Phosphorus (TP)	22	2	2
Dissolved Reactive Phosphorus (DRP)	5	12	9

All TN, all but one NO_3-N, and approximately two thirds of the NH_4-N data sets showed a positive C-D relationship. No negative C-D relationship was found for any of the N forms. This means that all significant relationships were positive, i.e. N concentrations at all 26 monitoring sites generally increase with increasing discharge.

However, it is crucial to acknowledge that there can be substantial variability in the C-D relationships in spite of being statistically highly significant. This is demonstrated in Fig. 4 for the example of four highly significant NO_3-N C-D relationships.

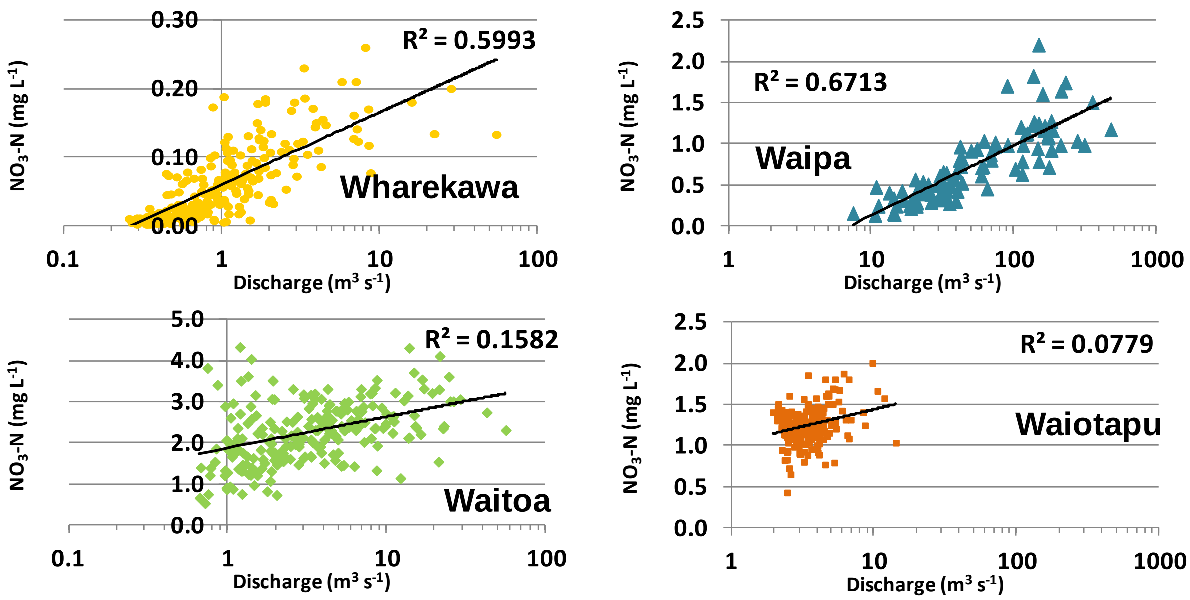


Fig. 4: Four examples of highly significant C-D relationship for NO_3-N.

The relationships shown in the top row of Fig. 4 (Wharekawa and Waipa) explain 60 and 67% of the observed variability in NO_3-N concentrations and are amongst the data sets with the highest coefficient of determination (R^2; observed maximum = 71%). The Waitoa and Waiotapu examples represent the low end of R^2 values amongst significant C-D relationships and explain only 16 and 8%, respectively, of the observed variability in NO_3-N concentrations.

Consequently, substantial uncertainty has to be expected if such C-D relationships are used to estimate loads or catchment yields. Monitoring in higher temporal resolution and advanced calculation techniques (that take hysteresis, seasonality and trends into account) can reduce this uncertainty, but this is beyond the scope of this paper (see Woodward, 2014).

As for all N forms, positive C-D relationships were also found at most sites for TP (Table 1). However, there were two notable exceptions where negative relationships were found. In both instances (Piako River, Waitoa River), these negative relationships were caused by point-source discharges that resulted in high concentrations at low stream flow rates. These examples highlight that point-source discharges can seriously change the relationships that would apply to general diffuse pollution.

Of all N and P forms analysed, DRP showed the least number of significant C-D relationships. However, it had the highest number of negative relationships, i.e. decreasing concentrations with increasing discharge. While two of these can be attributed to point-source discharges (as in the case of TP), in the other instances groundwater discharge appears to have higher DRP concentrations than near-surface flows (Waingaro River, Mangapu River, Puniu River, Waipa River (at Pirongia), Waiotapu River, Whareroa Stream, Tauranga-Taupo River).

Hydrograph separation

Hydrograph separation can help to explore the link between nutrient concentrations measured in the stream at a given discharge and the land-to-water transfer pathways that are responsible for the observed nutrient concentration.

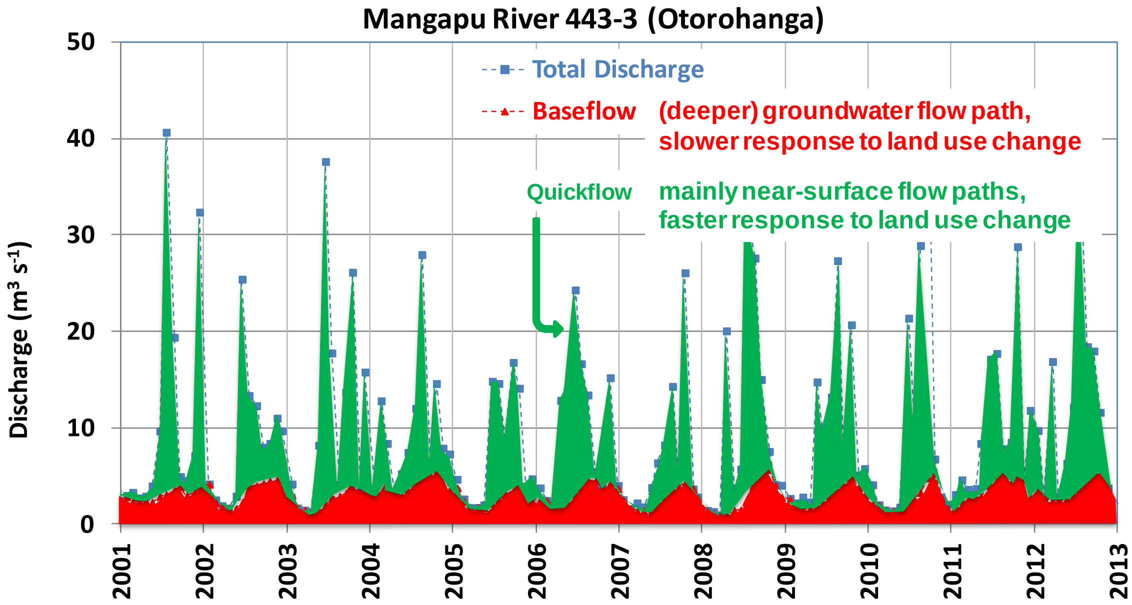


Fig. 5: Hydrograph for Mangapu River (at Otorohanga). Baseflow component shown in red, quickflow component in green.

As shown in Fig. 5 for Mangapu River, the observed total discharge can be split into a baseflow and a quickflow component. We determined the baseflow component using the two parameter digital filter of Eckhardt (2005). The baseflow represents the relatively steady contribution that the groundwater system makes to the flow in the river, while the much more dynamic quickflow is mainly due to near-surface flows, like surface runoff, interflow, and artificial drainage, but can also contain contributions from the groundwater system. Obviously, nutrient concentrations in quickflow respond more quickly to land management or land use changes than those in baseflow.

Stratification of monitoring data

Splitting all available monitoring data into those from sampling dates where baseflow dominated and those where quickflow dominated can provide insights into the role of different land-to-water transfer pathways for the nutrient concentrations observed in a river and any possibly occurring concentration trends.

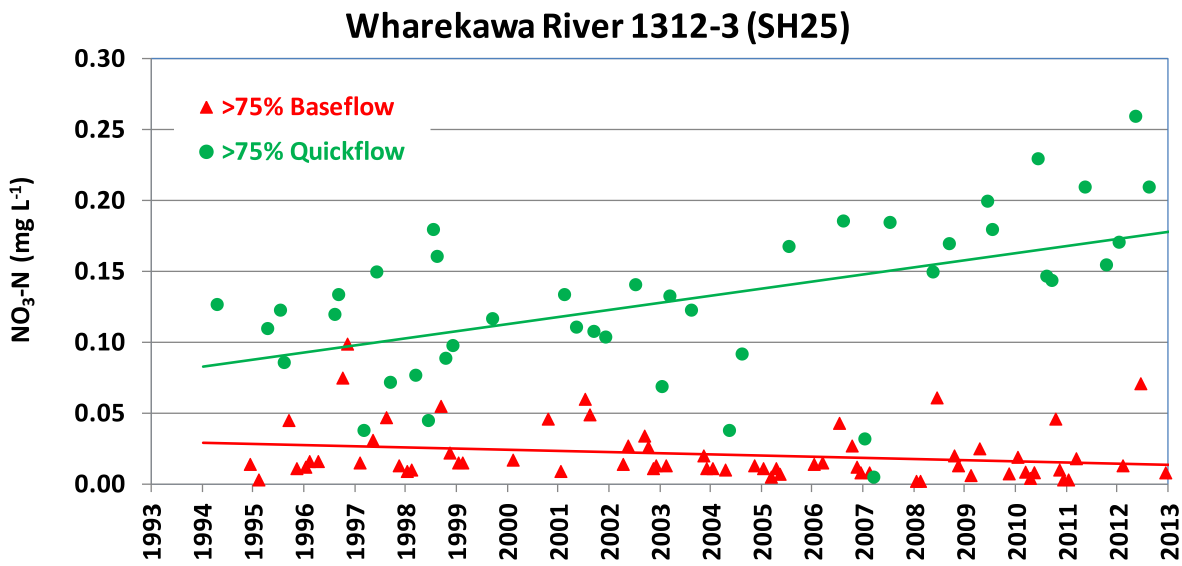


Fig. 6: NO_3-N concentration time series of Wharekawa River (Coromandel). Baseflow-dominated sampling dates shown in red, quickflow-dominated dates in green.

This analysis suggests, for example, that the rising nitrate concentrations in the Wharekawa River in the Coromandel are due to near-surface transfers from the land to the river, which cause concentration increases at quickflow-dominated sampling dates (Fig. 6). In contrast, concentrations observed at baseflow-dominated sampling dates have remained stable and lower. This suggests that we are seeing the early response in the river to relatively recent land use intensification, while the nitrate lost from the root zone has either not yet reached the groundwater or the recharged nitrate has been denitrified within the groundwater system (Stenger et al., 2013).

In contrast, the rising nitrate concentrations in the Ohinemuri River (Fig. 7) are presumably due to rising concentrations in groundwater discharge, as concentrations at baseflow-dominated sampling dates have now reached the relatively stable level of quickflow-dominated dates. This pattern is likely to reflect the gradual response of the groundwater system to an earlier phase of land use intensification.

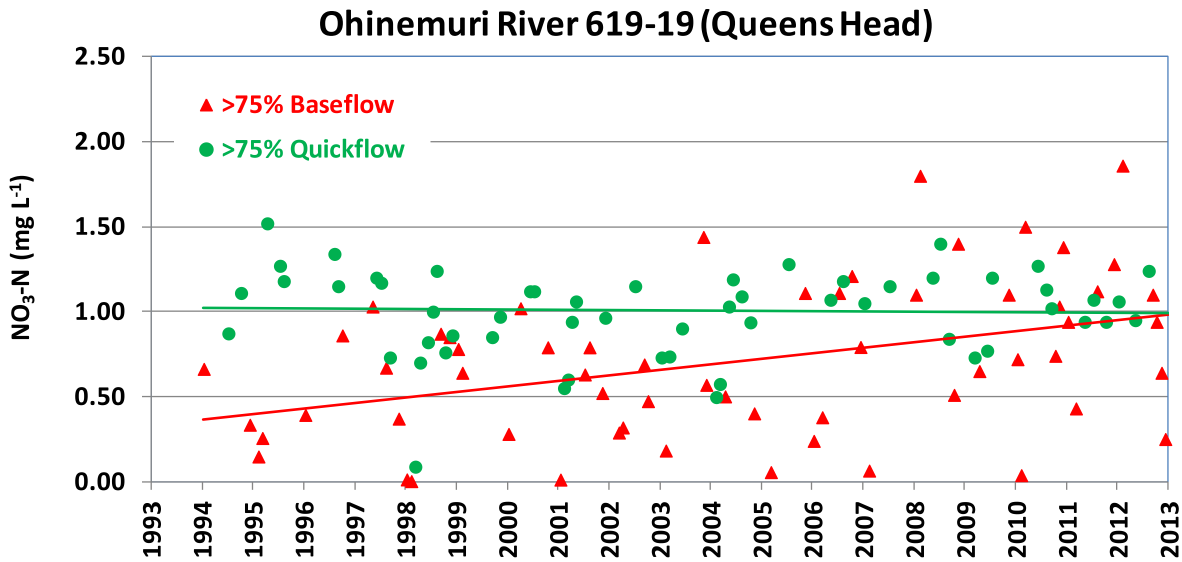


Fig. 7: NO_3-N concentration time series of Ohinemuri River (Coromandel). Baseflow-dominated sampling dates shown in red, quickflow-dominated dates in green.

Decreasing nitrate concentrations in the Mangatangi River (Fig. 8) are due to decreasing near-surface concentrations. The fairly steady and low baseflow concentrations would suggest there may have been a trend reversal before the groundwater system was affected.

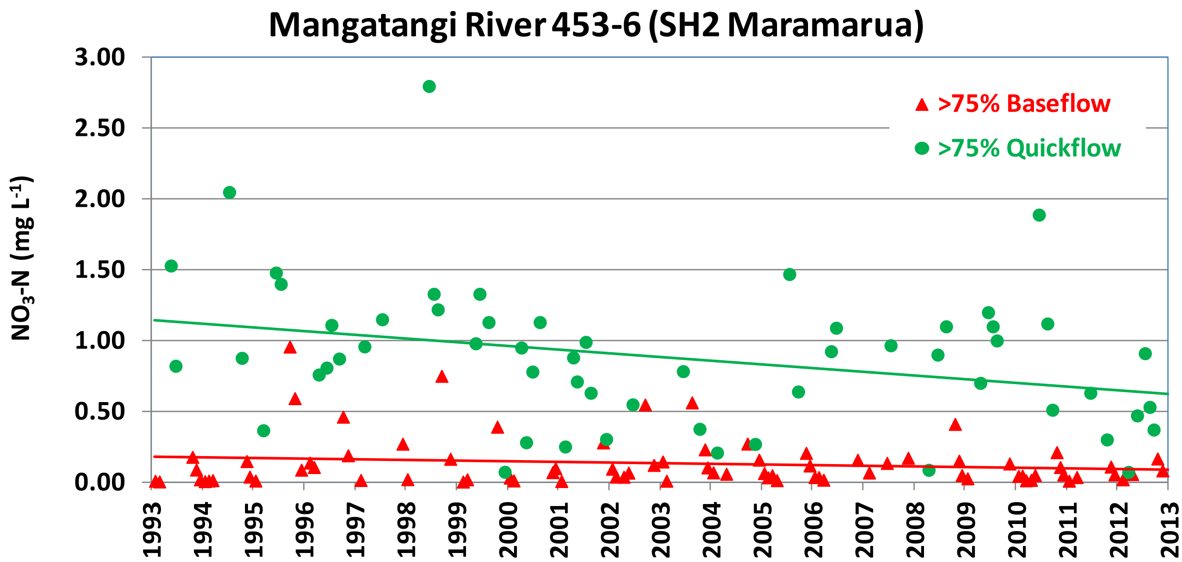


Fig. 8: NO_3-N concentration time series of Mangatangi River (Lower Waikato). Baseflow-dominated sampling dates shown in red, quickflow-dominated dates in green.

Conclusion

Initial results from this ongoing study have shown that the combined analysis of concentration and discharge data can provide insights into the relative importance of near-surface vs. groundwater flow paths, both for the absolute level of nutrient concentrations in rivers and for any trends in them. This improved understanding of flow path effects on river concentrations allows them to be more defensibly linked to the land use changes that have caused them.

Acknowledgments

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