Appendix 2 – Adjusting for changes in laboratory analysis of total nitrogen and total phosphorus

Introduction

Changes in laboratory methods for analysing total nitrogen (TN), total phosphorus (TP) and dissolved reactive phosphorus (DRP) occurred in late 2008 and 2009 (see Appendix 1). The recent laboratory changes have resulted in less variability of results but also caused a step change decrease in TN results and a step change increase in TP (Table A3.1). This complicates the assessment of trends in water quality and may affect the calculation of the TLI and comparisons with target values.

When there is a change in laboratory or laboratory method it is best practice to undertake a period of cross calibration - where duplicate samples were analysed by the different methods to ensure consistency. This did not occur. Furthermore it is difficult to undertake this calibration process retrospectively because the old laboratory methods are no longer routinely run. In the absence of this calibration information statistical methods were used to quantify the difference in TN and TP results that can be attributed to the change in laboratory methods.

Method

Lakes and rivers with few pressures and relatively stable water quality were selected and median values of TN and TP were calculated for the four year period of July 2004 to June 2008 (before the method changes) and July 2010 to June 2014 (after the method changes). A regression was made between the two periods. The analysis was repeated using seasonal data rather than four year medians and the results were very similar.

Sites used in the analysis were: Lakes Ōkāreka, Ōkataina, Rotomā, Rotomahana, Tarawera and Tikitapu. Rivers used in the analysis were Utuhina Stream, Waiohewa Stream, Waiowhiro Stream and Omanawa River. Data from other rivers in the region were not used to quantify the effect of the laboratory method change because of either changing pressures in the catchments or too few data points or because they had trends in nitrate concentration (a substantial component of TN in rivers). For lake samples the results from surface waters, bottom waters and hypoxic bottom waters were used independently in the analysis.

The sites used in the analysis were further refined based trends in TN, TP or nitrate that was apparent before or after the time of laboratory changes. The TN analysis did not include Waiowhiro Stream or Omanawa River because concentrations of nitrate were significantly different between the periods. The TP analysis did not include: Lake Tarawera, Ōkāreka (bottom and bottom x), Rotomahana (bottom), or Utuhina Stream. This was because these lake sites had significant trends in TP during the period after January 2010 and alum dosing occurs in the Utuhina Stream (see Table A3.2).

No lake had completely stable water quality for all variables but the lakes with few pressures and reasonably stable TN and TP concentrations for the 5 year period before July 2008 and the five years after January 2010 were:

- Ōkāreka: TN showed no significant trend in 5 year period before but a decline in 5 year period after (PAC -2.3%). TP showed no significant trend before and or after.

- Ōkataina: TN showed no significant trend before but a decline in the 5 year period after (PAC -4.2%). TP had no significant trend before or after.

- Rotomā: TN showed an increasing trend before July 2008 (PAC 4.7%) but no trend after. TP showed no significant trend before or after.

- Rotomahana: TN showed no significant trend before or after the period. TP showed no significant trend before or after.

- Tarawera: TN showed an increasing trend before July 2008 (PAC 13%) but no trend after. TP showed no significant trend before or after.

- Tikitapu: TN and TP showed no significant trend before or after the period.

TP was reasonably stable in all these lakes for the five year periods before and after the method change. However the only lakes that showed no trend in TN were Rotomahana and Tikitapu. Tarawera and Rotomā had an increasing trend before July 2008 so including these lakes in the analysis might make a more conservative assessment of declines due to method changes.

Results

The new laboratory method appears to have resulted in a step change increase in total nitrogen of about 50.7 mg/m^3 ([TN old method] = 1.0008 [TN new method] + 50.7 mg/m^3, R^2 = 0.9992, n = 20).

The analysis confirmed that the new laboratory method reports lower TP values compared to the old method. The relationship between the two methods can be expressed by the equation:

[TP old method] = 0.829 [TP new method] R^2 = 0.99, n = 15.

Dissolved inorganic nitrogen (DIN) is a large component of total nitrogen in rivers but usually a small component of TN in lakes. The changes in the ratio of TN:DIN was used to confirm the effect of a lab method change. The TN:DIN ratio for the periods before and after the lab method change was compared from nine tributaries to Lake Rotorua and eleven other rivers throughout the region. All sites had an apparent decline in the TN:DIN ratio occurring in late 2009 when laboratory methods changed (CUSMUM test). A statistically significant decline occurred in 15 out of the 20 sites.

Table A3.1: *Arithmetic mean (ppb) and standard error of mean of lake surface water samples for the four year periods before July 2008 and after July 2010*

Arithmetic mean

	TN		TP		DRP	
Lake	**before**	**after**	**before**	**after**	**before**	**after**
Ōkāreka	220.6	183.9	8.68	9.71	2.73	2.73
Ōkataina	154.3	90.6	8.21	11.76	3.49	4.67
Rotomā	174.2	101.0	5.26	6.27	2.14	3.16
Rotomahana	223.3	196.3	36.74	46.70	10.58	20.74
Tarawera	149.2	90.2	9.88	19.33	5.05	10.60
Tikitapu	212.4	162.3	5.85	4.36	2.56	1.50

Standard Deviation

	TN		TP		DRP	
Lake	**before**	**after**	**before**	**after**	**before**	**after**
Ōkāreka	47.17	20.07	3.931	4.010	2.616	1.267
Ōkataina	68.66	12.43	3.775	4.998	3.245	1.329
Rotomā	80.68	16.98	3.091	2.789	1.906	2.079
Rotomahana	56.63	23.13	14.835	7.313	5.388	4.618
Tarawera	88.96	22.48	4.470	4.007	3.968	2.368
Tikitapu	40.03	39.52	4.524	2.015	2.406	1.716

Table A3.2: *Median TN (ppb) and TP for the four year periods before July 2008 and after July 2010 for stable sites used in the analysis.*

		TN		TP		
site	**layer**	**before**	**after**	**before**	**after**	**comment**
Lake Ōkāreka	top	221	182	9	9	
Lake Ōkāreka	bottom	215.75	159			Upward TP trend since 2010
Lake Ōkāreka	bottom x	229	179			Upward TP trend since 2010
Lake Ōkataina	top	145	89	7.5	11	
Lake Ōkataina	bottom	121.5	78	9	12	
Lake Ōkataina	bottom x	129.25	90	14	16	
Lake Rotomā	top	152	100	4	6	
Lake Rotomā	bottom	131	80	4	5	
Lake Rotomā	bottom x	145.5	91	5	6	
Lake Rotomahana	top	213	194	36	47	
Lake Rotomahana	bottom	228	195			Upward TP trend since 2010
Lake Rotomahana	bottom x	248.5	210	44	51	
Lake Tarawera	top	136.5	88			
Lake Tarawera	bottom	108.75	61.5			Upward TP trend since 2010
Lake Tarawera	bottom x	116	70			
Lake Tikitapu	top	213.75	156	5	4	
Lake Tikitapu	bottom	232.5	159	6	5	
Lake Tikitapu	bottom x	251.75	169.5	7	5	
Omanawa River	river			29	38.25	Upward nitrate trend
Utuhina River	river	815.5	729			Alum dosing for P
Waiohewa Stream	river	2640	2595	62	72.5	
Waiowhiro Stream	river			45	54.5	Upward nitrate trend

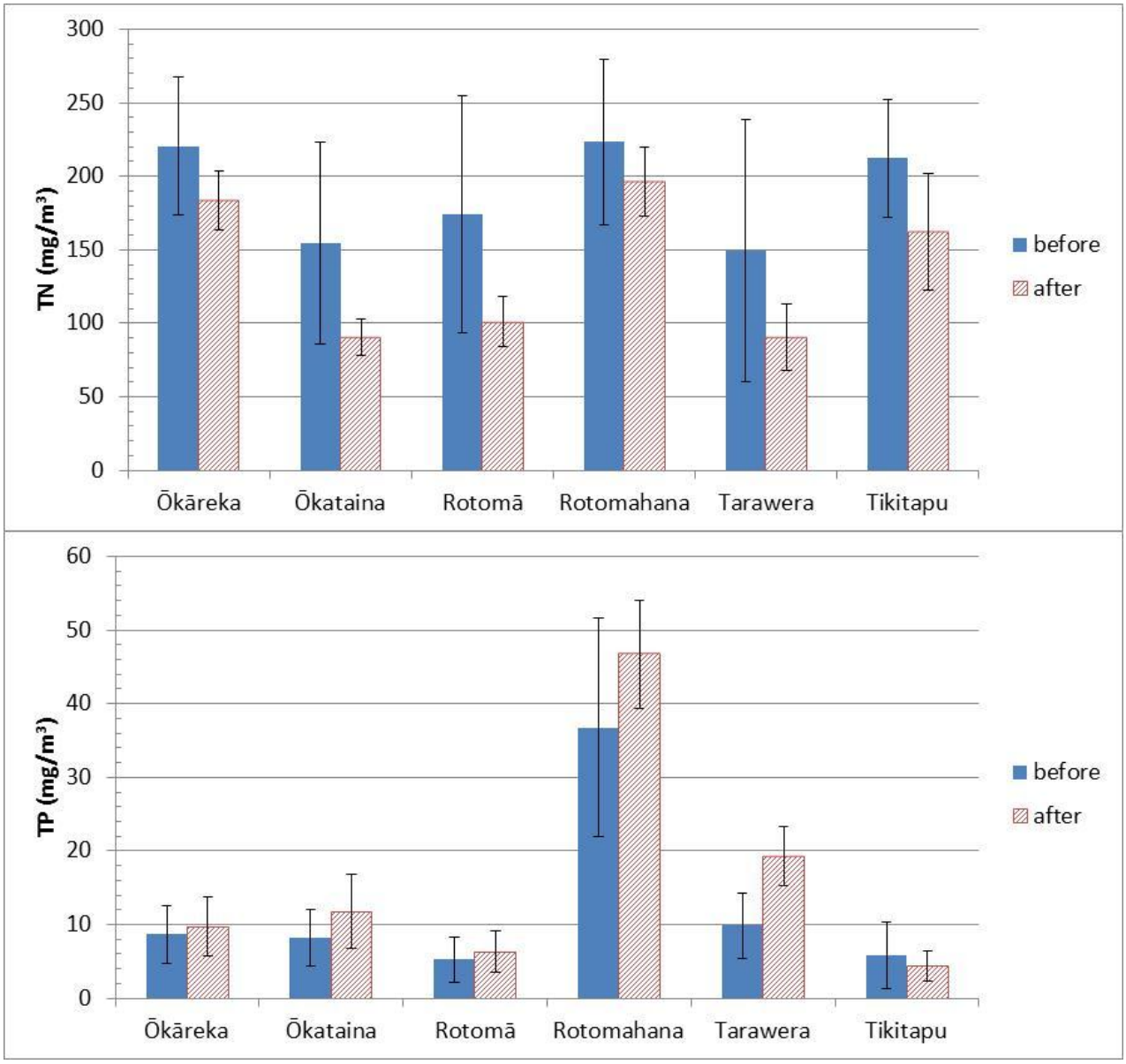
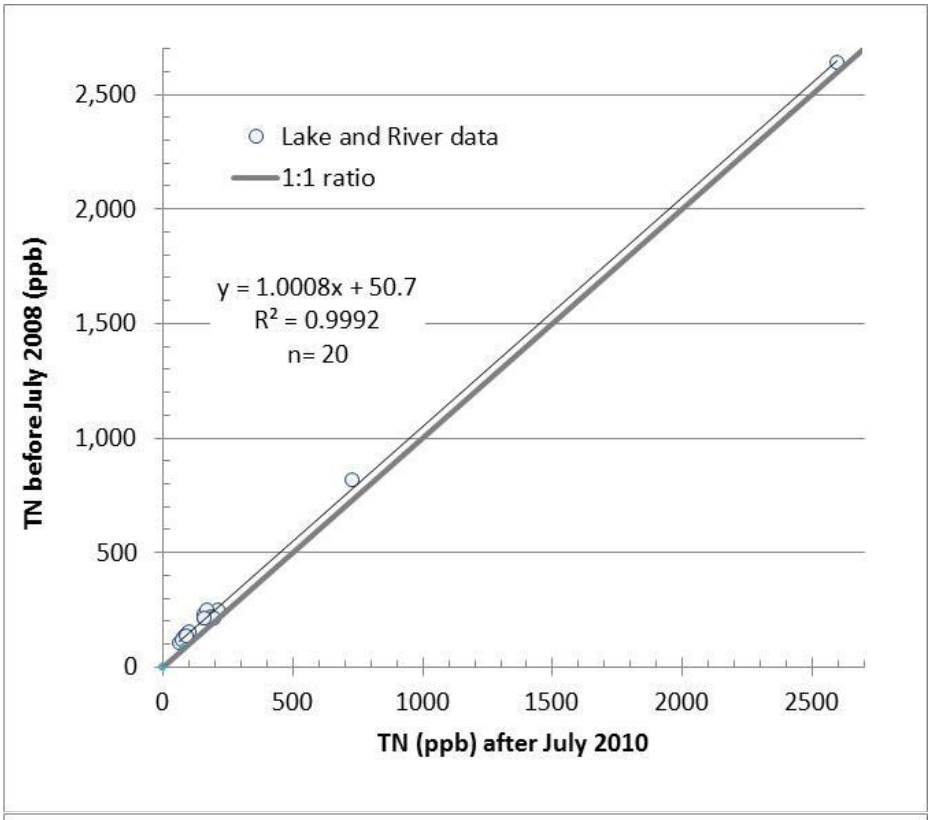


Figure A3.1: *Comparison of average TN (top) and TP (bottom) results for the three year period before July 2009 and after July 2010. For Rotorua lakes with relatively stable water quality the changes in laboratory methods resulted in lower TN, higher TP and less variation. Error bars are one standard deviation.*



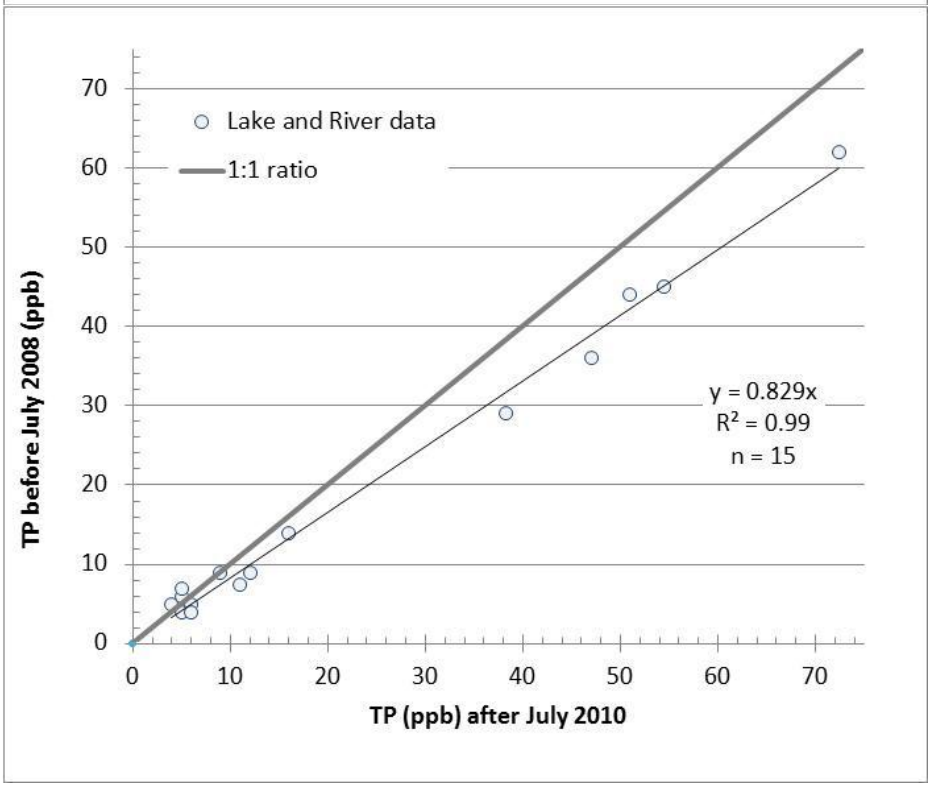


Figure A3.2: *Four year median TN (top) and TP (bottom) in stable lakes and rivers compared before and after laboratory method changes. The 1:1 ratio indicates the relationship if there was no difference between the time periods.*

Conclusions

It is recommended that the following adjustment factors are applied to data since November 2009 prior to undertaking trend analysis that spans the period August 2008 to November 2009:

- [TN old method] = [TN new method] + 50.7 mg/m^3
- [TP old method] = 0.829 [TP new method]

It is possible that the adjustment is also applicable for data since August 2008 for TP and since October 2008 for TN but this could not be confirmed by the analysis.

The recent laboratory changes have resulted in a decrease in TN results and an increase in TP results. For the purpose of calculating TLI scores, these changes mostly cancel each other out and there is very little impact on the TLI score.

The formulas calculated in this analysis provide an approximate adjustment factor. A more accurate way to assess the effect of changes in laboratory method would be to analysis a range of water samples using both the new and the old method. Unfortunately, the old laboratory methods are no longer routinely run, so this approach would require a separate investigation.