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Land-to-water transfer of nutrients: What knowledge can be gained by combined analysis of river water quality and flow records?

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Land-to-water transfer of nutrients: What knowledge can be gained by combined analysis of river water quality and flow records?

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15 September 2014

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EXECUTIVE SUMMARY

Waikato Regional Council currently collects monthly grab samples for monitoring of water quality at 114 sites throughout the region, both from the Waikato River and from smaller stream and rivers. The samples are analysed for a range of water quality parameters, and since 2004, long term water quality trend analysis has been carried out at 5-yearly intervals.

Although water flow has not been recorded at many of the sites, flow adjustment has routinely been carried out as part of this process, in an attempt to remove the effects of flow trends from the analysis. However, access to flow records that are matched to water quality sampling sites also allows a wider range of analyses to be performed. The purpose of this report was to investigate potential advantages of establishing flow recording in parallel to the existing monthly water quality sampling programme, in order to allow a greater degree of information to be extracted from the water quality data.

The report identified 26 water quality sampling sites across the Waikato Region where continuous flow records were available, either at the sampling site, or nearby. These flow records were used in several ways to better understand the time series of total nitrogen (TN), nitrate-nitrite nitrogen (NNN), ammoniacal nitrogen (NH4), total phosphorus (TP), dissolved reactive phosphorus (DRP) and the non reactive phosphorus fraction (TP-DRP) collected at these sites. Silica concentration (Si) and electrical conductivity (EC) were also considered, as possible indicators of water age.

Four sets of analyses were carried out.

First, the frequency distribution of stream flow at time of water quality sampling was compared with the frequency distribution of stream flow in the continuous record. Since contaminant concentrations are often correlated to stream flow, differences in these distributions indicate where the water quality sampling programme might have been biased. In most cases these biases occur due to under-sampling of high flow conditions, which occur relatively infrequently, but typically comprise a significant proportion of the annual water flow and contaminant flux. The results showed that monthly grab sampling frequently gives a biased sample of flow conditions even after many years, and that within a single year, bias is almost guaranteed. This problem may be solved in the future with the advent of low cost, automated water quality monitoring systems.

Second, correlations between water quality and stream flow was identified for each site by analysis of the concentration-discharge relationships. Such correlations exist because observed stream flow is the combination of water simultaneously discharged from a range of flow paths with different chemical characteristics, from older, deeper groundwater that dominates stream flow during low flow conditions, to younger water contributing a greater proportion of total flow to the stream along surface and near-surface flow paths during and following storm events. Short term changes in concentration are therefore driven by changes in the proportions of older and younger water in response to flow conditions.

For each analyte, a linear regression was carried out between concentration and the logarithm of stream flow. TN, NNN and NH4 concentrations were strongly positively correlated with flow at many sites, indicating relatively low nitrate concentrations in deeper groundwater discharge, reflecting either water that was recharged prior to agricultural intensification, or nitrate assimilation in the subsurface. TP and TP-DRP concentrations were also positively correlated with flow at most sites, reflecting low TP-DRP concentrations in the subsurface coupled with increased surface runoff at high flows. DRP concentrations were negatively correlated with flow at 9 sites. This could be due to relatively high DRP concentrations in the discharging groundwater of these catchments being diluted during storm events.

Statistically significant correlations between Si and EC and flow were always negative. Concentrations of both of these analytes tend to increase with time in the subsurface, so that they reflect water age. The negative concentration-discharge relationships therefore reflect the older age of low flow water, compared with relatively young, high flow water.

Third, the stream flow information was used to stratify the water quality samples, in an attempt to identify those samples that primarily represent older water and those that primarily represent younger water. This was done either by stratifying the samples according to flow percentile at time of sampling (bottom quartile or top quartile), or by stratifying the samples based on the old water fraction as estimated by hydrograph separation (calibrated to either silica or EC). Although the hydrograph separation method has a stronger theoretical basis, the non-parametric flow percentile method gave more consistent results. After stratifying the water quality samples into low flow or high flow subsets, trend analysis was carried out. In some cases this was able to show that water quality trends previously identified by WRC could be attributed to changes in either low flow concentrations (reflecting older groundwater discharge) or high flow concentrations (reflecting more recent land use).

Finally, the water quality data were combined with the flow records to calculate annual contaminant loads (kg y^{-1}) and yields (kg ha^{-1} y^{-1}) for each catchment. The non-parametric Beale Ratio Estimator was found to be more robust for this purpose than the regression model approach, which relies on a strong correlation between concentration and flow. As expected, per hectare yields were higher in those catchments with relatively high levels of intensive agriculture. Known municipal or industrial point sources were also evident, as were geothermal influences. Year to year variation in yields was high for nutrients transported on near-surface flow paths (TN, NNN, NH4, TP and TP-DRP), whereas variation in DRP yields was much less, highlighting the importance of deeper flow paths for this analyte. Further analysis requires detailed land use information, which was beyond the scope of this study.

The analysis has been complicated by inconsistencies in the quality of the data (missing data, mismatch between water quality and flow recording sites and periods, changes in analytical methods) as well as by point source and geothermal impacts of water quality in some catchments. This has frequently hampered systematic comparison between catchments.

Ideally water quality sampling programmes should be accompanied by matched stream flow recording, in order to maximize the value of the sampling programme. When focusing on a single site, however, consideration of already available stream flow records can nevertheless provide substantial additional insight gained into stream contaminant dynamics and processes.

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TABLE OF CONTENTS:

Executive Summary **2**

1 Introduction **6**

2 Regularisation of Stream Flow Data **11**

3 Water Quality Sampling Bias **17**

4 Concentration-Discharge Relationships **25**

4.1 Introduction 25

4.2 Nitrogen Species 30

4.3 Phosphorus Species 36

4.4 Silica 42

4.5 Electrical Conductivity 46

5 Data Stratification **48**

5.1 Introduction 48

5.2 Data Stratification Approaches 48

5.2.1 Stratification based on Flow Percentiles 48

5.2.2 Stratification based on Hydrograph Separation 51

5.2.3 Discussion 68

5.3 Trend Analysis 68

5.3.1 Comparison with WRC (2013) Method 68

5.3.2 Trends in the Stratified Data 71

6 Load And Yield Estimation **77**

6.1 Regression Approach 77

6.2 Beale Ratio Estimator Approach 85

6.3 Catchment Comparisons 91

Conclusions **95**

Acknowledgments **96**

References **97**

Appendix 1: Concentration Discharge Relationships **100**

Appendix 2: Data Stratification Based on Flow **127**

1 INTRODUCTION

Since 1993, Waikato Regional Council has collected monthly grab samples at 114 stream and river sites across the region for water quality monitoring purposes (WRC, 2004). Ten of these sites represent the main stem of the Waikato River itself, and are not considered further in this report, while the remaining 104 represent other streams and rivers. The samples are analysed for a wide range of properties, including pH, electrical conductivity (EC), turbidity (Turb-N), dissolved oxygen (DO), nitrate-nitrite nitrogen (NNN), ammoniacal nitrogen (NH4), total Kjeldahl nitrogen (TKN), dissolved reactive phosphorus (DRP) and total phosphorus (TP); as well as the cations calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) and the anions chloride (Cl), sulphate (SO4) (1994, 2005 and July 2010 to June 2011 only) and silica (Si) (October 2010 to September 2011 only).

Water quality trends in 8 of these variables were reported by WRC (2013) for the first 20 years of data. Statistically significant trends ($p<0.05$) were identified using the Seasonal Kendall Trend Test, and those trends with concentration changes of more than ±1% of the median concentration per year were considered “important”. The analysis was carried out on both raw and “flow adjusted” concentrations. In the latter, a non parametric method was used to remove the long term dependence of concentration on stream flow based on flow recorded at the site or at a nearby site.

The purpose of the current report was to study the relationship between water quality and stream flow in more depth. Our hypothesis is that consideration of stream flow alongside water quality can enhance our understanding of water quality data and trends, particularly with regard to the transfer processes from the land to the stream monitoring site. Attention was focused on the key water quality parameters associated with pastoral farming; TN, NNN, NH4, TP and DRP. TN was calculated as the sum of NNN and TKN. In addition to these, the non-dissolved phosphorus fraction was calculated (TP-DRP). A nominal detection limit of 0.003 mg L^{-1} was assumed for TP-DRP in cases where the difference between TP and DRP was less that 0.003 mg L^{-1}. Two further analytes (Si and EC) were included for their potential to reflect groundwater age; these are discussed in more detail in Section 4.

In order to investigate the influence of stream flow on water quality, we analysed continuous stream flow data alongside the water chemistry sampling records at 26 sites (Figure 1, Table 1). These sites represent mesoscale catchments (10–1000 km^2) that cover all subregions of the Waikato region.

At 15 of the sites, stream flow was recorded at the same location from which the water quality samples were taken (although not always for the entire period). At a further 3 sites (Waitoa River (Landsdowne Road), Tahunaatara Stream, Whareroa Stream) the stream flow recording location was close enough that it could be considered to be co-located. At the remaining 8 sites, (Waiwawa River, Wharekawa River, Matahuru Stream, Mangapu River, Waipa River (Pirongia), Waipa River (Otorohanga), Waiotapu Stream, Waitetuna River) potentially significant ungauged tributaries enter between the (upstream) flow recorder and the (downstream) water quality sampling site. Accordingly, particular caution is required when interpreting the concentration-discharge relationships established for these sites (Section 4). These 8 sites are flagged “MF” (mismatched flow) in Table 1.

A further complication arises due to significant point source (PS) or geothermal (G) discharges being present in several of the catchments (Table 1). Details on residential and industrial point source discharges in the Hauraki region, for example, can be found in WRC (2011). WRC (2004) suggested that significant point source discharges could be indicated by elevated electrical conductivity (EC) in the stream water, and proposed that median EC values above 20 mS m^{-1} could be used to screen for significant point sources discharges. This criterion correctly identifies the geothermal influences in the Otamakokore and Waiotapu streams, and the point source discharges above the Piako River (Paeroa-Tahuna Road) and Waitoa River (Mellon Road) monitoring sites. In the current report we consider that point source discharges significantly affect water quality measurements at a further 3 sites (Whakapipi Stream, Mangapu River and Ohinemuri River) which have median EC above 17 mS m^{-1}. Point source and geothermal discharges are flagged in Table 1.

In 2004-2005 changes were made to the laboratory methods used for analysing both total phosphorus (TP) and dissolved reactive phosphorous (DRP), the details of which are described in WRC (2013). Inspection of the data showed that at some sites these changes had noticeably affected the long term records of TP and DRP. Data affected included the TP measurements for the geothermal Otamakokore and Waiotyapu stream, and the DRP measurements for the Kauaeranga, Ohinemuri, Tapu, Waiwawa, Wharekawa, Waipa (Pirongia) and Oparau river sites. TP and DRP data from these sites is noted as “suspect” in Table 1. In fact TP data were missing from the database at the two sites, Waiotapu Stream and Otamakokore Stream, for the 2005-2011 period.

Following WRC (2013), the 20 year period 1 January 1993 to 31 December 2012 was chosen as a reference period to facilitate comparisons between the sites. Monthly water quality data was available at all sites for most of this period (sampling began in 1994 at 9 sites, and in December 2000 at Whareroa Stream). Stream flow data availability was a lot more variable, with only 17 of the 26 sites having stream flow data available for the full 20 year period. Figure 2 shows the period for which water chemistry data was available at each site, and whether flow data was also available or not at these times. Sites with a short data series are also flagged in Table 1.

Based on this dataset, the following data analysis was carried out:

- Preprocessing of the flow data to convert it from various and variable time steps onto to a regular time step (Section 2),
- Analysis of the frequency distribution of flow at time of water quality sampling, to assess the possibility of bias in the water quality sampling (Section 3),
- Analysis of the concentration-discharge relationships for 8 key water quality variables (Section 4),
- Exploring the possibility of extracting additional information by stratifying the data on the basis of flow percentile or hydrograph separation (Section 5),
- Calculations and comparisons of annual contaminant loads and yields (Section 6).

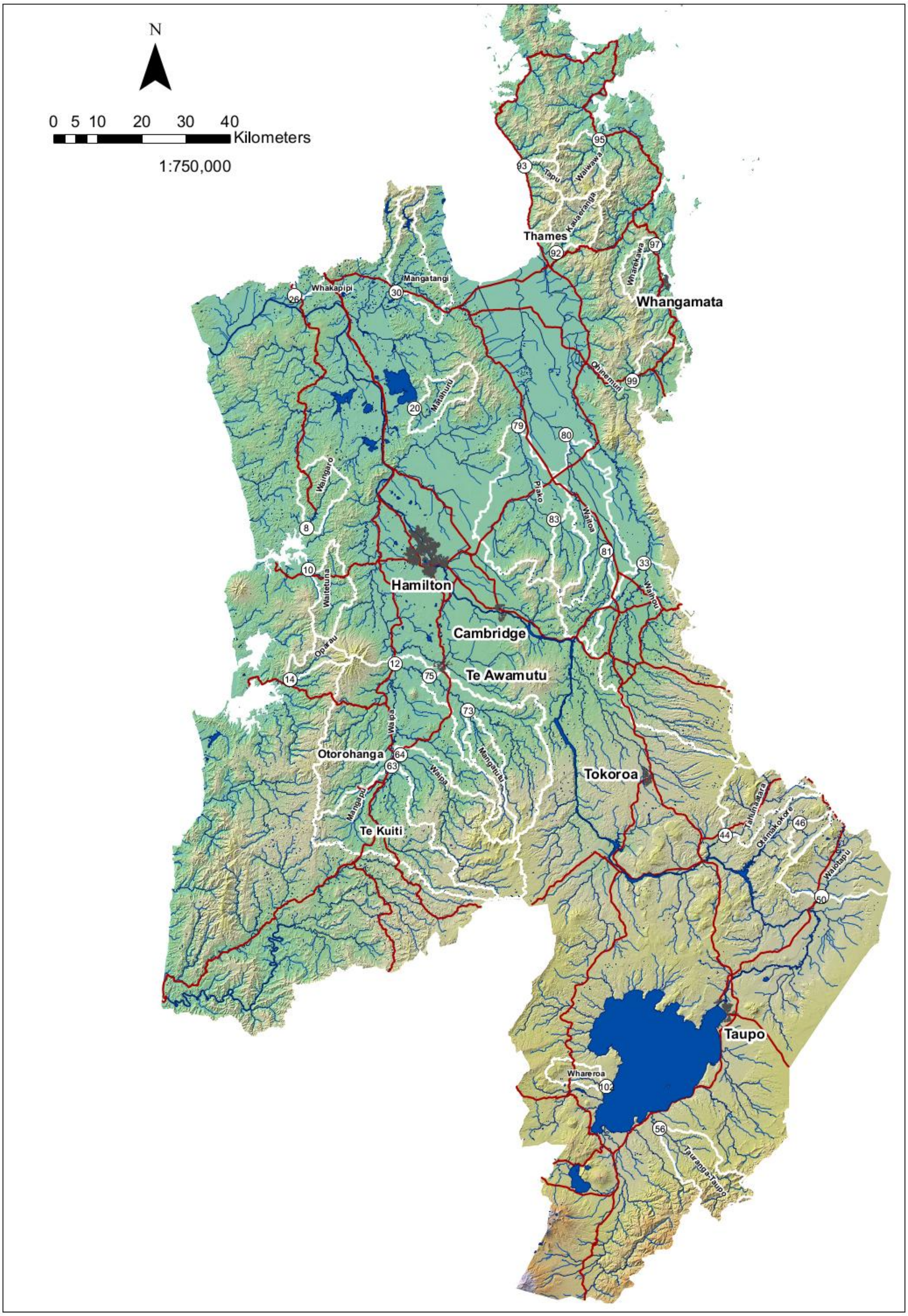


Figure 1: Map showing selected water quality monitoring sites (numbered circles) and topographical catchment boundaries (in white). The site names are listed in Table 1.

Table 1: Water quality sampling locations considered in this report, and associated stream flow monitoring sites. “Area” is the topographical catchment area above the water sampling location in km^2. “Point” flags indicates significant point source (PS) or geothermal (G) discharges. “Flow” flags indicates mismatched flow (MF), where significant tributaries enter the stream between the water quality and flow monitoring locations, or short data series (SS) (see Figure 2). “Lab” flags identifies sites affected by changes to TP and DRP laboratory procedures as described in the text.

Region	Map Key	Site Name	Sample Location	ChemID	Area	ChemStart	Flow Location	Flow ID	FlowStart	Point	Flow	Lab
Coromandel												
	92	Kauaeranga River	Smiths Cableway/Recorder	234-11	119.5	11-Jan-94	Smiths Cableway/Recorder	234-11	16-Feb-59	-	-	DRP
	99	Ohinemuri River	Queens Head	619-19	135.7	11-Jan-94	Queens Head Rock	619-19	19-Aug-83	PS	-	DRP
	93	Tapu River	Tapu-Coroglen Rd	954-5	26.1	11-Jan-94	Tapu-Coroglen Road	954-5	1-Jul-91	-	-	DRP
	95	Waiwawa River	SH25 Coroglen	1257-3	132	11-Jan-94	Rangihau Road Ford	1257-2	3-Jul-91	-	MF	DRP
	97	Wharekawa River	SH25	1312-3	55.4	11-Jan-94	Adams Farm Br	1312-1	10-Jun-91	-	MF	DRP
Hauraki												
	83	Piako River	Kiwitahi	749-10	103.6	13-Jan-94	Kiwitahi	749-10	23-Apr-80	-	-	-
	79	Piako River	Paeroa-Tahuna Rd Br	749-15	537	13-Jan-94	Paeroa-Tahuna Road Bridge	749-15	3-Jul-72	PS	-	-
	33	Waihou River	Okauia	1122-18	802.1	28-Jan-93	Okauia	1122-18	23-Mar-82	-	-	-
	81	Waitoa River	Landsdowne Rd Br	1249-15	121.8	13-Jan-94	Waharoa Control	1249-38	18-May-84	-	-	-
	80	Waitoa River	Mellon Rd Recorder	1249-18	409.3	13-Jan-94	Mellon Road	1249-18	2-May-86	PS	-	-
Lower Waikato												
	30	Mangatangi River	SH2 Maramarua	453-6	194.5	26-Jan-93	SH2 Maramarua	453-6	19-May-86	-	-	-
	20	Matahuru Stm	Waiterimu Road Below Confl	516-5	105.4	26-Jan-93	Myjers Farm Bridge	516-22	17-Jul-06	-	MF, SS	-
	26	Whakapipi Stm	SH22 Br	1282-8	45.4	25-Feb-93	SH22 Bridge	1282-8	5-Mar-84	PS	-	-
Waipa												
	63	Mangapu River	Otorohanga	443-3	445.5	3-Feb-93	SH3 + Mangaokewa	443-4	17-Oct-00	PS	MF, SS	-
	73	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	121.9	5-Feb-93	Walker Road Bridge	476-7	8-Jun-04	-	SS	-
	75	Puniu River	Bartons Corner Rd Br	818-2	519.1	5-Feb-93	Bartons Corner Road Bridge	818-2	6-May-85	-	-	-
	64	Waipa River	SH3 Otorohanga	1191-12	457.6	3-Feb-93	SH31 - Mangapu - Mangaokewa	1191-13	17-Oct-00	-	MF, SS	-
	12	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	2184.1	25-Jan-93	Pukehoua Bridge on Baffin Road	1191-2	22-Dec-04	-	MF, SS	DRP
Upper Waikato												
	46	Otamakokore Stm	Hossack Rd	683-4	45.6	28-Jan-93	Hossack Road	683-4	9-Dec-86	G	-	TP
	44	Tahunaatara Stm	Ohakuri Rd	934-1	208.1	28-Jan-93	Ohakuri Rd (NIWA)	1-3	16-Apr-64	-	-	-
	50	Waiotapu Stm	Homestead Rd Br	1186-4	297.5	28-Jan-93	Reporoa (NIWA)	1-4	24-Feb-60	G	MF	TP
West Coast												
	14	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	58.5	25-Jan-93	Langdon Road (Off Okupata Road)	658-1	12-Dec-07	-	SS	DRP
	8	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	118.5	25-Jan-93	Ruakiwi Road Off SH22	1167-4	30-Nov-01	-	SS	-
	10	Waitetuna River	Te Uku-Waingaro Rd	1247-2	124.4	25-Jan-93	SH23 Raglan	1247-1	7-Dec-07	-	MF, SS	-
Taupo												
	56	Tauranga-Taupo River	Te Kono Slackline	971-4	197.3	29-Jan-93	Te Kono	971-4	11-Feb-76	-	-	-
	102	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	59.2	6-Dec-00	Fish Trap	1318-5	8-May-02	-	SS	-

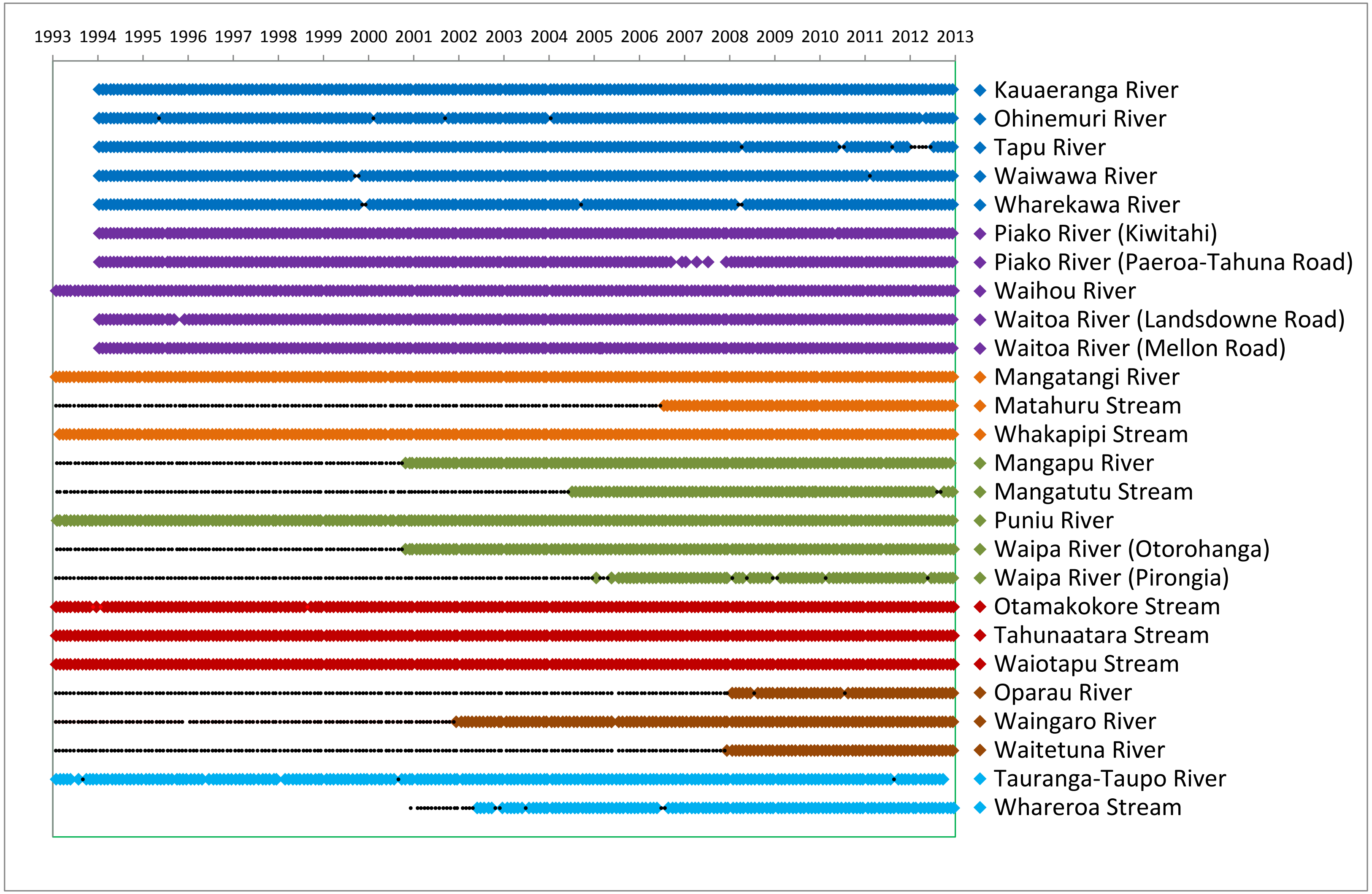


Figure 2: Summary of stream flow data availability for the 26 sites studied. Large diamonds indicate that stream flow data was available at the time of water quality sampling. Small black diamonds indicate that no flow data was available at the time of water quality sampling.

2 REGULARISATION OF STREAM FLOW DATA

Before water quality-stream flow interactions could be considered, the flow data required standardisation. Waikato Regional Council stream flow data is stored in a database system as a series of date/time-flow pairs. In most cases stream stage recordings are taken at regular intervals (typically 5, 10 or 15 minutes), converted into stream flow in cumecs (m^3 s^{-1}) using a rating curve, and then entered into database software.

In some cases, particularly prior to 2004, the logger or the database software has included algorithms (the details of which are unknown) to remove data points where stream flow has not changed significantly between time steps. This has presumably been done to reduce data storage requirements (“data reduction”). As a result, there may be large gaps in the stored data that must be filled by interpolation. If interpolation is not carried out, there will be more stream flow data points in winter (when flow changes often) than summer (when flow may be stable for longer periods of time). This will bias any statistics calculated on the raw flow data.

In some cases there are also (typically short) periods of “missing data”, which have been tagged in the data files. Periods of missing data up to two days in length have been filled by interpolation. No attempt has been made in this study to fill periods of missing data longer than two days.

For example, Table 2 shows the header and first few data rows from the flow file for Waitoa River (Waharoa Control) recording site (Location 1249-38) used to represent stream flow at the Waitoa River (Landsdowne Rd Br) water quality sampling site (Location 1249-15). The entire text file of flow data for this site has 1.36 million rows and is 58 megabytes in size. During the short period shown, recordings were taken at irregular intervals, presumably automatically triggered by stage (water level) changes. Furthermore, during the 1993-2012 period, the base time step also appears to have changed several times, as shown in Table 3. Flow seems to have been recorded at 15 minute intervals from 1994 to 1996, then every 5 minutes from 1996 to 2004, but data reduction algorithms have been applied either in the logger or later in the database software, so the flow records could be separated by as much as 18 hours in extreme cases. After 2004, a constant 5 minute interval seems to have been used.

Table 4 summarises the stream flow data available for the 26 monitoring sites. The period of flow data, raw time steps, and evidence of data reduction are summarised.

As described in Section 1, several of the flow files used do not correspond directly to water quality monitoring sites. As noted in Table 1, in some cases significant tributaries enter the stream between the flow recording site and the water quality sampling site. Further complications arise in the upper Waipa catchment, where water quality sites lie on different branches to the flow sites. As a result, stream flow for the Mangapu River water quality site (443-3) was calculated as the sum of stream flow from the Mangapu (443-4) and Mangaokewa (414-13) River flow recorders. Even so, additional tributaries remain unaccounted for. Stream flow for the Waipa (Otorohanga) water quality site (1191-12) was similarly calculated from Waipa River flow recorder at SH31 (1191-13), less the combined stream flow from the Mangapu (443-4) and Mangaokewa (414-13) Rivers. This method is particularly

Table 2: Stream flow data file sample excerpt.

```
Station Site:     Waitoa River
Station Name:     Waharoa Control
Station Number:   38
LocalX:     ---
LocalY:     ---
Datum:      ---
Parameter Name:   Flow
Parameter Type:   Q
Parameter Type Name:    ---
Time series Name: 1249/38/Flow/Cmd.P
Time series Unit: cumec
GlobalX:    1841868.000000
GlobalY:    5817036.000000
Longitude:  175.745733
Latitude:   -37.762043
Date,Time,Value [cumec],State of value
08/02/1984,10:20:00,---,missing, calc
18/05/1984,15:15:00,---,missing, calc
18/05/1984,15:16:00,0.185429,20 (20), calc
19/05/1984,09:40:58,0.196445,20 (20), calc
19/05/1984,15:40:06,0.192246,20 (20), calc
20/05/1984,00:26:15,0.192246,20 (20), calc
20/05/1984,18:32:11,0.203634,20 (20), calc
21/05/1984,18:45:57,0.197863,20 (20), calc
24/05/1984,07:59:15,0.217165,20 (20), calc
24/05/1984,13:49:39,0.266121,20 (20), calc
24/05/1984,17:05:28,0.391083,20 (20), calc
25/05/1984,03:30:31,0.388222,20 (20), calc
25/05/1984,08:20:36,0.665439,20 (20), calc
25/05/1984,11:11:31,1.025007,20 (20), calc
25/05/1984,15:19:09,1.135484,20 (20), calc
25/05/1984,21:34:37,1.246047,20 (20), calc
26/05/1984,06:23:50,1.157612,20 (20), calc
26/05/1984,09:48:35,1.371256,20 (20), calc
26/05/1984,12:29:49,1.721128,20 (20), calc
26/05/1984,15:39:16,1.966082,20 (20), calc
26/05/1984,18:46:41,2.156900,20 (20), calc
27/05/1984,01:03:24,2.316224,20 (20), calc
27/05/1984,03:50:08,2.583245,20 (20), calc
27/05/1984,06:52:03,---,missing, calc
27/05/1984,09:35:25,3.301062,20 (20), calc
27/05/1984,12:42:14,3.720578,20 (20), calc
27/05/1984,15:41:39,3.686912,20 (20), calc
Etc…
```

Table 3: Frequency of data time steps (in minutes) in the flow file in Table 2. For each year, the number of time steps of different lengths are counted, In 5 minute intervals, from 0 (i.e. less than 5 minutes) to 60. Time steps 65 minutes or longer are not shown.

Waitoa River 1249-38 (Waharoa Control)													
	0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
1994	0	0	0	2545	0	0	2895	0	0	861	0	0	913
1995	0	33	0	4236	14	0	4285	7	0	990	5	0	1193
1996	0	5999	8705	1770	1868	613	1642	262	275	421	154	111	545
1997	0	9894	6828	1198	1577	663	504	396	318	233	208	186	177
1998	0	25749	3481	1478	1019	662	479	416	317	283	241	215	171
1999	0	20313	2656	1294	909	656	543	430	349	315	266	222	220
2000	0	20174	2981	1469	911	653	496	382	309	312	279	228	204
2001	0	29484	3718	1801	1017	694	554	445	352	272	246	181	190
2002	4	39416	6039	3409	1482	824	1802	680	212	185	423	193	335
2003	1	25373	3673	2744	993	1009	1110	489	561	706	176	180	142
2004	0	77534	1811	441	320	363	792	106	72	70	50	45	37
2005	2	105098	2	2	0	0	0	0	0	0	0	0	0
2006	1	103565	46	6	2	0	1	0	0	1	0	0	0
2007	0	105020	27	0	0	0	0	1	0	0	0	0	0
2008	1	105229	5	1	0	2	1	2	0	0	0	0	1
2009	0	104974	4	2	4	1	0	1	1	0	0	0	0
2010	0	105037	18	0	1	1	0	1	1	0	0	1	1
2011	0	104987	4	1	1	1	0	2	1	2	1	0	1
2012	0	105217	28	0	1	1	0	0	1	0	0	0	0

Table 4: Summary of stream flow data used for analysis of the water chemistry data. ChemFlowStart and ChemFlowEnd show the period of flow data used, “Short” indicates the proportion of water chemistry data not covered by this, and “Missing” is the proportion of missing data in this period. “Time Step” is the default time step(s) in minutes and “Data Reduction” is described in the text. Two flow data files were obtained from NIWA, as indicated.

Region	Site Name	Flow Location	Flow ID	ChemFlowStart	ChemFlowEnd	Short	Missing	Time Step	Data Reduction
Coromandel									
	Kauaeranga River	Smiths Cableway/Recorder	234-11	1-Jan-94	31-Dec-12	0%	0%	5	prior to 2004
	Ohinemuri River	Queens Head Rock	619-19	1-Jan-94	31-Dec-12	0%	2%	5/10	prior to 2004
	Tapu River	Tapu-Coroglen Road	954-5	1-Jan-94	31-Dec-12	0%	5%	10	yes
	Waiwawa River	Rangihau Road Ford	1257-2	1-Jan-94	31-Dec-12	0%	1%	5	prior to 2004
	Wharekawa River	Adams Farm Br	1312-1	1-Jan-94	31-Dec-12	0%	2%	5	prior to 2004
Hauraki									
	Piako River	Kiwitahi	749-10	1-Jan-94	31-Dec-12	0%	0%	5	prior to 2004
	Piako River	Paeroa-Tahuna Road Bridge	749-15	1-Jan-94	31-Dec-12	0%	0%	5	prior to 2004
	Waihou River	Okauia	1122-18	1-Jan-93	31-Dec-12	0%	0%	5	prior to 2004
	Waitoa River	Waharoa Control	1249-38	1-Jan-94	31-Dec-12	0%	0%	5	prior to 2004
	Waitoa River	Mellon Road	1249-18	1-Jan-94	31-Dec-12	0%	0%	5	prior to 2004
Lower Waikato									
	Mangatangi River	SH2 Maramarua	453-6	1-Jan-93	31-Dec-12	0%	0%	5	prior to 2004
	Matahuru Stm	Myjers Farm Bridge	516-22	1-Jul-06	31-Dec-12	67%	1%	10	no
	Whakapipi Stm	SH22 Bridge	1282-8	1-Feb-93	31-Dec-12	0%	0%	5	prior to 2004
Waipa									
	Mangapu River	SH3 + Mangaokewa	443-4	1-Oct-00	30-Nov-12	39%	1%	10	no
	Mangatutu Stm (Waikeria)	Walker Road Bridge	476-7	1-Jul-04	31-Dec-12	57%	2%	10	no
	Puniu River	Bartons Corner Road Bridge	818-2	1-Feb-93	31-Dec-12	0%	0%	5	prior to 2004
	Waipa River	SH31 - Mangapu - Mangaokewa	1191-13	1-Oct-00	31-Dec-12	38%	1%	10	no
	Waipa River	Pukehoua Bridge on Baffin Road	1191-2	1-Jan-05	31-Dec-12	60%	8%	5	no
Upper Waikato									
	Otamakokore Stm	Hossack Road	683-4	1-Jan-93	31-Dec-12	0%	1%	10	yes
	Tahunaatara Stm	Ohakuri Rd (NIWA)		1-Jan-93	31-Dec-12	0%	0%	15	no
	Waiotapu Stm	Reporoa (NIWA)		1-Jan-93	31-Dec-12	0%	0%	15	no
West Coast									
	Oparau River	Langdon Road (Off Okupata Road)	658-1	1-Jan-08	31-Dec-12	75%	3%	5/10/15	no
	Waingaro River (Pukemiro)	Ruakiwi Road Off SH22	1167-4	1-Dec-01	31-Dec-12	45%	1%	5	prior to 2004
	Waitetuna River	SH23 Raglan	1247-1	1-Dec-07	31-Dec-12	75%	0%	10	no
Taupo									
	Tauranga-Taupo River	Te Kono	971-4	1-Jan-93	30-Sep-12	0%	1%	5/15	prior to 2010
	Whareroa Stm (Taupo)	Fish Trap	1318-5	1-May-02	31-Dec-12	12%	4%	5	prior to 2006

problematic: due to the time delays between the three flow sites, and as a result the estimated flow at the Waipa River water quality site (1191-12) is sometimes very small or even negative (and so currently treated as missing data). Additional tributaries are also unaccounted for at this site. A more sophisticated flow estimate is possible, but is beyond the scope of this study.

Unevenly spaced data requires interpolation onto a fixed time step (a process we call "regularisation"). Linear interpolation is usually used, or logarithmic interpolation, both of which tend to slightly "flatten" the peaks and troughs of the signal, especially if relatively large time steps are used (this flattening can be ameliorated by use of more sophisticated algorithms, such as Savitzky-Golay filtering (Press et al., 1992), but these have not been pursued here). In our analysis, we used logarithmic interpolation of the flow data onto 15-minute intervals (although longer time intervals, even up to a day, give almost identical results statistically). Logarithmic interpolation is preferred over linear interpolation in this case because of the positively skewed nature of flow data. In this method, flow Q_t at time t is estimated from flow Q_a and time t_a and Q_b and time t_b (where $t_a < t < t_b$) as:

$$lnQ_t = lnQ_a + (lnQ_b - lnQ_a)\frac{t\ -t_a}{t_b - t_a}$$

Figure 3 shows how regularisation corrects the frequency distribution of the flow data at the Waitoa River (Waharoa Control) site. Flow measurement frequency is plotted against the day of the year to show the seasonality of data collection. The red diamonds show the frequency of raw data points stored in the database, which are not evenly spaced throughout the year, being affected by the logger and database data reduction algorithms, so that winter data are more frequent, as this is the time of year when flow changes most rapidly. If flows were sampled with a fixed time step, we would expect every day would contribute a fraction of 1/365 or 0.27% to the annual record. After interpolation ("regularisation") of the flow data onto 15-minute intervals, the black triangle series was achieved, which is almost constant, with deviations being due to small amounts of missing data.

Figure 4 demonstrates the effect of regularisation on flow data with larger gaps at the Oparau River site. The original data for this site was on a regular time step (although the time step changed from 10 minutes to 15 minutes to 5 minutes over the years). Long periods of missing data result in a "step" pattern where some periods are under-represented, principally in the winter (spring is consequently over-represented). It is not possible to reconstruct the missing data, as the gaps are too large for meaningful interpolation. The missing data could result in biased annual flow statistics for this site, therefore, as different times of year (for example) are not equally represented. The proportion of missing data at each site is indicated in Table 4.

A full set of frequency charts is given in Appendix 1. Logarithmic interpolation was used to regularise all flow data onto a 15 minute time step.

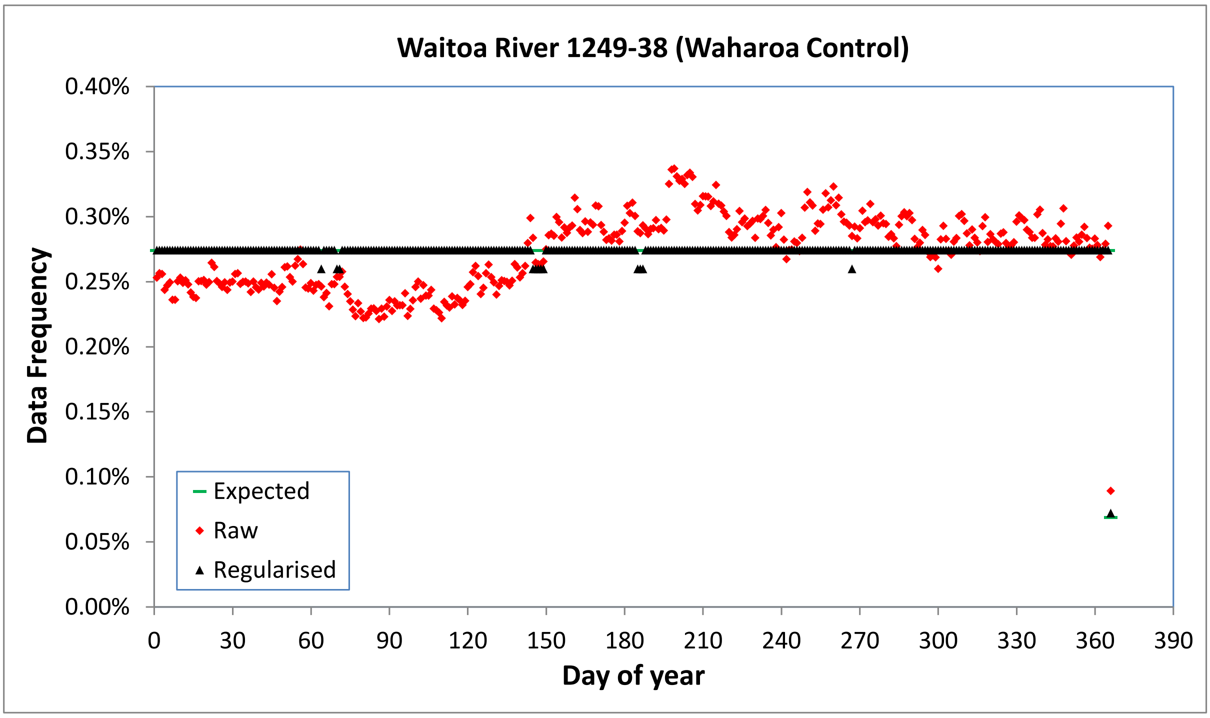


Figure 3: Frequency of raw stream flow data compared with frequency of stream flow data interpolated onto a regular 15 minute time step, for a site where data reduction algorithms have been applied to the raw data.

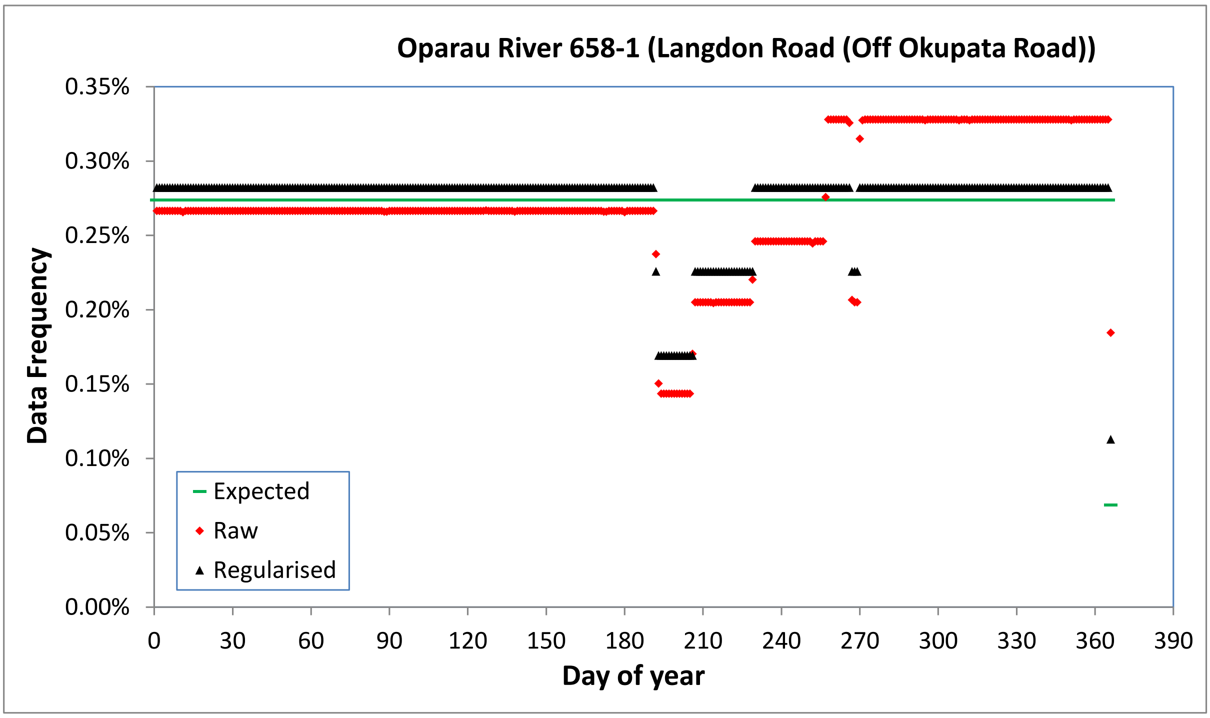


Figure 4: Frequency of raw stream flow data compared with frequency of stream flow data interpolated onto a 15 minute time step, for a site where the raw data is on a fixed time step, but has missing periods.

3 WATER QUALITY SAMPLING BIAS

A key question in periodic (e.g. monthly) stream water quality sampling is how representative the samples are of overall conditions. Stream flow and water quality are typically very dynamic, changing rapidly in response to rainfall events, and monthly sampling may give a limited picture of the range of conditions experienced. The picture may also be biased, for example if few (or many) samples are taken during storm flow conditions which, though short-lived, may represent a large portion of the annual water flow and contaminant load.

The high-resolution stream flow time series data can be used to determine whether the flow conditions under which the monthly water quality samples were taken, are representative of the overall flow conditions observed at a site. To do this, the stream flow at the time of the monthly water quality sampling was estimated by interpolation from the regularised flow time series.

For example, Figure 5 shows the monthly TN, NNN and NH4 samples from the Whareroa Stream 1318-4 (Taupo) water quality site, as well as stream flows measured at the Whareroa Stream 1318-5 (Fish Trap) flow recorder, approximately 900 m upstream (both daily and at the time of water quality sampling). This site was chosen as an example, despite the fact that it does not cover the whole 20 year period, because its hydrograph is less dynamic than those of most other sites, which makes it easier to visually interpret the concentration and flow data.

In Figure 5 we can recognise strong, synchronised, seasonal trends in TN, NNN and flow. Furthermore, we might suspect that TN and NNN are increasing over time. Indeed WRC (2013) confirmed the likelihood of increasing TN and NNN trends at this site. NH4 concentrations, on the other hand, are consistently low, near detection limit (0.01 mg L^{-1}) at this site.

Comparison between the sampled stream flows (blue squares) and the daily stream flows (blue dotted line) in Figure 5 shows that most peak flows are missed in the monthly sampling schedule. In order to assess any bias possibly resulting from fixed monthly sampling schedules, therefore, the frequency distribution of stream flow at time of monthly water quality sampling was compared with the frequency distribution of the continuous high-resolution stream flow record at every site. This allows us to determine to what extent the range of stream flows sampled was representative of the overall flow hydrograph.

Figure 6 shows the “regularised” (interpolated, continuous) flow distribution for the Whareroa Stream compared with the flow distribution based only on the monthly “sampled” dates. The x-axis is subdivided logarithmically in steps of $10^{0.2}$ m^3 s^{-1}.(i.e. 5 bins for each order of magnitude) The distributions are compared as (1) the frequency of samples in each flow range, and (2) the total flow sampled in each flow range. The former is more relevant for the purposes of estimating concentrations, for example, while the latter is more relevant for estimating loads.

This shows that for this site, the highest flow categories were under-sampled, but across the entire flow range, the sampled flows were fairly similar to the overall flow record in terms of both % of samples, and % of annual flow sampled (Figure 6).

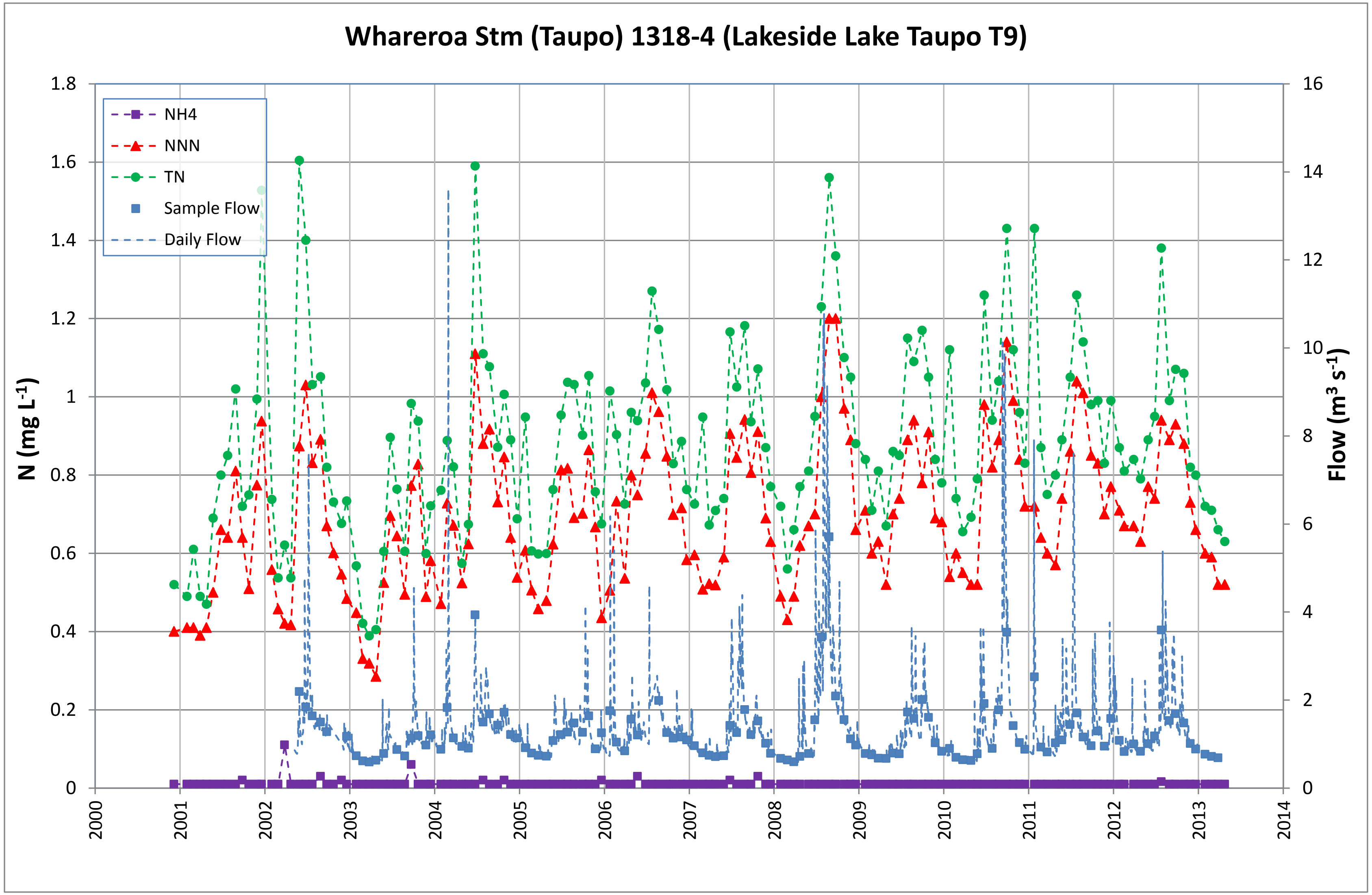
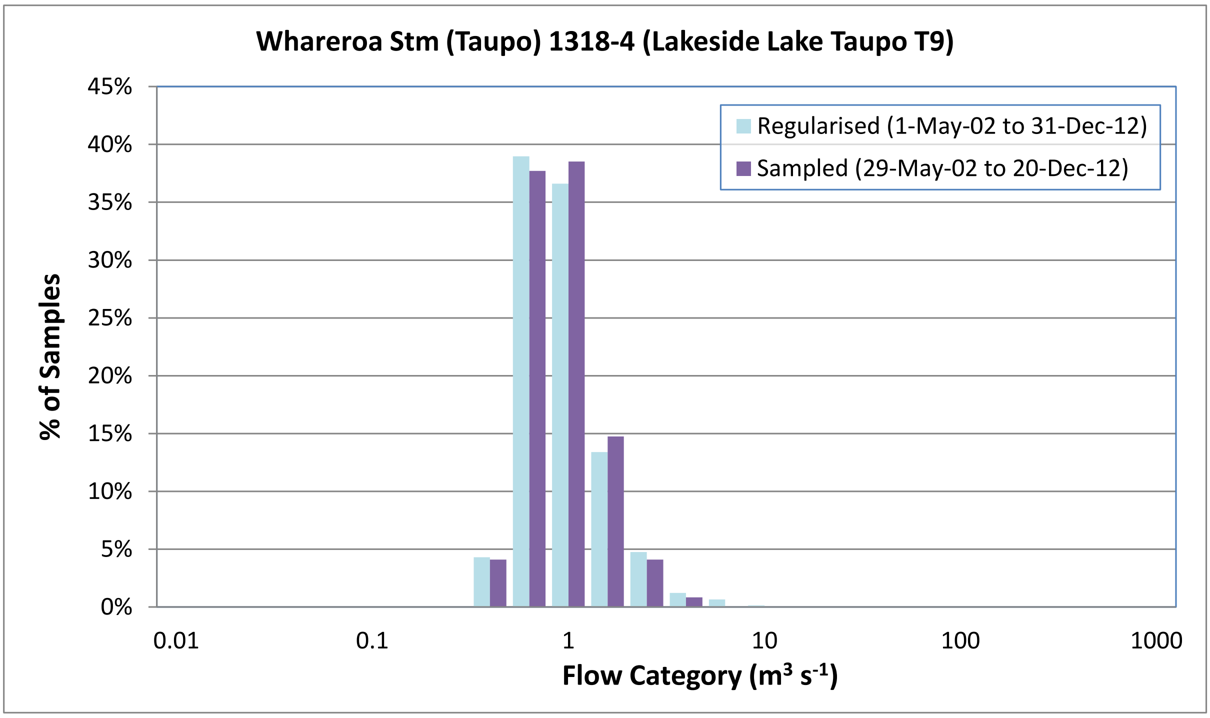


Figure 5: Time series of nitrogen species concentrations at Whareroa Stream (Taupo), and associated flows (both daily and at time of water quality sampling).



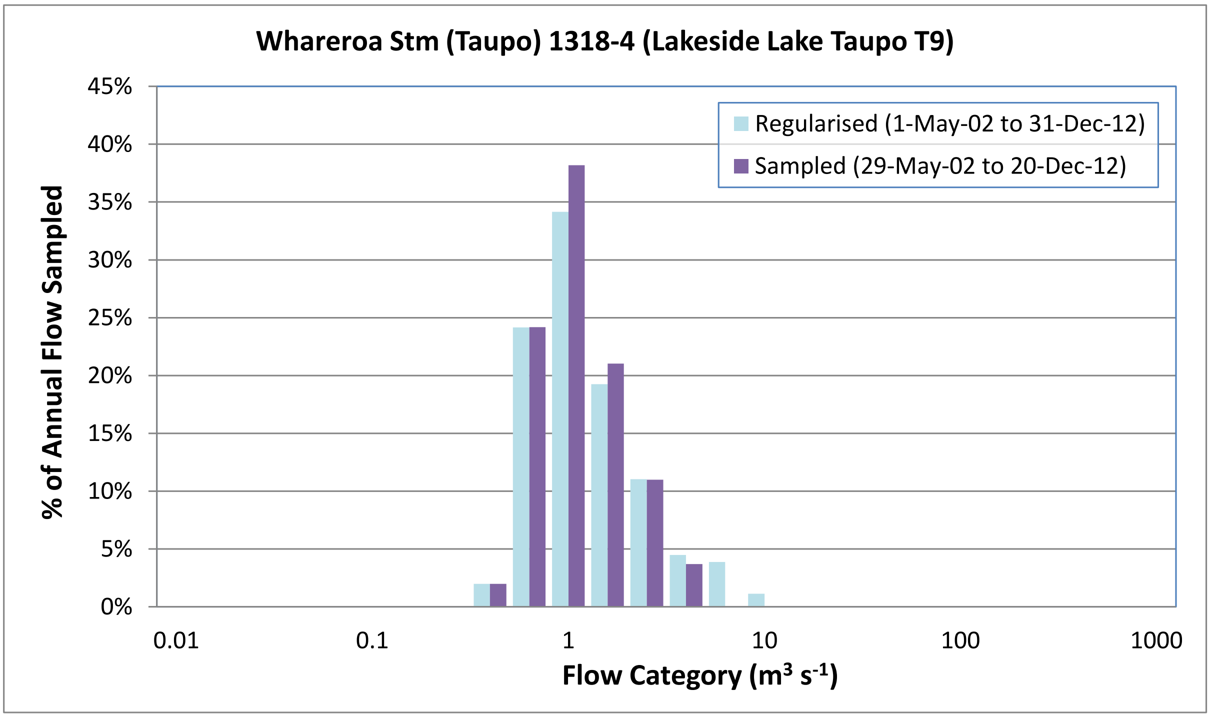


Figure 6: Bias in water quality sampling expressed in two ways, showing under-sampling of high flows.

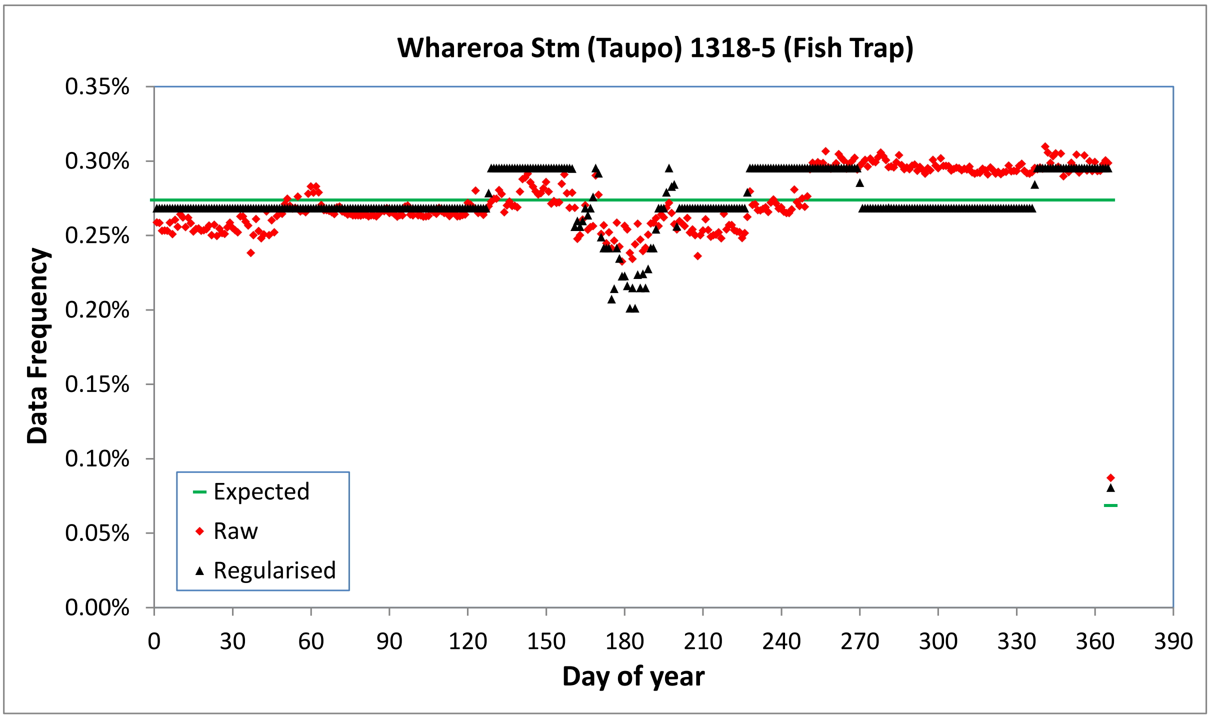
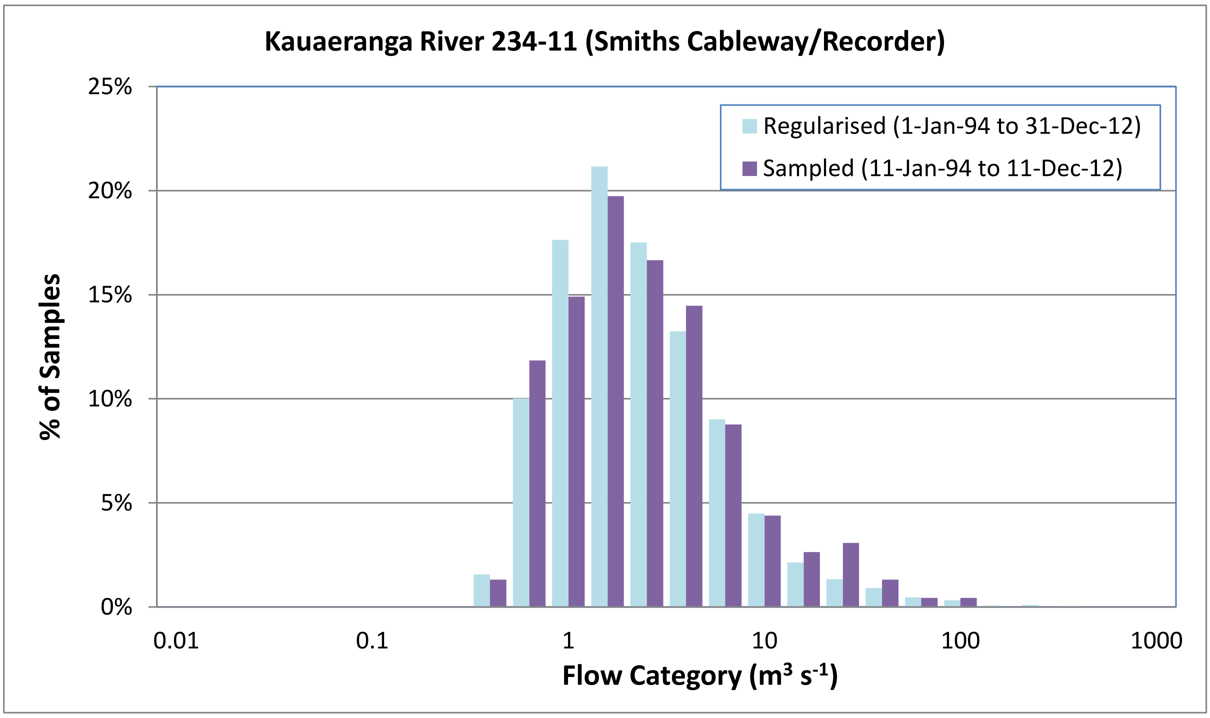


Figure 7: Frequency of raw stream flow data compared with frequency of stream flow data interpolated onto a regular 15 minute time step, for Whareroa Stream.

Caution must be exercised when comparing the monthly sampled flows with the continuous regularised flows however, as the regularised flows may themselves be biased. While both sets of flows are taken from the same time period (that for which water quality and stream flow data are both available), many of the stream flow records contain periods of missing data (Table 4). In the case of Whareroa Stream, certain times of year are slightly overrepresented in the regularised flow data, while a period in midwinter is underrepresented (Figure 7). While the comparison in Figure 6 is valid therefore, since missing data is missing from both distributions, it may not accurately represent the long term flow frequency distribution at this site.

In contrast to the Whareroa Stream data, Figure 8 shows the “regularised” (interpolated, continuous) flow distribution for the Kauaeranga River site compared with the distribution based only on the monthly “sampled” dates. The Kauaeranga River site was chosen as an example of a river with a very dynamic flow hydrograph, which dominate the monitoring sites. The frequency distributions in this case show that flows of $10^{1.4}$-$10^{1.8}$ (25-63) $m^3 s^{-1}$ were overrepresented in the water quality samples, whereas flows above $10^{2.2}$ (158) $m^3 s^{-1}$ were not sampled at all (which represented 12% of the total water flow). This will lead to biases in the water quality data in the many instances where an analyte concentration is correlated with stream flow (c.f. Section 4).

At the Piako River (Paeroa-Tahuna Road) site, on the other hand, the highest flows were over-represented in the water quality samples, as shown in Figure 9. This is probably due to random chance: infrequent (e.g. monthly) sampling results in great variability in the sampling of rare, short duration, high flow events.



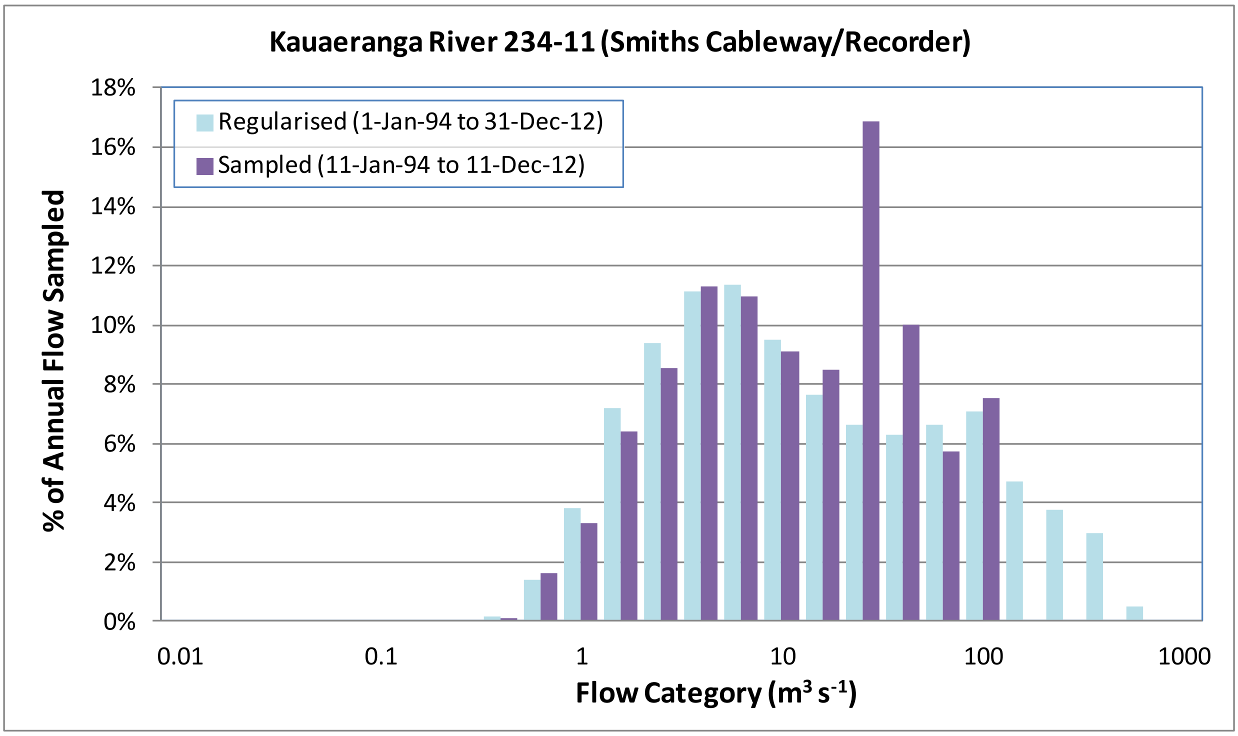
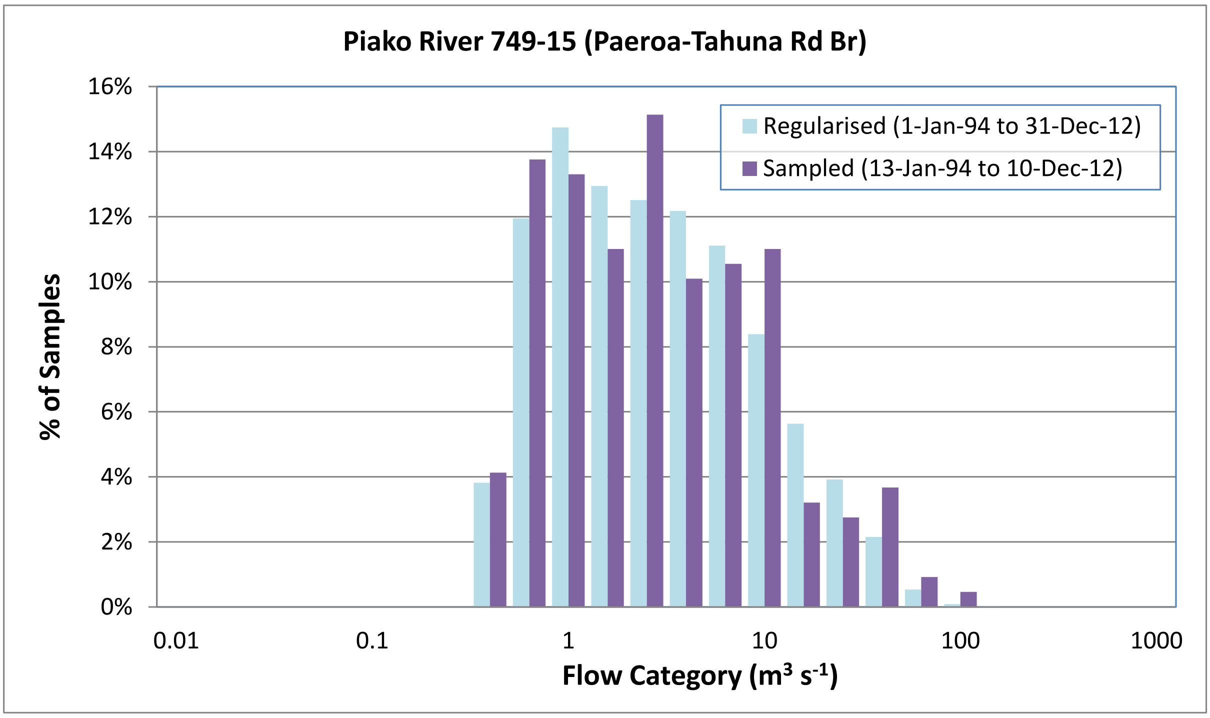


Figure 8: Bias in water quality sampling expressed in two ways, showing under-sampling of high flows.



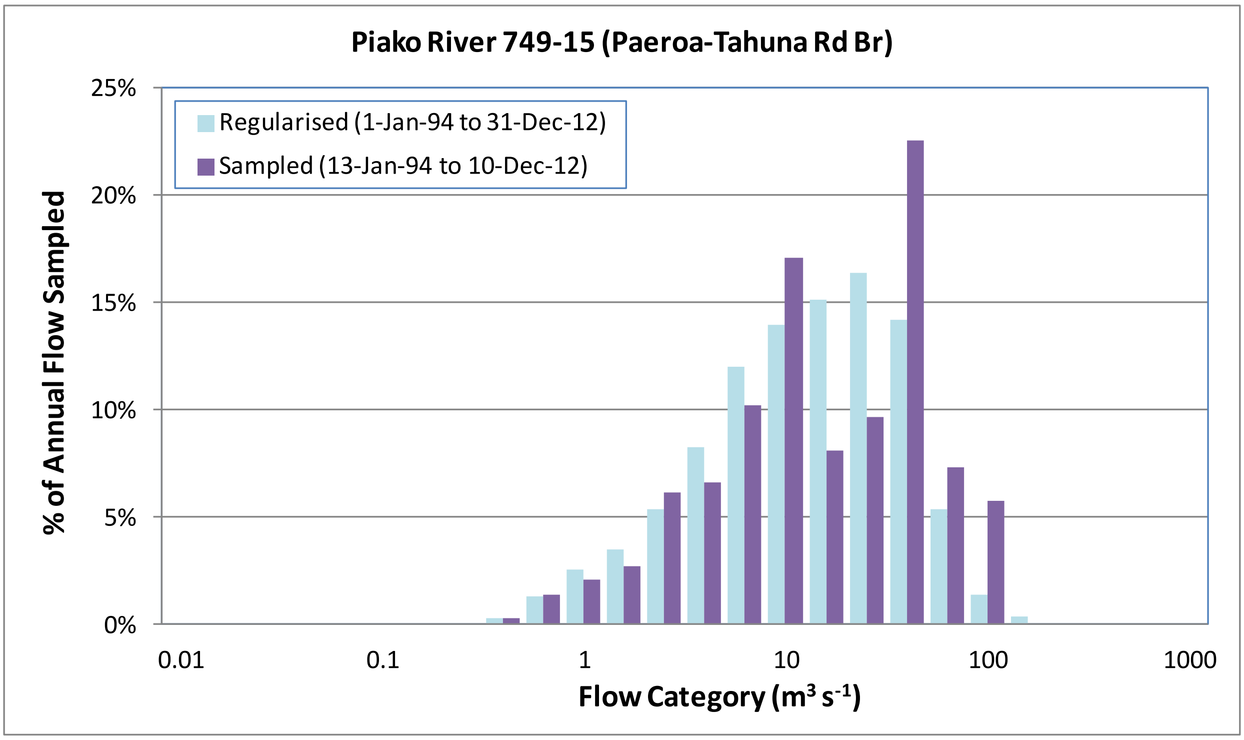
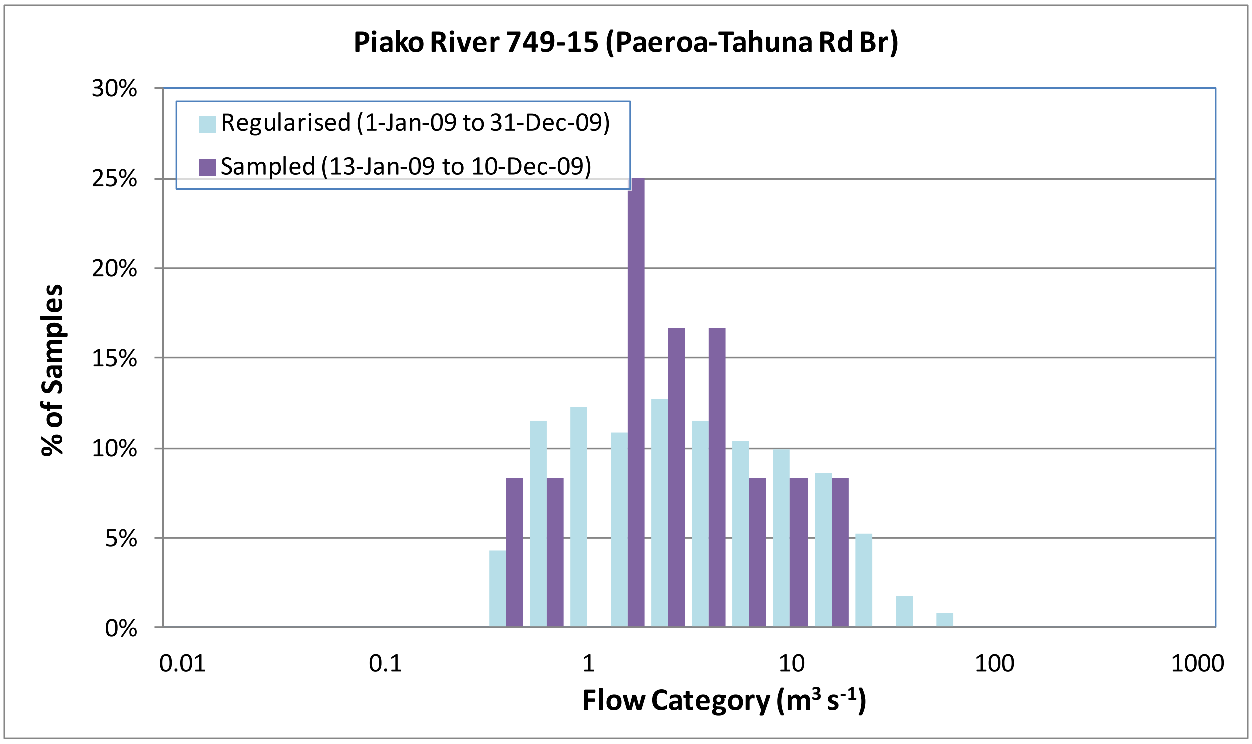


Figure 9: Bias in water quality sampling expressed in two ways, showing over-sampling of high flows.



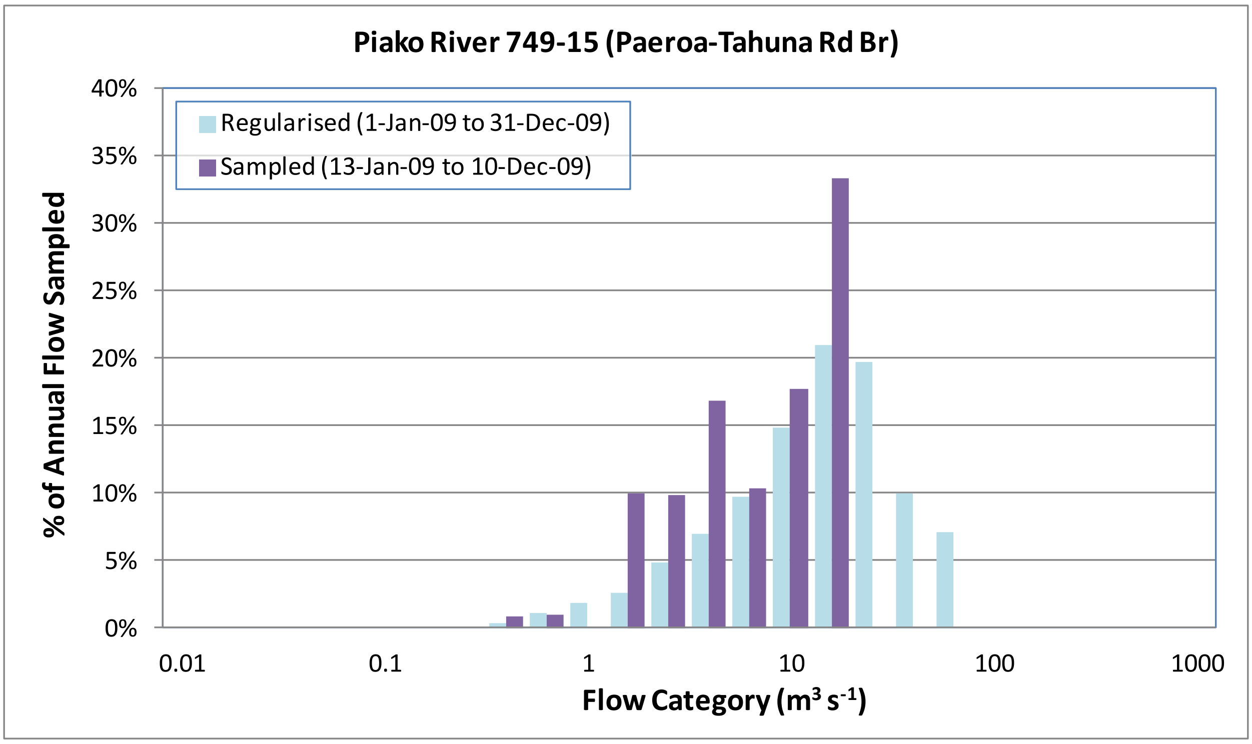


Figure 10: Bias in water quality sampling expressed in two ways for a single year.

Based on such flow frequency comparisons across all sites, under-sampling of high flows (e.g. Figure 8) occurred at more than half of all sites (14 out of 26 sites) whereas over-sampling of high flows (e.g. Figure 9) was less common (3 out of 26 sites). Those sites with under-sampling of high flows also tended to over-sample medium-range flows (9 out of 14 sites, e.g. Figure 8). Relatively unbiased sampling was achieved at only 4 out of the 26 sites, and 3 of these were in the Upper Waikato sub-region: sites that are characterised by little variation in flow rates.

It should be noted that the sampling bias may differ on different time scales. Even data sets that show little bias when the entire 20-year period is considered may show biased results for individual years. For example, Figure 10 shows sampling bias for the 2009 calendar year for the Piako River (Paeroa-Tahuna Road) site (c.f. Figure 9). Monthly sampling of the flow distribution is even less reliable on this shorter timescale, and instead of showing over-sampling of the highest flows, as observed for the long term record (Figure 8), it shows the opposite.

This variability is due to infrequent sampling, and is the reason that load estimates calculated from such data are often inaccurate (biased) and imprecise (variable) (Aulenbach, 2013) (c.f. Section 6). Increasing the length of the time series (by sampling for multiple years) will only improve concentration and load estimates if the flow and concentration distributions, and concentration-discharge relationships (see next section), do not change through time. Increasing the frequency of sampling, especially during high flows, is far more effective for obtaining accurate and precise results (Aulenbach, 2013). High-resolution sampling is still in its infancy in New Zealand, but is gradually increasing.

Working with a historical data set based on monthly sampling, we have to accept that the accuracy and precision of concentration-discharge relationships, and yield and load estimates may be poor. This poses a challenge for the limit-setting process at the water management unit scale as stipulated by the National Policy Statement for Freshwater Management.

The complete set of flow frequency histograms for all sites is provided in Appendix 1.

4 CONCENTRATION-DISCHARGE RELATIONSHIPS

4.1 INTRODUCTION

While analysing flow frequency enables us to assess bias in the water quality sampling programme (Section 3), stream flow data are particularly valuable for the exploration of concentration-discharge relationships (i.e. the correlation between concentration and stream flow). By highlighting differences in concentration under different flow regimes, such relationships provide insight into the dynamics of land-to-water transfers and contaminant discharges from catchments. Periods of high rainfall, for example, may increase stream flow via activation or strengthening of mechanisms such as surface runoff, interflow in the vadose zone, flow in artificial drains, and increased groundwater discharge (resulting from rising water tables), each of which may contribute water with different concentrations to the stream. The relative contribution of these mechanisms will vary depending on the pre-event conditions and over time (during and after a rain event). Onset of turbulent stream flow and associated disturbance of stream bed sediments at increased flow rate may also directly impact concentrations of certain nutrients in the stream water exiting a catchment.

While the importance and complexity of these processes vary from catchment to catchment, in the simplest cases they may be reflected in a correlation between concentration and discharge at the catchment outlet. A simple way to identify a dependence of concentration on discharge therefore is to plot concentration against flow. Such “concentration-discharge plots” are commonly used to study the hysteresis between high resolution flow and concentration dynamics during individual storm events (Chanat et al., 2002; Burt et al., 2014). In contrast, concentration-discharge relationships derived from long-term, periodic monitoring allow high-level insights to be gained into the overall contaminant flux dynamics in a catchment.

Concentration-discharge relationships were analysed for nitrogen species (TN, NNN, NH4), phosphorus species (TP, DRP, and their difference TP-DRP), silica (Si) and electrical conductivity (EC) by fitting a regression line to concentration and flow for the 20-year period as a whole. This is valid provided (1) the data are representative of the population (i.e. no sampling bias) and (2) the underlying relationship between the data is linear (Kirchner, 2001). As flow varies by up to 3 orders of magnitude at many of our sites, a log transform was used for flow. The linearity assumption then appears reasonable.

The key output of the regression is the coefficient of determination (R^2), which is interpreted as the proportion of the variance in the dependent variable (concentration) that is predictable from the independent variable (flow). The probability that the slope was significantly different from zero was also calculated for each regression, using the Student’s t-test. Such a calculation is valid provided the regression residuals are also (1) homoscedastic, (2) independent, and (3) Gaussian (Kirchner, 2001). The first and third of these conditions are certainly not satisfied in many of the plots (for example where variance increases with flow (perhaps due to event hysteresis) or large “outliers” exist) so the significance test must be treated with caution. Nevertheless it provides a useful screening test for potentially important relationships.

Concentration-discharge plots can also be interpreted qualitatively. Figure 11 shows a complete set of concentration-discharge plots for the Piako River (Kiwitahi) site. Linear regression slopes and coefficients of determination are shown for each plot. Several water quality measurements exhibited strong correlations with stream flow at this site.

For example, total nitrogen (TN) was strongly correlated with stream flow ($R^2 = 0.7945$) with a positive slope, Conc = 0.9373 ln(Flow) + 1.8989. The slope of this relationship was highly statistically significant ($p<0.005$) (i.e. very likely to be different from zero).

A strong positive correlation such as this could indicate several mechanisms at work. Low concentrations at low flow could indicate contaminant assimilation in the subsurface, and/or reflect the quality of water that was recharged in the past, prior to land use intensification. High concentrations at high flow, on the other hand, could indicate contaminant flushing, where relatively immobile contaminants at or near the ground surface or in the stream bed become mobilised during storm events. This is commonly observed for contaminants that become adsorbed to sediment particles, such as non dissolved phosphorus species (TP-DRP).

By contrast, the electrical conductivity (EC) concentration-discharge relationship at Piako River (Kiwitahi) is negatively correlated with stream flow ($R^2 = 0.1532$), albeit weakly. The regression line in this case is Conc = -0.462 ln(Flow) + 14.351. The slope of this relationship was again highly statistically significant ($p<0.005$).

A negative correlation can likewise indicate various mechanisms. High concentrations at low flow can indicate geogenic sources (i.e. ions picked up during water’s passage through the subsurface), and/or contaminants leached into the subsurface due to intensive land use in the past, whereas low concentrations at high flow are often the result of simple dilution, as rainfall events dilute concentrations discharged from deeper flow paths.

The actual slope of the concentration-flow relationship is difficult to interpret, since a small slope may be considered important in a catchment where concentrations are consistently low, while the same slope might be considered unimportant in a catchment with generally higher levels of contamination. On the other hand, a small slope may be considered unimportant even when water quality is consistently low. The coefficient of determination (R^2) gives the importance of the slope *relative to the magnitude of the concentration*, i.e. a high R^2 value may accompany a small slope when the magnitudes of the concentrations are also small.

Concentration-discharge relationships with relatively low R^2 values may still be statistically significant. The plot of TP against flow in Figure 11 has a relatively weak positive relationship between flow and concentration Conc = 0.0229 ln(Flow) + 0.1265 ($R^2 = 0.0907$) but is nevertheless highly statistically significant ($p<0.005$). The reason for this is that regression equations tend to have low p-values when there are a large number of data points, even when the correlation is relatively weak. The coefficient of determination (R^2) indicates the proportion of variance in the concentration that can be explained by the flow, whereas the p-value indicates the probability that this relationship is the result of chance.

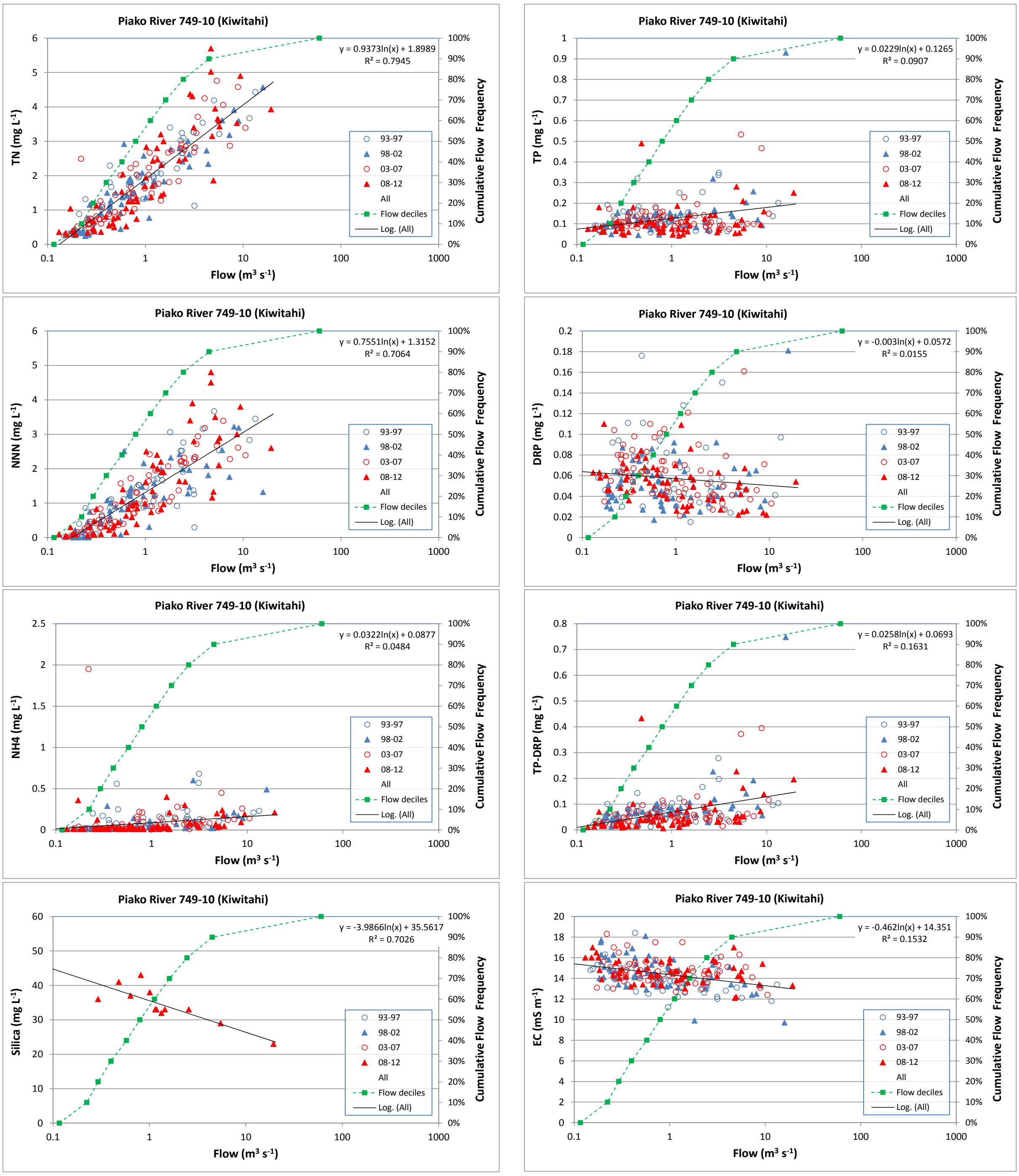


Figure 11: Concentration-discharge plots for Piako River (Kiwitahi). Data points are coloured in 5-year periods, and the trend line is for the entire period 1993-2012. Cumulative flow frequencies are marked as green squares.

Table 5: Coefficients of determination (R^2) of linear regressions between log stream flow and water quality variables. Highlighted values indicate slopes that were highly significantly different from zero ($p<0.005$). Values are highlighted red for positive correlations and blue for negative correlations. Flags are explained in Table 1.

				CDR RSQ								
Region	**Site Name**	**Sample Location**	**ChemID**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**	**Flags**
Coromandel												
	Kauaeranga River	Smiths Cableway/Recorder	234-11	0.43	0.31	0.00	0.08	0.01	0.07	0.75	0.59	DRP
	Ohinemuri River	Queens Head	619-19	0.21	0.18	0.09	0.15	0.01	0.23	0.65	0.41	PS, DRP
	Tapu River	Tapu-Coroglen Rd	954-5	0.43	0.41	0.03	0.41	0.05	0.37	0.55	0.74	DRP
	Waiwawa River	SH25 Coroglen	1257-3	0.26	0.39	0.00	0.23	0.00	0.22	0.93	0.69	MF, DRP
	Wharekawa River	SH25	1312-3	0.24	0.59	0.01	0.06	0.00	0.05	0.90	0.64	MF, DRP
Hauraki												
	Piako River	Kiwitahi	749-10	0.79	0.71	0.05	0.09	0.02	0.16	0.70	0.15	-
	Piako River	Paeroa-Tahuna Rd Br	749-15	0.56	0.42	0.40	0.10	0.20	0.17	0.60	0.41	PS
	Waihou River	Okauia	1122-18	0.48	0.18	0.34	0.37	0.00	0.53	0.93	0.00	-
	Waitoa River	Landsdowne Rd Br	1249-15	0.61	0.37	0.24	0.31	0.09	0.29	0.79	0.60	-
	Waitoa River	Mellon Rd Recorder	1249-18	0.28	0.14	0.11	0.12	0.15	0.01	0.76	0.58	PS
Lower Waikato												
	Mangatangi River	SH2 Maramarua	453-6	0.71	0.51	0.35	0.46	0.07	0.45	0.18	0.03	-
	Matahuru Stm	Waiterimu Road Below Conflu	516-5	0.52	0.31	0.32	0.50	0.00	0.53	0.16	0.05	MF, SS
	Whakapipi Stm	SH22 Br	1282-8	0.15	0.10	0.24	0.35	0.04	0.35	0.31	0.48	PS
Waipa												
	Mangapu River	Otorohanga	443-3	0.50	0.40	0.20	0.03	0.40	0.38	0.71	0.71	PS, MF, SS
	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	0.49	0.50	0.11	0.14	0.00	0.14	0.67	0.07	SS
	Puniu River	Bartons Corner Rd Br	818-2	0.55	0.58	0.27	0.08	0.15	0.11	0.75	0.07	-
	Waipa River	SH3 Otorohanga	1191-12	0.67	0.66	0.06	0.24	0.00	0.27	0.20	0.38	MF, SS
	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	0.59	0.66	0.21	0.14	0.12	0.19	0.70	0.41	MF, SS, DRP
Upper Waikato												
	Otamakokore Stm	Hossack Rd	683-4	0.62	0.34	0.12	0.14	0.04	0.25	0.90	0.54	G, TP
	Tahunaatara Stm	Ohakuri Rd		0.56	0.37	0.09	0.27	0.01	0.30	0.79	0.06	-
	Waiotapu Stm	Homestead Rd Br		0.54	0.09	0.45	0.31	0.19	0.39	0.92	0.47	G, MF, TP
West Coast												
	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	0.61	0.44	0.07	0.30	0.10	0.29	0.56	0.70	SS, DRP
	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	0.60	0.59	0.13	0.15	0.18	0.16	0.00	0.65	SS
	Waitetuna River	Te Uku-Waingaro Rd	1247-2	0.55	0.42	0.03	0.25	0.04	0.26	0.32	0.61	MF, SS
Taupo												
	Tauranga-Taupo River	Te Kono Slackline	971-4	0.07	0.00	0.00	0.02	0.34	0.06	0.93	0.76	-
	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	0.75	0.63	0.01	0.16	0.40	0.28	0.69	0.72	SS

Table 5 summarises the coefficient of determination and slope of the relationships between flow and key water quality parameters at the 26 sites in this study. Highlighted R^2 values indicate slopes that were highly significantly different from zero ($p<0.005$). Red highlighting indicates positive correlations and blue highlighting indicates negative correlations. Flags indicating point source effects (PS, G), mismatched flow data (MF), and laboratory analysis issues (DRP, TP) are also shown (these are explained in more detail in Table 1).

Nitrogen concentrations (TN, NNN, NH4) were generally positively correlated with stream flow, as was total phosphorus (TP) and non-DRP phosphorus (TP-DRP), while dissolved reactive phosphorus (DRP) was either positively or negatively correlated with stream flow in those instances where a correlation was observed. Silica (Si) concentrations and electrical conductivity (EC) were always negatively correlated with stream flow.

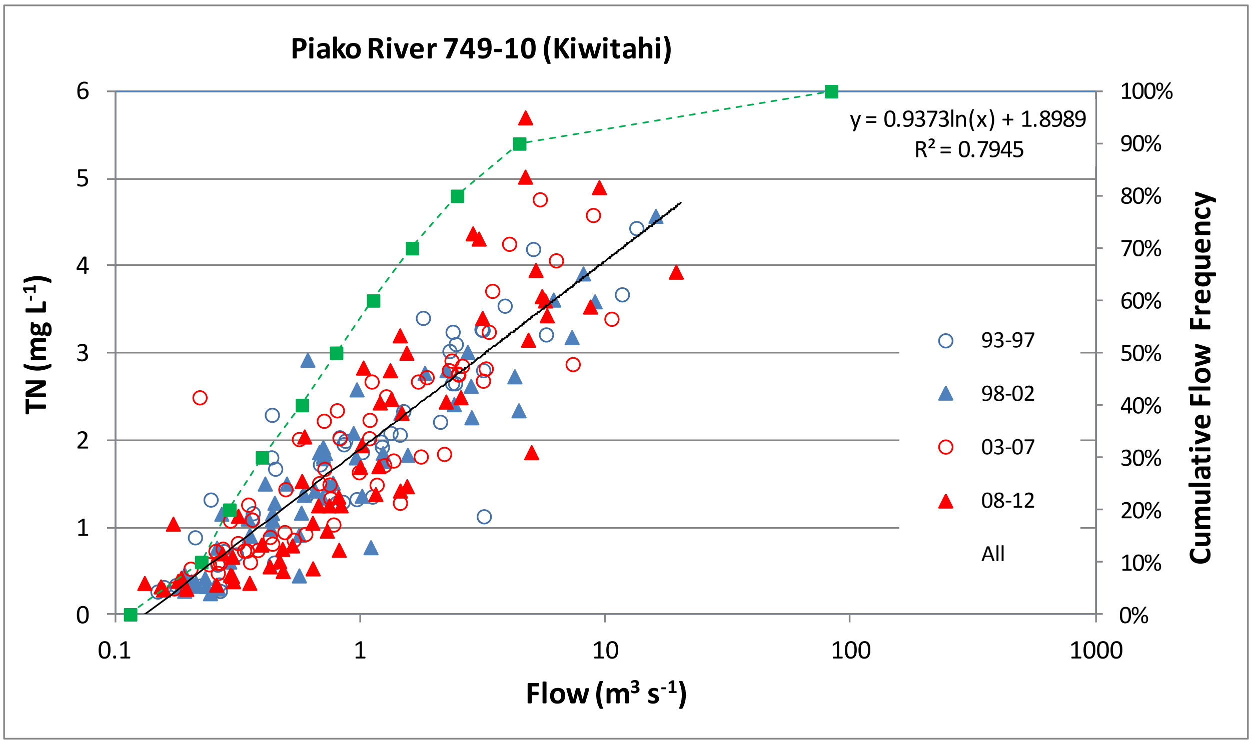
Concentration-discharge relationships identify stable correlations between water quality and stream flow. When studying these plots, it should be remembered that a low R^2 does not necessarily mean that water quality is random, or that the measurements have a large error. Water quality depends on a wide variety of factors, including land use changes, or soil factors which may not be correlated with stream flow. On the other hand, concentration may indeed be correlated with stream flow, but the relationship may change over time, so that the correlation is weak when the data series is viewed as a whole. In our study, temporal changes in the concentration-discharge relationships were studied by plotting the data for each 5-year period separately, and calculating the regression for each 5-year period, as shown in Figure 11. The 5-year slopes and the probability that these changed over time are tabulated for each site in Appendix 1, along with the concentration discharge plots for each site

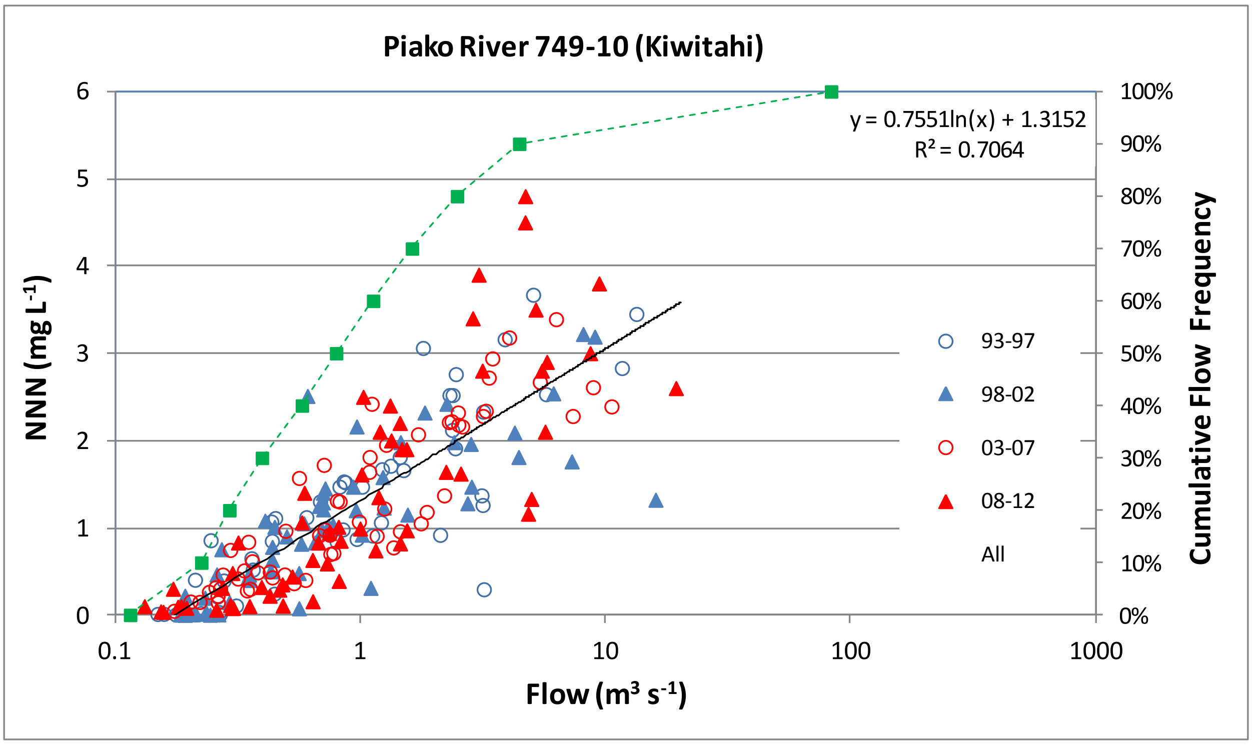
4.2 NITROGEN SPECIES

Strong positive correlations between flow and nitrogen species (TN, NNN, NH4) were commonly observed regardless of the absolute level of the concentrations. The consistency of these relationships across the Waikato Region is somewhat striking, as it is by no means universal, and in other parts of the world negative correlations may be more common (e.g. Aubert et al, 2013), reflecting contaminated groundwater and increasing dilution with increasing runoff. The TN, NNN and NH4 concentration-discharge relationships shown for Piako River (Kiwitahi) in Figure 12 are typical.

Concentration-discharge relationships were similar between TN and NNN, because NNN is the major constituent of TN in most Waikato streams, and were almost always strongly positive. This suggests that deeper groundwater concentrations are typically low in NNN in the region, with storm flow activating shallower flow paths with higher concentrations of NNN.

Three sites had clear evidence of point source nitrogen discharges at low flows: Ohinemuri River (NNN), Piako River (Paeroa-Tahuna Road) (NNN), and Waitoa River (Mellon Road) (NNN and NH4, Figure 13). The Ohinemuri River and Piako River (Paeroa-Tahuna Road) sites both had evidence of point source NNN discharges in the 2008-2013 period, while the Waitoa River (Mellon Road) discharges were all prior to 2008.





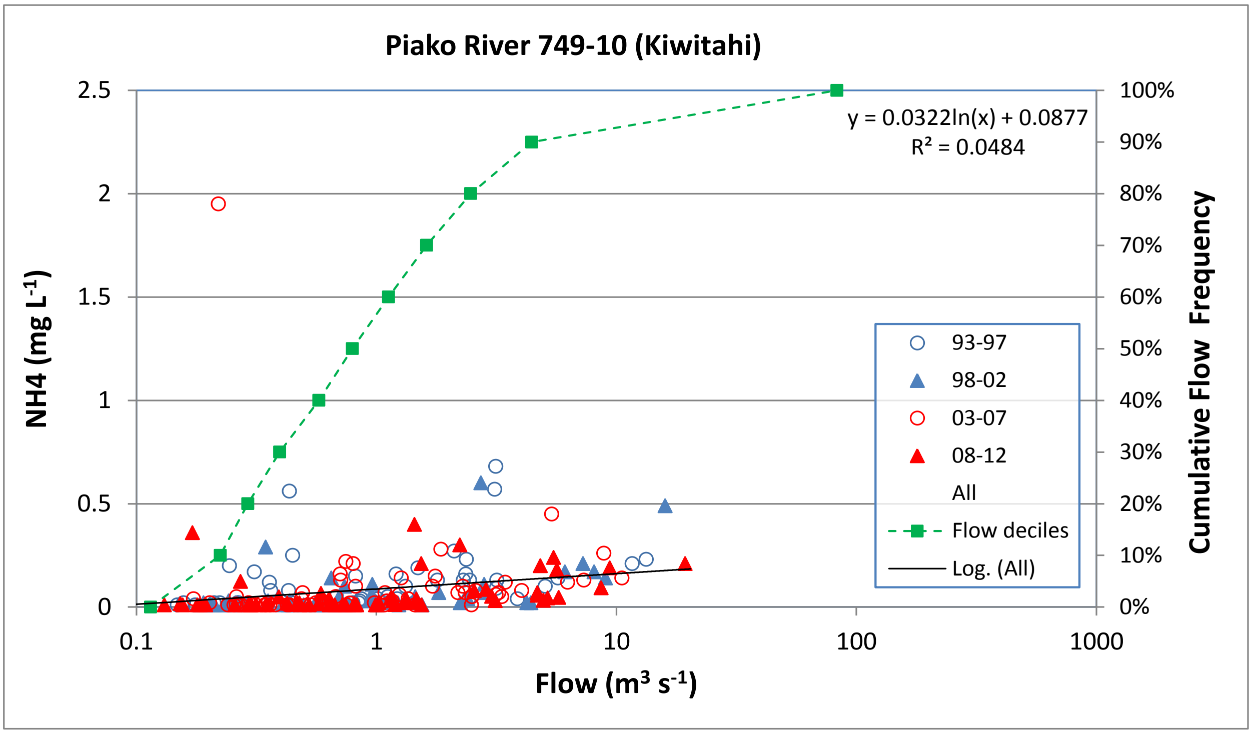
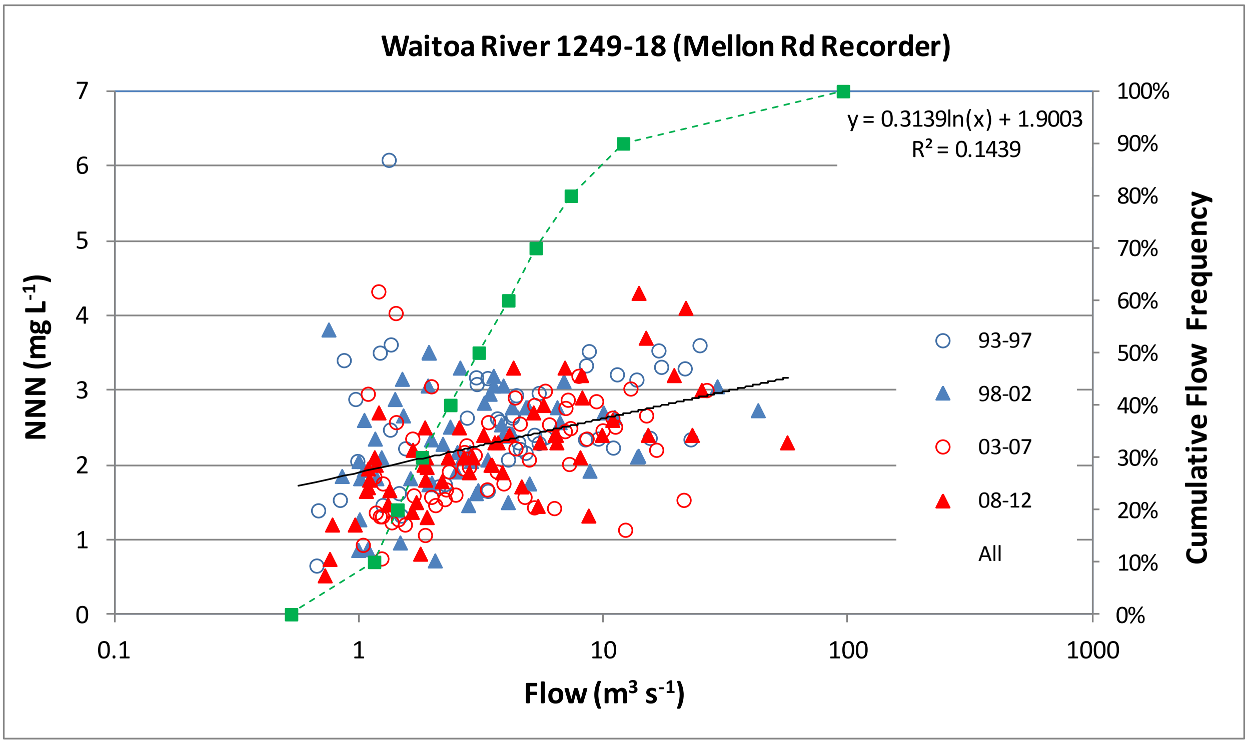


Figure 12: Concentration-discharge relationships for nitrogen species in the Piako River (Kiwitahi).



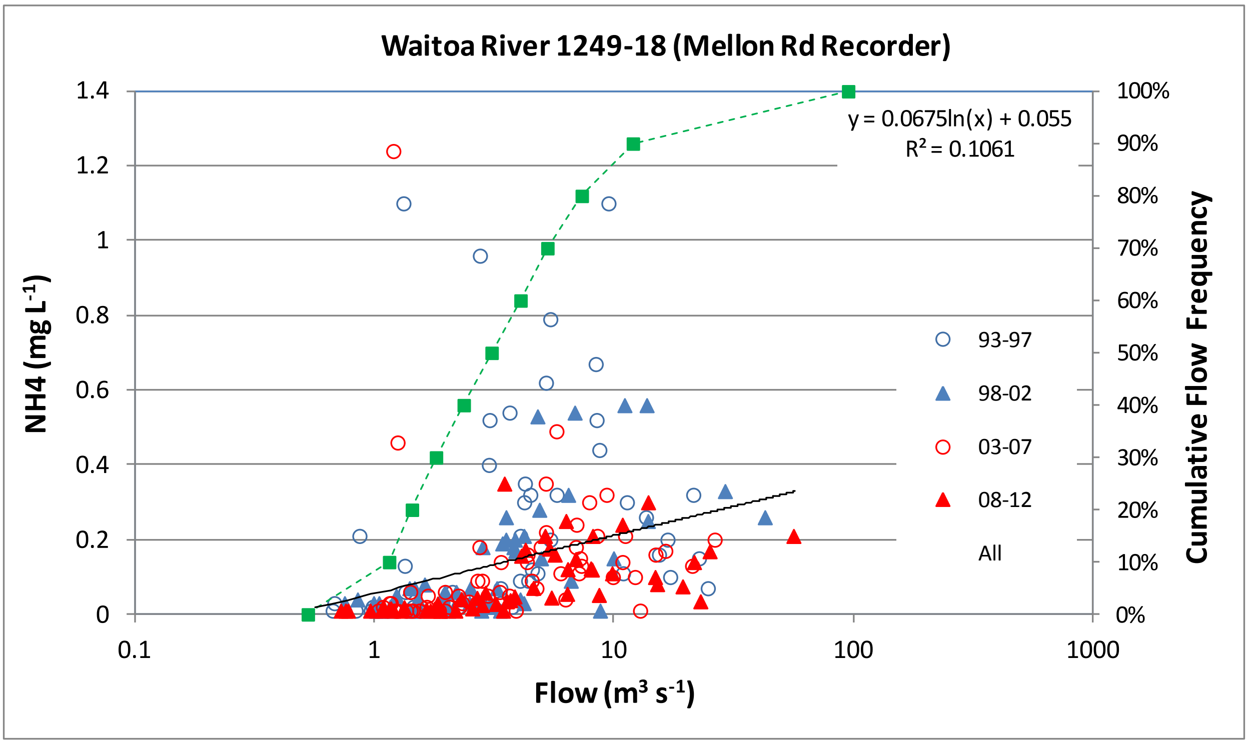


Figure 13: Unusually high concentrations of NNN and NH4 at low stream flows in the Waitoa River at Mellon Road, due to point source discharges.

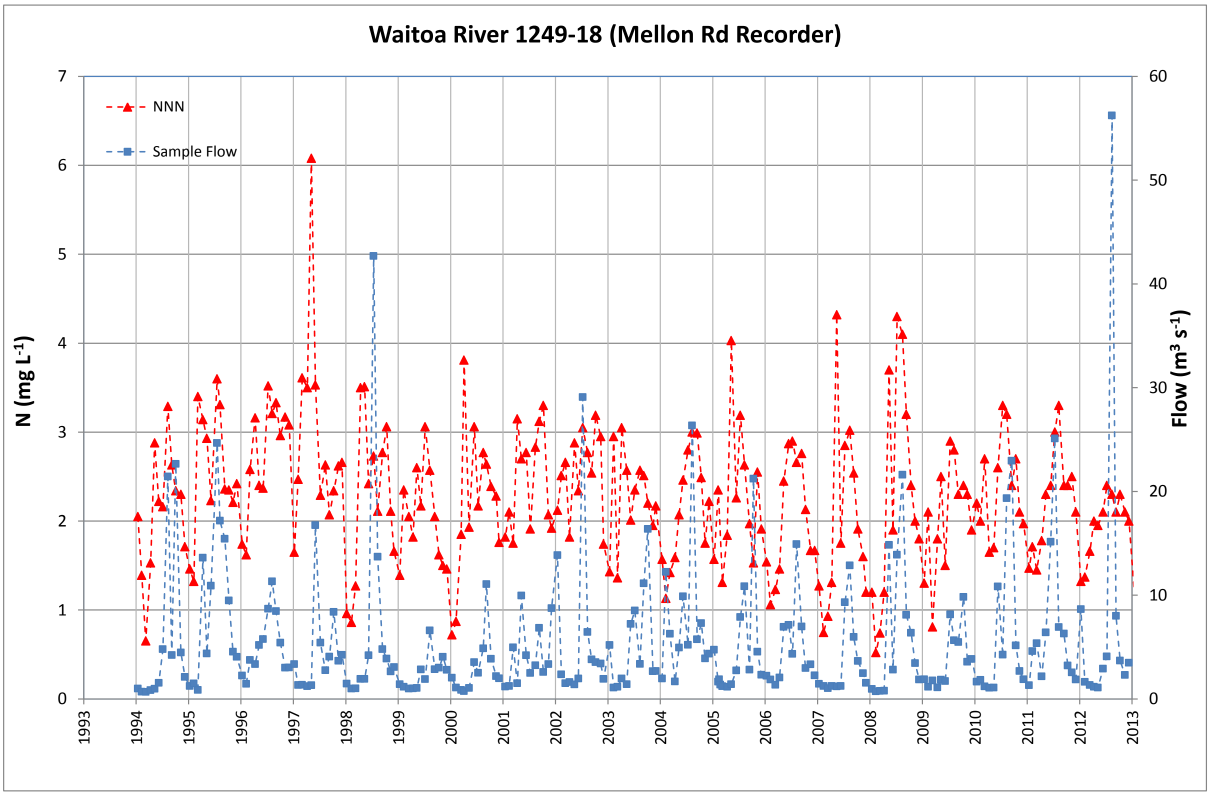
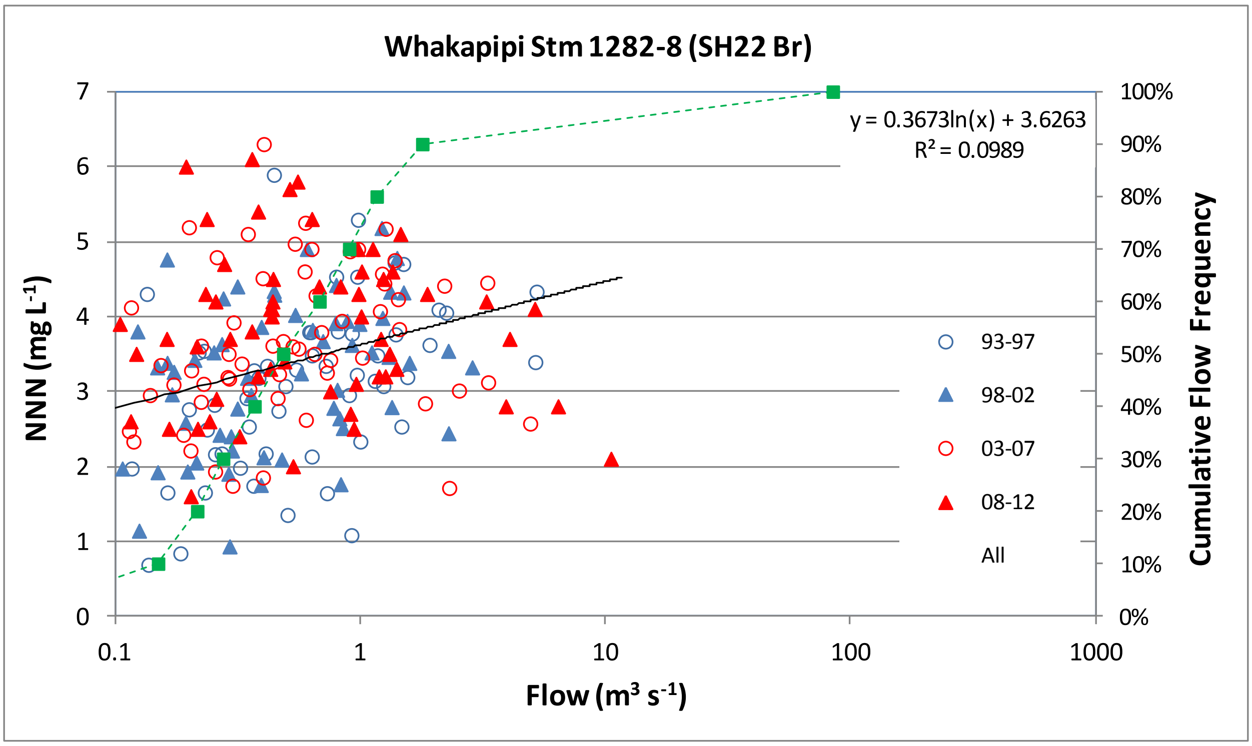


Figure 14: Time series plot of NNN concentrations for Waitoa River (Mellon Road).

WRC (2011) has previously discussed point sources discharges in these Hauraki rivers. The concentration-discharge plot allows easy identification of such features that are less obvious in a simple time series plot (compared Figure 13 and Figure 14).

Only two sites had weak C-D relationships for TN and NNN. These were Whakapipi Stream and Tauranga-Taupo River (Figures 15 and 16). One further site, Waiotapu Stream, had a strong C-D relationship for TN, but a weak one for NNN. In the case of Whakapipi Stream, a strong seasonal pattern of TN and NNN is apparent in the time series plot (Figure 16), but because this changes over time, the C-D relationship appears weak. This site may also be affected by point source discharges (Table 1). In the Tauranga-Taupo River, TN and NNN have much lower absolute concentrations and weaker seasonality, which also changes over time, so that any flow dependence is obscured by other processes. Waiotapu Stream, had strong seasonality in TN, but weak seasonality in NNN which changes over time. This highlights one weakness of the C-D relationship approach: changes in concentration over time, due to land use change, for example, will result in weak C-D relationships. These static plots are less useful in this case.

Compared with TN and NNN, NH4 concentrations were much lower, and more weakly correlated with flow at all sites. A number of sites had very little NH4 observed (those with non-highlighted R^2 values in Table 5), and no site had a concentration-discharge relationship for NH4 with R^2>50%. The highest correlations were for the geothermally-influenced Waiotapu Stream (R^2=45%) and the Piako River (Paeroa-Tahuna Road) site (R^2=40%), which includes point source effects.



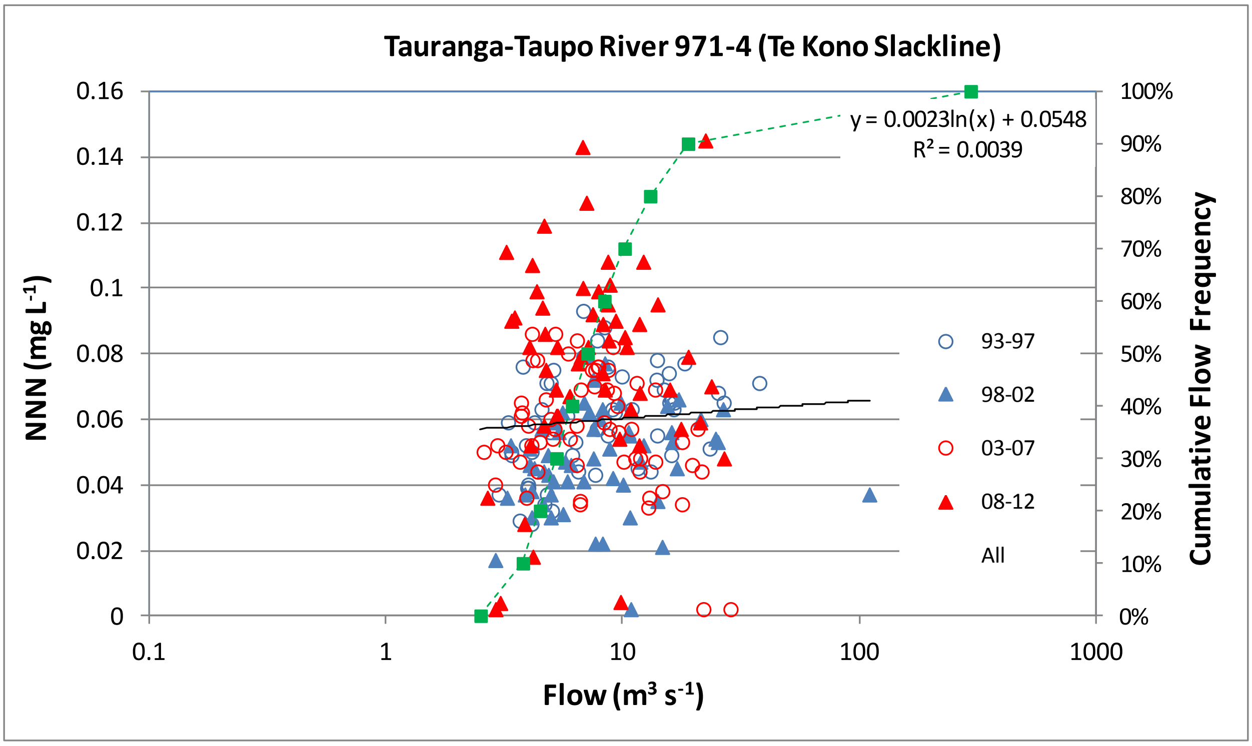


Figure 15: Unusually weak correlations between nitrate/nitrite-nitrogen concentration (NNN) and stream flow at Whakapipi Stream and Tauranga-Taupo River.

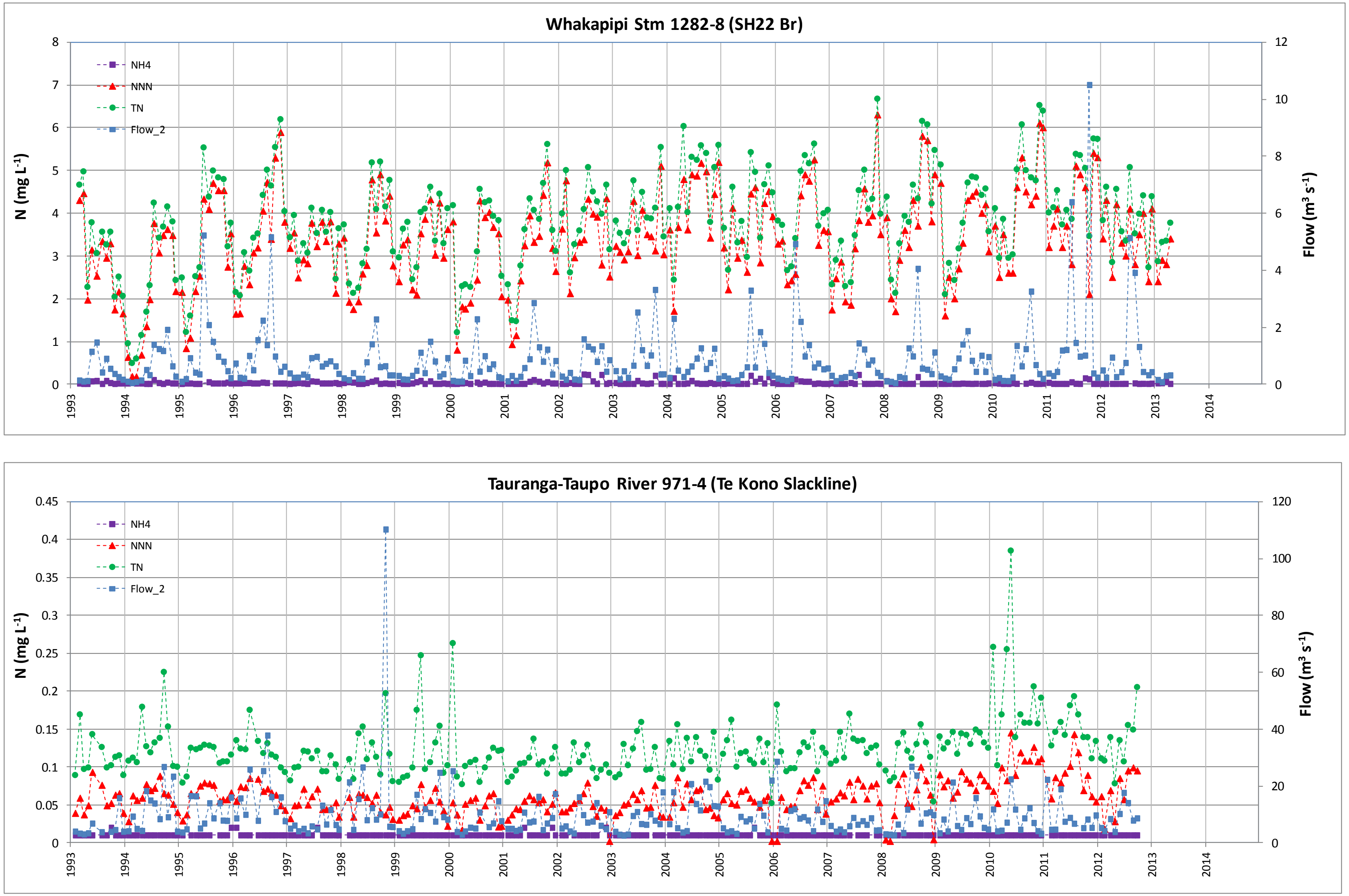


Figure 16: Time series plots of N species concentrations at Whakapipi Stream and Tauranga-Taupo River.

4.3 PHOSPHORUS SPECIES

The correlations between total phosphorus (TP), dissolved reactive phosphorus (DRP) and other phosphorus (TP-DRP) concentrations and stream flow were not as strong or as consistent as those observed for nitrogen species (Table 5). Furthermore, concentrations of DRP and/or TP were often very low, to the point of being near detection limit (0.003 or 0.004 mg L^{-1}, depending on the analytical method) at some sites, particularly those in the Coromandel. Non-dissolved phosphorus TP-DRP was calculated as the difference between TP and DRP, with a nominal detection limit of 0.003 mg L^{-1} being assumed.

Weak positive C-D relationship were the norm for TP and TP-DRP, the R^2 of these relationships being better than 50% only at Matahuru Stream (TP and TP-DRP) and Waihou River (TP-DRP only) (Table 5). Increasing TP-DRP with flow is likely to be associated with increased sediment/particulate content. Only two sites had significant C-D relationships for TP that were negative: Piako River (Paeroa-Tahuna Road) and Waitoa River (Mellon Road), and both of these were the result of historical point source discharges.

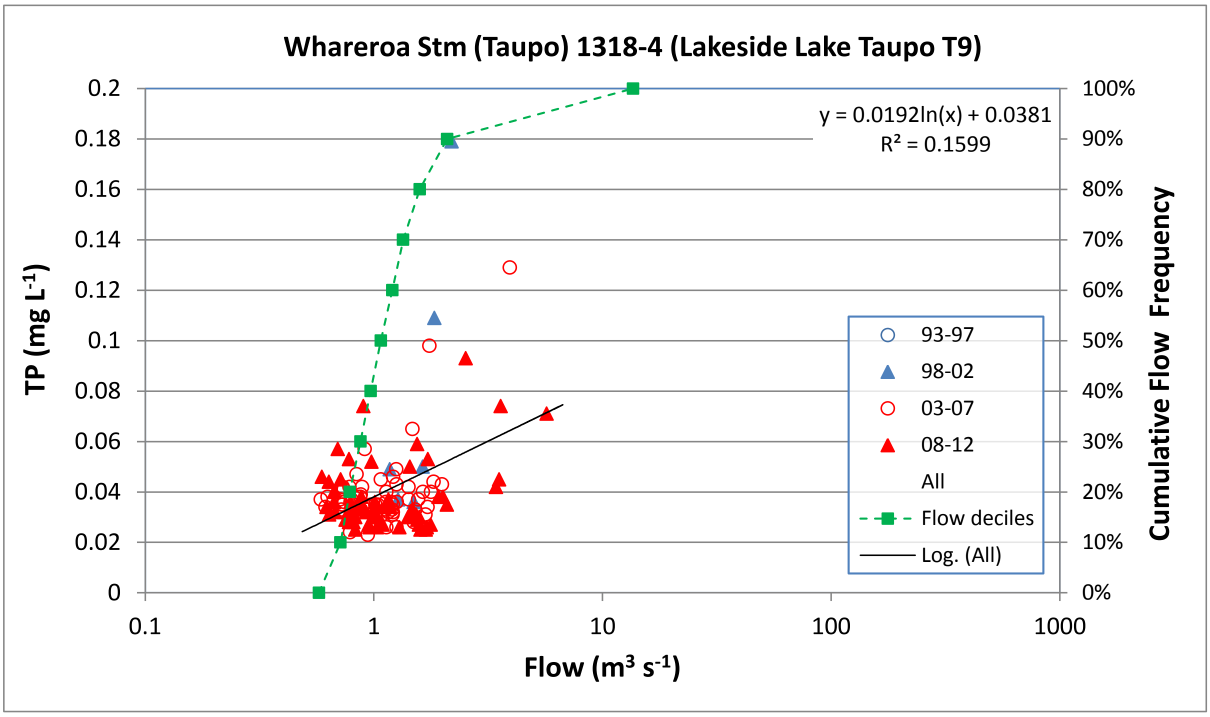
Statistically significant C-D relationships for DRP were positive at 5 sites and negative at 9 sites. The positive C-D relationships were all weak however (R^2 less than 10%), while the negative C-D relationships for DRP were more defined, with R^2 from 12% to 40%. This suggests that DRP is predominantly delivered through groundwater discharge, which is most appreciable at low flows, and reduced DRP concentrations at high flows are the result of dilution.

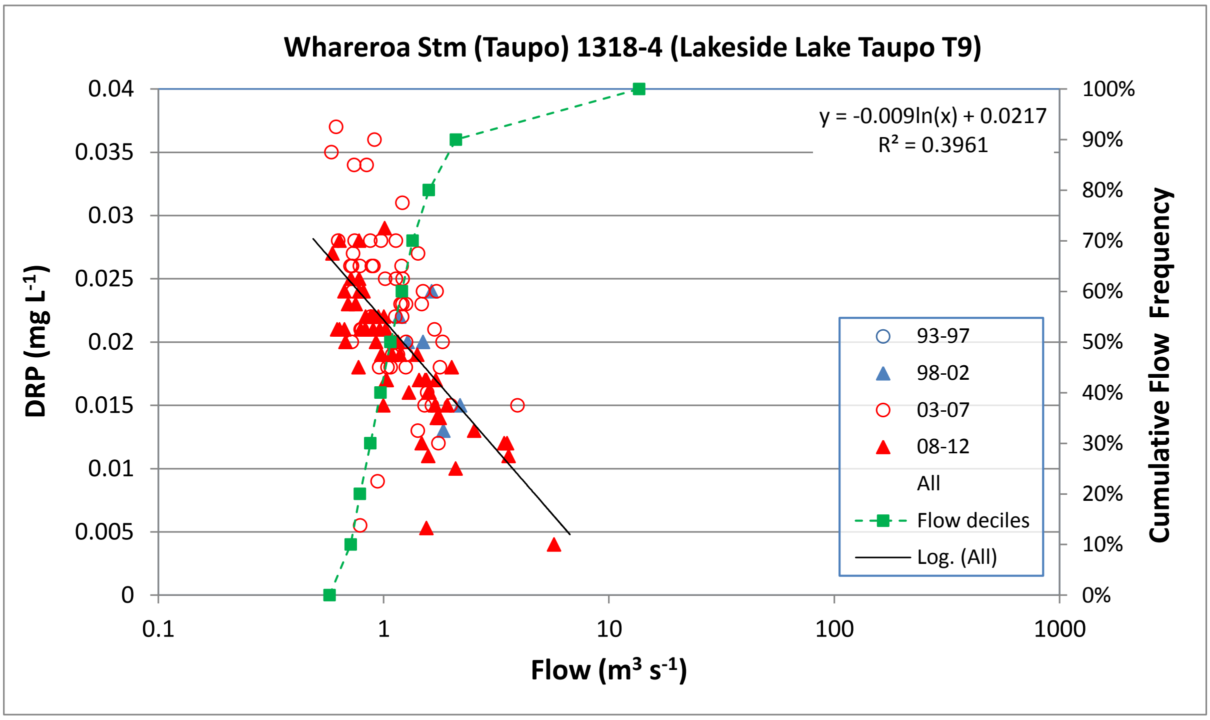
Figure 17 shows example relationships between TP, DRP, and TP-DRP and stream flow at the Whareroa Stream site. Increasing concentrations of TP-DRP at high flow rates may indicate initiation of overland flow processes at high rainfall intensity, and/or release of streambed nutrients due to the onset of turbulent flow, both of which would tend to increase particulate phosphorus fractions in the stream water. DRP concentrations at this site, on the other hand, are negatively correlated with flow (R^2 = 40%), indicating transmission via groundwater flow paths, and dilution at higher flows.

The average ratio of DRP to TP varied between sites (Figure 18). In order to avoid problems with calculating ratios between small concentrations, the ratio was calculated as DRP / (DRP + TP-DRP). This tends to give values near 0.5 when DRP and TP-DRP are near detection limit (typically 0.003 or 0.004 mg L^{-1}), as evident at several of the Coromandel sites where phosphorus levels were consistently low. The ratio typically varied throughout the year (e.g. Figure 19), sometimes showing a strong seasonal cycle. A few sites had consistently high DRP fractions. In some cases (Waihou River, Otamakokore Stream) these may be associated with high groundwater contributions that have elevated concentrations of geogenic DRP, although other groundwater dominated streams (e.g. Waiotapu Stream) had lower-than-average DRP fractions. Lower DRP fractions in the Lower Waikato, Waipa and West Coast areas may reflect the high levels of sediment (and associated TP-DRP) typically observed in streams in these regions.

Historical point source discharges of phosphorus species were evident at several sites: Ohinemuri River (DRP), Piako River (Paeroa-Tahuna Road) (DRP) and Waitoa River (Mellon Road) (DRP and

TP-DRP, Figure 20). These discharges all occurred prior to 2008, probably due to improvements to sewerage treatment around 2005 (WRC, 2011).





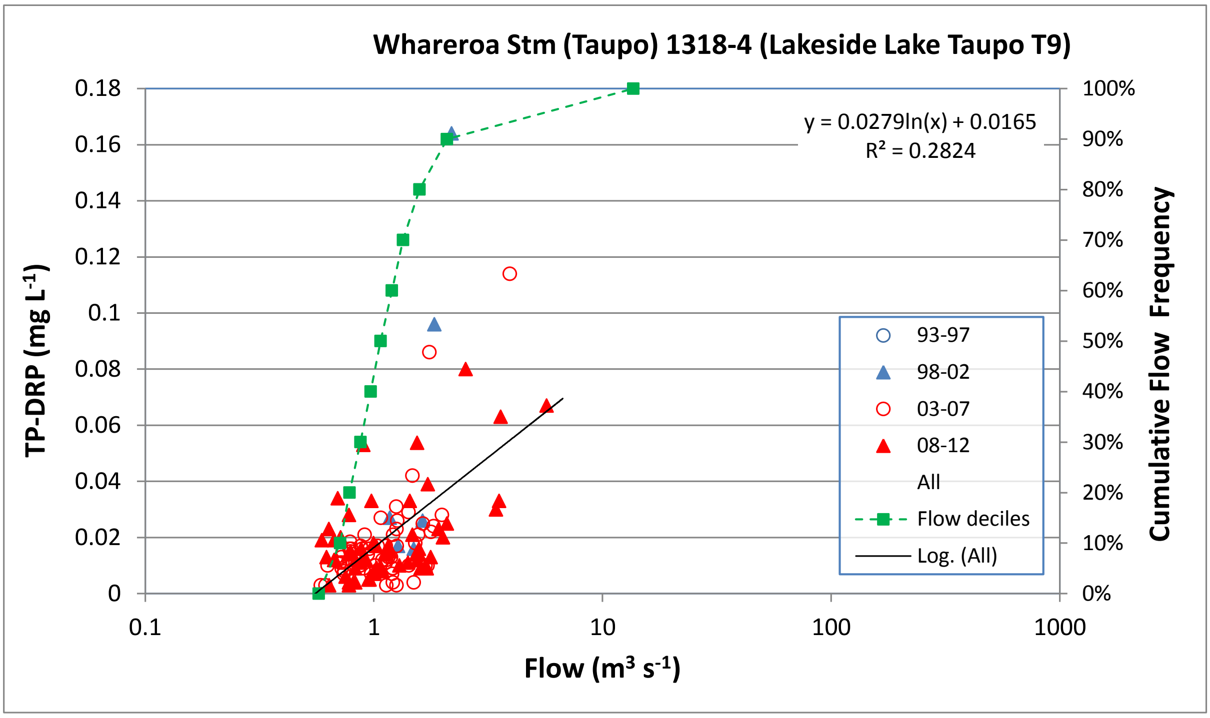


Figure 17: Correlations between TP, DRP, and TP-DRP and stream flow in Whareroa Stream . Data points are coloured in 5-year periods, and the trend line is for the entire period 1993-2012. Cumulative flow frequencies are marked as green squares.

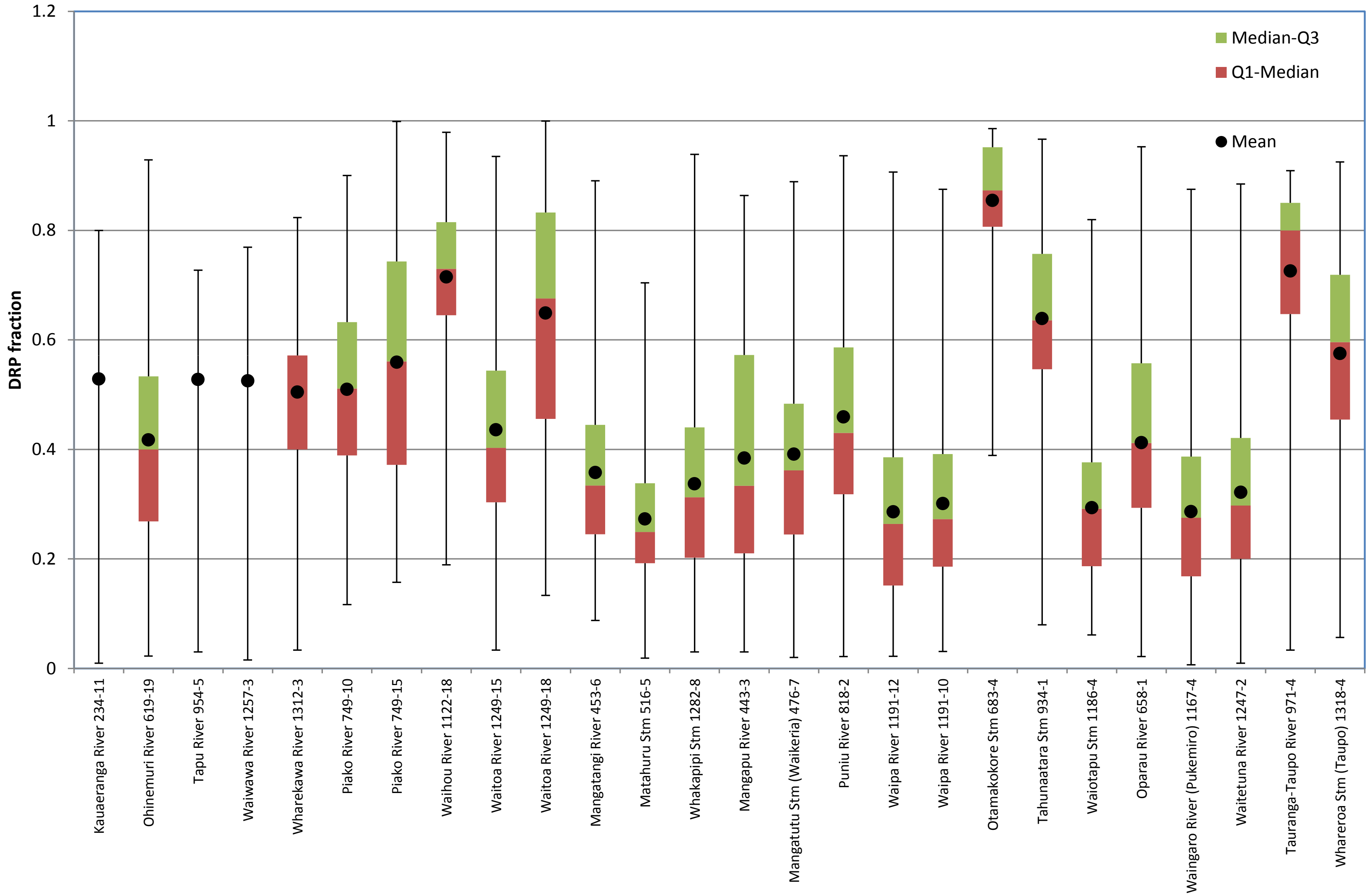


Figure 18: Box plot of DRP fraction of TP in water quality samples across the Waikato region. Q1 and Q3 are the first and third quartiles, respectively.

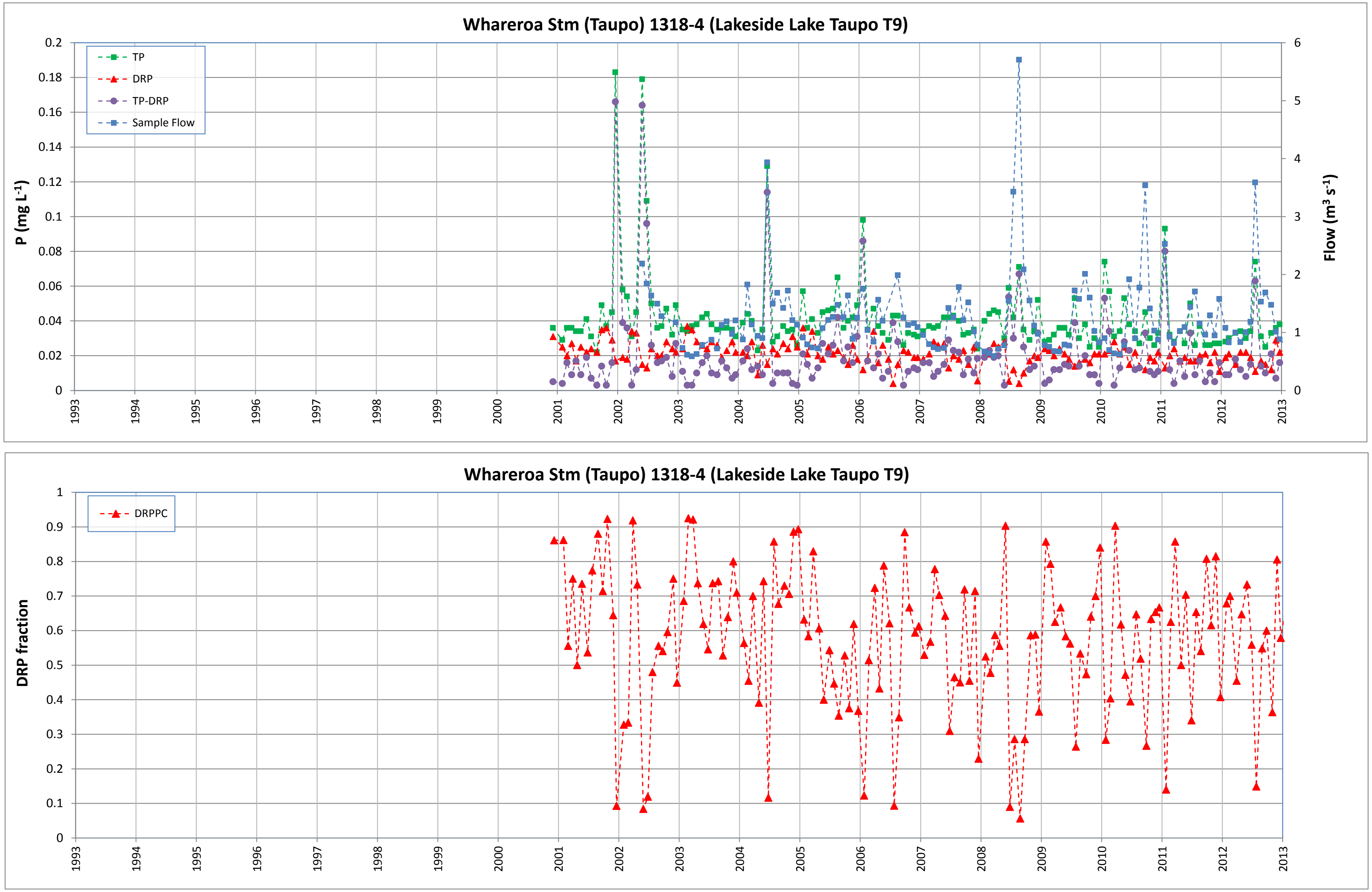
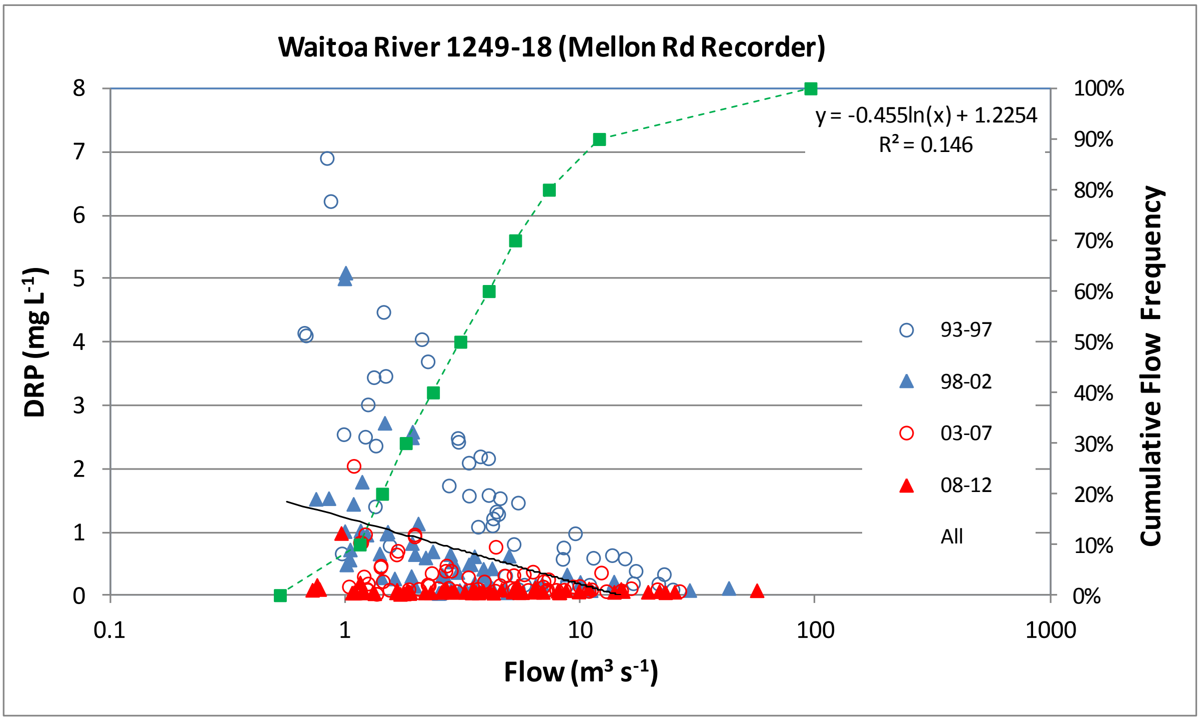


Figure 19: Time series of phosphorus species concentrations and DRP fraction at Whareroa Stream (Taupo).



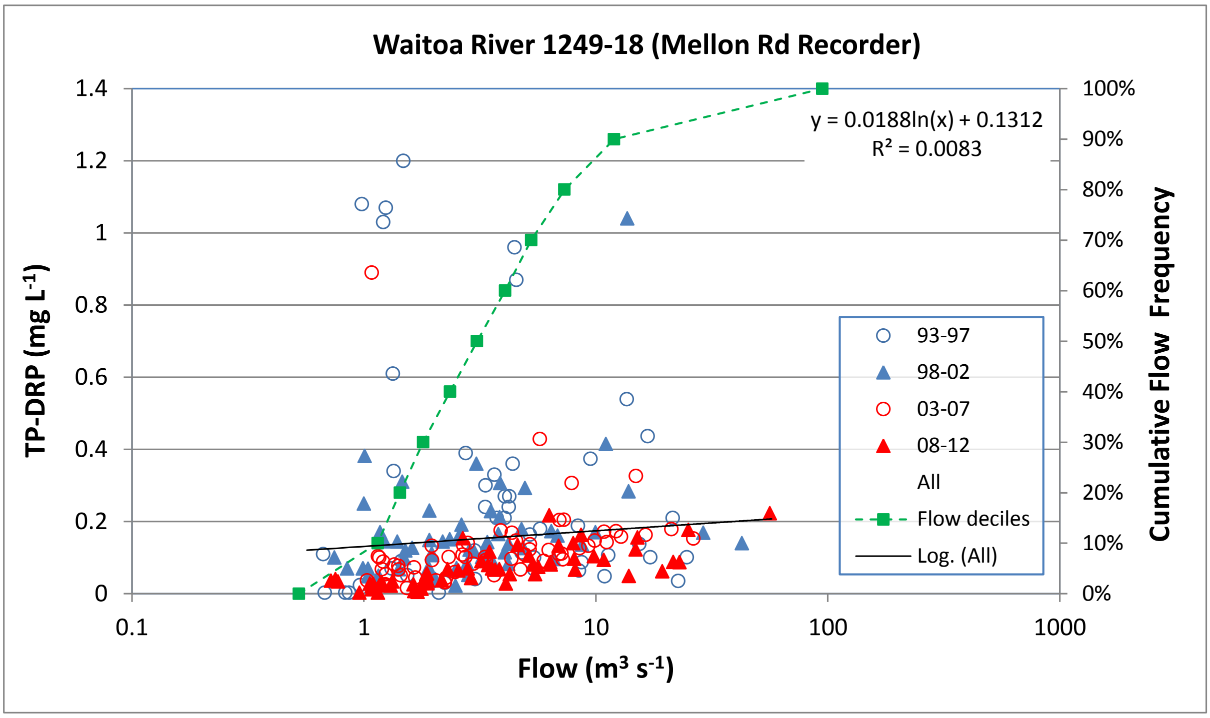


Figure 20: Unusually high concentrations of DRP and TP-DRP at low stream flows in the Waitoa River at Mellon Road, due to point source discharges.

4.4 SILICA

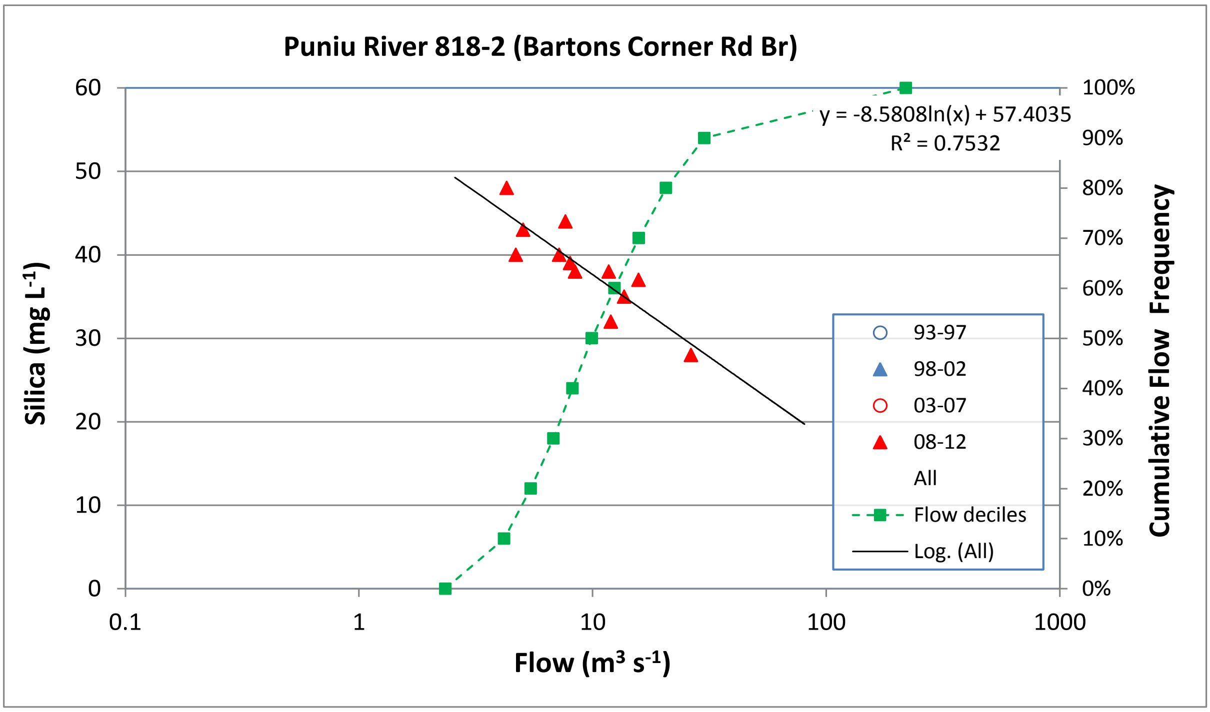
As well as nitrogen and phosphorus species, which are environmentally important due to their contribution to eutrophication, silica concentrations are also of interest for their potential use in indicating water age and land-to-water transfer paths (Morgenstern et al., 2010; Barkle et al., 2014). As water spends a longer period of time in the subsurface, concentrations of dissolved silica tend to increase (depending on the specific minerals present), and thus higher silica concentrations in the stream may indicate a predominance of older water. In this way, seasonal patterns of stream silica may point to seasonal changes in the contributions of young vs old water to stream flow.

Silica concentrations varied widely across the region (Figure 22), reflecting differences in silica content of the subsurface materials and differences between the catchments in the predominance of stream flow generating processes. Concentrations were lowest in the Coromandel, Lower Waikato, Waipa and West Coast areas, higher in the Hauraki and Taupo areas, and extremely high in those Upper Waikato streams affected by geothermal influences.

Despite the differences in absolute Si concentrations, Si exhibited strong negative correlations with flow at most sites (Table 5), although the very limited number of samples (monthly samples for a single year) meant that 8 of the 26 relationships were not highly statistically significant ($p>0.005$). The negative correlation is expected, as baseflows typically comprise older water (with high Si concentrations) while storm flows are dominated by younger water (with low Si).

Figure 21 shows typical relationships observed at Puniu River and Whareroa Stream. With such a small number of data points, it is apparent that errors in one or two points could drastically alter the apparent relationship. This is reflected in the relatively high (i.e. poor) p-values for silica C-D relationships.

Relatively low correlations in the three Lower Waikato sites were due to variable Si concentrations at low flow. In addition, the Waingaro River was unusual in that Si was uncorrelated with flow.



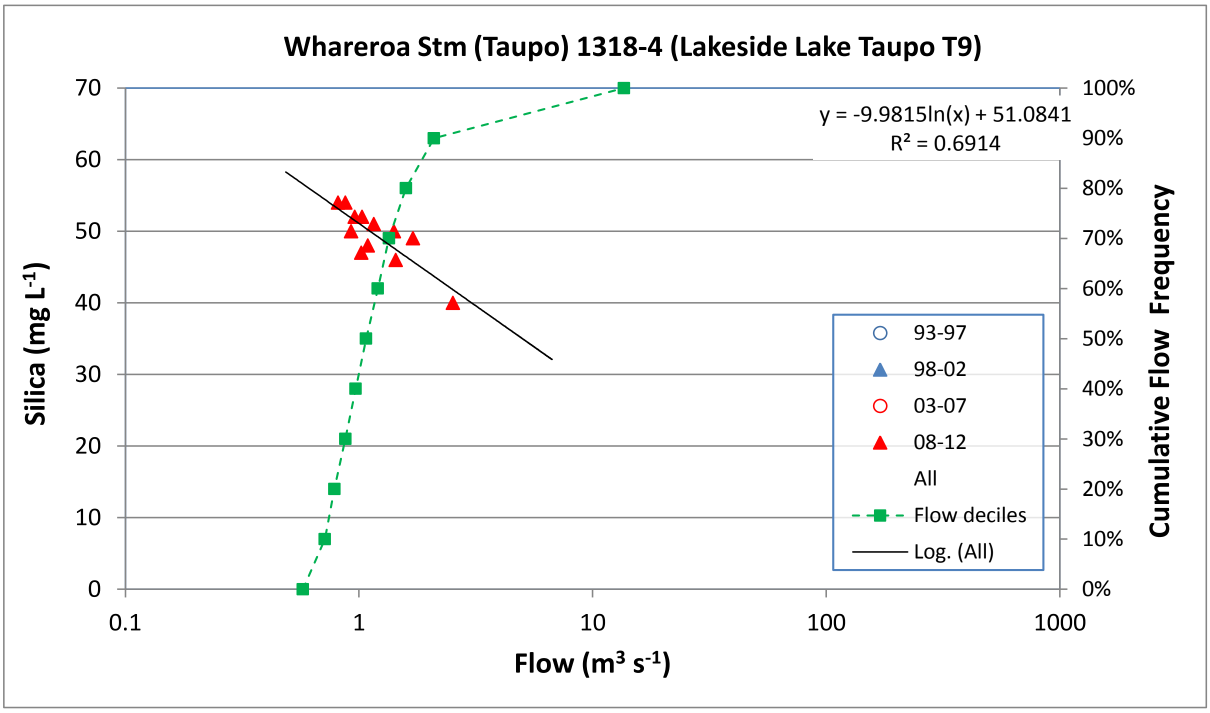


Figure 21: Typical negative correlation between silica concentration and flow at Puniu River and Whareroa Stream.

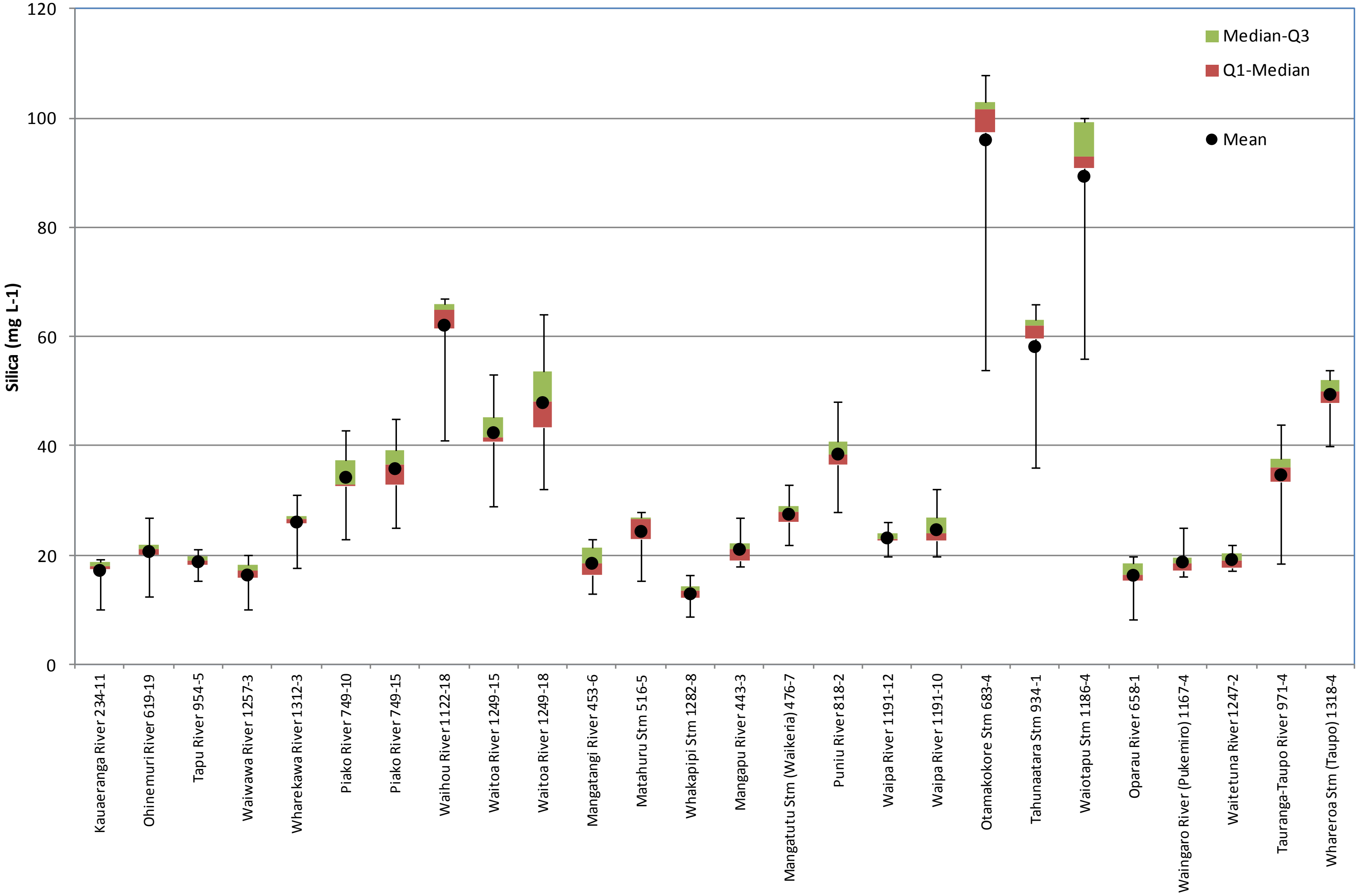


Figure 22: Box plot of silica concentrations across all 26 sites.

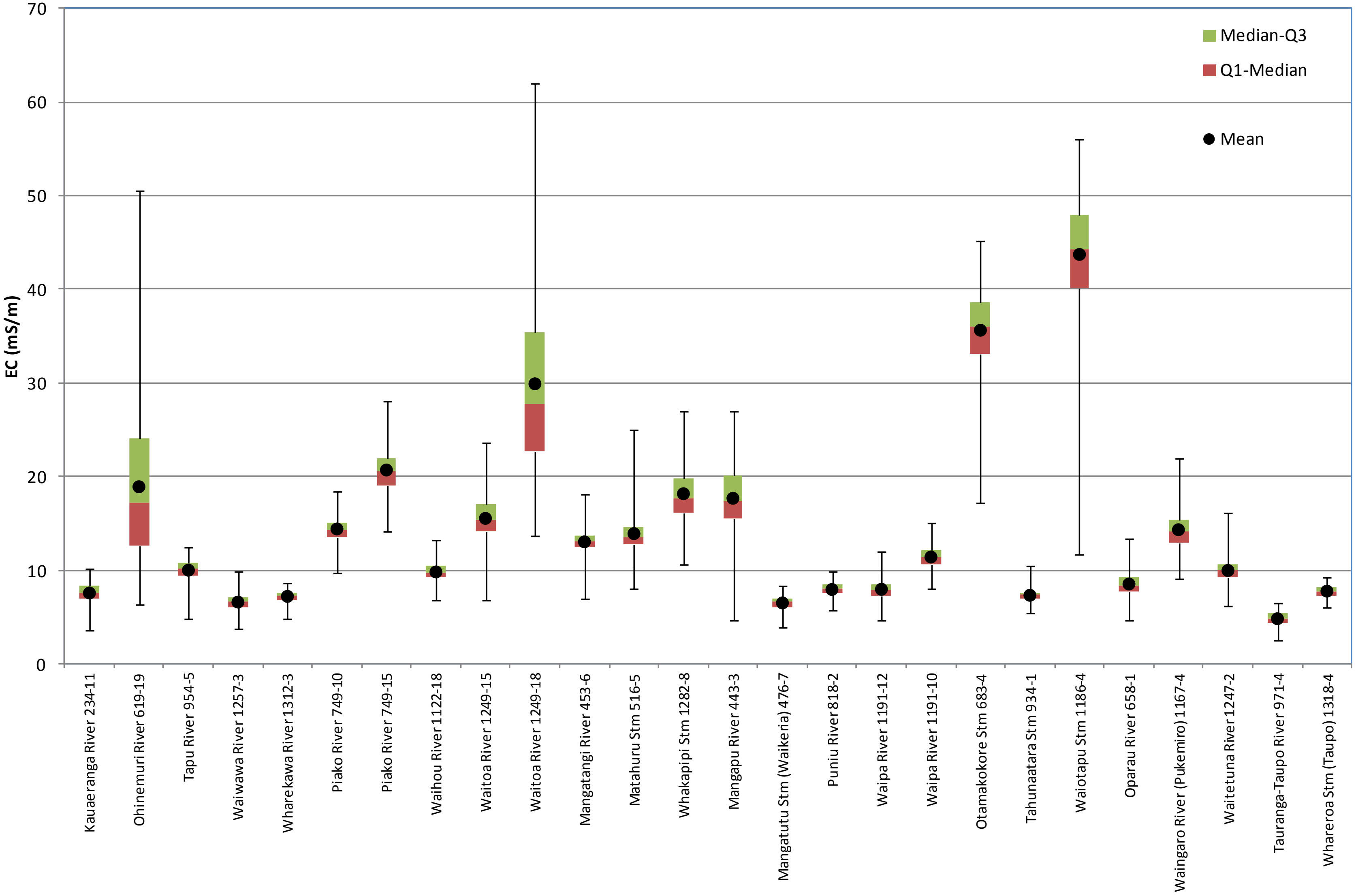


Figure 23: Box plot of electrical conductivity across all 26 sites.

4.5 ELECTRICAL CONDUCTIVITY

Electrical conductivity (EC) is a measure of the ability of water to pass an electrical current. It is very closely correlated to the content of cations and anions in the water (expressed in units of meq L^{-1}). Combined analysis of two 12-month periods for which cation/anion balance data is available (2005, 2010/11) indicates that averaged across all sites, bicarbonate contributes 46% to the anion charge, chloride 34%, sulphate 10%, and nitrate 4%. Sodium contributes 48% of the cation charge, calcium 26%, magnesium 18%, potassium 6%, and ammonium less than 1%. While land use activity affects the concentrations of some of these ions, conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Accordingly, it could potentially be an alternative to silica as indicator of contact time of water in the subsurface system (c.f. Section 5). In contrast to the very small silica data sets, EC data is typically available for the entire length of the water quality time series.

Figure 23 shows that the highest EC values are found in catchments with point source discharges (Ohinemuri River, Piako River (Paeroa_Tahuna Road), Waitoa River (Mellon Road), Whakapipi Stream, Mangapu River) or geothermal influence (Otamakokore Stream, Waiotapu Stream). As previously discussed, elevated EC was used by WRC (2004) as an indicator of point source discharges.

Negative correlations between EC and flow were observed at all sites (Table 5), presumably reflecting dilution of groundwater discharge with higher EC by discharge from near-surface flow paths with lower EC. Most of these relationships were highly statistically significant ($p<0.005$). Figure 24 shows one such EC-flow relationship (Kauaeranga River). The only sites where EC was only weakly related to flow were Waihou River, Mangatangi River, Matahuru Stream, Mangatutu Stream, Puniu River and Tahunaatara Stream.

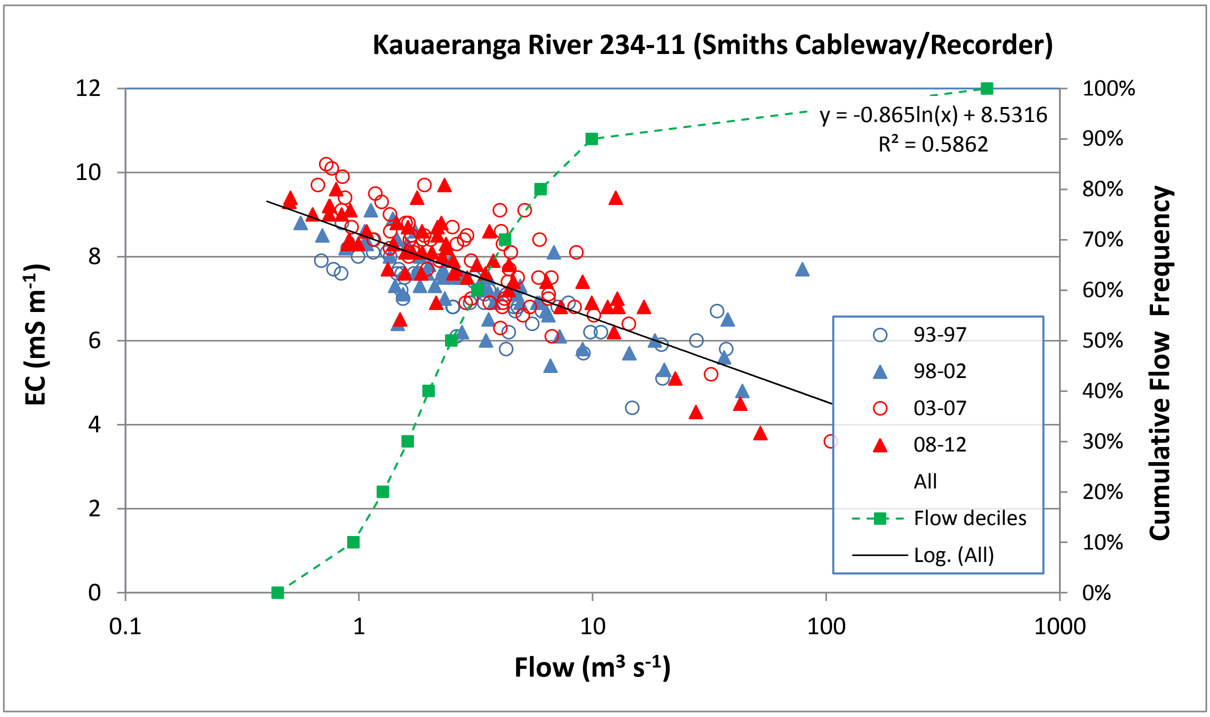


Figure 24: Typical negative correlation between EC and flow at Kauaeranga River.

5 DATA STRATIFICATION

5.1 INTRODUCTION

The strong concentration-discharge relationships observed for many variables in this study (Table 5) are considered to largely result from different flow paths being dominant in low flow compared with high flow conditions, while the effect of in-stream processes like plant uptake or denitrification is considered to be secondary in these mesoscale catchments. Low stream flows are typically fed from discharge of relatively old groundwater reservoirs, whereas high stream flows occur in response to significant rainfall events, which both displace water from the unsaturated zone (interflow) and shallower groundwater layers, and tend to contribute a larger proportion of overland or near-surface flow (e.g. through artifical drains) (McGlynn & McDonnell, 2003). While specific evidence for the validity of this relationship is not available for our monitoring sites, it has been demonstrated for Toenepi Stream through tritium-based water dating (Morgenstern et al., 2010) and modelling (Woodward et al., 2013).

On this basis, stream flow can potentially be used to “stratify” the water quality samples into those that represent predominantly older, groundwater discharge, and those that represent predominantly younger water discharged from shallower reservoirs. These two data subsets can then be compared and analysed to gain insight into the differences between the older and younger water that produce the observed stream flow and concentration patterns. This could then allow us to address the following questions:

1. Are there concentration differences between the reservoirs?
2. Can this sample stratification help to ascertain which reservoir is responsible for concentration trends (WRC, 2013) observed in some streams?

5.2 DATA STRATIFICATION APPROACHES

There are various approaches to stratifying the water quality data. The most widely applicable is to stratify the data based upon the stream flow at time of sampling, for example according to flow percentile. Alternatively, a hydrochemical tracer can be used to estimate the proportions of young and old water in the stream through time. In the current study we first tested stratification by flow percentile, and then stratification based on hydrograph separation calibrated to either silica or electrical conductivity (EC). These approaches will now be described.

5.2.1 STRATIFICATION BASED ON FLOW PERCENTILES

Assuming that low flows represent older water while high flows represent younger water, one method of stratifying the water quality data is according to flow percentile at time of sampling. Water quality samples taken at low flow thus fall into a low percentile, whereas high flow samples correspond to a high percentile. This offers a means for determining whether there is a statistically significant difference between the water quality at low vs high flow.

Following this approach, the monitoring data was stratified into low flow (flow percentile less than 25%) and high flow (flow percentile above 75%) samples. The 25% and 75% cut-offs were chosen to provide sufficient differentiation between the low and high flow samples, while maintaining a sufficient number of samples for meaningful statistical comparison.

The means of the concentrations of the low flow and high flow samples were each calculated, and the differences are presented in Table 6. The probability that the means were significantly different was also calculated using a Student's t-test (two-tailed, unequal variance); differences were considered highly statistically significant if the p-value was less than 0.005. This is closely related to the question of whether the slope of the concentration-discharge relationship is statistically significantly different to zero, in Section 4.

The results of this stratification (Table 6) matched the analysis of the concentration discharge relationships (Table 5) closely, and showed that TN, NNN, NH4 and TP-DRP concentrations were lower in the low flow (and therefore older) samples compared with the high flow (and therefore younger) samples, whereas EC was higher in the low flow samples compared with the high flow samples (highly statistically significant at most sites). At 15 sites, there were no significant DRP concentration differences between the two subsets. However, DRP was higher in the low flow samples compared with the high flow samples at 8 sites, but lower at 3 sites. Higher DRP concentrations at low flow could indicate that groundwater discharge may have greater DRP concentrations in these catchments (Whareroa Stream, Tauranga-Taupo River, Waiotapu Stream, Puniu River, Mangapu River, Waingaro River) than the shallower water reservoirs, or could be due to the effect of point-source discharges (Waitoa River (Mellon Road), Piako River (Paeroa-Tahuna Road)).

TP was lower in the low flow samples compared with the high flow samples at 12 sites, but higher at the 2 sites noted above for point-source discharges. Silica concentrations were always higher in the low flow samples compared with the high flow samples, but these differences were never highly statistically significant due to the small number of silica samples (between 0 and 5 silica samples per subset). This is in contrast to the slopes of the concentration-discharge relationships for silica, which were generally highly statistically significantly different from zero (based on 12 samples).

One advantage of data stratification by flow percentile is that approximately equal numbers of samples are classified as high flow or low flow, which means that differences in water quality are more likely to be statistically significant. On the other hand, as the shape of the hydrograph differs substantially between streams, the high flow and low flow samples do not necessarily correspond to particular water flow paths or associated water ages. While the flow percentile approach is likely to result in a good separation of old and young water in very dynamic streams with a spiky hydrograph, even the high percentile samples may represent discharge of relatively old groundwater in a baseflow dominated stream. In order to stratify the data on a more physical basis, we explored the use of hydrochemical tracers as a basis for identifying samples as being predominantly consisting of young or old water.

Table 6: Differences in concentration (mS m^{-1} for EC, mg L^{-1} for other analytes) between high flow and low flow water quality samples, as stratified according to flow percentile. N Low and N High are the number of samples classified as low flow and high flow respectively (Flow%<25% and Flow%>75%), and N Moderate are the remaining samples. Significant concentration differences (p<0.005) are highlighted red if positive and blue if negative. Flags are described in Table 1.

							Concentration Difference (Conc High - Conc Low)								
Region	**Site Name**	**Sample Location**	**ChemID**	**N High**	**N Moderate**	**N Low**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**	**Flags**
Coromandel															
	Kauaeranga River	Smiths Cableway/Recorder	234-11	57	121	50	0.16	0.07	0.00	0.02	0.00	0.02	-6.40	-2.28	DRP
	Ohinemuri River	Queens Head	619-19	56	112	55	0.54	0.43	0.05	0.03	0.00	0.03	-6.50	-13.87	PS, DRP
	Tapu River	Tapu-Coroglen Rd	954-5	53	116	49	0.14	0.03	0.00	0.02	0.00	0.01	-3.35	-2.53	DRP
	Waiwawa River	SH25 Coroglen	1257-3	55	123	47	0.14	0.03	0.00	0.02	0.00	0.02	-8.28	-1.96	MF, DRP
	Wharekawa River	SH25	1312-3	59	113	51	0.11	0.11	0.00	0.00	0.00	0.00	-7.65	-1.30	MF, DRP
Hauraki															
	Piako River	Kiwitahi	749-10	59	118	51	2.75	2.24	0.08	0.06	-0.01	0.07	-7.67	-1.22	-
	Piako River	Paeroa-Tahuna Rd Br	749-15	56	107	55	1.91	1.41	0.14	-0.22	-0.32	0.09	-11.50	-4.23	PS
	Waihou River	Okauia	1122-18	56	124	60	0.53	0.30	0.03	0.03	-0.01	0.04	-	0.23	-
	Waitoa River	Landsdowne Rd Br	1249-15	56	115	55	1.40	0.91	0.07	0.11	0.02	0.10	-13.50	-4.29	-
	Waitoa River	Mellon Rd Recorder	1249-18	59	112	59	1.23	0.68	0.15	-1.21	-1.22	0.01	-11.60	-19.36	PS
Lower Waikato															
	Mangatangi River	SH2 Maramarua	453-6	65	119	56	1.28	0.84	0.04	0.07	0.01	0.06	-1.98	-0.15	-
	Matahuru Stm	Waiterimu Road Below Confl	516-5	20	40	18	1.86	1.19	0.09	0.11	0.00	0.11	-	-0.85	MF, SS
	Whakapipi Stm	SH22 Br	1282-8	55	127	57	1.20	1.00	0.07	0.07	0.01	0.06	-4.15	-4.94	PS
Waipa															
	Mangapu River	Otorohanga	443-3	42	67	37	0.78	0.57	0.03	0.01	-0.05	0.06	-4.92	-6.38	PS, MF, SS
	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	25	55	22	0.73	0.58	0.01	0.03	0.00	0.03	-11.00	-0.57	SS
	Puniu River	Bartons Corner Rd Br	818-2	61	120	59	1.08	0.77	0.04	0.04	-0.01	0.05	-15.67	-0.54	-
	Waipa River	SH3 Otorohanga	1191-12	36	68	43	0.75	0.56	0.01	0.05	0.00	0.05	-1.67	-1.71	MF, SS
	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	29	39	19	1.18	0.86	0.04	0.06	-0.01	0.06	-8.20	-2.02	MF, SS, DRI
Upper Waikato															
	Otamakokore Stm	Hossack Rd	683-4	59	116	62	0.92	0.52	0.06	0.04	0.00	0.04	-20.75	-8.05	G, TP
	Tahunaatara Stm	Ohakuri Rd	934-1	56	124	60	0.59	0.26	0.01	0.06	0.00	0.05	-13.75	-0.21	-
	Waiotapu Stm	Homestead Rd Br	1186-4	57	121	62	0.74	0.15	0.28	0.10	-0.02	0.12	-	-11.13	G, MF, TP
West Coast															
	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	15	33	10	0.35	0.25	0.00	0.03	0.00	0.03	-5.35	-2.59	SS, DRP
	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	34	64	35	1.16	0.79	0.01	0.12	0.00	0.12	0.02	-3.77	SS
	Waitetuna River	Te Uku-Waingaro Rd	1247-2	16	30	15	0.69	0.43	0.01	0.10	0.00	0.10	-2.08	-1.90	MF, SS
Taupo															
	Tauranga-Taupo River	Te Kono Slackline	971-4	60	106	64	0.02	0.00	0.00	0.01	-0.01	0.01	-20.65	-1.84	-
	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	35	58	30	0.48	0.37	0.00	0.01	-0.01	0.02	-9.50	-1.29	SS

5.2.2 STRATIFICATION BASED ON HYDROGRAPH SEPARATION

While stratification of water quality samples according to flow percentile identifies many significant concentration differences between low flow and high flow samples, this method does not consider to what extent stream water quality samples are the product of mixing of the discharges from the two flow paths. Furthermore, stratifying the water quality samples by flow percentile does not take seasonality into consideration, so that a summer event flow sample could possibly be stratified as “low flow” while a winter low flow sample could be stratified as “high flow”. Therefore, we explored whether a stratification method that takes the available information on the temporal variation in stream flow (i.e. the ‘hydrograph’) into account could achieve a more process-based separation.

5.2.2.1 Hydrodynamic Analysis

Hydrograph separation methods are a variety of approaches for separating a flow hydrograph into two (or more) components. By taking a process point of view, these methods allow for the fact that flows may change with time, so that, for example, groundwater discharge may increase in winter as water tables rise.

Most commonly, hydrograph separation is used for “baseflow separation”, i.e. for estimating the non-event (“baseflow”) and event (“quickflow”) portions of a stream flow hydrograph through time. In this application, quickflow is often equated with overland flow, while baseflow is equated with groundwater discharge. However, this can be misleading since baseflow separation methods work on short term vs longer term flow responses (i.e. hydrodynamics), which do not necessarily correspond to particular physical flow paths. In reality, not only base flow, but also a significant portion of event flow can be provided by discharge of shallow groundwater (McGlynn & McDonnell, 2003; Bidwell et al., 2008; Gonzales et al., 2009; Barkle et al., 2014).

A recent and successful method of automatic hydrograph separation is the two parameter digital filter of Eckhardt (Eckhardt 2005, 2008; Gonzales et al., 2009; Russell, 2013; Collischonn & Fan, 2013, Rimmer & Hartmann, 2014). In the Eckhardt model, the low frequency flow fraction at time step k, b_k, is estimated from the total stream flow, y_k, as,

$$b_k = \min\left(\frac{(1-\beta)\alpha b_{k-1} + (1-\alpha)\beta y_k}{1-\alpha\beta}; y_k\right)$$

where b_{k-1} is the low frequency flow fraction at the previous time step, and α and β are site-specific parameters to be determined. The high frequency flow fraction at time step k is then equal to ($y_k - b_k$). The method requires the hydrograph data to be on a fixed time step with no missing values. When applied to baseflow separation, the Eckhardt filter has been shown to perform well by comparison with other methods (Eckhardt, 2008; Gonzales et al., 2009).

In order to use the Eckhardt filter, the parameters α and β must be estimated. For baseflow separation, the parameters are typically estimated using the hydrodynamic characteristics of the hydrograph, by tuning the hydrograph separation so that the recession portions of the hydrograph are identified as being baseflow (Vogel & Kroll, 1996; Eckhardt, 2008; Collischonn & Fan, 2013). Stewart

(2014), however, argues that this approach does not properly represent the hydrodynamics of baseflow, which has been shown in isotopic or conservative tracer studies to be much more dynamic during rain events than during periods of stream recession. Consequently, the dynamics of baseflow (or more accurately, "pre-event" water, that includes both fast and slow components) must be determined by some method other than recession analysis (Stewart, 2014).

5.2.2.2 Calibration Based on Silica Data

Several authors have performed "hydrochemical separation", by tuning the hydrograph separation so that it matches water chemistry data. Gonzales et al. (2009) used this approach with a variety of tracers (EC, Ca, Mg, silica, deuterium) to estimate the groundwater contribution to flow in a lowland stream in The Netherlands during a 3 week period. Rimmer & Hartmann (2014) similarly used this approach to calibrate the digital hydrograph separation filter of Eckhardt (2005, 2008) to (geogenic) sulphate and total suspended solids measurements in two small streams in Israel.

In the present study, we are interested in identifying stream water quality changes due to recent land use compared with water quality changes due to past land use. As such, we would like to separate the stream flow into its "younger" and "older" fractions. Water quality samples taken when "younger" water is dominant are considered to reflect recent land use, while samples taken when "older" water is dominant are considered to reflect past land use.

As water age data is not available, we proposed in the first instance to use silica (SiO_2) concentrations as a proxy for water age. Silica concentration reflects water contact time with subsurface materials, and so is generally correlated with water age (Morgenstern et al., 2010; Barkle et al. 2014). Furthermore, silica concentrations are usually unaffected by other sources of contamination such as agricultural or point source discharges. It is however crucial to be aware that silica concentrations differ strongly between different geological settings. Accordingly, a given silica concentration may represent 'younger' water in one geological setting, but 'older' water in another. Unfortunately, the present data set includes only one year's monthly silica samples for each catchment (October 2010 to September 2011), which restricts stringent statistical analysis.

As mentioned above, Rimmer & Hartmann (2014) extended the Eckhardt method to perform a hydrochemical separation by firstly assuming that the low and high frequency components could be assigned fixed concentration values (C_b and C_s respectively), and then by calibrating the resulting mixing model (C_y) to stream concentration data.

$$C_y = \frac{C_b b_k + C_s (y_k - b_k)}{y_k}$$

This requires not only that the flow data are on a fixed time step, with no missing values, but that the time steps coincide with water quality sampling times.

Following this approach, the Eckhardt filter was applied to daily stream flow data for the 26 catchments in our study for the 1993-2012 period. Daily stream flow was determined by interpolating the raw stream flow records. Missing flow records were assumed to be equal to the previous available record, for the purpose of filtering. The time of each day at which daily stream flow was estimated was adjusted gradually through time (using a linearly interpolated correction factor) so that interpolated daily stream flow would correspond with time of sampling on water quality sampling days. This was necessary because stream flow and chemistry changes sometimes occur at a much shorter time scale than 1 day, so that using stream flow at a fixed time of day (e.g. noon) would not necessarily represent the flow at the time of water quality sampling.

The filter parameter α, and the concentrations C_b and C_s, were automatically adjusted for each site to minimise the sum of squared errors between C_y and the recorded stream silica concentrations. This was done in Microsoft Excel 2010 using a genetic algorithm optimisation tool. Each time the parameter α was changed, the parameter β was recalculated using the backward filter method of Collischonn & Fan (2013).

The resulting hydrograph separation (using the calibrated parameters α and β) thus provided a separation between low silica (younger) and high silica (older) water contributions to stream flow. The reliability of this separation depends both on the simplifications inherent in the conceptual model described above, and the quality and quantity of available (silica) calibration data. Because it depends on the silica concentrations, it separates flow based on the concentration changes, and not just flow hydrodynamics. This allows for dynamic changes in the discharges from the younger and older water reservoirs.

Figure 25, for example, shows the resulting hydrograph separation for the Whareroa Stream. The silica-calibrated hydrograph separation model (shown in red in Figure 25) explained 88% (NSE) of the variation in the silica data, and predicted that older water contributed 67% (OWI) of long term stream flow (when the model was run over the period of available stream flow data: 11 years in this case). NSE (Nash-Sutcliffe Efficiency) is the proportion of variation in the measured silica data explained by the silica model, and OWI (Old Water Index) is the long term average proportion of older (high silica) water in the stream.

It is clear from Figure 25 that a single year’s monthly silica data will not usually be sufficient for reliable calibration of the hydrograph separation, even for the short time period shown in the graph. Stream water is a dynamic mixture of discharges from different flow paths with a wide variety of response times, which can result in rapid changes to water quality in response to storm events. The range of resulting silica concentrations is unlikely to get captured by monthly sampling over a 1-year period (c.f. Figure 25).

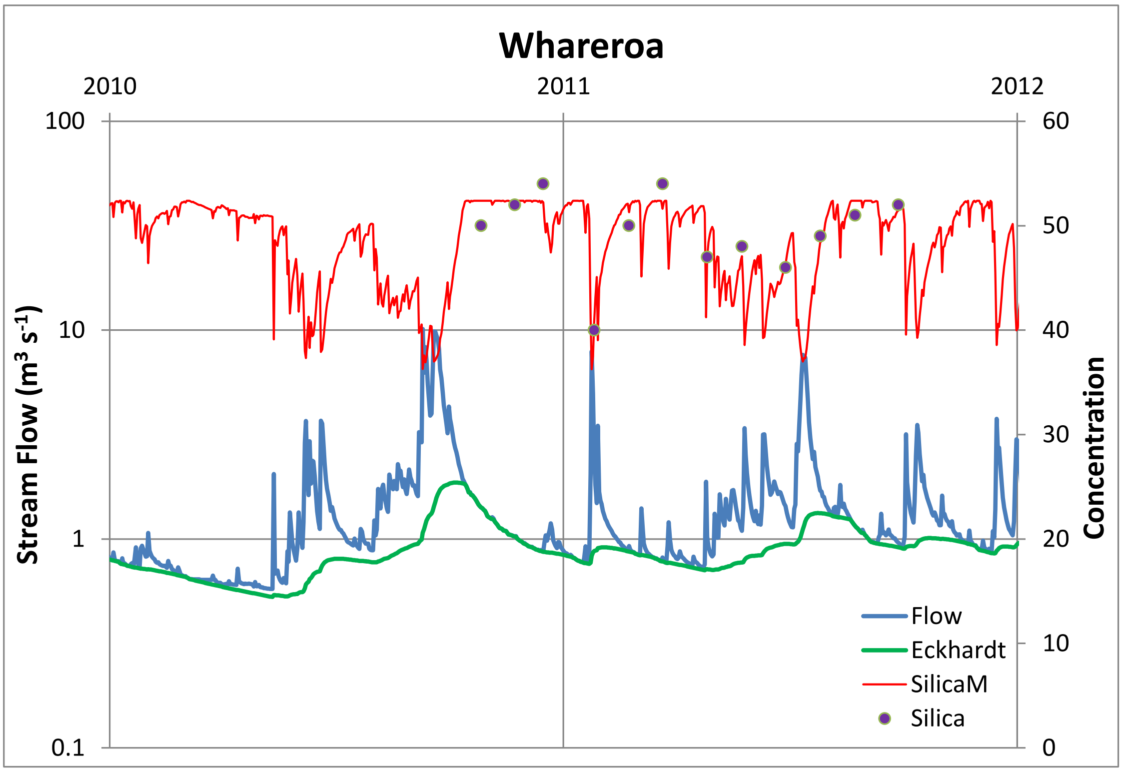


Figure 25: Silica-calibrated hydrograph separation for Whareroa Stream, showing daily stream flow (blue), predicted old water contribution (green), predicted silica concentration (red) and measured silica (dots).

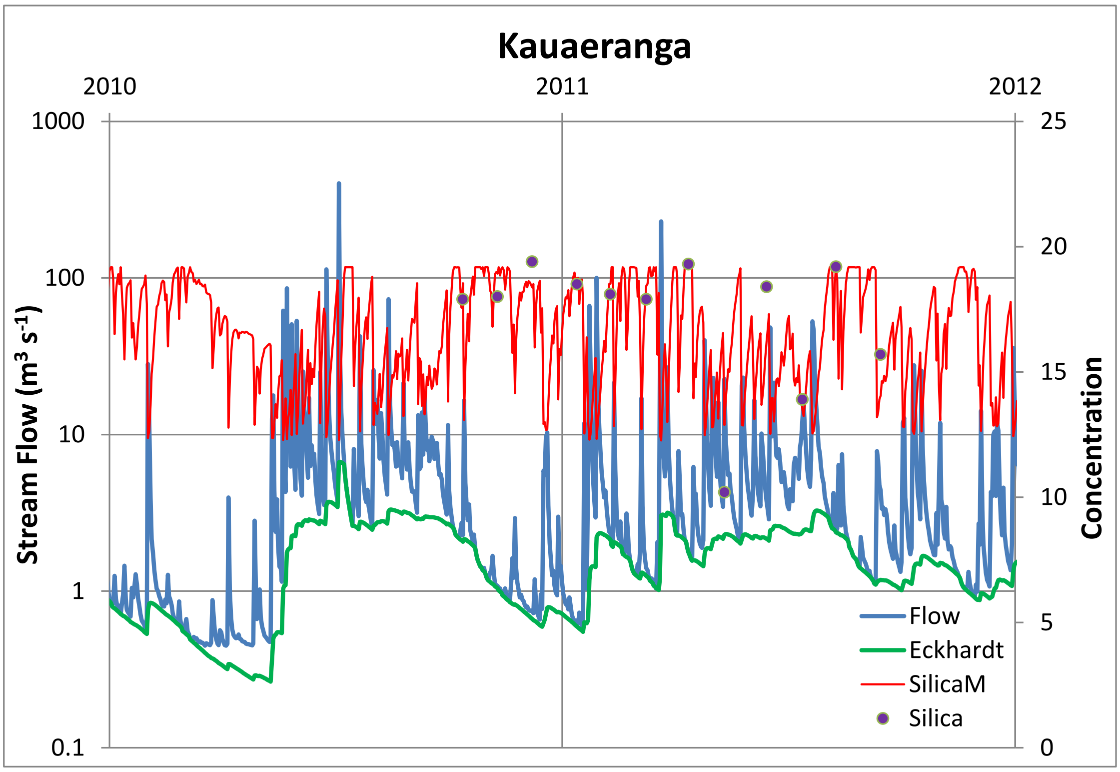


Figure 26: Silica-calibrated hydrograph separation for Kauaeranga River, showing daily stream flow (blue), predicted old water contribution (green), predicted silica concentration (red) and measured silica (dots).

Table 7: Silica-calibrated hydrograph separation results. The Eckhardt filter parameters α and β, and the silica concentrations C_b and C_s, are described in the text. NSE (Nash-Sutcliffe Efficiency) is the proportion of variation in the measured silica data explained by the silica model. OWI (Old Water Index) is the long term average proportion of old (high silica) water in the stream. P is the probability that the NSE is not significantly different to 0, and sites with P>0.005 are greyed out to indicate their low reliability.

Region	Site	LOC	alpha	beta	Cb	Cs	NSE	OWI	P
Coromandel									
	Kauaeranga	234-11	0.983049	0.327563	19.2	12.2	0.7802	0.2842	0.0001
	Ohinemuri	619-19	0.996999	0.189548	25.4	16.8	0.5858	0.1601	0.0037
	Tapu	954-5	0.987704	0.364627	19.9	16.3	0.5489	0.3218	0.0091
	Waiwawa	1257-3	0.983564	0.355136	18.8	10.0	0.8490	0.3116	0.0001
	Wharekawa	1312-3	0.995354	0.288754	30.0	19.8	0.7462	0.2503	0.0003
Hauraki									
	Piako (Kiwitahi)	749-10	0.996037	0.183552	40.9	30.0	0.3736	0.1506	0.0347
	Piako (Paeroa-Tahuna Road)	749-15	0.913974	0.724505	41.3	16.0	0.5537	0.6853	0.0055
	Waihou	1122-18	0.998922	0.813900	67.6	34.8	0.8921	0.7824	0.0000
	Waitoa (Landsdowne Road)	1249-15	0.994726	0.279519	50.3	35.3	0.6211	0.2388	0.0023
	Waitoa (Mellon Road)	1249-18	0.994864	0.385016	59.6	33.9	0.8163	0.3349	0.0001
Lower Waikato									
	Mangatangi	453-6	0.995314	0.267144	20.3	16.1	0.1974	0.2234	0.1479
	Matahuru	516-5	0.756048	0.810133	29.3	1.0	0.4432	0.7843	0.0248
	Whakapipi	1282-8	0.992873	0.313048	15.7	9.9	0.4890	0.2706	0.0114
Waipa									
	Mangapu	443-3	0.999297	0.184329	28.6	17.2	0.8310	0.1616	0.0000
	Mangatutu	476-7	0.997189	0.305100	33.6	22.7	0.6633	0.2776	0.0013
	Puniu	818-2	0.997783	0.323292	47.6	28.8	0.7638	0.2755	0.0002
	Waipa (Otorohanga)	1191-12	0.980459	0.547744	24.3	19.4	0.2777	0.5015	0.0784
	Waipa (Pirongia)	1191-10	0.999608	0.180970	37.8	20.4	0.8485	0.1512	0.0000
Upper Waikato									
	Otamakokore	683-4	0.991690	0.899213	103.8	31.8	0.9015	0.8721	0.0000
	Tahunaatara	934-1	0.993296	0.778224	64.2	30.4	0.9200	0.7435	0.0000
	Waiotapu	1186-4	0.996146	0.828564	97.8	47.8	0.9026	0.7973	0.0000
West Coast									
	Oparau	658-1	0.982030	0.492508	19.9	10.1	0.6679	0.4444	0.0012
	Waingaro	1167-4	0.974254	0.449174	19.3	17.4	0.0367	0.4032	0.5509
	Waitetuna	1247-2	0.982533	0.478443	20.8	16.5	0.5909	0.4296	0.0035
Taupo									
	Tauranga-Taupo	971-4	0.998625	0.387459	44.0	18.1	0.8606	0.3435	0.0001
	Whareroa	1318-4	0.996450	0.717458	52.4	34.4	0.8800	0.6673	0.0000

This is even more evident in more dynamic rivers such as Kauaeranga River (Figure 26). The silica-calibrated hydrograph separation for this catchment predicts an extremely dynamic pattern of water age, but which fits the silica data very well (NSE = 78%). This greater dynamism is presumably due to the relatively small capacity for water storage in this steep rocky catchment compared with the sediments available in the Whareroa Stream catchment. As a result, the "older" water fraction in this catchment is likely to represent much younger water compared with the older water fraction in Whareroa Stream. This is also suggested by the much lower silica concentrations (although these also reflect the different mineralogies).

The calibrated parameters for all sites are presented in Table 7. In order to assess the reliability of the model calibration, the probability (p) that the calibrated NSE was not significantly different to zero was also calculated for each site, using the Student's t-test. Calibrations with $p>0.005$ are greyed out in Table 7, and are considered unreliable. Comparison with Table 5 shows that no significant concentration-discharge relationships for silica had been detected at most of these sites (except Piako River sites).

In general, sites whose concentration-discharge relationship for silica had a high R^2 (Table 5) also achieved good calibrations to silica (high NSE values) using the hydrograph separation method. Figure 27 shows the relationships between the R^2 value of the concentration-discharge relationship for silica, against the calibrated NSE for all sites. The correlation between these two statistics reflects the fact that the hydrograph separation method also depends on the relationship between concentration and discharge, and the relatively poor values for many sites reflects the low number of silica measurements available. Accordingly, the most confident interpretation of silica-based hydrograph separation is possible for the 18 sites plotting in the top half of Figure 27 (see black sites in Table 7). (Oparau River and Waitetuna River both had concentration-discharge relationships with $p>0.005$, but model calibration was nevertheless highly statistically significant ($p<0.005$) at these sites.)

For those sites where it was statistically significant, the calibrated hydrograph separation model was used to predict the old water fraction for the whole 1993-2012 period, particularly at the times of water quality sampling (e.g. Figure 29). This allowed each water quality sample to be stratified according to the estimated proportion of young vs old water in the stream at that point in time. Samples were stratified as being predominantly old water when the modelled old water fraction was greater than 75%, and stratified as being predominantly young water when the modelled old water fraction was less than 25%. The aim was to be able to understand changes in stream water quality in terms of changes in the origins of that water.

For example, Figure 28 shows the TN data for Kauaeranga River, stratified as young or old. In this catchment, young water is consistently higher in TN than old water. When the average TN concentration of young water was compared with the average TN concentration of old water, the difference (0.16 mg L^{-1}) was found to be highly significant ($p<0.005$).

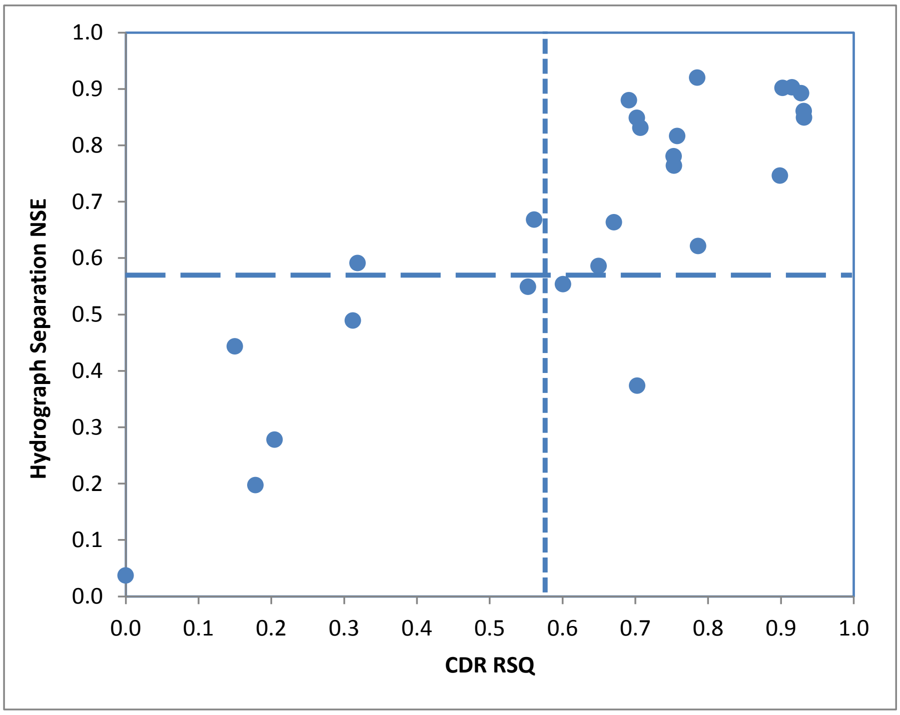


Figure 27: Nash-Sutcliff Efficiency (NSE) of silica-calibrated hydrograph separations compared with Coefficient of Determination for the silica Concentration-Discharge Relationships (CDR RSQ) for all 26 catchments. CDR RSQ values to the left of the dotted line were not statistically significant (p>0.005) and NSE values below the dashed line were not statistically significant (p>0.005).

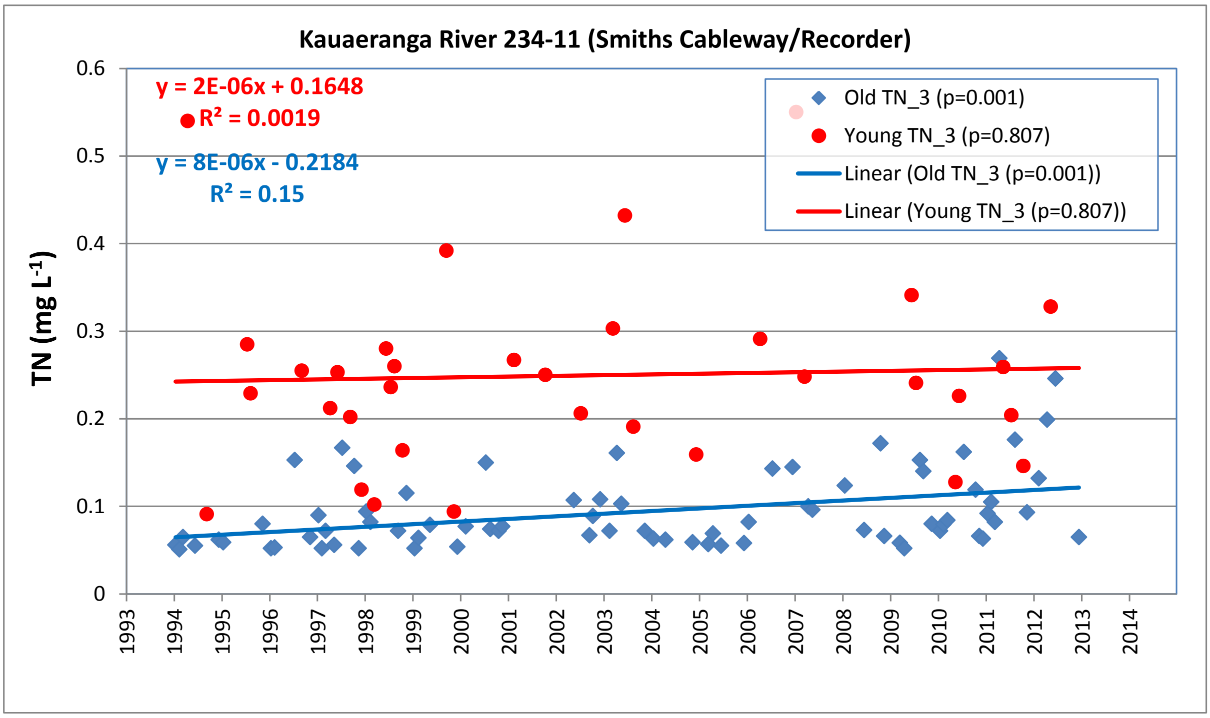
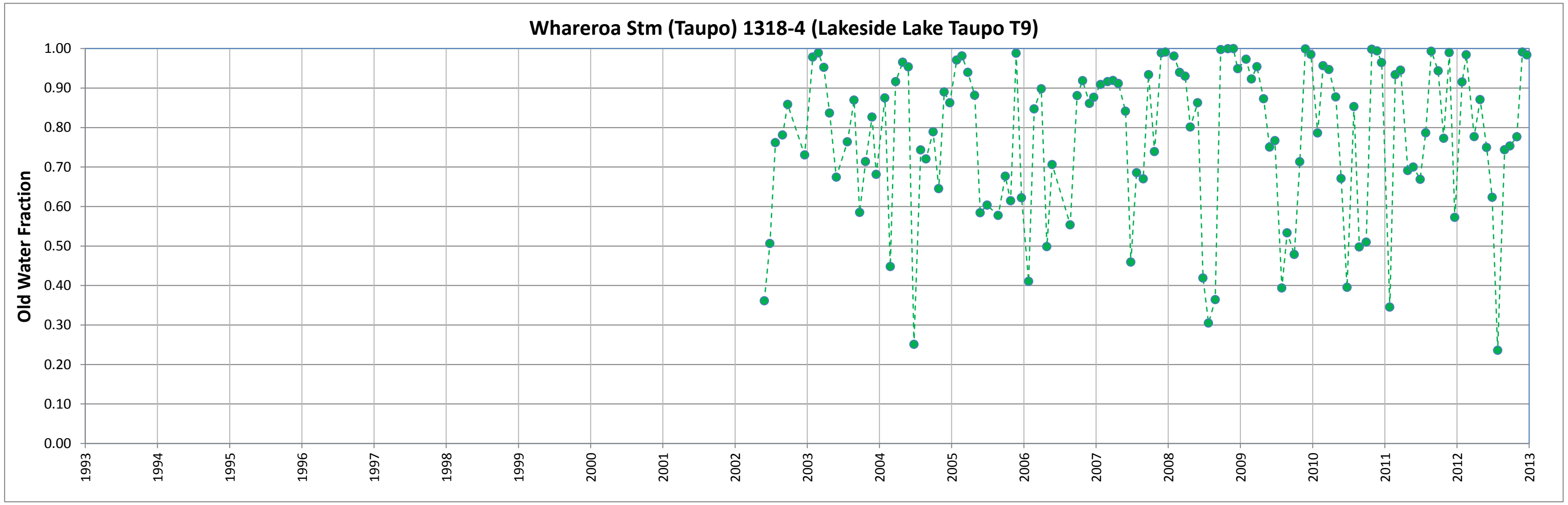


Figure 28: Total Nitrogen concentrations in the Kauaeranga River, stratified by silica-calibrated hydrograph separation as being Old or Young. Reported p-values are the probability that the trendline slope is not different from zero.



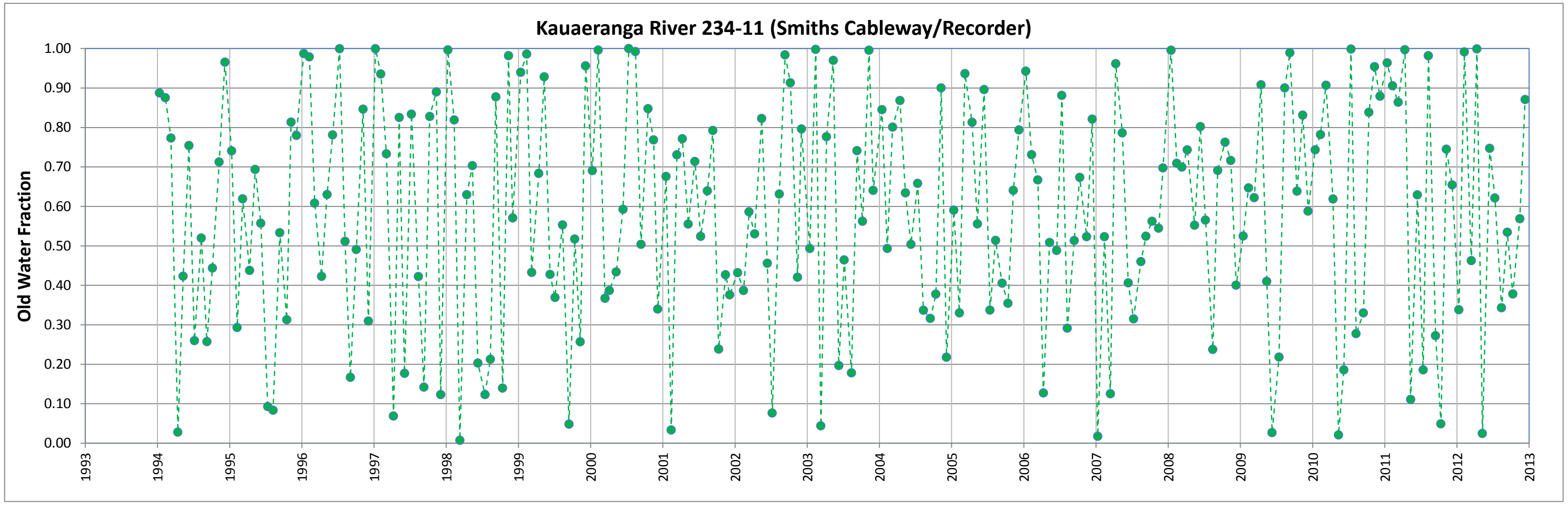


Figure 29: Estimated old water fraction at times of water quality sampling at two sites. Based on silica-calibrated hydrograph separation.

Table 8: Differences in water quality samples based on silica-calibrated hydrograph separation. N Old and N Young are the number of samples stratified as old and young respectively (OW%>75% and OW%<25%), and N Mixed are the remaining samples. Significant concentration differences (p<0.005) are highlighted red if positive and blue if negative.

							Concentration Difference (Conc High - Conc Low)								
Region	**Site Name**	**Sample Location**	**ChemID**	**N Young**	**N Mixed**	**N Old**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**	**Flags**
Coromandel															
	Kauaeranga River	Smiths Cableway/Recorder	234-11	34	117	77	0.16	0.04	0.00	0.02	0.00	0.02	-6.49	-2.38	DRP
	Ohinemuri River	Queens Head	619-19	98	98	27	0.36	0.34	0.03	0.02	0.00	0.02	-7.00	-14.04	PS, DRP
	Tapu River	Tapu-Coroglen Rd	954-5	28	112	78	0.23	0.03	0.00	0.03	0.00	0.03	-3.96	-2.38	DRP
	Waiwawa River	SH25 Coroglen	1257-3	37	108	80	0.20	0.02	0.00	0.02	0.00	0.02	-7.26	-1.64	MF, DRP
	Wharekawa River	SH25	1312-3	47	118	58	0.11	0.10	0.00	0.00	0.00	0.00	-10.30	-1.20	MF, DRP
Hauraki															
	Piako River	Kiwitahi	749-10	93	97	38	2.21	1.88	0.02	0.03	0.00	0.03	-9.00	-0.95	-
	Piako River	Paeroa-Tahuna Rd Br	749-15	0	78	140	-	-	-	-	-	-	-	-	PS
	Waihou River	Okauia	1122-18	1	51	188	0.68	0.05	0.10	0.18	-0.02	0.20	-	-2.03	-
	Waitoa River	Landsdowne Rd Br	1249-15	54	119	53	1.18	0.79	0.05	0.10	0.02	0.08	-13.00	-3.77	-
	Waitoa River	Mellon Rd Recorder	1249-18	48	103	79	1.34	0.76	0.15	-0.82	-0.87	0.05	-21.00	-16.84	PS
Lower Waikato															
	Mangatangi River	SH2 Maramarua	453-6	70	108	62	1.11	0.74	0.03	0.05	0.01	0.04	-5.83	0.14	-
	Matahuru Stm	Waiterimu Road Below Confl	516-5	0	15	62	-	-	-	-	-	-	-	-	MF, SS
	Whakapipi Stm	SH22 Br	1282-8	58	124	57	-0.28	-0.46	0.06	0.06	0.00	0.06	-3.45	-3.85	PS
Waipa															
	Mangapu River	Otorohanga	443-3	71	53	22	0.69	0.50	0.03	0.00	-0.05	0.05	-7.87	-5.92	PS, MF, SS
	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	26	56	20	0.72	0.57	0.01	0.03	0.00	0.03	-9.00	-0.39	SS
	Puniu River	Bartons Corner Rd Br	818-2	66	138	36	1.08	0.76	0.03	0.05	-0.01	0.06	-16.00	-0.39	-
	Waipa River	SH3 Otorohanga	1191-12	7	78	62	0.70	0.33	0.02	0.11	0.00	0.11	-	-0.42	MF, SS
	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	45	35	7	1.10	0.82	0.03	0.05	0.00	0.05	-	-2.01	MF, SS, DR
Upper Waikato															
	Otamakokore Stm	Hossack Rd	683-4	0	17	220	-	-	-	-	-	-	-	-	G, TP
	Tahunaatara Stm	Ohakuri Rd	934-1	2	53	185	2.21	0.16	0.12	0.36	0.06	0.30	-22.20	0.46	-
	Waiotapu Stm	Homestead Rd Br	1186-4	2	42	196	1.28	0.07	0.30	0.44	-0.01	0.44	-32.30	-13.15	G, MF, TP
West Coast															
	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	7	30	21	0.39	0.11	0.00	0.06	0.00	0.06	-9.95	-2.55	SS, DRP
	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	15	59	59	1.41	0.73	0.02	0.14	0.00	0.15	-	-1.96	SS
	Waitetuna River	Te Uku-Waingaro Rd	1247-2	7	29	25	0.93	0.35	0.02	0.17	0.00	0.18	-2.40	-0.71	MF, SS
Taupo															
	Tauranga-Taupo River	Te Kono Slackline	971-4	40	143	47	0.03	0.01	0.00	0.00	-0.01	0.01	-21.73	-2.19	-
	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	2	44	77	0.67	0.36	0.00	0.07	-0.01	0.08	-	-1.82	SS

Table 8 summarises the concentration differences between young and old samples for all catchments, as stratified using this method. In some catchments, few or no samples could be stratified as being predominantly consisting of young water. Catchments with significant groundwater storage and discharge, for example, remained dominated by old water except during the largest storm events, which are rarely sampled by a monthly programme (e.g. Whareroa Stream, Figures 25 and 29). Furthermore, even when the old water contribution was more modest, periods of young water dominance are typically short lived (Stewart, 2014), and may be under-represented in a data set based on a fixed monthly sampling schedule (e.g. Kauaeranga River, Figures 26 and 29). Higher resolution sampling would be required to accurately separate event responses from old water flow in such cases.

Water quality classification based on silica-calibrated hydrograph separation (Table 8) identified fewer statistically significant differences in water quality parameters between younger and older water than the method based on flow percentiles (Table 6). This is primarily due to the small amount of silica data available, and hence the low statistical significance of the tests. In some cases the low numbers of young water samples in a catchment was due to the reality of old water dominance in spring-fed catchments (Waihou River, Otamakokore Stream, Tahunaatara Stream, Waiotapu Stream, Whareroa Stream). Furthermore, the high variability in the water quality parameters of “young” samples (e.g. Figure 28) also affects the statistical significance of the differences.

Electrical conductivity was considered as a possible alternative indicator of water age, and will be discussed in the next section.

5.2.2.3 Calibration Based on Electrical Conductivity

Despite the close link between silica concentration and water age, use of silica as a proxy is restricted by it not being widely measured. The silica samples in the Waikato data set, for example, were collected as part of a specific campaign, for the duration of a single year only.

A possible alternative is electrical conductivity (EC). EC is straightforward to measure, and as a consequence, is routinely measured in most long term water quality monitoring programmes. As explained in Section 4, EC is a measure of the ability of water to pass an electrical current, and is very closely correlated to the content of cations and anions in the water (expressed in units of meq L^{-1}). While land use activity affects the concentrations of some of these ions, in the absence of large point-source discharges, conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows (USEPA, 2012). Accordingly, it could potentially be an alternative to silica as an indicator of contact time of water in the subsurface system. In contrast to the very small silica data sets, EC data is typically available for the entire length of the water quality time series.

Encouraged by the observation that C-D relationships for silica and EC were generally similar (see Section 4), EC was therefore tested as an alternative proxy for water age. As before, the filter parameter α, and the concentrations C_b and C_s, were automatically adjusted for each site to minimise the sum of squared errors between C_y and the recorded stream EC concentrations. Each time the parameter α was changed, the parameter β was calculated using the method of Collischonn & Fan (2013).

The resulting hydrograph separation (using the calibrated parameters α and β) provided a separation between low EC (younger) and high EC (older) water contributions to stream flow. As before, the reliability of this separation depends both on the simplifications inherent in the conceptual model described above, and the quality and quantity of available (EC) calibration data. As EC is routinely measured in the monthly sampling programme, a much larger amount of data was available compared with silica. However, EC values are less closely tied to water age, and can be affected by other processes including point source discharges and agricultural runoff. Furthermore, because the EC data spans a longer period of time, up to 20 years, the possibility that trends may exist in the EC data must be considered, as a result of land use or other changes. The hydrograph separation model for EC does not consider the possibility of changes in EC with time, other than those associated with changes in flow.

Figure 30 shows the calibrated hydrograph separation for the Whareroa Stream, both for the 2010-2012 period (for comparison with Figure 25) as well as for the entire data period for this site (2002-2012). The EC-calibrated hydrograph separation model (shown in red in Figure 30) explained 76% (NSE) of the variation in the EC data, and predicted that old water contributed 58% (OWI) of long term stream flow (11 years in this case), similar to the results obtained from calibration to silica. NSE (Nash-Sutcliffe Efficiency) is the proportion of variation in the measured EC data explained by the EC model, and OWI (Old Water Index) is the long term average proportion of old (high EC) water in the stream. Comparison with Figure 25 shows that the predicted old water fraction was similar with that derived from calibration to the silica data.

The calibrated parameters for all sites are presented in Table 9. The longer time series for EC data compared with silica provides a much more reliable basis for calibration of the hydrograph separation; this is reflected in the much lower p-values in Table 9 compared with Table 7. In general, sites whose concentration-discharge relationship for EC had a high R^2 (Table 5) also achieved good calibrations to EC (high NSE values) using the hydrograph separation method. Figure 31 shows the relationships between the R^2 value of the concentration-discharge relationship for EC, against the calibrated NSE for all sites. Interestingly, only two sites had hydrograph separations that were not statistically significant (Matahuru Stream and Puniu River). However, due to the high number of EC data, several sites were statistically significant, but had rather low NSE and R^2 values (c.f. Figures 27 and 31).

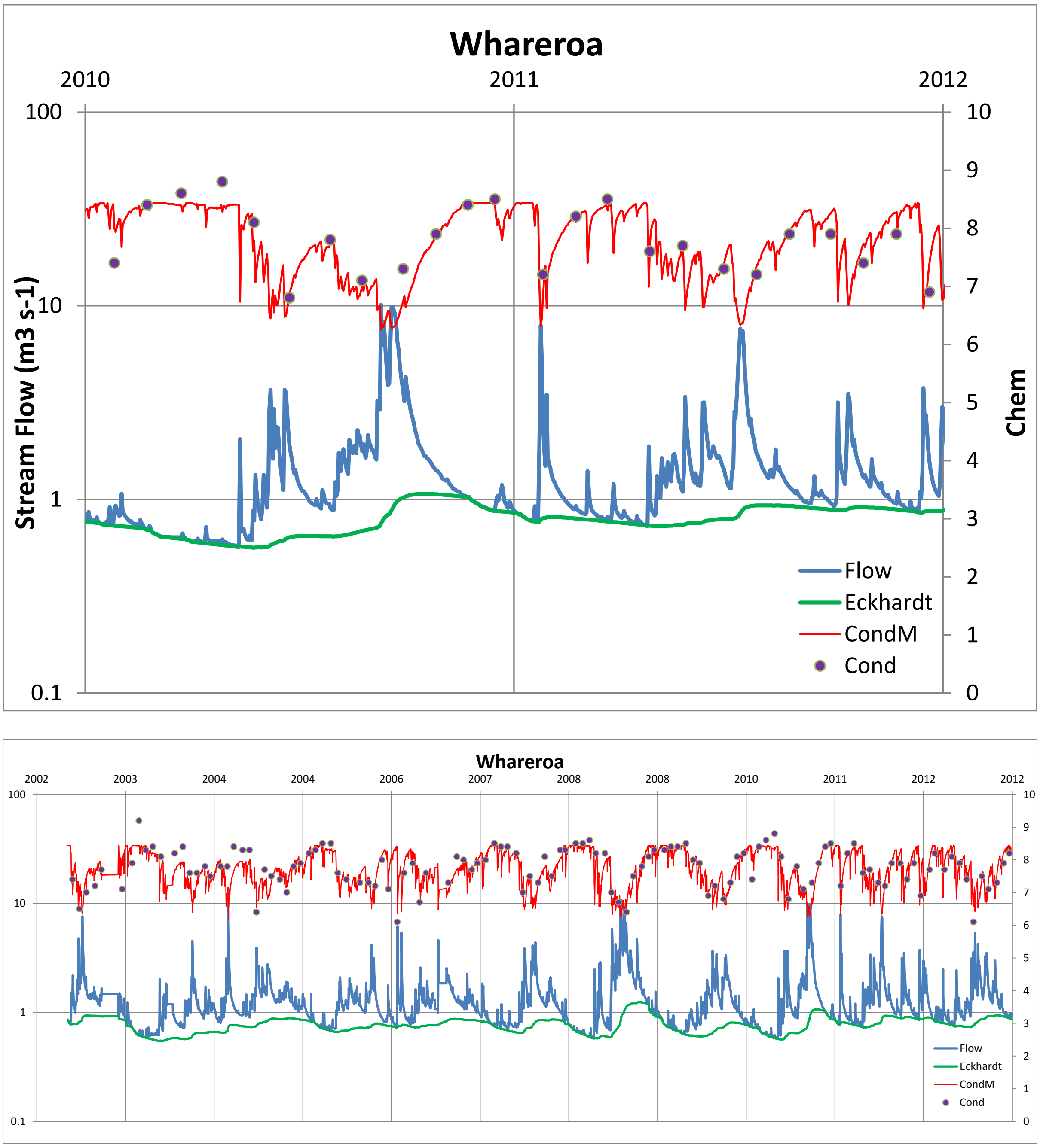


Figure 30: EC-calibrated hydrograph separation for Whareroa Stream, showing daily stream flow (blue), predicted old water contribution (green), predicted EC concentration (red) and measured EC (dots).

Table 9: EC-calibrated hydrograph separation results. The Eckhardt filter parameters α and β, and the EC concentrations C_b and C_s, are described in the text. NSE (Nash-Sutcliffe Efficiency) is the proportion of variation in the measured EC data explained by the EC model. OWI (Old Water Index) is the long term average proportion of old (high EC) water in the stream. P is the probability that the NSE is not significantly different to 0, and sites with P>0.005 are greyed out to indicate their low reliability.

Region	Site	LOC	alpha	beta	Cb	Cs	NSE	OWI	P
Coromandel									
	Kauaeranga	234-11	0.990803	0.273720	8.9	6.1	0.4989	0.2361	0.0000
	Ohinemuri	619-19	0.997725	0.172224	32.0	12.0	0.4257	0.1453	0.0000
	Tapu	954-5	0.999528	0.163007	12.6	8.6	0.6022	0.1384	0.0000
	Waiwawa	1257-3	0.999303	0.142532	8.8	5.7	0.5632	0.1178	0.0000
	Wharekawa	1312-3	0.999751	0.161995	8.6	6.5	0.5684	0.1405	0.0000
Hauraki									
	Piako (Kiwitahi)	749-10	0.999890	0.092016	16.0	13.8	0.1490	0.0814	0.0000
	Piako (Paeroa-Tahuna Road)	749-15	0.999407	0.092155	25.8	18.9	0.4804	0.0764	0.0000
	Waihou	1122-18	0.992575	0.887677	10.0	8.1	0.0683	0.8634	0.0000
	Waitoa (Landsdowne Road)	1249-15	0.999188	0.159629	19.4	13.6	0.4874	0.1354	0.0000
	Waitoa (Mellon Road)	1249-18	0.999795	0.180689	52.1	20.0	0.6458	0.1468	0.0000
Lower Waikato									
	Mangatangi	453-6	0.617924	0.903994	13.8	4.9	0.0634	0.8979	0.0001
	Matahuru	516-5	0.725353	0.827197	14.5	12.5	0.0087	0.8060	0.4198
	Whakapipi	1282-8	0.998466	0.162585	23.4	15.9	0.4611	0.1295	0.0000
Waipa									
	Mangapu	443-3	0.998573	0.210457	23.2	15.5	0.6193	0.1826	0.0000
	Mangatutu	476-7	0.983382	0.585060	7.1	5.9	0.1967	0.5366	0.0000
	Puniu	818-2	0.496574	0.998945	7.8	120.0	0.0018	0.9989	0.5049
	Waipa (Otorohanga)	1191-12	0.999408	0.141189	10.0	7.6	0.2727	0.1177	0.0000
	Waipa (Pirongia)	1191-10	0.999353	0.192820	13.5	10.8	0.3141	0.1652	0.0000
Upper Waikato									
	Otamakokore	683-4	0.999779	0.719744	41.2	20.8	0.4562	0.6703	0.0000
	Tahunaatara	934-1	0.989488	0.809522	7.4	6.6	0.0710	0.7797	0.0000
	Waiotapu	1186-4	0.999999	0.549430	52.7	29.6	0.4050	0.5390	0.0000
West Coast									
	Oparau	658-1	0.999930	0.211747	11.7	7.1	0.7156	0.1502	0.0000
	Waingaro	1167-4	0.998695	0.122057	17.7	12.8	0.5102	0.1124	0.0000
	Waitetuna	1247-2	0.999718	0.175226	12.6	9.4	0.3872	0.0954	0.0000
Taupo									
	Tauranga-Taupo	971-4	0.997550	0.427366	6.1	3.2	0.7929	0.3786	0.0000
	Whareroa	1318-4	0.998344	0.631447	8.4	6.1	0.7592	0.5798	0.0000

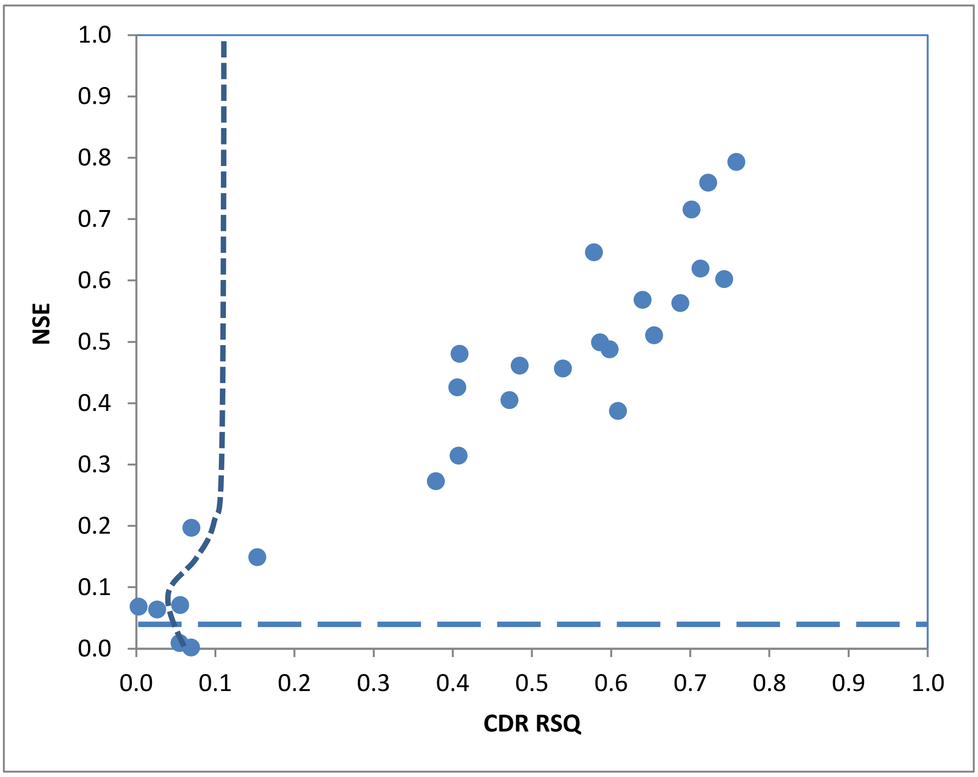


Figure 31: Nash-Sutcliff Efficiency (NSE) of EC-calibrated hydrograph separations compared with Coefficient of Determination for the EC concentration-discharge relationships (CDR RSQ) for all 26 catchments. CDR RSQ values to the left of the dotted line were not statistically significant (p>0.005) and NSE values below the dashed line were not statistically significant (p>0.005).

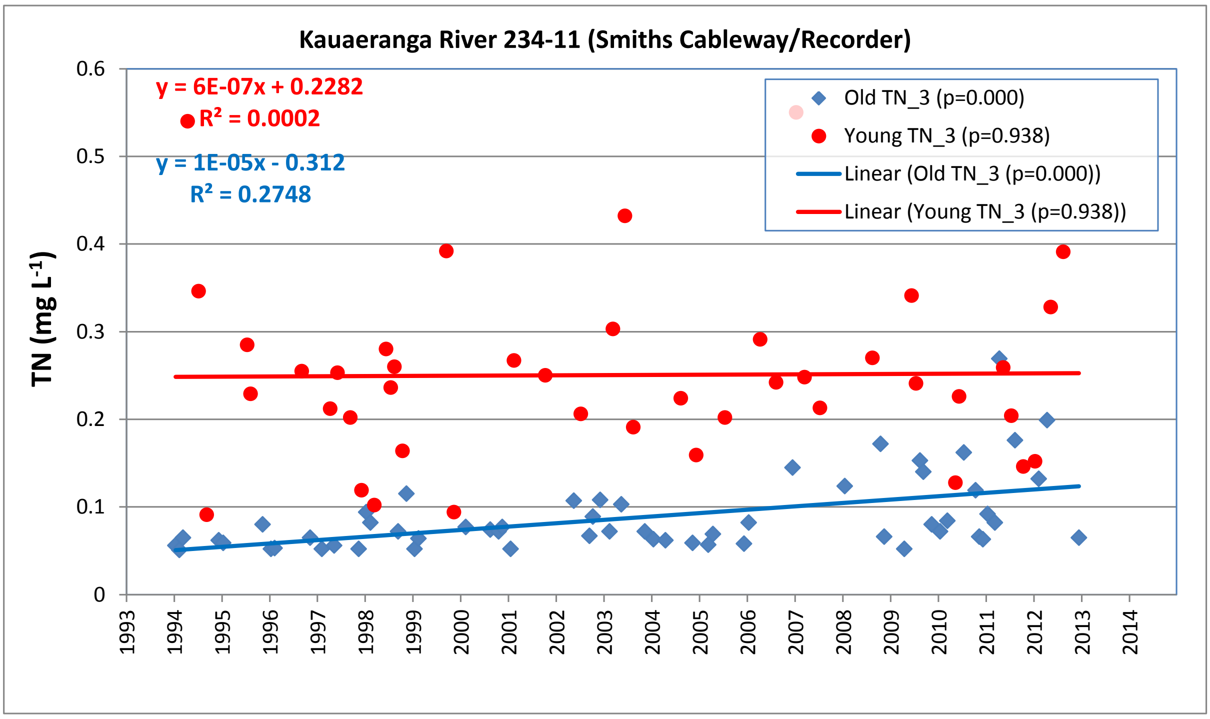


Figure 32: Total Nitrogen concentrations in the Kauaeranga River, stratified by EC-calibrated hydrograph separation as being Old or Young. Reported p-values are the probability that the trendline slope is not different from zero.

As before, the calibrated hydrograph separation model for each site was used to predict the old water fraction for the whole 1993-2012 period, particularly at the times of water quality sampling (Figure 33). Samples were stratified as being predominantly old water when the modelled old water fraction was greater than 75%, and stratified as being predominantly young water when the modelled old water fraction was less than 25%.

Figure 32 shows the TN data for Kauaeranga River, stratified as old or young. At this site, data stratification based on EC gave very similar results to that based on silica (Figure 28) or flow percentiles (Appendix 2).

Table 10 summarises the concentration differences between old and young samples for all catchments, as classified using this method. As with silica-calibrated separation (Table 8), in some catchments, few or no samples could be stratified as being predominantly consisting of young water. Furthermore, at several sites the opposite problem was observed, i.e., few samples being stratified as old water.

The EC-calibrated hydrograph separations were similar to the silica-calibrated hydrograph separations at only 11 sites: Kauaeranga River, Ohinemuri River , Piako River (Kiwitahi), Waihou River, Waitoa River (Landsdowne Rd), Mangapu River, Waipa River (Pirongia), Otamakokore Stream, Tahunaatara Stream, Tauranga-Taupo River and Whareroa Stream (compare Figure 29 and Figure 33). At these sites, the parameter beta and the variable OWI (Table 7 and Table 9), as well as the number of samples stratified as young or old, and the differences in their concentrations (Table 8 and Table 10) were similar (although the concentration difference estimates were not always statistically significant). At the remaining 9 sites where both hydrograph separation methods yielded a statistically significant relationship between predicted and observed water age (i.e. Si or EC, respectively), the parameter beta and the variable OWI were quite different between the two methods. This could indicate either that hydrograph separations based on Si or EC result in separation between different water fractions, or that the calibration process is itself non-unique, and therefore insufficiently reliable for general use.

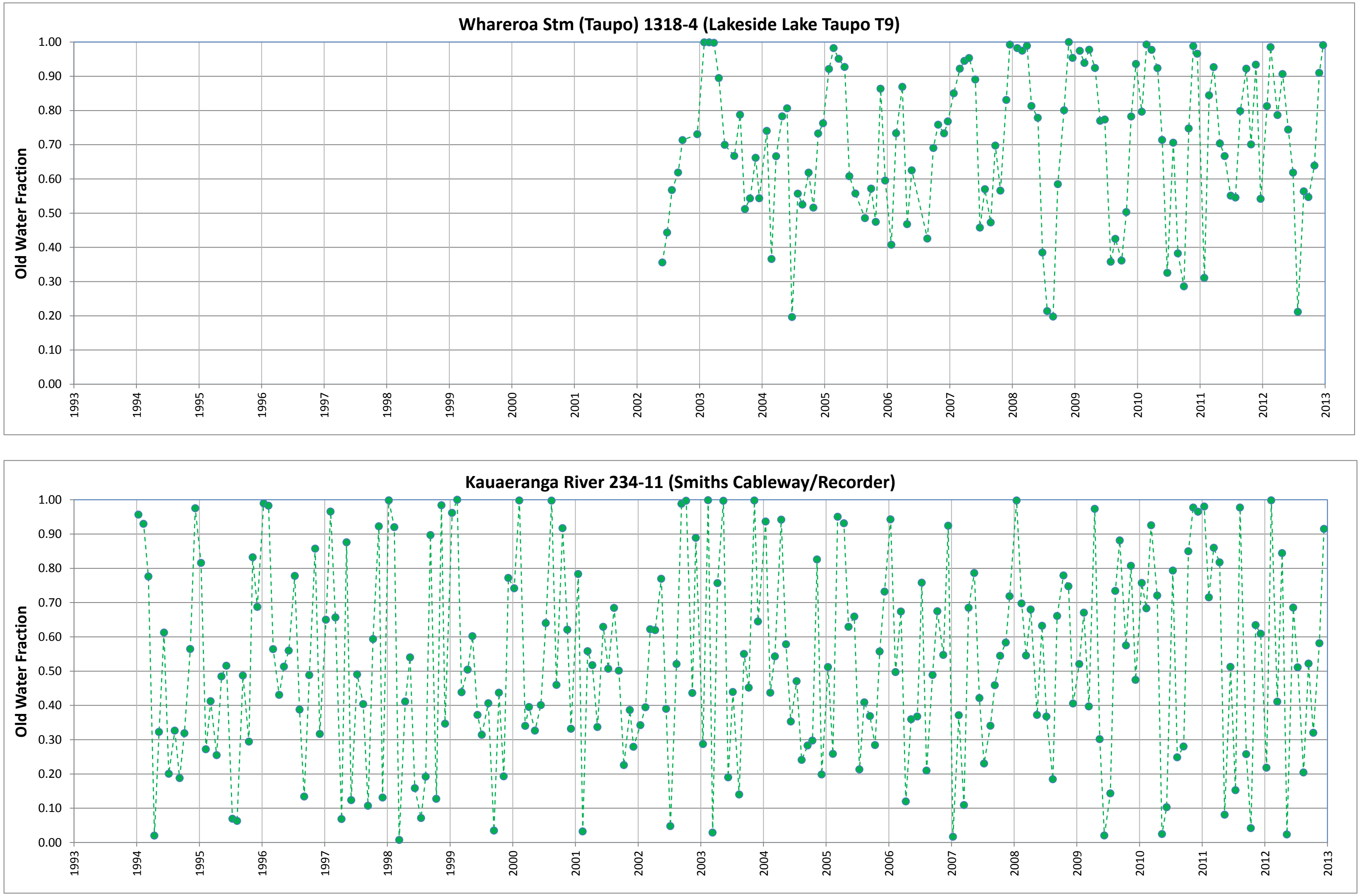


Figure 33: Estimated old water fraction at times of water quality sampling at two sites, based on EC-calibrated hydrograph separation.

Table 10: Differences in water quality samples based on EC-calibrated hydrograph separation. N Old and N Young are the number of samples stratified as old and young respectively (OW%>75% and OW%<25%), and N Mixed are the remaining samples. Significant concentration differences are highlighted red if positive and blue if negative.

							Concentration Difference (Conc High - Conc Low)								
Region	**Site Name**	**Sample Location**	**ChemID**	**N Young**	**N Mixed**	**N Old**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**	**Flags**
Coromandel															
	Kauaeranga River	Smiths Cableway/Recorder	234-11	42	128	58	0.16	0.05	0.00	0.02	0.00	0.02	-6.55	-2.30	DRP
	Ohinemuri River	Queens Head	619-19	106	93	24	0.32	0.30	0.03	0.01	-0.01	0.02	-7.50	-14.36	PS, DRP
	Tapu River	Tapu-Coroglen Rd	954-5	82	126	10	0.10	0.02	0.00	0.01	0.00	0.01	-0.30	-2.48	DRP
	Waiwawa River	SH25 Coroglen	1257-3	116	99	10	0.06	0.03	0.00	0.01	0.00	0.01	-	-1.66	MF, DRP
	Wharekawa River	SH25	1312-3	102	107	14	0.07	0.09	0.00	0.00	0.00	0.00	-	-1.35	MF, DRP
Hauraki															
	Piako River	Kiwitahi	749-10	140	74	14	2.08	1.72	0.08	0.05	0.00	0.05	-	-1.71	-
	Piako River	Paeroa-Tahuna Rd Br	749-15	134	72	12	1.01	0.72	0.11	-0.57	-0.67	0.10	-	-5.72	PS
	Waihou River	Okauia	1122-18	1	19	220	0.64	0.02	0.10	0.18	-0.02	0.20	-	-2.06	-
	Waitoa River	Landsdowne Rd Br	1249-15	110	86	30	1.17	0.80	0.06	0.09	0.02	0.07	-5.43	-3.75	-
	Waitoa River	Mellon Rd Recorder	1249-18	119	101	10	1.55	1.10	0.18	-1.13	-1.16	0.03	-	-25.60	PS
Lower Waikato															
	Mangatangi River	SH2 Maramarua	453-6	0	0	240	-	-	-	-	-	-	-	-	-
	Matahuru Stm	Waiterimu Road Below Confl	516-5	0	11	66	-	-	-	-	-	-	-	-	MF, SS
	Whakapipi Stm	SH22 Br	1282-8	130	91	18	0.99	0.91	0.03	0.04	0.01	0.03	-	-5.25	PS
Waipa															
	Mangapu River	Otorohanga	443-3	65	57	24	0.71	0.52	0.03	0.00	-0.05	0.05	-8.55	-5.96	PS, MF, SS
	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	5	43	54	0.81	0.22	0.01	0.11	0.00	0.11	-	-0.92	SS
	Puniu River	Bartons Corner Rd Br	818-2	0	0	240	-	-	-	-	-	-	-	-	-
	Waipa River	SH3 Otorohanga	1191-12	103	40	4	0.45	0.32	0.01	0.03	0.00	0.03	-	-0.88	MF, SS
	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	43	37	7	1.12	0.83	0.03	0.05	0.00	0.05	-	-2.04	MF, SS, DR
Upper Waikato															
	Otamakokore Stm	Hossack Rd	683-4	1	117	119	2.15	0.74	0.00	-	0.06	-	-	-20.75	G, TP
	Tahunaatara Stm	Ohakuri Rd	934-1	0	0	240	-	-	-	-	-	-	-	-	-
	Waiotapu Stm	Homestead Rd Br	1186-4	6	173	61	1.48	0.30	0.32	0.24	-0.02	0.25	-	-16.97	G, MF, TP
West Coast															
	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	31	26	1	0.26	0.21	0.00	0.01	0.00	0.01	-	-3.30	SS, DRP
	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	63	57	13	0.95	0.70	0.01	0.07	0.00	0.07	0.46	-3.80	SS
	Waitetuna River	Te Uku-Waingaro Rd	1247-2	43	16	2	0.46	0.35	0.00	0.04	0.00	0.04	-	-1.76	MF, SS
Taupo															
	Tauranga-Taupo River	Te Kono Slackline	971-4	36	135	59	0.03	0.01	0.00	0.00	-0.01	0.01	-20.65	-2.17	-
	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	4	62	57	0.67	0.44	0.00	0.04	-0.01	0.06	-	-1.82	SS

5.2.3 DISCUSSION

In summary, the flow percentile method has several advantages over the hydrograph separation method. It relies only on the flow data, it is applicable in all catchments for which flow data exist, and it can be expected to produce approximately equal numbers of samples in the high flow and low flow strata, so that differences are more easily identified and more likely to be statistically significant.

However, because the stratification is based solely on flow percentiles, its meaning may vary from catchment to catchment. As there is no direct link to dominant flow paths or associated water age, differences are only relative to the range captured by the monthly observations; i.e. “high flow” represents the “younger water” while “low flow” represents the “older water” within the age range of water sampled at this site. In catchments with significant groundwater discharge, for example, even samples stratified as “high flow” may in fact predominantly comprise “old water” (in absolute terms).

Data stratification based on hydrograph separation would appear to be a more defensible approach, since it is linked to physical processes. The fact that similar results were obtained from silica-calibrated and EC-calibrated stratification at 11 sites provides some confidence that the method works in principle. Identification of a suitable tracer, however, remains as an issue. Silica is not generally available and may not be useful in all catchments (c.f. Table 5), and EC is, in some catchments, substantially affected by processes other than contact with the subsurface. Furthermore, consistent calibration of non-linear models is often non-trivial, so that obtaining reliable estimates of the model parameters can present a challenge.

For these reasons, the flow percentile method currently provides the best “benchmark” for practical use.

In the next section we used these methods to explore trends in the stratified data.

5.3 TREND ANALYSIS

Apart from identifying concentration differences between (older) low flow and (younger) high flow water, data stratification can also potentially be used to identify trends in the low flow or high flow concentrations at a site through time. These then can potentially explain the origins of concentration trends in the complete series of concentration data.

5.3.1 COMPARISON WITH WRC (2013) METHOD

Trend analysis of the Waikato Regional Council data has previously been carried out by WRC (2013), who used Seasonal Kendall Trend analysis to identify long term trends in the flow-adjusted concentrations of nitrogen and phosphorus species (among other constituents) at 114 Waikato sites from 1993-2012 (Table 11). Water quality data was available from 1993-2012 or 1994-2012 at all 26 of the sites considered in the current report, with the exception of Whareroa Stream, where water quality sampling only began in 2000 (Figure 1). The majority of sites which recorded significant trends ($p<0.01$) had increasing concentrations of TN (17 out of 21) and NNN (16 out of 19), while decreasing concentrations of NH4 (10 out of 10), TP (6 out of 8) and DRP (8 out of 10) were more common.

Some of these trends may have been influenced by point source discharges, or changes in TP and DRP sample analysis, as described in Section 1 and flagged in Table 11.

Data stratification potentially allows these trends to be explored in more depth, and potentially identified as being predominantly due to changes in old water, or in young water. To do this, several changes were made to the trend analysis method:

Firstly, the WRC (2013) method uses “flow adjusted” concentration data. Flow adjustment is useful to remove any dependence of water quality parameters on stream flow from the trend analysis. It does this by assuming that the slope of the concentration-discharge relationship does not change with time, and then adjusts the concentration data so that the slope of the flow adjusted concentration-discharge relationship is zero (no flow dependence). Here, however, we are interested in the differences in concentration between samples stratified under different flow regimes, so that flow adjustment is not appropriate.

Secondly, WRC (2013) analysed the entire 1993-2012 data set. In order to use data stratification based on the flow record, as discussed in the previous section, we were only able to consider periods for which water quality and flow data were both available (only the large diamonds in Figure 1). Many of the sites did not have available flow data for the full period, and so trends can only be analysed for the shorter period for which flow data is also available.

Thirdly, WRC (2013) used the Seasonal Kendall Trend analysis. Our analysis was done using Microsoft Excel 2010, which does not provide this statistical functionality. For this reason, we used linear regression analysis as an alternative, although this is not as powerful for analysing trends in seasonal data. This is reasonable however, as the water quality of the stratified data is likely to be much less seasonal.

As a first step, therefore, linear regression was used to estimate trends in the raw (i.e., not flow adjusted) water quality data for the period for which flow data was also available. The trends estimated in this way were compared with those previously identified by WRC (2013) in order to assess the equivalence of the two methods.

Correspondence between the trends identified using this method and those identified by WRC (2013) are indicated in Table 11. In general the trends were similar between the two methods: linear regression identified 22 out of the 37 statistically significant positive trends (in TN, NNN, NH4, TP and DRP) and 12 out of the 31 statistically significant negative trends identified by WRC (2013). The linear regression analysis also indicated statistically significant trends (all negative) in 7 cases where Seasonal Kendall Trend analysis found no significant trend. Of these 41 discrepancies, 21 occurred in the catchments where limited availability of stream flow data meant that the data period considered differed greatly between the two studies.

Table 11: Water quality trends identified by WRC (2013) for the 1993-2012 period using Seasonal Kendall Trend analysis. Values indicate the slope of the trend line, expressed as percentage change in flow-adjusted concentration per year, with the p-value being given in brackets. The coloured highlighting indicates correspondence with significant trends (p<0.01) in the raw (i.e. non flow-adjusted) data identified using linear regression. Flags are described in Table 1.

					Trend % Change Per Year (P Value)						
Region	**Map Key**	**Site Name**	**Sample Location**	**ChemID**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**EC**	**Flags**
Coromandel											
	92	Kauaeranga River	Smiths Cableway/Recorder	234-11	3.3 (<1)	2.1 (3)	-0.1 (<1)	0.0 (9)	-0.2 (4)	0.6 (<1)	DRP
	99	Ohinemuri River	Queens Head	619-19	1.2 (<1)	1.0 (<1)	-0.2 (91)	-6.7 (<1)	-10.8 (<1)	2.4 (<1)	PS, DRP
	93	Tapu River	Tapu-Coroglen Rd	954-5	0.4 (52)	-2.6 (9)	-0.1 (1)	-0.4 (32)	-0.6 (1)	0.1 (1)	DRP
	95	Waiwawa River	SH25 Coroglen	1257-3	0.0 (99)	-1.9 (3)	-0.1 (10)	-0.7 (19)	-0.4 (<1)	0.0 (98)	MF, DRP
	97	Wharekawa River	SH25	1312-3	2.2 (<1)	2.9 (<1)	-0.6 (<1)	-1.3 (8)	-1.0 (<1)	0.3 (<1)	MF, DRP
Hauraki											
	83	Piako River	Kiwitahi	749-10	-0.4 (10)	-0.5 (23)	-5.3 (<1)	-1.5 (<1)	-0.4 (37)	0.5 (<1)	-
	79	Piako River	Paeroa-Tahuna Rd Br	749-15	-0.8 (<1)	-1.0 (1)	-4.1 (<1)	-0.9 (3)	-0.3 (61)	0.7 (<1)	PS
	33	Waihou River	Okauia	1122-18	1.0 (<1)	1.0 (<1)	-2.3 (1)	-0.6 (<1)	-1.0 (<1)	0.7 (<1)	-
	81	Waitoa River	Landsdowne Rd Br	1249-15	-0.1 (85)	-0.4 (24)	-4.5 (<1)	-1.5 (<1)	-1.4 (2)	0.7 (<1)	-
	80	Waitoa River	Mellon Rd Recorder	1249-18	-0.8 (<1)	-0.8 (<1)	-4.6 (<1)	-18.0 (<1)	-27.9 (<1)	0.2 (22)	PS
Lower Waikato											
	30	Mangatangi River	SH2 Maramarua	453-6	-1.2 (<1)	-3.1 (<1)	-1.5 (1)	0.7 (<1)	-0.4 (33)	-0.1 (62)	-
	20	Matahuru Stm	Waiterimu Road Below Conflu	516-5	-0.9 (<1)	-2.1 (<1)	-1.9 (<1)	0.8 (1)	-1.1 (6)	0.2 (2)	MF, SS
	26	Whakapipi Stm	SH22 Br	1282-8	1.4 (<1)	1.5 (<1)	-4.7 (<1)	1.7 (<1)	4.3 (<1)	1.2 (<1)	PS
Waipa											
	63	Mangapu River	Otorohanga	443-3	1.3 (<1)	1.5 (<1)	-0.9 (33)	0.2 (73)	1.2 (2)	0.7 (<1)	PS, MF, SS
	73	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	2.0 (<1)	2.0 (<1)	-1.5 (5)	0.0 (90)	0.0 (52)	0.6 (<1)	SS
	75	Puniu River	Bartons Corner Rd Br	818-2	2.0 (<1)	1.9 (<1)	1.4 (1)	0.6 (8)	0.0 (65)	0.7 (<1)	-
	64	Waipa River	SH3 Otorohanga	1191-12	1.9 (<1)	2.0 (<1)	-1.5 (<1)	-1.0 (4)	-1.6 (1)	0.4 (<1)	MF, SS
	12	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	1.2 (<1)	1.3 (<1)	-1.4 (6)	0.0 (84)	0.0 (78)	0.5 (<1)	MF, SS, DRP
Upper Waikato											
	46	Otamakokore Stm	Hossack Rd	683-4	1.7 (<1)	2.3 (<1)	-4.6 (<1)	-0.4 (20)	0.5 (<1)	0.8 (<1)	G, TP
	44	Tahunaatara Stm	Ohakuri Rd	934-1	2.1 (<1)	2.5 (<1)	-0.7 (3)	-0.2 (50)	-0.6 (1)	0.6 (<1)	-
	50	Waiotapu Stm	Homestead Rd Br	1186-4	1.2 (<1)	1.3 (<1)	-0.5 (5)	0.0 (99)	-0.5 (12)	0.5 (<1)	G, MF, TP
West Coast											
	14	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	1.0 (1)	0.9 (12)	-0.3 (3)	-0.6 (45)	-1.7 (1)	0.0 (76)	SS, DRP
	8	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	1.1 (<1)	1.5 (<1)	-1.8 (2)	-0.2 (54)	-1.8 (<1)	0.1 (14)	SS
	10	Waitetuna River	Te Uku-Waingaro Rd	1247-2	1.5 (<1)	1.9 (<1)	-0.9 (19)	0.3 (70)	-0.8 (2)	0.1 (5)	MF, SS
Taupo											
	56	Tauranga-Taupo River	Te Kono Slackline	971-4	1.6 (<1)	1.3 (<1)	0.0 (25)	-0.7 (1)	-1.3 (<1)	0.0 (98)	-
	102	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	1.4 (<1)	2.1 (<1)	-0.1 (21)	-2.8 (<1)	-2.3 (<1)	0.1 (27)	SS

5.3.2 TRENDS IN THE STRATIFIED DATA

The second step in the trend analysis was to use the linear regression method to identify trends in the stratified data. The analysis was done for each of the 3 data stratification methods described in the previous section (flow percentile, silica-calibrated hydrograph separation, EC-calibrated hydrograph separation). Linear regression was used to identify statistically significant trends in the low flow/old water and high flow/young water data for TN, NNN, NH4, TP, DRP and EC.

The 3 data stratification methods produced very similar results in some catchments, and very different results in others. These similarities and differences reflect the number and selection of samples stratified as low flow/old water or high flow/young water. Figures 34, 35 and 36, for example, show the NNN data from Waiwawa River stratified using the three methods. The flow percentile method identified approximately equal numbers of high flow and low flow samples (by design), while the silica-based stratification suggested a relatively larger number of old water samples, and the EC-based method suggested a larger number of young water samples at this site. WRC (2013) identified a negative concentration trend in this data, and this can be seen in the young water samples in Figure 36 (EC-based method), although the trend is not statistically significant.

There were 6 sites at which the flow-, silica- and EC-based methods all gave similar results (Kauaeranga River, Ohinemuri River, Tapu River, Waitoa River (Landsdowne Road), Mangapu River, Tauranga-Taupo River). However is it difficult to provide a physical explanation as to why this might be the case. Silica and EC concentrations are typically highly correlated with flow rate (Table 5) and in some cases, hydrograph separation calibration simply reflects this.

By contrast, the results were very different between methods at many sites, particularly where groundwater discharge dominates stream flow (Waihou River, Otamakokore Stream, Tahunaatara Stream Waiotapu Stream, Whareroa Stream). At these sites, the silica- and EC-based stratification identified few or no samples representing primarily young water, while the flow-based stratification again identified roughly equal numbers of samples in each category. While the silica- and EC-based methods could be considered to be correct from a physical point of view (water quality at these sites is indeed dominated by old water), in this instance they are less useful in stratifying the data. Although the flow percentile method is not tied to physical processes, it is statistically robust and better able to adapt to different situations.

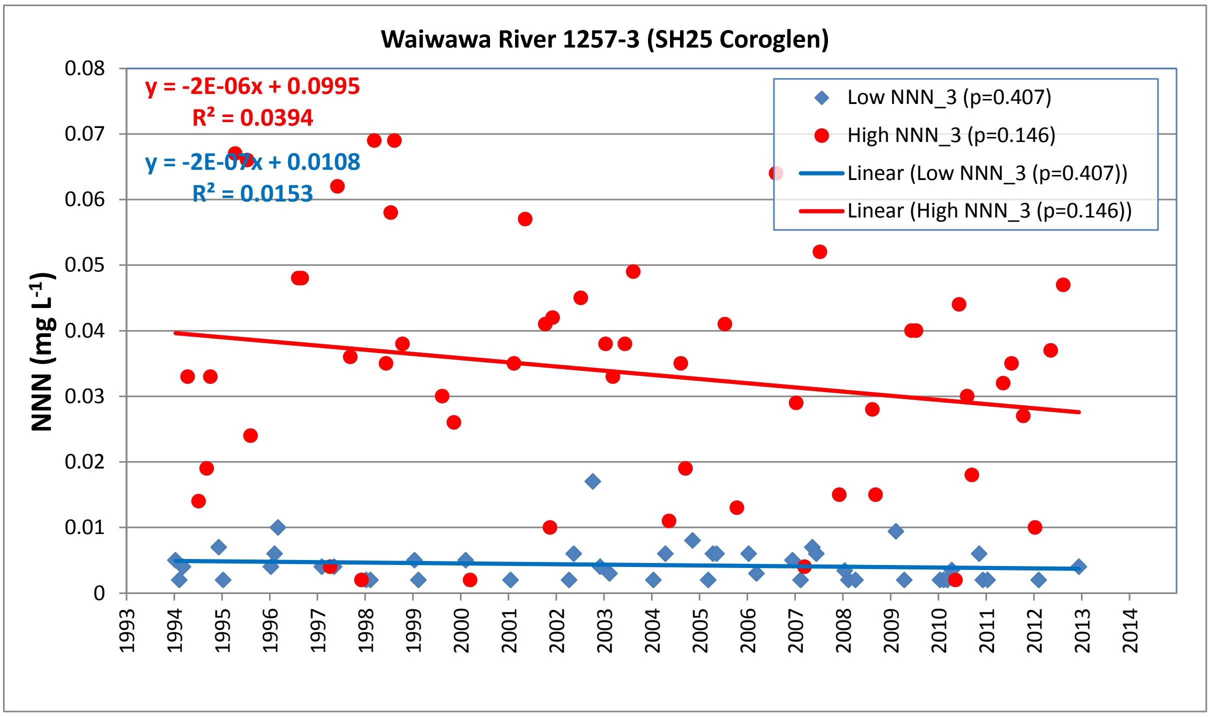


Figure 34: NNN trends in high flow compared with low flow water at Waiwawa River, stratified using flow percentiles.

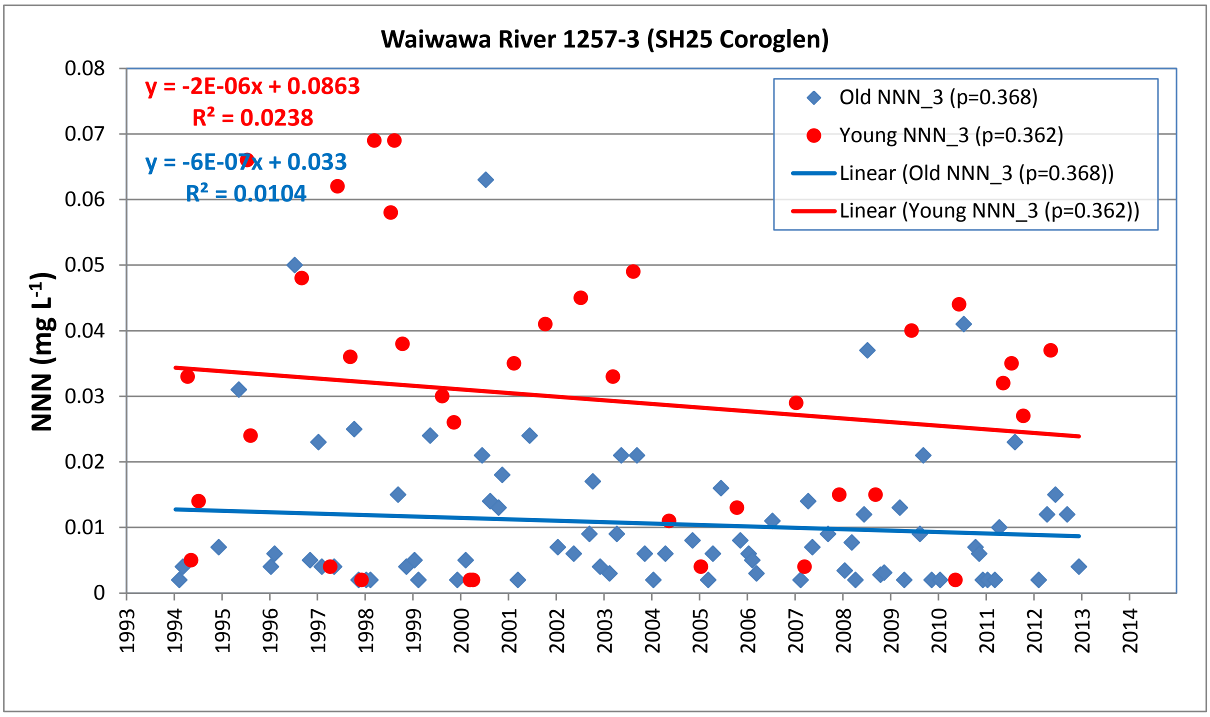


Figure 35: NNN trends in young compared with old water at Waiwawa River, stratified using silica-calibrated hydrograph separation.

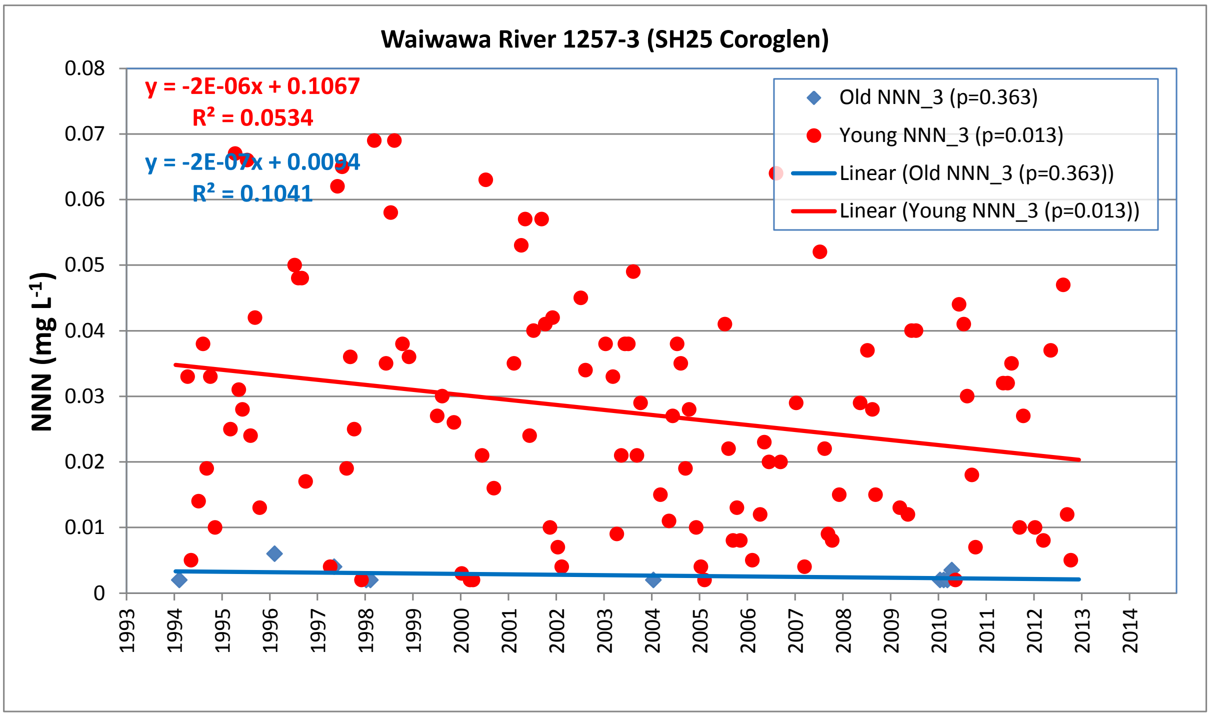


Figure 36: NNN trends in young compared with old water at Waiwawa River, stratified using EC-calibrated hydrograph separation.

Table 12 shows the concentration trends (% change per year) identified in the full series (not stratified) of water quality-stream flow data (not flow adjusted) at each site using linear regression. Only data from the period for which stream flow data was also available was used. Corresponding concentration trends in the stratified low flow or high flow samples are indicated by highlighting. In this way, significant concentration trends can potentially be matched with underlying trends in the older water or younger water flow paths in the catchment.

For example, a statistically significant trend of increasing NNN was identified for the Wharekawa River at a rate of 4.0% of the median concentration per year. Figure 37 shows the stratified low flow and high flow NNN concentrations for the Wharekawa River site, and trends identified in these by linear regression. NNN concentrations in high flow samples increased over time (p<0.01), whereas low flow samples remained at a very low concentration. WRC (2013) also identified increasing NNN concentrations at this site (Table 11), and our analysis indicates that the trend can be attributed to increases in high flow concentrations, presumably reflecting recent land use intensification, possibly coupled with groundwater assimilation of nitrate.

In contrast, the increasing NNN trend in the Whareroa Stream, which flows into Lake Taupo, can be shown to be due mainly to increases in low flow concentration (Figure 38). This pattern could indicate that the effect of earlier land use intensification has now reached the groundwater body that discharges into the stream.

A third example shows the decreasing trend in NNN concentrations in the Mangatangi River (Figure 39). Data stratification suggests that this trend is due to a decline in the NNN concentrations in the younger water entering the river, and thus reflects recent improvements in land use practices in the catchment. NNN concentrations in the older water at this site are consistently very low, again possibly indicating groundwater assimilation of nitrate.

A complete set of stratified data trend analysis is given in Appendix 2.

The low flow and high flow trend analysis is summarised in Table 12, as described in the legend. While some increasing and decreasing trends can be ascribed to changes in either low flow or high flow concentrations, many of the observed trends were not reflected in significant trends of either low flow or high flow samples. Several factors can contribute to this discrepancy. Firstly, splitting the data set into subsets (low flow vs. high flow) reduces the number of observations available for statistical analysis of each trend, making it potentially more difficult to reach significance limits. Secondly, the high flow concentrations tend to be quite variable in many instances (see Figures 37, 38, 39), so that any trends are less likely to be statistically significant. Thirdly, many of the data series are affected by external factors such as point source discharges or mismatched flow data (flagged in Table 12), introducing an additional source of uncertainty that may obscure the trends of interest.

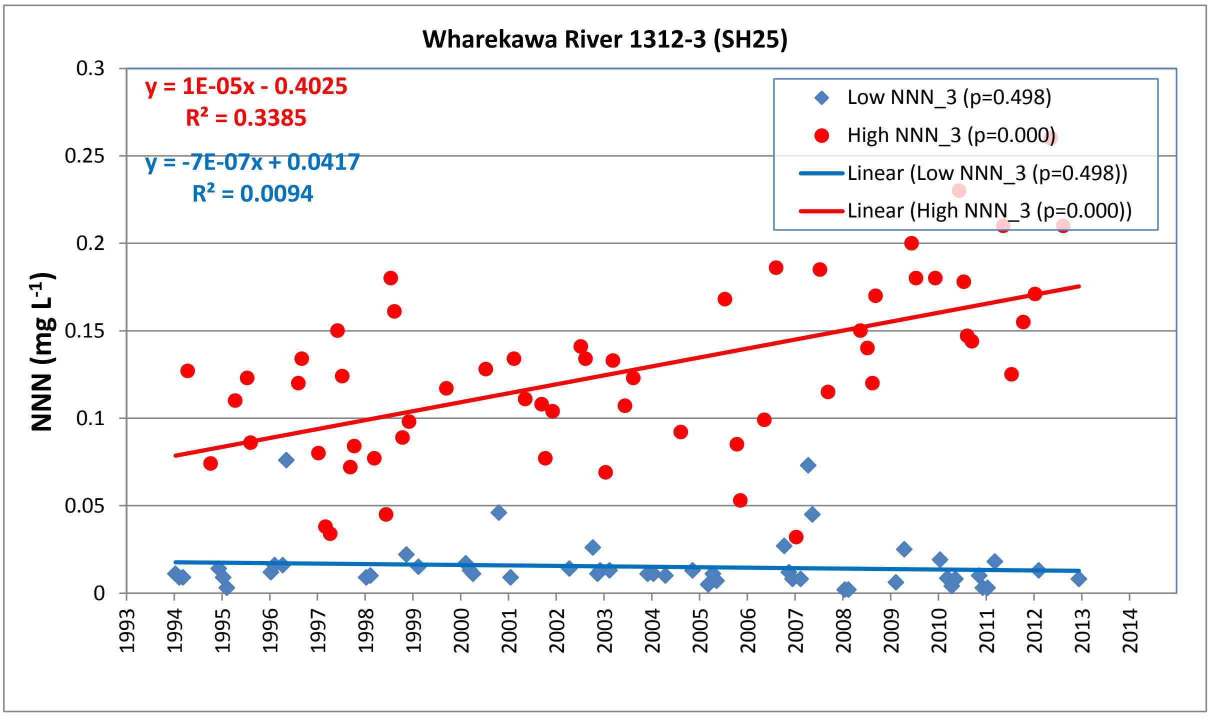


Figure 37: NNN trends in high flow compared with low flow water at Wharekawa River, stratified using flow percentile.

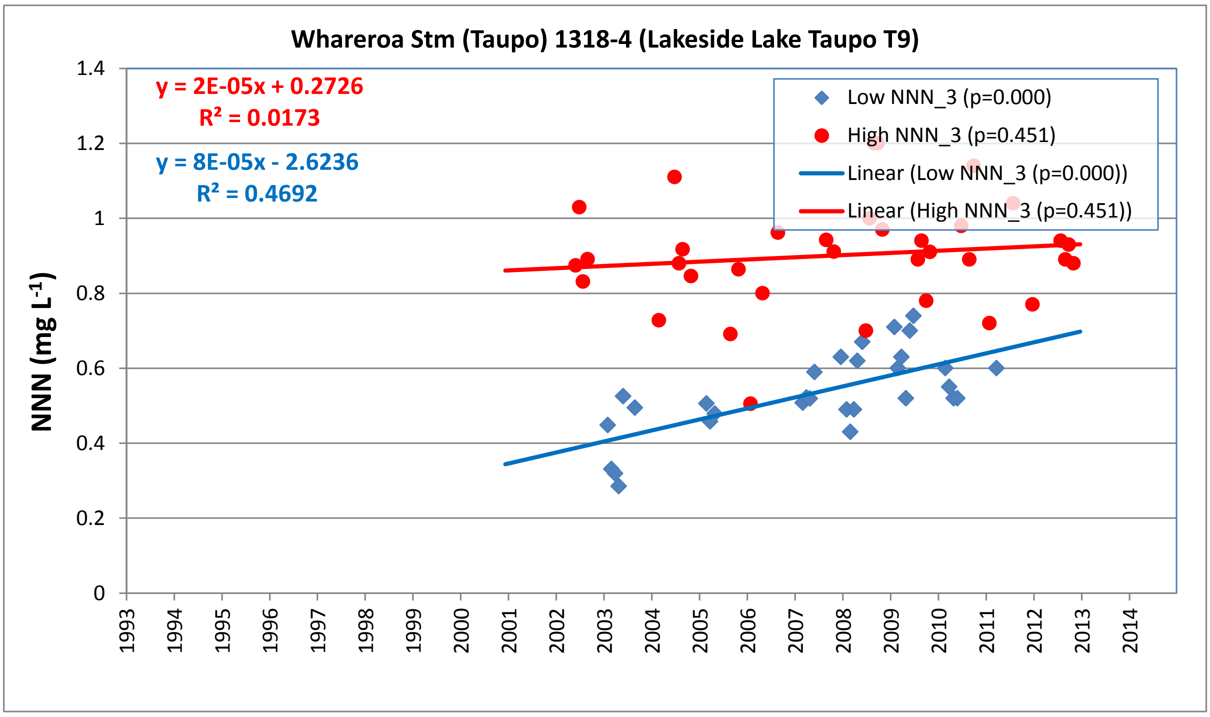


Figure 38: NNN trends in high flow compared with low flow water at Whareroa Stream River, stratified using flow percentile.

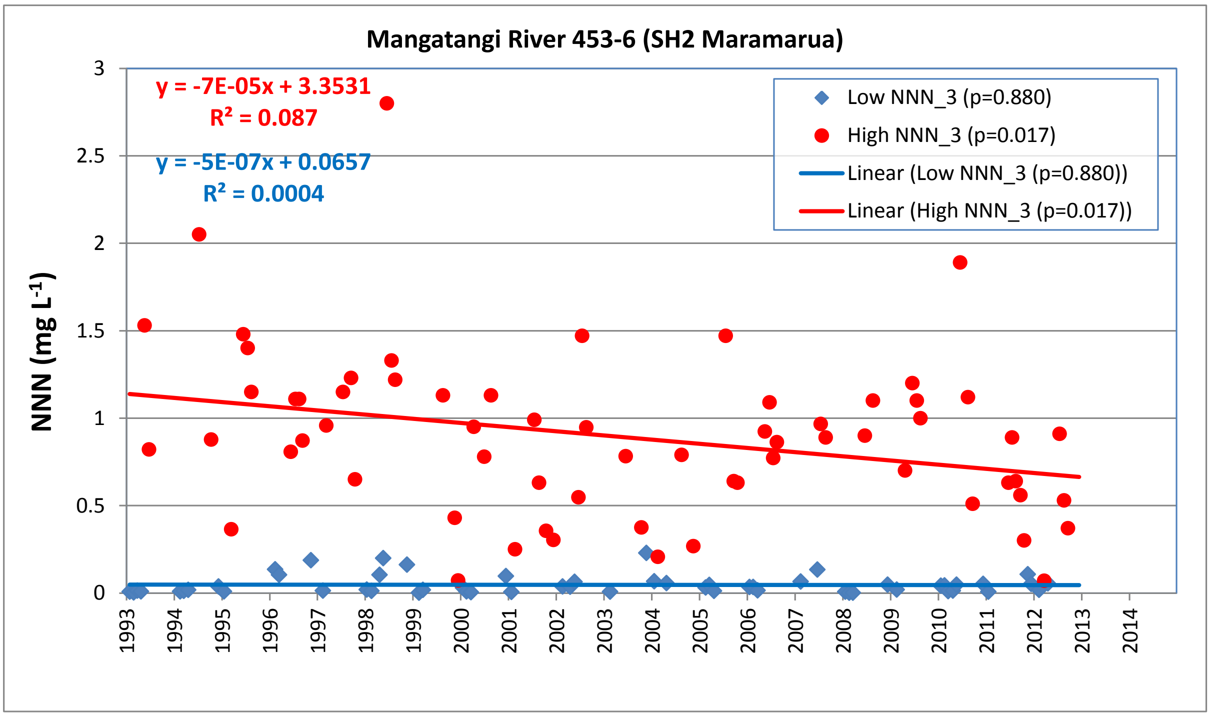


Figure 39: NNN trends in high flow compared with low flow water at Mangatangi River, stratified using flow percentile.

Table 12: Water quality trends identified using linear regression. Values indicate the slope of the trend line, expressed as percentage change in flow-adjusted concentration per year, with the p-value being given in brackets. The coloured highlighting indicates significant trends (p<0.01) in the low flow and/or high flow water samples, stratified based on flow percentile. Flags are described in Table 1.

					Trend % Change Per Year (P Value)						
Region	**Map Key**	**Site Name**	**Sample Location**	**ChemID**	**TN**	**NNN**	**NH4**	**TP**	**DRP***	**EC**	**Flags**
Coromandel											
	92	Kauaeranga River	Smiths Cableway/Recorder	234-11	2.1 (5)	1.4 (62)	-4.0 (12)	-4.2 (67)	0.0 (96)	0.8 (<1)	DRP
	99	Ohinemuri River	Queens Head	619-19	1.8 (<1)	1.9 (<1)	-0.6 (82)	-6.5 (<1)	-12.8 (<1)	3.0 (<1)	PS, DRP
	93	Tapu River	Tapu-Coroglen Rd	954-5	-0.3 (87)	-23.5 (<1)	-1.1 (13)	-0.2 (96)	-0.4 (23)	0.3 (6)	DRP
	95	Waiwawa River	SH25 Coroglen	1257-3	-0.6 (76)	-4.3 (4)	-0.9 (2)	-0.6 (91)	-0.6 (10)	0.0 (87)	MF, DRP
	97	Wharekawa River	SH25	1312-3	2.5 (<1)	4.0 (<1)	-1.3 (2)	0.2 (93)	-1.8 (<1)	0.2 (2)	MF, DRP
Hauraki											
	83	Piako River	Kiwitahi	749-10	0.4 (65)	0.8 (51)	-8.8 (19)	-1.8 (7)	-0.6 (35)	0.3 (2)	-
	79	Piako River	Paeroa-Tahuna Rd Br	749-15	-0.1 (84)	-0.1 (87)	-6.3 (<1)	-3.8 (<1)	-5.0 (2)	0.4 (1)	PS
	33	Waihou River	Okauia	1122-18	1.0 (<1)	0.7 (<1)	-5.4 (6)	-0.8 (3)	-1.3 (<1)	0.7 (<1)	-
	81	Waitoa River	Landsdowne Rd Br	1249-15	0.1 (74)	0.0 (100)	-6.8 (6)	-1.3 (34)	-1.1 (14)	0.5 (<1)	-
	80	Waitoa River	Mellon Rd Recorder	1249-18	-0.9 (2)	-0.9 (2)	-13.1 (<1)	-35.8 (<1)	-62.5 (<1)	-0.5 (25)	PS
Lower Waikato											
	30	Mangatangi River	SH2 Maramarua	453-6	-1.3 (22)	-4.6 (<1)	-0.2 (97)	1.1 (7)	-0.9 (9)	-0.1 (51)	-
	20	Matahuru Stm	Waiterimu Road Below Conflu	516-5	-1.8 (67)	-3.6 (51)	-18.4 (5)	6.0 (19)	-10.4 (<1)	-2.8 (<1)	MF, SS
	26	Whakapipi Stm	SH22 Br	1282-8	1.8 (<1)	1.9 (<1)	-0.6 (89)	3.9 (<1)	7.5 (<1)	1.0 (<1)	PS
Waipa											
	63	Mangapu River	Otorohanga	443-3	2.3 (<1)	2.9 (<1)	1.3 (56)	-3.7 (<1)	-6.4 (<1)	0.1 (84)	PS, MF, SS
	73	Mangatutu Stm (Waikeria)	Walker Rd Br	476-7	0.8 (78)	0.5 (87)	-9.9 (5)	0.3 (96)	-3.1 (11)	-0.1 (73)	SS
	75	Puniu River	Bartons Corner Rd Br	818-2	2.3 (<1)	1.9 (1)	0.1 (95)	2.4 (13)	0.0 (96)	0.7 (<1)	-
	64	Waipa River	SH3 Otorohanga	1191-12	1.5 (25)	2.6 (9)	-7.7 (6)	-7.1 (3)	-7.7 (<1)	0.1 (73)	MF, SS
	12	Waipa River	Pirongia-Ngutunui Rd Br	1191-10	-3.3 (27)	-1.6 (58)	-14.1 (6)	-4.5 (35)	-5.9 (<1)	-0.3 (61)	MF, SS, DRP
Upper Waikato											
	46	Otamakokore Stm	Hossack Rd	683-4	2.8 (<1)	3.2 (<1)	-5.0 (54)	-0.7 (15)	0.5 (3)	0.7 (<1)	G, TP
	44	Tahunaatara Stm	Ohakuri Rd	934-1	3.0 (<1)	2.9 (<1)	-6.1 (4)	0.4 (77)	-1.5 (6)	0.5 (<1)	-
	50	Waiotapu Stm	Homestead Rd Br	1186-4	1.4 (<1)	1.5 (<1)	-0.2 (73)	-0.5 (59)	-0.7 (8)	0.5 (<1)	G, MF, TP
West Coast											
	14	Oparau River	Langdon Rd (Off Okupata Rd)	658-1	-2.7 (74)	9.4 (63)	-1.1 (38)	-8.4 (68)	-1.3 (69)	-2.3 (5)	SS, DRP
	8	Waingaro River (Pukemiro)	Ruakiwi Rd Off SH22	1167-4	1.8 (50)	1.9 (55)	-9.8 (1)	2.6 (74)	-2.5 (7)	0.2 (55)	SS
	10	Waitetuna River	Te Uku-Waingaro Rd	1247-2	7.3 (27)	2.9 (65)	15.6 (44)	31.1 (22)	4.3 (35)	-2.3 (<1)	MF, SS
Taupo											
	56	Tauranga-Taupo River	Te Kono Slackline	971-4	1.4 (<1)	2.2 (<1)	-0.6 (25)	-3.0 (8)	-1.3 (<1)	0.4 (6)	-
	102	Whareroa Stm (Taupo)	Lakeside Lake Taupo T9	1318-4	1.8 (2)	2.4 (<1)	-3.4 (4)	-4.5 (<1)	-3.0 (<1)	0.0 (90)	SS

Legend

black	black text = significant positive trend
red	red text = significant negative trend
🟦	blue = significant trend in lowflow samples
🟧	peach = significant trend in highflow samples
🟪	purple = significant trends in lowflow and highflow samples

6 LOAD AND YIELD ESTIMATION

The need to calculate mass fluxes, e.g. annual loads (t y^{-1}) or yields (kg ha^{-1} y^{-1}), is the most common incentive for collecting matched water quality and flow data. If water quality information could be collected with a temporal resolution high enough to capture the entire concentration range occurring at a particular site across the whole flow range, then load calculations would simply be a matter of summing the loads (flow x concentration) occurring during these time steps through time. More commonly, as here, high resolution flow information is available (e.g. 15 min resolution), but water quality sampling is much less frequent (e.g. monthly). In this case, much care is required in order to calculate load estimates that are as accurate and precise (unbiased) as possible and the users of such estimates need to be aware of the substantial uncertainties involved. In general, “loads estimated from monthly data are … highly uncertain” (Aqualinc, 2014). It should also be noted that yield estimates (kg ha^{-1} y^{-1}) carry a higher degree of uncertainty than load estimates (t y^{-1}), as the catchment area contributing a contaminant to a monitoring site is often poorly defined,

6.1 REGRESSION APPROACH

One method which has gained popularity in recent years is the use of regression models as the basis for estimating water quality in between sampling times (Quilbé et al., 2006; Verma et al., 2012). If a high correlation between concentration and discharge (and/or time) has been established, such relationships can be used to provide an estimate for concentration at points in time where flow information is available, but concentration has not been measured. This allows mass flux to be estimated and integrated through time to calculate annual loads (t y^{-1}) or yields (kg ha^{-1} y^{-1}).

One commonly used regression model for load estimation is the seven parameter model of Cohn et al. (1992), in which instantaneous concentration is modelled as a function of stream flow and time:

$$\ln(C) = b_0 + b_1 \ln(Q) + b_2 \ln^2(Q) + b_3 T + b_4 T^2 + b_5 \sin(2 \pi T) + b_6 \cos(2 \pi T) + \varepsilon$$

where C is the concentration, Q is (usually daily average) stream flow, T is the time in years and ε is the residual. This model improves on simpler flow-based regression models by incorporating seasonal and long term trends, and has been shown to perform reasonably well for monthly concentration samples, although higher resolution concentration data is preferred (Verma et al. 2012; Aulenbach, 2013).

Russell (2013) recommended modifying this model for small, flashy watersheds of similar size to many in this report, by using instantaneous (15 minute) flow instead of daily average flow for Q, and by adding an additional term $b_7 \ln(dQ)$ to represented the instantaneous rate of change of Q with time, where

$$\ln(dQ) = \Delta \ln(Q) / \Delta t$$

where Δt is the time step. This addition is intended to allow the model to simulate hysteretic behaviour where concentrations (or more particularly, sediment load) may be higher during the rising limb of a peak compared with the falling limb.

$$\ln(C) = b_0 + b_1 \ln(Q) + b_2 \ln^2(Q) + b_3 T + b_4 T^2 + b_5 \sin(2 \pi T) + b_6 \cos(2 \pi T) + b_7 \ln(dQ) + \varepsilon$$

This regression model was calibrated to the concentration data for each contaminant by multiple linear regression using the LINEST function of Microsoft Excel (which provides the R^2 and p-values of the regression, among other statistics). The $b_2 \ln^2(Q)$ and $b_7 \ln(dQ)$ terms, however, tended to give unrealistically high predictions of concentration during some storm events. This was exacerbated by fitting the regression model to ln(C) instead of C. An example is given in Figure 40 for NNN measurements at Piako River (Kiwitahi). Although this regression had a high R^2 of 75% (considering the residuals in log space), the predictions do not match the obvious structure in the data, predicting a wide spread of concentrations at moderate flows, but low concentrations at extremely high flows. Furthermore, the "spikes" in Figure 40 are a result of difficulties in estimating ln(dQ) from real world data, although this could be improved by smoothing the hydrograph prior to estimation of ln(dQ).

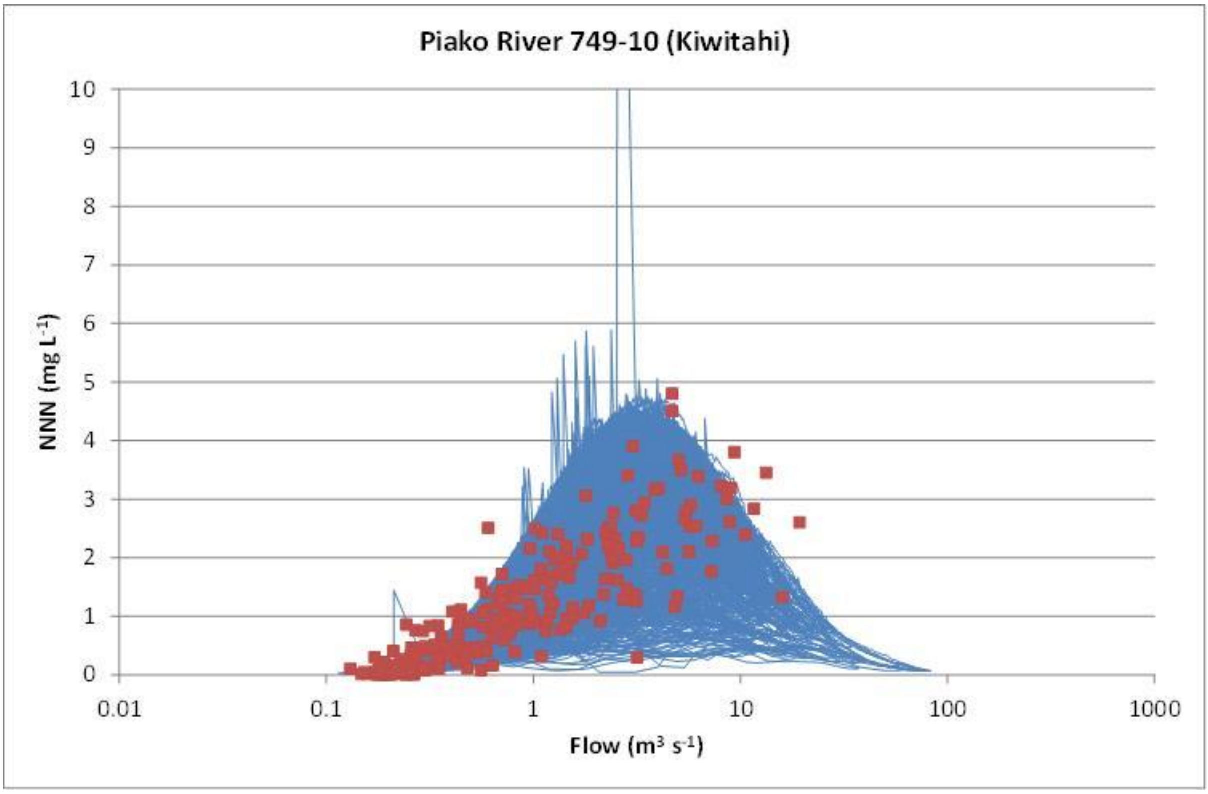


Figure 40: Example of linear regression fit using the Cohn et al. (1992) model as modified by Russell (2013). Vertical spikes are due to Russell's ln(dQ) term, and the wide spread at high flow is a result of fitting in log space.

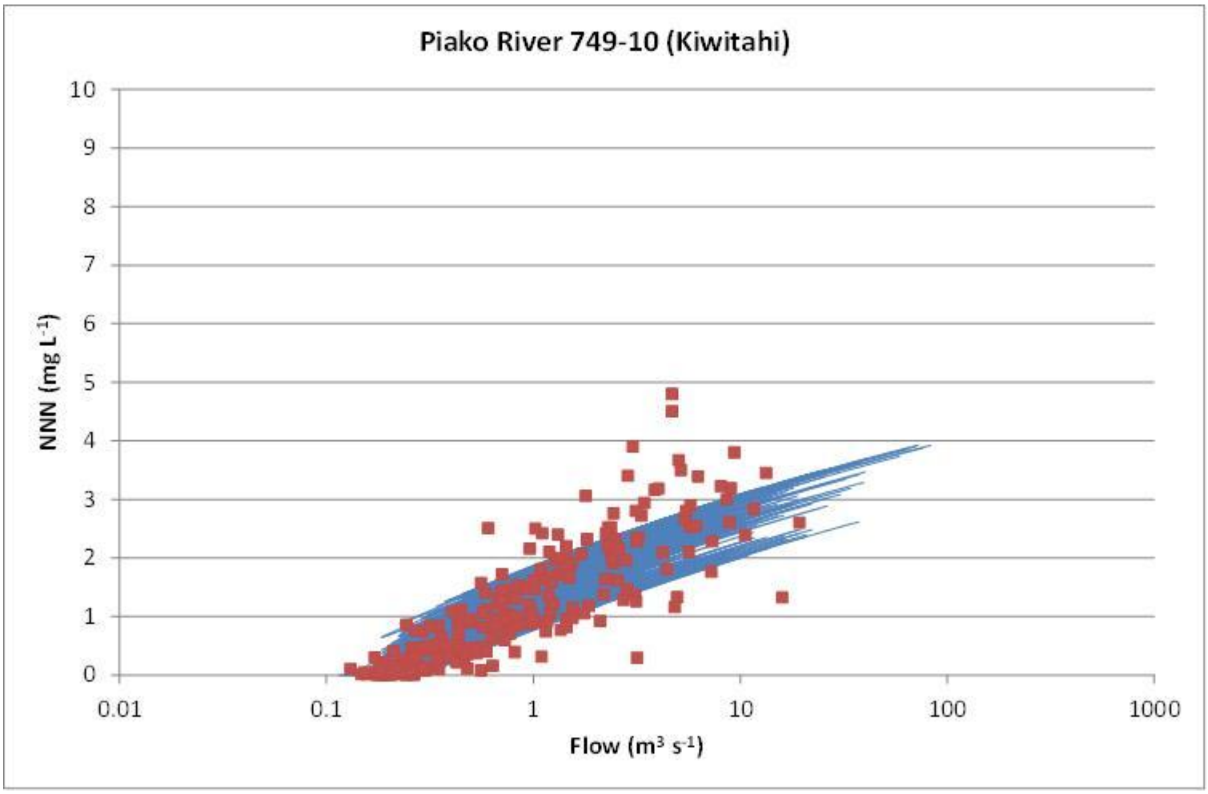


Figure 41: Example of linear regression fit using the Cohn et al. (1992) model, in normal (not log) space.

Fitting in log space was originally proposed in order to deal with modelling of sediment loads, which typically vary over several orders of magnitude (Cohn et al., 1992; Aulenbach, 2013). When modelling less variable contaminants, log space fitting continues to be used (1) because measurement errors may be expected to increase with concentration, (2) to avoid undue influence being exerted by extremely large concentration values, and (3) in order to prevent predictions from having negative values.

However there are also several drawbacks from fitting the model in log space: (1) small concentrations are given relatively more weight in the regression compared with large ones, even though the latter dominate the load calculations, (2) overestimates of ln(C) at high flows can lead to dramatic overestimations of mass flux, (3) and it is awkward to represent the linear relationship between C and ln(Q) observed in many concentration-discharge relationships (see Section 4) in log space (it can be done with a term of the form ln(ln(Q)-ln(Q*)), where Q* is a constant representing the flow below which C = 0, but Q* must be determined a priori). As a result of these factors, and after some trial and error, a modified version of the Cohn et al. (1992) model was developed. This model is calibrated in normal linear (not log) space, uses instantaneous discharge for Q, and does not include the ln(dQ) term of Russell (2013):

$$C = b_0 + b_1 \ln(Q) + b_2 \ln^2(Q) + b_3 T + b_4 T^2 + b_5 \sin(2 \pi T) + b_6 \cos(2 \pi T) + \varepsilon$$

Figure 41 shows the regression in Figure 40 redone with this revised model. The flow terms (i.e. those containing Q in the equation above) are clearly stronger, whereas the time terms are less strong (as indicated by the smaller spread). This regression had an R^2 of 80% (considering the residuals in normal space), and appears to be a much more defensible representation of the data than that in Figure 40

The ε error residual terms in a regression model can be considered to be either errors in the data (e.g. measurement error), or errors in the model (e.g. due to additional mechanisms that are not captured in the model). If we take the position that the concentration data are largely accurate, load calculations based on regression models can be further improved by adding a correction based on interpolation between the regression residuals through time, so that the resulting "composite" model passes through the concentration samples exactly (Aulenbach & Hooper, 2006; Verma et al., 2012; Aulenbach, 2013; Russell, 2013). In this approach the regression model provides the dynamics of concentration that are correlated to flow and time, and the correction then modifies this up or down to match the known concentrations through time. The resulting composite model can then be used to calculate instantaneous mass flux, and therefore long term contaminant loads in the stream.

Figure 42 shows the results of applying such a correction to the regression in Figure 41. The general pattern of predictions is maintained, but the trace now passes exactly through the data points. For this purpose, predicted concentrations less than zero are truncated to zero. Figure 43 shows the same data plotted as a time series for a two year period. For this site, as the regression model gives a good prediction of NNN concentration (R^2 = 80%), the correction is relatively minor.

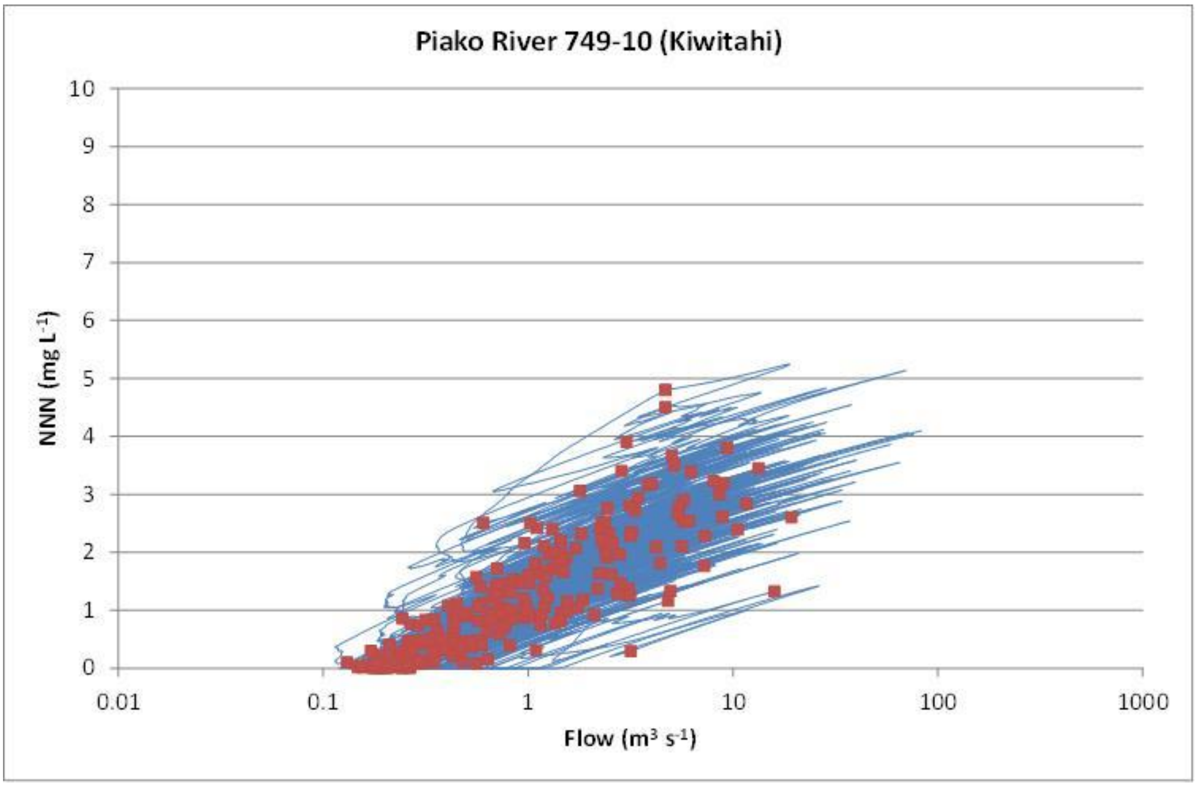


Figure 42: Linear regression fit using the modified Cohn et al. (1992) model, in normal (not log) space, with a linearly interpolated correction applied to force the prediction through the measured data exactly.

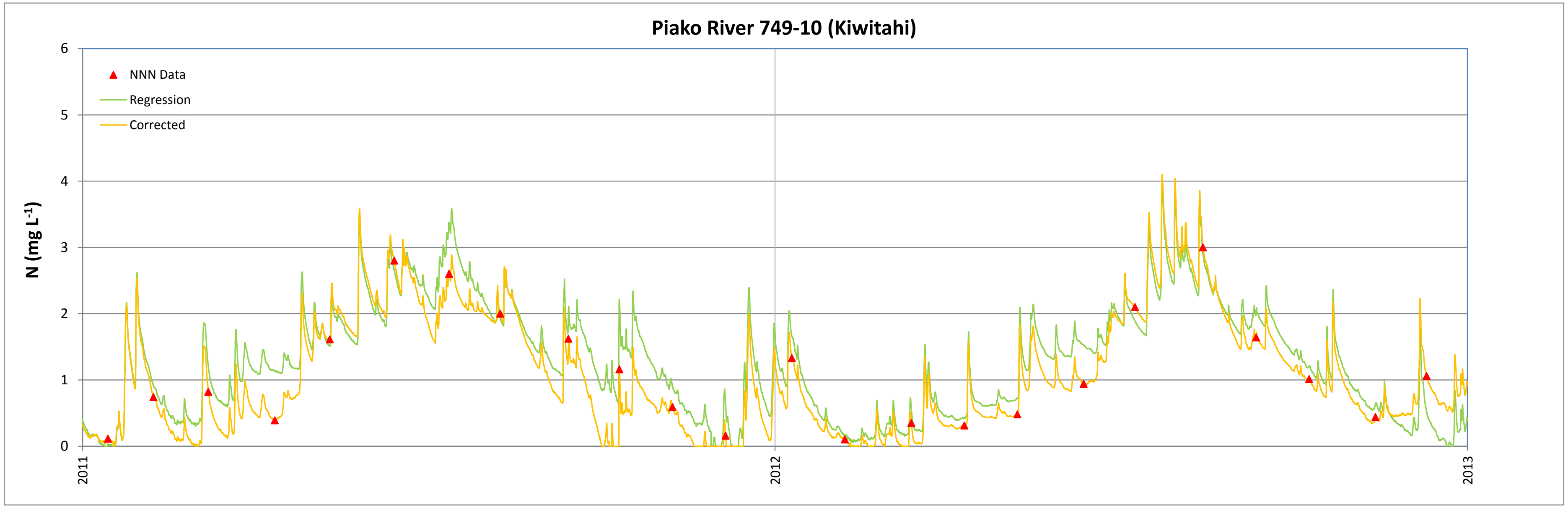


Figure 43: Example of corrected regression model used in calculating continuous mass fluxes and annual yields. This 2 year excerpt for Piako River (Kiwitahi) shows the NNN data, as well as the modified Cohn et al. (1992) regression model, and the corrected model (corrected to pass through the data points exactly).

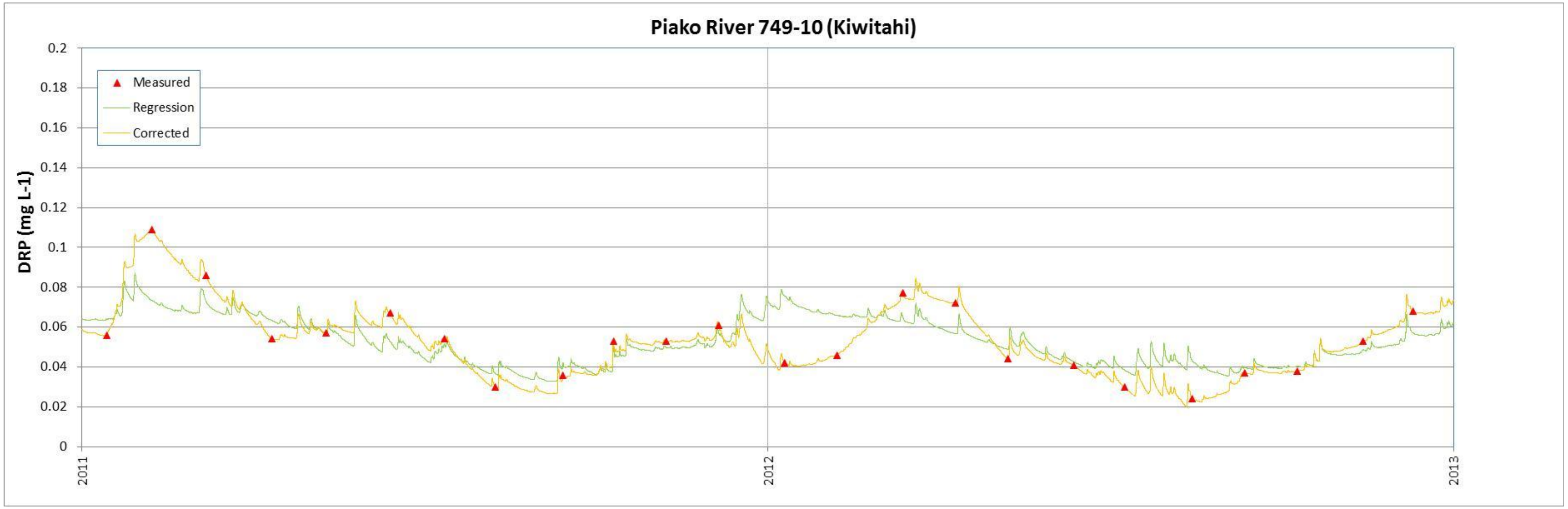


Figure 44: Example of corrected regression model used in calculating continuous mass fluxes and annual yields. This 2 year excerpt for Piako River (Kiwitahi) shows the DRP data, as well as the modified Cohn et al. (1992) regression model, and the corrected model (corrected to pass through the data points exactly).

Table 13: Coefficients of determination (RSQ) for the concentration regression model of Cohn et al (1992) applied in normal (not log) space. The area of each catchment (km^2), number of years with less than 25% missing flow data, and long term average flow (m^3 s^{-1}) are shown. RSQ values above 50% are highlighted in red. Flags are explained in Table 1.

						Load Model RSQ							
Region	**Site Name**	**ChemID**	**Area**	**Years**	**Flow**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**		**Flags**
Coromandel													
	Kauaeranga River	234-11	119.5	19	5.9	0.47	0.50	0.02	0.14	0.05	0.13		DRP
	Ohinemuri River	619-19	135.7	19	5.3	0.34	0.34	0.15	0.47	0.41	0.50		PS, DRP
	Tapu River	954-5	26.1	18	0.9	0.67	0.48	0.05	0.78	0.20	0.75		DRP
	Waiwawa River	1257-3	132	19	6.8	0.43	0.55	0.03	0.43	0.05	0.41		MF, DRP
	Wharekawa River	1312-3	55.4	19	1.9	0.32	0.75	0.06	0.18	0.16	0.15		MF, DRP
Hauraki													
	Piako River	749-10	103.6	19	1.7	0.84	0.80	0.08	0.22	0.16	0.28		-
	Piako River	749-15	537	19	7.3	0.61	0.52	0.48	0.27	0.37	0.35		PS
	Waihou River	1122-18	802.1	20	27.4	0.65	0.48	0.38	0.48	0.15	0.57		-
	Waitoa River	1249-15	121.8	19	1.5	0.69	0.57	0.32	0.37	0.22	0.34		-
	Waitoa River	1249-18	409.3	19	5.1	0.41	0.34	0.22	0.58	0.56	0.18		PS
Lower Waikato													
	Mangatangi River	453-6	194.5	20	2.8	0.77	0.70	0.47	0.63	0.15	0.61		-
	Matahuru Stm	516-5	105.4	6	1.5	0.64	0.55	0.47	0.76	0.47	0.77		MF, SS
	Whakapipi Stm	1282-8	45.4	20	0.9	0.42	0.42	0.36	0.59	0.23	0.61		PS
Waipa													
	Mangapu River	443-3	445.5	12	10.2	0.60	0.56	0.23	0.30	0.54	0.48		PS, MF, SS
	Mangatutu Stm (Waikeria)	476-7	121.9	8	3.9	0.60	0.73	0.20	0.19	0.15	0.19		SS
	Puniu River	818-2	519.1	20	14.8	0.66	0.78	0.33	0.11	0.24	0.14		-
	Waipa River	1191-12	457.6	12	18.5	0.74	0.80	0.13	0.32	0.09	0.35		MF, SS
	Waipa River	1191-10	2184.1	8	77.5	0.67	0.75	0.31	0.23	0.27	0.26		MF, SS, DRP
Upper Waikato													
	Otamakokore Stm	683-4	45.6	20	1.1	0.69	0.65	0.21	0.46	0.40	0.43		G, TP
	Tahunaatara Stm	934-1	208.1	20	4.5	0.74	0.75	0.15	0.57	0.05	0.62		-
	Waiotapu Stm	1186-4	297.5	20	3.7	0.67	0.40	0.59	0.36	0.28	0.43		G, MF, TP
West Coast													
	Oparau River	658-1	58.5	5	3.0	0.73	0.77	0.16	0.63	0.19	0.62		SS, DRP
	Waingaro River (Pukemiro)	1167-4	118.5	11	2.7	0.70	0.72	0.20	0.19	0.30	0.21		SS
	Waitetuna River	1247-2	124.4	5	3.3	0.69	0.74	0.06	0.58	0.21	0.59		MF, SS
Taupo													
	Tauranga-Taupo River	971-4	197.3	19	10.1	0.25	0.43	0.03	0.16	0.46	0.17		-
	Whareroa Stm (Taupo)	1318-4	59.2	10	1.3	0.80	0.80	0.08	0.41	0.50	0.47		SS

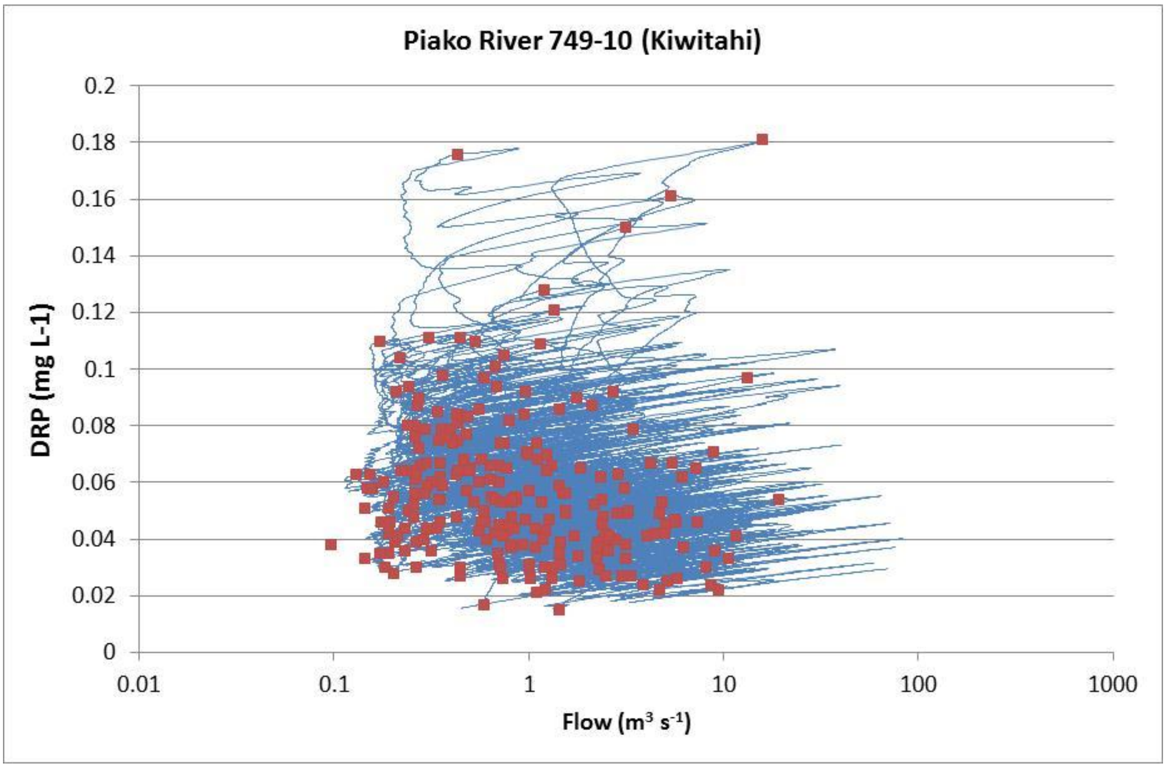


Figure 45: Linear regression fit using the modified Cohn et al. (1992) model, in normal (not log) space, with a linearly interpolated correction applied to force the prediction through the measured data exactly.

Figure 45 shows the same approach applied to the DRP data from the same site. At this site, DRP is not strongly correlated with flow, and the seasonal terms dominate the regression. Figure 44 again shows the regression model and data plotted as a time series for the two year period. In this case, the regression model provides only a weak prediction of DRP concentration (R^2 = 16%), and as a result, the corrected model approximates a linear interpolation of the data itself. In the extreme case where the regression provides no information (R^2 = 0%) the corrected model would be equivalent to simply linearly interpolating the concentration data. In this case, the model may still be used as a basis for estimation of load, although this might not be the preferred method.

Quilbé et al. (2006) suggested that regression models might be most suitable for "sediments, particulate and total P, as well as pesticides, but more rarely for mobile chemicals such as nitrate or chlorides." They propose that load estimates based on regression models with R^2 values of less than 50% could be less accurate than load estimates based on alternative calculation methods. After fitting the revised regression model to the 126 water quality times series (26 sites x 6 constituents) considered in our study (Table 13), only 58 of these achieved coefficients of determination (R^2) above 50%, although in contrast to Quilbé et al.'s statement, these were mainly those describing TN and NNN. This reflects the typically strong correlation between flow and nitrate concentrations in our catchments (Table 5).

Furthermore, the regression model approach assumes that the relationship between concentration and flow remains relatively constant over time, with only a quadratic long term trend and a sinusoidal seasonal trend available to account for changes. Model fits at sites known to be affected by point source discharges, for example, are expectedly poor, even when R^2 values are above 50% (e.g. for DRP at the Waitoa River (Mellon Road) site). In the case where the changes in, e.g., land use or unknown point source discharges are more complex, the regression model could provide a similarly poor representation of concentration dynamics, which would not be picked up without detailed examination of the observed and predicted concentration time series.

For this reason, a non-parametric method was also tested, that makes fewer assumptions about the relationship between concentration, flow and time, and may thus be more widely applicable across our sites.

6.2 BEALE RATIO ESTIMATOR APPROACH

Ratio estimators are a class of statistical approaches for estimating the time integral of an infrequently measured variable (e.g. contaminant load) on the basis of a frequently measured variable (e.g. stream flow). One simple estimate for (e.g.) annual load (L_a) is to assume that it is equal to the average of the sampled loads,

$$L_a = \frac{1}{n}\sum_{i=1}^{n} C_i Q_i = \overline{CQ}$$

where n is the number of samples, C_i are the sampled concentrations and Q_i are the sampled stream flows (i.e. the stream flows at the times of water quality sampling). Since stream flow is often measured much more frequently, the estimate can be improved by multiplying by the ratio of total to sampled stream flow,

$$L_a = \frac{1}{n}\sum_{i=1}^{n} C_i Q_i \frac{\frac{1}{N}\sum_{i=1}^{N} Q_i}{\frac{1}{n}\sum_{i=1}^{n} Q_i} = \overline{CQ}\frac{\mu_Q}{\bar{Q}}$$

where N is the number of “continuous” stream flow measurements, and μ_Q is the average stream flow calculated from the continuous record. If the concentration data does not represent the entire flow range, as is typically the case, this estimate will be biased (Quilbé et al., 2006). Beale (1962) derived a factor to correct for this bias based on the covariance between flow and load. This covariance is generally high, given that load is the product of concentration and flow, and flow is usually more dynamic than concentration. The Beale Ratio Estimator for annual load is then,

$$L_a = \overline{CQ}\frac{\mu_Q}{\bar{Q}}\left(\frac{1+\left(\frac{1}{n}-\frac{1}{N}\right)\frac{S_{CQQ}}{\overline{CQ}\,\bar{Q}}}{1+\left(\frac{1}{n}-\frac{1}{N}\right)\frac{S_{QQ}}{\bar{Q}\bar{Q}}}\right)$$

where S_{CQQ} is the unbiased covariance between C_iQ_i and Q_i, and S_{QQ} is the unbiased variance of Q_i,

$$S_{CQQ} = \frac{1}{n-1}\left(\sum_{i=1}^{n} C_i Q_i^2 - n\overline{CQ}\,\bar{Q}\right)$$

$$S_{QQ} = \frac{1}{n-1}\left(\sum_{i=1}^{n} Q_i^2 - n\bar{Q}\bar{Q}\right)$$

Table 14: Average annual flow ($m^3 s^{-1}$) and contaminant load ($t y^{-1}$) calculated using the Beale Ratio Estimator approach for the 1993-2012 period. Years indicates the number of years with at least 9 water quality samples and where at least 90% of the flow data is available.

						Average Load ($t y^{-1}$) by Beale Ratio Method						
Region	**Site Name**	**ChemID**	**Area**	**Years**	**Flow**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Flags**
Coromandel												
	Kauaeranga River	234-11	119.5	19	5.9	41.8	10.5	2.5	5.5	0.9	4.9	DRP
	Ohinemuri River	619-19	135.7	17	5.3	252.2	165.9	14.2	13.6	2.7	10.9	PS, DRP
	Tapu River	954-5	26.1	17	1.0	8.5	0.9	0.4	1.0	0.2	0.9	DRP
	Waiwawa River	1257-3	132	18	6.8	66.2	6.4	2.3	7.4	1.0	6.6	MF, DRP
	Wharekawa River	1312-3	55.4	16	1.9	16.3	7.2	0.7	1.1	0.3	0.8	MF, DRP
Hauraki												
	Piako River	749-10	103.6	19	1.7	174.0	126.6	7.7	9.2	3.0	6.2	-
	Piako River	749-15	537	18	7.3	869.4	605.3	40.2	64.8	25.1		PS
	Waihou River	1122-18	802.1	20	27.4	1231.4	988.9	25.4	98.0	62.4	35.7	-
	Waitoa River	1249-15	121.8	19	1.5	136.2	97.7	4.4	7.2	1.8	5.4	-
	Waitoa River	1249-18	409.3	19	5.1	580.3	429.6	31.6	80.6	53.5	27.1	PS
Lower Waikato												
	Mangatangi River	453-6	194.5	20	2.8	131.3	71.0	5.2	11.3	3.0	8.4	-
	Matahuru Stm	516-5	105.4	6	1.5	118.9	61.3	5.5	11.3	1.4	9.9	MF, SS
	Whakapipi Stm	1282-8	45.4	20	0.9	114.9	98.4	2.3	3.0	0.6	2.4	PS
Waipa												
	Mangapu River	443-3	445.5	12	10.2	505.1	351.7	15.1	36.0	8.7	27.2	PS, MF, SS
	Mangatutu Stm (Waikeria)	476-7	121.9	7	3.9	118.6	76.5	2.6	7.0	1.2	5.8	SS
	Puniu River	818-2	519.1	20	14.8	643.5	428.9	19.5	42.2	10.2	31.9	-
	Waipa River	1191-12	457.6	12	18.5	585.9	394.4	14.5	39.2	5.5	33.6	MF, SS
	Waipa River	1191-10	2184.1	5	73.6	3271.2	2179.1	102.1	196.5	39.6	156.9	MF, SS, DRP
Upper Waikato												
	Otamakokore Stm	683-4	45.6	20	1.1	38.8	26.0	1.2	6.1	5.3	1.1	G, TP
	Tahunaatara Stm	934-1	208.1	20	4.5	129.5	76.8	3.1	13.2	5.6	7.7	-
	Waiotapu Stm	1186-4	297.5	20	3.7	232.3	147.2	38.5	19.9	4.2	15.6	G, MF, TP
West Coast												
	Oparau River	658-1	58.5	4	3.0	41.7	19.5	1.0	4.7	0.6	4.1	SS, DRP
	Waingaro River (Pukemiro)	1167-4	118.5	11	2.7	126.7	69.6	2.1	12.7	0.8	11.9	SS
	Waitetuna River	1247-2	124.4	5	3.3	107.1	55.3	2.3	15.4	1.1	14.2	MF, SS
Taupo												
	Tauranga-Taupo River	971-4	197.3	20	10.1	42.6	19.2	3.5	8.9	4.2	5.0	-
	Whareroa Stm (Taupo)	1318-4	59.2	9	1.3	42.2	33.2	0.5	1.8	0.8	1.0	SS

Table 15: Average annual flow ($m^3\ s^{-1}$) and contaminant yield ($kg\ ha^{-1}\ y^{-1}$) calculated using the Beale Ratio Estimator approach for the 1993-2012 period. Years indicates the number of years with at least 9 water quality samples and where at least 90% of the flow data is available.

						Average Yield (kg ha^{-1} y^{-1}) by Beale Ratio Method						
Region	**Site Name**	**ChemID**	**Area**	**Years**	**Flow**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Flags**
Coromandel												
	Kauaeranga River	234-11	119.5	19	5.9	3.50	0.88	0.21	0.46	0.07	0.41	DRP
	Ohinemuri River	619-19	135.7	17	5.3	18.59	12.23	1.05	1.00	0.20	0.80	PS, DRP
	Tapu River	954-5	26.1	17	1.0	3.24	0.34	0.16	0.38	0.06	0.33	DRP
	Waiwawa River	1257-3	132	18	6.8	5.02	0.49	0.18	0.56	0.07	0.50	MF, DRP
	Wharekawa River	1312-3	55.4	16	1.9	2.94	1.30	0.13	0.20	0.06	0.15	MF, DRP
Hauraki												
	Piako River	749-10	103.6	19	1.7	16.80	12.22	0.74	0.89	0.29	0.60	-
	Piako River	749-15	537	18	7.3	16.19	11.27	0.75	1.21	0.47		PS
	Waihou River	1122-18	802.1	20	27.4	15.35	12.33	0.32	1.22	0.78	0.45	-
	Waitoa River	1249-15	121.8	19	1.5	11.18	8.02	0.36	0.59	0.15	0.44	-
	Waitoa River	1249-18	409.3	19	5.1	14.18	10.50	0.77	1.97	1.31	0.66	PS
Lower Waikato												
	Mangatangi River	453-6	194.5	20	2.8	6.75	3.65	0.27	0.58	0.15	0.43	-
	Matahuru Stm	516-5	105.4	6	1.5	11.28	5.81	0.52	1.07	0.13	0.94	MF, SS
	Whakapipi Stm	1282-8	45.4	20	0.9	25.30	21.68	0.51	0.66	0.14	0.52	PS
Waipa												
	Mangapu River	443-3	445.5	12	10.2	11.34	7.89	0.34	0.81	0.20	0.61	PS, MF, SS
	Mangatutu Stm (Waikeria)	476-7	121.9	7	3.9	9.73	6.28	0.21	0.57	0.10	0.48	SS
	Puniu River	818-2	519.1	20	14.8	12.40	8.26	0.38	0.81	0.20	0.61	-
	Waipa River	1191-12	457.6	12	18.5	12.80	8.62	0.32	0.86	0.12	0.73	MF, SS
	Waipa River	1191-10	2184.1	5	73.6	14.98	9.98	0.47	0.90	0.18	0.72	MF, SS, DRP
Upper Waikato												
	Otamakokore Stm	683-4	45.6	20	1.1	8.51	5.70	0.27	1.34	1.16	0.25	G, TP
	Tahunaatara Stm	934-1	208.1	20	4.5	6.22	3.69	0.15	0.64	0.27	0.37	-
	Waiotapu Stm	1186-4	297.5	20	3.7	7.81	4.95	1.29	0.67	0.14	0.52	G, MF, TP
West Coast												
	Oparau River	658-1	58.5	4	3.0	7.12	3.33	0.18	0.80	0.10	0.70	SS, DRP
	Waingaro River (Pukemiro)	1167-4	118.5	11	2.7	10.69	5.88	0.18	1.07	0.07	1.01	SS
	Waitetuna River	1247-2	124.4	5	3.3	8.61	4.44	0.19	1.23	0.09	1.14	MF, SS
Taupo												
	Tauranga-Taupo River	971-4	197.3	20	10.1	2.16	0.97	0.18	0.45	0.21	0.25	-
	Whareroa Stm (Taupo)	1318-4	59.2	9	1.3	7.13	5.60	0.08	0.30	0.13	0.18	SS

Table 16: Average annual flow (m^3 s^{-1}) and contaminant load (t y^{-1}) calculated using the Beale Ratio Estimator approach for the 2008-2012 period. Years indicates the number of years with at least 9 water quality samples and where at least 90% of the flow data is available.

						Average Load (t y^{-1}) by Beale Ratio Method						
Region	**Site Name**	**ChemID**	**Area**	**Years**	**Flow**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Flags**
Coromandel												
	Kauaeranga River	234-11	119.5	5	5.9	44.6	10.8	1.9	2.4	0.8	1.8	DRP
	Ohinemuri River	619-19	135.7	5	5.9	305.8	188.8	17.9	16.7	2.1	14.6	PS, DRP
	Tapu River	954-5	26.1	3	1.0	13.3	0.6	0.3	1.5	0.1	1.4	DRP
	Waiwawa River	1257-3	132	5	7.1	52.4	6.2	2.2	4.6	0.9	3.9	MF, DRP
	Wharekawa River	1312-3	55.4	4	2.1	22.6	10.7	0.7	1.3	0.3	1.1	MF, DRP
Hauraki												
	Piako River	749-10	103.6	5	2.1	224.0	170.7	7.2	8.5	2.7	5.8	-
	Piako River	749-15	537	5	9.3	1115.2	798.0	34.1	64.2	27.4		PS
	Waihou River	1122-18	802.1	5	27.7	1371.2	1051.0	23.5	105.3	54.0	51.3	-
	Waitoa River	1249-15	121.8	5	1.9	165.7	121.7	3.4	6.6	1.6	5.0	-
	Waitoa River	1249-18	409.3	5	6.2	697.3	520.7	25.0	34.9	12.8	22.1	PS
Lower Waikato												
	Mangatangi River	453-6	194.5	5	3.0	139.2	68.5	5.7	11.8	2.5	9.3	-
	Matahuru Stm	516-5	105.4	5	1.6	127.6	65.3	5.5	12.5	1.4	11.1	MF, SS
	Whakapipi Stm	1282-8	45.4	5	1.0	131.5	110.3	2.3	4.3	0.7	3.5	PS
Waipa												
	Mangapu River	443-3	445.5	5	10.8	590.6	426.2	16.6	31.9	7.0	24.9	PS, MF, SS
	Mangatutu Stm (Waikeria)	476-7	121.9	4	4.1	138.5	85.3	2.7	8.8	1.2	7.6	SS
	Puniu River	818-2	519.1	5	15.7	849.8	531.0	18.0	58.0	9.7	48.3	-
	Waipa River	1191-12	457.6	5	19.7	673.0	476.3	11.9	33.2	4.3	28.9	MF, SS
	Waipa River	1191-10	2184.1	3	78.3	3319.5	2389.7	70.2	163.0	36.0	127.0	MF, SS, DRP
Upper Waikato												
	Otamakokore Stm	683-4	45.6	5	1.1	47.5	31.2	0.7	5.7	5.8	0.2	G, TP
	Tahunaatara Stm	934-1	208.1	5	4.7	179.2	92.5	2.5	20.3	5.5	14.8	-
	Waiotapu Stm	1186-4	297.5	5	3.8	270.4	170.2	41.6	19.7	3.7	15.5	G, MF, TP
West Coast												
	Oparau River	658-1	58.5	4	3.0	41.7	19.5	1.0	4.7	0.6	4.1	SS, DRP
	Waingaro River (Pukemiro)	1167-4	118.5	5	2.9	139.4	77.2	1.3	16.1	0.7	15.4	SS
	Waitetuna River	1247-2	124.4	5	3.3	107.1	55.3	2.3	15.4	1.1	14.2	MF, SS
Taupo												
	Tauranga-Taupo River	971-4	197.3	5	10.4	51.1	26.1	3.3	5.5	3.7	2.1	-
	Whareroa Stm (Taupo)	1318-4	59.2	5	1.4	49.2	38.6	0.5	1.9	0.7	1.2	SS

Table 17: Average annual flow (m^3 s^{-1}) and contaminant yield (kg ha^{-1} y^{-1}) calculated using the Beale Ratio Estimator approach for the 2008-2012 period. Years indicates the number of years with at least 9 water quality samples and where at least 90% of the flow data is available.

						Average Yield (kg ha^{-1} y^{-1}) by Beale Ratio Method						
Region	**Site Name**	**ChemID**	**Area**	**Years**	**Flow**	**TN**	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Flags**
Coromandel												
	Kauaeranga River	234-11	119.5	5	5.9	3.73	0.91	0.16	0.20	0.06	0.15	DRP
	Ohinemuri River	619-19	135.7	5	5.9	22.54	13.91	1.32	1.23	0.16	1.07	PS, DRP
	Tapu River	954-5	26.1	3	1.0	5.11	0.24	0.12	0.59	0.05	0.55	DRP
	Waiwawa River	1257-3	132	5	7.1	3.97	0.47	0.17	0.35	0.07	0.29	MF, DRP
	Wharekawa River	1312-3	55.4	4	2.1	4.08	1.93	0.12	0.23	0.05	0.20	MF, DRP
Hauraki												
	Piako River	749-10	103.6	5	2.1	21.62	16.48	0.70	0.82	0.26	0.56	-
	Piako River	749-15	537	5	9.3	20.77	14.86	0.63	1.20	0.51		PS
	Waihou River	1122-18	802.1	5	27.7	17.10	13.10	0.29	1.31	0.67	0.64	-
	Waitoa River	1249-15	121.8	5	1.9	13.60	9.99	0.28	0.54	0.13	0.41	-
	Waitoa River	1249-18	409.3	5	6.2	17.04	12.72	0.61	0.85	0.31	0.54	PS
Lower Waikato												
	Mangatangi River	453-6	194.5	5	3.0	7.16	3.52	0.29	0.61	0.13	0.48	-
	Matahuru Stm	516-5	105.4	5	1.6	12.11	6.20	0.52	1.19	0.13	1.06	MF, SS
	Whakapipi Stm	1282-8	45.4	5	1.0	28.97	24.30	0.50	0.94	0.16	0.78	PS
Waipa												
	Mangapu River	443-3	445.5	5	10.8	13.26	9.57	0.37	0.72	0.16	0.56	PS, MF, SS
	Mangatutu Stm (Waikeria)	476-7	121.9	4	4.1	11.37	7.00	0.22	0.72	0.10	0.63	SS
	Puniu River	818-2	519.1	5	15.7	16.37	10.23	0.35	1.12	0.19	0.93	-
	Waipa River	1191-12	457.6	5	19.7	14.71	10.41	0.26	0.72	0.09	0.63	MF, SS
	Waipa River	1191-10	2184.1	3	78.3	15.20	10.94	0.32	0.75	0.17	0.58	MF, SS, DRP
Upper Waikato												
	Otamakokore Stm	683-4	45.6	5	1.1	10.41	6.83	0.15	1.24	1.28	0.05	G, TP
	Tahunaatara Stm	934-1	208.1	5	4.7	8.61	4.45	0.12	0.98	0.26	0.71	-
	Waiotapu Stm	1186-4	297.5	5	3.8	9.09	5.72	1.40	0.66	0.12	0.52	G, MF, TP
West Coast												
	Oparau River	658-1	58.5	4	3.0	7.12	3.33	0.18	0.80	0.10	0.70	SS, DRP
	Waingaro River (Pukemiro)	1167-4	118.5	5	2.9	11.76	6.51	0.11	1.36	0.06	1.30	SS
	Waitetuna River	1247-2	124.4	5	3.3	8.61	4.44	0.19	1.23	0.09	1.14	MF, SS
Taupo												
	Tauranga-Taupo River	971-4	197.3	5	10.4	2.59	1.32	0.17	0.28	0.19	0.10	-
	Whareroa Stm (Taupo)	1318-4	59.2	5	1.4	8.30	6.52	0.08	0.32	0.12	0.20	SS

Annual load (t y^{-1}), and after dividing by catchment area, annual contaminant yield (kg ha^{-1} y^{-1}), were calculated for each year x site x contaminant using the Beale Ratio Estimator method just described, implemented in Microsoft Excel. Although the Beale Ratio Estimator is not as accurate as the regression approach in the ideal case (Verma et al., 2012), it is less sensitive to the calibration period or structure in the data, and was therefore considered to be preferable for our purposes.

Table 14 and Table 15 give the average contaminant loads and yields for each site based on the entire available data series (Figure 1), as well as the average annual flow (expressed in m^3 s^{-1}). Only years with at least 9 water quality samples and where at least 90% of the flow data was available were included. As noted in Section 1, TP and TP-DRP data were additionally missing from the database at the two sites, Waiotapu Stream and Otamakokore Stream, for the 2005-2011 period.

The results generally reflect the level of agricultural production in each catchments, with the Hauraki and Waipa streams having high yield of TN and NNN. Influences from point course discharges are also apparent, e.g., as the high yields in the Ohinemuri River stand out from the other results in the Coromandel, as does the Whakapipi Stream in the Lower Waikato.

In order to reduce the influence of point source discharges, which were most significant prior to 2004, and differences in data availability (Figure 1), the average loads and yields were also calculated for the 5-year period 2008-2012, during which both water quality and stream flow data were available for all sites (Table 16 and Table 17). This resulted in 3-5 years with at least 9 water quality samples and where at least 90% of the flow data was available at all sites. Again, TP and TP-DRP data were additionally missing at Waiotapu Stream and Otamakokore Stream for the 2005-2011 period.

In the Coromandel, generally low loads and yields reflect the relatively small amount of intensive agriculture in these catchments. The relatively high N and P yields in the Ohinehuri River again stand out, and may reflect the relatively larger proportion of pastoral agriculture in this catchment compared with other Coromandel catchments. Higher NNN yields in the Wharekawa River possibly have the same pastoral origin.

High loads and yields in the Hauraki, Lower Waikato and Waipa catchments can similarly be attributed to widespread farming in these areas. The extremely high N yields in the Whakapipi Stream have previously been noted by WRC (2007), who attributed them to non-specific “point source” discharges; a survey of land use in the area suggests the origin is market gardening.

Geothermal influences in two catchments in the Upper Waikato are reflected in elevated NH4 (Waiotapu Stream) or DRP (Otamakokore Stream) at these sites.

Full interpretation of the load and yield results would require a thorough study of catchment areas and land use patterns. One might expect that loads and yields reflected the proportion of low versus high intensity land uses in the catchment, and differences from this expectation could be attributed to spatially varying extents of natural attenuation and lengths of subsurface time lags. Such analysis, however, is beyond the scope of the current study.

6.3 CATCHMENT COMPARISONS

In order to assess the year to year variability of contaminant loads/yields, the distributions of annual yield were compared between the different catchments for TN, NNN, NH4, TP, DRP and TP-DRP for the 2008-2012 period. As before, years which had less than 9 water quality samples, or less than 90% available flow data were excluded (see Table 17) in order to maximise the number of years that were included while still ensuring that sufficient data were available for a meaningful analysis.

The box plots in Figures 46-51 show the minimum, 1st quartile, median, 3rd quartile, maximum and mean annual yield values for each catchment. Although the box plots represent only 5 data points for most sites, they provide an impression of the variability of annual yield in each catchments.

The annual yields again reflect the patterns previously identified: elevated yields in catchments with significant pastoral agriculture (Hauraki, Waipa, West Coast), or where significant point source or geothermal influences are known to exist (Upper Waikato), and lower yields in catchments with a greater proportion of exotic forestry or native bush (e.g. Coromandel, Tauranga-Taupo River).

One point of interest is the relatively large variation in annual yields on a year to year basis. TN, NNN and NH4 yields often vary by a factor of two between the lowest and highest annual values, while TP and TP-DRP yields are even more variable, possibly reflecting the infrequency of large storm events that displace large amounts of sediment and associated adsorbed nutrients.

DRP yield variations, on the other hand, are much smaller (Figure 50). As observed in Section 4, DRP concentrations are often negatively correlated with stream flow, suggesting that DRP concentrations are generally higher in discharged deeper groundwater compared with near-surface flow paths. As groundwater discharge is relatively constant compared with near-surface flow (Section 3, Section 5), this may explain the small variation in annual DRP yield compared with NNN, for example, which is primarily discharged via shallow flow paths that experience a greater degree of annual variation.

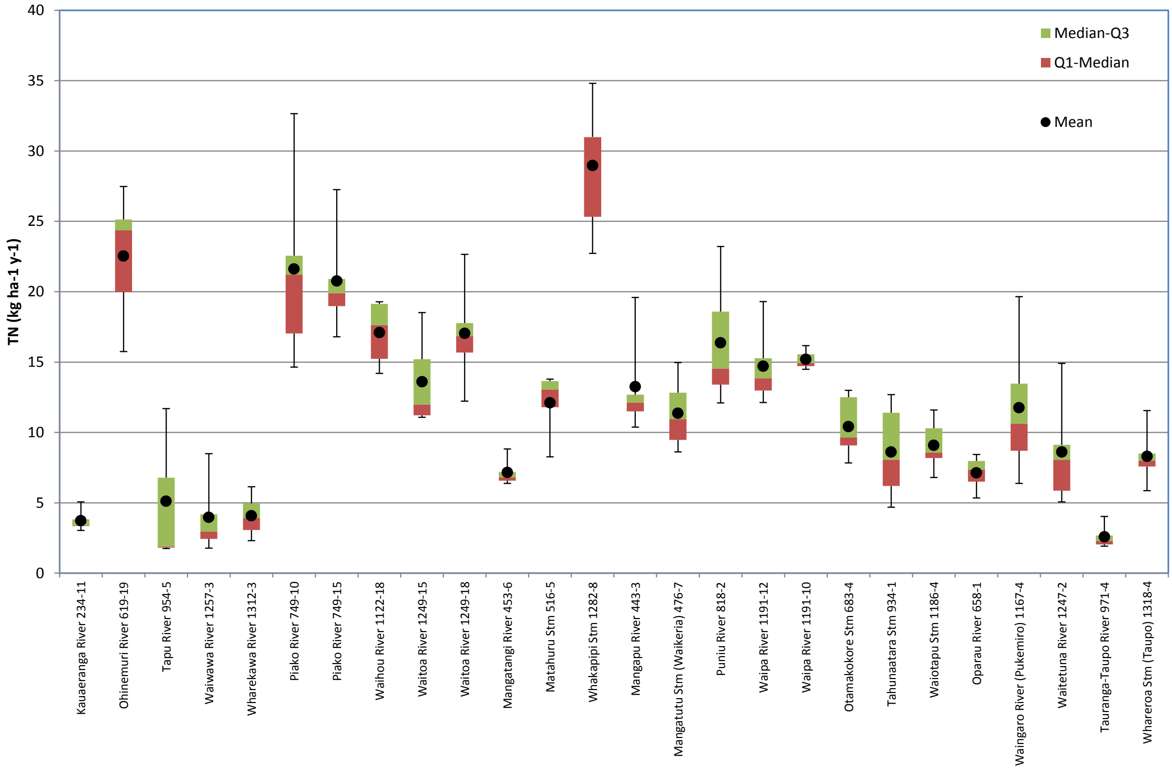


Figure 46: Box plot of TN concentrations across all 26 sites for the 2008-2012 period, and estimated annual TN yield.

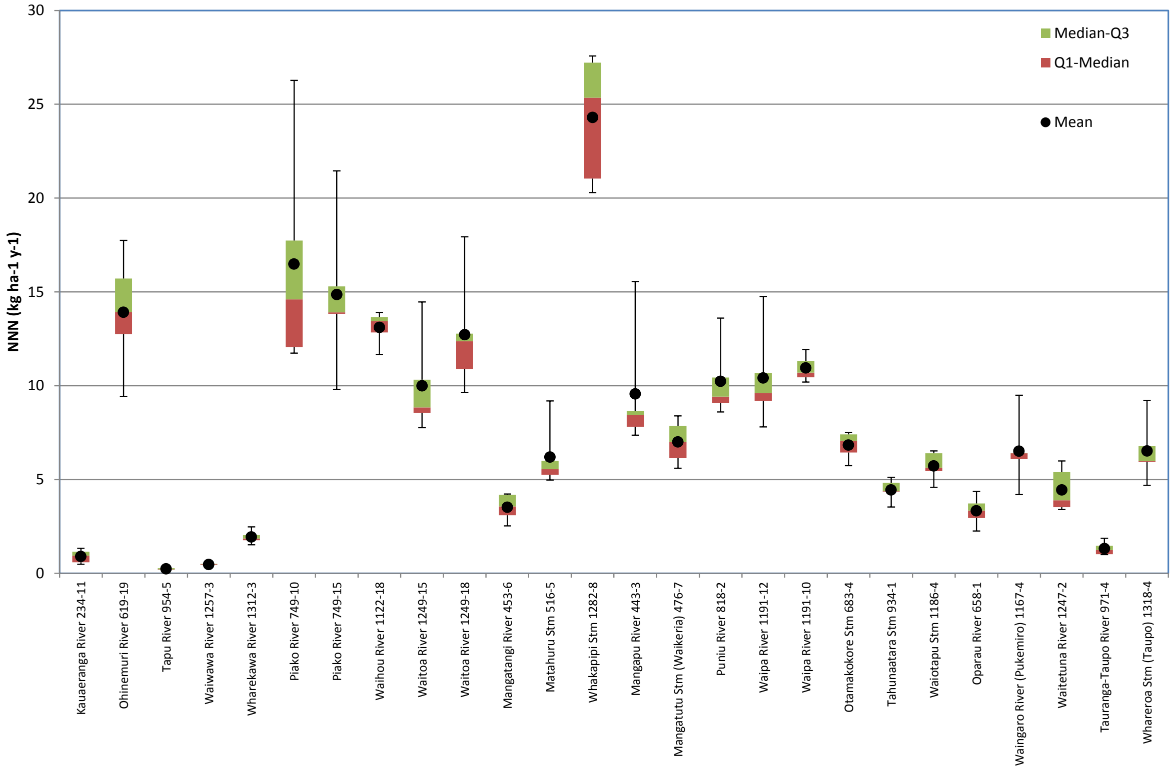


Figure 47: Box plot of NNN concentrations across all 26 sites for the 2008-2012 period, and estimated annual NNN yield.

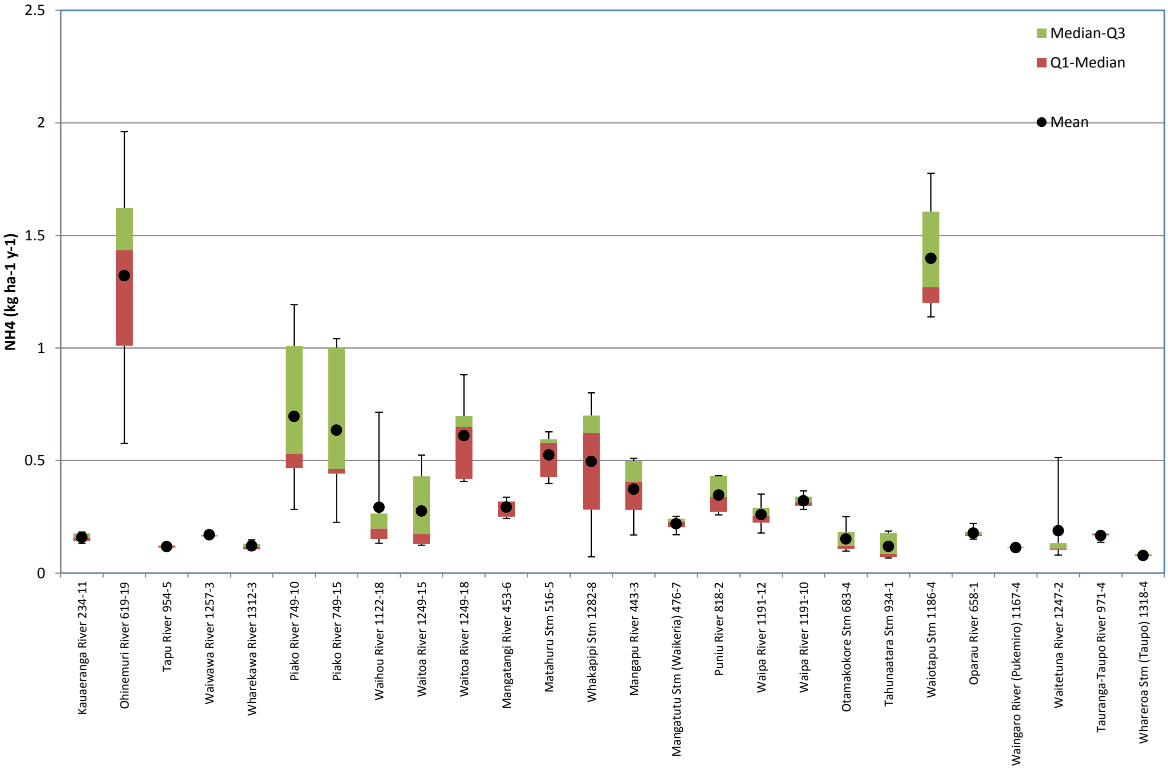


Figure 48: Box plot of NH4 concentrations across all 26 sites for the 2008-2012 period, and estimated annual NH4 yield.

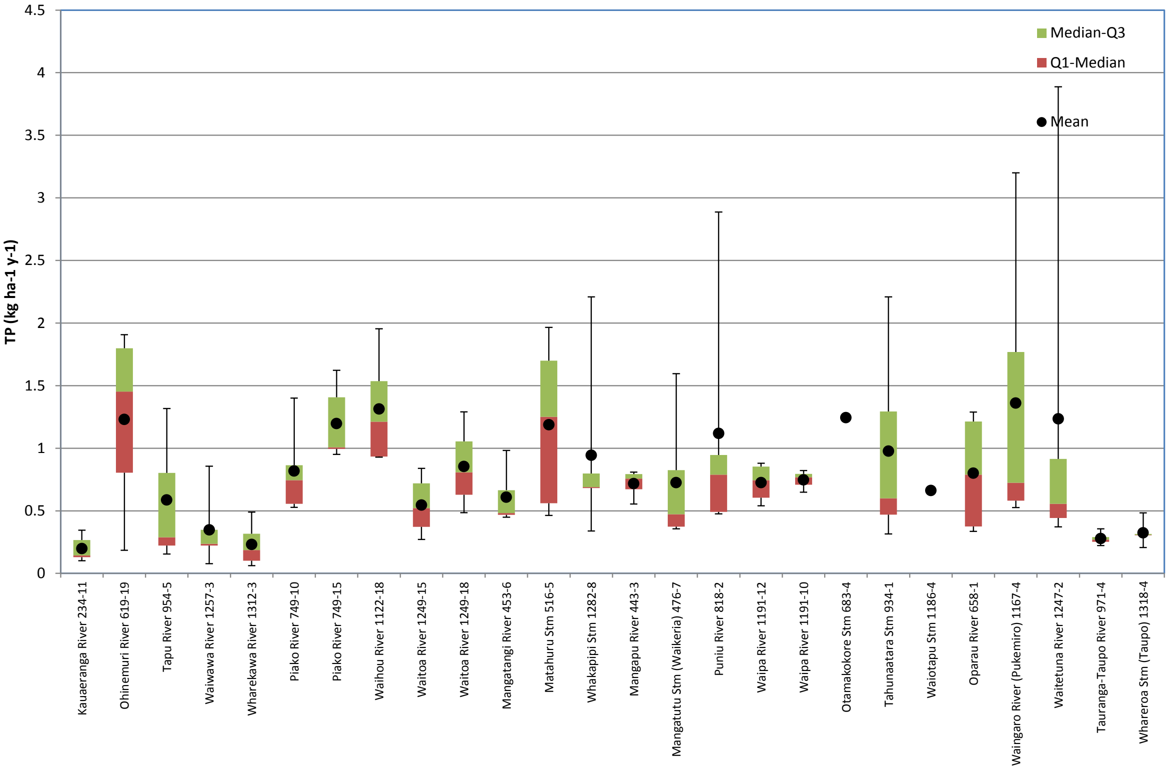


Figure 49: Box plot of TP concentrations across all 26 sites for the 2008-2012 period, and estimated annual TP yield.

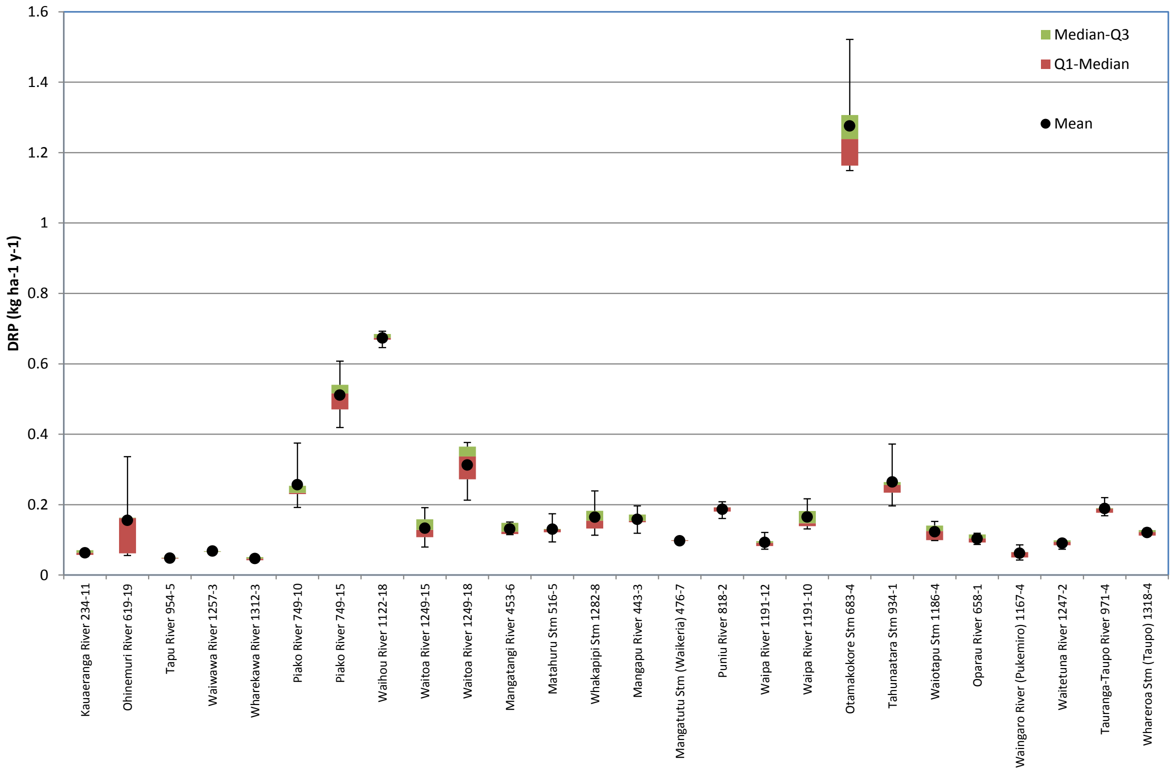


Figure 50: Box plot of DRP concentrations across all 26 sites for the 2008-2012 period, and estimated annual DRP yield.

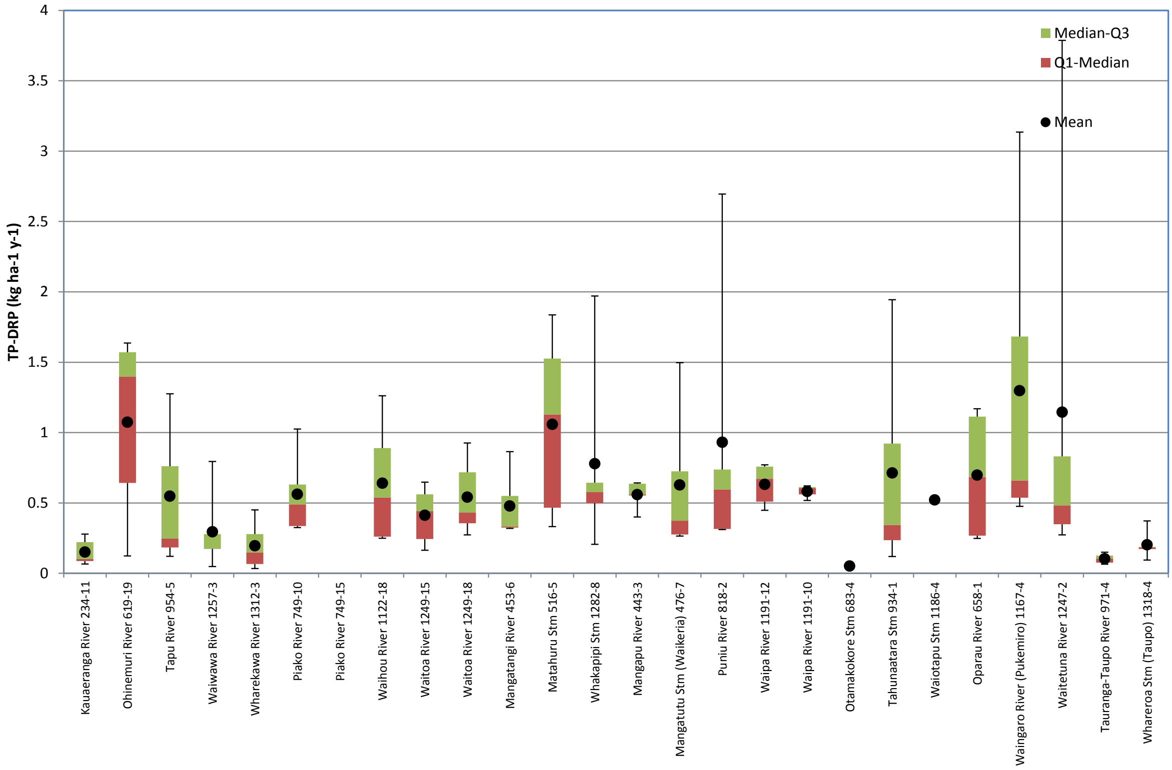


Figure 51: Box plot of TP-DRP concentrations across all 26 sites for the 2008-2012 period, and estimated annual TP-DRP yield.

CONCLUSIONS

To date, analysis of stream water quality time series data has often been done based on concentrations alone. This is partly due to the fact that there are many more water quality monitoring sites than stream flow monitoring sites and there is often a poor overlap of these monitoring programmes. At most, flow data has been used to apply a “flow correction” to water quality time series (which assumes that such a correction would be stable over time), or in the calculation of contaminant loads.

However, contaminant concentrations are often correlated with stream flow, and these correlations can be used to better understand the processes driving contaminant discharge. In this report we have proposed several additional ways in which stream flow data can be used to elucidate information from water quality sampling:

1. Comparison of stream flow distributions at time of sampling with stream flow distributions from the continuous flow record can indicate where water quality sampling might have been biased by under- or over-sampling, particularly of rare, high flow conditions (Section 3);
2. Plotting of contaminant concentrations against stream flow may indicate strong correlations between concentration and discharge (“concentration-discharge relationships”). Such correlations may be due to alternative flow paths (e.g. overland flow, interflow, and shallow or deep groundwater discharge) being more or less dominant under low or high flow conditions , and may thus provide insight into the relative importance of the different flow paths for land-to-water transfer of contaminants in a particular catchment (Section 4);
3. Stratification of water quality time series based on stream flow conditions at time of sampling (e.g. according to flow percentile, or hydrograph separation) can allow identification of concentration trends in the alternative flow paths, which may reflect historical or recent changes in land use and/or point source discharges (Section 5);
4. Parallel water quality and flow information allow calculation of mass fluxes (loads or yields). While high resolution data is preferable, the Beale Ratio Estimator method provides unbiased estimation of annual mass flux that makes the best use of infrequent concentration measurements when continuous flow records are available (Section 6).

The analysis has been complicated by inconsistencies in the quality of the data (missing data, mismatch between water quality and flow recording sites and periods, changes in analytical methods) as well as by point source and geothermal impacts of water quality in some catchments. This has made comparison between catchments sometimes problematic.

Ideally water quality sampling programmes should be accompanied by matched stream flow recording, in order to maximize the value of the sampling programme. When focusing on a single site, however, consideration of already available stream flow records can nevertheless provide much additional insight into stream contaminant dynamics and processes.

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REFERENCES

Aqualinc (2014) Contaminant load calculator. Prepared for Environment Southland. Aqualinc Report No C14098/1.

Aubert, A.H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., Grimaldi, C., Hamon, Y., Jaffrézic, A., Lecoz-Boutnik, M., Molénat, J., Petitjean, P., Ruiz, L., Merot, P. (2013) Solute transport dynamics in small shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study. Hydrology and Earth System Sciences 17, 1379-1391. doi:10.5194/hess-17-1379-2013.

Aulenbach, B.T. (2013) Improving regression-model-based streamwater constituent load estimates derived from serially correlated data. Journal of Hydrology 503, 55-66.

Aulenbach, B.T. & Hooper, R.P. (2006) Improving stream solute load estimation by the composite method: A comparative analysis using data from the Panola Mountain Research Watershed. In: Hatcher, K.J. (ed.) Proceedings of the 2005 Georgia Water Resources Conference, 25-27 April 2005, Institute of Ecology, University of Georgia, Athens, GA, USA.

Barkle, G.F., Stenger, R., Burgess, C., Wall, A. (2014) Quantifying groundwater contribution to stream flow generation in a steep headwater catchment. Journal of Hydrology (NZ) 53(1), 23-40.

Beale, E.M.L. (1962) Some uses of computers in operational research. Industrielle Organisation 31, 51-52.

Bidwell, V.J., Stenger, R., Barkle, G.F. (2008) Dynamic analysis of groundwater discharge and partial area contribution to Pukemanga Stream. New Zealand. Hydrology and Earth System Sciences 12, 975 987.

Burt, T.P., Worrall, F., Howden, N.J.K., Anderson, M.G. (2014) Shifts in discharge-concentration relationships as a small catchment recover from sever drought. Hydrological Processes. doi:10.1002/hyp.10169

Chanat, J.G., Rice, K.C., Hornberger, G.H. (2002) Consistency of patterns in concentration-discharge plots. Water Resources Research 38(8). doi:10.1029/2001WR000971

Chen, D., Dahlgren, R.A., Lu, J. (2013) A modified load apportionment model for identifying point and diffuse source nutrient inputs to river from stream monitoring data. Journal of Hydrology, 501: 25-34.

Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., Summers, R.M. (1992) The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay. Water Resources Research 28, 2353-2363.

Collischonn, W., Fan, F.M. (2013) Defining parameters for Eckhardt's digital baseflow filter. Hydrological Processes 27, 2614-2622.

Eckhardt, K. (2005) How to construct recursive digital filters for baseflow separation. Hydrological Processes 19, 507-515.

Eckhardt, K. (2008) A comparison of baseflow indices, which were calculated with seven different baseflow separation methods. Journal of Hydrology 352, 168-173.

Furey, P.R., Gupta, V.K. (2001) A physically base filter for separating base flow from streamflow time series. Water Resources Research 37(11), 2709-2722.

Gonzales, A.L., Nonner, J., Heijkers, J., Uhlenbrook, S. (2009) Comparison of different base flow separation methods in a lowland catchment. Hydrology and Earth System Sciences 13, 2055-2068.

Kirchner, J. (2001) Data Analysis Toolkit #10: Simple linear regression. Department of Earth & Planetary Science, University of California, Berkeley. http://seismo.berkeley.edu/~kirchner/eps_120/Toolkits/Toolkit_10.pdf

Krakauer, N.Y., Temimi, M. (2011) Stream recession curves and storage variability in small watersheds. Hydrology and Earth System Sciences 15, 2377-2389.

Littlewood, I.G. (1992) Estimating contaminant loads in rivers: A review. Institute of Hydrology Report No. 117, Oxfordshire, UK.

Loftis, J.C., Phillips, R.D., Ward, R.C., Taylor, C.H. (1989) WQSTAT II: A water quality statistics package. Groundwater 27(6): 866-873.

McGlynn, B.L., McDonnell, J.J. (2003) Quantifying the relative contributions of riparian and hillslope zones to catchment runoff. Water Resources Research 39(11), 1310.

Moore, R.D., Richards, G., Story, A. (2008) Electrical conductivity as an indicator of water chemistry and hydrologic process. Streamline Waterhed Management Bulletin 11(2): 25-29.

Morgenstern, U., Stewart, M.K., Stenger, R. (2010) Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. Hydrology and Earth System Sciences 14, 2289-2301, doi:10.5194/hess-14-2289-2010.

Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P. (1992) Numerical Recipes in Fortran 77: The Art of Scientific Computing. Second Edition. Cambridge University Press, New York, USA.

Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P. (2007) Numerical Recipes: The Art of Scientific Computing. Third Edition. Cambridge University Press, New York, USA.

Quilbé, R., Rousseau, A.N., Duchemin, M., Poulin, A., Gangbazo, G., Villeneuve, J.P. (2006) Selecting a calculation method to estimate sediment and nutrient loads in streams: Application to the Beaurivage River (Québec, Canada). Journal of Hydrology 326, 295-310.

Rimmer, A., Hartmann, A. (2014) Optimal hydrograph separation filter to evaluate transport routines of hydrological models. Journal of Hydrology 514, 249–257.

Russell, A.M. (2013) Suspended sediment and total phosphorus loadings from small agricultural watersheds in western Illinois. M.Sc. thesis, University of Illinois, Urbana-Champaign, IL, USA.

Smith, D.G., McBride, G.B., Bryers, G.G., Wisse, J., Mink, D.F.J. (1999) Trends in New Zealand's national river water quality network. New Zealand Journal of Marine and Freshwater Science, 30: 485-500.

Stewart, M.K. (2014) New baseflow separation and recession analysis approaches for streamflow. Hydrology and Earth System Sciences Discussions 11, 7089-7131.

Stonger, R.W. (2000) Trends in precipitation and streamflow and changes in stream morphology in the Fountain Creek watershed, Colorado, 1939-1999. U.S. Geological Survey, Water-Resources Investigation Report 00-4130.

USEPA (2012) Conductivity. United States Environmental Protection Agency, Water Monitoring and Assessment Website. http://water.epa.gov/type/rsl/monitoring/vms59.cfm

Van de Griend, A.A., De Vries, J.J., Seyhan, E. (2002) Groundwater discharge from areas with variable specific drainage resistance. Journal of Hydrology 259, 203-220.

Verma, S., Markus, M., Cooke, R.A. (2012) Development of error correction techniques for nitrate-N load estimation methods. Journal of Hydrology 432-433, 12-25.

Vogel, R.M., Kroll, C.N. (1996) Estimation of baseflow recession constants. Water Resources Management 10, 303-320.

WRC (2004) Trends in river water quality in the Waikato Region, 1987-2002. Environment Waikato Technical Report 2004/02.

WRC (2007) Potential for reducing the nutrient loads from the catchments of shallow lakes in the Waikato Region. Environment Waikato Technical Report 2006/54.

WRC (2011) Water quality of the Hauraki Rivers and Southern First of Thames, 2000-2009. Waikato Regional Council Technical Report 2011/06.

WRC (2013) Trends in river water quality in the Waikato Region, 1993-2012. Waikato Regional Council Technical Report 2013/20.

Woodward, S.J.R., Stenger, R., Bidwell, V.J. (2013) Dynamic analysis of stream flow and water chemistry to infer subsurface water and nitrate fluxes in a lowland dairying catchment. Journal of Hydrology 505, 299–311. http://dx.doi.org/10.1016/j.jhydrol.2013.07.044

APPENDIX 1: CONCENTRATION DISCHARGE RELATIONSHIPS

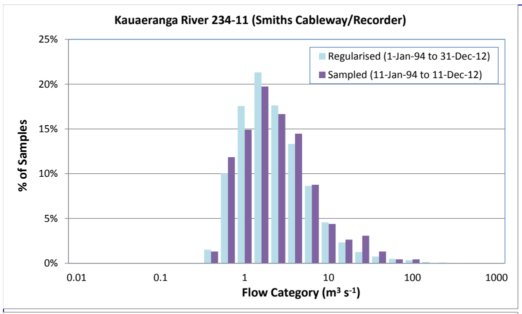
This appendix provides concentration-discharge charts for each of the Waikato water quality sampling sites, sorted by subregion (Coromandel, Hauraki, Lower Waikato River, Waipa, Upper Waikato River, West Coast, Lake Taupo).

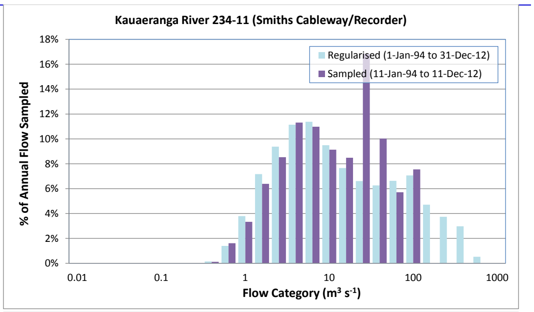
For each site there are 11 charts. In the top row, the right hand chart shows the frequency of flow data before and after regularisation (interpolation onto a 15 minute time step). The left hand chart compares the amount of stream flow sampled during water quality sampling during 1993-2012 (purple) compared with the amount of water from the continuous flow record over the same period (blue). The differences in these histograms indicate bias in the water quality samples (e.g. over- or under-sampling of high flows).

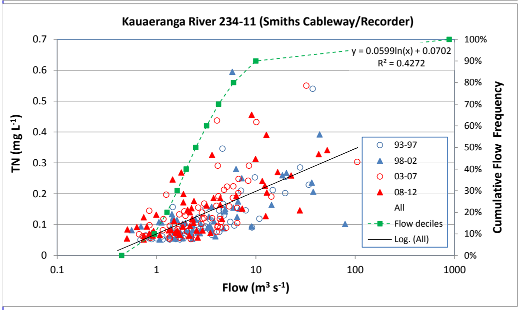
The following 8 charts show the relationship between stream flow (cumecs on a log scale) and water quality measurements (mg L^{-1}, or mS m^{-1} for EC). Water quality measurements are separated into five year periods (1993-1997, 1998-2002, 2003-2007, 2008-2012). The log regression between stream flow and concentration is also shown for the whole period (1993-2012). Cumulative flow frequency is also shown in green.

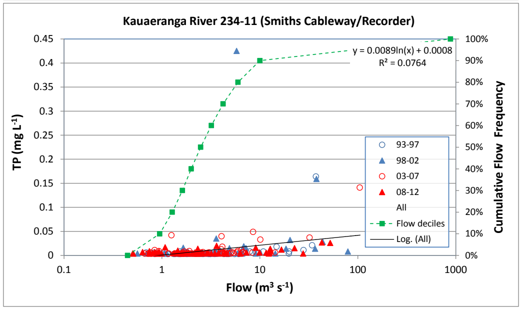
The final chart on the bottom line, shows the frequency of the raw stream flow data plotted against the day of the year, as well as the frequency of the regularised stream flow data. At some sites this shows the greater frequency of raw stream flow data in the winter. Periods of missing data are also identified as those where the frequency is lower than expected.

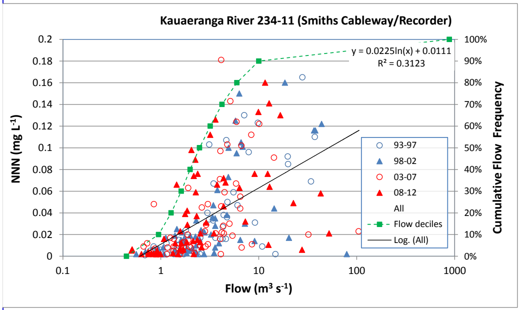
The regression statistics for each water quality variable are summarised in a small table, including the R^2, slope, and p-values from the chart trendlines, the median concentration, and the slopes and significance of the concentration-discharge relationships for each 5-year period.

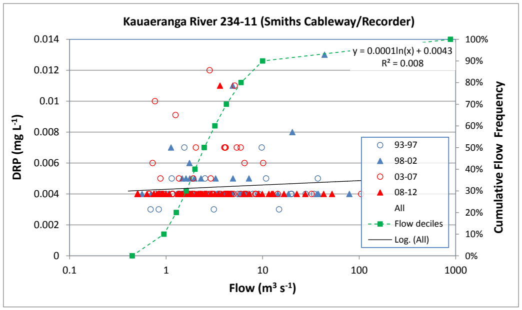


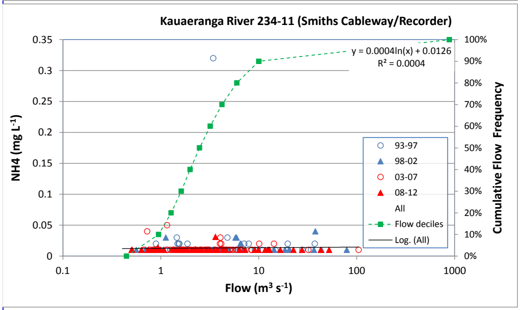


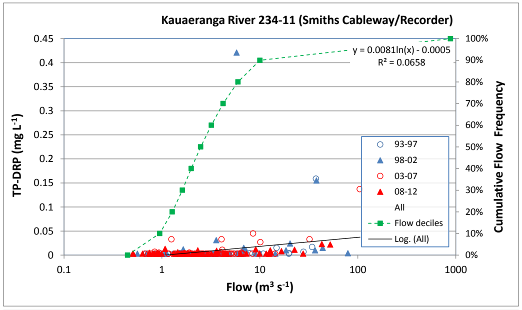


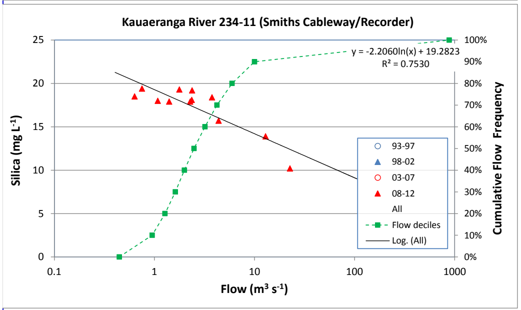


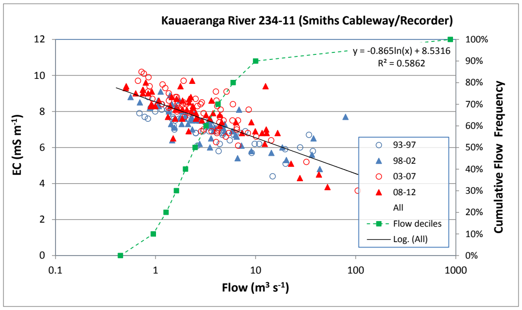










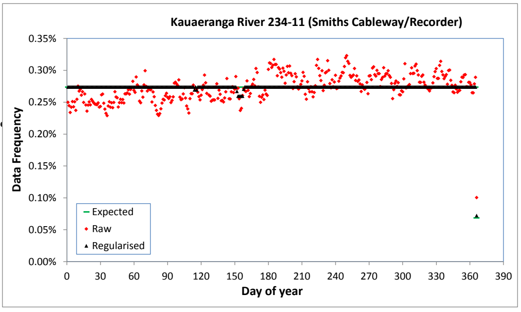


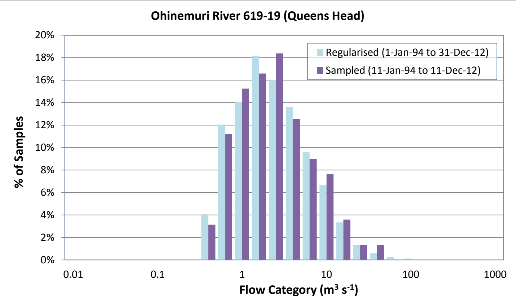
C-D relationship for the 20 year period, highlighted if significant.

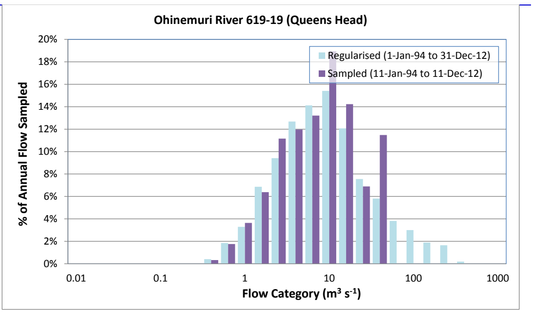
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	228	12	228	228	228	228	228	228
MEDIAN	0.02	18.05	0.01	0.00	0.00	0.00	0.11	7.60
RSQ	31%	75%	0%	1%	8%	7%	43%	59%
SLOPE	0.023	-2.206	0.000	0.000	0.009	0.008	0.060	-0.865
P-VALUE	0.000	0.000	0.754	0.179	0.000	0.000	0.000	0.000

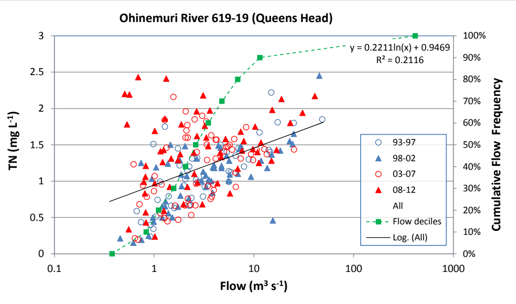
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

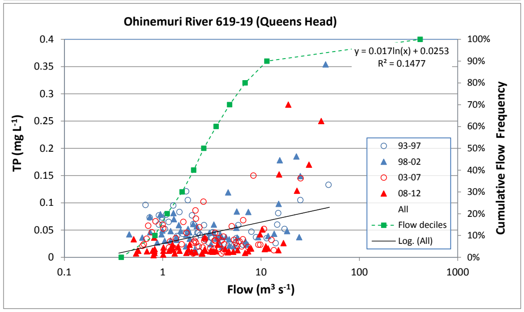
93-97	0.028		0.000	0.000	0.009	0.009	0.068	-0.694
98-02	0.025		0.001	0.000	0.013	0.011	0.048	-0.670
03-07	0.019		-0.001	0.000	0.013	0.012	0.074	**-1.113**
08-12	0.020	-2.206	0.000	0.000	**0.002**	**0.002**	0.059	-0.918

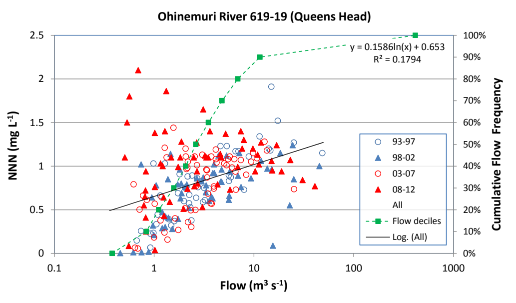


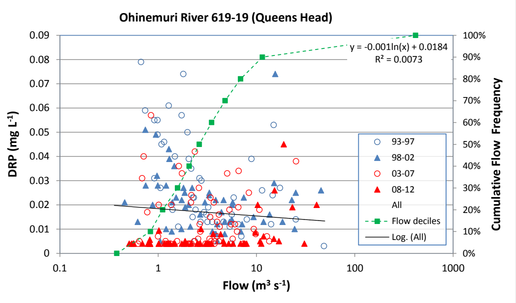


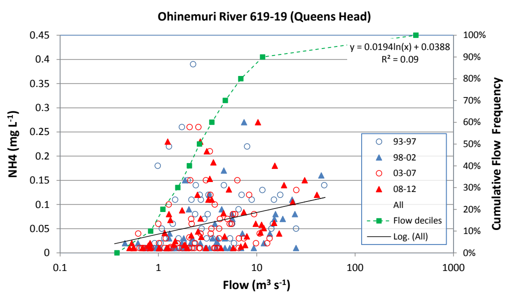


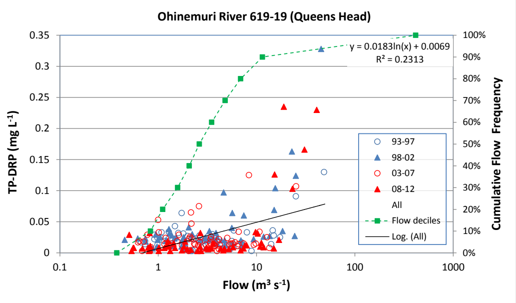


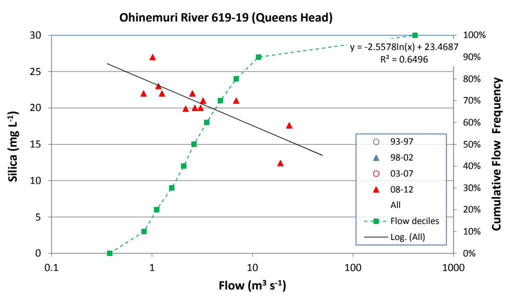


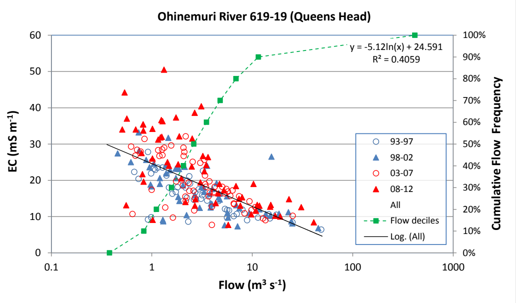










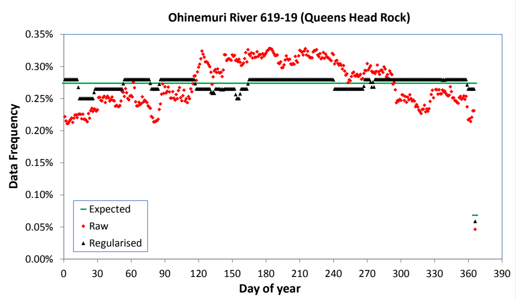


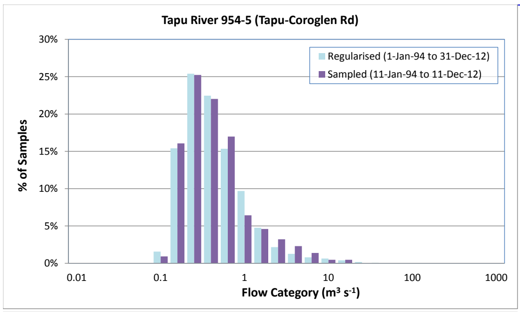
C-D relationship for the 20 year period, highlighted if significant.

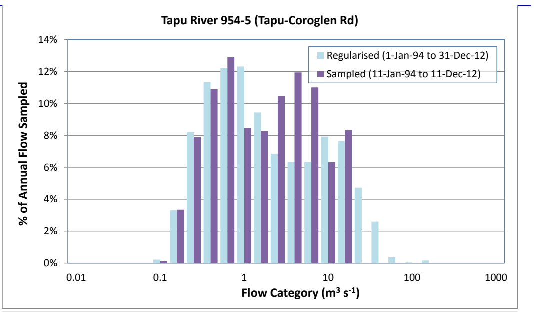
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	223	12	223	223	223	223	223	223
MEDIAN	0.86	21.00	0.03	0.01	0.03	0.02	1.22	17.20
RSQ	18%	65%	9%	1%	15%	23%	21%	41%
SLOPE	0.159	-2.558	0.019	-0.001	0.017	0.018	0.221	-5.120
P-VALUE	0.000	0.002	0.000	0.204	0.000	0.000	0.000	0.000

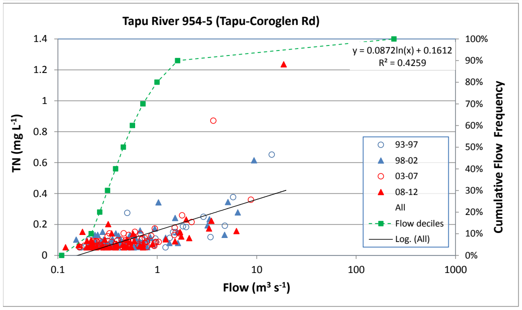
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

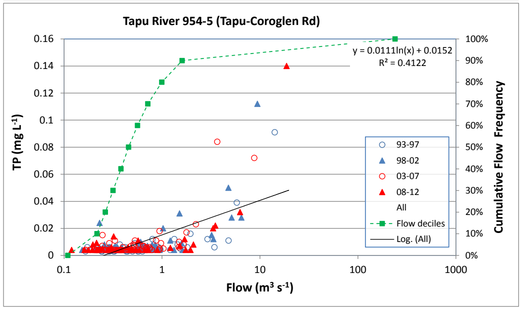
93-97	0.308		0.012	-0.010	-0.002	0.008	0.323	-3.913
98-02	**0.170**		0.021	**-0.001**	**0.025**	**0.026**	0.275	-4.231
03-07	0.217		0.016	-0.001	**0.006**	**0.006**	0.230	-5.146
08-12	**0.040**	-2.558	0.025	0.003	**0.027**	**0.024**	0.128	-6.284

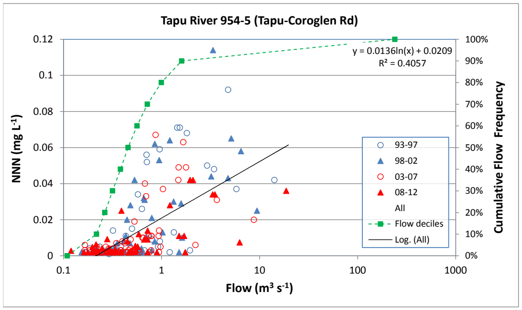


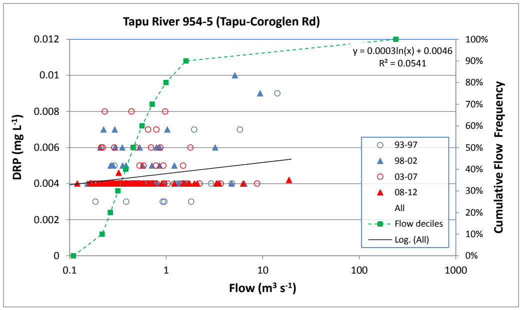


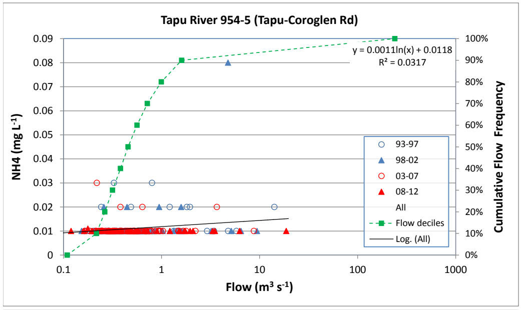


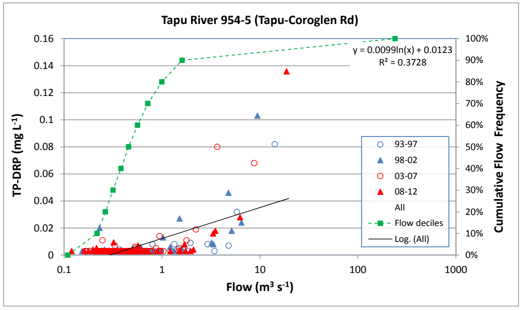


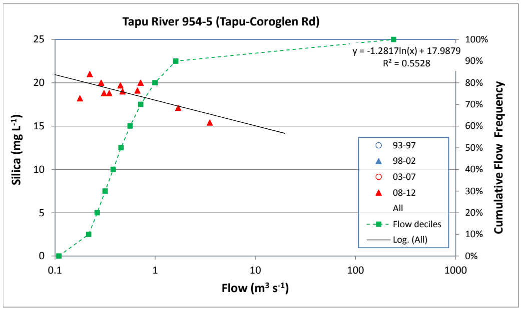


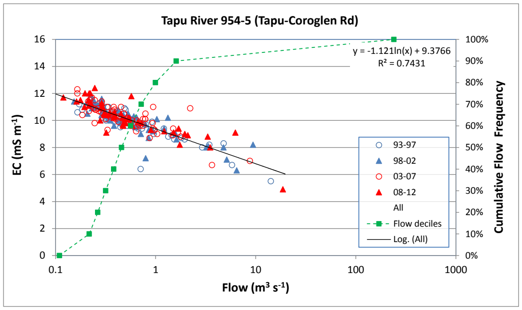










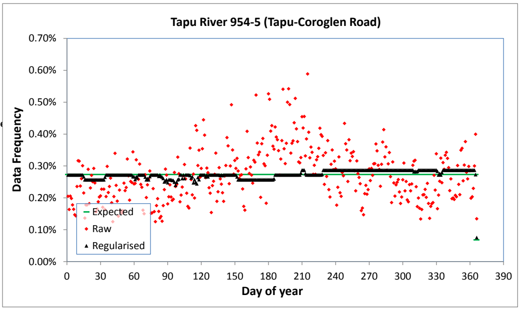


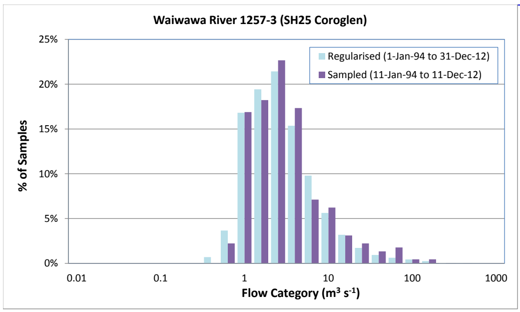
C-D relationship for the 20 year period, highlighted if significant.

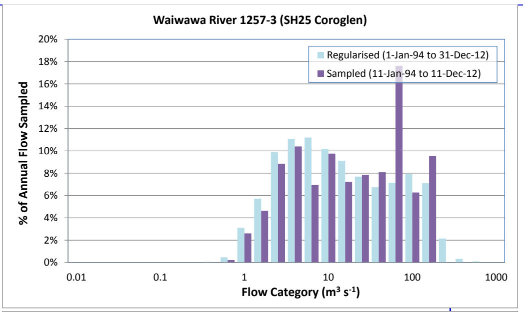
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	218	11	218	218	218	218	218	218
MEDIAN	0.00	19.00	0.01	0.00	0.00	0.00	0.08	10.10
RSQ	41%	55%	3%	5%	41%	37%	43%	74%
SLOPE	0.014	-1.282	0.001	0.000	0.011	0.010	0.087	-1.121
P-VALUE	0.000	0.009	0.008	0.001	0.000	0.000	0.000	0.000

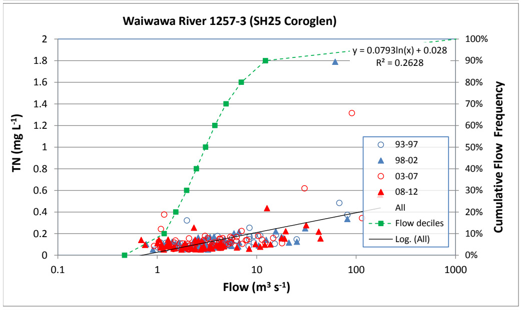
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

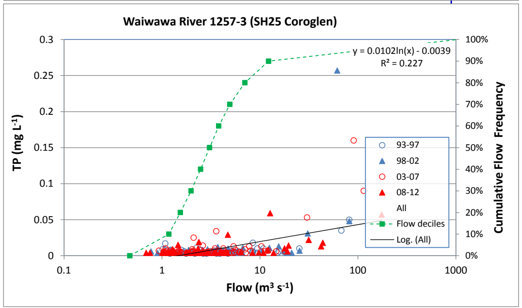
93-97	0.017		0.001	0.001	0.009	0.008	0.081	-1.169
98-02	0.017		0.003	0.000	0.011	0.010	0.071	-1.106
03-07	0.012		**0.000**	0.000	0.012	0.011	0.094	-1.049
08-12	0.008	-1.282	0.000	0.000	0.013	0.012	0.106	-1.114

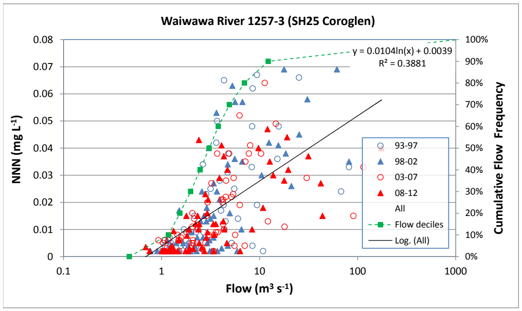


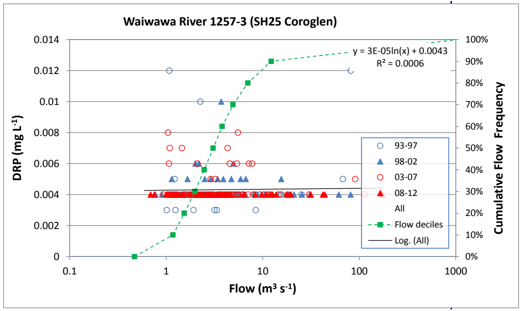


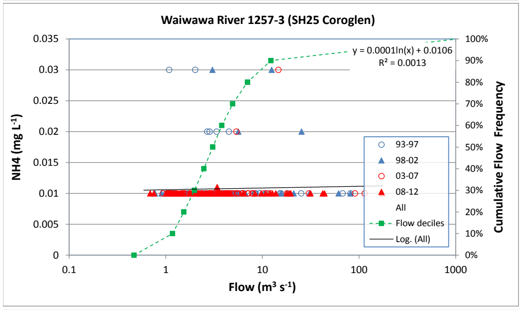


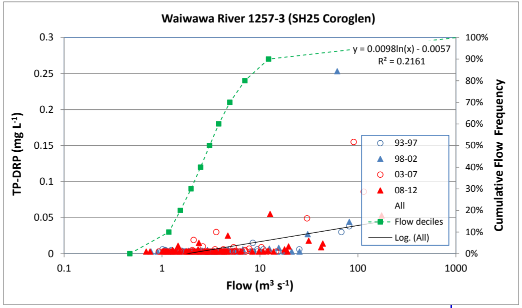


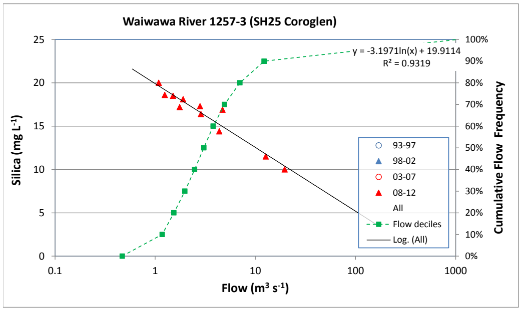


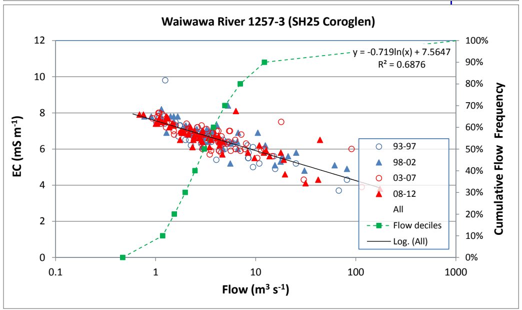










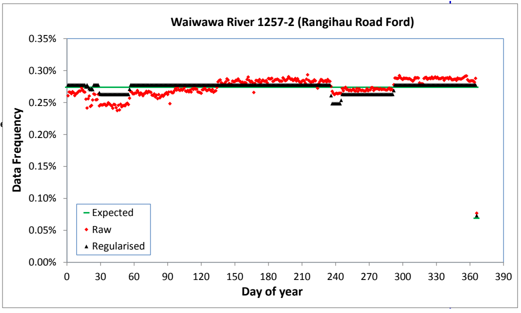


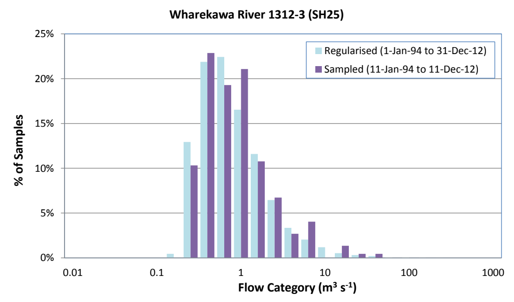
C-D relationship for the 20 year period, highlighted if significant.

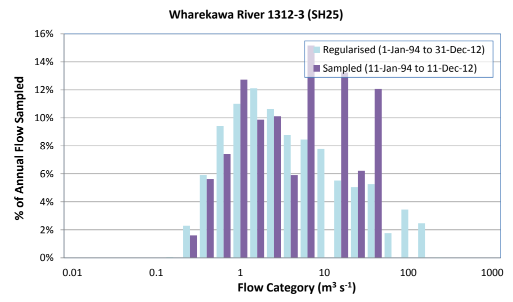
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	225	11	225	225	225	225	225	225
MEDIAN	0.01	17.20	0.01	0.00	0.01	0.00	0.10	6.70
RSQ	39%	93%	0%	0%	23%	22%	26%	69%
SLOPE	0.010	-3.197	0.000	0.000	0.010	0.010	0.079	-0.719
P-VALUE	0.000	0.000	0.585	0.723	0.000	0.000	0.000	0.000

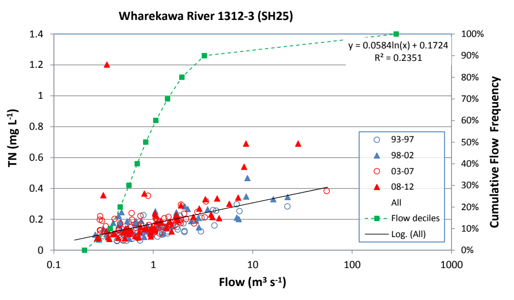
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

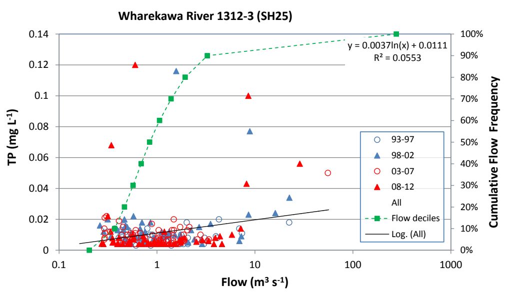
93-97	0.011		-0.001	0.000	0.005	0.004	0.059	-0.904
98-02	0.014		0.001	0.000	**0.016**	**0.016**	0.113	**-0.681**
03-07	**0.008**		0.001	0.000	0.015	0.015	0.103	-0.623
08-12	0.009	-3.197	0.000	0.000	**0.005**	**0.005**	**0.047**	-0.709

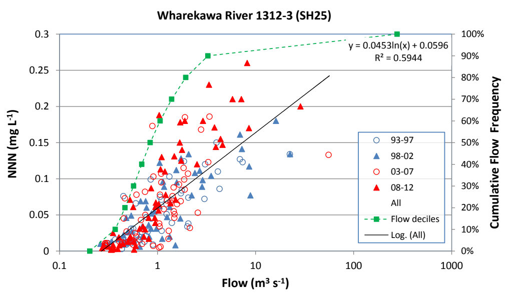


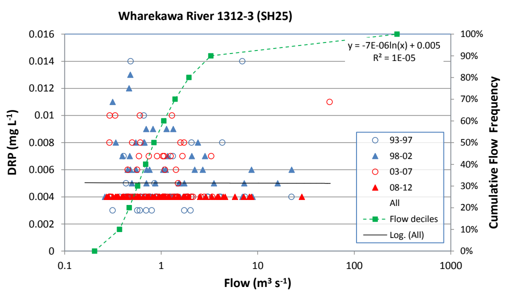


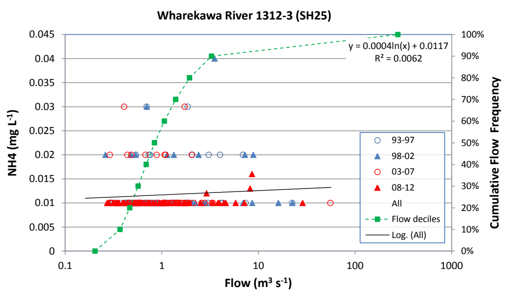


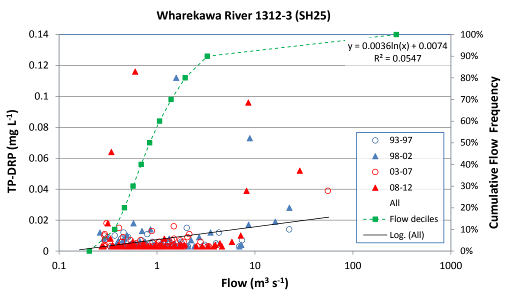


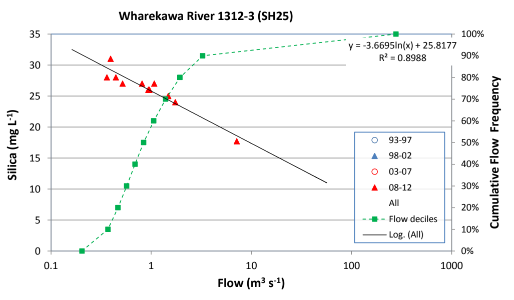


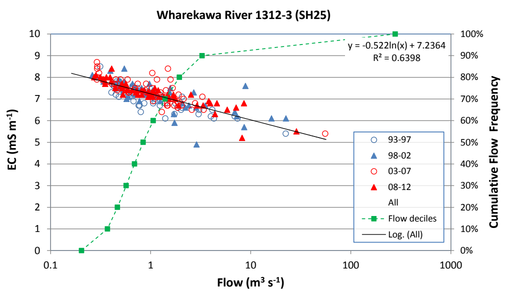










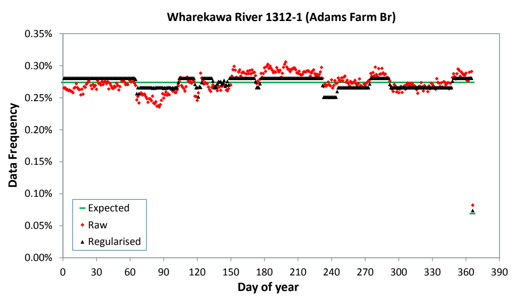


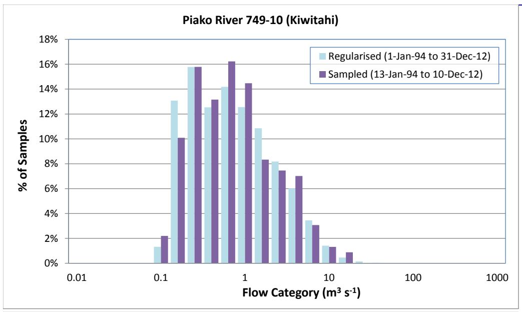
C-D relationship for the 20 year period, highlighted if significant.

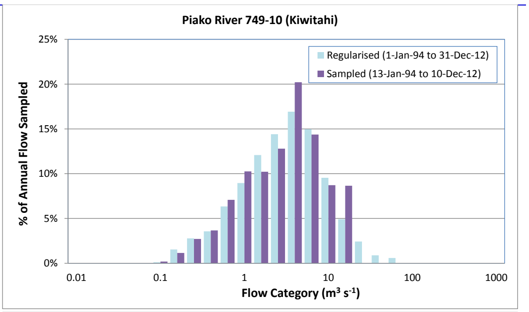
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	223	12	223	223	223	223	223	223
MEDIAN	0.05	26.50	0.01	0.00	0.01	0.00	0.15	7.20
RSQ	59%	90%	1%	0%	6%	5%	24%	64%
SLOPE	0.045	-3.670	0.000	0.000	0.004	0.004	0.058	-0.522
P-VALUE	0.000	0.000	0.243	0.960	0.000	0.000	0.000	0.000

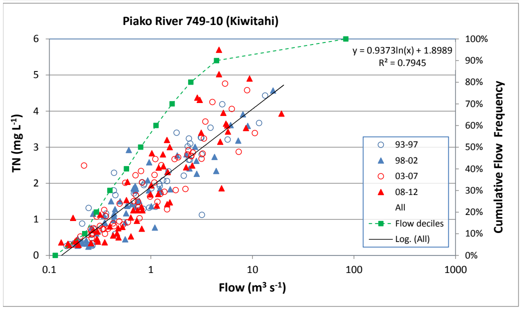
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

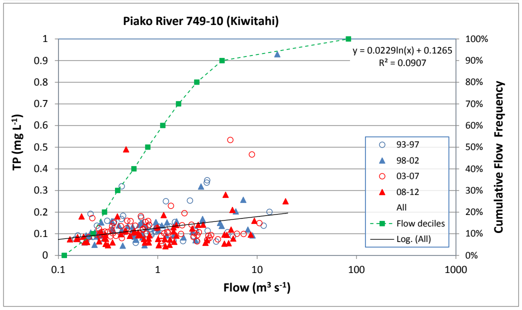
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.037		0.001	0.000	0.001	0.000	0.052	-0.539
98-02	0.038		0.001	0.000	0.005	**0.005**	0.054	-0.500
03-07	0.037		-0.001	0.000	0.003	0.003	0.040	-0.537
08-12	**0.064**	-3.670	0.000	0.000	0.005	0.005	0.082	-0.507

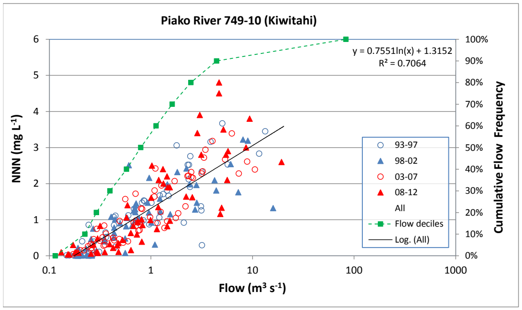


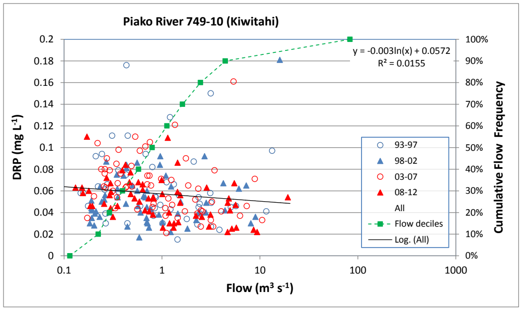


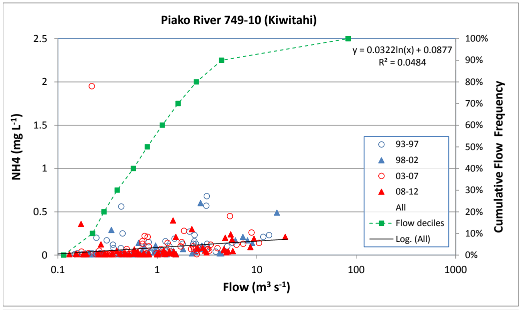


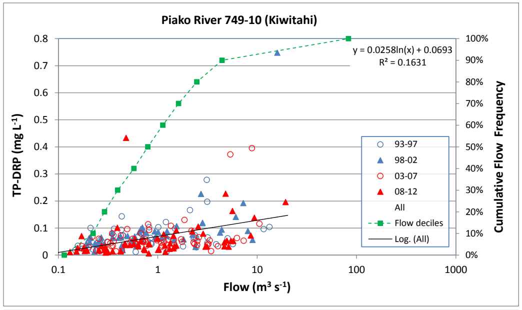


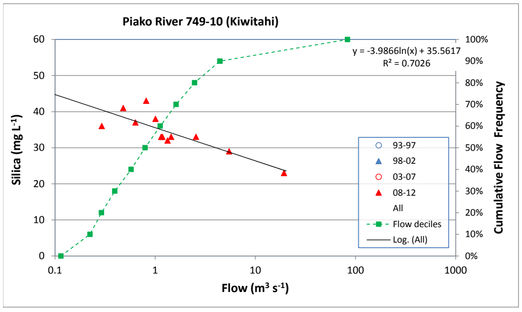


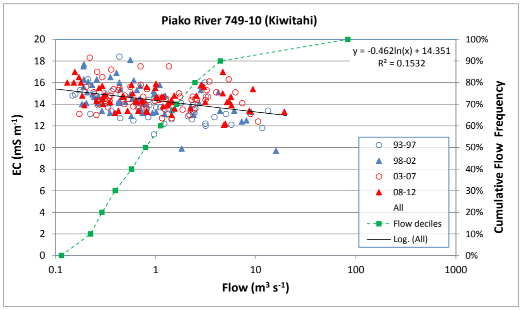










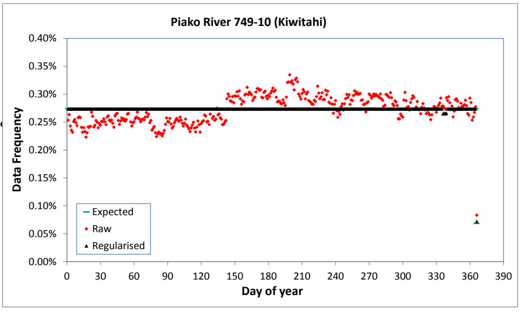


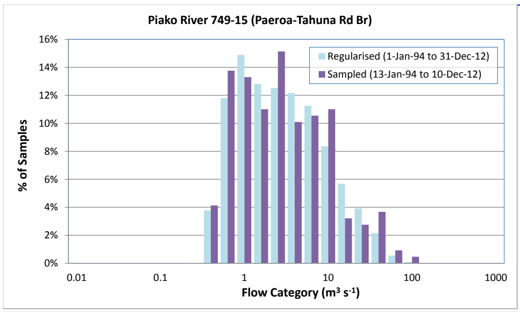
C-D relationship for the 20 year period, highlighted if significant.

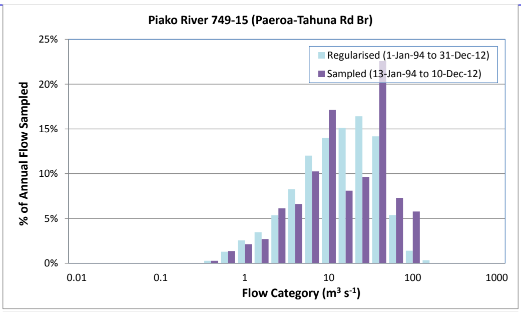
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	228	12	228	228	228	228	228	228
MEDIAN	1.01	33.00	0.03	0.05	0.11	0.05	1.52	14.30
RSQ	71%	70%	5%	2%	9%	16%	79%	15%
SLOPE	0.755	-3.987	0.032	-0.003	0.023	0.026	0.937	-0.462
P-VALUE	0.000	0.001	0.001	0.061	0.000	0.000	0.000	0.000

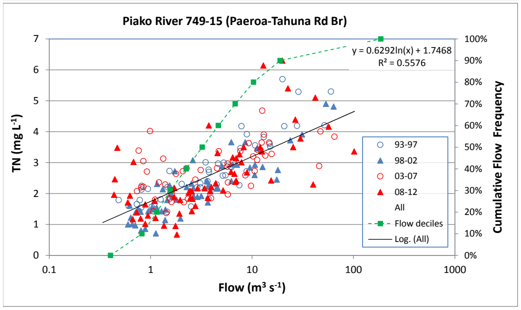
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

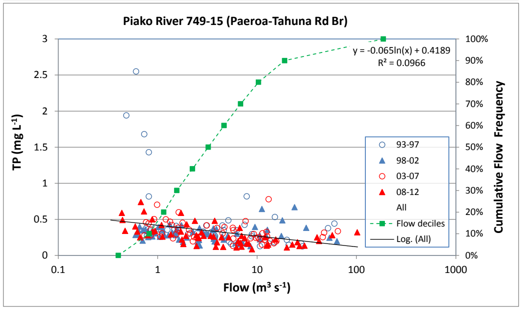
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.744		0.046	-0.005	0.008	0.013	0.882	-0.558
98-02	0.618		0.051	0.005	**0.053**	**0.047**	0.857	-0.775
03-07	**0.767**		0.001	**-0.006**	**0.021**	0.027	0.930	**-0.250**
08-12	0.862	-3.987	0.028	-0.007	0.011	0.018	1.043	-0.280

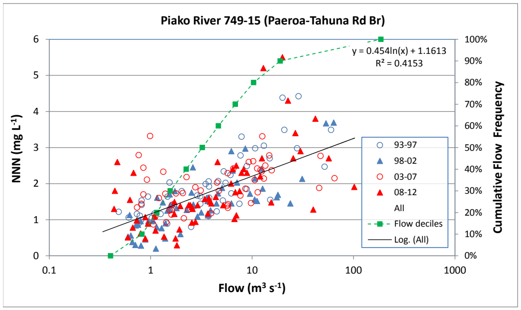


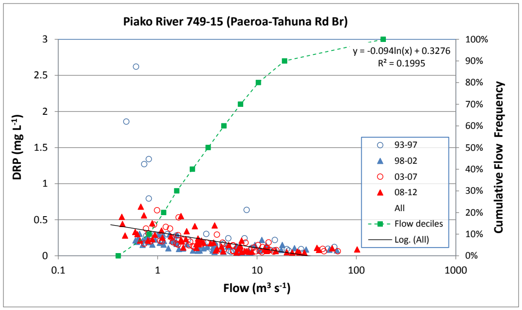


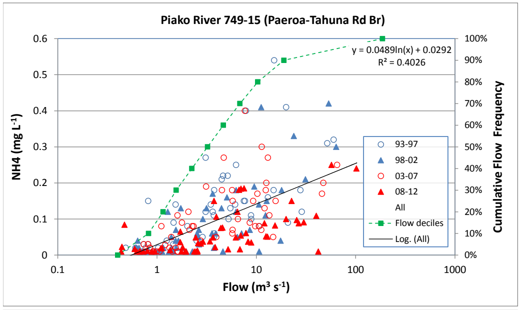


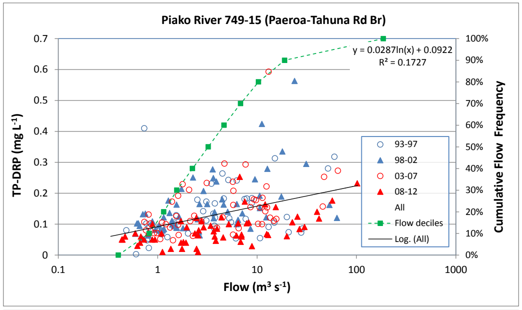


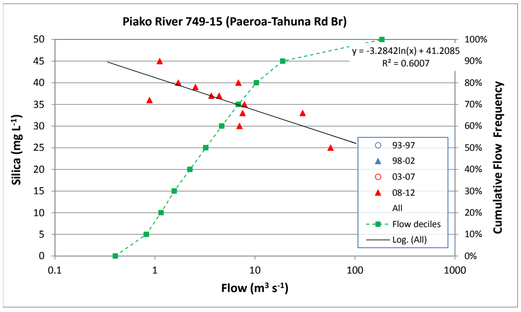


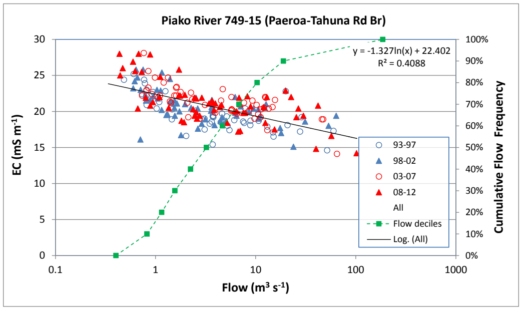










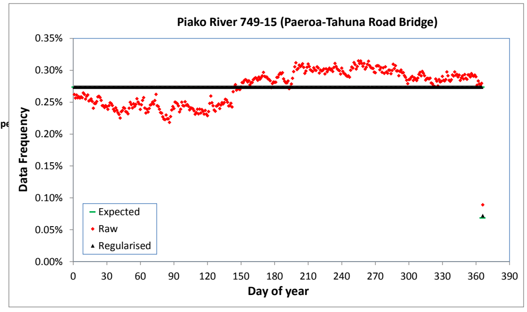


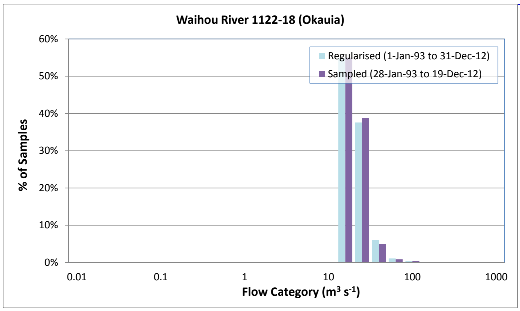
C-D relationship for the 20 year period, highlighted if significant.

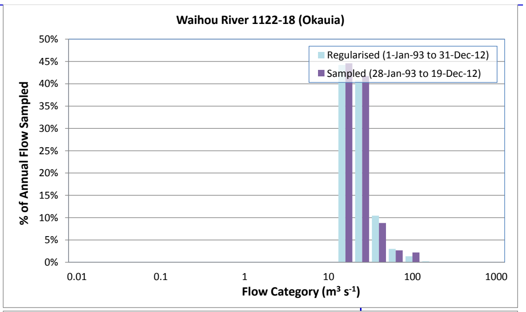
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	218	12	218	218	218	218	218	218
MEDIAN	1.57	36.50	0.06	0.15	0.29	0.11	2.33	20.50
RSQ	42%	60%	40%	20%	10%	17%	56%	41%
SLOPE	0.454	-3.284	0.049	-0.094	-0.065	0.029	0.629	-1.327
P-VALUE	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000

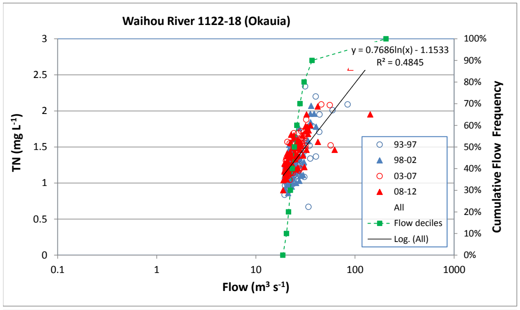
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

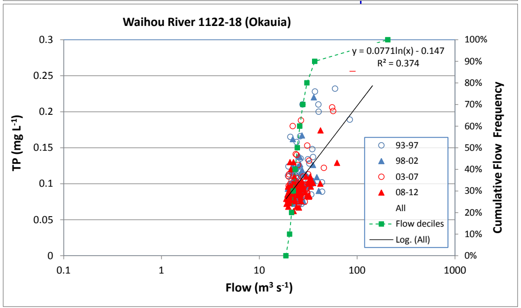
93-97	0.562		0.062	-0.215	-0.190	0.023	0.759	-1.388
98-02	0.493		0.061	**-0.039**	**0.005**	0.044	0.700	-1.123
03-07	**0.198**		0.050	**-0.072**	**-0.038**	0.034	**0.368**	-1.352
08-12	**0.483**	-3.284	**0.029**	-0.081	-0.060	0.021	**0.620**	-1.505

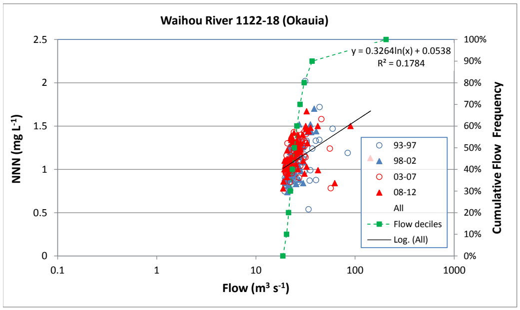


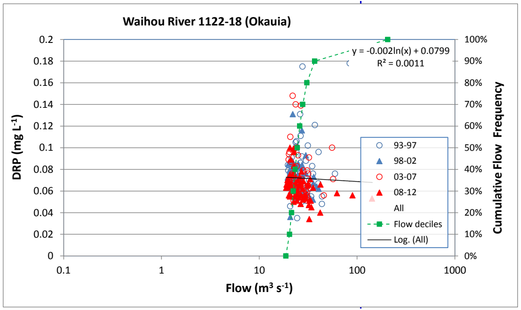


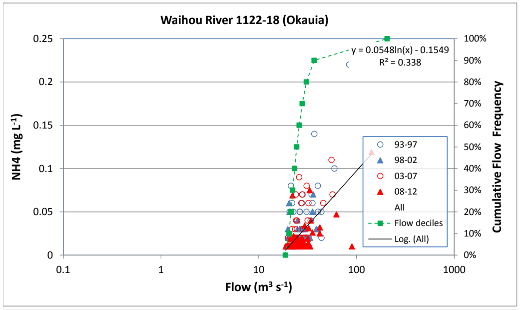


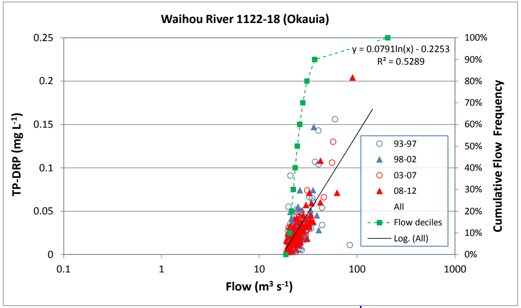


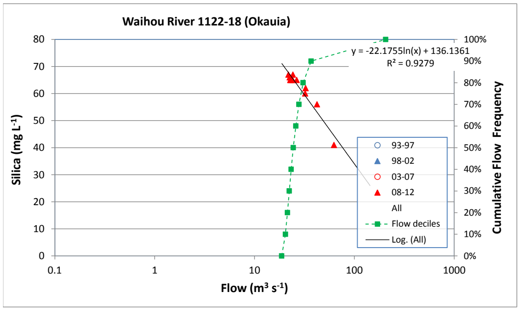


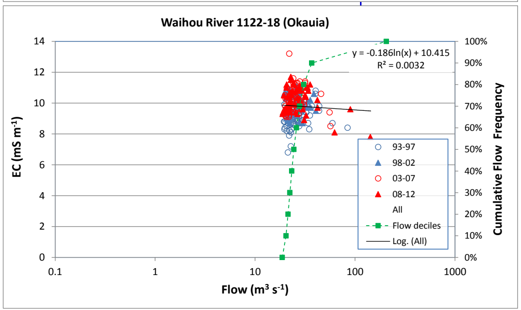










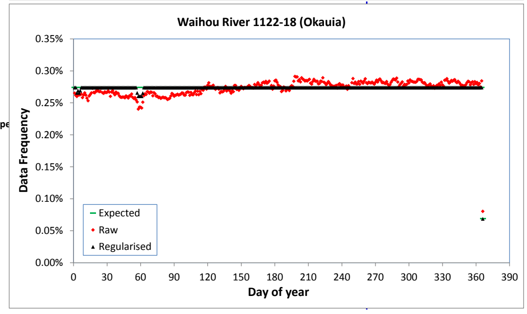


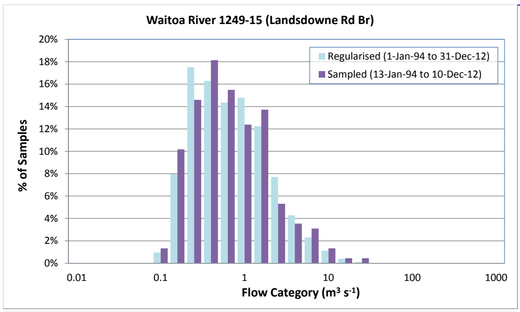
C-D relationship for the 20 year period, highlighted if significant.

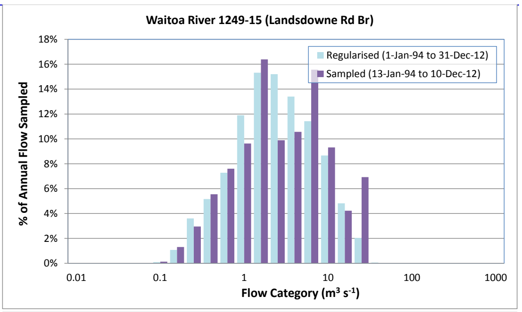
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	240	12	240	240	240	240	240	240
MEDIAN	1.09	65.00	0.01	0.07	0.10	0.03	1.29	9.75
RSQ	18%	93%	34%	0%	37%	53%	48%	0%
SLOPE	0.326	-22.175	0.055	-0.002	0.077	0.079	0.769	-0.186
P-VALUE	0.000	0.000	0.000	0.615	0.000	0.000	0.000	0.383

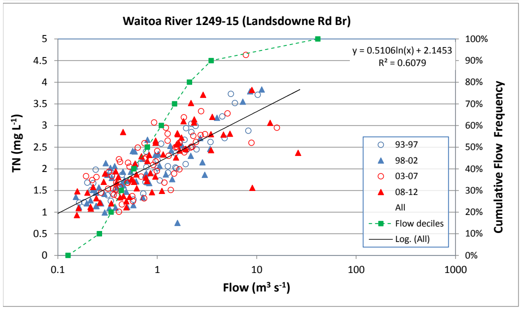
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

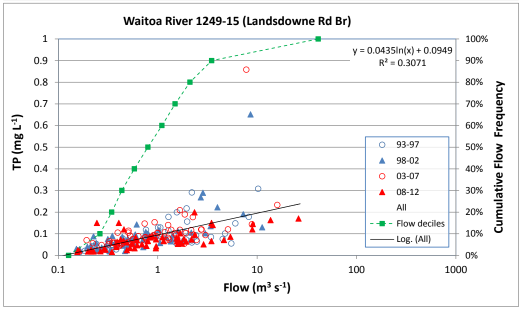
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.421		0.093	0.024	0.078	0.054	0.906	0.784
98-02	**0.859**		**0.027**	**-0.017**	0.045	0.062	1.182	0.090
03-07	**0.298**		**0.066**	-0.008	0.075	0.081	**0.820**	0.025
08-12	0.165	-22.175	**0.033**	-0.013	0.084	0.097	0.586	-0.595

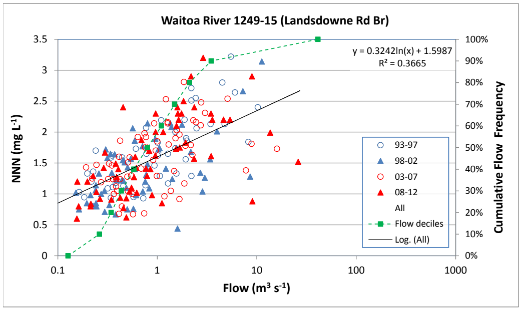


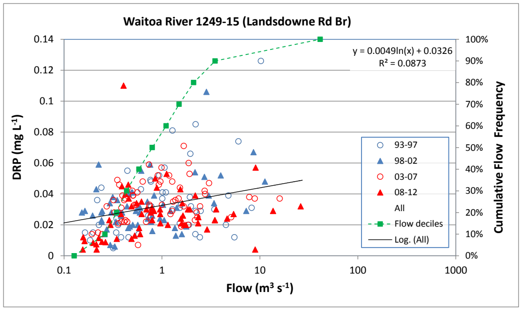


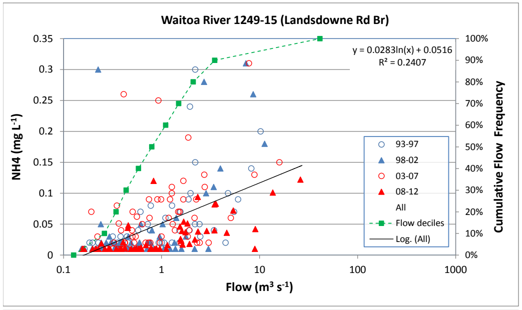


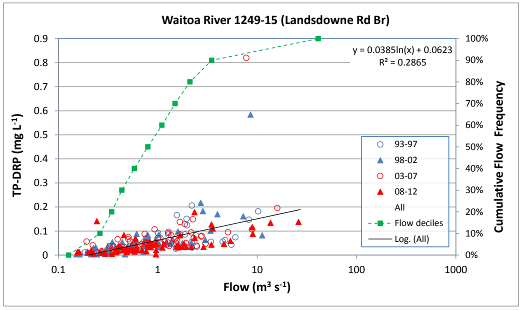


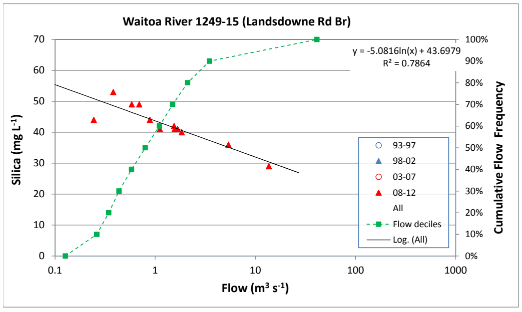


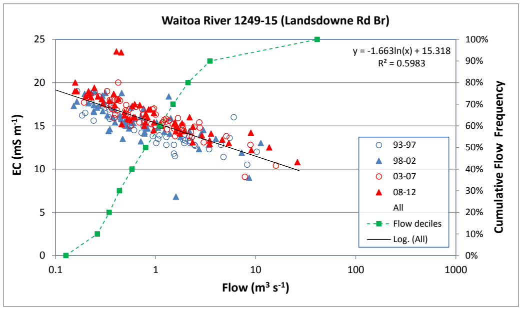










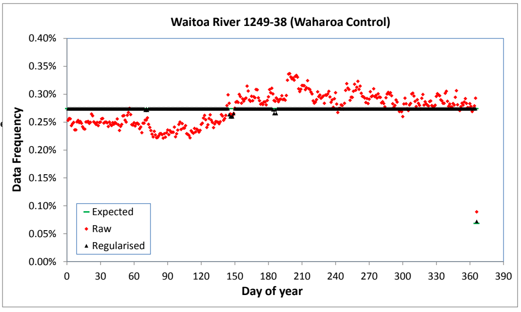


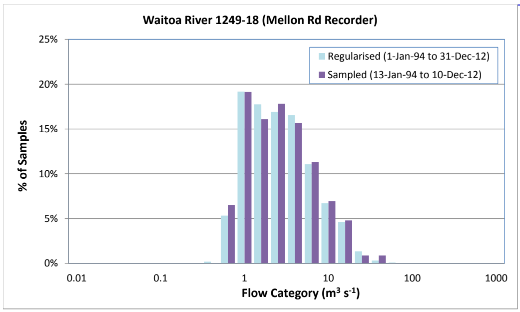
C-D relationship for the 20 year period, highlighted if significant.

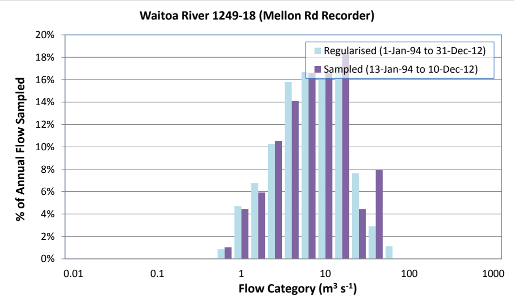
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	226	12	226	226	226	226	226	226
MEDIAN	1.49	41.50	0.02	0.03	0.07	0.04	1.95	15.40
RSQ	37%	79%	24%	9%	31%	29%	61%	60%
SLOPE	0.324	-5.082	0.028	0.005	0.044	0.038	0.511	-1.663
P-VALUE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

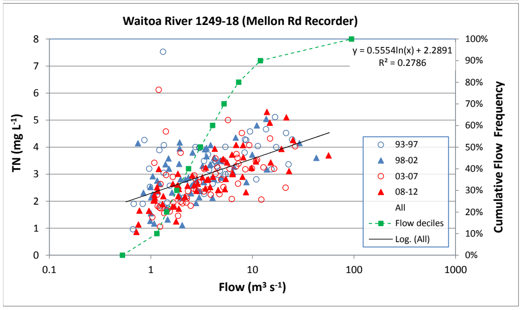
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

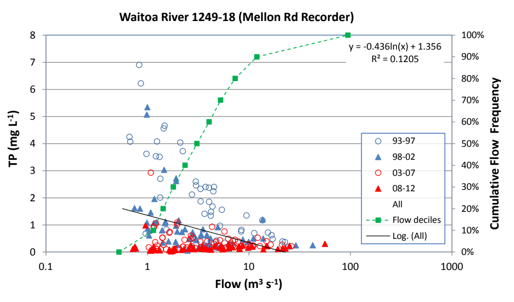
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.383		0.032	0.009	0.038	0.029	0.537	-1.498
98-02	0.287		0.041	0.006	**0.063**	**0.056**	0.520	-1.641
03-07	0.265		0.030	0.003	0.061	0.058	0.517	-1.831
08-12	0.323	-5.082	0.016	0.003	**0.024**	**0.022**	0.464	-1.755

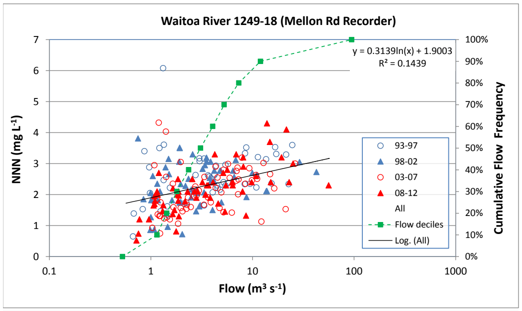


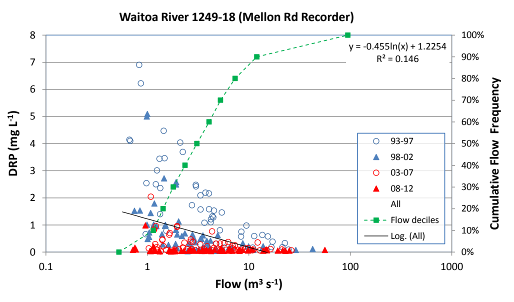


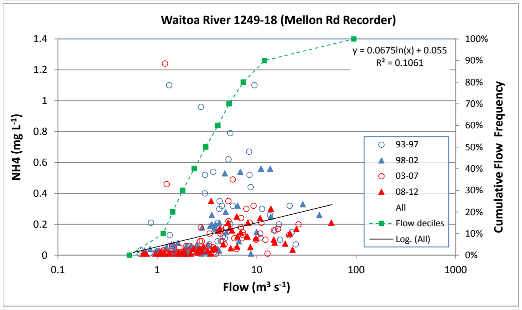


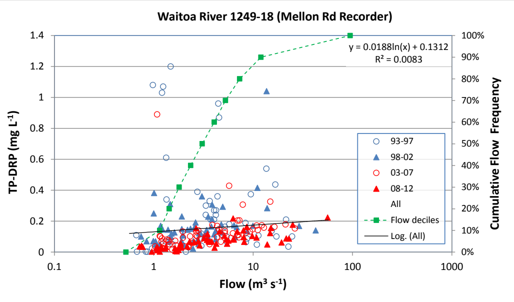


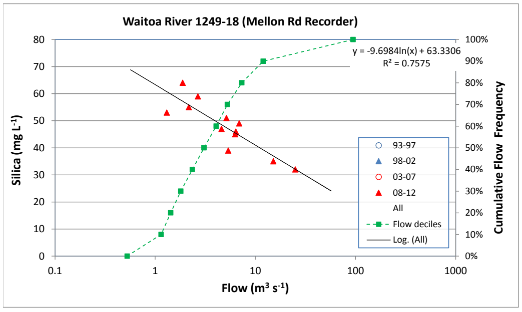


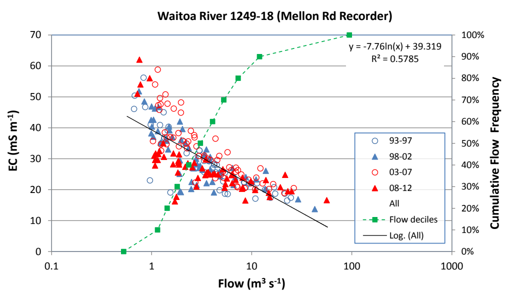










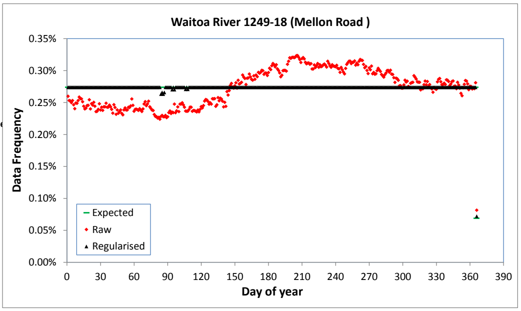


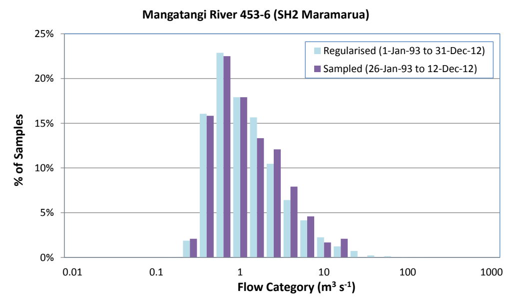
C-D relationship for the 20 year period, highlighted if significant.

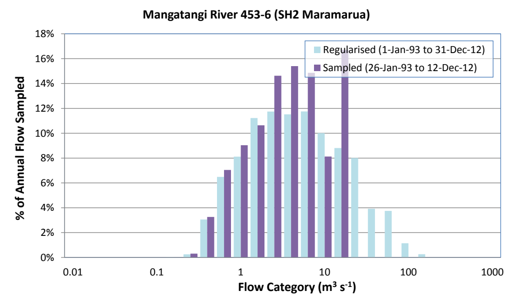
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	228	12	228	228	228	228	228	230
MEDIAN	2.30	48.00	0.06	0.18	0.36	0.10	2.89	27.80
RSQ	14%	76%	11%	15%	12%	1%	28%	58%
SLOPE	0.314	-9.698	0.067	-0.455	-0.436	0.019	0.555	-7.760
P-VALUE	0.000	0.000	0.000	0.000	0.000	0.171	0.000	0.000

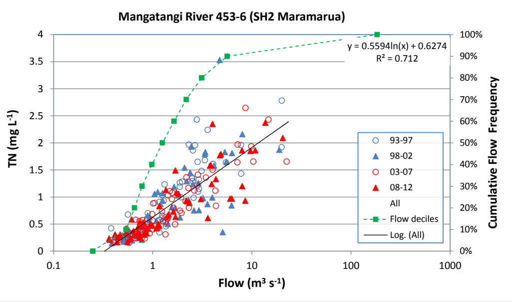
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

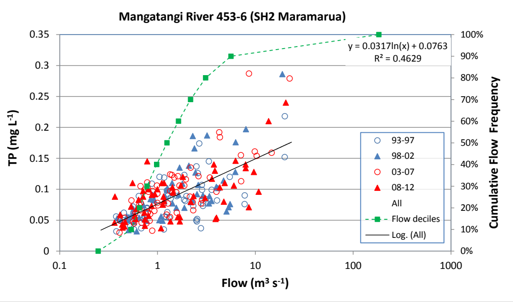
93-97	0.243		0.069	-1.218	-1.275	-0.059	0.453	-8.287
98-02	0.215		0.115	**-0.591**	**-0.530**	**0.061**	0.545	-8.056
03-07	0.257		**0.030**	**-0.171**	**-0.140**	0.031	0.465	-9.465
08-12	0.487	-9.698	0.052	**-0.020**	**0.017**	0.037	0.712	**-5.985**

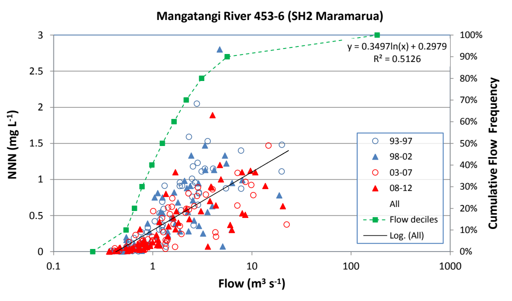


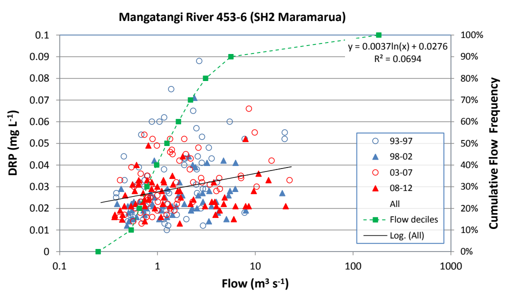


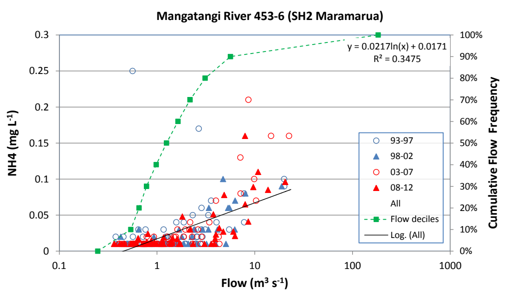


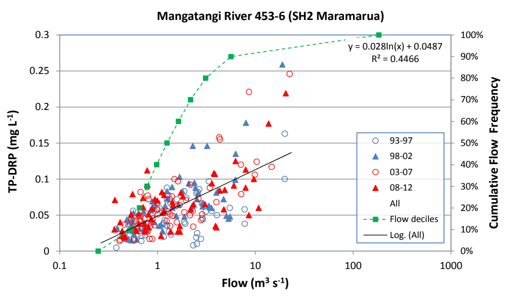


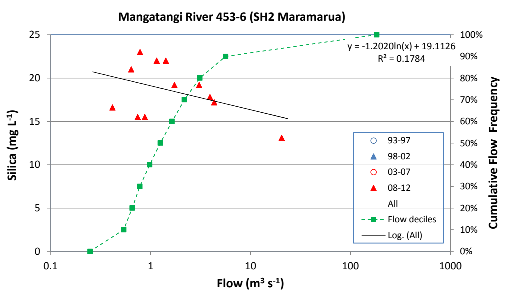


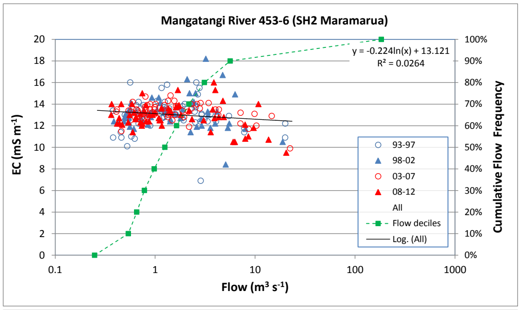










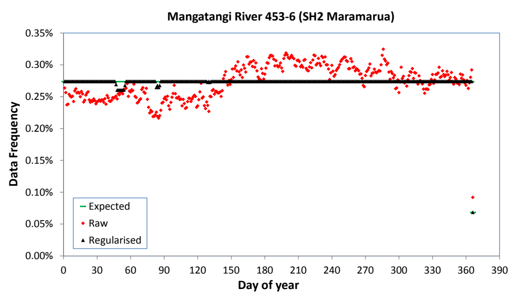


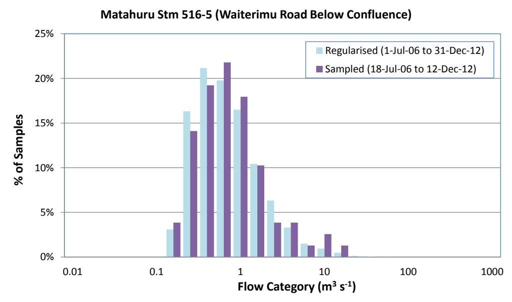
C-D relationship for the 20 year period, highlighted if significant.

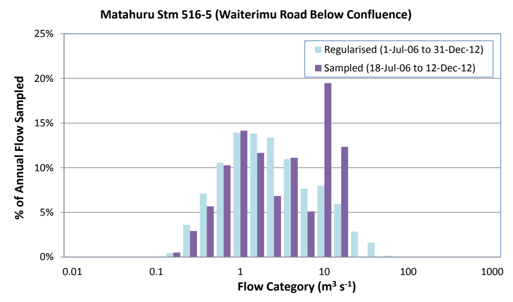
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	240	12	240	240	240	240	240	240
MEDIAN	0.29	18.50	0.01	0.03	0.08	0.05	0.66	13.10
RSQ	51%	18%	35%	7%	46%	45%	71%	3%
SLOPE	0.350	-1.202	0.022	0.004	0.032	0.028	0.559	-0.224
P-VALUE	0.000	0.171	0.000	0.000	0.000	0.000	0.000	0.012

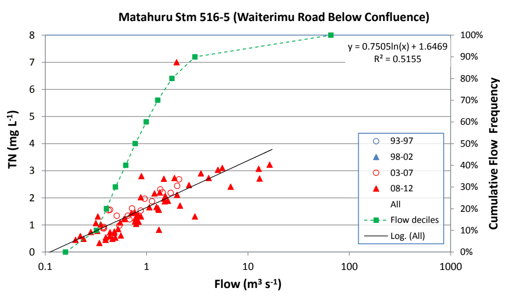
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

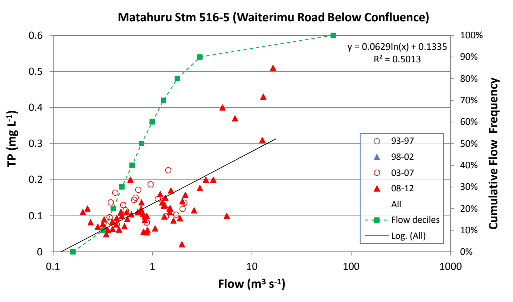
93-97	0.464		0.014	0.007	0.025	0.018	0.641	-0.083
98-02	0.379		0.016	0.003	0.037	**0.033**	0.561	-0.114
03-07	0.288		**0.036**	0.005	0.042	0.037	0.558	-0.297
08-12	0.297	-1.202	**0.021**	**0.001**	**0.024**	**0.024**	0.503	-0.346

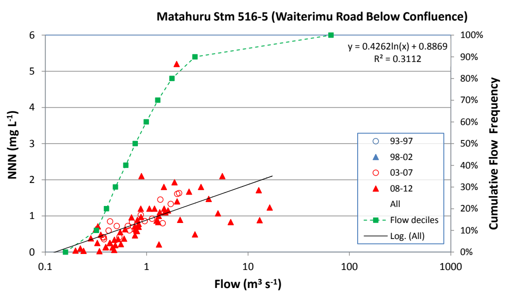


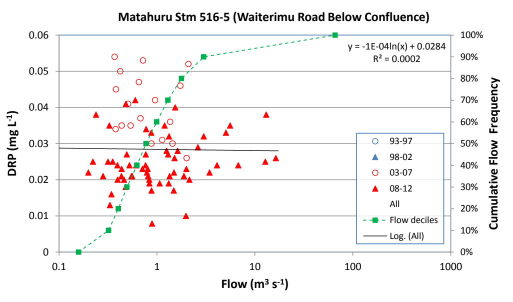


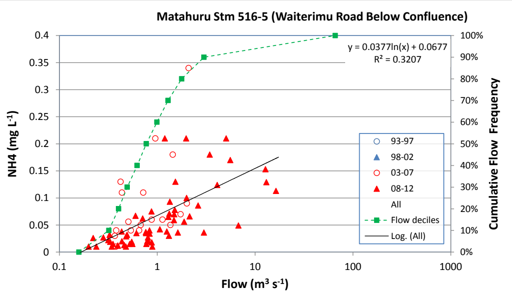


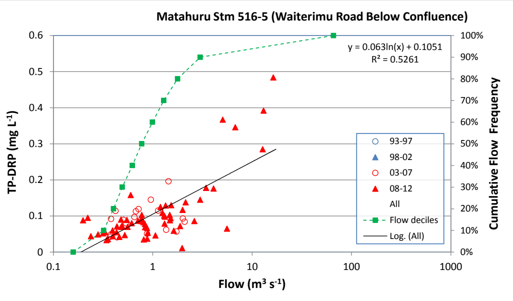


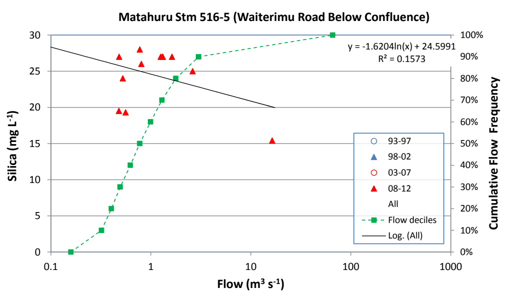


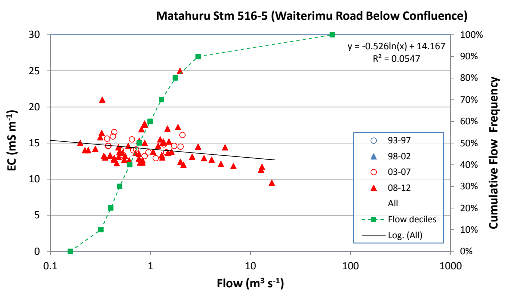










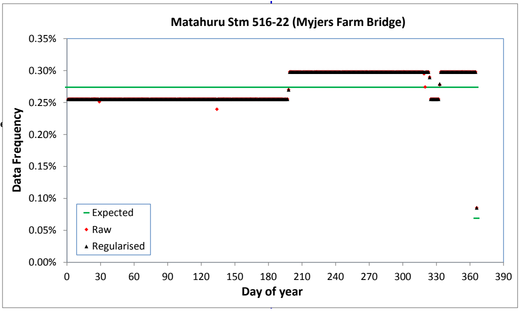


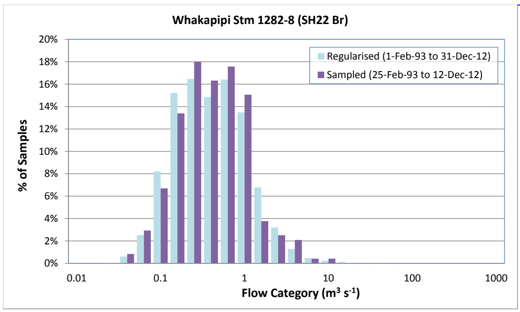
C-D relationship for the 20 year period, highlighted if significant.

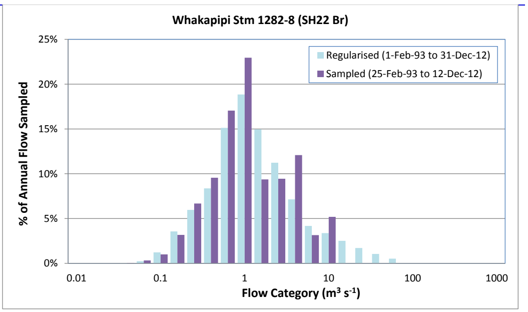
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	78	12	78	78	78	78	78	78
MEDIAN	0.79	26.50	0.04	0.03	0.11	0.09	1.40	13.80
RSQ	31%	16%	32%	0%	50%	53%	52%	5%
SLOPE	0.426	-1.620	0.038	0.000	0.063	0.063	0.750	-0.526
P-VALUE	0.000	0.202	0.000	0.904	0.000	0.000	0.000	0.039

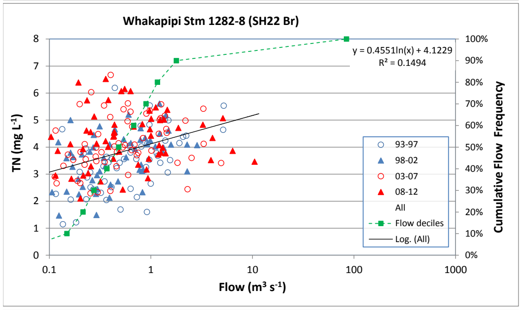
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

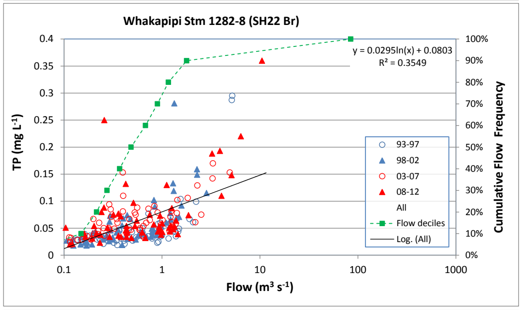
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02								
03-07	0.602		0.069	-0.004	0.015	0.018	0.872	-0.325
08-12	0.415	-1.620	0.037	0.001	**0.069**	**0.068**	0.752	-0.527

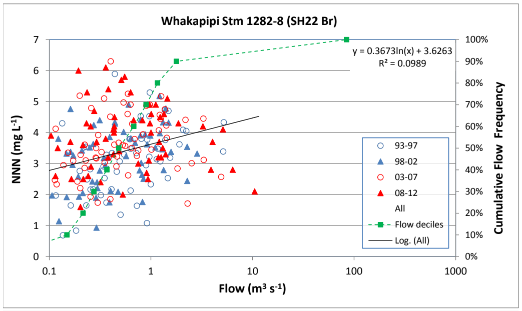


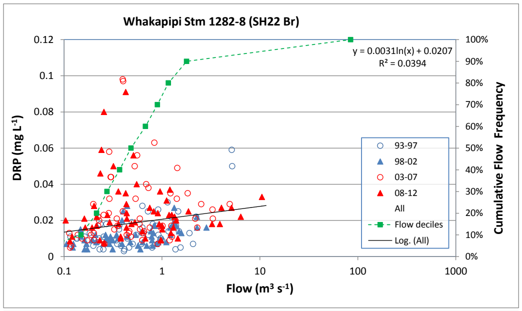


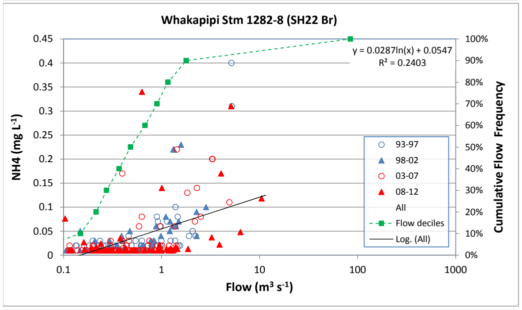


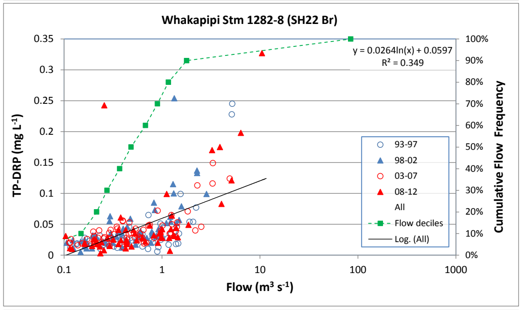


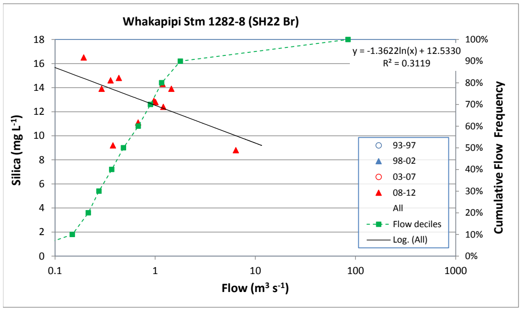


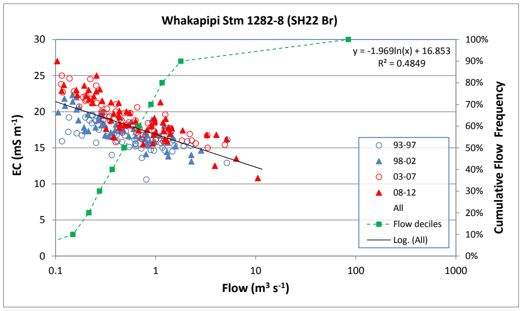










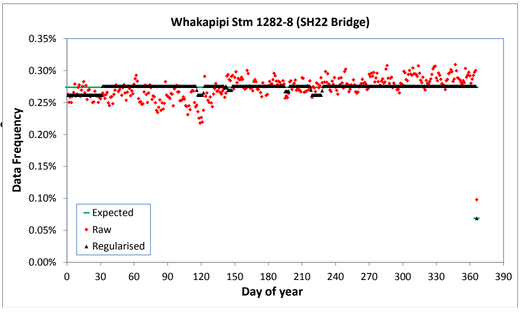


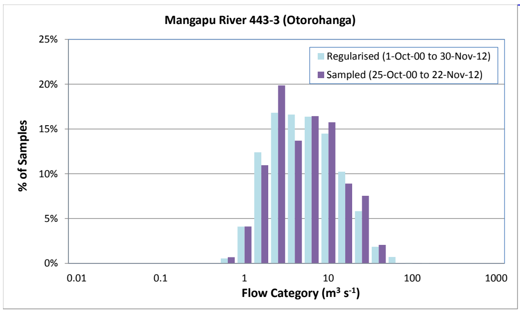
C-D relationship for the 20 year period, highlighted if significant.

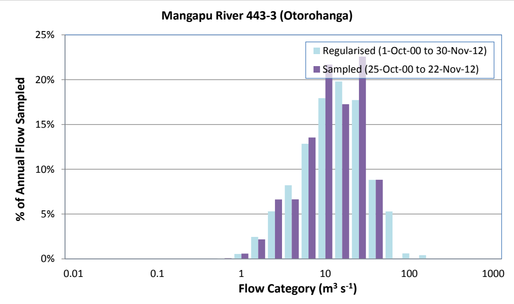
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	239	12	239	239	239	239	239	239
MEDIAN	3.40	13.40	0.02	0.01	0.05	0.03	3.86	17.70
RSQ	10%	31%	24%	4%	35%	35%	15%	48%
SLOPE	0.367	-1.362	0.029	0.003	0.030	0.026	0.455	-1.969
P-VALUE	0.000	0.059	0.000	0.002	0.000	0.000	0.000	0.000

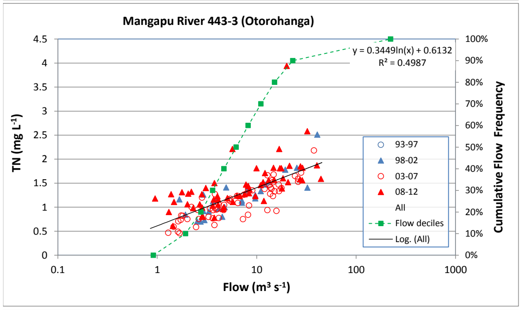
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

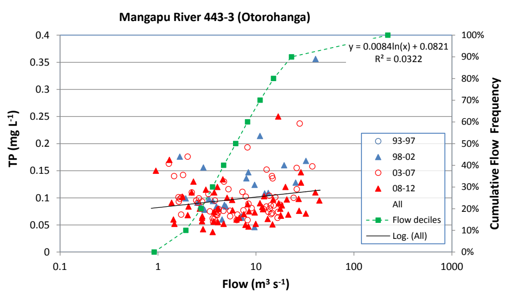
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.661		0.034	0.005	0.027	0.022	0.731	-1.095
98-02	0.481		0.031	0.003	0.032	0.029	0.568	**-2.163**
03-07	0.210		0.035	0.003	0.023	0.021	0.285	-2.361
08-12	0.089	-1.362	0.020	0.000	0.032	0.032	0.195	-2.577

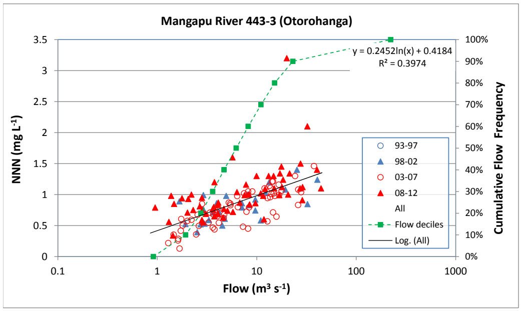


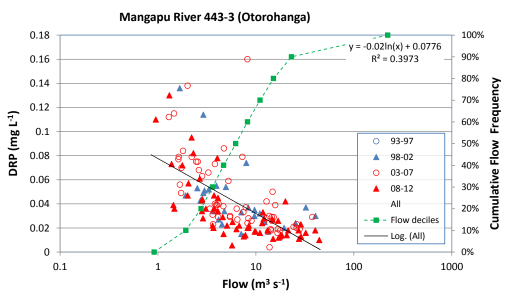


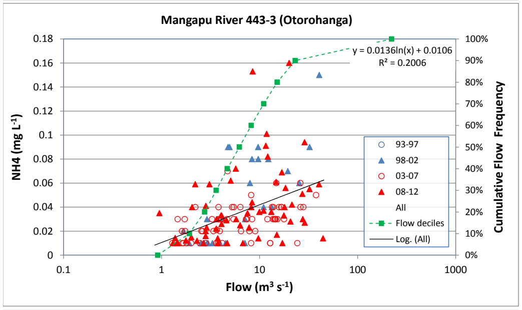


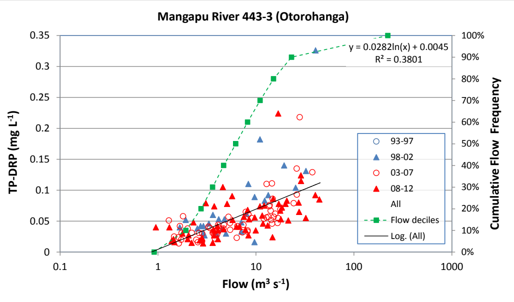


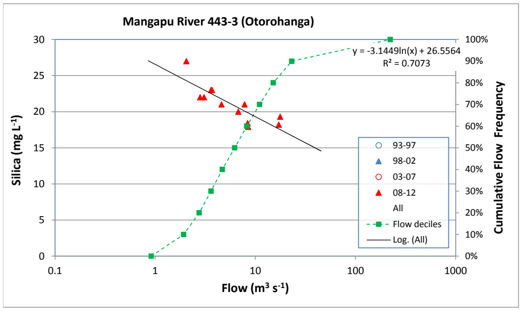


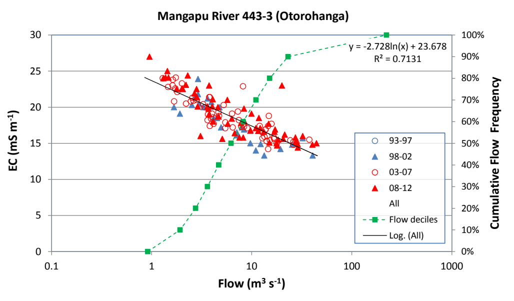










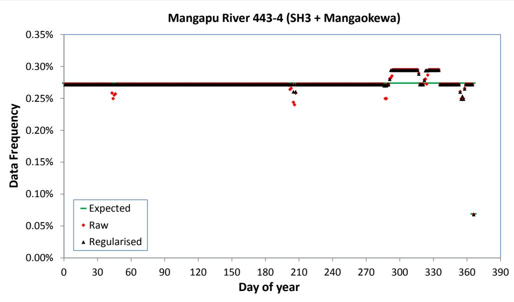


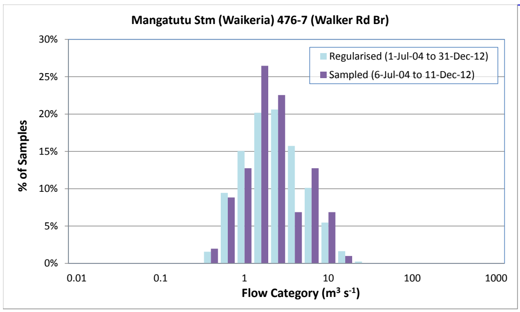
C-D relationship for the 20 year period, highlighted if significant.

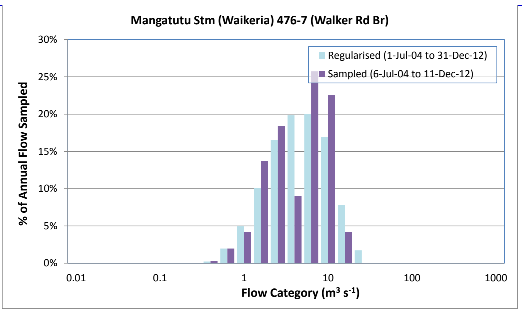
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	146	12	146	146	146	146	146	146
MEDIAN	0.85	21.00	0.03	0.03	0.09	0.05	1.23	18.10
RSQ	40%	71%	20%	40%	3%	38%	50%	71%
SLOPE	0.245	-3.145	0.014	-0.020	0.008	0.028	0.345	-2.728
P-VALUE	0.000	0.001	0.000	0.000	0.030	0.000	0.000	0.000

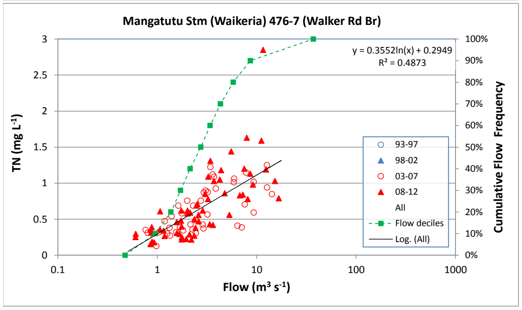
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

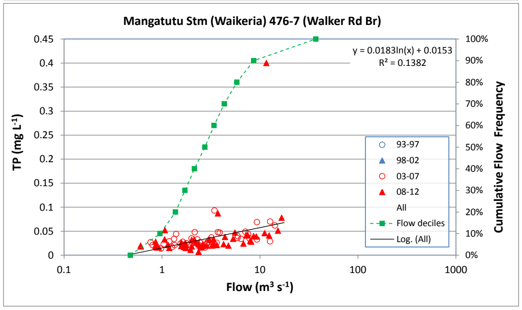
93-97								
98-02	0.192		0.033	-0.017	0.038	0.055	0.379	-2.901
03-07	0.267		**0.007**	-0.022	**0.005**	**0.027**	0.346	-2.665
08-12	0.233	-3.145	0.012	-0.018	0.003	0.021	0.319	-2.754

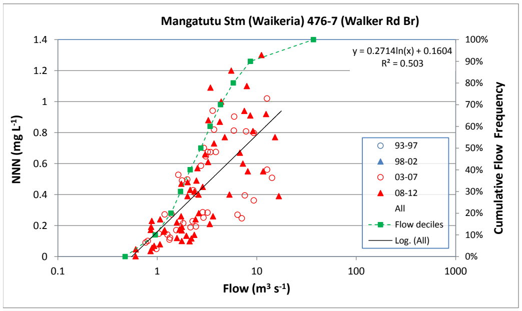


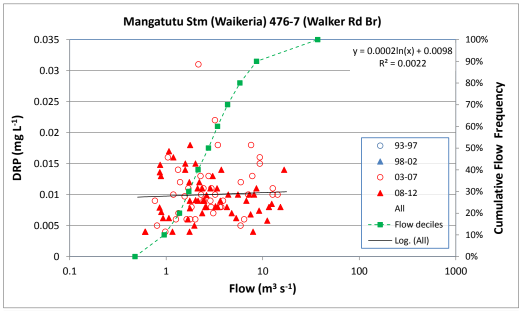


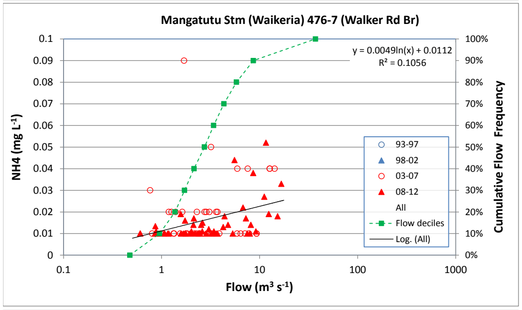


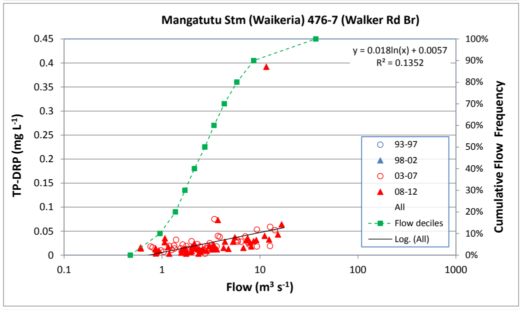


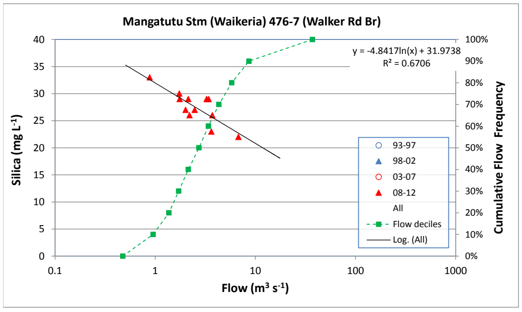


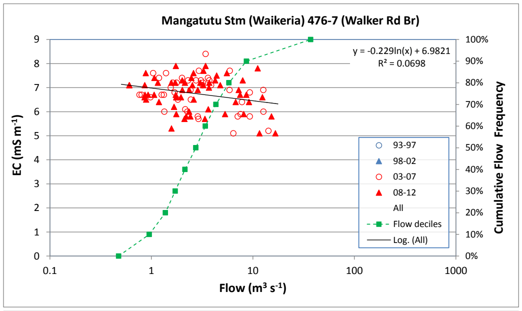










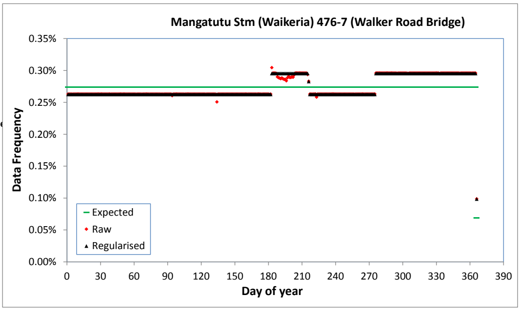


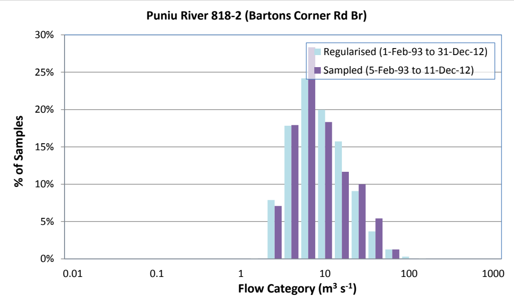
C-D relationship for the 20 year period, highlighted if significant.

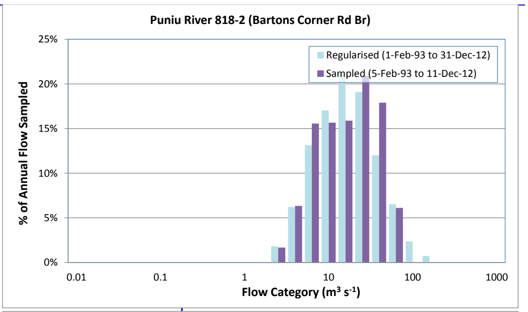
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	100	12	100	100	100	100	100	102
MEDIAN	0.39	28.00	0.01	0.01	0.03	0.02	0.57	6.85
RSQ	50%	67%	11%	0%	14%	14%	49%	7%
SLOPE	0.271	-4.842	0.005	0.000	0.018	0.018	0.355	-0.229
P-VALUE	0.000	0.001	0.001	0.643	0.000	0.000	0.000	0.007

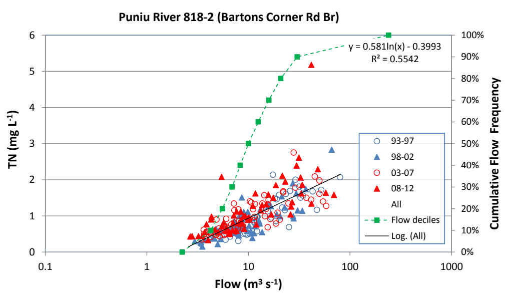
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

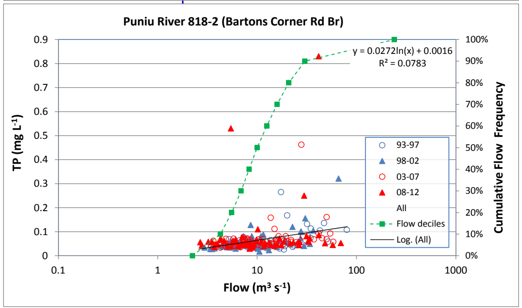
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02								
03-07	0.221		0.004	0.001	0.011	0.010	0.261	-0.314
08-12	0.304	-4.842	0.006	0.000	0.023	0.023	**0.415**	-0.178

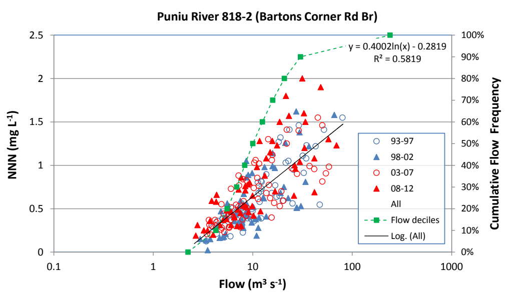


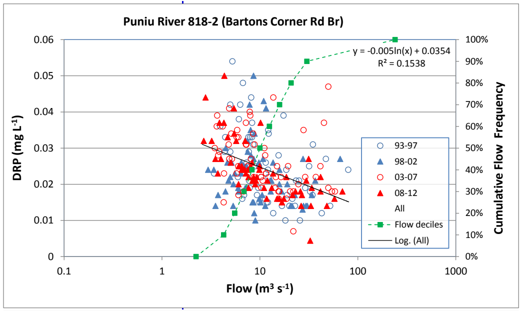


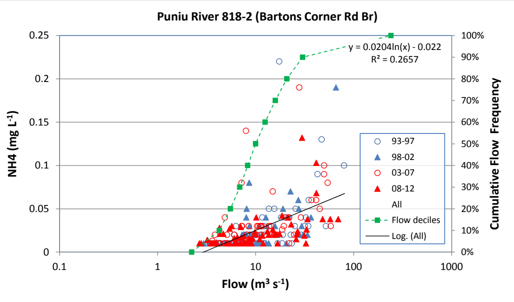


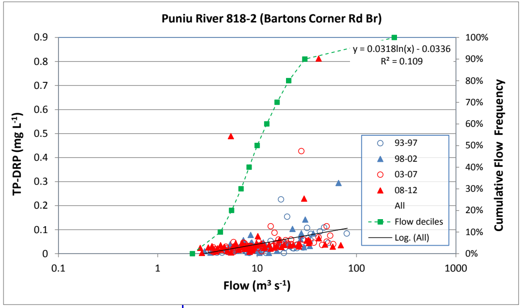


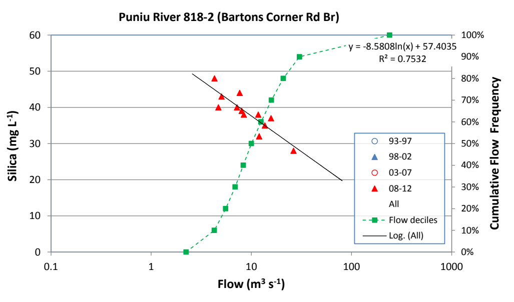


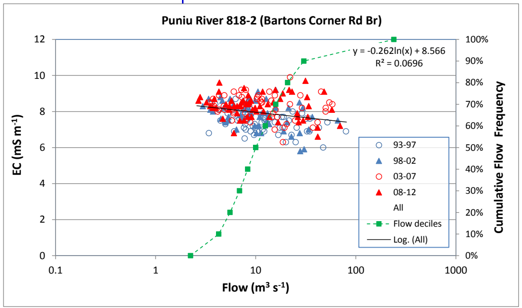










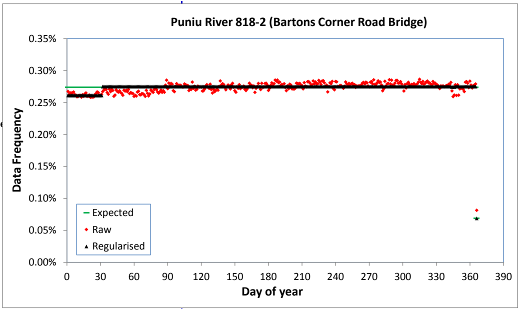


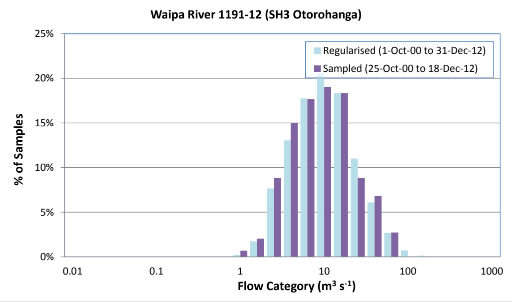
C-D relationship for the 20 year period, highlighted if significant.

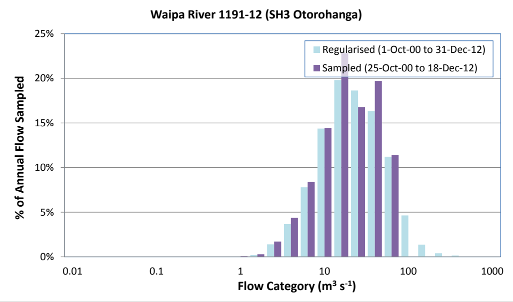
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	240	12	240	240	240	240	240	240
MEDIAN	0.56	38.50	0.02	0.02	0.05	0.03	0.85	8.00
RSQ	58%	75%	27%	15%	8%	11%	55%	7%
SLOPE	0.400	-8.581	0.020	-0.005	0.027	0.032	0.581	-0.262
P-VALUE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

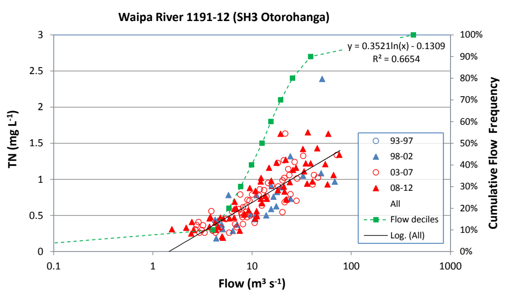
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

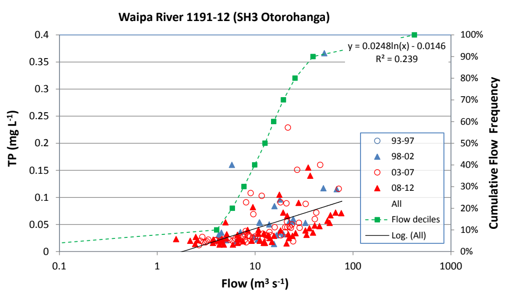
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.433		0.026	-0.007	0.023	0.029	0.619	-0.257
98-02	0.391		0.024	**-0.002**	0.037	0.039	0.562	-0.462
03-07	0.338		0.021	-0.003	0.026	0.029	0.496	-0.132
08-12	0.442	-8.581	0.014	**-0.007**	0.026	0.033	0.655	-0.162

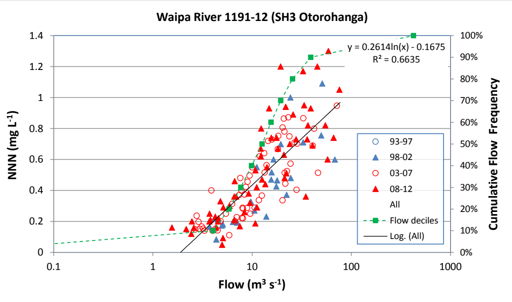


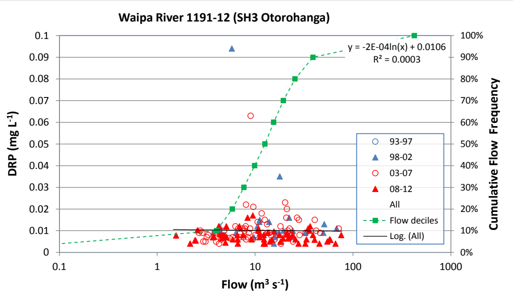


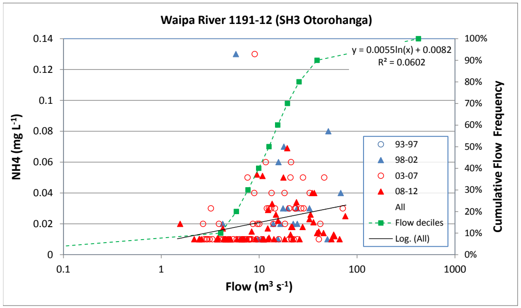


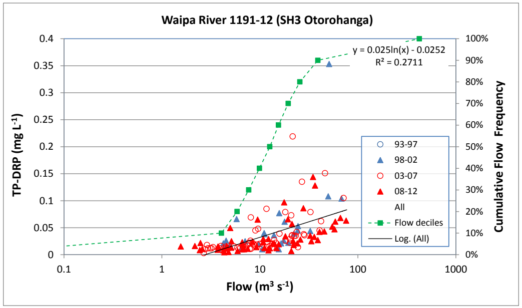


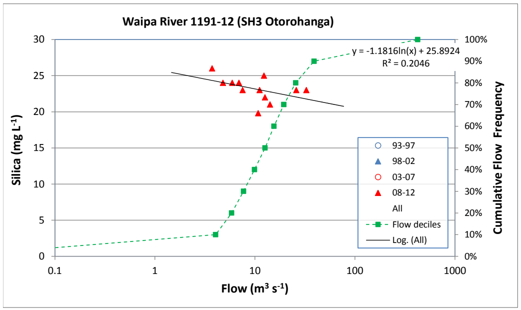


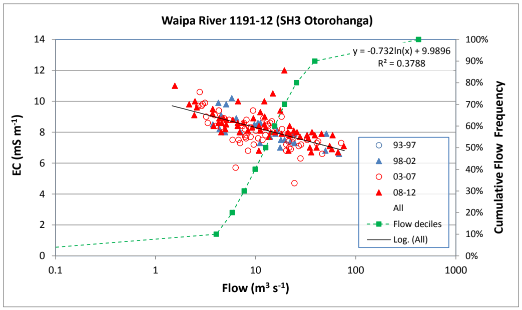










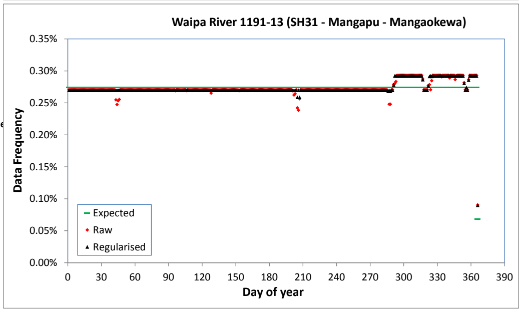


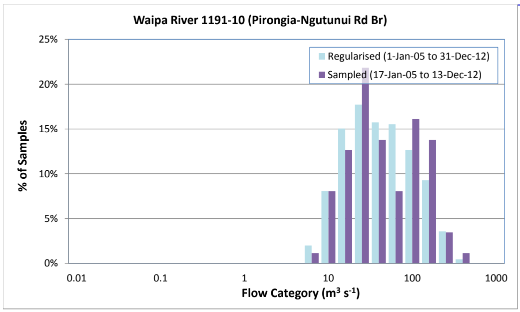
C-D relationship for the 20 year period, highlighted if significant.

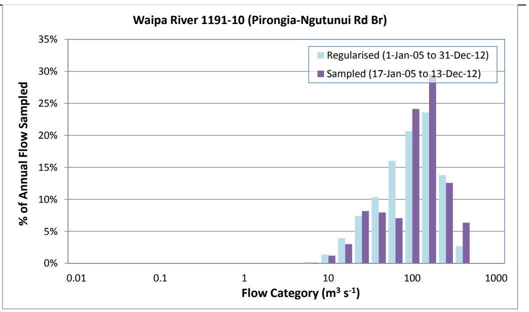
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	147	12	147	147	147	147	147	147
MEDIAN	0.42	23.00	0.01	0.01	0.03	0.02	0.70	8.10
RSQ	66%	20%	6%	0%	24%	27%	67%	38%
SLOPE	0.261	-1.182	0.006	0.000	0.025	0.025	0.352	-0.732
P-VALUE	0.000	0.140	0.003	0.835	0.000	0.000	0.000	0.000

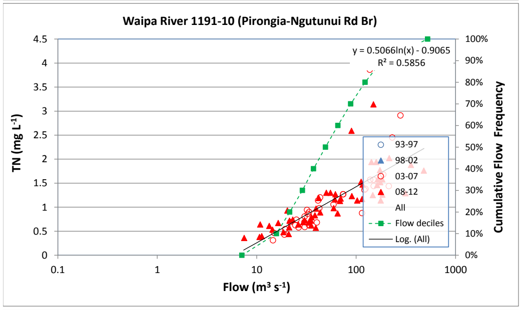
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

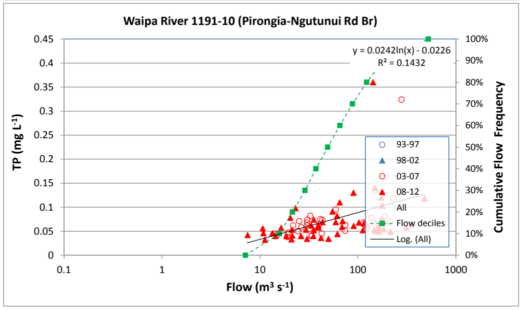
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02	0.261		0.008	-0.003	0.043	0.046	0.398	-0.808
03-07	0.245		0.007	0.001	0.029	0.027	0.340	-0.837
08-12	0.273	-1.182	0.004	0.000	0.016	0.017	0.346	-0.665

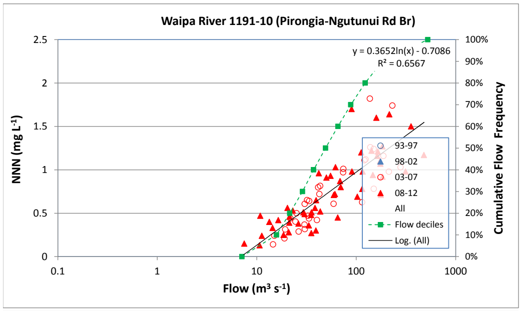


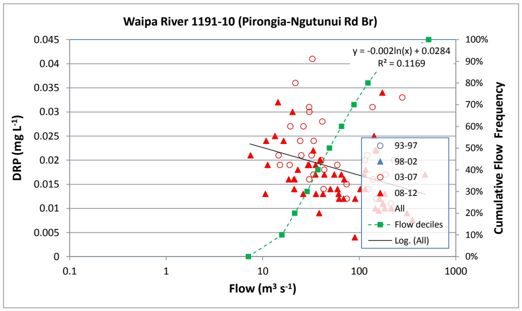


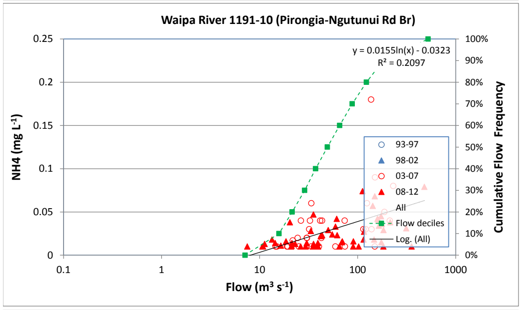


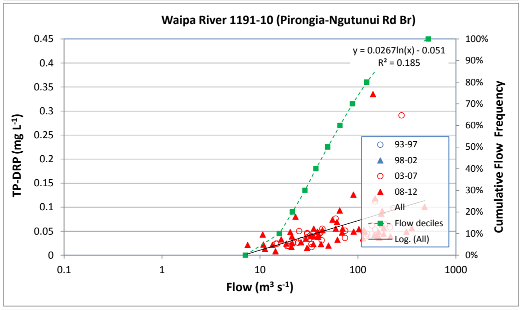


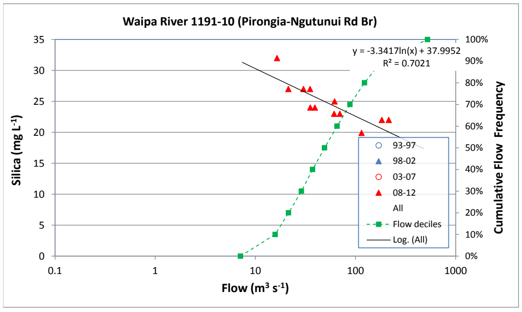


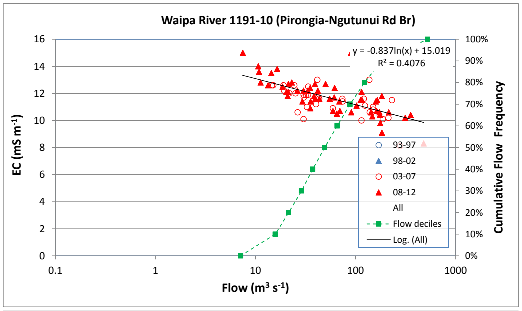










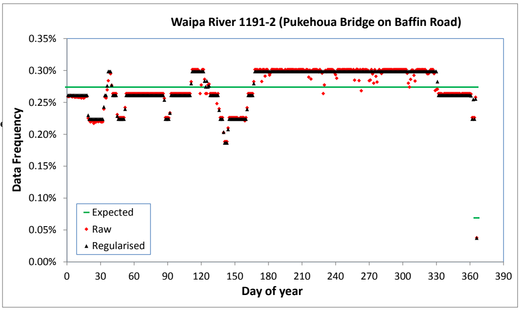


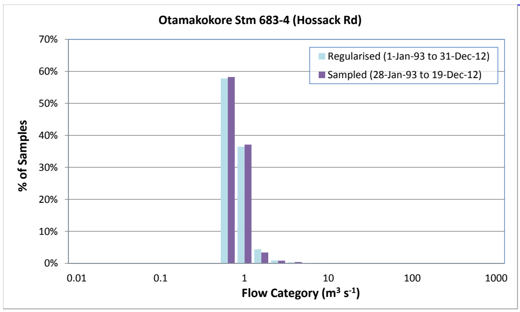
C-D relationship for the 20 year period, highlighted if significant.

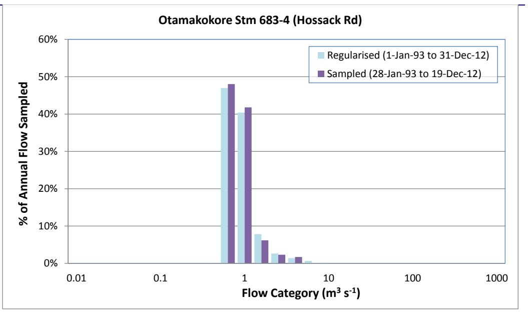
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	87	12	87	87	87	87	87	87
MEDIAN	0.69	24.00	0.02	0.02	0.06	0.04	0.98	11.60
RSQ	66%	70%	21%	12%	14%	19%	59%	41%
SLOPE	0.365	-3.342	0.015	-0.002	0.024	0.027	0.507	-0.837
P-VALUE	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000

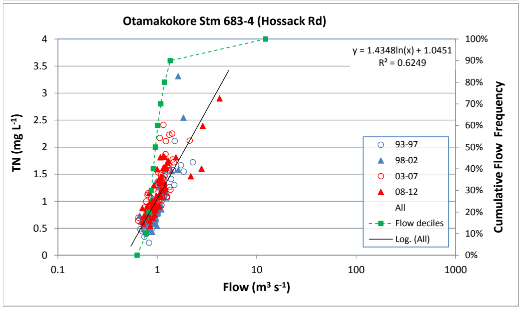
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

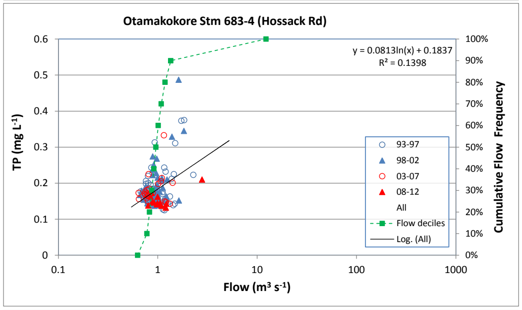
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02								
03-07	0.406		0.031	-0.002	0.044	0.046	0.662	-0.716
08-12	0.346	-3.342	**0.009**	-0.003	0.016	0.018	**0.438**	-0.898

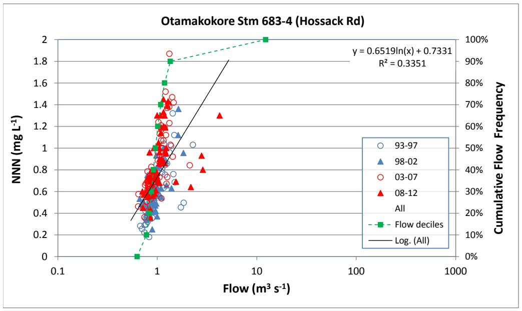


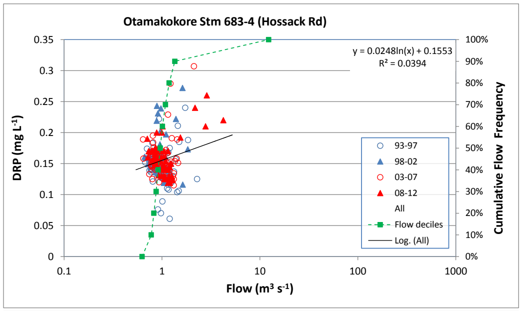


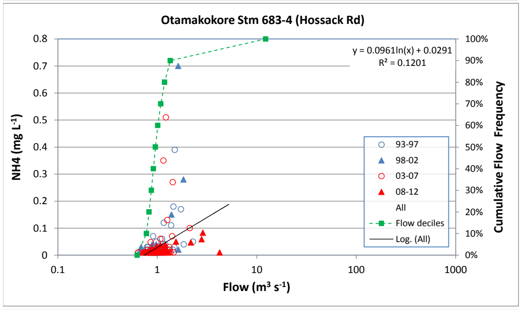


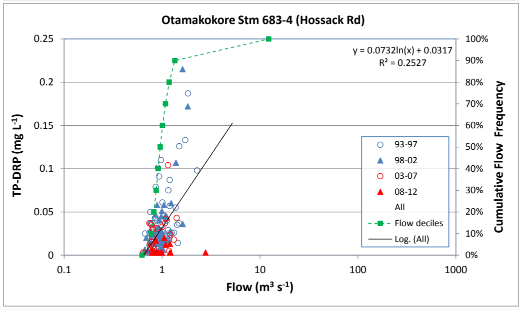


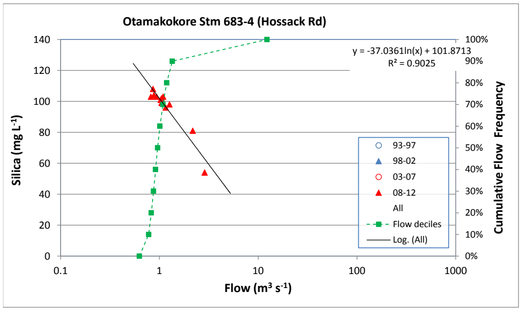


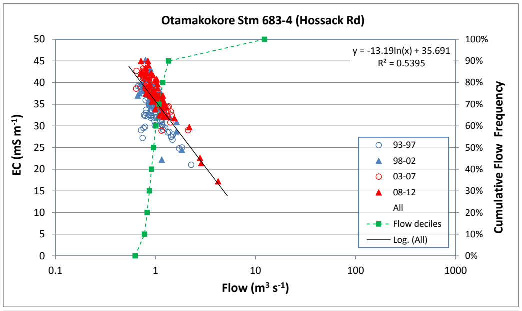










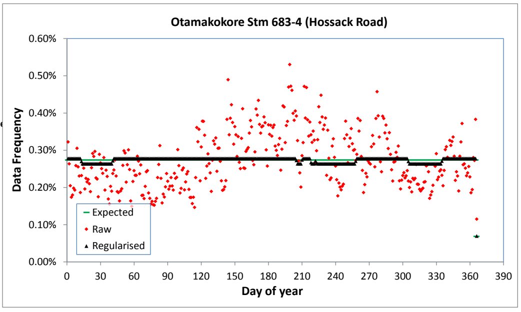


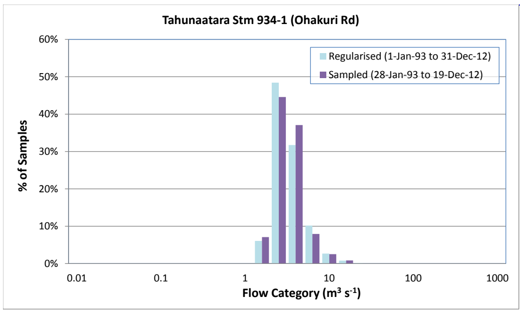
C-D relationship for the 20 year period, highlighted if significant.

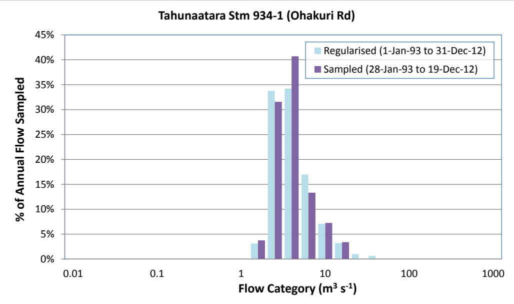
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	237	12	237	237	154	154	237	237
MEDIAN	0.67	101.50	0.01	0.15	0.17	0.02	0.91	36.10
RSQ	34%	90%	12%	4%	14%	25%	62%	54%
SLOPE	0.652	-37.036	0.096	0.025	0.081	0.073	1.435	-13.194
P-VALUE	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000

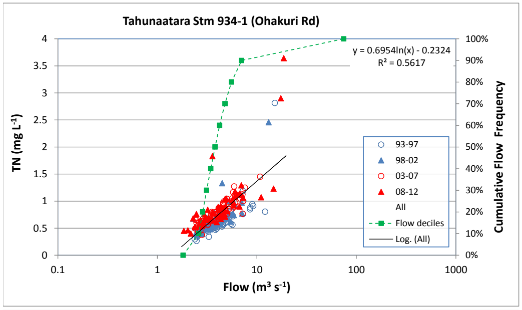
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

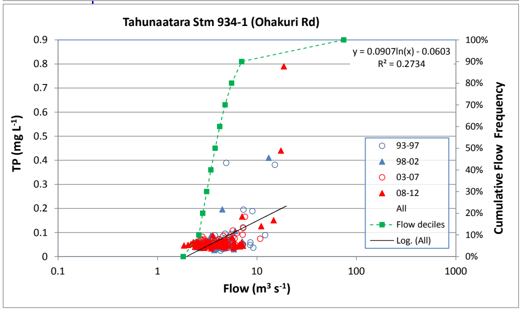
93-97	0.686		0.110	0.003	0.081	0.078	1.389	-11.481
98-02	0.759		**0.284**	0.021	0.158	**0.135**	**1.946**	-14.732
03-07	0.969		**0.117**	0.030	**0.046**	**0.049**	1.598	-13.525
08-12	**0.347**	-37.036	**0.027**	0.037	0.040	**-0.002**	**1.141**	-14.532

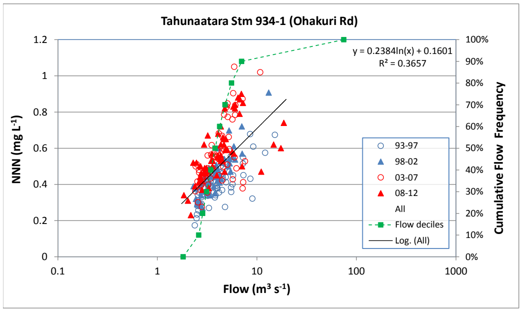


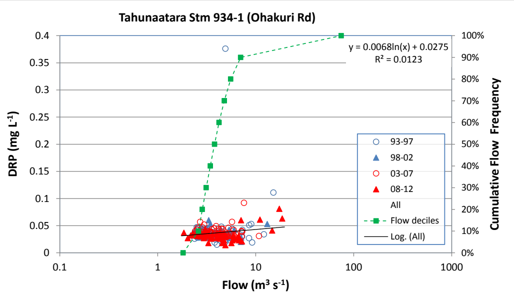


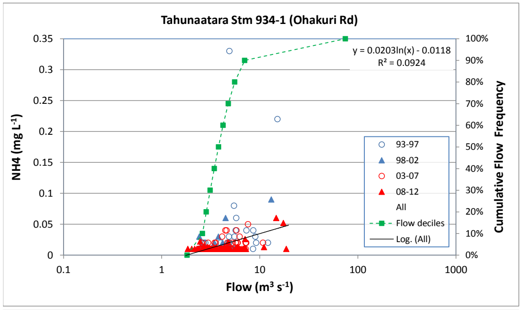


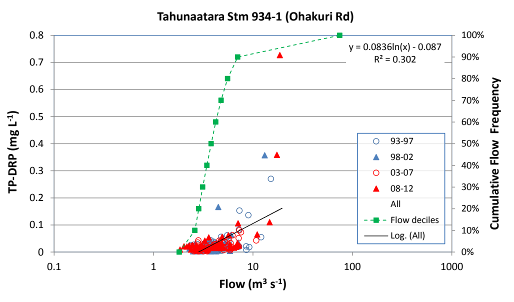


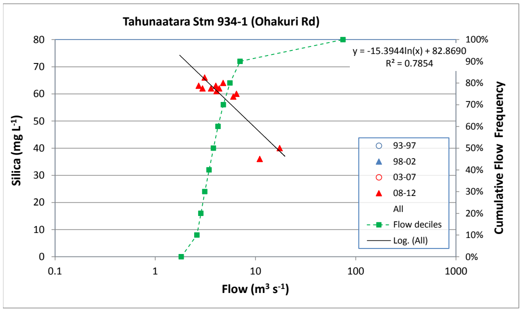


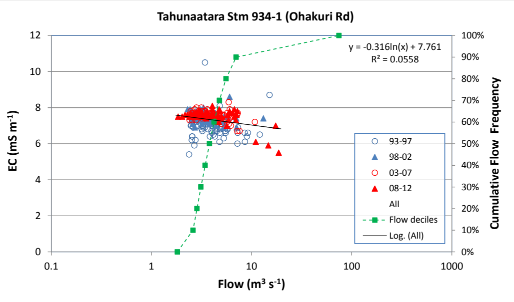










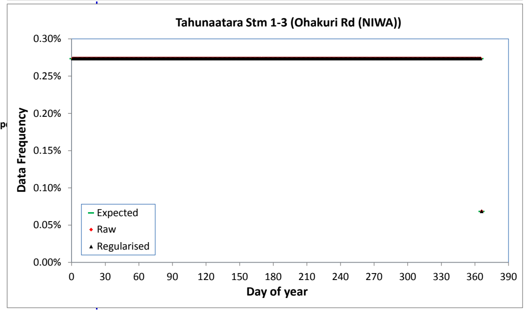


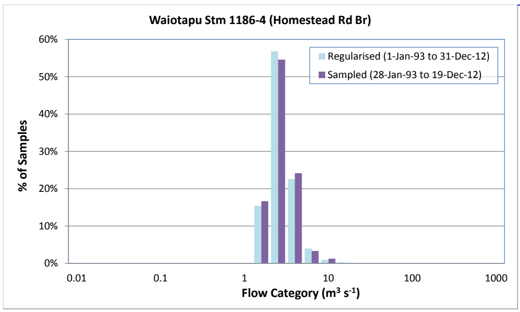
C-D relationship for the 20 year period, highlighted if significant.

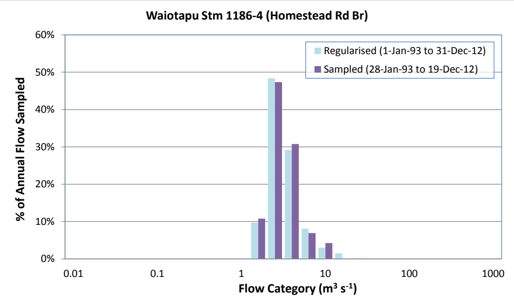
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	240	12	240	240	240	240	240	240
MEDIAN	0.47	62.00	0.01	0.03	0.05	0.02	0.66	7.40
RSQ	37%	79%	9%	1%	27%	30%	56%	6%
SLOPE	0.238	-15.394	0.020	0.007	0.091	0.084	0.695	-0.316
P-VALUE	0.000	0.000	0.000	0.087	0.000	0.000	0.000	0.000

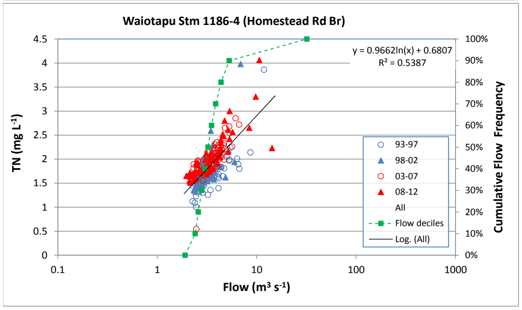
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

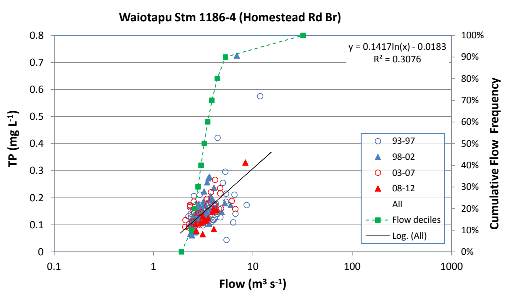
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97	0.191		0.042	0.013	0.073	0.060	0.623	0.013
98-02	**0.317**		0.017	-0.003	0.086	0.088	0.686	-0.235
03-07	0.312		0.012	0.002	**0.029**	**0.026**	0.559	-0.276
08-12	0.193	-15.394	0.009	0.010	**0.139**	**0.129**	**0.817**	**-0.553**

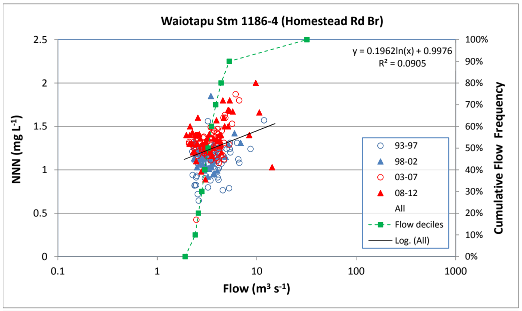


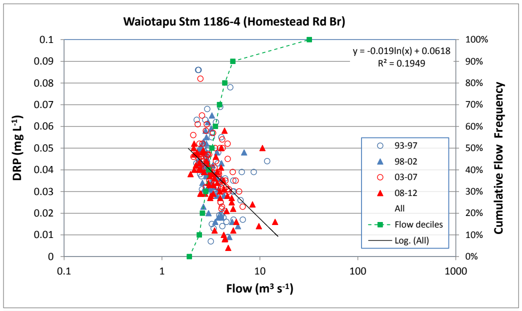


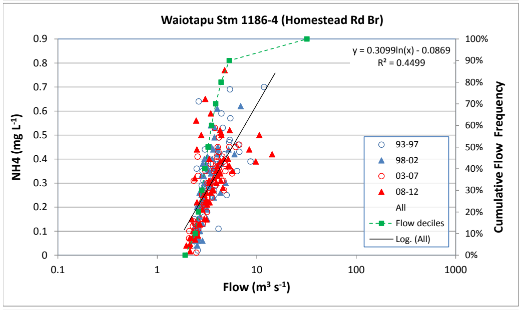


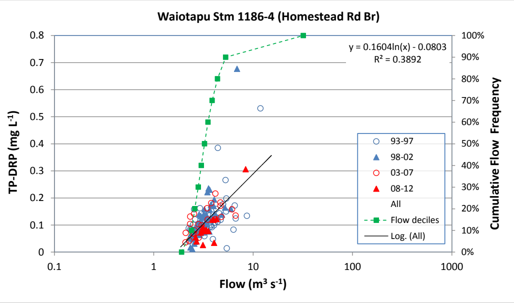


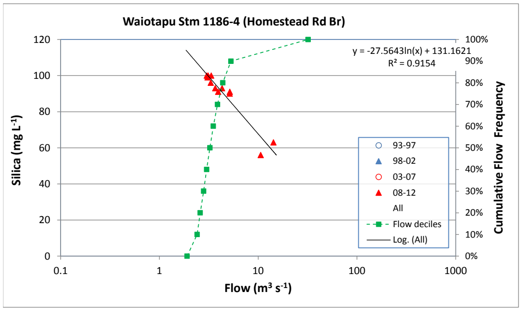


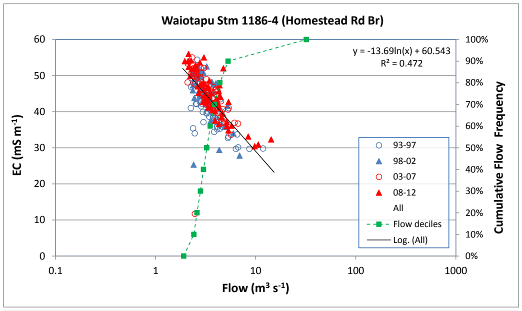










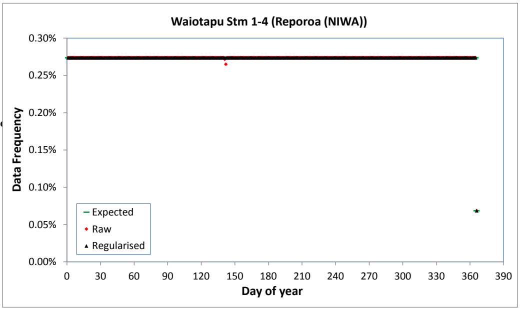


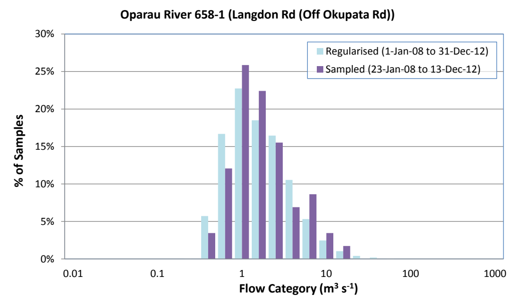
C-D relationship for the 20 year period, highlighted if significant.

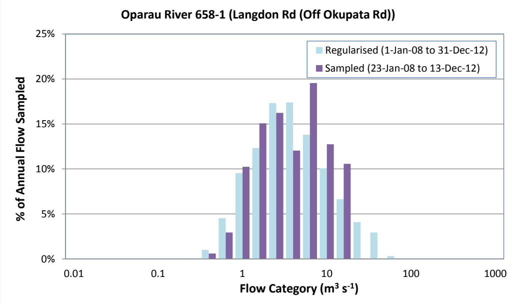
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	240	12	240	240	157	157	240	240
MEDIAN	1.24	93.00	0.30	0.04	0.14	0.10	1.80	44.30
RSQ	9%	92%	45%	19%	31%	39%	54%	47%
SLOPE	0.196	-27.564	0.310	-0.019	0.142	0.160	0.966	-13.694
P-VALUE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

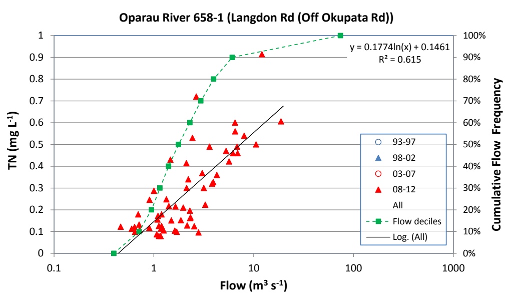
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

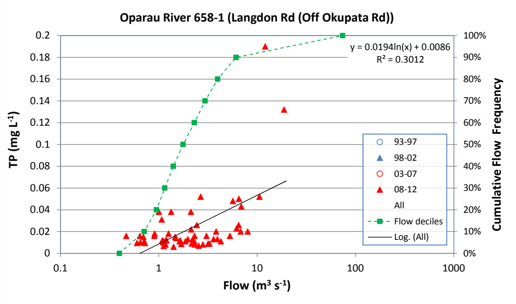
93-97	0.209		0.317	-0.019	0.116	0.135	0.946	-11.986
98-02	0.066		**0.492**	-0.026	**0.262**	**0.288**	1.195	-15.255
03-07	0.290		**0.342**	-0.023	**0.084**	**0.099**	1.011	-13.459
08-12	0.179	-27.564	0.233	-0.016	**0.201**	**0.214**	0.917	-13.848

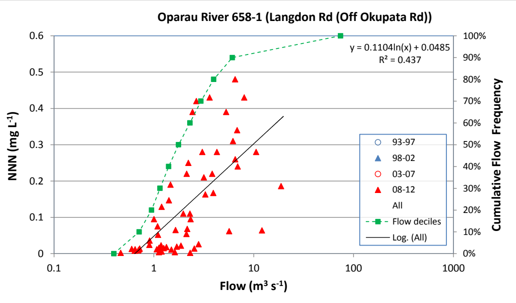


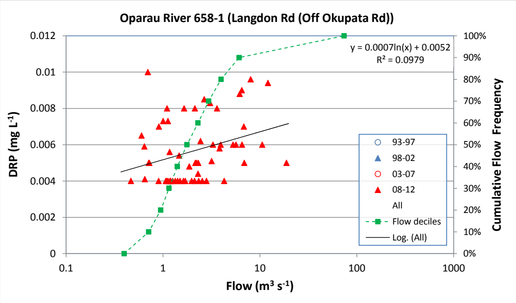

Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

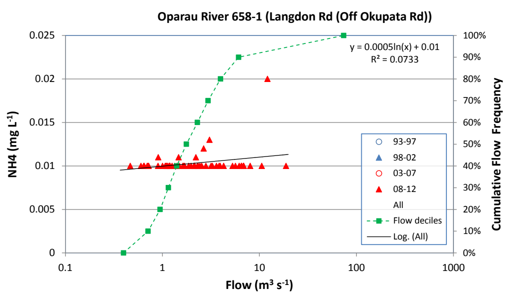

Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

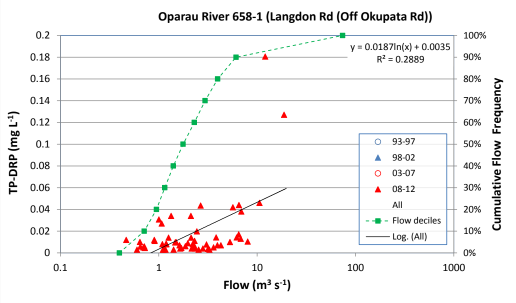

Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

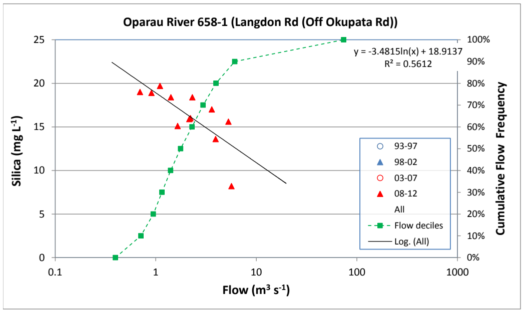

Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

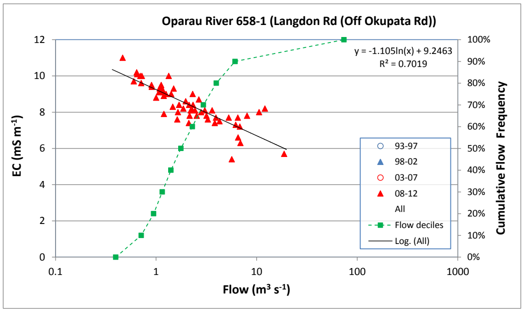

Oparau River 658-1 (Langdon Rd (Off Okupata Rd))


Oparau River 658-1 (Langdon Rd (Off Okupata Rd))


Oparau River 658-1 (Langdon Rd (Off Okupata Rd))


Oparau River 658-1 (Langdon Rd (Off Okupata Rd))


Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

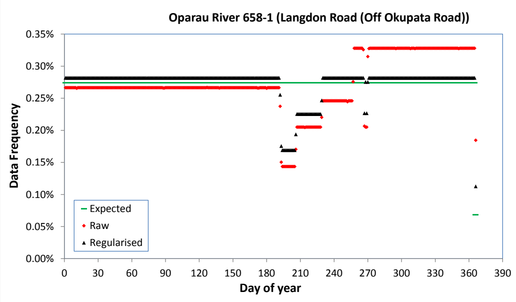

Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

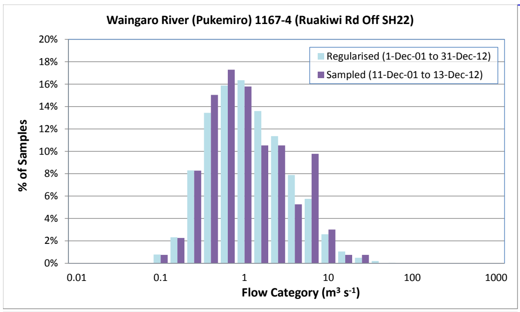
C-D relationship for the 20 year period, highlighted if significant.

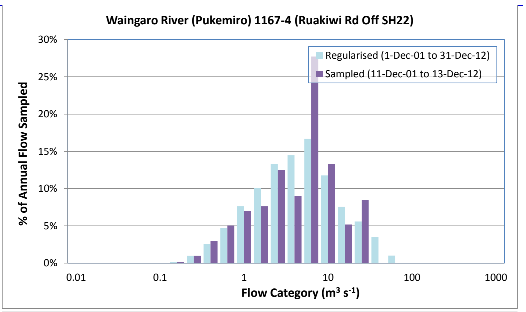
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	58	12	58	58	58	58	58	58
MEDIAN	0.07	16.50	0.01	0.01	0.01	0.01	0.21	8.25
RSQ	44%	56%	7%	10%	30%	29%	61%	70%
SLOPE	0.110	-3.482	0.000	0.001	0.019	0.019	0.177	-1.105
P-VALUE	0.000	0.005	0.040	0.017	0.000	0.000	0.000	0.000

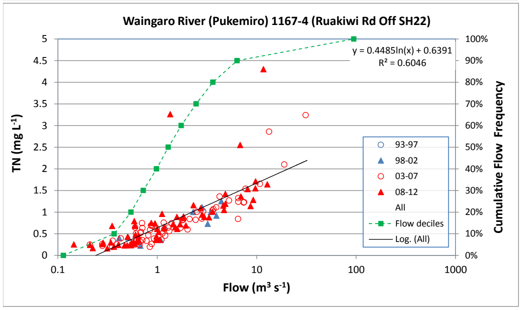
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slop

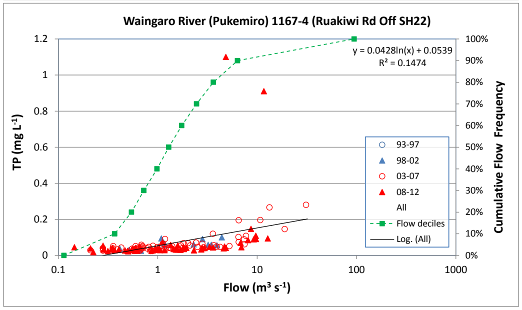
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02								
03-07								
08-12	0.110	-3.482	0.000	0.001	0.019	0.019	0.177	-1.105

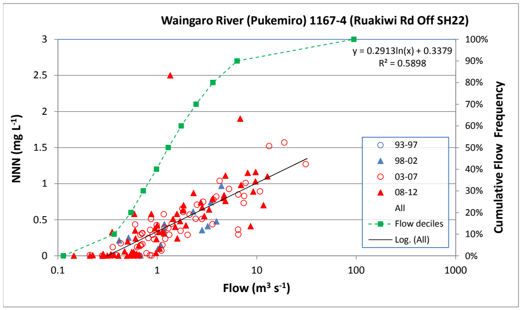

Oparau River 658-1 (Langdon Road (Off Okupata Road))

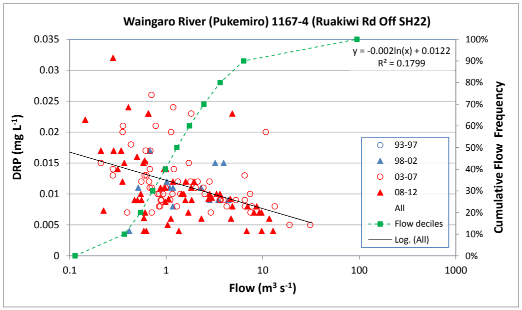


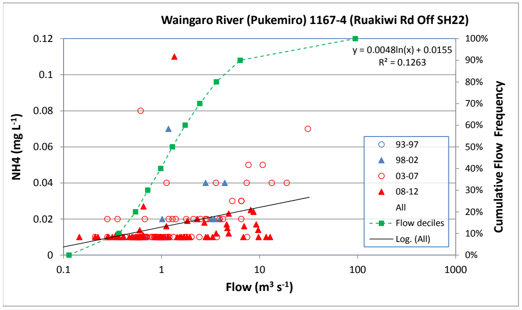


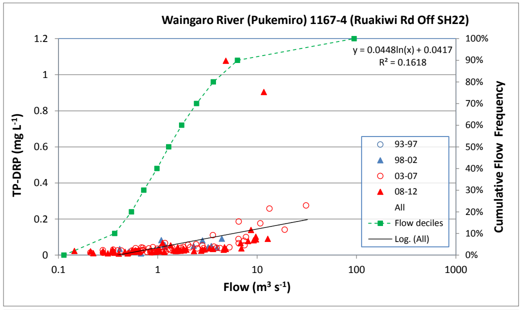


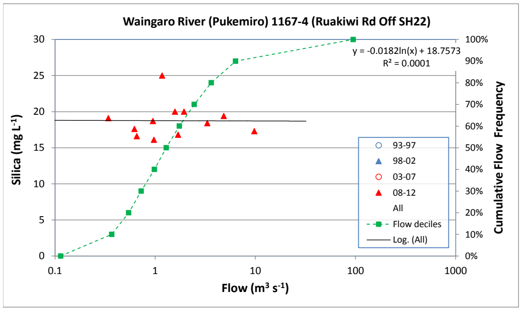


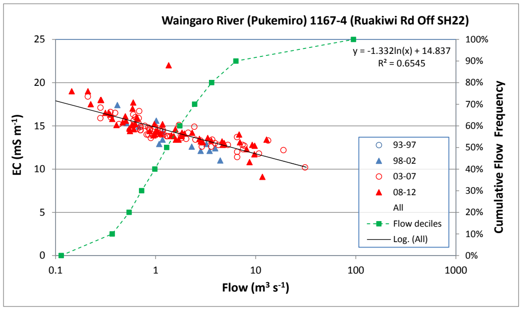










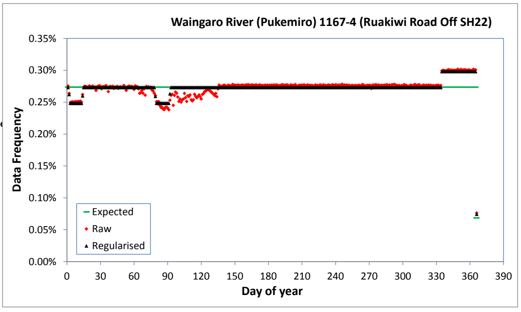


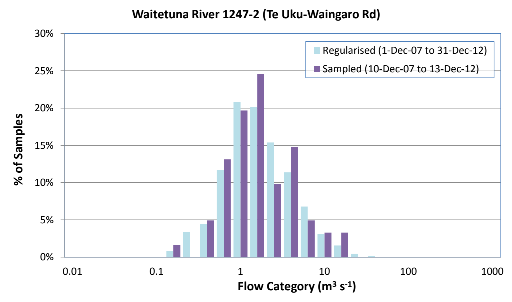
C-D relationship for the 20 year period, highlighted if significant.

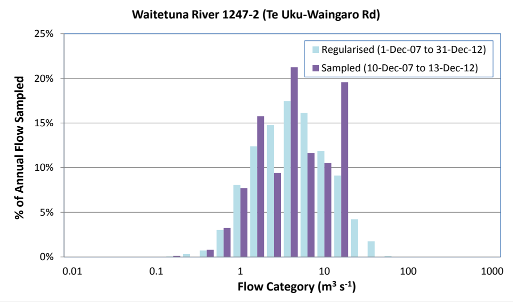
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	133	12	133	133	133	133	133	133
MEDIAN	0.36	18.55	0.01	0.01	0.04	0.03	0.65	14.20
RSQ	59%	0%	13%	18%	15%	16%	60%	65%
SLOPE	0.291	-0.018	0.005	-0.002	0.043	0.045	0.448	-1.332
P-VALUE	0.000	0.982	0.000	0.000	0.000	0.000	0.000	0.000

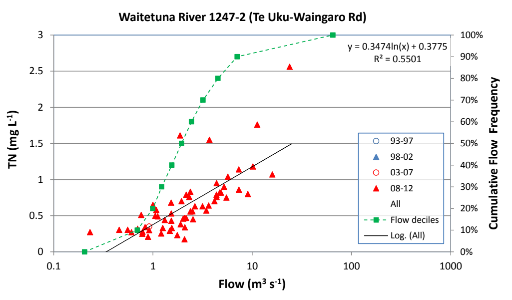
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

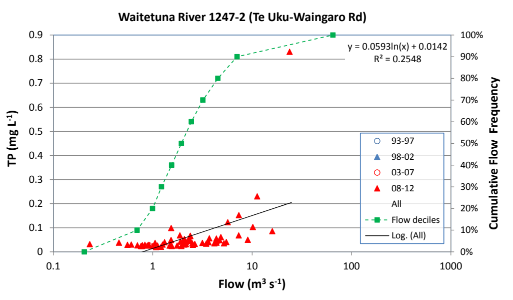
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02	0.253		0.007	0.001	0.018	0.017	0.362	-2.003
03-07	0.295		0.008	-0.002	**0.035**	**0.037**	0.466	**-1.175**
08-12	0.297	-0.018	**0.001**	-0.003	0.053	0.056	0.447	-1.390

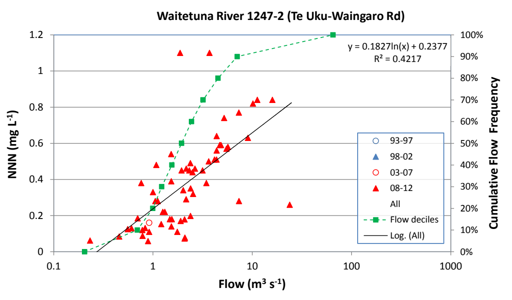


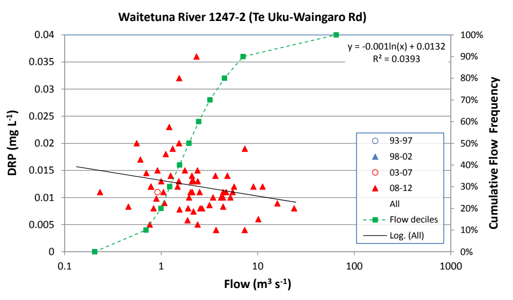


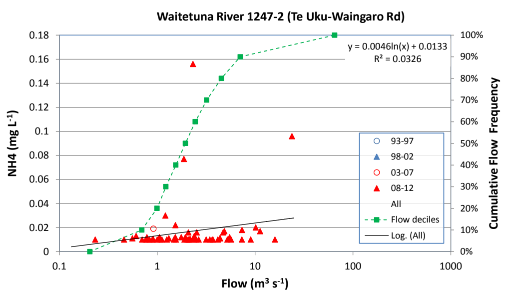


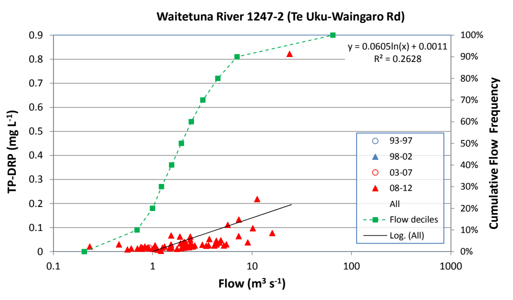


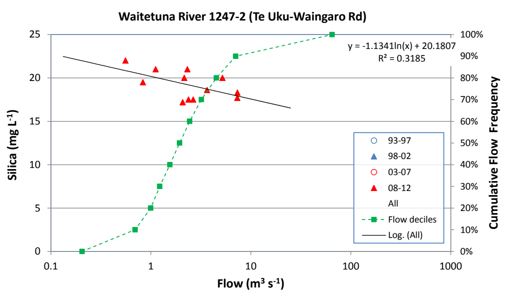


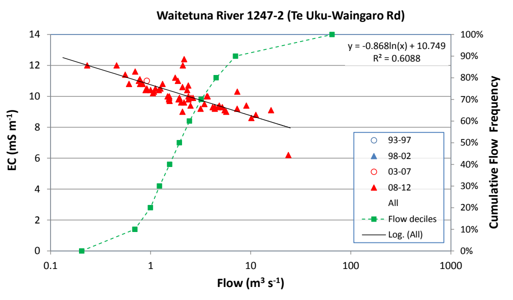










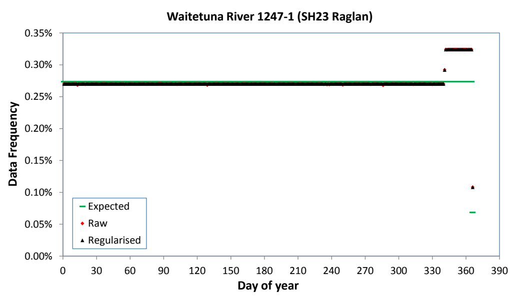


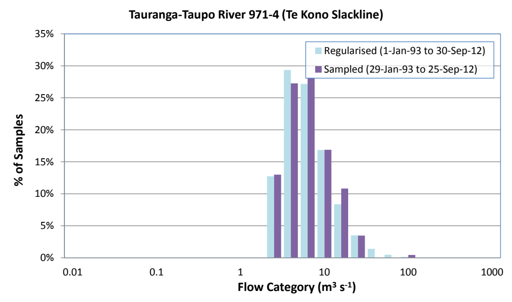
C-D relationship for the 20 year period, highlighted if significant.

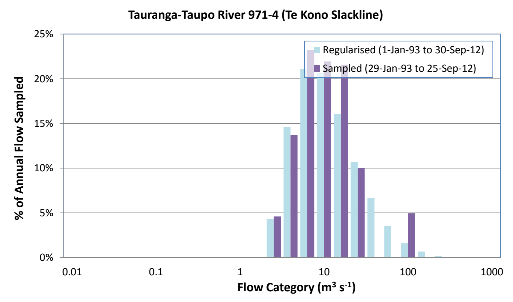
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	61	12	61	61	61	61	61	61
MEDIAN	0.34	19.05	0.01	0.01	0.04	0.03	0.56	10.00
RSQ	42%	32%	3%	4%	25%	26%	55%	61%
SLOPE	0.183	-1.134	0.005	-0.001	0.059	0.060	0.347	-0.868
P-VALUE	0.000	0.056	0.164	0.126	0.000	0.000	0.000	0.000

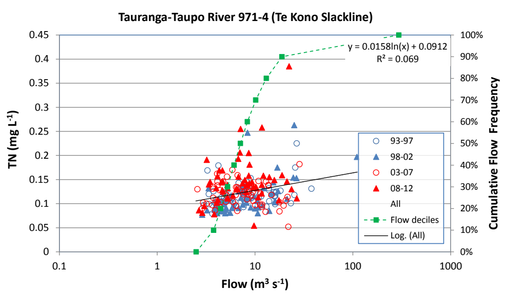
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

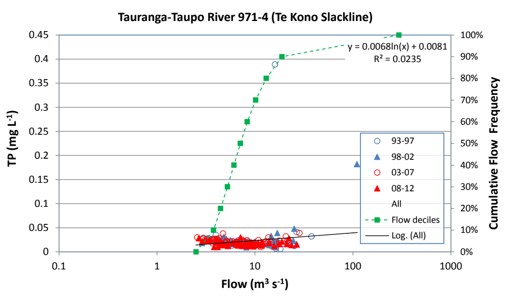
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02								
03-07								
08-12	0.182	-1.134	0.005	-0.001	0.060	0.061	0.348	-0.865

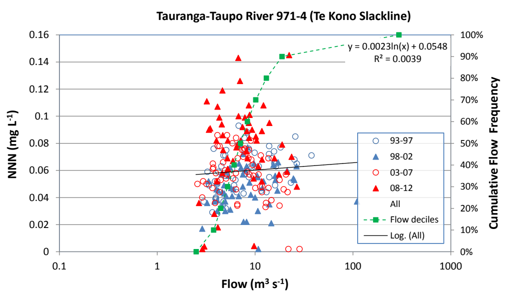


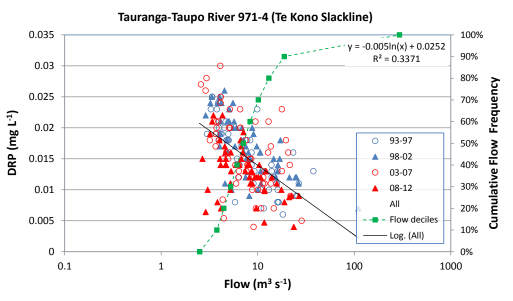


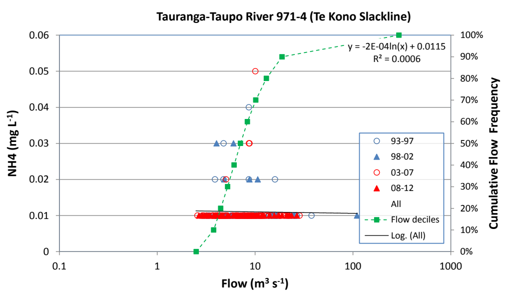


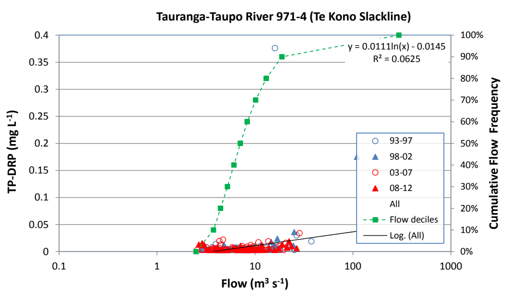


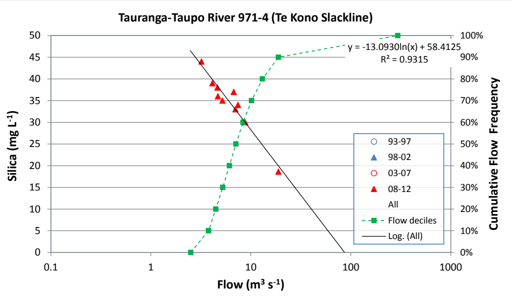


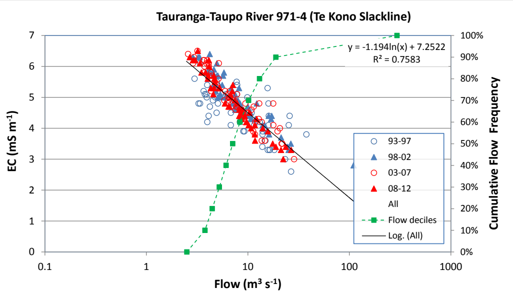










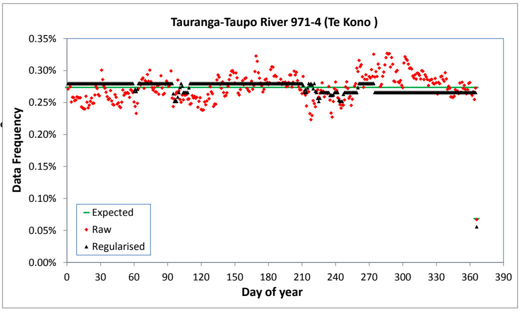


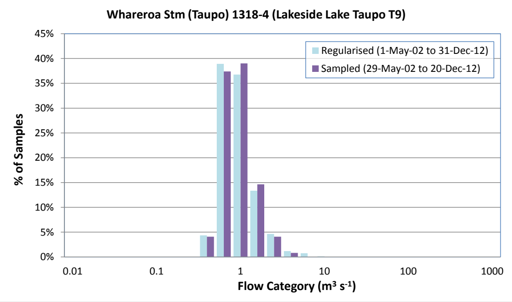
C-D relationship for the 20 year period, highlighted if significant.

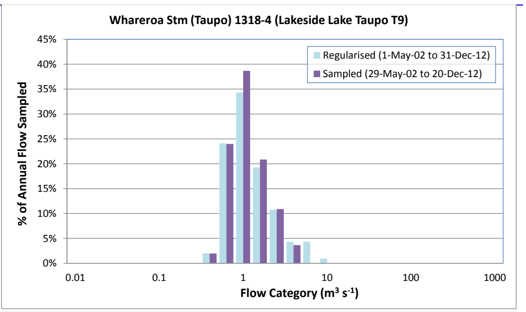
	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	230	10	230	230	230	230	230	230
MEDIAN	0.06	35.50	0.01	0.02	0.02	0.00	0.12	4.80
RSQ	0%	93%	0%	34%	2%	6%	7%	76%
SLOPE	0.002	-13.093	0.000	-0.005	0.007	0.011	0.016	-1.194
P-VALUE	0.343	0.000	0.717	0.000	0.020	0.000	0.000	0.000

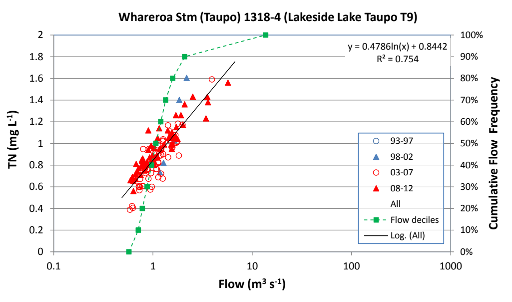
C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

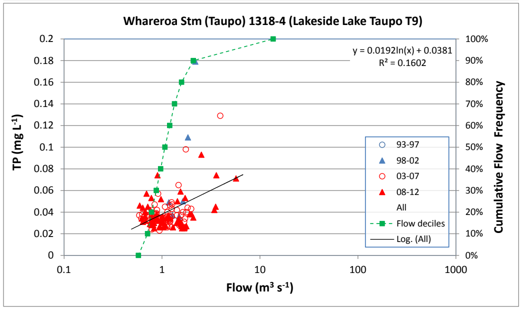
93-97	0.011		-0.001	-0.006	0.008	0.013	0.014	-0.839
98-02	0.004		-0.001	-0.005	0.018	0.022	**0.031**	**-1.167**
03-07	**-0.011**		0.001	-0.005	**-0.002**	**0.003**	**-0.003**	**-1.371**
08-12	**0.009**	-13.093	0.000	-0.004	-0.002	0.001	**0.025**	-1.490

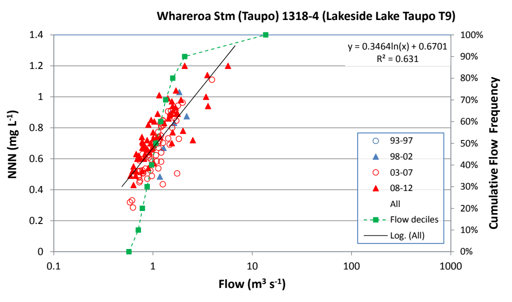


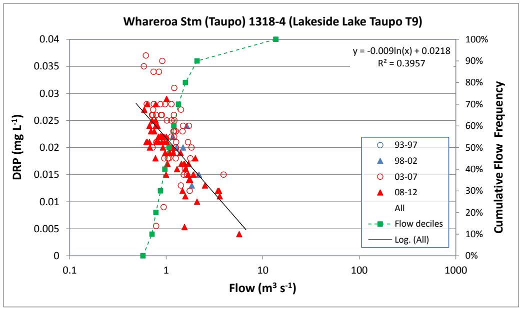


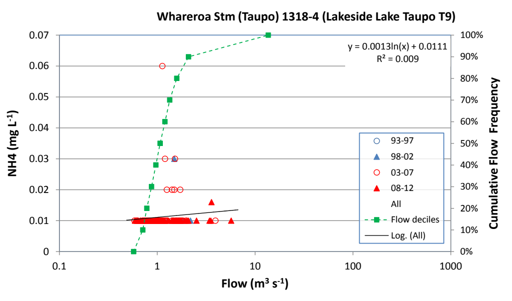


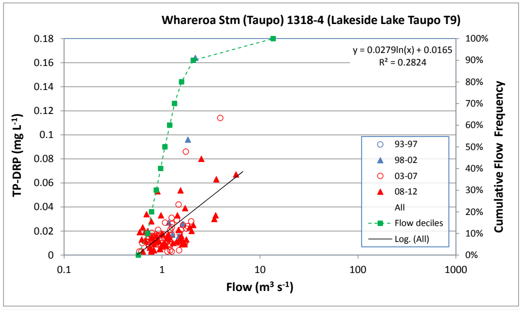


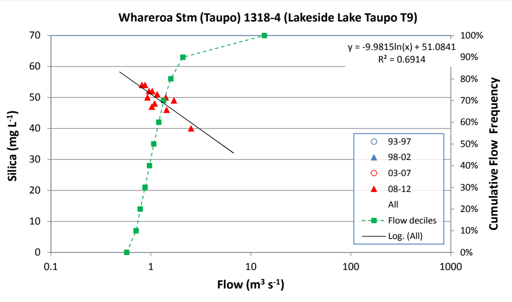


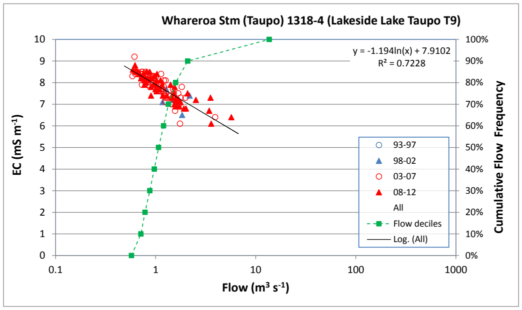










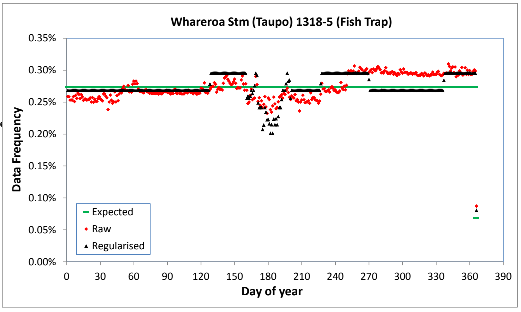


C-D relationship for the 20 year period, highlighted if significant.

	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
N	123	12	123	123	123	123	123	123
MEDIAN	0.70	50.00	0.01	0.02	0.04	0.01	0.89	7.80
RSQ	63%	69%	1%	40%	16%	28%	75%	72%
SLOPE	0.346	-9.982	0.001	-0.009	0.019	0.028	0.479	-1.194
P-VALUE	0.000	0.001	0.296	0.000	0.000	0.000	0.000	0.000

C-D relationship for each 5 year period, highlighted if significant, and bold if significantly different to the previous 5 year slope

	NNN	Si	NH4	DRP	TP	TP-DRP	TN	EC
93-97								
98-02	0.663		-0.004	-0.012	0.211	0.223	1.421	-0.479
03-07	0.414		0.003	-0.009	**0.023**	**0.031**	**0.546**	-1.326
08-12	**0.302**	-9.982	0.000	-0.009	**0.010**	0.019	**0.411**	-1.114



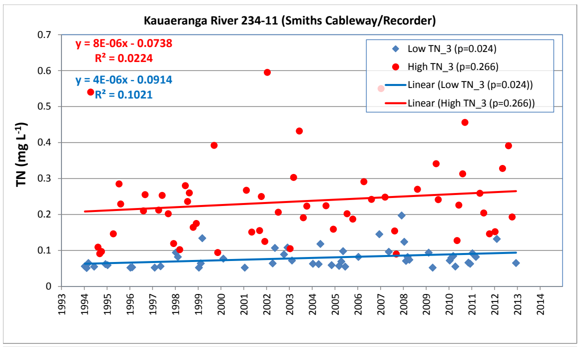
APPENDIX 2: DATA STRATIFICATION BASED ON FLOW

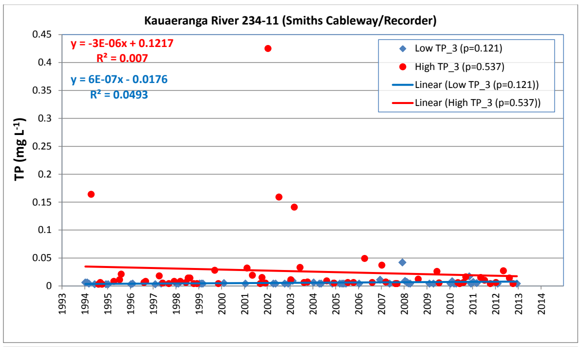
This appendix documents the results of stratification of the water quality data based on flow percentiles, as described in Section 5.2 of this report. Charts are included that show the water quality measurements corresponding to the top 25% of flows, and the bottom 25% of flows, for each of the Waikato water quality sampling sites, sorted by subregion (Coromandel, Hauraki, Lower Waikato River, Waipa, Upper Waikato River, West Coast, Lake Taupo).

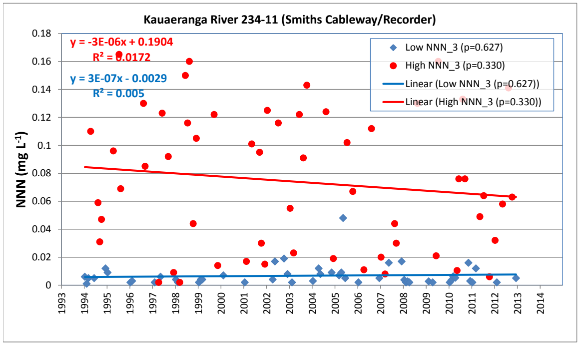
For each of 8 contaminants (TN, NNN, NH4, TP, DRP, TP-DRP, Si, EC), linear trends are shown for the high flow and low flow samples, and the p-value for the slope of these trends is reported in the chart legend (the trend is considered to be highly statistically significant if $p<0.005$).

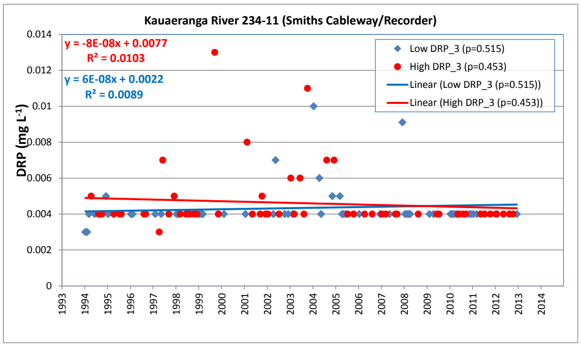
The table at the bottom of each page summarises the characteristics of samples stratified as Low Flow (bottom 25%) or High Flow (top 25%), and as well as the characteristics of all of the samples together ("All Flow"). For each of these stratifications the number of samples (N), mean, median, trend slope, and trend slope p-value (P) are reported. "P Difference" is the probability that the Low Flow and High Flow means are not significantly different to zero. These p-values are based on the Student's t-test. The trend slope or concentration difference is considered to be highly statistically significant if $P<0.005$, in which case the p-value is highlighted.

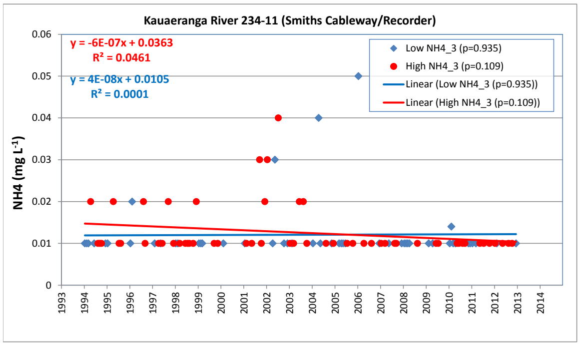
The statistical analysis cannot necessarily be taken at face value however. As indicated in Table 1 of this report, some of the water quality data sets are affected by point source discharges (which may have changed over time), geothermal influences or changes in laboratory analysis procedures (WRC, 2011, 2013). Furthermore, the flow data used for data stratification is not always from the same location as the water quality samples, or for the same period. Because of these issues, interpretation must be done with caution.

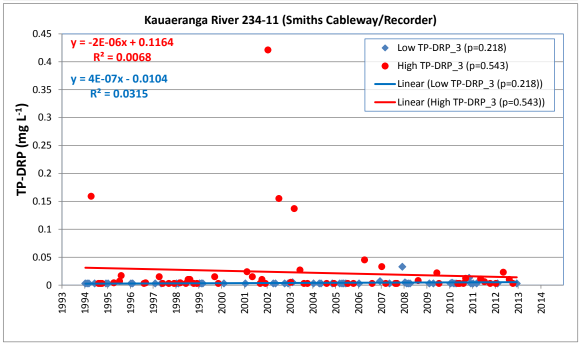


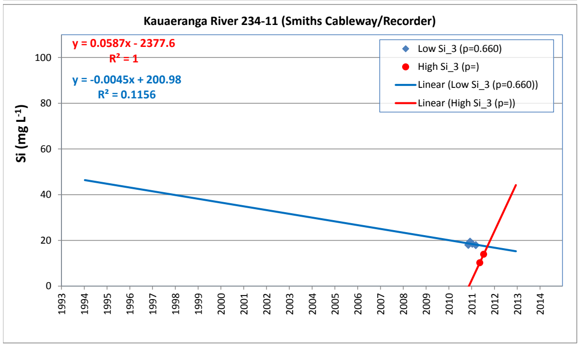


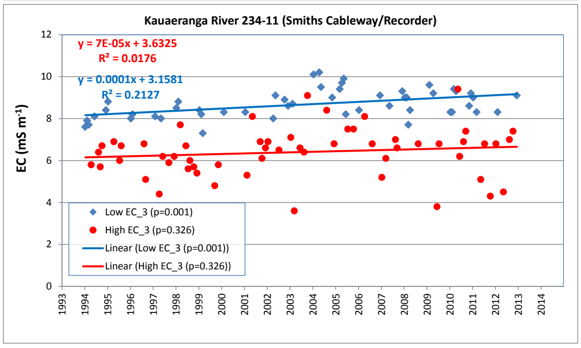








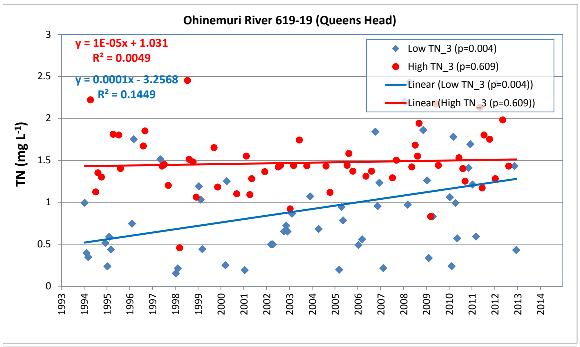


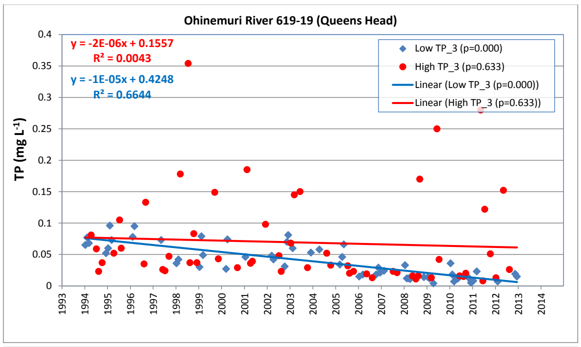


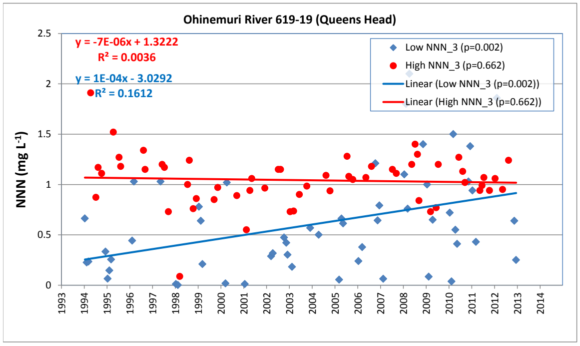
Kauaeranga River 234-11 (Smiths Cableway/Recorder)

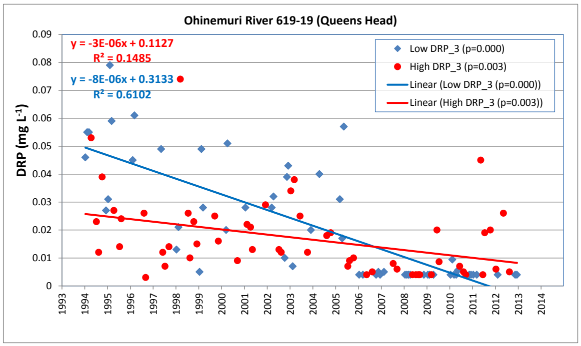
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	50	50	50	50	50	50	4	50
Mean Low Flow Sam	0.079	0.007	0.012	0.006	0.004	0.004	18.450	8.680
Median Low Flow Sa	0.070	0.005	0.010	0.004	0.004	0.003	18.250	8.600
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.005	0.000
P Low Flow Samples	0.024	0.627	0.935	0.121	0.515	0.218	0.660	0.001
N High Flow Samples	57	57	57	57	57	57	2	57
Mean High Flow Sam	0.236	0.074	0.013	0.026	0.005	0.023	12.050	6.402
Median High Flow Sa	0.223	0.069	0.010	0.008	0.004	0.003	12.050	6.600
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.000
P High Flow Samples	0.266	0.330	0.109	0.537	0.453	0.543		0.326
P Difference	0.000	0.000	0.682	0.018	0.343	0.029	0.169	0.000
N All Flow Samples	228	228	228	228	228	228	12	228
Mean All Flow Samp	0.137	0.036	0.013	0.011	0.004	0.009	17.208	7.561
Median All Flow Sam	0.105	0.017	0.010	0.004	0.004	0.003	18.050	7.600
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.009	0.000
P All Flow Samples	0.050	0.624	0.116	0.672	0.960	0.580	0.267	0.000

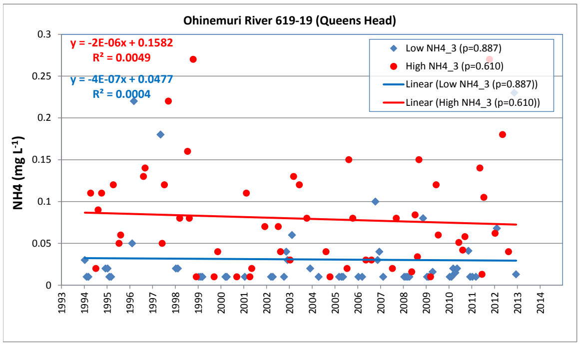
(p values < 0.005 are highlighted as being highly statistically significant)

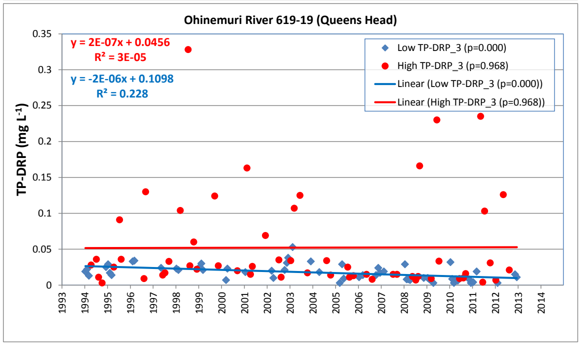


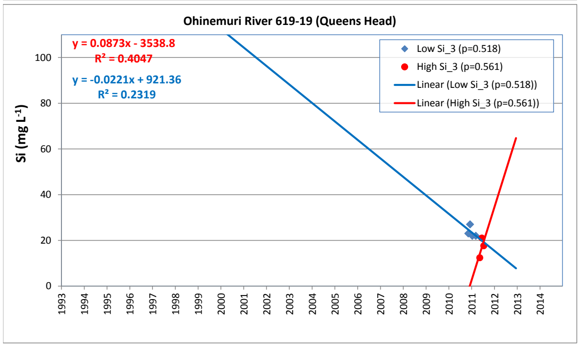


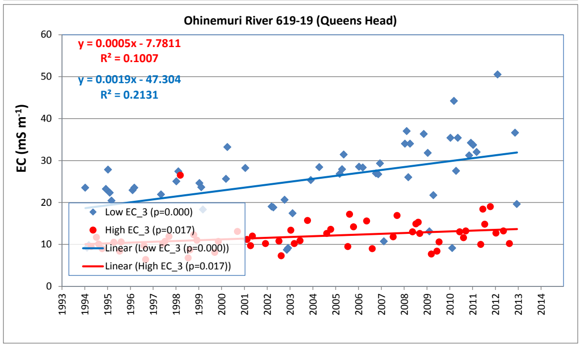








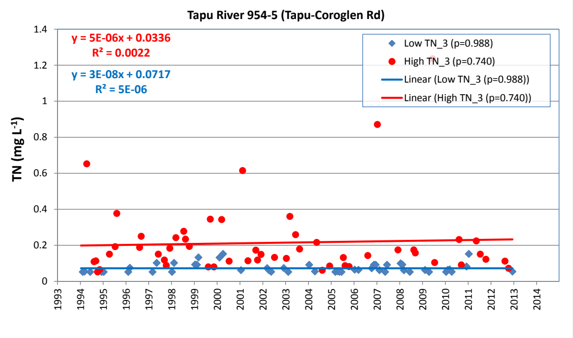


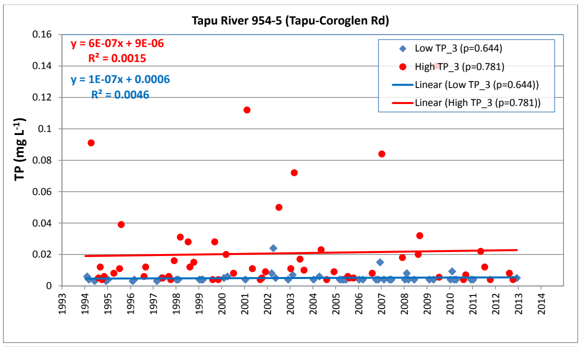


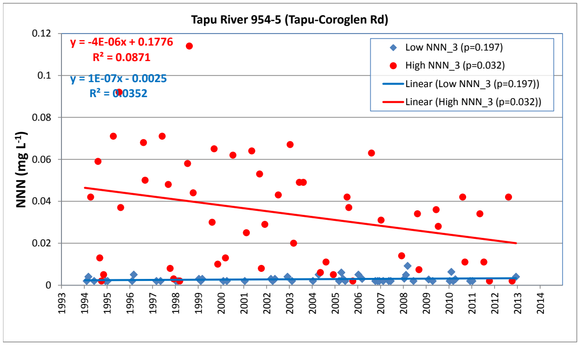
Ohinemuri River 619-19 (Queens Head)

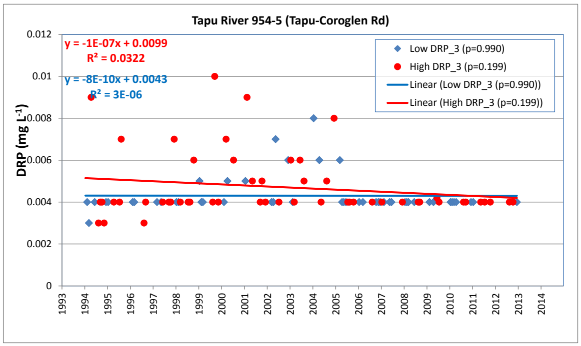
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	55	55	55	55	55	55	4	55
Mean Low Flow Sam	0.926	0.609	0.031	0.039	0.021	0.018	23.500	25.773
Median Low Flow Sa	0.784	0.501	0.010	0.033	0.009	0.017	22.500	26.700
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.022	0.002
P Low Flow Samples	0.004	0.002	0.887	0.000	0.000	0.000	0.518	0.000
N High Flow Samples	56	56	56	56	56	56	3	56
Mean High Flow Sam	1.470	1.044	0.080	0.069	0.017	0.052	17.000	11.898
Median High Flow Sa	1.432	1.065	0.066	0.037	0.013	0.025	17.600	11.100
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.087	0.001
P High Flow Samples	0.609	0.662	0.610	0.633	0.003	0.968	0.561	0.017
P Difference	0.000	0.000	0.000	0.005	0.216	0.000	0.103	0.000
N All Flow Samples	223	223	223	223	223	223	12	223
Mean All Flow Samp	1.192	0.828	0.060	0.044	0.017	0.027	20.658	18.926
Median All Flow Sam	1.218	0.860	0.030	0.033	0.012	0.018	21.000	17.200
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.013	0.001
P All Flow Samples	0.000	0.000	0.815	0.000	0.000	0.184	0.188	0.000

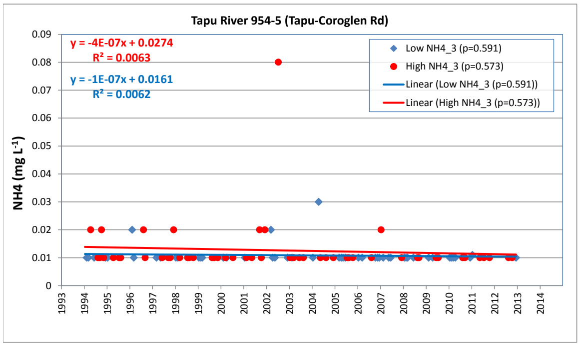
(p values < 0.005 are highlighted as being highly statistically significant)

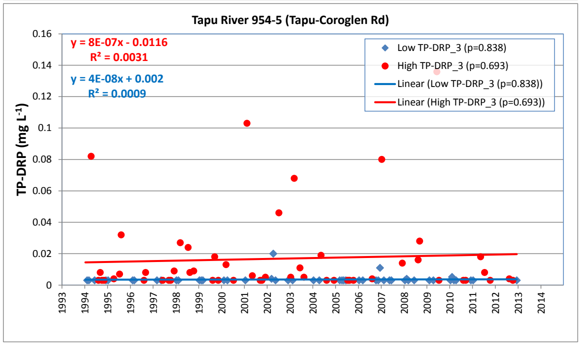


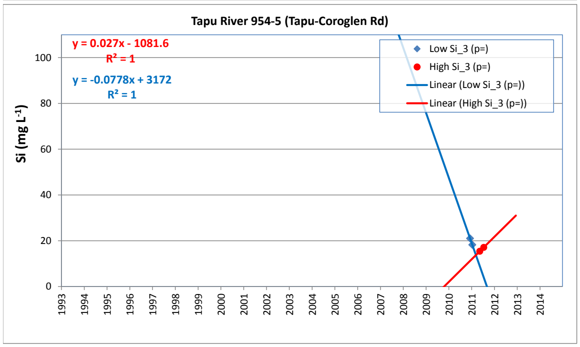


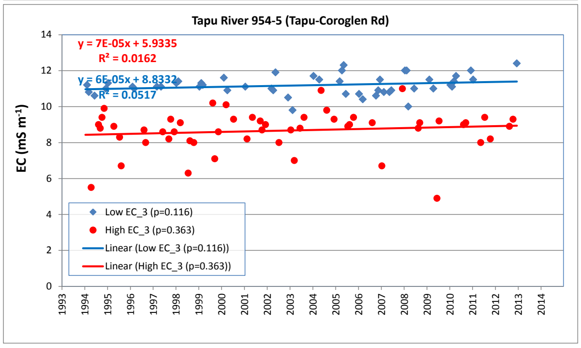








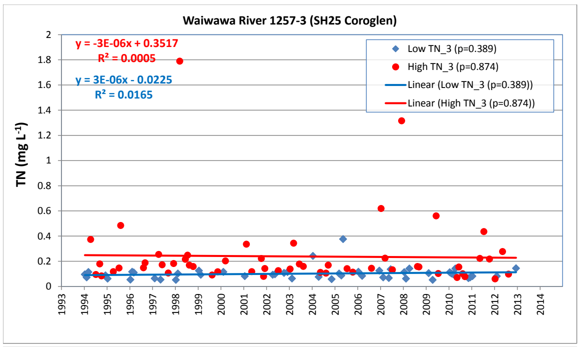


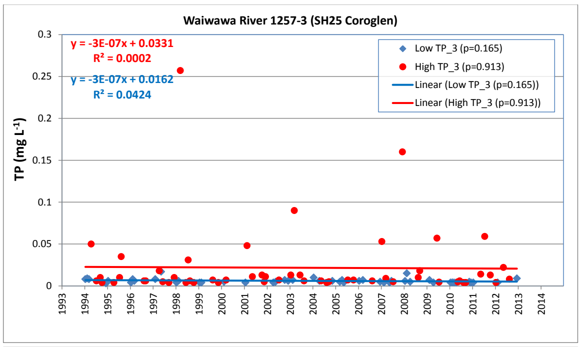


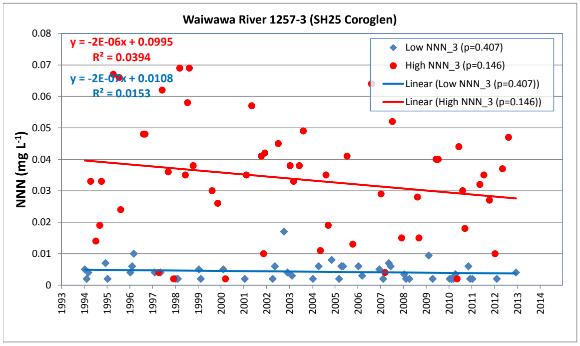
Tapu River 954-5 (Tapu-Coroglen Rd)

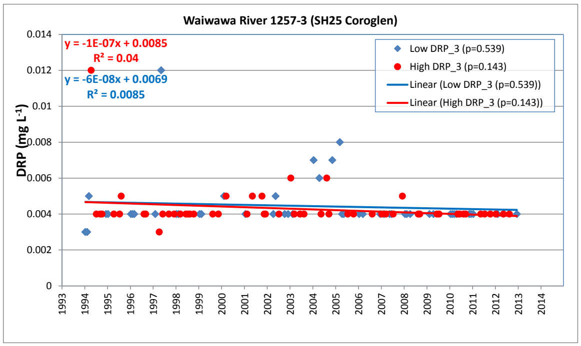
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	49	49	49	49	49	49	2	49
Mean Low Flow Sam	0.073	0.003	0.011	0.005	0.004	0.004	19.600	11.188
Median Low Flow Sa	0.062	0.002	0.010	0.004	0.004	0.003	19.600	11.100
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.078	0.000
P Low Flow Samples	0.988	0.197	0.591	0.644	0.990	0.838		0.116
N High Flow Samples	53	53	53	53	53	53	2	53
Mean High Flow Sam	0.214	0.035	0.013	0.021	0.005	0.017	16.250	8.662
Median High Flow Sa	0.151	0.034	0.010	0.010	0.004	0.005	16.250	8.900
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.027	0.000
P High Flow Samples	0.740	0.032	0.573	0.781	0.199	0.693		0.363
P Difference	0.000	0.000	0.222	0.000	0.096	0.001	0.204	0.000
N All Flow Samples	218	218	218	218	218	218	11	218
Mean All Flow Samp	0.111	0.013	0.011	0.009	0.004	0.007	18.827	10.016
Median All Flow Sam	0.077	0.003	0.010	0.004	0.004	0.003	19.000	10.100
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.006	0.000
P All Flow Samples	0.870	0.004	0.131	0.961	0.229	0.974	0.184	0.055

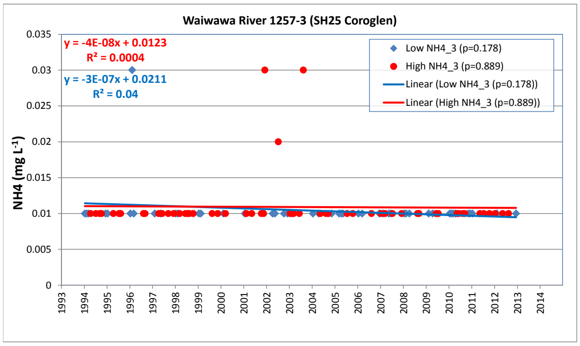
(p values < 0.005 are highlighted as being highly statistically significant)

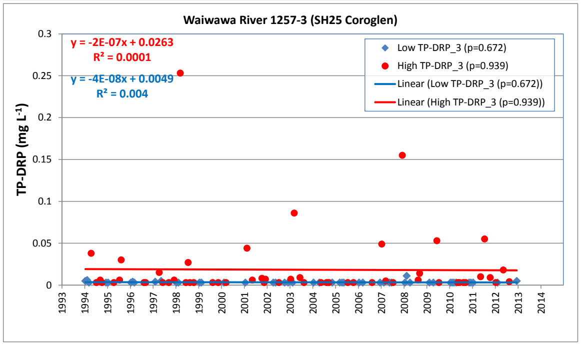


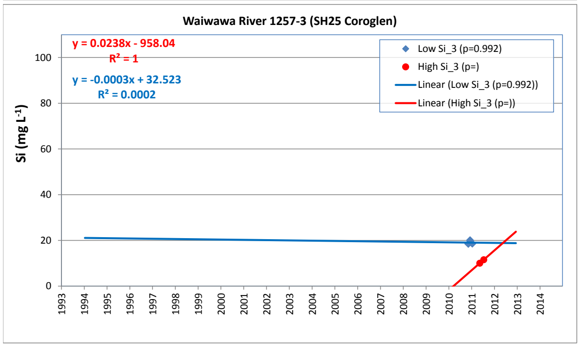


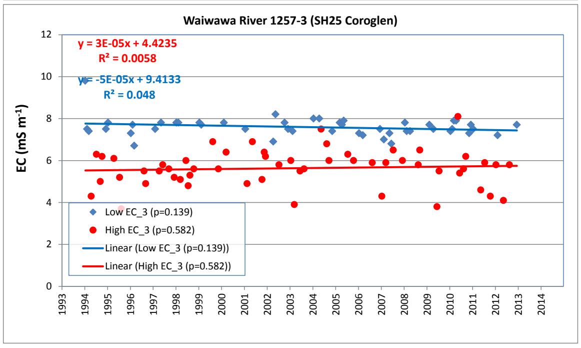








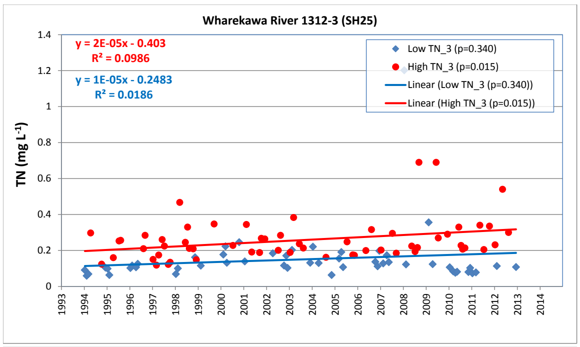


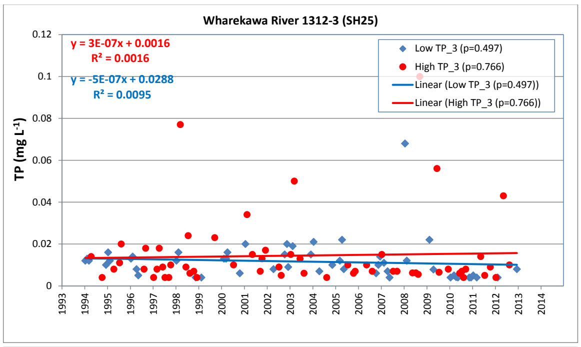


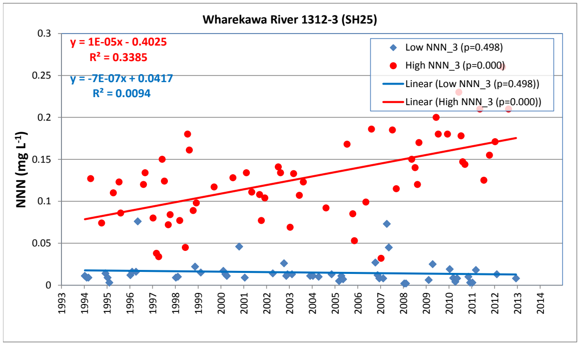
Waiwawa River 1257-3 (SH25 Coroglen)

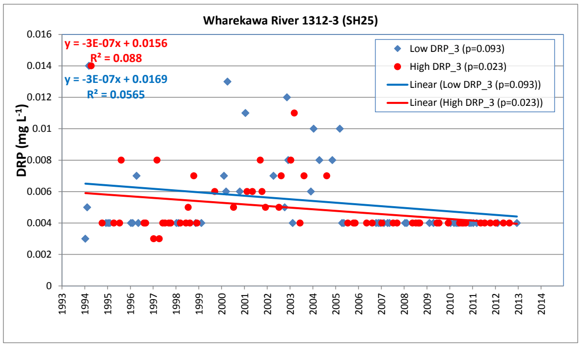
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	47	47	47	47	47	47	3	47
Mean Low Flow Sam	0.102	0.004	0.010	0.006	0.004	0.003	19.033	7.596
Median Low Flow Sa	0.095	0.004	0.010	0.005	0.004	0.003	18.600	7.500
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P Low Flow Samples	0.389	0.407	0.178	0.165	0.539	0.672	0.992	0.139
N High Flow Samples	55	55	55	55	55	55	2	55
Mean High Flow Sam	0.238	0.034	0.011	0.022	0.004	0.018	10.750	5.635
Median High Flow Sa	0.158	0.035	0.010	0.007	0.004	0.003	10.750	5.800
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.024	0.000
P High Flow Samples	0.874	0.146	0.889	0.913	0.143	0.939		0.582
P Difference	0.001	0.000	0.482	0.007	0.557	0.009	0.015	0.000
N All Flow Samples	225	225	225	225	225	225	11	225
Mean All Flow Samp	0.134	0.018	0.011	0.010	0.004	0.007	16.264	6.603
Median All Flow Sam	0.102	0.010	0.010	0.005	0.004	0.003	17.200	6.700
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.014	0.000
P All Flow Samples	0.757	0.038	0.021	0.909	0.096	0.973	0.105	0.869

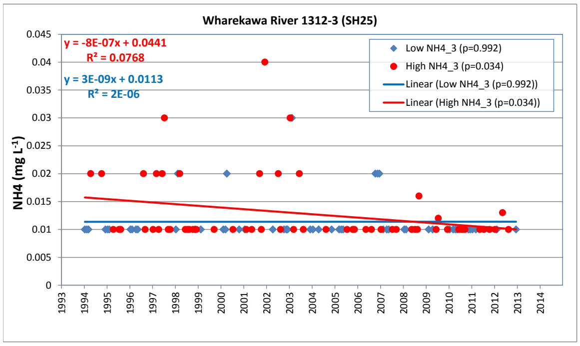
(p values < 0.005 are highlighted as being highly statistically significant)

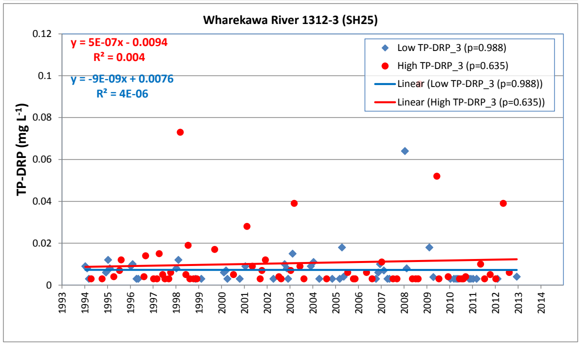


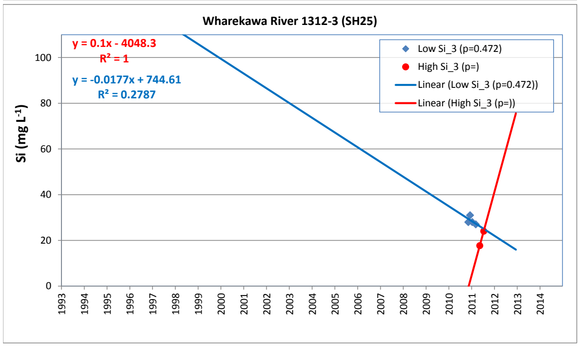


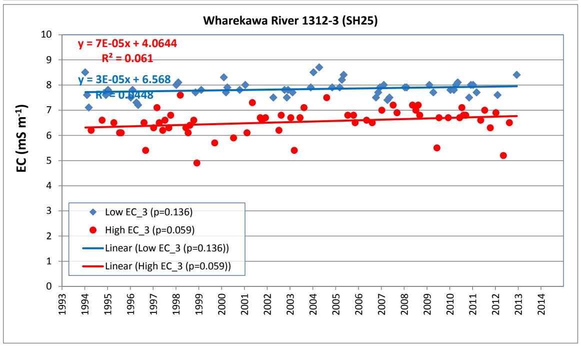








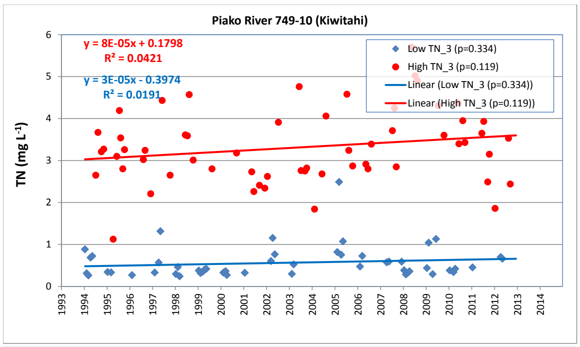


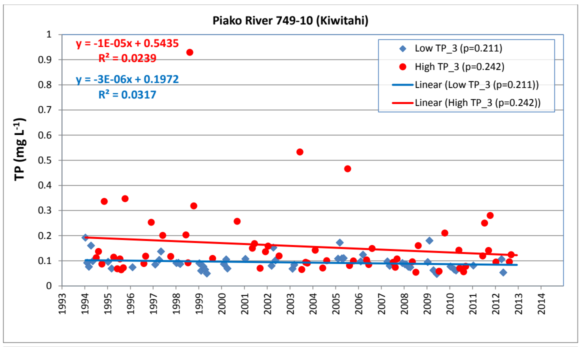


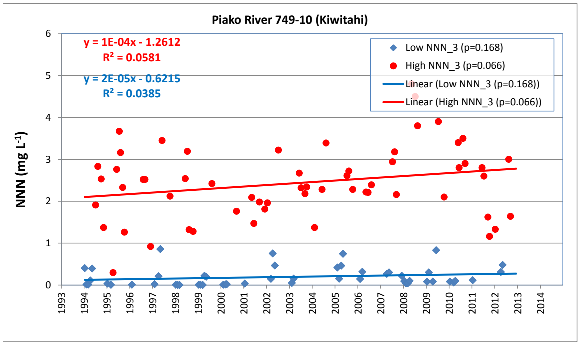
Wharekawa River 1312-3 (SH25)

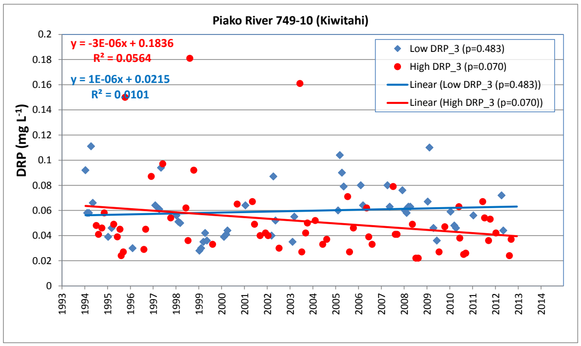
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	51	51	51	51	51	51	4	51
Mean Low Flow Sam	0.150	0.015	0.011	0.012	0.005	0.007	28.500	7.835
Median Low Flow Sa	0.116	0.011	0.010	0.010	0.004	0.004	28.000	7.800
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.018	0.000
P Low Flow Samples	0.340	0.498	0.992	0.497	0.093	0.988	0.472	0.136
N High Flow Samples	59	59	59	59	59	59	2	59
Mean High Flow Sam	0.257	0.127	0.013	0.014	0.005	0.011	20.850	6.539
Median High Flow Sa	0.228	0.124	0.010	0.008	0.004	0.004	20.850	6.600
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.100	0.000
P High Flow Samples	0.015	0.000	0.034	0.766	0.023	0.635		0.059
P Difference	0.000	0.000	0.120	0.285	0.250	0.210	0.229	0.000
N All Flow Samples	223	223	223	223	223	223	12	223
Mean All Flow Samp	0.176	0.063	0.012	0.011	0.005	0.008	26.058	7.202
Median All Flow Sam	0.150	0.047	0.010	0.008	0.004	0.003	26.500	7.200
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.011	0.000
P All Flow Samples	0.007	0.004	0.018	0.926	0.003	0.559	0.206	0.022

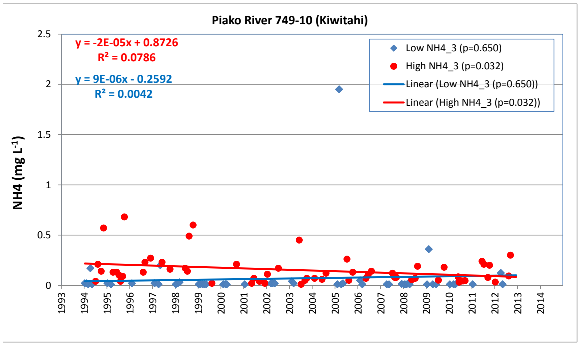
(p values < 0.005 are highlighted as being highly statistically significant)

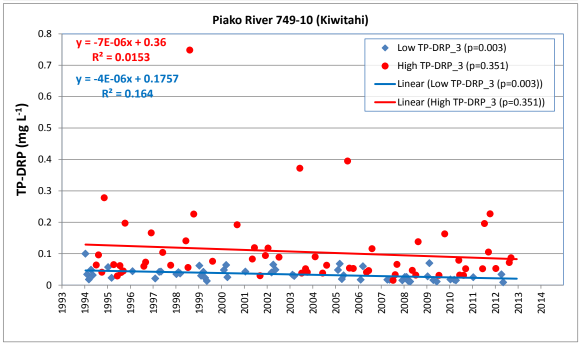


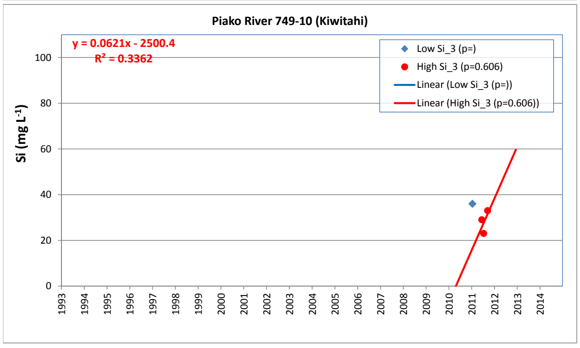


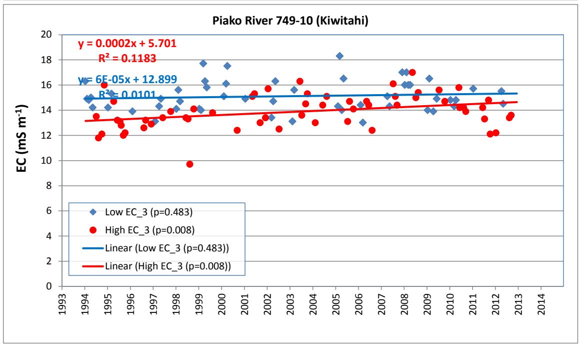








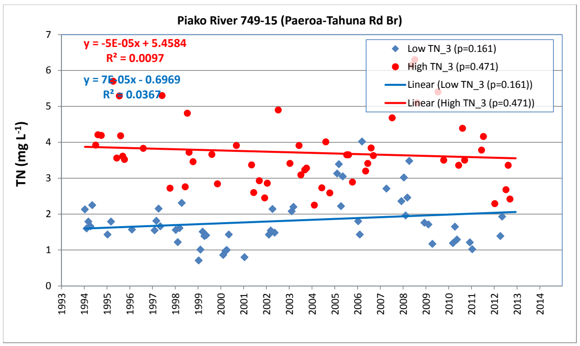


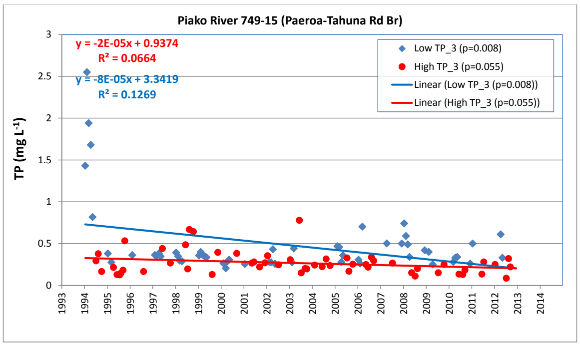


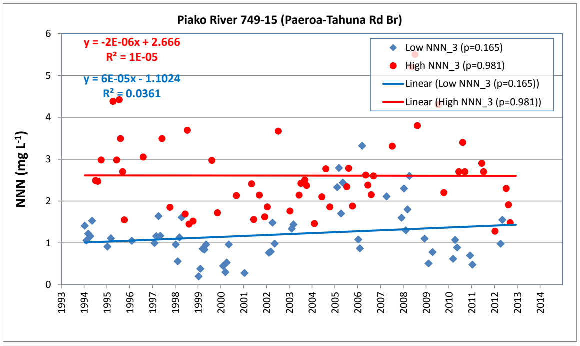
Piako River 749-10 (Kiwitahi)

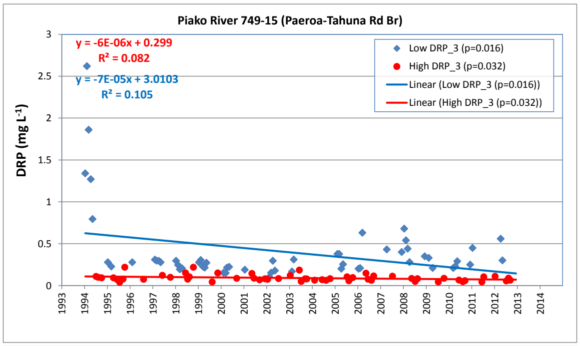
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	51	51	51	51	51	51	1	51
Mean Low Flow Sam	0.565	0.193	0.068	0.094	0.059	0.034	36.000	15.112
Median Low Flow Sa	0.419	0.100	0.010	0.087	0.058	0.031	36.000	14.900
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P Low Flow Samples	0.334	0.168	0.650	0.211	0.483	0.003		0.483
N High Flow Sample:	59	59	59	59	59	59	3	59
Mean High Flow Sam	3.312	2.437	0.152	0.158	0.052	0.106	28.333	13.893
Median High Flow Sa	3.240	2.390	0.110	0.112	0.042	0.065	29.000	13.900
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.062	0.000
P High Flow Samples	0.119	0.066	0.032	0.242	0.070	0.351	0.606	0.008
P Difference	0.000	0.000	0.054	0.001	0.127	0.000		0.000
N All Flow Samples	228	228	228	228	228	228	12	228
Mean All Flow Samp	1.799	1.234	0.084	0.124	0.057	0.067	34.250	14.400
Median All Flow Sam	1.520	1.010	0.030	0.106	0.053	0.052	33.000	14.300
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.021	0.000
P All Flow Samples	0.651	0.510	0.186	0.069	0.347	0.069	0.159	0.016

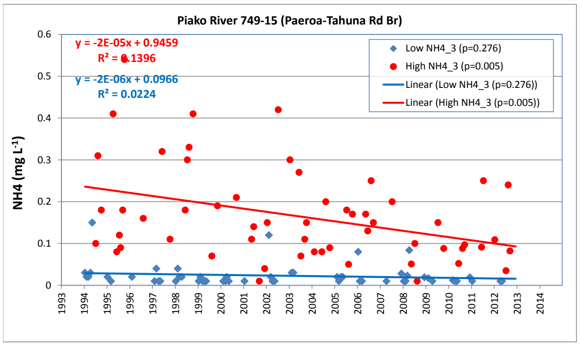
(p values < 0.005 are highlighted as being highly statistically significant)

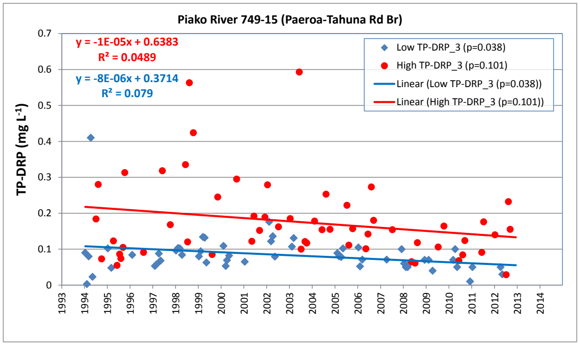


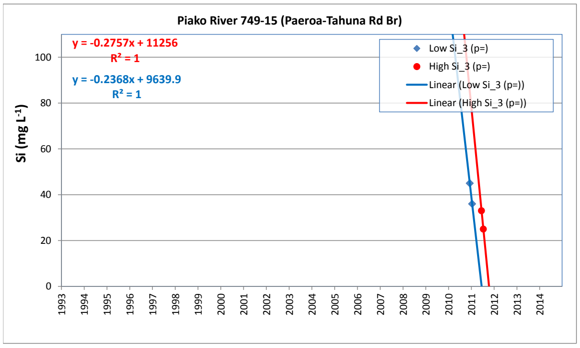


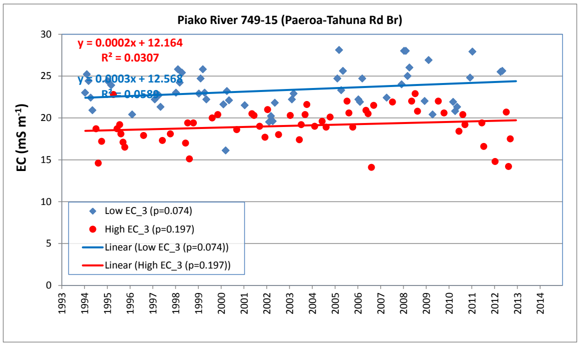








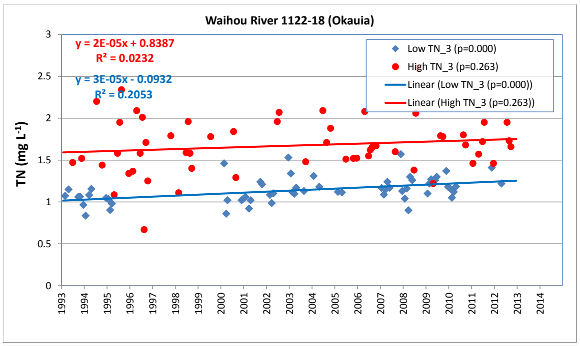


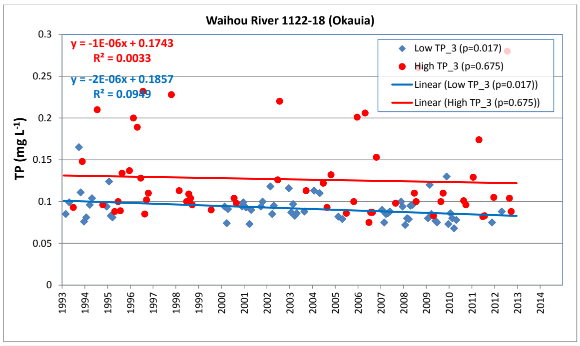


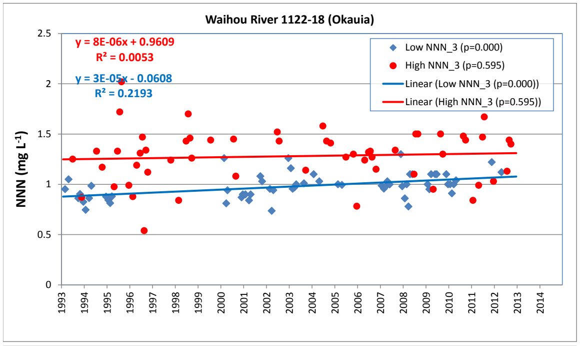
Piako River 749-15 (Paeroa-Tahuna Rd Br)

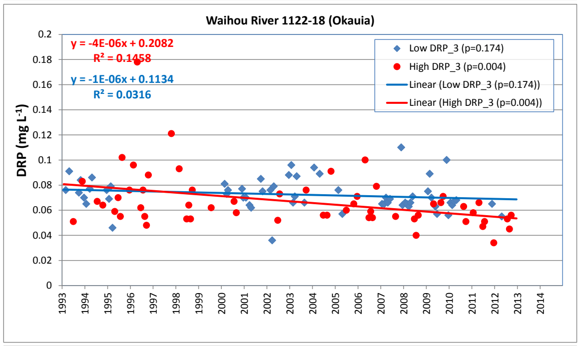
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	55	55	55	55	55	55	2	55
Mean Low Flow Sam	1.807	1.203	0.023	0.491	0.408	0.084	40.500	23.315
Median Low Flow Sa	1.650	1.070	0.012	0.357	0.279	0.079	40.500	23.000
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.237	0.000
P Low Flow Samples	0.161	0.165	0.276	0.008	0.016	0.038		0.074
N High Flow Samples	56	56	56	56	56	56	2	56
Mean High Flow Sam	3.717	2.609	0.165	0.267	0.091	0.176	29.000	19.089
Median High Flow Sa	3.585	2.445	0.145	0.244	0.082	0.154	29.000	19.200
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.276	0.000
P High Flow Samples	0.471	0.981	0.005	0.055	0.032	0.101		0.197
P Difference	0.000	0.000	0.000	0.001	0.000	0.000	0.198	0.000
N All Flow Samples	218	218	218	218	218	218	12	218
Mean All Flow Samp	2.553	1.743	0.092	0.336	0.207	0.129	35.833	20.701
Median All Flow Sam	2.330	1.565	0.060	0.290	0.150	0.106	36.500	20.500
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.026	0.000
P All Flow Samples	0.843	0.867	0.001	0.000	0.017	0.000	0.063	0.012

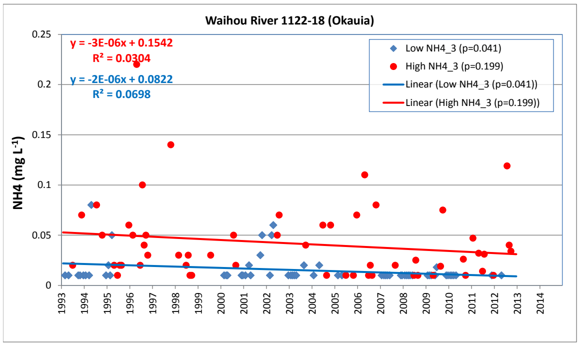
(p values < 0.005 are highlighted as being highly statistically significant)

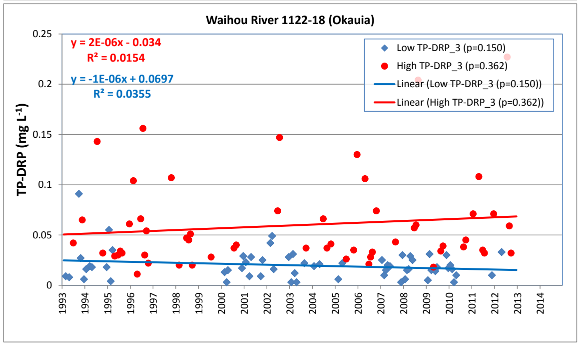


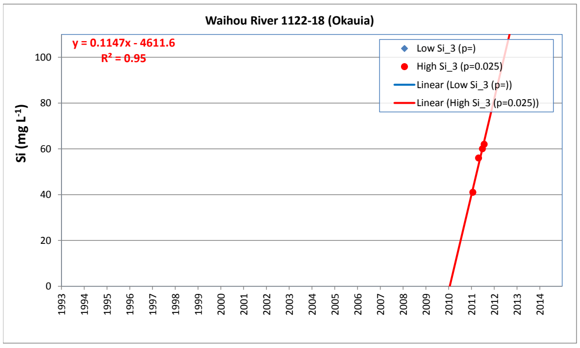


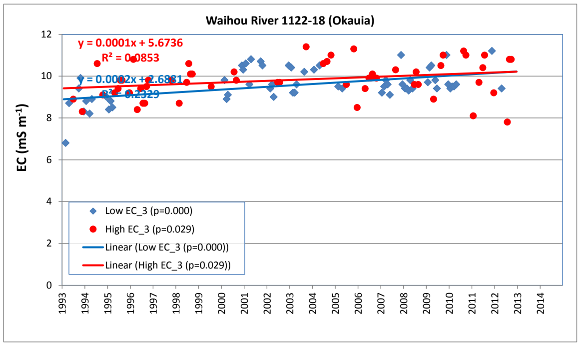








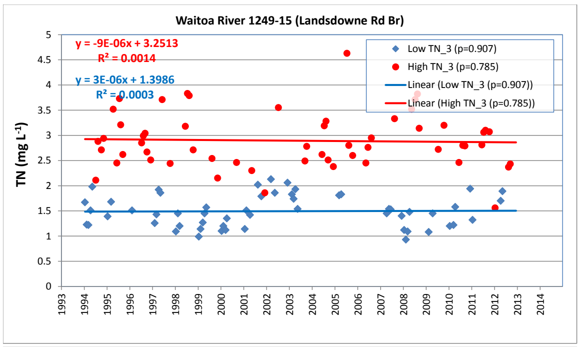


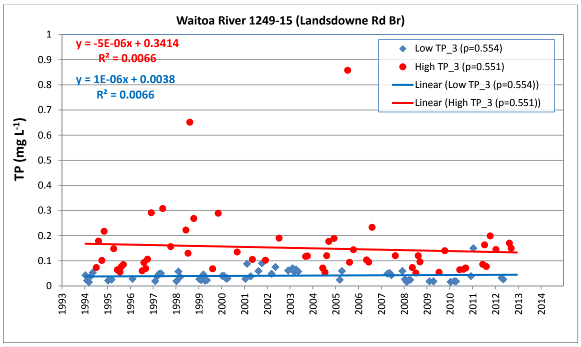


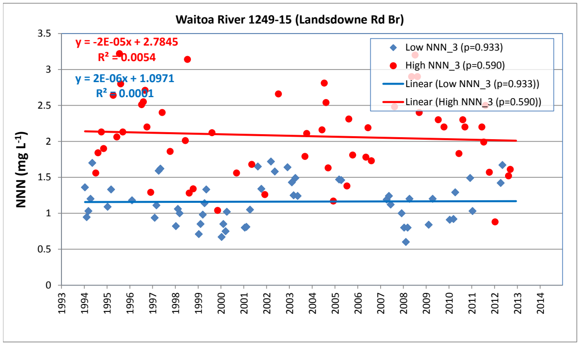
Waihou River 1122-18 (Okauia)

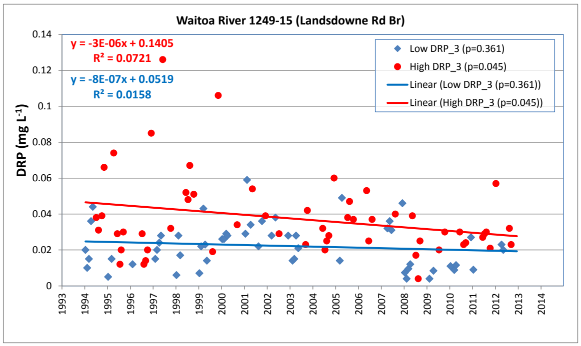
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	60	60	60	60	60	60	0	60
Mean Low Flow Sam	1.141	0.982	0.015	0.092	0.072	0.020		9.590
Median Low Flow Sa	1.125	0.986	0.010	0.088	0.070	0.018		9.500
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P Low Flow Samples	0.000	0.000	0.041	0.017	0.174	0.150		0.000
N High Flow Samples	56	56	56	56	56	56	4	56
Mean High Flow Sam	1.673	1.280	0.042	0.127	0.067	0.060	54.750	9.820
Median High Flow Sa	1.655	1.315	0.030	0.104	0.062	0.042	58.000	9.800
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.115	0.000
P High Flow Samples	0.263	0.595	0.199	0.675	0.004	0.362	0.025	0.029
P Difference	0.000	0.000	0.000	0.000	0.120	0.000		0.136
N All Flow Samples	240	240	240	240	240	240	12	240
Mean All Flow Samp	1.348	1.116	0.023	0.104	0.072	0.032	62.083	9.809
Median All Flow Sam	1.290	1.090	0.010	0.095	0.068	0.027	65.000	9.750
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000
P All Flow Samples	0.000	0.000	0.056	0.033	0.000	0.815	0.707	0.000

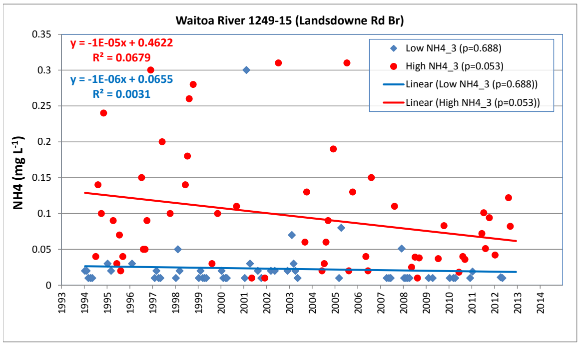
(p values < 0.005 are highlighted as being highly statistically significant)

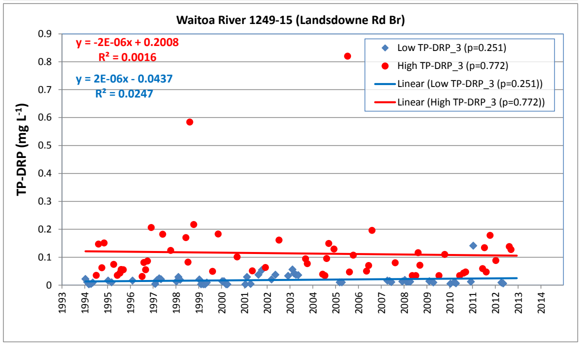


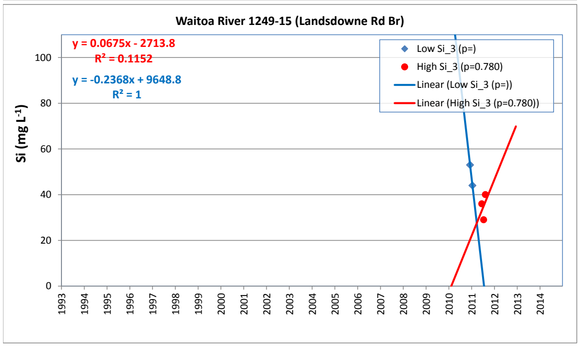


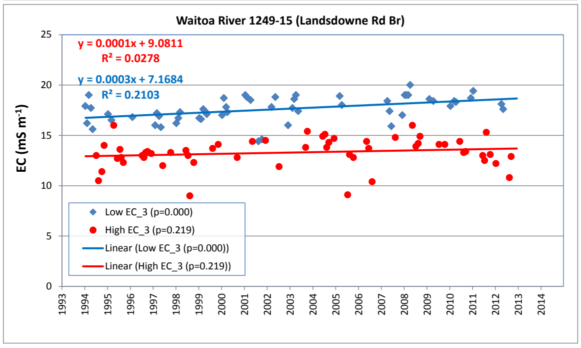








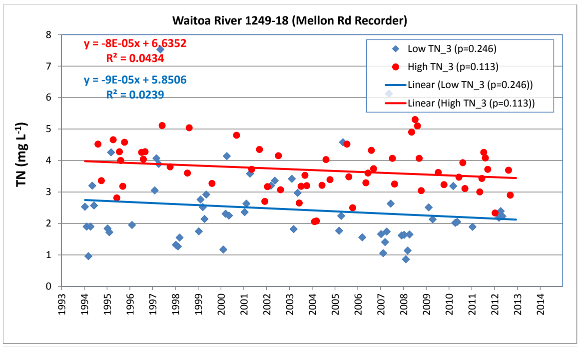


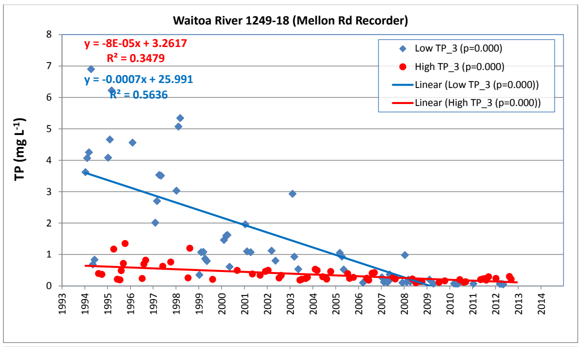


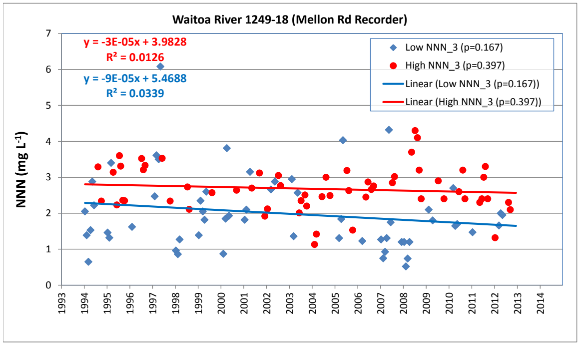
Waitoa River 1249-15 (Landsdowne Rd Br)

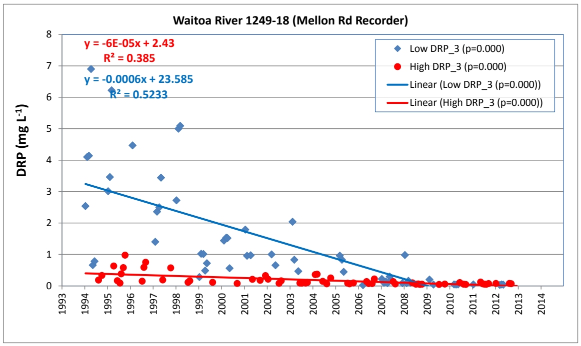
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	55	55	55	55	55	55	2	55
Mean Low Flow Sam	1.493	1.162	0.023	0.041	0.022	0.019	48.500	17.595
Median Low Flow Sa	1.450	1.140	0.010	0.038	0.022	0.013	48.500	17.700
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.237	0.000
P Low Flow Samples	0.907	0.933	0.688	0.554	0.361	0.251		0.000
N High Flow Sample:	56	56	56	56	56	56	3	56
Mean High Flow Sam	2.894	2.076	0.096	0.151	0.037	0.114	35.000	13.302
Median High Flow Sa	2.800	2.125	0.077	0.118	0.031	0.081	36.000	13.350
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.067	0.000
P High Flow Samples	0.785	0.590	0.053	0.551	0.045	0.772	0.780	0.219
P Difference	0.000	0.000	0.000	0.000	0.000	0.000	0.134	0.000
N All Flow Samples	226	226	226	226	226	226	12	226
Mean All Flow Samp	2.079	1.556	0.048	0.089	0.032	0.057	42.417	15.536
Median All Flow Sam	1.945	1.490	0.020	0.073	0.029	0.043	41.500	15.400
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.033	0.000
P All Flow Samples	0.736	0.999	0.062	0.341	0.139	0.477	0.047	0.002

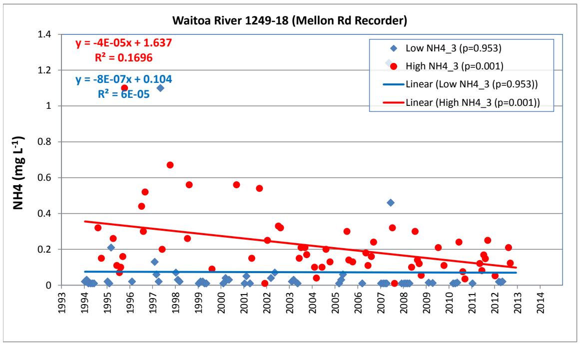
(p values < 0.005 are highlighted as being highly statistically significant)

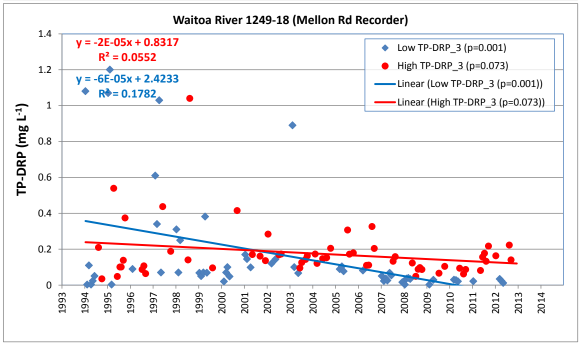


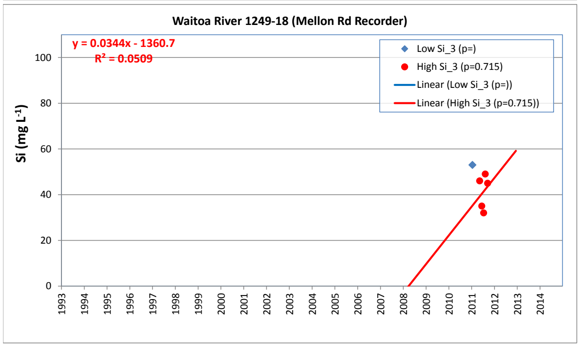


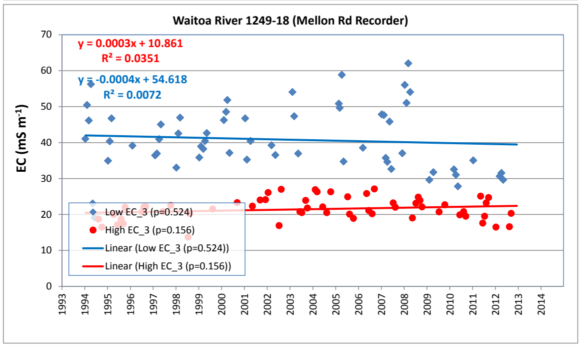








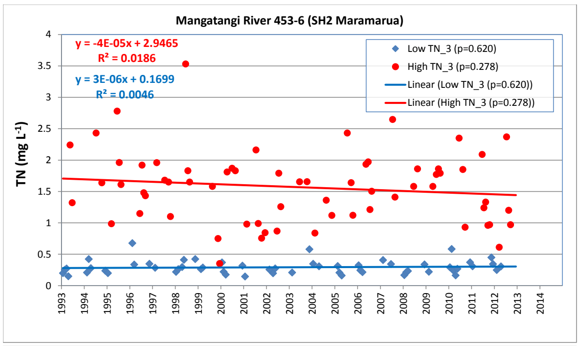


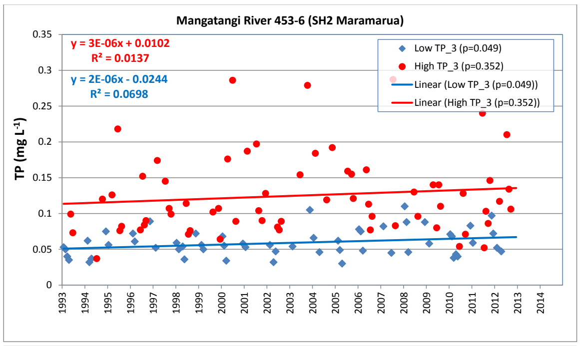


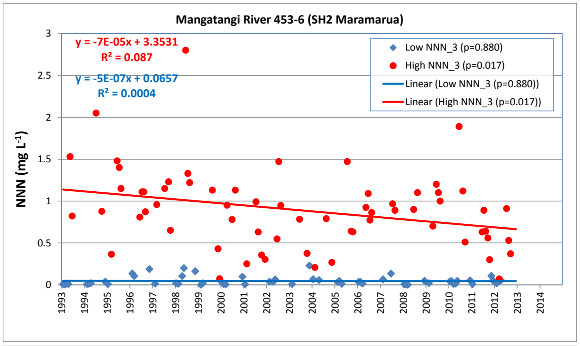
Waitoa River 1249-18 (Mellon Rd Recorder)

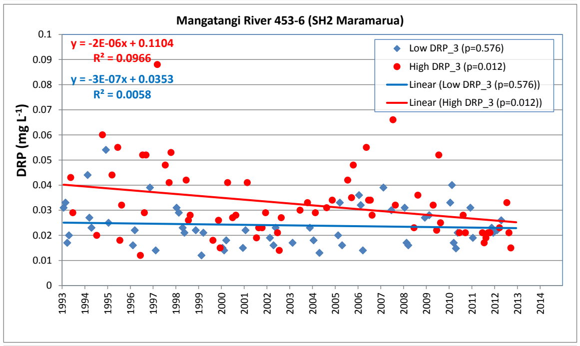
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	58	58	58	58	58	58	1	59
Mean Low Flow Sam	2.467	2.001	0.073	1.570	1.401	0.170	53.000	40.846
Median Low Flow Sa	2.205	1.810	0.015	0.898	0.806	0.068	53.000	39.200
Trend Low Flow Sam	0.000	0.000	0.000	-0.001	-0.001	0.000		0.000
P Low Flow Samples	0.246	0.167	0.953	0.000	0.000	0.001		0.524
N High Flow Samples	59	59	59	59	59	59	5	59
Mean High Flow Sam	3.695	2.680	0.219	0.361	0.185	0.176	41.400	21.485
Median High Flow Sa	3.620	2.630	0.160	0.253	0.104	0.140	45.000	21.500
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.034	0.000
P High Flow Samples	0.113	0.397	0.001	0.000	0.000	0.073	0.715	0.156
P Difference	0.000	0.000	0.000	0.000	0.000	0.892		0.000
N All Flow Samples	228	228	228	228	228	228	12	230
Mean All Flow Samp	2.966	2.283	0.137	0.824	0.670	0.154	47.917	29.907
Median All Flow Sam	2.890	2.295	0.060	0.355	0.183	0.102	48.000	27.800
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.053	0.000
P All Flow Samples	0.023	0.019	0.001	0.000	0.000	0.000	0.034	0.254

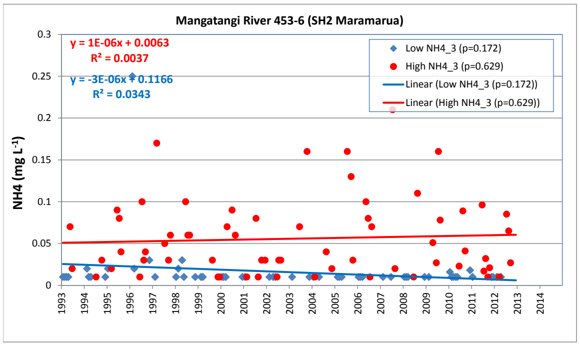
(p values < 0.005 are highlighted as being highly statistically significant)

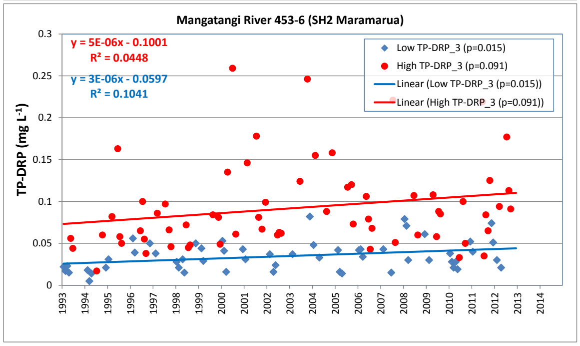


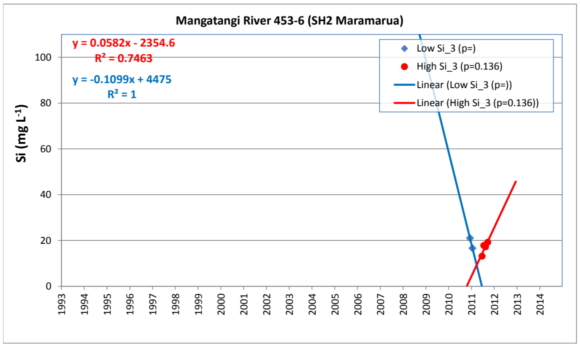


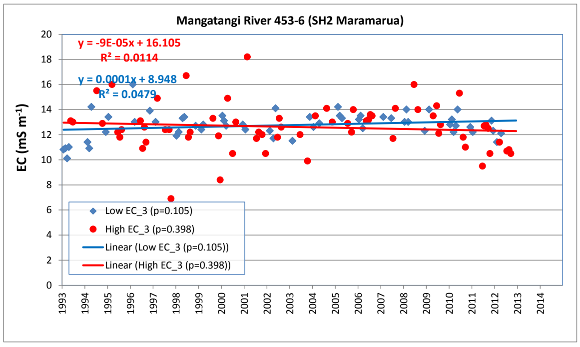








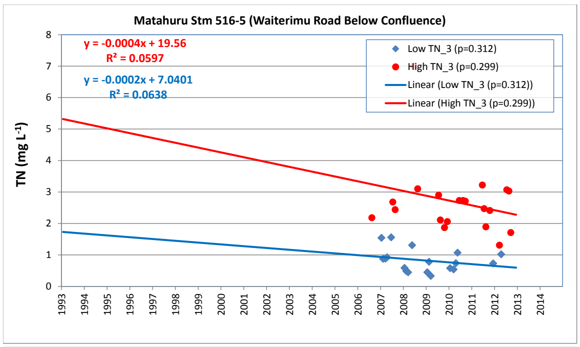


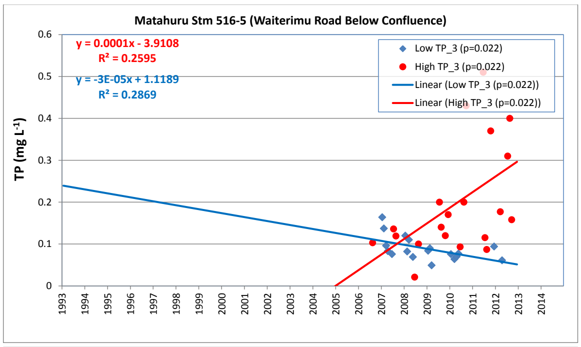


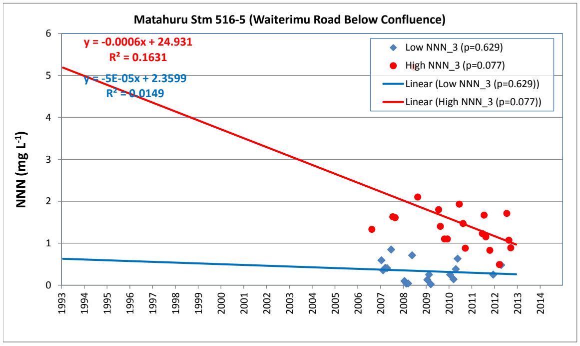
Mangatangi River 453-6 (SH2 Maramarua)

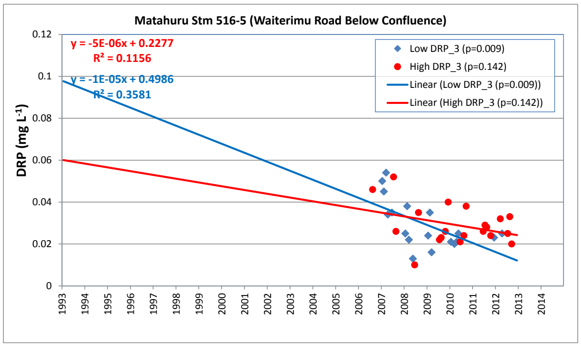
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	56	56	56	56	56	56	2	56
Mean Low Flow Sam	0.292	0.047	0.016	0.059	0.024	0.035	18.800	12.755
Median Low Flow Sa	0.274	0.031	0.010	0.056	0.022	0.031	18.800	12.800
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.110	0.000
P Low Flow Samples	0.620	0.880	0.172	0.049	0.576	0.015		0.105
N High Flow Samples	65	65	65	65	65	65	4	65
Mean High Flow Sam	1.569	0.892	0.056	0.125	0.032	0.093	16.825	12.608
Median High Flow Sa	1.610	0.890	0.040	0.110	0.029	0.081	17.500	12.600
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.058	0.000
P High Flow Samples	0.278	0.017	0.629	0.352	0.012	0.091	0.136	0.398
P Difference	0.000	0.000	0.000	0.000	0.000	0.000	0.530	0.584
N All Flow Samples	240	240	240	240	240	240	12	240
Mean All Flow Samp	0.862	0.445	0.026	0.090	0.029	0.060	18.508	13.028
Median All Flow Sam	0.660	0.289	0.010	0.083	0.026	0.054	18.500	13.100
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.012	0.000
P All Flow Samples	0.218	0.008	0.966	0.066	0.094	0.009	0.160	0.511

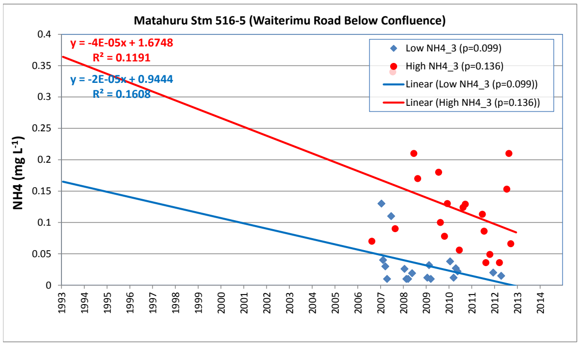
(p values < 0.005 are highlighted as being highly statistically significant)

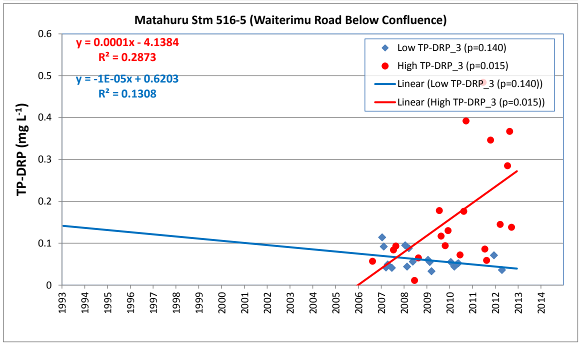


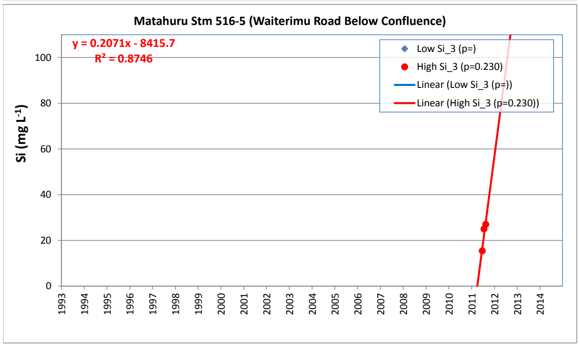


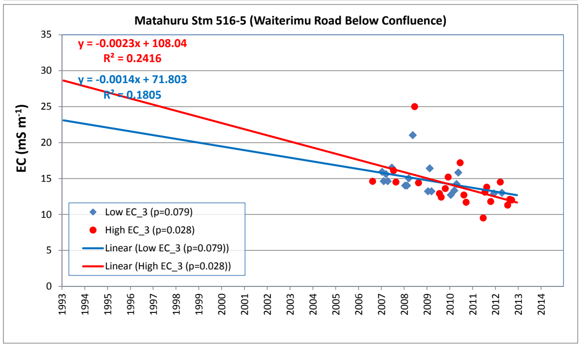








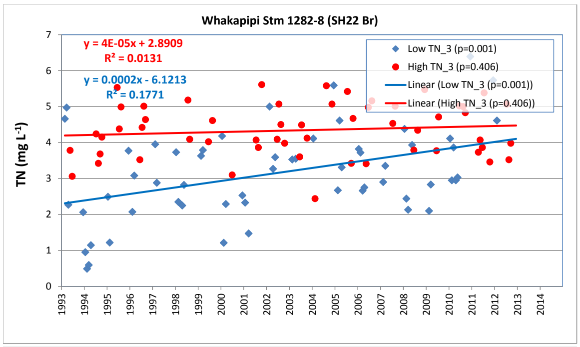


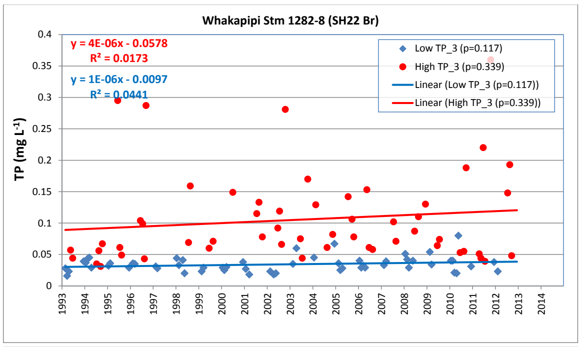


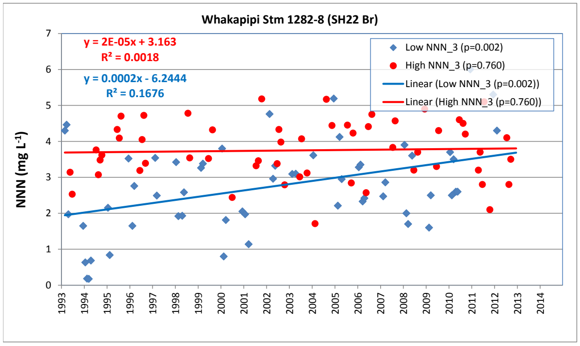
Matahuru Stm 516-5 (Waiterimu Road Below Confluence)

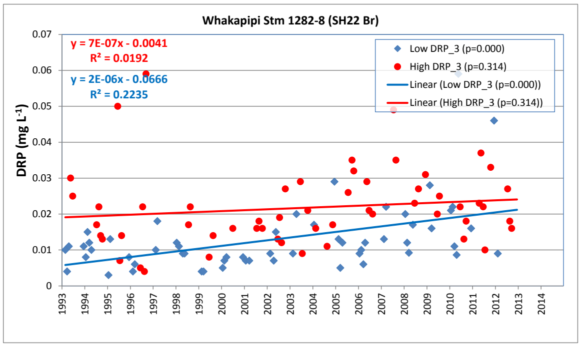
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	18	18	18	18	18	18	0	18
Mean Low Flow Sam	0.826	0.335	0.032	0.089	0.029	0.060		14.772
Median Low Flow Sa	0.760	0.303	0.021	0.083	0.025	0.054		14.400
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		-0.001
P Low Flow Samples	0.312	0.629	0.099	0.022	0.009	0.140		0.079
N High Flow Samples	20	20	20	20	20	20	3	20
Mean High Flow Sam	2.681	1.530	0.121	0.198	0.029	0.169	22.467	13.920
Median High Flow Sa	2.575	1.365	0.107	0.149	0.026	0.124	25.000	13.350
Trend High Flow Sam	0.000	-0.001	0.000	0.000	0.000	0.000	0.207	-0.002
P High Flow Samples	0.299	0.077	0.136	0.022	0.142	0.015	0.230	0.028
P Difference	0.000	0.000	0.000	0.002	0.950	0.002		0.322
N All Flow Samples	78	78	78	78	78	78	12	78
Mean All Flow Samp	1.616	0.869	0.066	0.131	0.028	0.103	24.350	14.188
Median All Flow Sam	1.400	0.789	0.040	0.110	0.026	0.086	26.500	13.800
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.001
P All Flow Samples	0.674	0.515	0.051	0.191	0.000	0.060	0.985	0.002

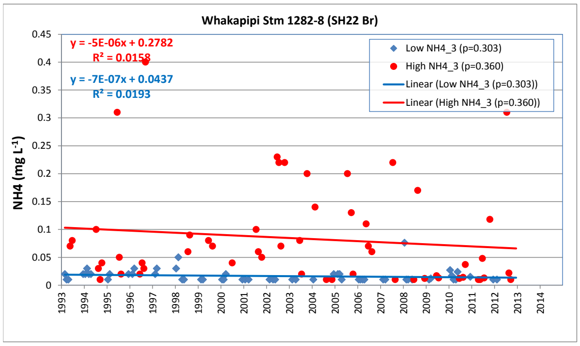
(p values < 0.005 are highlighted as being highly statistically significant)

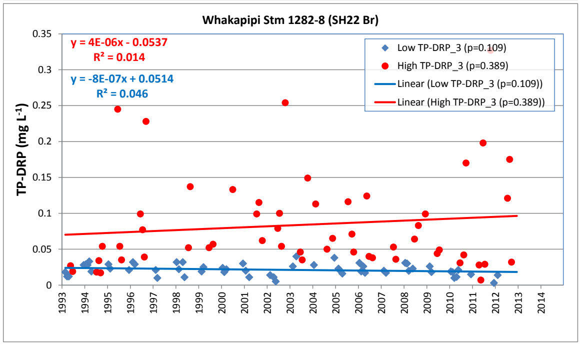


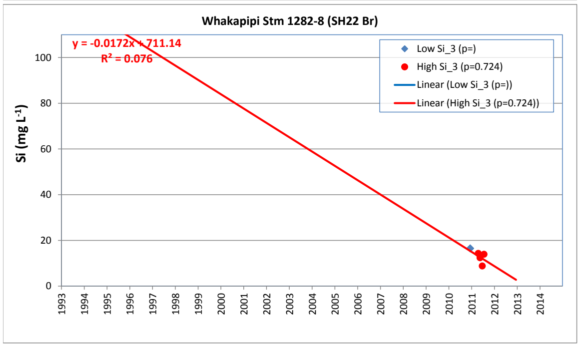


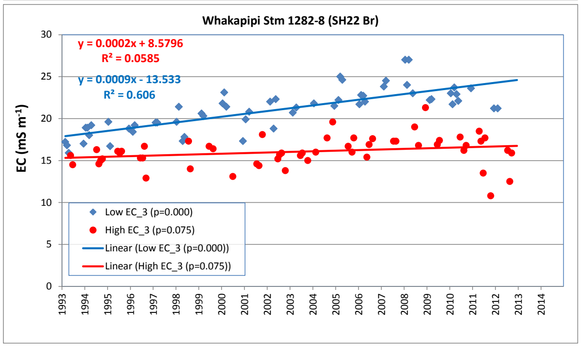








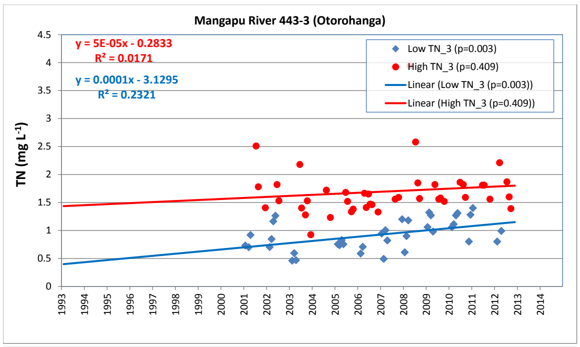


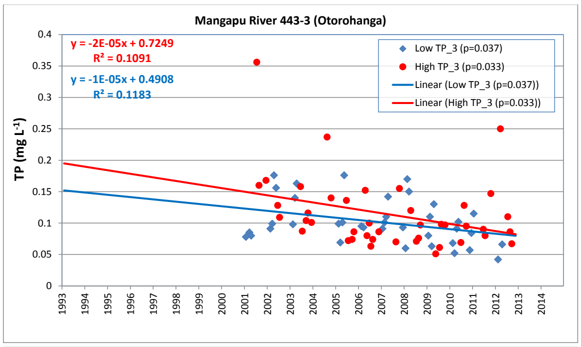


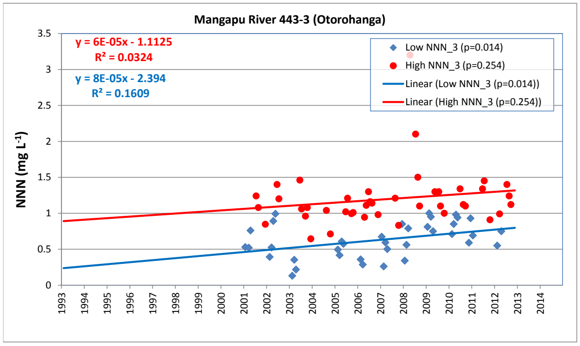
Whakapipi Stm 1282-8 (SH22 Br)

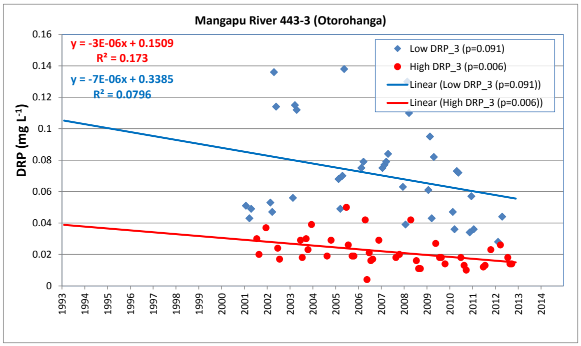
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	57	57	57	57	57	57	1	57
Mean Low Flow Sam	3.141	2.752	0.016	0.034	0.013	0.021	16.500	21.009
Median Low Flow Sa	3.030	2.600	0.010	0.032	0.010	0.021	16.500	21.400
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.001
P Low Flow Samples	0.001	0.002	0.303	0.117	0.000	0.109		0.000
N High Flow Sample:	55	55	55	55	55	55	4	55
Mean High Flow Sam	4.344	3.751	0.084	0.106	0.022	0.084	12.350	16.073
Median High Flow Sa	4.340	3.700	0.050	0.078	0.020	0.054	13.150	16.100
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.017	0.000
P High Flow Samples	0.406	0.760	0.360	0.339	0.314	0.389	0.724	0.075
P Difference	0.000	0.000	0.000	0.000	0.000	0.000		0.000
N All Flow Samples	239	239	239	239	239	239	12	239
Mean All Flow Samp	3.819	3.381	0.036	0.061	0.019	0.042	12.933	18.168
Median All Flow Sam	3.860	3.400	0.015	0.046	0.014	0.029	13.400	17.700
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.003	0.000
P All Flow Samples	0.000	0.000	0.887	0.001	0.000	0.120	0.660	0.000

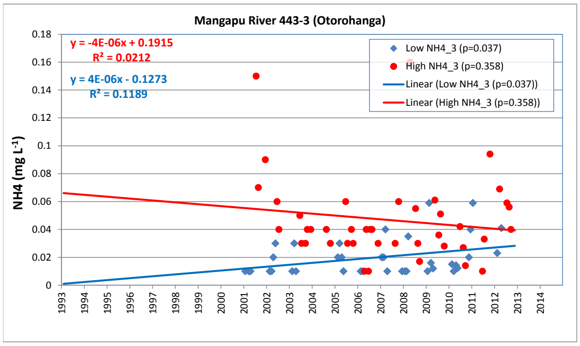
(p values < 0.005 are highlighted as being highly statistically significant)

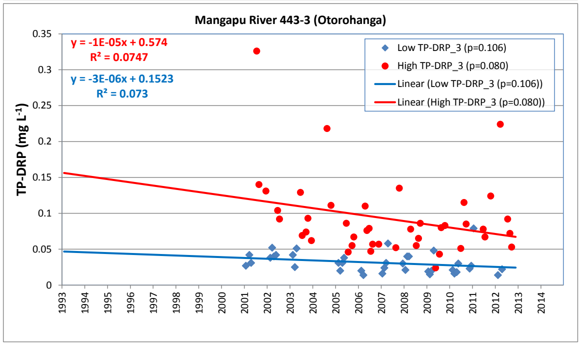


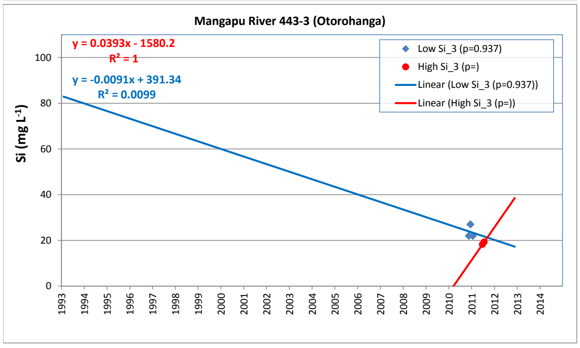


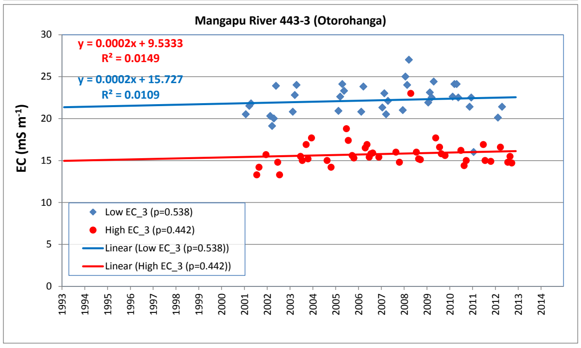








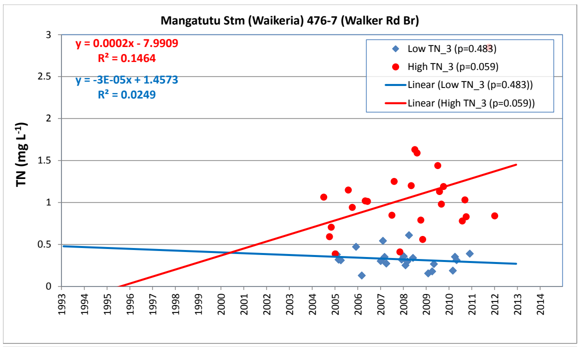


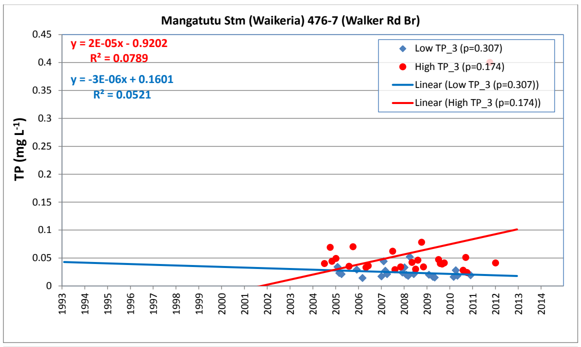


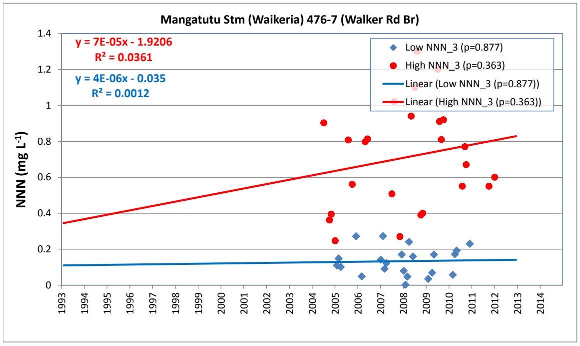
Mangapu River 443-3 (Otorohanga)

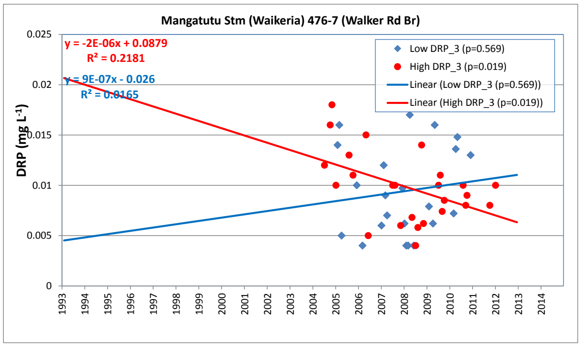
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	37	37	37	37	37	37	3	37
Mean Low Flow Sam	0.919	0.625	0.020	0.102	0.071	0.031	23.667	22.181
Median Low Flow Sa	0.900	0.594	0.014	0.095	0.068	0.030	22.000	22.500
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.009	0.000
P Low Flow Samples	0.003	0.014	0.037	0.037	0.091	0.106	0.937	0.538
N High Flow Sample:	42	42	42	42	42	42	2	42
Mean High Flow Sam	1.698	1.196	0.047	0.114	0.022	0.093	18.750	15.800
Median High Flow Sa	1.585	1.115	0.040	0.098	0.019	0.079	18.750	15.500
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.039	0.000
P High Flow Samples	0.409	0.254	0.358	0.033	0.006	0.080		0.442
P Difference	0.000	0.000	0.000	0.251	0.000	0.000	0.087	0.000
N All Flow Samples	146	146	146	146	146	146	12	146
Mean All Flow Samp	1.257	0.876	0.036	0.098	0.041	0.057	21.067	18.584
Median All Flow Sam	1.231	0.850	0.030	0.087	0.032	0.046	21.000	18.100
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.013	0.000
P All Flow Samples	0.007	0.003	0.558	0.001	0.003	0.210	0.061	0.841

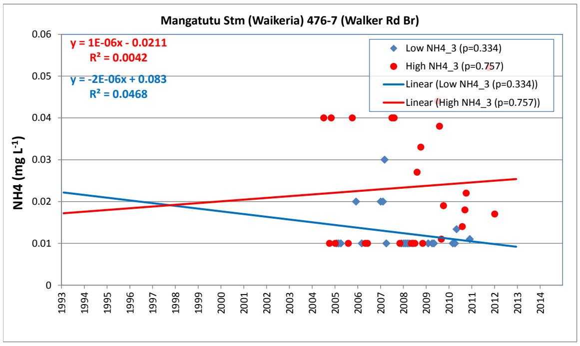
(p values < 0.005 are highlighted as being highly statistically significant)

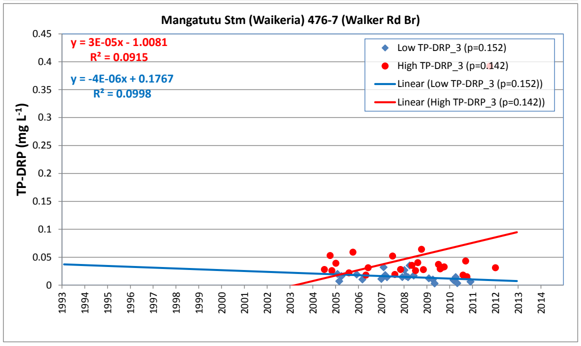


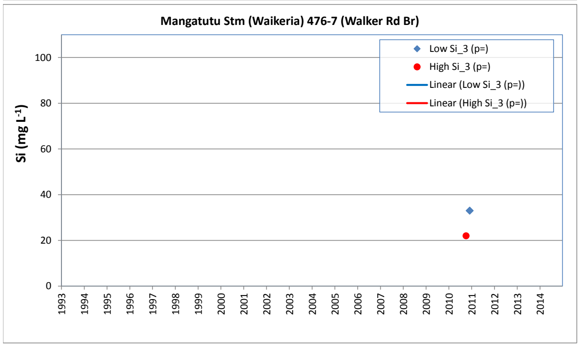


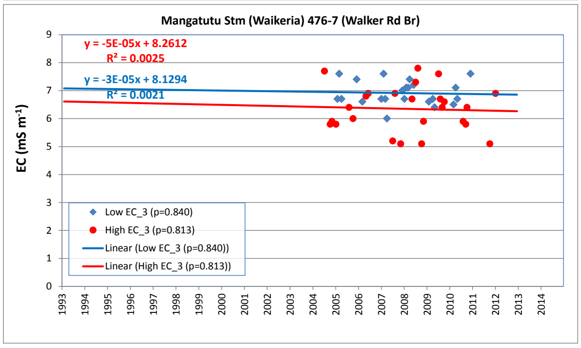








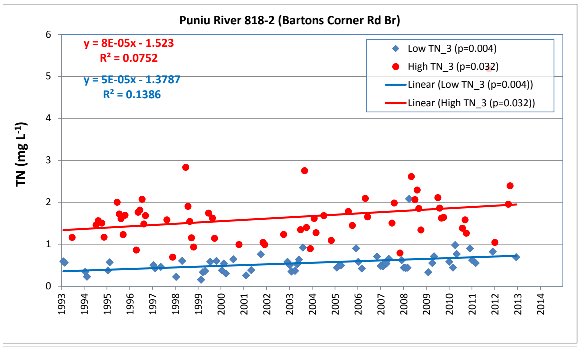


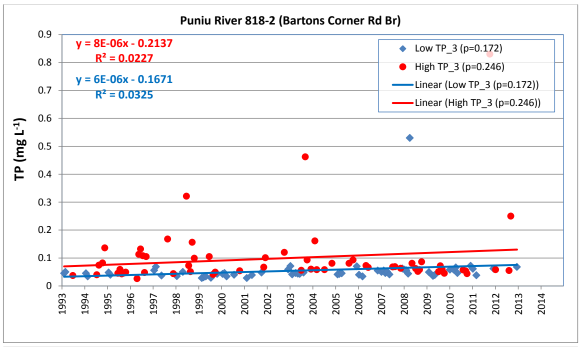


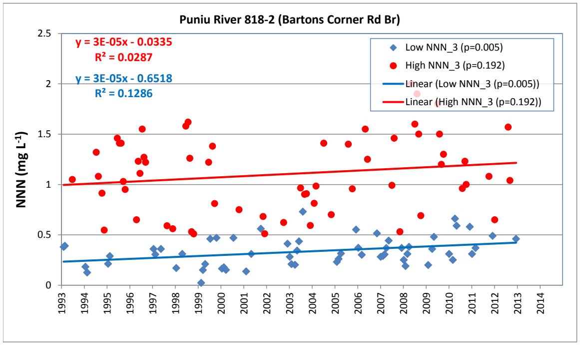
Mangatutu Stm (Waikeria) 476-7 (Walker Rd Br)

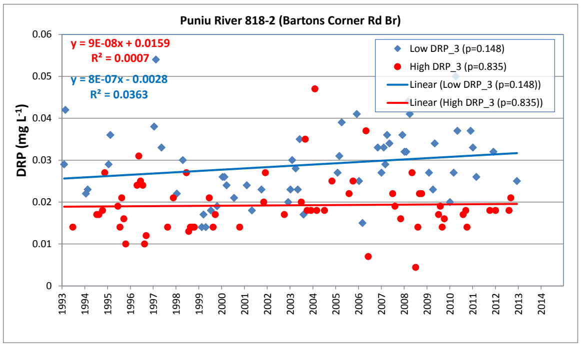
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	22	22	22	22	22	22	1	22
Mean Low Flow Sam	0.323	0.133	0.012	0.024	0.009	0.015	33.000	6.914
Median Low Flow Sa	0.316	0.132	0.010	0.021	0.008	0.014	33.000	6.700
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P Low Flow Samples	0.483	0.877	0.334	0.307	0.569	0.152		0.840
N High Flow Samples	25	25	25	25	25	25	1	25
Mean High Flow Sam	1.049	0.712	0.023	0.058	0.010	0.048	22.000	6.348
Median High Flow Sa	1.013	0.770	0.018	0.041	0.010	0.031	22.000	6.400
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P High Flow Samples	0.059	0.363	0.757	0.174	0.019	0.142		0.813
P Difference	0.000	0.000	0.001	0.031	0.737	0.034		0.004
N All Flow Samples	100	100	100	100	100	100	12	102
Mean All Flow Samp	0.662	0.441	0.016	0.034	0.010	0.024	27.500	6.746
Median All Flow Sam	0.572	0.393	0.010	0.027	0.009	0.017	28.000	6.850
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000
P All Flow Samples	0.782	0.870	0.053	0.963	0.111	0.819	0.373	0.734

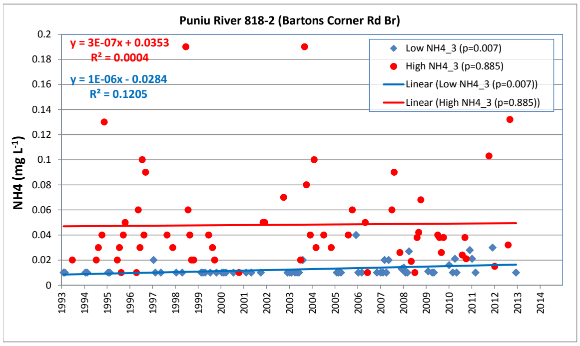
(p values < 0.005 are highlighted as being highly statistically significant)

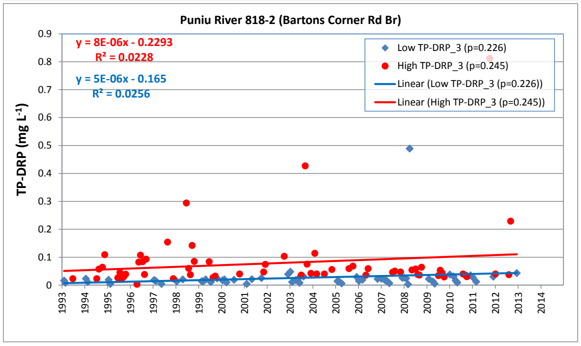


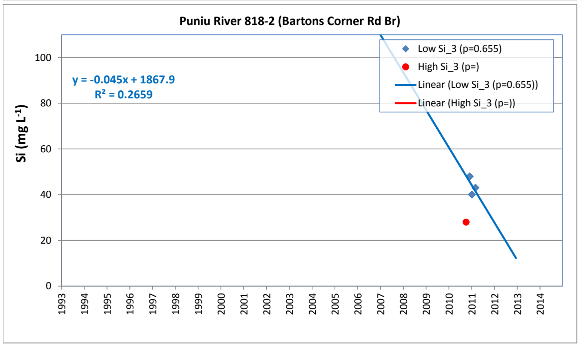


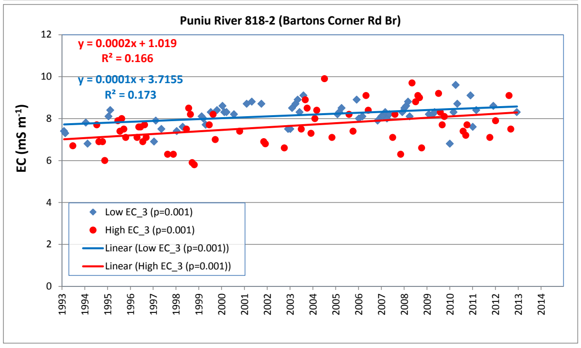








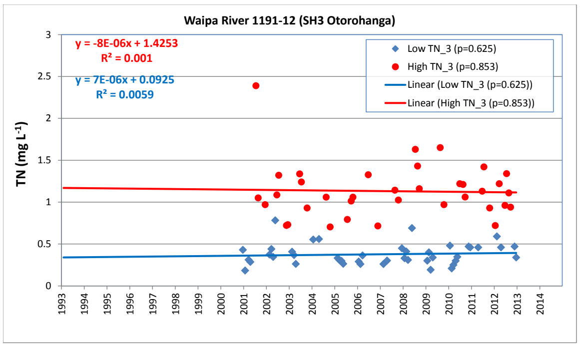


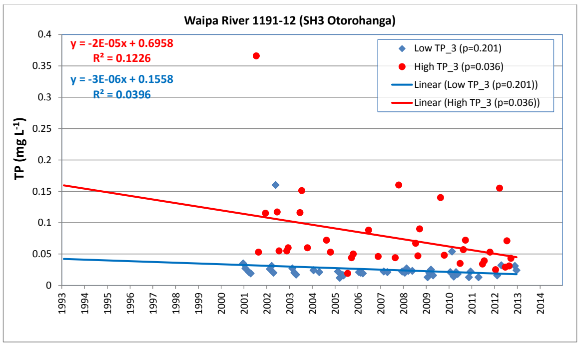


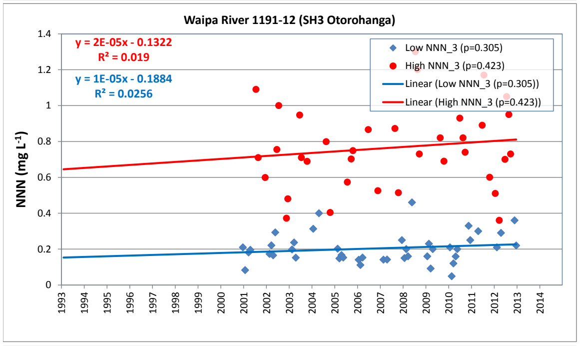
Puniu River 818-2 (Bartons Corner Rd Br)

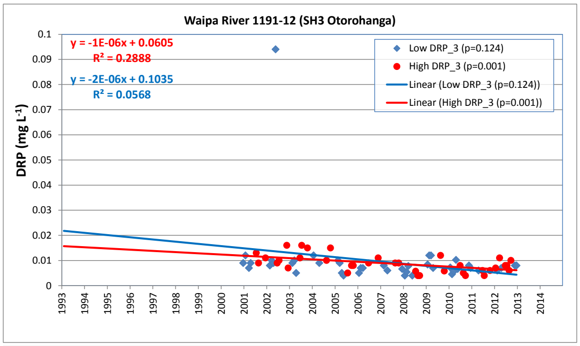
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	59	59	59	59	59	59	3	59
Mean Low Flow Sam	0.554	0.335	0.013	0.056	0.029	0.027	43.667	8.181
Median Low Flow Sa	0.538	0.310	0.010	0.046	0.028	0.018	43.000	8.300
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.045	0.000
P Low Flow Samples	0.004	0.005	0.007	0.172	0.148	0.226	0.655	0.001
N High Flow Sample:	61	61	61	61	61	61	1	61
Mean High Flow Sam	1.632	1.103	0.048	0.099	0.019	0.080	28.000	7.638
Median High Flow Sa	1.580	1.080	0.040	0.066	0.018	0.047	28.000	7.500
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P High Flow Samples	0.032	0.192	0.885	0.246	0.835	0.245		0.001
P Difference	0.000	0.000	0.000	0.013	0.000	0.002		0.000
N All Flow Samples	240	240	240	240	240	240	12	240
Mean All Flow Samp	0.988	0.673	0.027	0.067	0.024	0.042	38.500	7.940
Median All Flow Sam	0.853	0.556	0.020	0.051	0.023	0.028	38.500	8.000
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000
P All Flow Samples	0.002	0.013	0.949	0.126	0.961	0.126	0.630	0.000

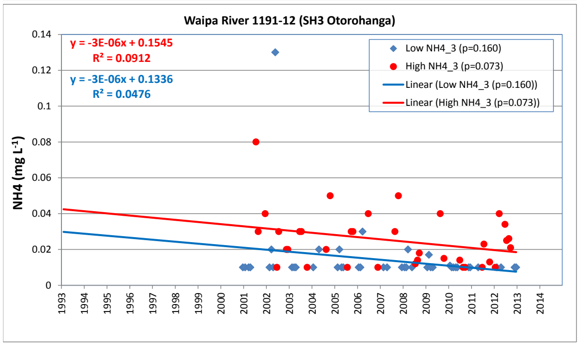
(p values < 0.005 are highlighted as being highly statistically significant)

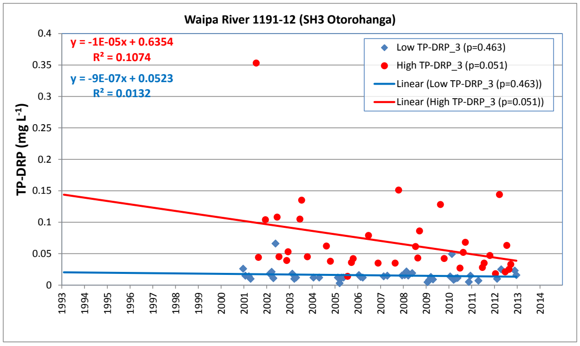


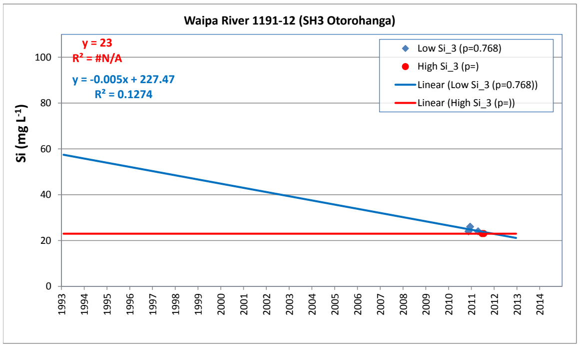


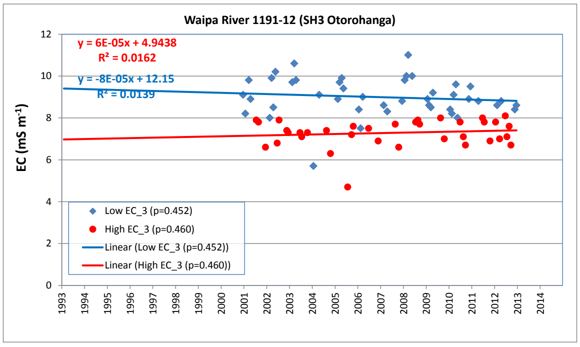








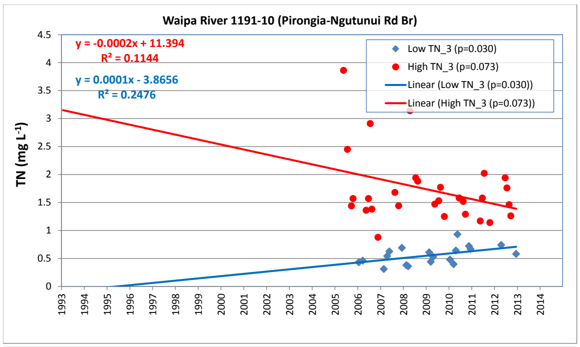


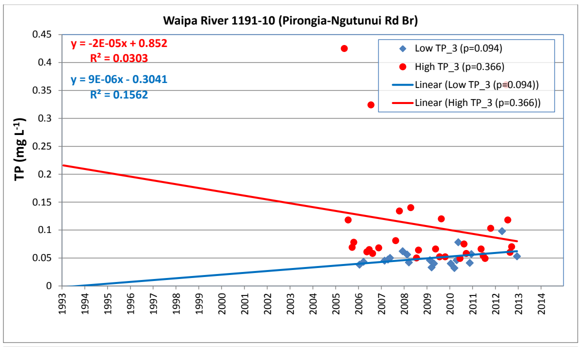


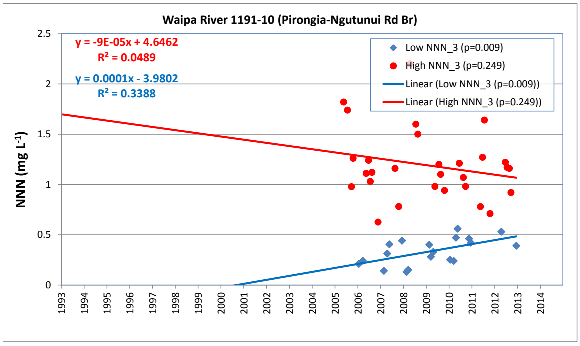
Waipa River 1191-12 (SH3 Otorohanga)

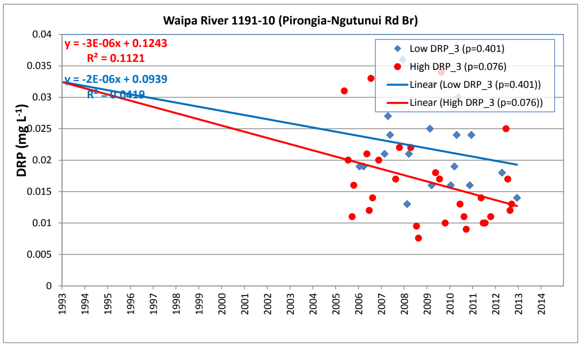
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	43	43	43	43	43	43	3	43
Mean Low Flow Sam	0.378	0.204	0.014	0.025	0.010	0.016	24.667	8.998
Median Low Flow Sa	0.345	0.198	0.010	0.021	0.008	0.013	24.000	8.900
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.005	0.000
P Low Flow Samples	0.625	0.305	0.160	0.201	0.124	0.463	0.768	0.452
N High Flow Samples	36	36	36	36	36	36	2	36
Mean High Flow Sam	1.131	0.765	0.025	0.077	0.009	0.068	23.000	7.286
Median High Flow Sa	1.073	0.735	0.022	0.055	0.009	0.045	23.000	7.350
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P High Flow Samples	0.853	0.423	0.073	0.036	0.001	0.051		0.460
P Difference	0.000	0.000	0.006	0.000	0.674	0.000	0.130	0.000
N All Flow Samples	147	147	147	147	147	147	12	147
Mean All Flow Samp	0.733	0.474	0.022	0.046	0.010	0.036	23.150	8.193
Median All Flow Sam	0.704	0.423	0.011	0.031	0.009	0.022	23.000	8.100
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
P All Flow Samples	0.247	0.092	0.063	0.033	0.002	0.120	0.764	0.728

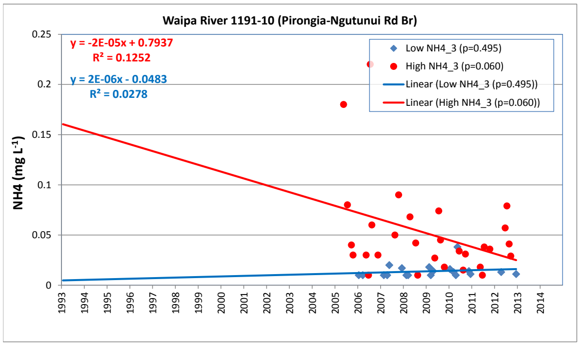
(p values < 0.005 are highlighted as being highly statistically significant)

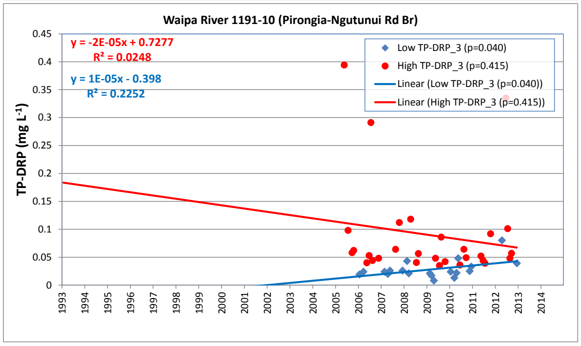


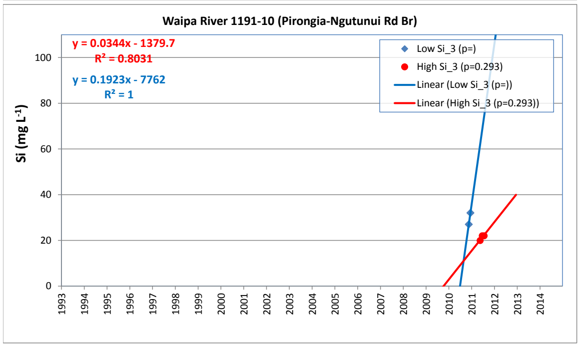


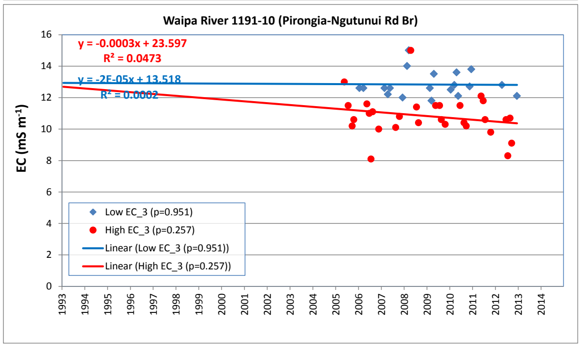








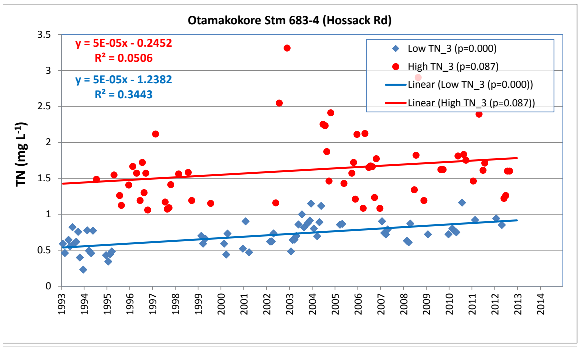


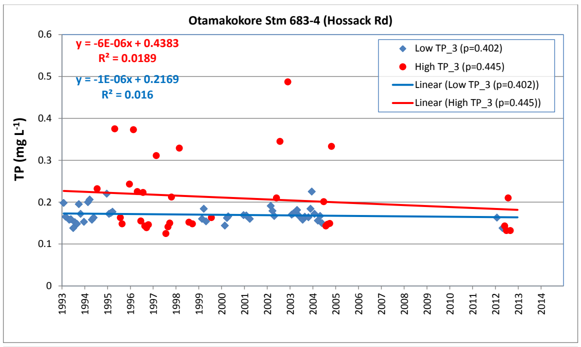


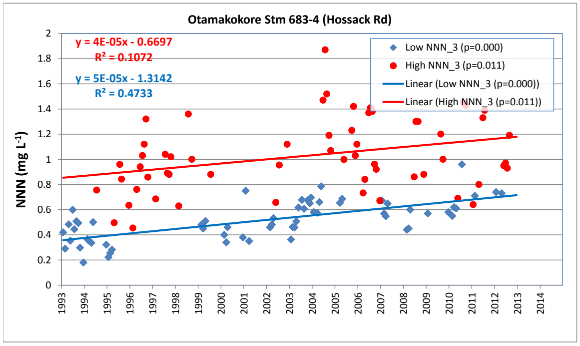
Waipa River 1191-10 (Pirongia-Ngutunui Rd Br)

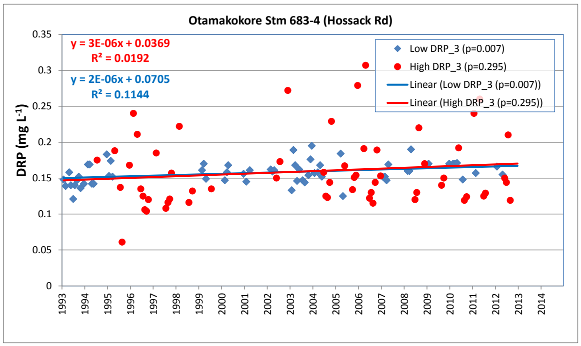
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	19	19	19	19	19	19	2	19
Mean Low Flow Sam	0.555	0.335	0.014	0.050	0.022	0.028	29.500	12.837
Median Low Flow Sa	0.543	0.330	0.011	0.046	0.021	0.024	29.500	12.600
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.192	0.000
P Low Flow Samples	0.030	0.009	0.495	0.094	0.401	0.040		0.951
N High Flow Samples	29	29	29	29	29	29	3	29
Mean High Flow Sam	1.732	1.190	0.051	0.106	0.017	0.090	21.300	10.821
Median High Flow Sa	1.570	1.160	0.038	0.068	0.014	0.056	22.000	10.600
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.034	0.000
P High Flow Samples	0.073	0.249	0.060	0.366	0.076	0.415	0.293	0.257
P Difference	0.000	0.000	0.000	0.004	0.011	0.001	0.167	0.000
N All Flow Samples	87	87	87	87	87	87	12	87
Mean All Flow Samp	1.133	0.762	0.030	0.075	0.018	0.056	24.658	11.652
Median All Flow Sam	0.980	0.690	0.020	0.061	0.017	0.044	24.000	11.600
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.013	0.000
P All Flow Samples	0.272	0.578	0.063	0.345	0.002	0.541	0.148	0.607

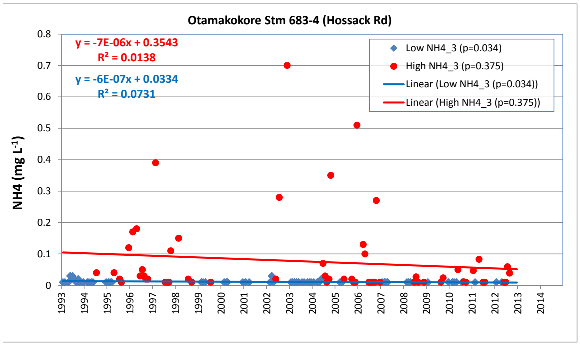
(p values < 0.005 are highlighted as being highly statistically significant)

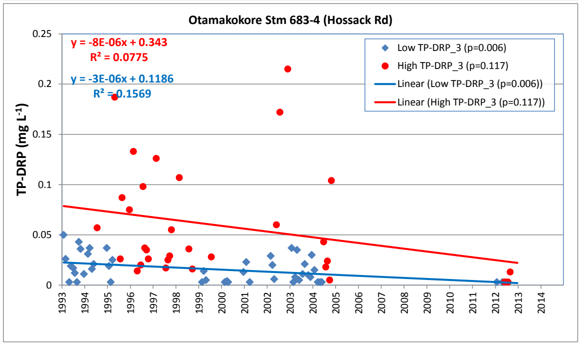


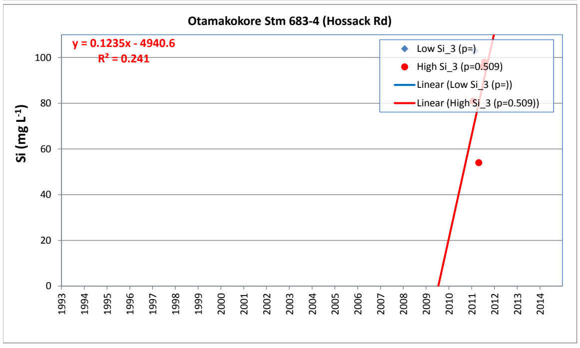


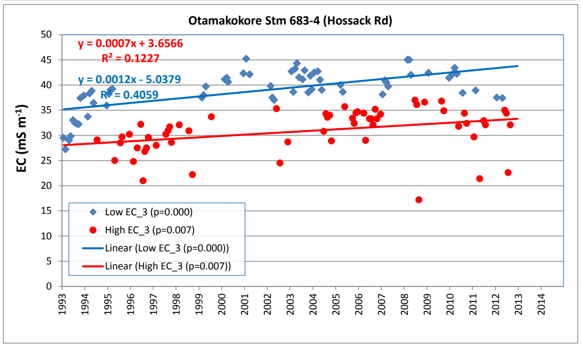








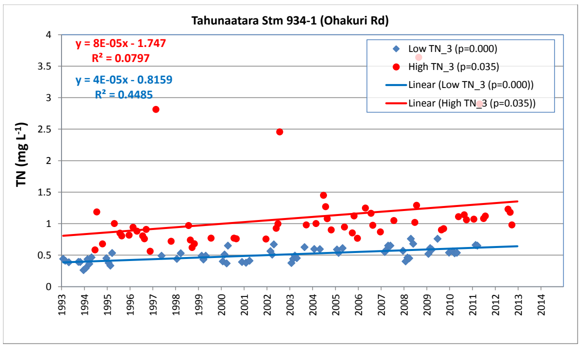


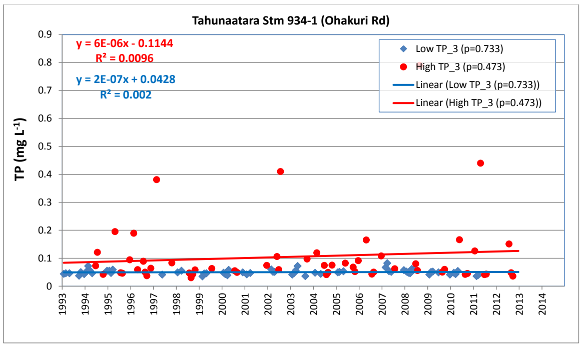


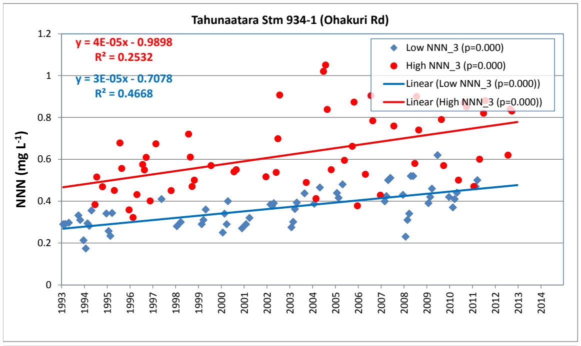
Otamakokore Stm 683-4 (Hossack Rd)

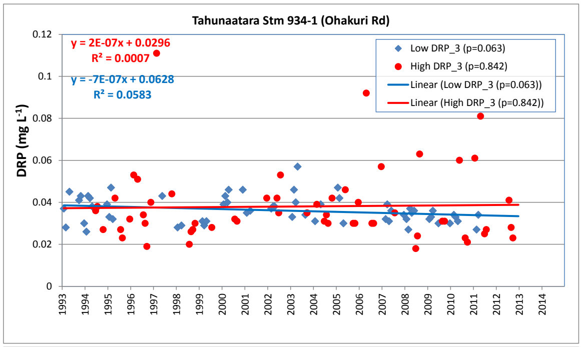
	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	62	62	62	46	62	46	1	62
Mean Low Flow Sam	0.703	0.515	0.011	0.170	0.158	0.016	103.000	38.952
Median Low Flow Sa	0.719	0.508	0.010	0.167	0.158	0.013	103.000	39.150
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.001
P Low Flow Samples	0.000	0.000	0.034	0.402	0.007	0.006		0.000
N High Flow Samples	59	59	59	33	59	33	4	59
Mean High Flow Sam	1.619	1.031	0.076	0.210	0.160	0.057	82.250	30.902
Median High Flow Sa	1.570	0.998	0.020	0.163	0.144	0.035	88.500	32.100
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.123	0.001
P High Flow Samples	0.087	0.011	0.375	0.445	0.295	0.117	0.509	0.007
P Difference	0.000	0.000	0.000	0.019	0.767	0.000		0.000
N All Flow Samples	237	237	237	154	237	154	12	237
Mean All Flow Samp	1.048	0.734	0.029	0.181	0.155	0.030	96.000	35.666
Median All Flow Sam	0.910	0.672	0.010	0.167	0.152	0.020	101.500	36.100
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.004	0.001
P All Flow Samples	0.000	0.000	0.537	0.154	0.026	0.003	0.932	0.000

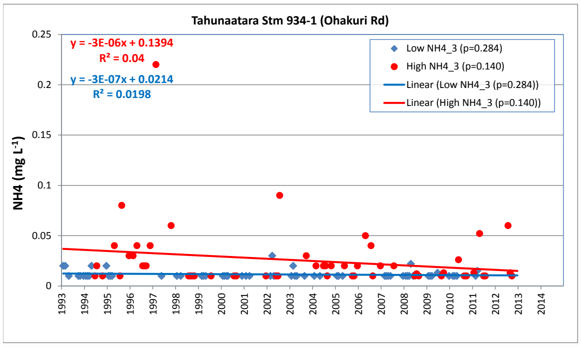
(p values < 0.005 are highlighted as being highly statistically significant)

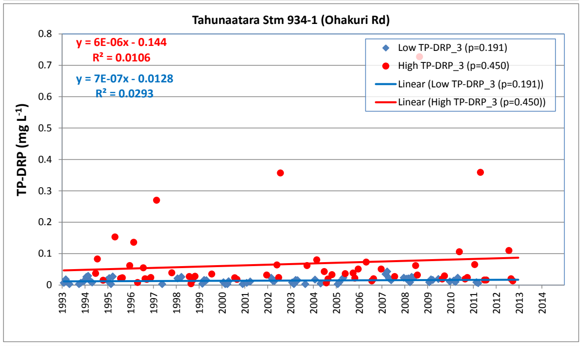


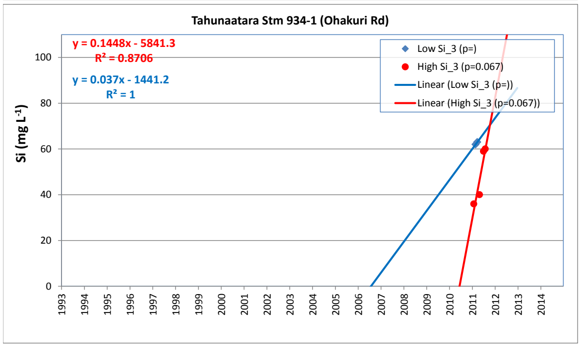


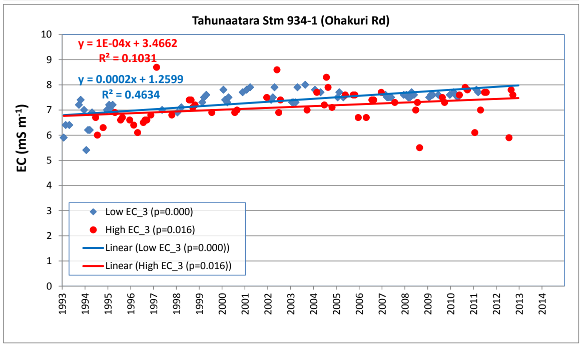








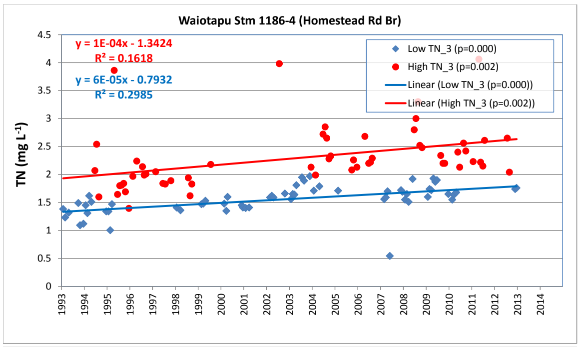


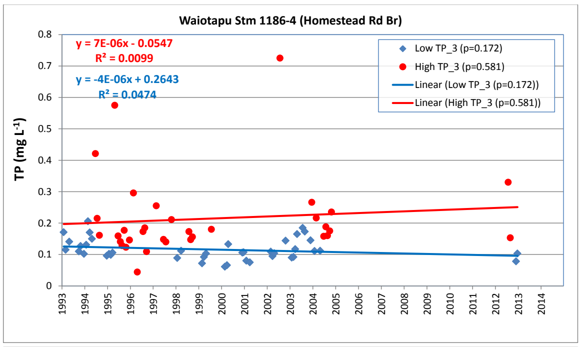


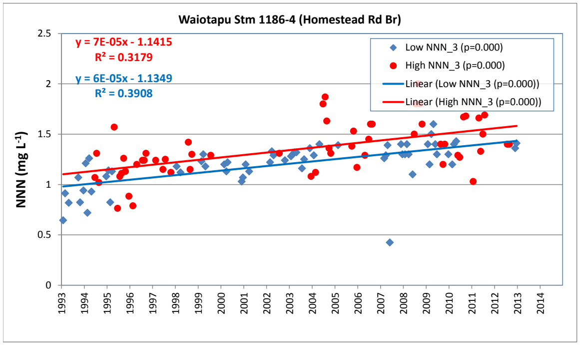
Tahunaatara Stm 934-1 (Ohakuri Rd)

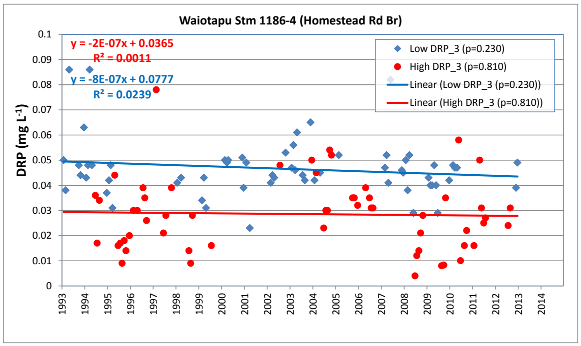
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	60	60	60	60	60	60	2	60
Mean Low Flow Sam	0.505	0.365	0.012	0.050	0.036	0.014	62.500	7.347
Median Low Flow Sa	0.500	0.361	0.010	0.049	0.036	0.014	62.500	7.500
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.037	0.000
P Low Flow Samples	0.000	0.000	0.284	0.733	0.063	0.191		0.000
N High Flow Samples	56	56	56	56	56	56	4	56
Mean High Flow Sam	1.091	0.628	0.026	0.106	0.038	0.068	48.750	7.134
Median High Flow Sa	0.972	0.578	0.013	0.063	0.032	0.031	49.500	7.150
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.145	0.000
P High Flow Samples	0.035	0.000	0.140	0.473	0.842	0.450	0.067	0.016
P Difference	0.000	0.000	0.002	0.002	0.453	0.001	0.115	0.052
N All Flow Samples	240	240	240	240	240	240	12	240
Mean All Flow Samp	0.739	0.493	0.016	0.066	0.037	0.030	58.167	7.320
Median All Flow Sam	0.660	0.467	0.010	0.052	0.034	0.018	62.000	7.400
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.000
P All Flow Samples	0.000	0.000	0.041	0.766	0.062	0.295	0.790	0.000

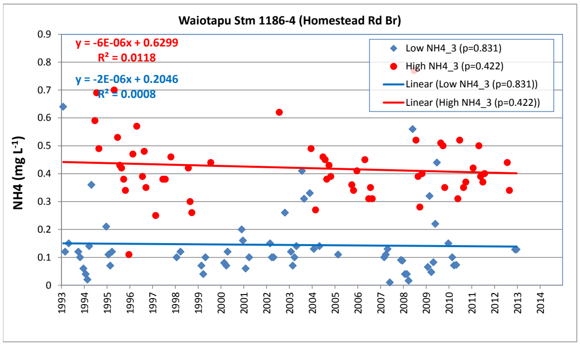
(p values < 0.005 are highlighted as being highly statistically significant)

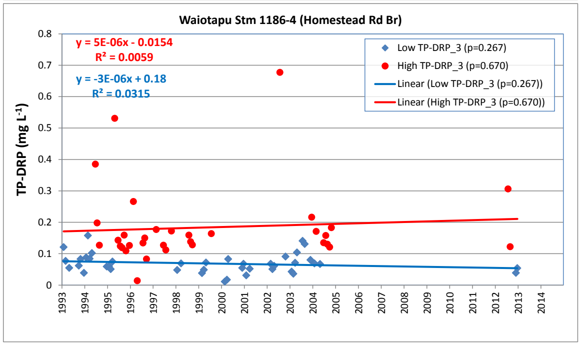


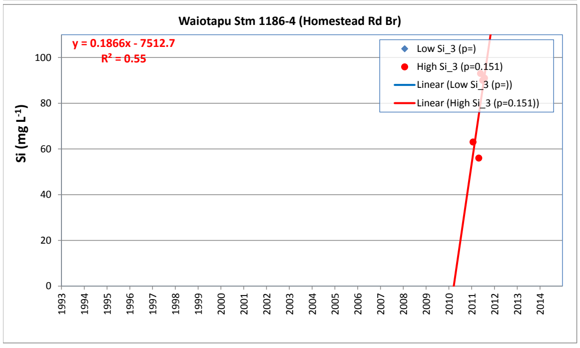


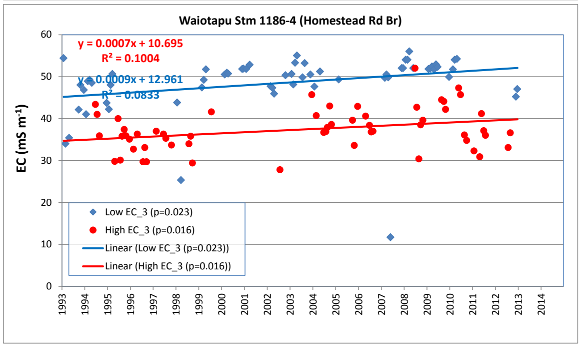








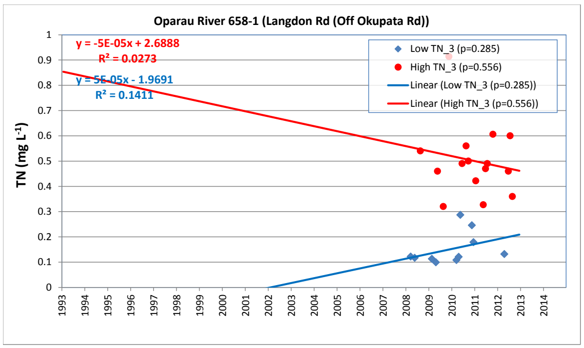


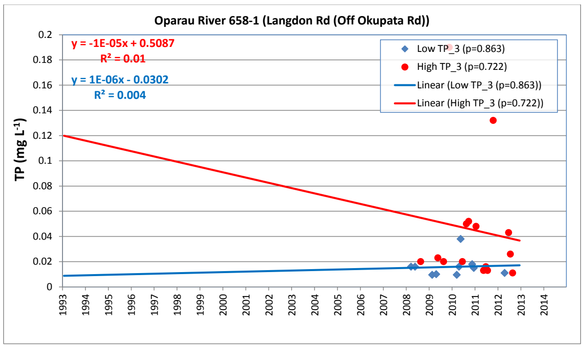


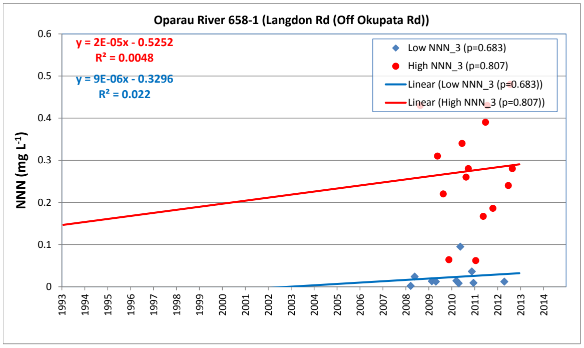
Waiotapu Stm 1186-4 (Homestead Rd Br)

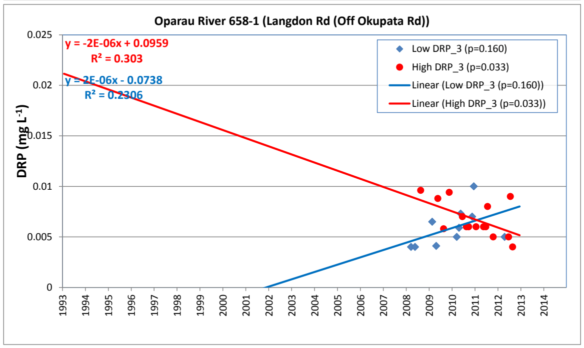
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	62	62	62	41	62	41	0	62
Mean Low Flow Sam	1.555	1.198	0.144	0.116	0.047	0.069		48.502
Median Low Flow Sa	1.590	1.245	0.110	0.107	0.046	0.067		50.500
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.001
P Low Flow Samples	0.000	0.000	0.831	0.172	0.230	0.267		0.023
N High Flow Samples	57	57	57	33	57	33	5	57
Mean High Flow Sam	2.296	1.351	0.421	0.214	0.029	0.184	78.600	37.374
Median High Flow Sa	2.200	1.310	0.400	0.173	0.028	0.143	90.000	36.800
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.187	0.001
P High Flow Samples	0.002	0.000	0.422	0.581	0.810	0.670	0.151	0.016
P Difference	0.000	0.001	0.000	0.000	0.000	0.000		0.000
N All Flow Samples	240	240	240	157	240	157	12	240
Mean All Flow Samp	1.867	1.239	0.294	0.154	0.038	0.115	89.333	43.726
Median All Flow Sam	1.800	1.240	0.300	0.143	0.039	0.102	93.000	44.300
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
P All Flow Samples	0.000	0.000	0.730	0.591	0.084	0.616	0.978	0.003

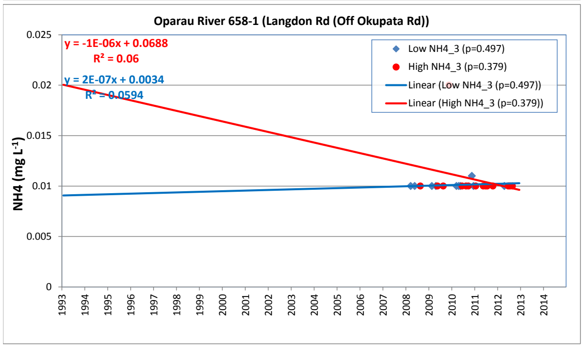
(p values < 0.005 are highlighted as being highly statistically significant)

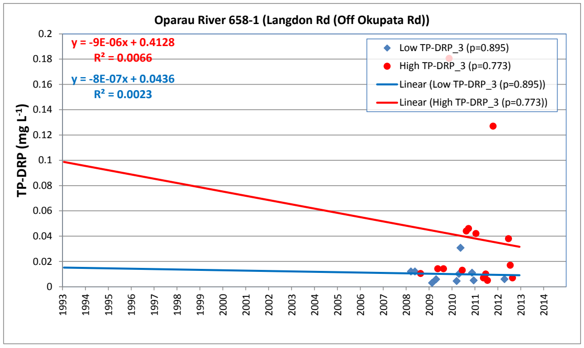


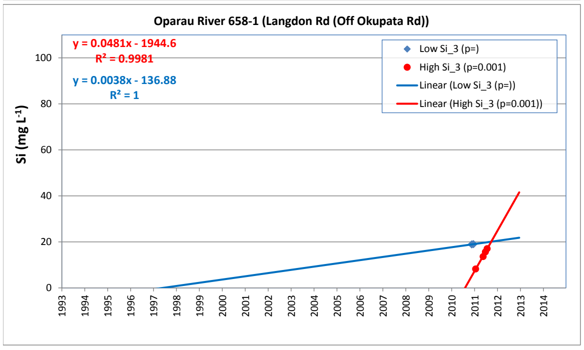


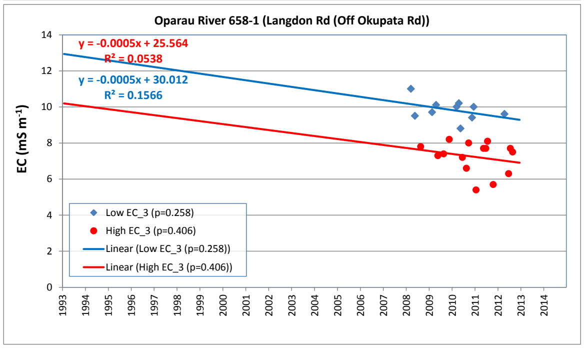








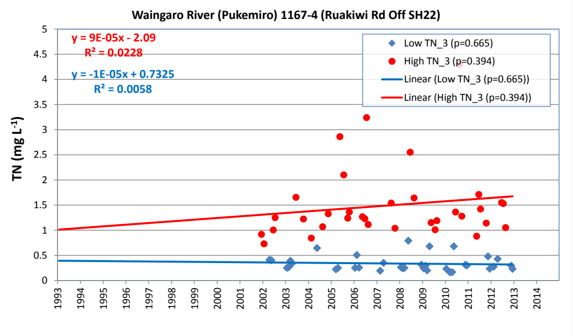


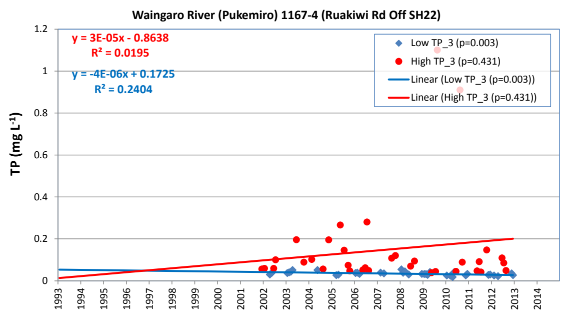


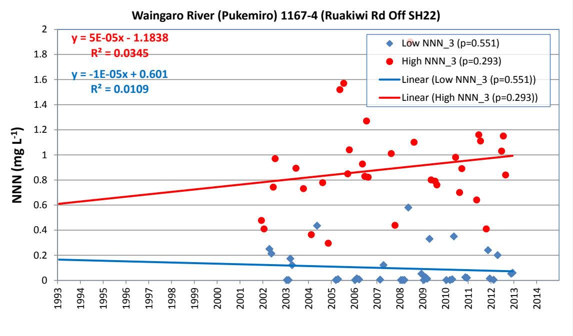
Oparau River 658-1 (Langdon Rd (Off Okupata Rd))

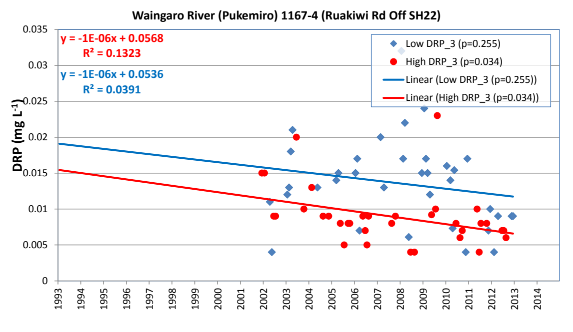
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	10	10	10	10	10	10	2	10
Mean Low Flow Sam	0.152	0.023	0.010	0.016	0.006	0.010	18.950	9.830
Median Low Flow Sa	0.122	0.013	0.010	0.016	0.005	0.008	18.950	9.850
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.004	-0.001
P Low Flow Samples	0.285	0.683	0.497	0.863	0.160	0.895		0.258
N High Flow Samples	15	15	15	15	15	15	4	15
Mean High Flow Sam	0.501	0.276	0.011	0.045	0.007	0.038	13.600	7.240
Median High Flow Sa	0.490	0.280	0.010	0.023	0.006	0.014	14.600	7.500
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.048	0.000
P High Flow Samples	0.556	0.807	0.379	0.722	0.033	0.773	0.001	0.406
P Difference	0.000	0.000	0.414	0.043	0.251	0.048	0.069	0.000
N All Flow Samples	58	58	58	58	58	58	12	58
Mean All Flow Samp	0.279	0.131	0.010	0.023	0.006	0.017	16.317	8.421
Median All Flow Sam	0.213	0.067	0.010	0.014	0.005	0.008	16.500	8.250
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.001
P All Flow Samples	0.740	0.626	0.380	0.676	0.694	0.690	0.978	0.052

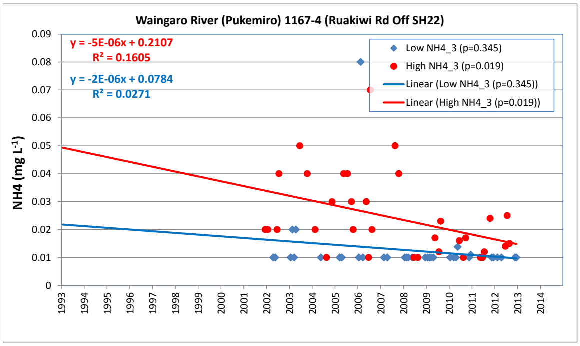
(p values < 0.005 are highlighted as being highly statistically significant)

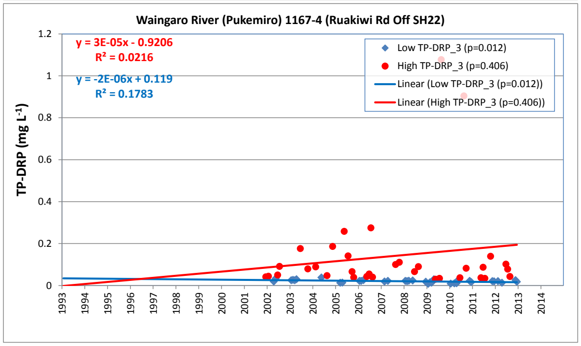


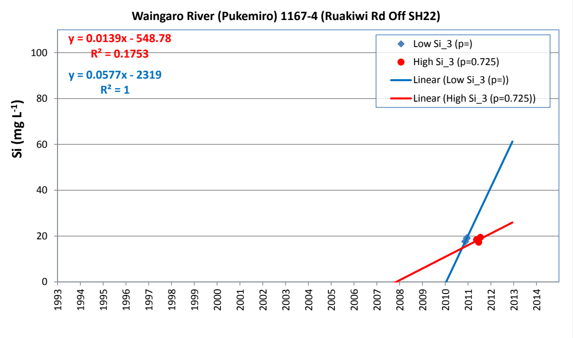


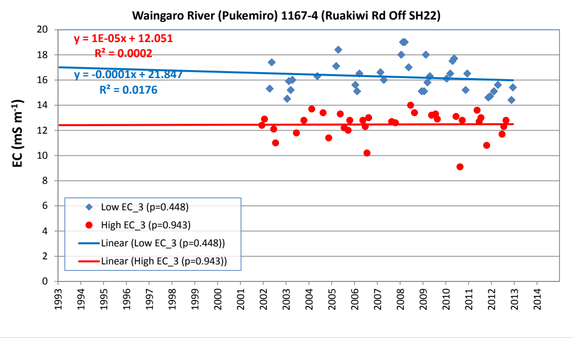








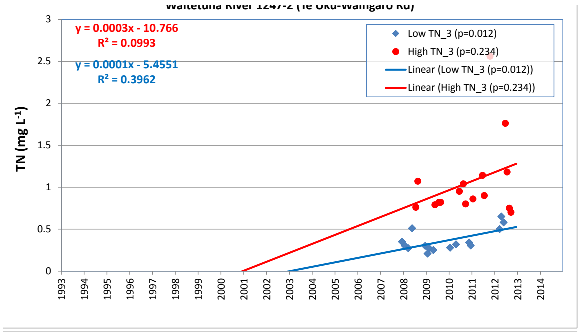


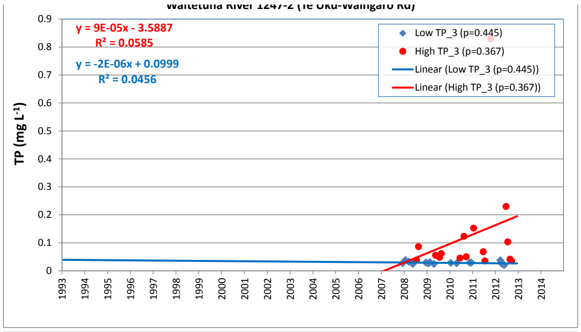


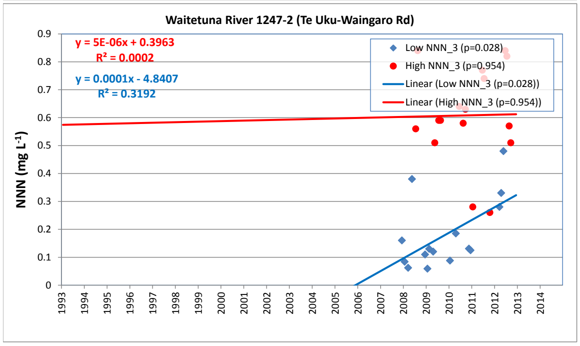
Waingaro River (Pukemiro) 1167-4 (Ruakiwi Rd Off SH22)

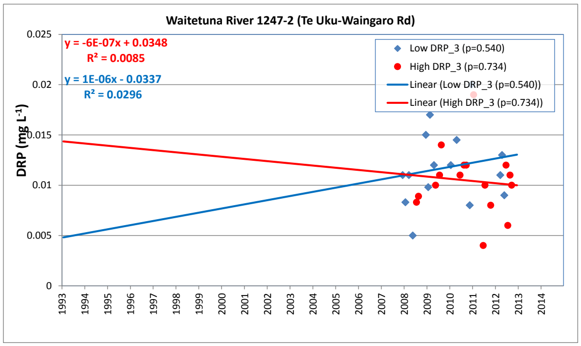
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	35	35	35	35	35	35	2	35
Mean Low Flow Sam	0.337	0.095	0.013	0.034	0.014	0.021	18.350	16.243
Median Low Flow Sa	0.274	0.015	0.010	0.033	0.014	0.021	18.350	16.000
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.058	0.000
P Low Flow Samples	0.665	0.551	0.345	0.003	0.255	0.012		0.448
N High Flow Sample	34	34	34	34	34	34	3	34
Mean High Flow Sam	1.493	0.888	0.024	0.149	0.009	0.140	18.367	12.474
Median High Flow Sa	1.258	0.845	0.020	0.087	0.008	0.079	18.400	12.800
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.000
P High Flow Samples	0.394	0.293	0.019	0.431	0.034	0.406	0.725	0.943
P Difference	0.000	0.000	0.001	0.006	0.001	0.004	0.988	0.000
N All Flow Samples	133	133	133	133	133	133	12	133
Mean All Flow Samp	0.798	0.441	0.017	0.069	0.012	0.058	18.750	14.365
Median All Flow Sam	0.650	0.355	0.010	0.043	0.010	0.030	18.550	14.200
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
P All Flow Samples	0.505	0.549	0.014	0.738	0.074	0.682	0.942	0.555

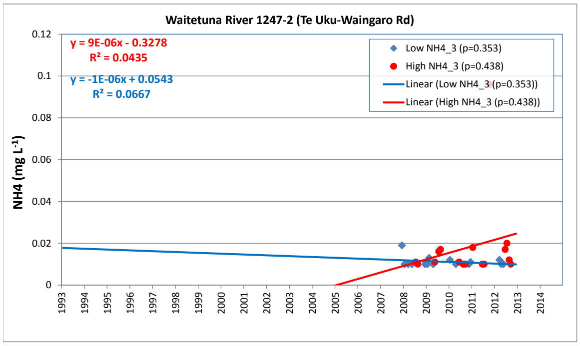
(p values < 0.005 are highlighted as being highly statistically significant)

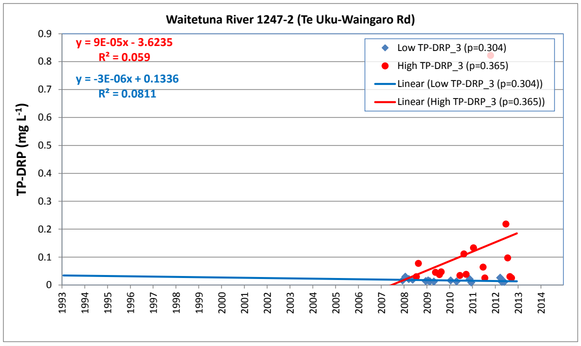


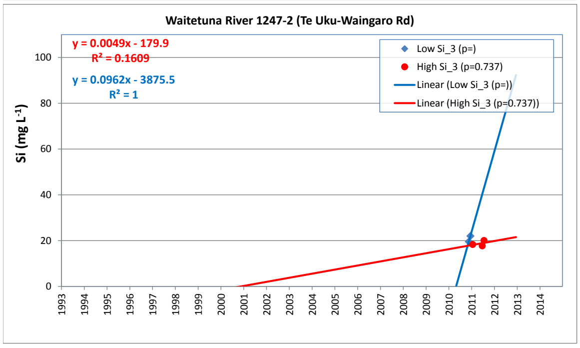


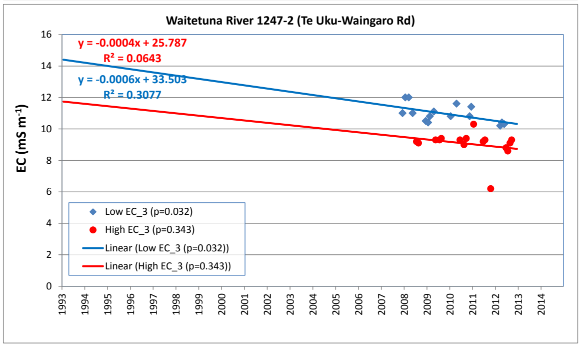








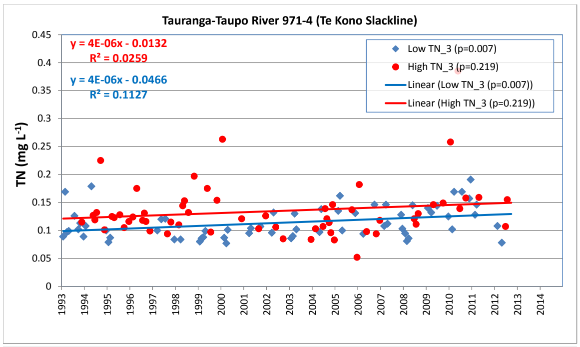


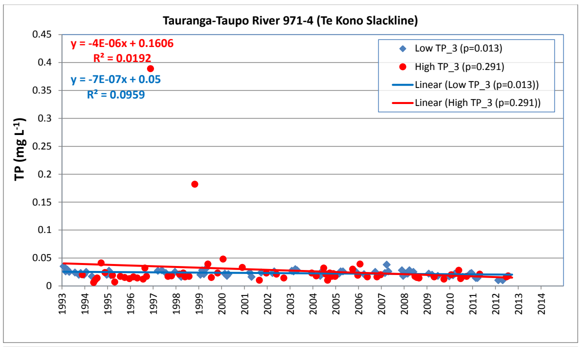


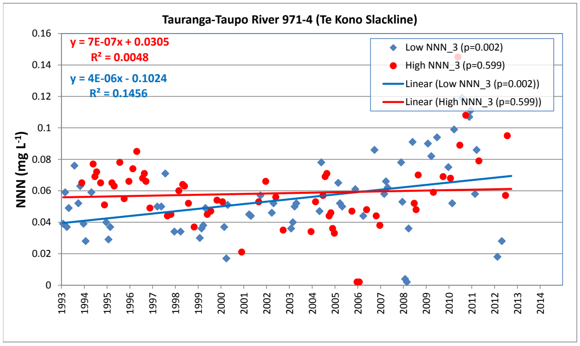
Waitetuna River 1247-2 (Te Uku-Waingaro Rd)

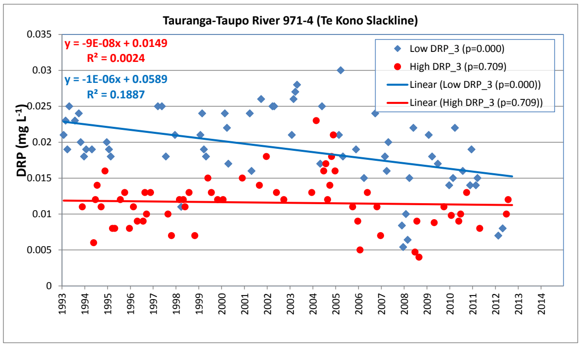
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	15	15	15	15	15	15	2	15
Mean Low Flow Sam	0.363	0.182	0.011	0.028	0.012	0.016	20.750	10.953
Median Low Flow Sa	0.305	0.130	0.010	0.028	0.011	0.016	20.750	10.800
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.096	-0.001
P Low Flow Samples	0.012	0.028	0.353	0.445	0.540	0.304		0.032
N High Flow Sample:	16	16	16	16	16	16	3	16
Mean High Flow Sam	1.056	0.608	0.018	0.125	0.010	0.115	18.667	9.050
Median High Flow Sa	0.880	0.590	0.011	0.058	0.011	0.046	18.300	9.250
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000
P High Flow Samples	0.234	0.954	0.438	0.367	0.734	0.365	0.737	0.343
P Difference	0.000	0.000	0.211	0.066	0.313	0.063	0.308	0.000
N All Flow Samples	61	61	61	61	61	61	12	61
Mean All Flow Samp	0.647	0.379	0.017	0.060	0.012	0.048	19.192	10.075
Median All Flow Sam	0.560	0.340	0.010	0.037	0.011	0.025	19.050	10.000
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.004	-0.001
P All Flow Samples	0.269	0.655	0.440	0.216	0.348	0.234	0.434	0.009

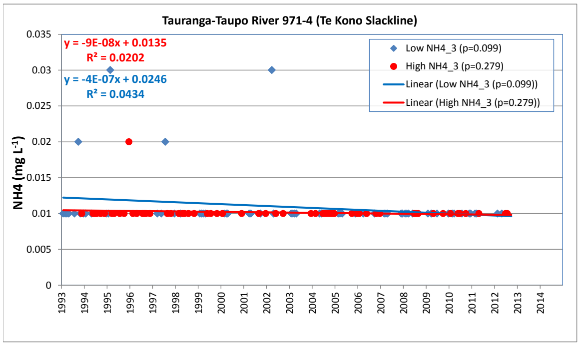
(p values < 0.005 are highlighted as being highly statistically significant)

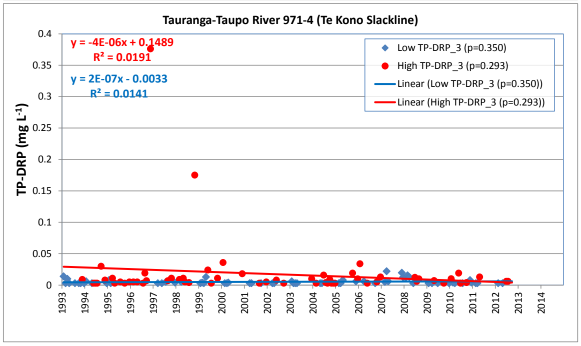


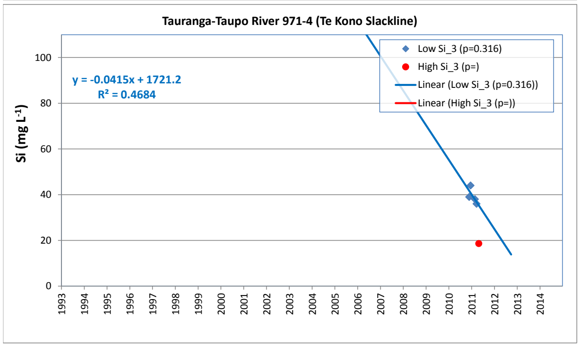


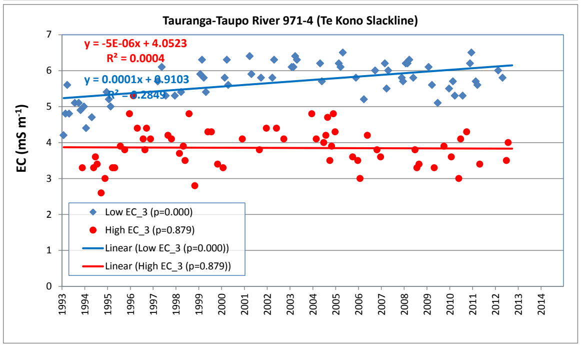








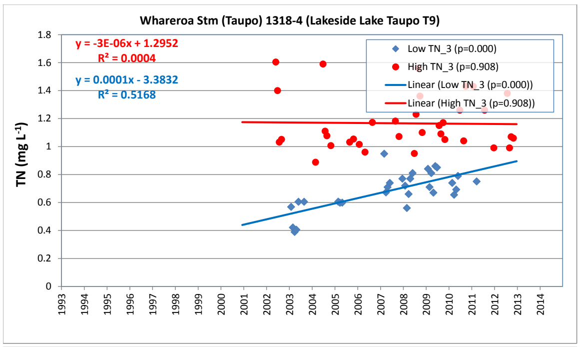


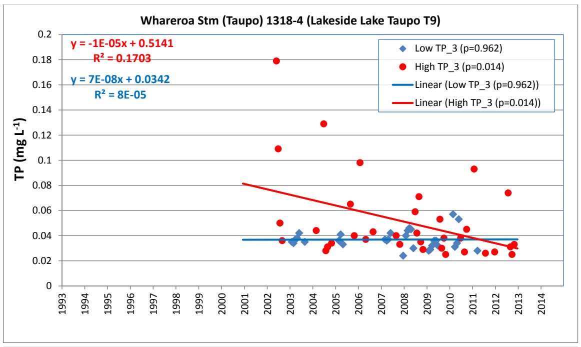


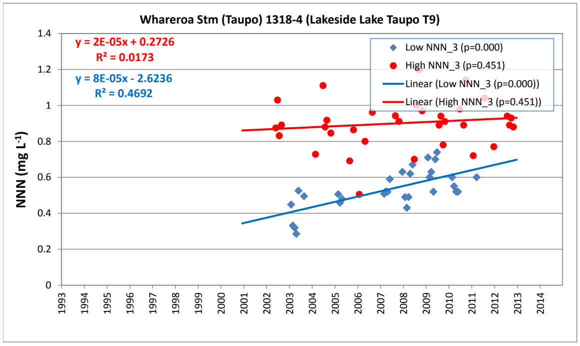
Tauranga-Taupo River 971-4 (Te Kono Slackline)

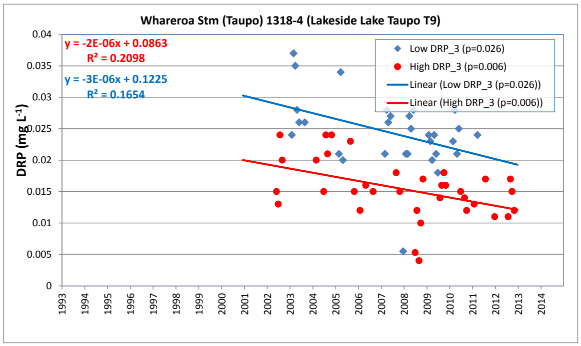
	TN	NNN	NH4	TP	DRP	TP-DRP	Si	EC
N Low Flow Samples	64	64	64	64	64	64	4	64
Mean Low Flow Sam	0.114	0.054	0.011	0.023	0.019	0.005	39.250	5.688
Median Low Flow Sa	0.104	0.051	0.010	0.023	0.019	0.003	38.500	5.800
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	-0.041	0.000
P Low Flow Samples	0.007	0.002	0.099	0.013	0.000	0.350	0.316	0.000
N High Flow Samples	60	60	60	60	60	60	1	60
Mean High Flow Sam	0.134	0.058	0.010	0.029	0.012	0.018	18.600	3.852
Median High Flow Sa	0.122	0.057	0.010	0.018	0.012	0.007	18.600	3.850
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P High Flow Samples	0.219	0.599	0.279	0.291	0.709	0.293		0.879
P Difference	0.008	0.345	0.136	0.396	0.000	0.069		0.000
N All Flow Samples	230	230	230	230	230	230	10	230
Mean All Flow Samp	0.123	0.060	0.011	0.022	0.015	0.008	34.460	4.815
Median All Flow Sam	0.118	0.058	0.010	0.019	0.015	0.003	35.500	4.800
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.018	0.000
P All Flow Samples	0.000	0.000	0.251	0.078	0.002	0.217	0.415	0.065

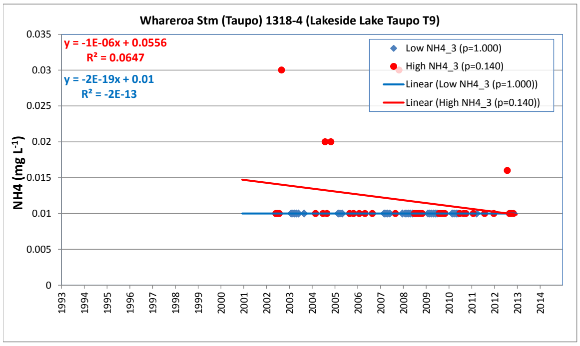
(p values < 0.005 are highlighted as being highly statistically significant)

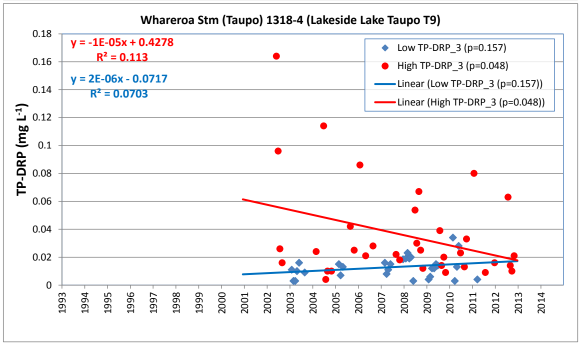


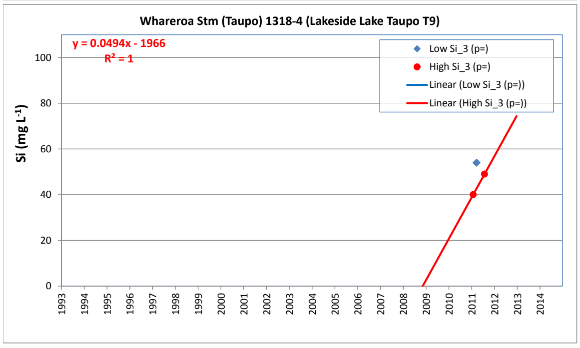


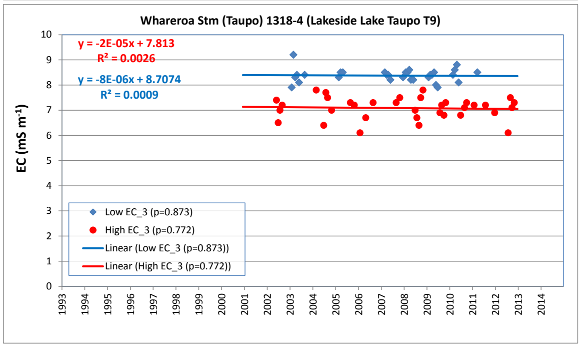












Whareroa Stm (Taupo) 1318-4 (Lakeside Lake Taupo T9)

	TN	**NNN**	**NH4**	**TP**	**DRP**	**TP-DRP**	**Si**	**EC**
N Low Flow Samples	30	30	30	30	30	30	1	30
Mean Low Flow Sam	0.684	0.534	0.010	0.037	0.024	0.013	54.000	8.377
Median Low Flow Sa	0.701	0.520	0.010	0.036	0.024	0.013	54.000	8.400
Trend Low Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000		0.000
P Low Flow Samples	0.000	0.000	1.000	0.962	0.026	0.157		0.873
N High Flow Sample	35	35	35	35	35	35	2	35
Mean High Flow Sam	1.166	0.901	0.012	0.051	0.015	0.036	44.500	7.086
Median High Flow Sa	1.090	0.891	0.010	0.038	0.015	0.023	44.500	7.200
Trend High Flow Sam	0.000	0.000	0.000	0.000	0.000	0.000	0.049	0.000
P High Flow Samples	0.908	0.451	0.140	0.014	0.006	0.048		0.772
P Difference	0.000	0.000	0.038	0.019	0.000	0.001		0.000
N All Flow Samples	123	123	123	123	123	123	12	123
Mean All Flow Samp	0.909	0.717	0.011	0.041	0.021	0.020	49.417	7.748
Median All Flow Sam	0.886	0.700	0.010	0.036	0.021	0.014	50.000	7.800
Trend All Flow Samp	0.000	0.000	0.000	0.000	0.000	0.000	-0.001	0.000
P All Flow Samples	0.020	0.002	0.040	0.006	0.000	0.119	0.916	0.905

(p values < 0.005 are highlighted as being highly statistically significant)