MULTIVARIATE ANALYSES OF THE EFFECTS OF LAND USE CHANGE ON RIVER WATER QUALITY: CASE STUDY OF MANAWATU RIVER WATERSHED, NEW ZEALAND

by

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DEDICATION

This work is dedicated to the Almighty God, who by his love and mercy bestowed me with inspiration and the required energy to conclude this research and produce this thesis. Not forgetting, my beloved parents who continually prayed for me and believed that I could achieve this feat.

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LIST OF ABBREVIATIONS

Abbreviation	Description
ANOVA	Analysis of Variance
ANZECC	Australia and New Zealand Environment and Conservative Council
APCS	Absolute Principal Component Score
BMP	Best Management Practices
BO	Barren/Other
CA	Cluster Analysis
Clar	Visual Clarity
Clr	Center-log-ratio
DO	Dissolved Oxygen
DO%	Dissolved Oxygen
DRP	Dissolved Reactive Phosphorus
E. coli	*Escherichia coli*
EC	Electrical Conductivity
EPA	Environmental Protection Agency
FA	Factor Analysis
Flow	Flow rate
HDPB	High Density Polyethene Bottles

HG	High producing Grassland
KMO	Kaiser Meyer Olken
K-S	Kolmogorov – Smirnov
LAWA	Land Air Water Aotearoa
LCDB	Land Cover Data Base
LUCAS	Land Use and Carbon Analysis System
LULC	Land Use and Land Cover
MDL	Minimum Detection Limit
MFE	Ministry for Environment
MLR	Multiple Linear Regression
NF	Non-plantation Forest
NH_4-N	Ammoniacal Nitrogen
NO_3-N	Nitrate
NRWQN	New Zealand River Water Quality Network
NZ	New Zealand
OW	Open Water
PCA	Principal Component Analysis
PF	Plantation Forest
pH	pH
PMF	Positive Matrix Factorization
SG	Shrub/Grassland

S/N	Signal-to-Noise ratio
SPSS	Statistical Package for Social Science
TN	Total Nitrogen
TP	Total Phosphorus
Turb	Turbidity
UR	Urban
USEPA	US Environmental Protection Agency
VW	Vegetated Wetland
WT	Water Temperature
WA7	Upland Monitoring Site
WA8	Intermediate Monitoring Site
WA9	Downstream Monitoring Site
WTP	Water Treatment Plant

ABSTRACT

Various land use land cover (LULC) properties can be very informative about pollution signatures or fingerprints in rivers. In addition, determining the quantity of pollution contributed to river water quality by different LULC is important to determine best management practices (BMPs) to adopt for effective water resource management. This study was initiated to identify pollution sources over spatiotemporal scales by using a combination of univariate trend analyses, multivariate statistical methods, and a receptor model. The multivariate method applied was principal component and factor analyses (PCA/FA). Thereafter, a positive matrix factorization (PMF) method, a receptor model was applied to apportion pollutants found within the Manawatu River Catchment in New Zealand. To achieve this, a 25-year (1989 – 2014) dataset comprising of 12 water quality variables from three different sites was used. LULC identified high-producing grassland (HG) as the most dominant class in all three sub-catchments, and was observed to be a major source of pollution at the three river monitoring sites. Univariate analyses and a Dunn-Bonferroni test conducted on categorized temporal values of pollutants revealed that nutrients and sediments were statistically significantly higher for the three sites when compared to initial monitoring years. There were multiple lines of evidence from both PCA/FA and PMF analyses that showed natural, domestic, and agricultural sources contributed to the water quality in the Manawatu river. The PMF analysis further revealed specific pollutants causing impairment and requiring attention by waste managers. Overall, the PMF model revealed point, natural, and agricultural sources

contributed close to 86%, 32%, and 75%, respectively in the downstream section of the river. At the intermediate sub-catchment, point, and agricultural sources contributed up to 100%, and 78% respectively, while soil erosion contributed 84%. For the upstream section of sub-catchment, agricultural pollution, and soil erosion were both 84% each. In addition, a combination of pollutant trends and these multivariate methods was significant in revealing the presence of point source pollution at the downstream site because of likely wastewater discharges. This study suggests that BMPs such as riparian buffers and constructed wetlands with high retention capacity are needed to filter the high concentrations of pollutants generated within the Manawatu Catchment.

1. INTRODUCTION

1.1 Introduction

Clean water is used for a multitude of daily activities and is required for good health (Jéquier & Constant, 2010; Mandal, Upadhyay, & Hasan, 2010). But with the advances in agricultural, industrial and urban development, retaining the quality of water to meet required standards has been difficult in recent times (Almeida, Quintar, González, & Mallea, 2007; Chelsea Nagy, Graeme Lockaby, Kalin, & Anderson, 2012; X. Li, Li, Anderson, & Xie, 2019; Peters, 2009; Tenebe, Emenike, & Daniel, 2018). There are several sources of water that can meet these daily needs and activities. These sources include rainwater (in the form of harvested rainwater), surface water, and groundwater (Emenike *et al.*, 2017), and the quality of these sources is a function of the components of the surrounding watershed, with land use activities identified as mostly responsible for impairment of water quality (Bowden, Mike, Josh, Keelie, & Shane, 2015; Hassan, Shah, Kanth, & Pandit, 2015; Huang, Zhan, Yan, Wu, & Deng, 2013). One of the main reasons may be due to how land use decisions are made without considering the watershed's assimilatory capacity (Tenebe, Ogbiye, Omole, & Emenike, 2016; Tenebe, Ogbiye, Omole, & Emenike, 2018). Larned *et al*., (2019) mentioned that excess influx of nutrient beyond river assimilation capacity result in poor water quality. When water quality is affected adversely, ecosystem functions are disrupted, and the consequence can lead to eutrophication and/or sedimentation (Woldeab, Ambelu, Mereta, & Beyene, 2018a). For example, phosphorus and nitrogen inclusion resulting from fertilizer applications in agricultural areas have been the major cause of pollution leading to algal bloom in rivers and lakes. These impairments can also reduce the aesthetic quality of the river by reducing clarity (Julian *et al*., 2013), as well as reducing oxygen levels when dead zones are created due to presence of decayed organic matter. Nutrients like nitrogen and phosphorus, and adjustments in the measurement of other variables such as dissolved oxygen, temperature, pH, and total suspended solids can affect ecosystem performance when they fall below recommended values.

Considering the negative effects of surface water pollution, consistent water quality monitoring is required to know the current state of water bodies as well as to be informed with the right policies, decisions, and management procedures. Consistent water quality monitoring can be achieved by building and operating water quality monitoring stations. This will enable relevant authorities to gather data that can be analyzed using univariate and multivariate statistical methods. The latter includes, but is not limited to, cluster analysis (CA), factor analysis (FA), and principal components analysis (PCA). These methods have been applied collectively to detect potential sources of pollution and identify relationships between variables in clusters. However, performing these analyses one after the other may yield poor inference and may also lead to the establishment of wrong policies. Several studies in the literature have utilized these techniques to propose cause- and-effect relationships of environmental pollution associated with groundwater (Adewale, 2010 ; Emenike, Tenebe, & Jarvis, 2018; Emenike, Tenebe, & Nnaji., 2018; Gulgundi & Shetty, 2016) and surface water (Chounlamany, Tanchuling, & Inoue, 2017).

New Zealand (NZ) has been identified as a nation that is experiencing recent surface water quality problems associated with intensive land uses (Rutherford *et al.,* 2008; Bruesewitz *et al.,* 2011; Julian *et al*., 2017; Scallenberg, 2019). Indeed, NZ is one of the world's major exporters of sheep products, powdered milk, and butter with the intention to increase agricultural productivity (OECD/FAO, 2015). Their dominance in agriculture is likely to put a stress on river water quality as more fertilizers will be required to increase agricultural production that the world requires.

According to World Health Organization (2017), consistent and accurate monitoring for water quality is critical for water resource management. NZ began consistently collecting and monitoring water quality data at the national scale in 1989 due to intense anthropogenic activities which led to surface water impairments (Smith & McBride, 1990). As reported by Davies-Colley et al., (2011), NZ's National River Water Quality Network (NRWQN) has been in operation and consistently monitored water quality variables for three decades. This robust dataset encompasses spatial and temporal variability of water quality, potentially exposing homogeneity or heterogeneity of individual variables or groups of variables. Seventy-Seven (77) sites were monitored across thirty-five rivers across NZ, with each site close to a hydrometric station for collection of water level and discharge. While several studies have used this dataset to reveal water quality issues at the national-scale (Ballantine & Davies-Colley, 2014; Julian, de Beurs, Owsley, Davies-Colley, & Ausseil, 2017; Larned, Snelder, Unwin, & McBride, 2016; McDowell, Larned, & Houlbrooke, 2009; Reff, Eberly, & Bhave, 2007; Smith, McBride, Bryers, Wisse, & Mink, 1996), very few studies have used it to focus on drivers of pollution at the regional and catchment watershed scale (Larned et al., 2016; Smith et al., 1996; Wilcock et al., 1999)

1.2 Study Goals

This study aims to apply multivariate statistical analysis using principal component and a receptor modelling technique to determine seasonal and spatial contributions to the water quality concerns identified in the Manawatu River Catchment, as well as to determine, and quantify individual contributions of measured water quality variables responsible for the pollution in the Manawatu River catchment.

1.3 Objectives

1. Conduct a spatiotemporal analysis on NZ's Manawatu River water quality for every 5-year period from 1989—2015 with a multivariate analysis using PCA, and FA to determine pollution sources and trends.
2. Assess the overall state of the watershed in terms of pollutant concentrations by apportioning sources using receptor modelling software (EPA PMF 5.0) developed by the United States Environmental Protection Agency (US EPA).
3. Determine land use effects on river water quality in Manawatu watershed.
4. Use the results above to develop adaptive management strategies that mitigate water pollution in rivers.

1.4 Justification

1. Water pollution issues are regional problems because they are largely dependent on natural processes and anthropogenic activities in the watershed. Drafting out policies or cause-and -effect studies from a national scale may not be adequate.
2. Conducting multivariate temporal analyses over 5-year periods is the appropriate scale for policy making and adaptive management.
3. A new modeling technique that incorporates PCA, FA, and PMF will be useful to

understand watershed-scale dynamics and anthropogenic effects on river water quality.

4. The United States and other countries are beginning to adopt the intensive agricultural practices of New Zealand. Thus, this study will give new insight on potential impacts of these intensive agricultural practices.

2. LITERATURE REVIEW

Surface water receives various inputs from the environment (Leng *et al*, 2019), and the issue of surface water pollution is now a global challenge. Monitoring of surface water bodies in the long-term and analyzing water quality variables have shown to be a way to access the performance or assimilatory capacities of watersheds and rivers. The information obtained from these analyses can be beneficial to water quality policy makers, and water managers on the right decisions to protect water bodies from incessant pollution. In addition, protecting surface waters from pollution gives assurance of satisfaction of different water needs by humans and ecosystem (Zanotti *et al*, 2019). River water quality exposes the various activities and properties of its surrounding catchment (Brierley, 2010). Water quality of rivers is usually best monitored by comparing water quality variables to a threshold value (Boesch 2002; Baron *et al*., 2002). However, information about the pollution source is equally important in managing river health (Brauman *et al*, 2007). With pollutants likely to emanate from more than one source, conducting bivariate or univariate analyses may not be enough to reveal those sources. The former involves understanding the relationships between variables, however understanding these correlations between river water quality and its catchment characteristics are complex to study as these interactions occur over space and time (Julian *et al*., 2017). Conducting univariate analyses require comparing measured values with local and international thresholds which is insufficient to identify pollution sources over space and time (Cambeg *et al*, 2013). The reason for this was attributed to the fact such monitoring and assessment are adequate for identifying point source pollution like wastewater from industries and treatment plant (Campbell *et al*., 2004); and unconsciously disregarding the contributory effects from diffuse source pollution (Vorosmarty *et al*, 2010).

2.1 River Water Quality in New Zealand

Over the years, the small country of NZ has devoted most of their economy to agriculture, which has resulted in them using intensive land use practices (OECD/FAO, 2015). Agriculture, forestry, and urban areas contribute a lot of pollution in the form of sediments and nutrients to surface water in NZ (Basher, 2013; Dymond et al, 2016). The presence of these pollutants can elevate algae presence and decimate species (Schallenberg and Sorrell 2009; Reid et al, 2011). Surface water quality in NZ is degrading in urban and pastural area and are likely to get worse in the future with increasing land use intensity (Ballantine and Davis-Colley, 2014). Several studies in the literature has uncovered the extent of pollution in NZ rivers at national, regional, and catchment scales (Learned *et al*, 2019). Close and Davies-Colley (1990) reported a positive correlation between planted forest (PF) coverage and mean DRP concentration as well as a reduction in TN with an increase in native-forest (NF) covers. Ballantine and Davies-Colley (2014) observed that median concentration values for TN, TP, DRP and NO_3-N increased as planted – forest, cropland and urban cover increased. Snelder *et al*., (2017) observed an increase in TN, NO_3-N and TP in agricultural areas from the assessment of 592 sites in New Zealand. On a regional scale, Hamill and McBride (2003) reported median DRP and NO_3-N concentration values increased at forest and dairy sites in Southland streams. McDowell (2009) observed elevated TP and orthophosphate concentration values in both diary, and sheep farming areas in the Otago Catchment located in the South Island from 24 sites investigated. Niyogi *et al*. (2007) reported that increased nutrients and sediments were associated with high PF covers in the Otago region as well. Similarly, at the catchment level, Cooper and Thomsen (1988) reported high TP, TN, DRP concentration values in Purukohukohu catchment, which is located between Rotorua and Taupo were associated within pastural catchment areas. Townsend *et al*., (1997) also obtained similar findings with TP concentration. Their study revealed higher concentration of TP were in pastural and NF catchment areas of Taieric catchment consisting of 60 sites. Young *et al*., (2005) reported higher values of TN, NO_3-N and *E. coli* from over 10 sites that were dominated by pastural and horticulture areas. Most recently, Weaver *et al*., (2017) reported increased TN and $N0_3$-N concentration from was eight (8) sites in lake Wanaka catchment and was strongly associated by the presence of high pastural cover. At the national scale, Julian, de Beurs, Owsley, Davies-Colley, & Ausseil, (2017a) considered river water quality of 77 catchments across NZ using a combination of time-series and regression analyses to assess the health status of NZ rivers. The study revealed that most of the lowland rivers in NZ have poor water quality due to legacy effect of intensive and prolonged agricultural practices. The study also identified that lowland rivers in NZ have become clearer, yet more nutrient-enriched, which may lead to toxic eutrophication. From all these studies on water quality in NZ, it is evident that land use activities play an important role towards pollution state of their rivers. Notably, most of these studies were carried out using different bivariate or multivariate approaches.

2.2 River Water Quality Assessment and Methods Applied

The use of multivariate statistical method in analysis of water quality data has been used widely revealing natural and anthropogenic processes having significantly affected water quality (Koh *et al*, 2016; Alberti *et al*., 2016; Devic *et al*., 2014; Phung *et al*., 2015; Sterfania *et al*, 2018). Recent literatures have reported river water quality conditions and the different method applied to conclude on their pollution status. These findings are summarized below:

Lenart-Boroń, Wolanin, Jelonkiewicz, & Żelazny, (2017) examined the spatial variation of anthropogenic pressures imposed on the surface water quality in Pohdale region in Southern Poland, which is known for tourism. Their study considered both microbial and chemical water characteristics, as well as the land use change pattern. Their study revealed that land use, particularly urbanization, has a significant effect on physio-chemical variables, more so than on bacteriological variables. Similarly, Chounlamany *et al*., (2017) conducted a spatiotemporal assessment of water quality on the Marikina River in the Philippines. The assessment included 12 water quality variables from a monitoring station for a period of one year. Multivariate analyses such as CA were used to cluster seasons and PCA was used to give information on anthropogenic effects. Their results showed that rainfall pattern within seasons and soil erosion were responsible for pollution of the river. Additionally, their methods suggest that not more than four stations within the river is required, thereby reducing cost. Khan *et al*., (2018) investigated water quality variables by randomly collecting water samples from seven different sites from River Swat watershed in Pakistan from the upstream and downstream section. These samples were collected for a year from 2015—2016. Multivariate analyses revealed that 96.7 % of surface water samples collected from the different sites were heavily contaminated with *Escherichia coli* (*E. coli)*, which they attributed to anthropogenic activities such as irrigation and indiscriminate sewage disposal of humans and animals. However, the study did not distinguish which of the sites contributed more to the pollution status of the river.

Alves *et al*., (2018) investigated a polluted river—Sinos River in Brazil-- which was used for water supply, and distribution. The authors used a two-year dataset (May 2013—April 2015) that was collected from a municipal water treatment plant (WTP), which they grouped into three periods using cluster analysis. Other multivariate analyses used were PCA and PMF methods. Their study revealed that *E. coli* was significantly lower in winter, and spring and was attributed to dilution effects, however their findings did not mention the effect of flow rate on *E. coli*, which was a possibility due to wash-off of algae and bacteria count. Generally, their study concluded that the use of multivariate statistics is very helpful in treating large datasets and giving new and relevant insight to water quality issues. Asare, Palamuleni, & Ruhiiga, (2018) investigated land use effects on water quality in a semi-arid region in South Africa by conducting land use mapping and accuracy assessment. The study revealed that increased rainfall within the study area increased vegetation which affected water quality variables like pH (from 8.6 to 10.6), and specific conductivity (from 379 to $780\mu s/cm$) to values unsuitable for irrigation purposes, while increased land use increased *E. coli* values. Bojarczuk, Jelonkiewicz, & Lenart-Boroń, (2018) studied anthropogenic effects on the water quality of River Bialka in Southern Poland by considering variation in *E. coli* and physio-chemical properties over time for two and a half years. Water samples were collected once a month for the study period from four different sites. Performing several statistics like PCA and Analysis of variance (ANOVA) with post-hoc test, the study suggested that pollution in the river was primarily due to point sources.

Furthermore, the study revealed that pollution patterns were affected by flow rate conditions. Specifically, the study showed that large pollutant concentrations were obtained in samples having low *E. coli* during high flow conditions. In conclusion, they emphasized that land use variability has a positive correlation with pollutant loads within the watershed. Woldeab, Ambelu, Mereta, & Beyene, (2018b) studied water quality issues of four tributaries in East African Highland, while considering several land use characteristics such as farmland, naturally vegetative land, and settlement from October 2014 to March 2015. Conducting water quality on 12 variables and using univariate and bivariate (Spearman correlation and Kolmogorov-smirnov (K-S) test) statistical methods revealed a significant difference between dry and wet seasons. Specifically, the study revealed that more pollution from agricultural land occurred in the wet season compared to the dry season, showing the importance of seasonal changes in water quality assessment. Cruz *et al.*, (2019) investigated cause-and-effect of land use/land cover and seasonality on the water quality of the Siriri River in Northeast Brazil. Twelve representative variables were collected from 2014 to 2015. By applying PCA, they were able to conclude that the major contribution to water quality degradation was from agricultural land use influence. However, despite the benefits mentioned about the use of PCA and FA techniques, there are some limitations in terms of parameter extraction and negative loading formation which makes it herculean for scientists to interpret. PCA is well able to suggest possible pollution sources based on factors extracted but complex receptor modelling like absolute principal component score—multiple linear regression (APCS—MLR) and PMF can quantify the variables or sources (H. Li, Liu, Du, Li, & Hopke, 2015). In another study, Salim *et al.*, (2019) compared the use of PMF and principal component analysis—multiple linear regression (PCA—MLR) on some runoff water quality data. Their study showed that PMF results gave better understanding and better results when compared with the use of dimensionless statistics.

Overall, few studies have applied PMF established by US EPA on water quality data since its release in 2014 (Yu *et al*, 2014; Gholizadeh *et al*., 2016). The proper use of PMF requires collection of large water quality for source identification (Wang *et al.*, 2018) and identifying sources is in turn needed for extensive characterization of water quality (Zanotti *et al*., 2019). PMF is a multivariate analytical method employed for source identification and apportionment. It was formulated to cater for data uncertainties (Paatero and Tapper 1994); which is a major issue with measurement obtained from field investigations. In addition, Reff *et al* (2007) reported that PMF gives a better characterization of sources identified than PCA. Yu *et al.,* (2014) applied FA and PMF on upper Yangtze River Chongqing in West of China to determine sources of pollution. Li *et al*., (2015) applied it to surface water quality data in Daliao River basin situated in North East China. Gholizadeh *et al*., (2016) applied a combination of PCA/FA, PMF and APCS—MLR to water quality data from three major rivers found in South Florida, United States. Their study, for now, appears to be the only one that has used a large set of water quality data (i.e., 2000—2014) to conduct source apportionment assessment. Alves *et al*., (2018) applied PCA, CA, and PMF to examine the pollution sources affecting Sinos River in Southern Brazil. Darlan *et al*., (2018b) investigated the chemical composition (pollutant) in three different areas in Southern Brazil. However, till now, no literature has applied these techniques to evaluate pollution sources and apportionment in

NZ, which is considered to have some of the most consistent water quality database and intensive agricultural land use in the world (Julian *et al*., 2017).

3. MATERIALS AND METHODS

3.1 Study Area

3.1.1 Physical Geography

The Manawatu catchment is situated on the southern tip of the North Island of NZ (Figure 3.1). It has an area of 5,879 km^2. Within this watershed, three NRWQN monitoring stations can be found which have been used to collect water quality variables since 1989. The first station on the upstream section is mainly surrounded by grassland and pasture while the midstream station has large adjacent built up areas. The last station is situated near the catchment outlet.

Larned *et al.* (2016) and Abbott *et al*. (2017) reported earlier that the Manawatu River is sediment impacted, largely as a result of intensive land uses on moderate-steep slopes with erodible soils. The Southern and Eastern regions of the Manawatu catchment are mountainous and hilly respectively and covered by natural forest and shrubland which serves as pasture for beef cattle, dairy and sheep farming (Dymond *et al*., 2016). It sits on soft sedimentary rocks characterized by mudstone and sandstones (Fuller *et al.,* 2018). The mountains contain hard dark grey-brown soils that produces fine deposit when eroded while the hills are characterized with tertiary aged mudstone or sandstone (Dymond *et al*., 2016) and large amount of sediments from this catchment (proliferated by land clearing) is generated to the ocean at the rate of Ca. 3.74Mt yr-1(Hicks *et al*., 2011)

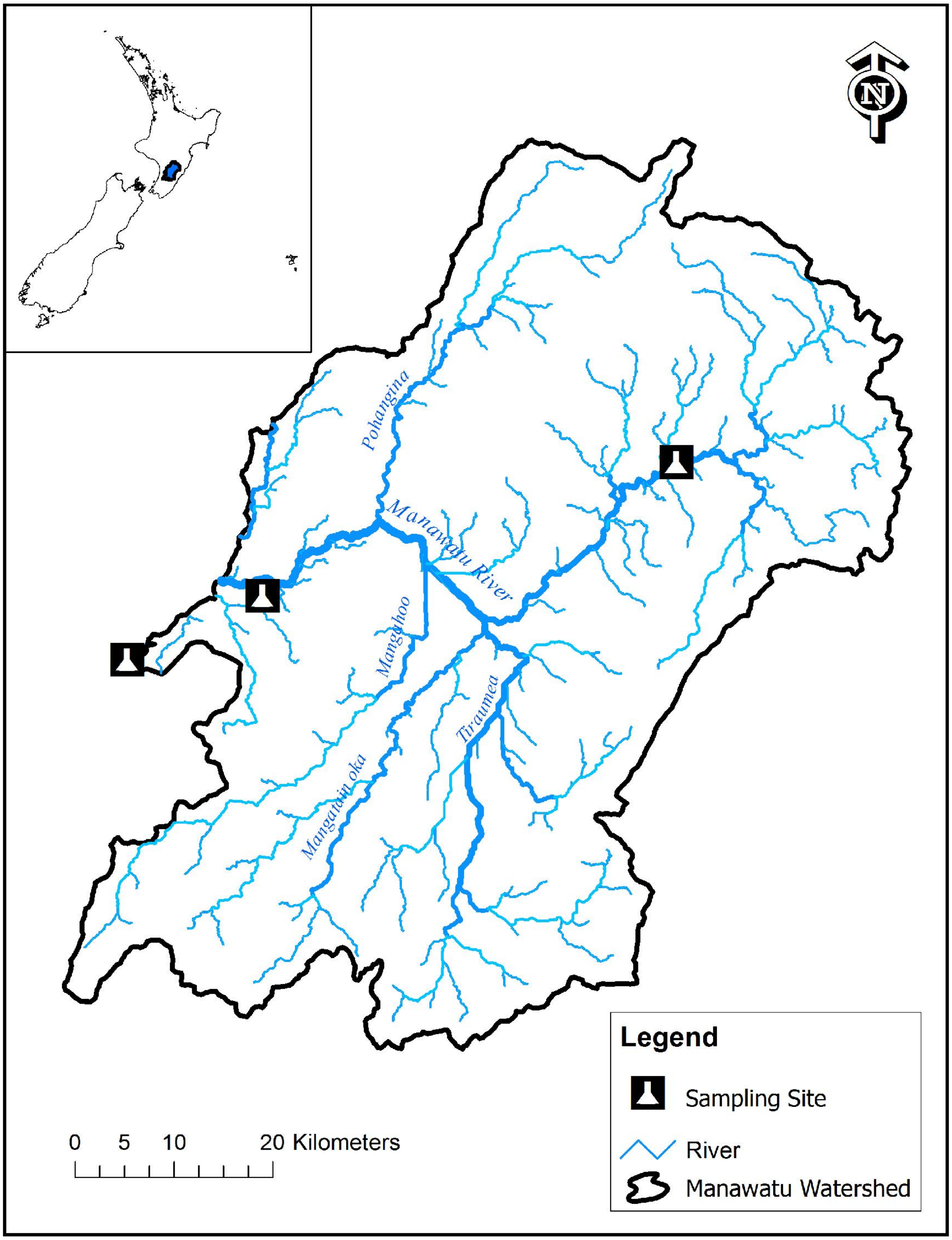


Figure 3.1: Manawatu River Catchment Showing Major River Networks & Sampling Sites.

According to the Land Air Water Aotearoa (2016), the Manawatu river itself is a long-stretched river, 235km long and has several large tributaries such as Mangahoo, Mangatain oka, Oroua, Pohangina and Tiraumea rivers that are 86km, 71km, 131km, 71km and 69km long respectively. The river starts from the Eastern part and gradually meanders to the Tasman sea. The predominant land use in the Manawatu catchment consist of agricultural areas (70%) and half of the agricultural land are used for sheep and beef farming (LAWA, 2016). Within the catchment, Palmerston North- where WA8 site is situated has the largest urban settlement with many other small communities. The settlers in these communities' practice intensive agriculture and have done this for years which suggests that the major consumptive use of the river within the catchment is mainly for irrigation purpose.

3.2 Methods for Assessing Water Quality in the Manawatu Catchment

The Manawatu catchment is located within the Manawatu-Wanganui region, which has some distinctive topography such as the Ruahine, Tararua, and Puketoi Ranges. These Ranges appear to be above 1000 m in elevation but soon dropped to form a ridge as they got closer to the Manawatu gorge. Water quality data was collected by the National Institute for Water and Atmospheric Research (NIWA) from three monitoring sites within the Manawatu Catchment monthly for 25 consecutive years (1989-2014). These three stations represent a longitudinal study, cutting across both upland river whose altitude is > 150 m and assumed to be less polluted (WA7) to lowland river with altitude <150 m. These lowland rivers are likely more polluted as accumulated diffuse pollution flows downstream (WA8 and WA9). The summary of the different site characteristics can be seen in Table 3.1. Specifically, WA7 (Manawatu at Weber Road) is located at the upstream section within the Manawatu catchment with a median temperature of 13^{0}C and catchment area of 705 km^2. At the intermediate point, WA8 (Manawatu at Teachers College) is found.

The catchment area is 3897 km^2 and it is located at the center of Palmerston North and has experienced significant soil erosion that has affected the water quality of the river due to its low elevation compared to WA7. It consists of major rivers with significant pastoral development and has a median temperature of 13.8^{0}C. At the downstream section of the river, WA9 (Manawatu at Opiki Bridge) is located. This catchment has a median temperature of 14.4^{0}C and receives majorly industrial and sewage discharges.

Table 3.1: Characteristics and Location of Monitoring Site in the Manawatu Catchment

Site code	Catchment area (km^2)	Site description
WA7	705.28	Located upstream
WA8	3897.37	Major river downstream located at center of Palmerston North
WA9	4222.22	Located downstream

The dataset used for this study included data collected from the inception of water quality monitoring program established by the NRWQN between Jan 1989 to Dec 2014 considering twelve variables (See Table 3.2). Out of the twelve parameters measured, five were measured *in situ* while seven others were measured in the laboratory. Water quality variables measured in the field were discharge (Q), dissolved oxygen (DO), water clarity (CLAR), turbidity (TURB), absorbance (Abs) and water temperature (T_w) while pH, total phosphorus (TP), total nitrogen (TN), dissolved reactive phosphorus (DRP), oxidized nitrogen (NO_x^-), and conductivity (COND) were measured in the laboratory (Smith & McBride, 1990). Smith & McBride (1990) and Davies-Colley *et al*., (2011) gave a detailed account on how water samples were collected. In the beginning of sampling years, samples taken for laboratory testing were collected into 2-liter High Density Polyethene Bottles (HDPB) at each site simultaneously up to 2004. But in 2005, the method of sampling with 2-liters HDPB was replaced with the use of a single 500ml HDPB of the same quality and manufacturer. Water samples were stored in an insulated bin filled in slush ice and immediately transported to the water quality center in Hamilton, New Zealand. These samples were transported quickly to ensure that both chemical and biological testing was conducted within 24 hrs according to laboratory standard. In order to determine the quality of the monitored river overtime as well as observing any change in water quality, the data set was grouped for every 5-year period from 1989 to 2014 with the exception of 1994, which was exempted for all variables due to contamination of ammoniacal nitrogen (NH_4)(Davies-Colley *et al*, 2011;Julian *et al*., 2017). This study used median values over mean values for comparison, and for monitoring water quality changes because the latter is sensitive to spread and extreme values. Median values of each 5-year period were calculated and compared to guidelines or trigger values prepared by the Australian and New Zealand for water quality assessment which varied across low and highland (Table 3.2) depending on where the sampling site stations were situated (Australian and New Zealand Environment and Conservation Council ANZECC, 2000). These trigger values do not necessarily suggest an immediate threat but rather a warning sign to future risk if not curtailed. Statistical testing procedures were carried out using SPSS package (V.23) and R package (R Core Team, 2020) while the receptor modelling was performed using EPA PMF 5.0. Before statistical and modeling was conducted, missing data were initially sorted by replacing each parameter with the overall median value. Thereafter, normality test using the Kolmogorov-Smirnov (K-S) test was conducted to determine the distribution of dataset. This step was important to determine the appropriate statistical test to implement moving forward. For example, a normality test showing non-normal distribution is usually analyzed by considering non-parametric statistical methods.

For this study, normality test showed that the dataset was not normally distributed ($p < 0.05$) except for one or two parameters at some sites. Median values for each 5-yr period were subjected to non-parametric median test—a form of non-parametric Kruskal Wallis test for all sample groups and where a difference is identified. A Dunn-Bonferroni post-hoc test was performed to determine significant differences among groups. Note that a statistical difference observed may not necessarily imply a concern as it may be due to a positive difference in the water quality parameter measured. i.e. values moving from high to low. Therefore, more emphasis should be given to the effect of the difference or non-difference relative to the stipulated trigger values. Seasonal pollution patterns were investigated for each site by stratification of datasets into seasons to determine which season might be an apparent contributor to the river water quality condition when compared to the overall pollution status especially trigger values. According to Abbott *et al*., (2017), the Manawatu watershed has two distinguishable seasons (Summer—November-May and Winter—June-October). Bearing this in mind, summer, winter, overall, and trigger comparison observations were carried out for both seasons to show contribution of seasonality to water quality variables measured at different sites.

A two-tailed non-parametric spearman correlation was applied to determine the relationship between variables while principal component analysis (PCA) was applied to the dataset in order to reveal latent characteristics of the variable that may have been hidden due to collinearity or serial correlation which is common in large dataset with similar measurements. The spearman correlation co-efficient values were reported while using the raw data because there was no change in the statistical significance which is important to the aim of the study. This study was more concerned with the direction and statistically significant difference developed by the variable rather than the co-efficient which was consistent when the transformed-Pearson's correlation coefficient was used. To carry out PCA/FA, it was necessary to determine whether the sample size was adequate for this process as this procedure is very sensitive to dataset size, serial correlation, or autocorrelation. This procedure known as the Bartlett test or Kaiser-Meyer-Olkin (KMO) Measure of Sampling test was conducted to determine the robustness of dataset, check for redundancy and to predict whether the variables can be well explained by factors generated from PCA/FA analysis with statistical significance set at 0.05. Kaiser (1974) reported that KMO values > 0.5 signify that variables can be subjected to PCA/FA but in 1999, Hutcheson and Sofroniou elaborated further by categorizing PCA/FA efficacies to different limits. The authors reported that values between 0.5 – 0.7 fall between moderate range, 0.7 – 0.8 are good, and 0.8 – 0.9 are very good values. Since the datasets were not normally distributed, it was necessary to transform the data before PCA/FA analysis. PCA/FA is governed by the same principles of linearity and it performs similar function of correlation as it was the intention of this study to determine whether factors or principal components generated are well correlated with the variables under investigation. Given that the raw or untransformed dataset is likely to be sensitive to deviations or skewness due to different measuring units, rescaling will be required to reduce variability and prevent the output from giving spurious results. To this end, a center-log-ratio transformation was adopted. This method was preferred over the Z-transformation because it maximized the variability explained when both methods were applied using a “brute force” technique. This method required the use of the Geometric mean (g(x)) as divisor and it is given as (Aitchson, 1986; Blake *et al*., 2016)

$$clr\ (x)\ =\ In\,\frac{Xi}{g(x)} \qquad \text{eq. (1)}$$

$$where\ g(x)\ = \sqrt[n]{X1X2\ldots Xn}, \qquad \text{eq. (2)}$$

where X represents the variable and n is the nth number of variables.

After PCA/FA was applied, an orthogonal rotation-varimax method was implemented to spread variability of the dataset to set aside any bias. The factors generated in the PCA matrix were interpreted based on the associated weight on the principal components (PCs) separated according to their level of contribution to the aim of the study or experiment. In this instance, the aim is the water quality condition based on the measured parameters. The output of the PCA methodologies was used to determine the presence of extracted variables which may be referred to as source identification. Kaiser (1974) suggested that components having PC(s) less than 1 should be excluded. This has been followed by many studies (Jin *et al*., 2019; Nnaji *et al*., 2019; Tenebe *et al*., 2016; Emenike *et al*., 2018; 2019). However, applying this rule to all studies may have a drawback for source identification measures. For source identification, suppressing PC with eigenvalues < 1 may not reveal the presence of variables whose identifiable presence could have led to a more robust finding. More specifically, suppressing the components without a clear understanding of the intended result can make a ridicule of the PCA/FA output and in some cases reduce the variability explained by the components. Generally, the first component of any PCA/FA process shows the highest explanation of variability which reduces as the principal components increases. The variability levels explained by each component is useful in both source identification and apportionment. Therefore, it is important to detect less variable factor with high loading during PCA. This process will assist in detecting pollutants of high background concentrations emanating from natural sources. For example, for a high loading to appear in a lower principal component, it may imply that the variable exists in the system in a natural form or as a legacy pollutant.

Unfortunately, neglecting less variable components simply by deploying higher eigenvalues may deprive the researcher from this observation Since the aim of the PCA/FA is to identify sources that explains the most variability, this study used the same number of factors obtained from EPA-PMF model as a guide for PCA/FA extraction except for cases where the PCs showed lesser variability. In that case, only factor loadings or components with loadings values > 0.75 (strong loadings) will be reported (Liu *et al*., 2003, Huang *et al*., 2010). Positive matrix factorization method (PMF) is a technique used on environmental datasets to identify sources and apportion weight in percentages to pollution parameters. It achieves this outcome by decomposing large temporal dataset into single quantified weight in the form of factor contributions, factor profiles or factor fingerprints. These factor profiles are sub divided into concentration of species (pollutants and their respective percentages). The percentage of these factor profiles are then interpreted as pollutant prevalence in the sites under investigation. The PMF model can be expressed by the general form.

$$X = GF + E \qquad \text{eq. (3)}$$

where X has α dimensions with n representing the sample space and m is the number of variables.

The X matrix is decomposed into G and F matrices, with the G representing the factor contribution and F factor profiles. The E matrix is the residual error which should be minimized. Minimizing these errors from each variable such that they tend to zero would almost guarantee that the dataset or variable was from a normal distribution. The PMF model generates co-variance and correlation matrices to be decomposed (Philips and Moya, 2014), with one of its strength being the generation of non-negative factors (Manousakas *et al*., 2017). For this study, the dataset was cleaned by ensuring no missing data existed. In the event of missing data, it was replaced with the median value of the specific variable and the file to be subjected to PMF modeling was termed the concentration file. Thereafter, the uncertainty concentration file was created. This refers to the minimum values that can be recorded by a measuring device, below this value, no reading can be obtained. Uncertainty dataset in modelling is important for pollution studies and risk assessment due to unknown processes or activities such as experimental precisions, instrumental errors, environmental instability effect (Climate change), seasonality variability effect that would have been introduced and affect the original data collected. This phenomenon may affect the output as well as the corresponding decision made when neglected as model results would have been significantly underestimated. The process of mathematically handling uncertainty data file using the PMF approach has been well documented elsewhere (Alves *et al*., 2018; EPA, 2014).

The Uncertainty concentration is obtained by:

$$= \sqrt{(Error\ fraction\ \times concentration)2 + (0.5\ \times MDL)2} \qquad \text{eq. (4)}$$

Where: MDL is the minimum detection limits

In performing the PMF analysis for this study, all data set entered showed a strong S/N ratio and this was attributed largely to the consistency of the data recorded, fewer missing values and large dataset or sample size which was used for the analysis (Table 3.2). Despite that, some of these variables were excluded from the analysis because the study was more concerned about variables directly involved in pollution without including strongly correlated variables that could be a surrogate of one another. Therefore, variables such as Temperature, DO%, Clarity, pH as "bad weight" so the program neglects those variables during computation. However, as a normal, "bad", "weak" or "strong" weight is given to dataset with large, average, and minimum missing value to give a heads-up to the software program. For this study, all variables used where allocated or described as strong by default. Regression plots were obtained showing corresponding R-squared values for each water quality variable.

3.3 Land Use Land Cover (LULC) Mapping

To determine the contribution of catchment characteristics—land cover and land use (LULC) activities on water quality, a map showing existing LULC of Manawatu catchment was developed. Land use refers to the usage of the earth's natural habitat towards the realization of a desired goal such as dairy farming, urban or industrialized settings. Land cover specifies the identifiable features on land which include the presence of crops, forest plantation or scrub-grassland covers (Learned *et al*., 2019). Identifying various LULC is important as it helps to give some insight as to sources of diffused pollution within a catchment. For this purpose, the LULC data obtained from the land cover database (LCDB v4.1, 2015) was used. Notably, the land use classes obtained gave up to 35 classes but showed some identical and conflicting classification with the Land Use and Carbon Analysis System (LUCAS) data which is operated by the NZ Ministry for the Environment (MFE, 2012). Julian *et al*., (2017) detailed these differences and re-classified the result obtained to be suitable for effectively connecting water-quality impairment relationship. Therefore, this study followed the same procedure for consistency of reporting with the authors detailed output.

3.4 Landscape Connectivity Analysis

I used an existing watershed connectivity model developed by Kamarinas (2018) to connect LULC to floodplains. This maps the LULC that is directly connected to the river via surface runoff. This model was carefully made following the detailed procedure reported in the literature by Kamarinas *et al*., (2016). The channel head for the Manawatu catchment was identified using 0.5 m rural aerial photos obtained from the Land Information, New Zealand using a two-year period data (2010-2012) as the reference point. After that, the watershed was delineated from the headwaters of the catchment to establish the flow direction from upstream to downstream in the flow direction. Each 15 m pixels on the hydrological model developed greater than 5^{o} slope along the flow direction as well as pixels adjacent to a river were categorized as "connected" whereas pixels less than 5^{o} slope along the flow direction were specified as "not connected". With the landscape connectivity map developed, it was clipped, combined, and re-classified to select catchment that are connected to flood plains for the Manawatu catchment area.

Table 3.2: Description of Water Quality Data Used for Analysis of Manawatu River in NZ from 1989-2014

Parameter	Unit	Abbreviation	Missing Data (%)	Trigger Values (Lowland, Highland)
Flow rate	m^3/s	Flow	1.4	
Water Temperature	^oC	WT	0.3	
Electrical conductivity	μScm^{-1}	EC	Nil	
Dissolved Oxygen	g/m^3	DO	1.3	6
Dissolved Oxygen (%)	%	DO%	1.3	98,99
pH	-	pH	0.2	7.2,7.3
Turbidity	NTU	Turb	Nil	5.6,4.1
Total Phosphorus	g/m^3	TP	0.3	33,26
Total Nitrogen	g/m^3	TN	0.6	614,295
Visual clarity	m^{-1}	Clar	Nil	0.8,0.6
Dissolved Reactive Phosphorus	g/m^3	DRP	Nil	10,9
Ammoniacal nitrogen	g/m^3	NH_4-N	Nil	21,10
Nitrate	g/m^3	NO_3-N	Nil	444,167

*DO % and pH: lower limits were considered

4. RESULTS

4.1 Land Use Map and Analysis

From the LULC mapping (Figure 4.1), there were different LULC categories observed from the three sites within the Manawatu Catchment. At the Upstream area (WA7), eight classes namely: Shrub/grassland (SG), Urban (UR), Non-plantation forest (NF), Plantation forest (PF), Vegetated Wetland (VW), High producing grassland (HG), Open water (OW), Barren/other (BO) were present. These categories revealed that perennial and annual cropland did not exist upstream. The catchment of WA7 was dominated by HG (88.5%), NF (3.4%), and PF (3%), respectively. For the intermediate site (WA8), Ten LULC categories were obtained, and as follows: SG, UR, NF, PF, VW, HG, OW, BO, PC, and AC. The catchment was dominated by HG (74.1%), SG (14.2%), NF (8%). For the downstream point of Manawatu Catchment (WA9), all LULC obtained for WA8 were present. The Nine categories observed were dominated by HG (74.5%), SG (10.8%), and NF (7.8%).

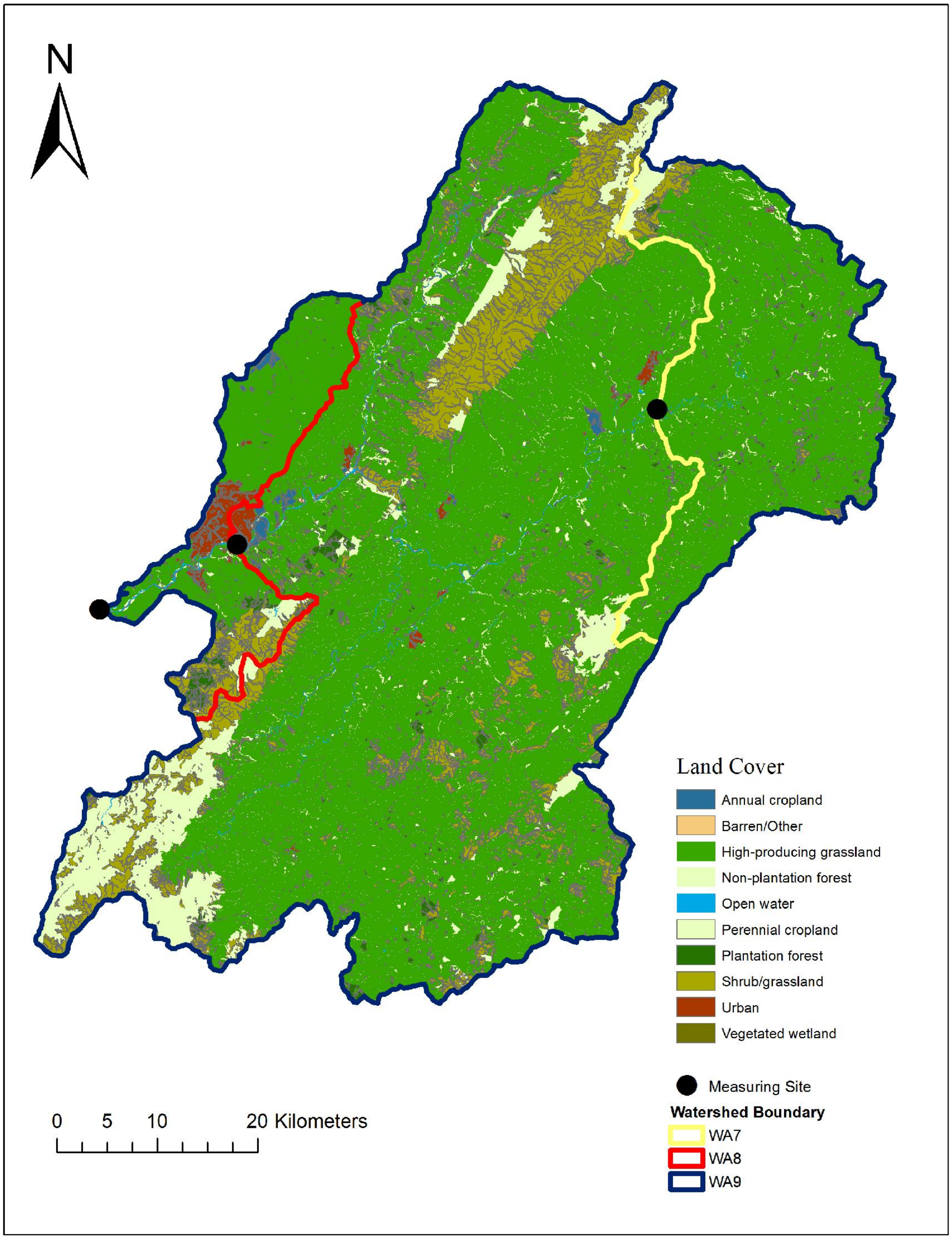


Figure 4.1: Land Use-Land Cover Map for Manawatu River Catchment

4.2 Landscape Connectivity

The landscape connectivity analyses (Table 4.1) revealed that 83.6 km^2 of WA7's catchment (or 11.9%) was directly connected to streams via surface runoff and located in floodplains. Another 196 km^2 (or 27.8%) were connected to streams via surface runoff, but not located in flood plain. That is, these were relatively steep hillslopes that directly contributed surface runoff to streams. In total, for WA7's catchment, 39.7% of the area was directly connecting to streams via surface runoff. Approximately 426 km^2, which is more than half of the catchment were not directly connected and contributing surface runoff to the Manawatu River. HG (88%) were mostly connected to a floodplain, which may suggest a significant pollution source to the Manawatu river from the upstream section. For the intermediate site (WA8), landscape connectivity result suggests that ~ 2191 km^2 from a total of 3897 km^2 of WA8's catchment (or 56.2%) were not directly connected to the river (Table 4.2). However, 11.3% of the total area in WA8 catchment (or 440.9km^2) was directly connected to the stream via surface runoff and located in floodplain. Also, 32.5% of WA8's catchment (or 1265.3km^2) were directly connected to stream via surface runoff and not located in floodplain. Of a note, HG (75.3%) dominated a large portion of the area connected to the floodplain, and ~ 64% (HG area connected + HG not connected to flood plains but catchment) of HG are somewhat contributing to the Manawatu River. Therefore, for WA8, 43.8% of the catchment were connected to streams via surface runoff. At the downstream sub-catchment (WA9), 483.9 km2 of the catchment (or 11.5%) was directly connected to the stream via surface runoff and located in flood plain. Another 1343.6 km^2 of WA9's catchment area (or 31.8%) was directly connected to the stream via surface runoff but not located in floodplain, and 2395.29 km^2

(or 56.7%) was not directly connected to either floodplain or the stream via surface runoff (Table 4.3). Similarly, HG (66%) was a dominant LC in all three sub-catchments.

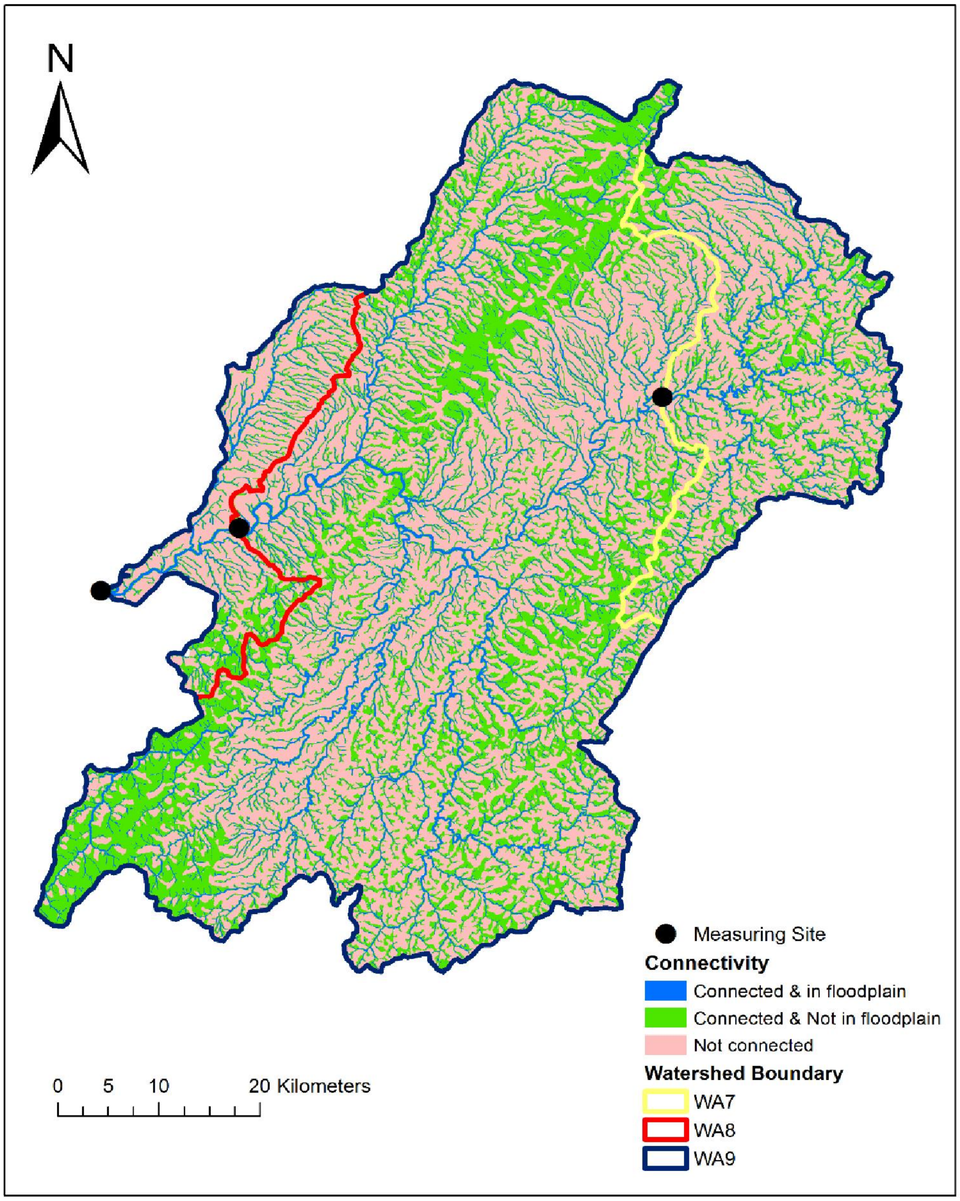


Figure 4.2: Landscape Connectivity Map for Manawatu River Catchment

To determine the extent to which measured water quality parameters were affected by watershed activities, a comparison was concurrently made with their corresponding trigger values, as stipulated by ANZECC.

Table 4.1: Reclassified Watershed Properties for Site WA7

Land use/Land cover category	Connected Area to floodplain (km^2)	Connected Area not to floodplain (km^2)	Area not connected (km^2)	Total (km2)
Shrub/grassland	3.39	14.20	15.67	33.26
Urban	0.12	0.12	0.36	0.60
Non-plantation forest	2.69	10.92	10.99	24.60
Plantation forest	3.36	6.77	11.11	21.24
Vegetated wetland	0.00	0.01	0.03	0.04
High-producing grassland	73.47	163.76	386.83	624.06
Open water	0.49	0.28	0.49	1.26
Barren/other	0.05	0.08	0.09	0.22
Perennial cropland	-	-	-	-
Annual cropland	-	-	-	-
Total (km^2)	83.57	196.14	425.57	705.28

Table 4.2: Reclassified Watershed Properties for Site WA8

Land use/Land cover category	Connected Area to floodplain (km^2)	Connected Area not to floodplain (km^2)	Area not connected (km^2)	Total (km^2)
Shrub/grassland	47.51	294.89	207.40	549.80
Urban	1.93	2.45	17.53	21.91
Non-plantation forest	35.27	174.98	100.38	310.63
Plantation forest	11.78	28.27	50.55	90.60
Vegetated wetland	0.1	0.18	0.58	0.86
High-producing grassland	332.21	756.14	1799.32	2887.67
Open water	6.86	3.34	4.26	14.28
Barren/other	3.75	3.77	3.19	10.71
Perennial cropland	0.07	0.07	0.31	0.45
Annual cropland	1.43	1.19	7.66	10.28
Total (km^2)	440.91	1265.28	2191.18	3897.37

Table 4.3: Reclassified Watershed Properties for Site WA9

Land use/Land cover category	Connected Area to floodplain (km^2)	Connected Area not to floodplain (km^2)	Area not connected (km^2)	Total (km^2)
Shrub/grassland	52.08	319.23	225.73	597.04
Urban	5.30	5.73	39.29	50.32
Non-plantation forest	37.51	181.05	105.76	324.32
Plantation forest	14.09	35.27	60.82	110.18
Vegetated wetland	0.10	0.18	0.58	0,86
High-producing grassland	360.67	792.61	1944.12	3097.40
Open water	8.01	3.82	5.05	16.88
Barren/other	4.22	3.92	3.45	11.59
Perennial cropland	0.08	0.09	0.41	0.58
Annual cropland	1.85	1.70	10.08	13.63
Total (km^2)	483.91	1343.60	2395.29	4222.22

4.2.1 Total Phosphorus (TP)

The TP values (Figure 4.3) for WA7 recorded an increasing trend for the first fifteen years of sampling and reduction for the last ten years during the monitoring period. However, the values recorded all through this period showed exceedance over the trigger values of 33 g/m^3 except for the first and last five years. Besides, the lowest median value measured in the first five years of sampling was initially lower than the trigger value but later increased between 2000 – 2004. For WA8 (Figure 4.3), a similar trend was observed, but a minor difference observed in the first and last five years. The first five years had slightly higher median values than the trigger values, while the last five-year period was less than the trigger values. This difference may be due to non-point source pollution at WA7 (upland river), which flowed to low land rivers (WA8 & WA9) as well as the increase in connected pasture areas connected into the floodplain in WA9 compared to WA7(Table 3.2 and 3.4 respectively). However, this was not the case for WA9. In the beginning and even till 2014, the values of TP recorded was more than the trigger values (Figure 4.3). The higher values of TP recorded all through may result from the accumulation of pollutants as they flow downstream. The seasonality comparison for all sites revealed similar trends for WA7 & WA8 (Figure 4.4). It showed that TP values were higher in the winter than in the summer periods, while the overall median values for both sites were higher than those of the stipulated trigger values. For WA9, that was not the case as summer, winter, and overall median values were higher than the trigger values (Figure 4.4).

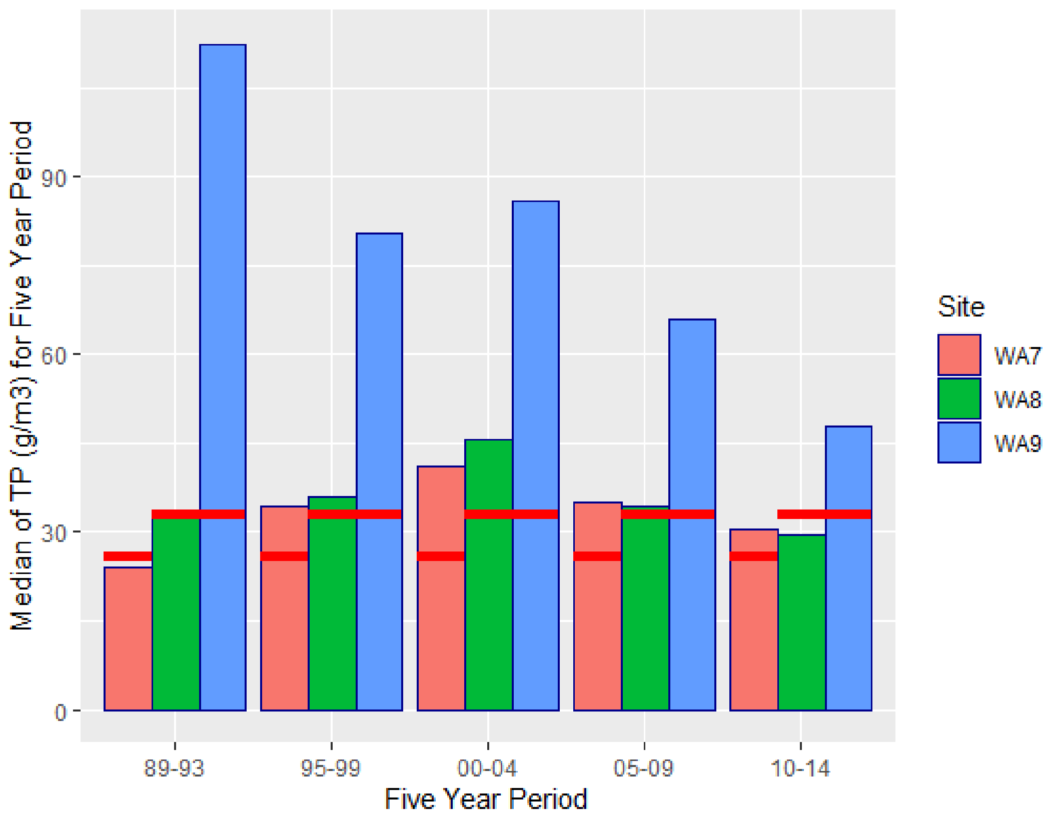


Figure 4.3: Total Phosphorus Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for TP.

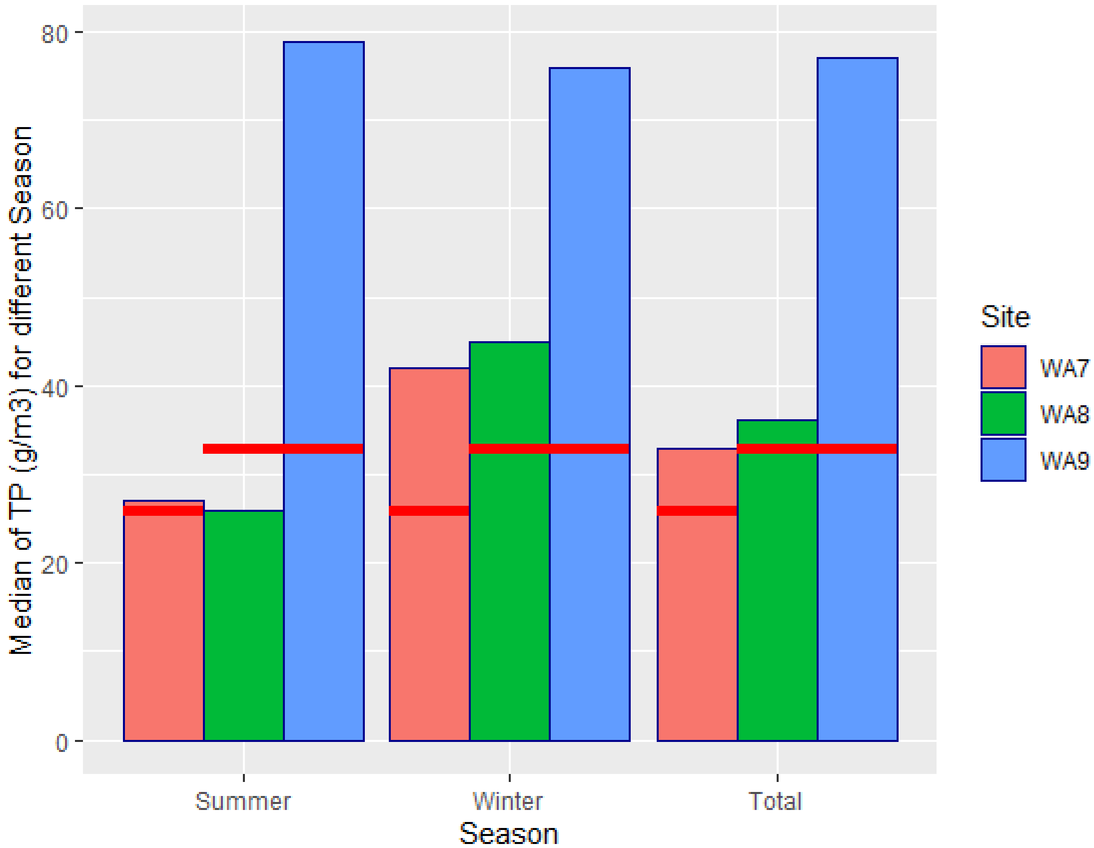


Figure 4.4: Total Phosphorus Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for TP.

4.2.2 Dissolved reactive phosphorus (DRP)

All through the monitoring periods, DRP values were higher than trigger values for WA9, which was 9 g/m^3 (Figure 4.5). Between 1989-1993 and 2005-2009, there was a reduction of DRP lower than the trigger values for WA7 and WA8. These values later increased in 2014 above the trigger values. Seasonality comparison for all site considering showed that seasonal values were higher than trigger values for WA9 (Figure 4.6), while the same was observed for only winter and overall median values for WA7 and WA8.

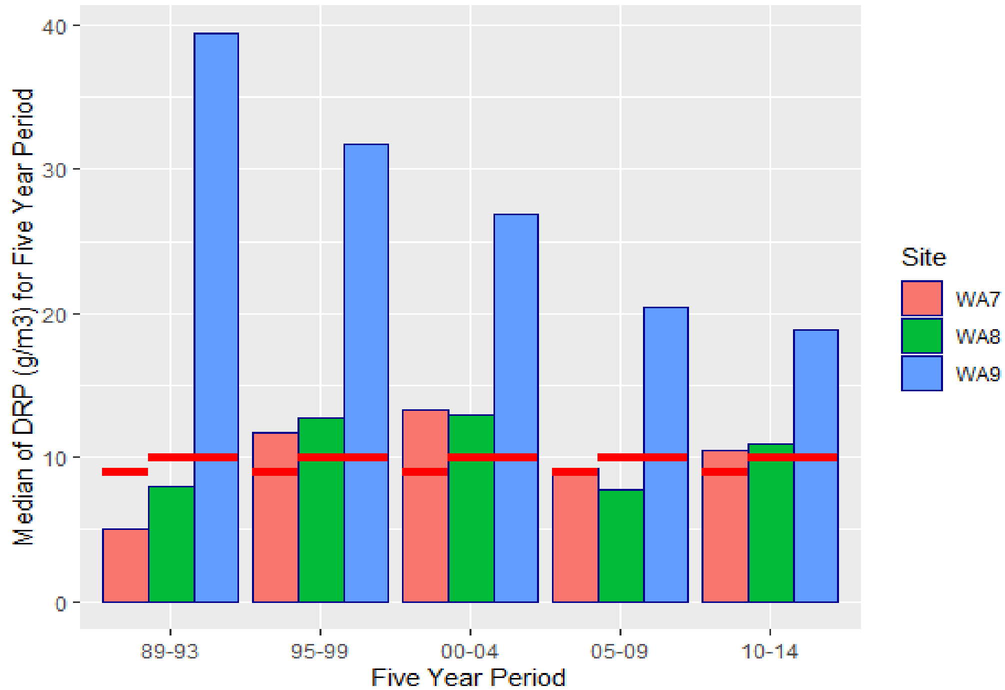


Figure 4.5: DRP Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for DRP

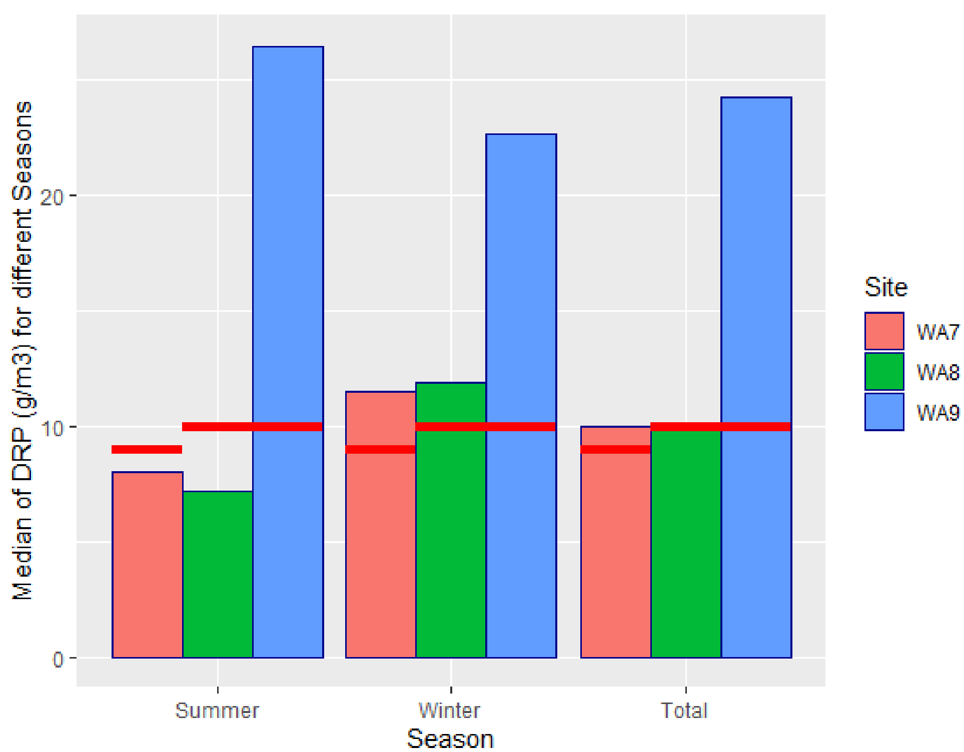


Figure 4.6: DRP Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for DRP.

4.2.3 Total Nitrogen

As for TN, all three sites (WA7, WA8, and WA9) (Figure 4.7) showed a similar distribution pattern with this pattern from the inception of the data. TN values recorded were above trigger values of 295 g/m^3 up till 2014. Interestingly, these values were significantly elevated between 2000-2004. Seasonality across sites revealed that summer, winter, and overall TN values exceeded trigger values for all sites (Figure 4.8).

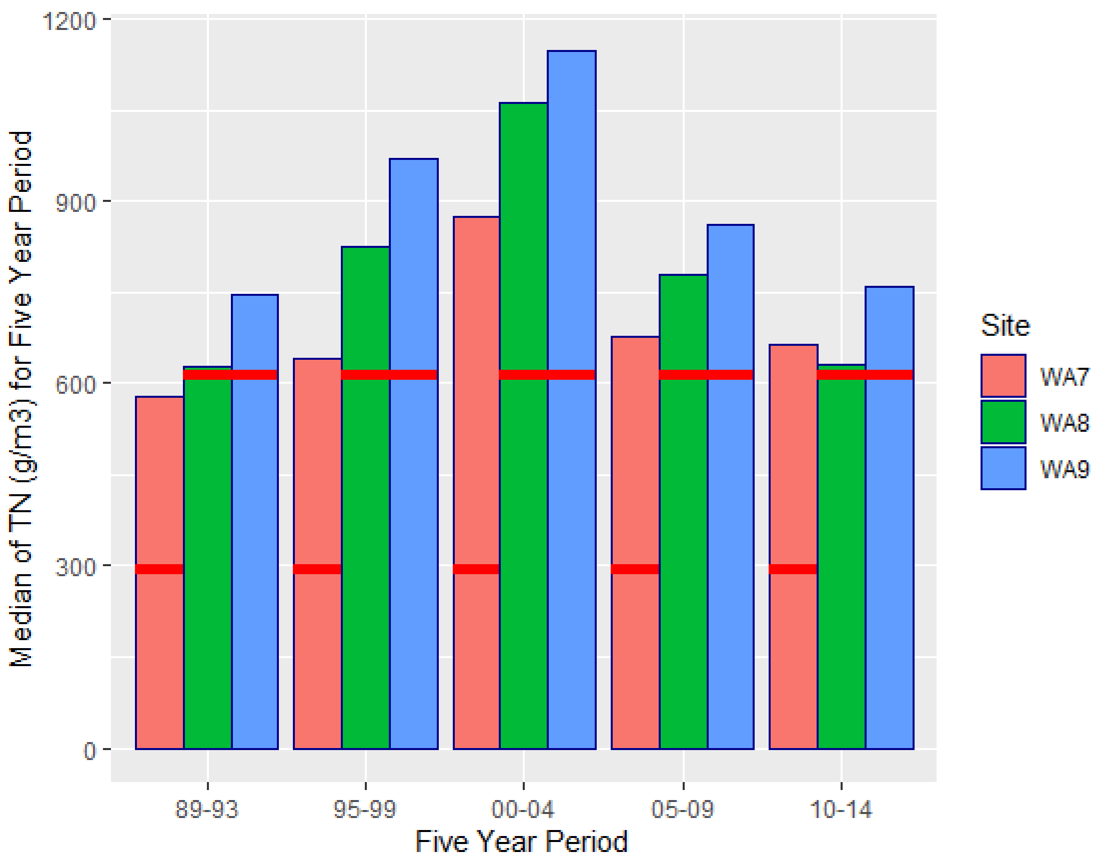


Figure 4.7: Total Nitrogen Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for TN.

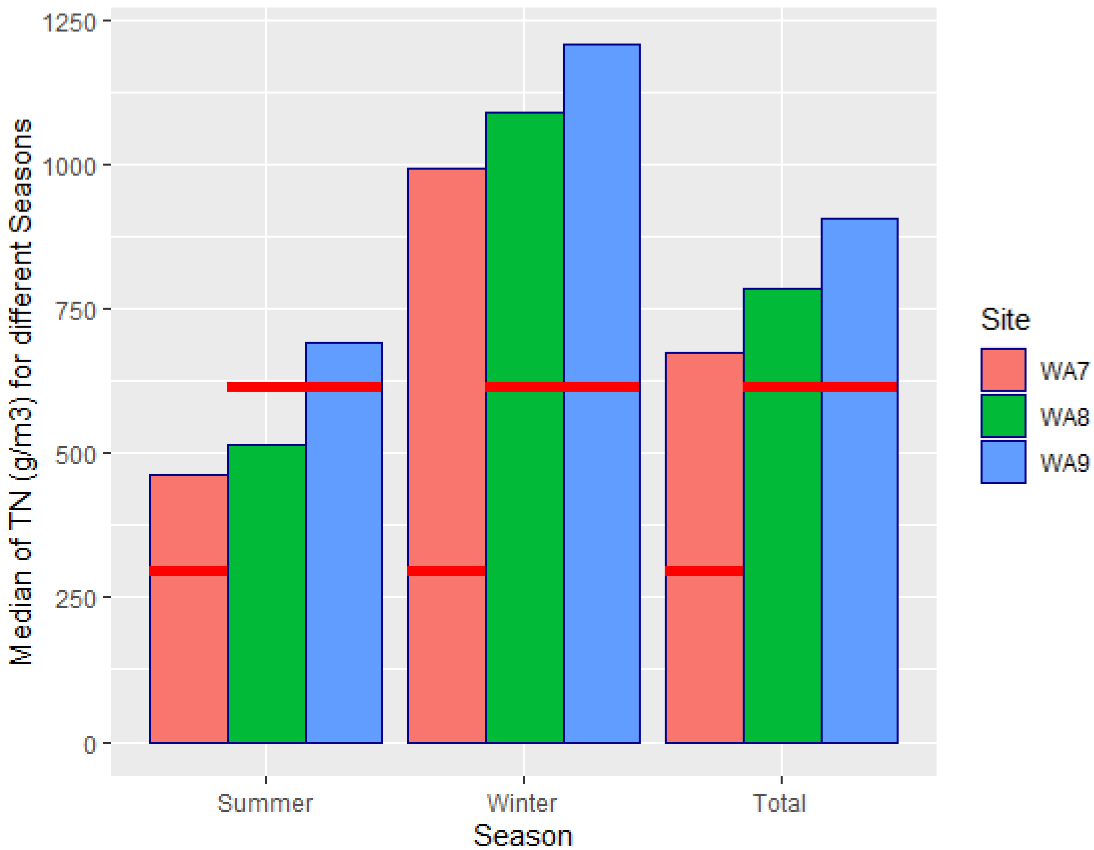


Figure 4.8: Total Nitrogen Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons. *The red lines represent the ANZECC trigger value for TN.

4.2.4 Oxidized Nitrogen (NO_3)

For NO_3, values recorded all through theses period were higher than the trigger values for all three sites (Figure 4.9). The high values above trigger values of 167 g/m^3 were measured during the winter and summer periods (Figure 4.10), indicating the continuous presence of this pollution over the years.

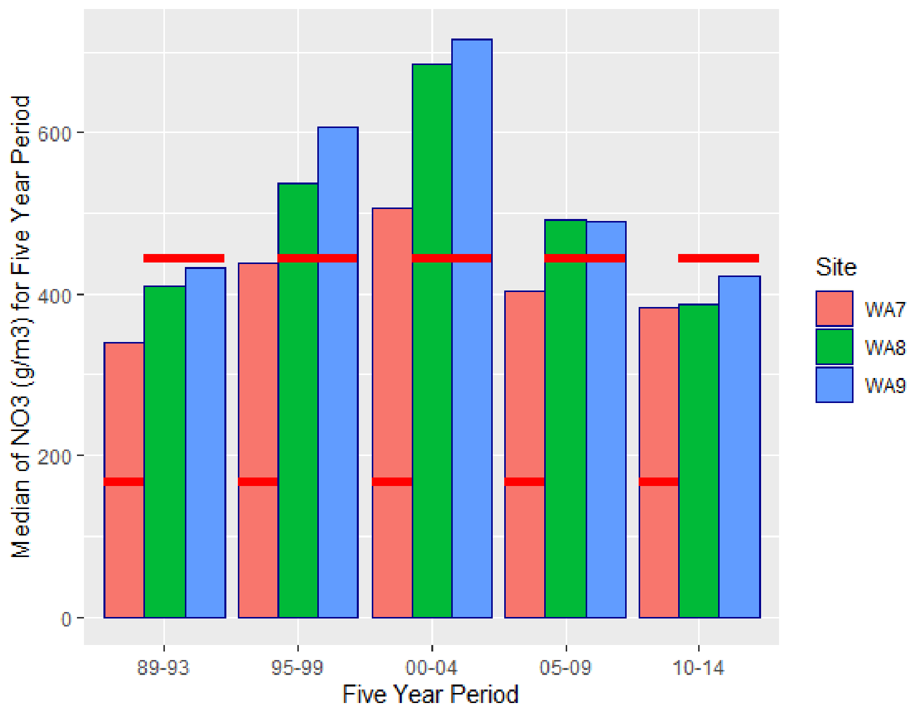


Figure 4.9: NO_3 Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for NO_3.

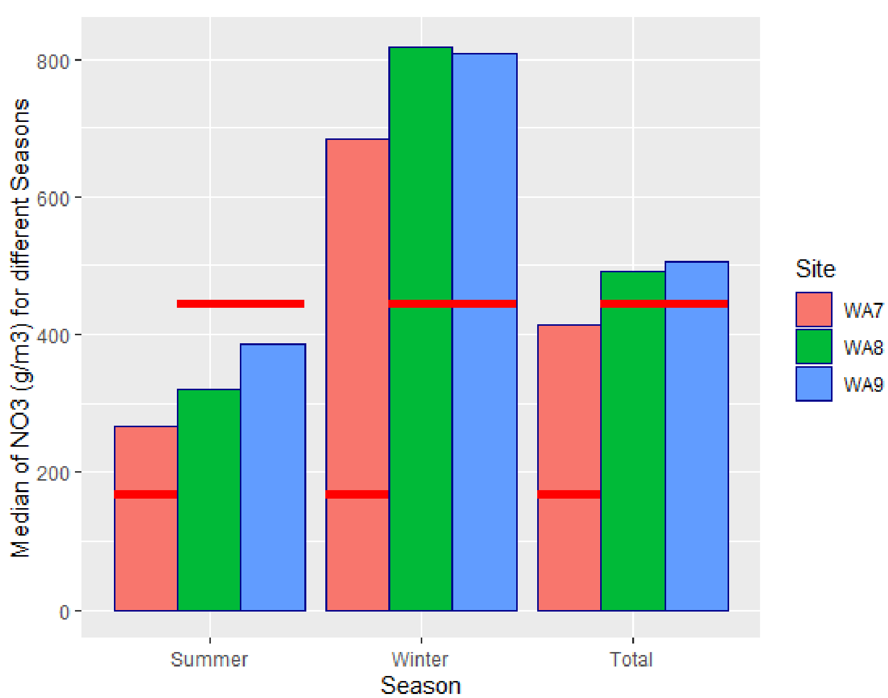


Figure 4.10: NO_3 Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for NO_3

4.2.5 Ammonium (NH_4)

As for NH_4, all the site concentration values monitored for 25 years showed that the trigger values of 10 g/m^3 were exceeded in different amounts (Figure 4.11). Specifically, NH_4 values recorded were much higher in WA9 than the other sites. Seasonality values also showed similar observations with winter, summer, and overall median values exceeding stipulated trigger values (Figure 4.12).

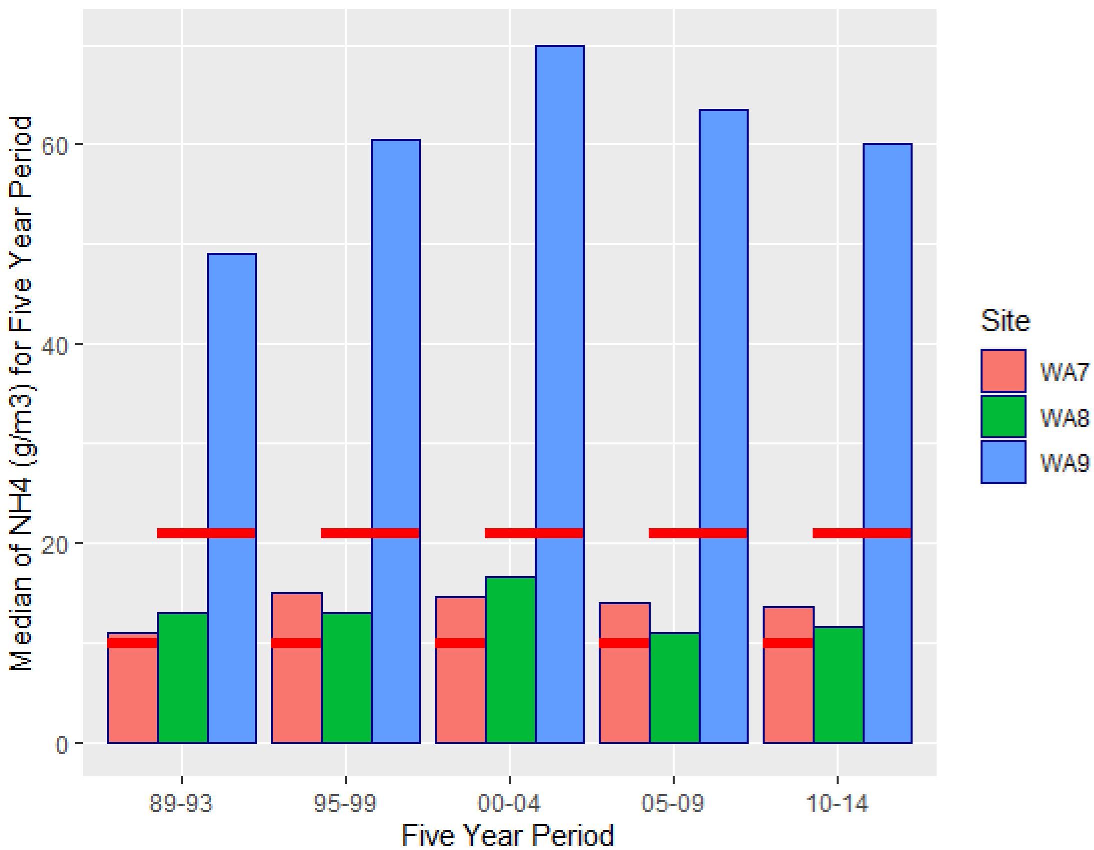


Figure 4.11: Ammonium Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.
*The red lines represent the ANZECC trigger value for NH_4

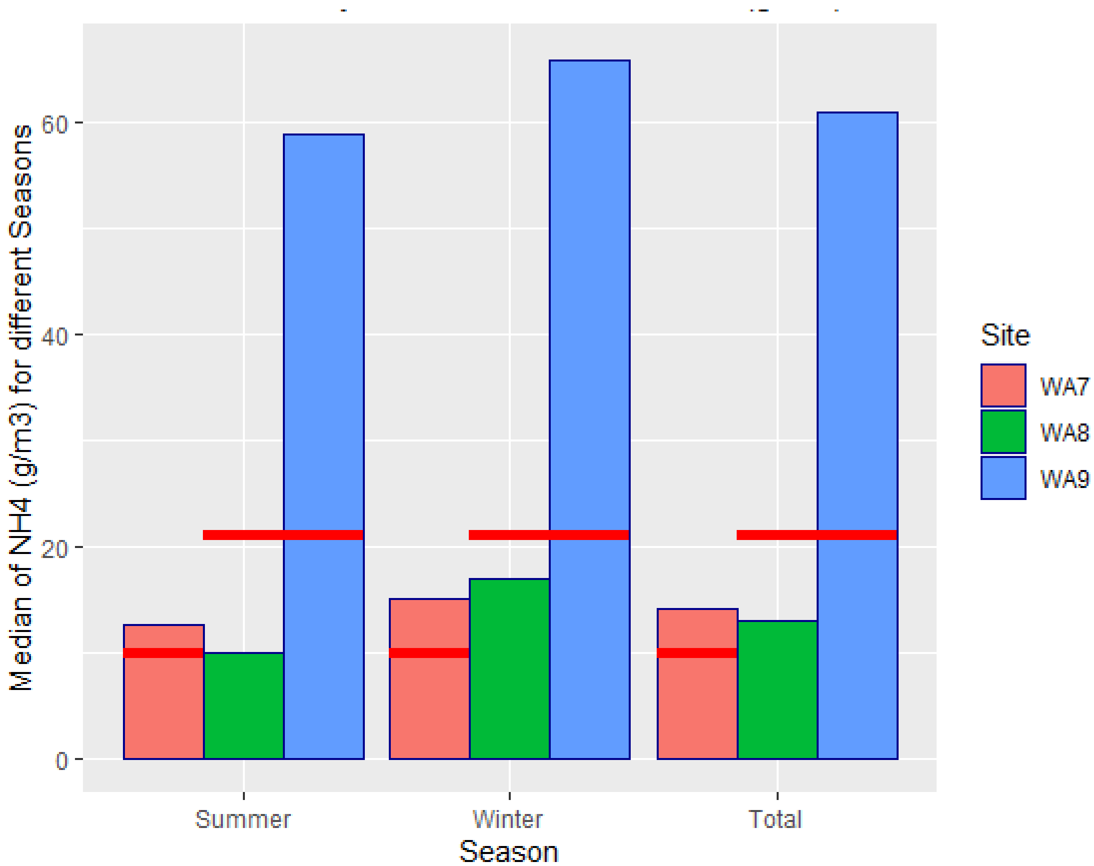


Figure 4.12: Ammonium for a Different Season. The red lines represent the ANZECC trigger value for NH_4

4.2.6 Dissolved oxygen (DO)

For DO, all sites (WA7, WA8, and WA9) had excellent values. All year long data revealed that despite the number of pollutants entering or present in the river, the DO values were significantly above the trigger values of 6 g/m^3 (Figures 4.13). The seasonality comparison also corroborates this. A functional reaeration capacity of the river allows for more oxygen re-introduced when used up owing to the bathymetry of the river (Figures 4.14). Also, observation of DO% revealed that all values measured were above the trigger values of 99 % for the different sites during the study periods (Figure 4.15). The same was observed with median values as seasonality was observed (Figure 4.16).

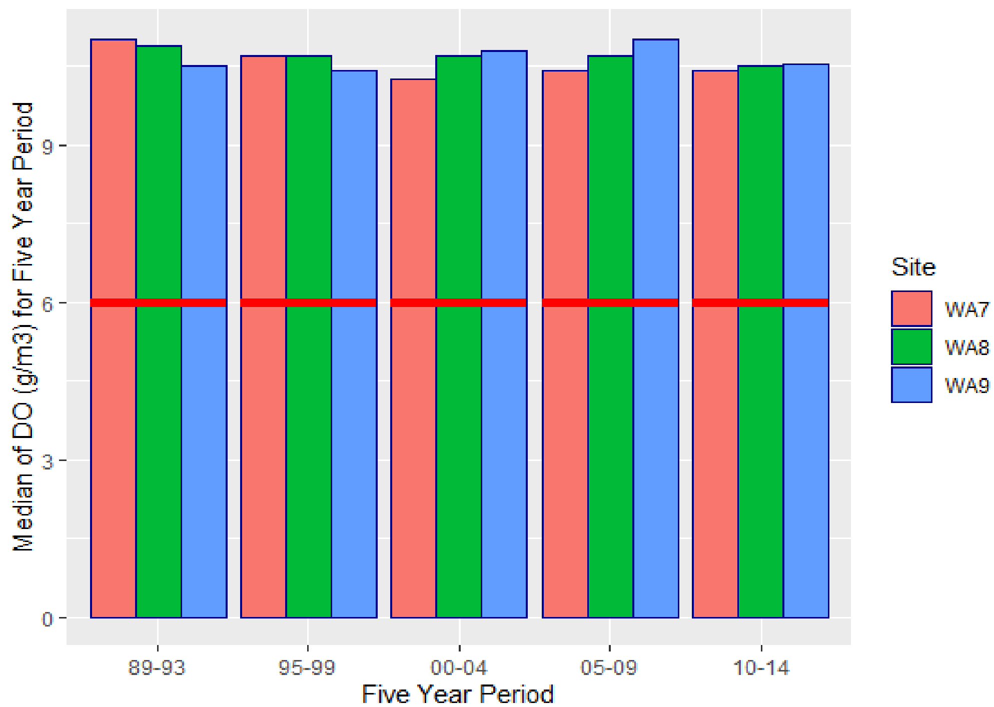


Figure 4.13: DO Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for DO

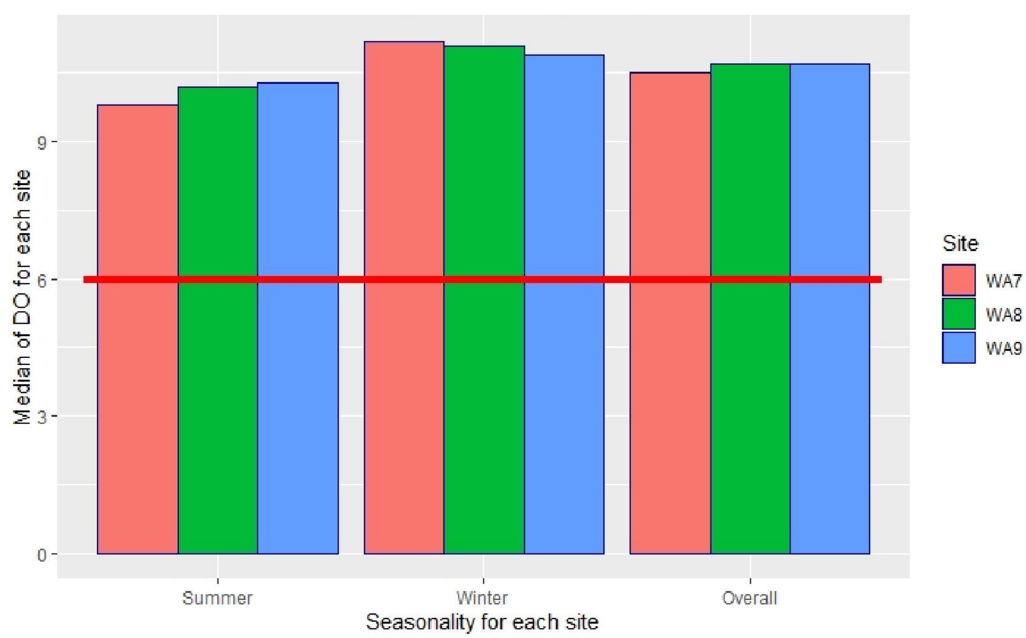


Figure 4.14: DO Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for DO

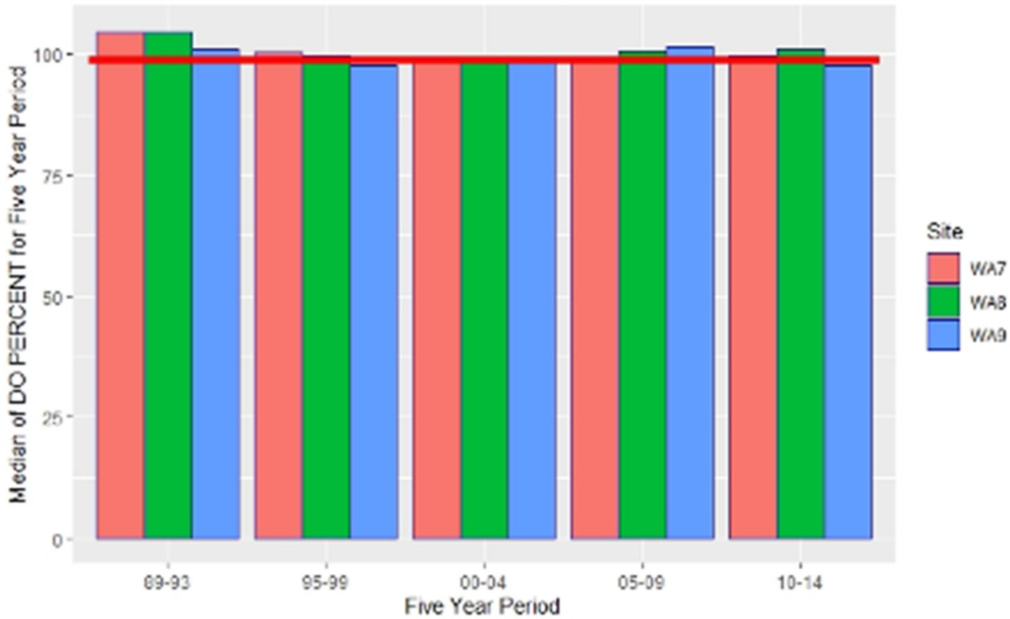


Figure 4.15: Dissolved Oxygen Percent (DO%) Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for DO%

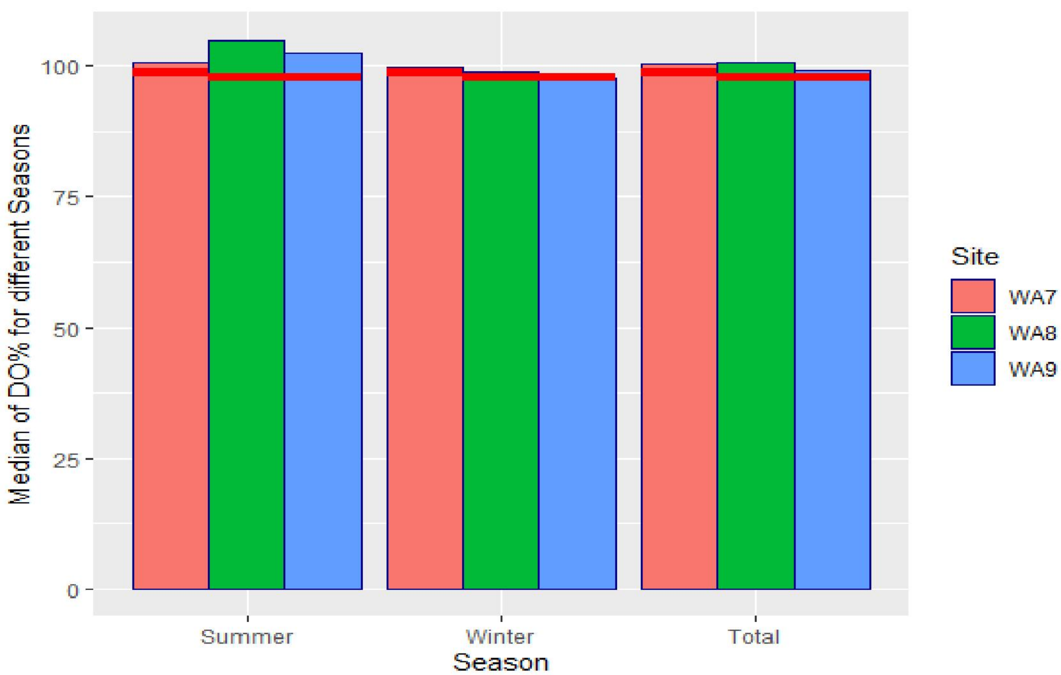


Figure 4.16: Dissolved Oxygen Percent (DO%) Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for DO PERCENT

4.2.7 pH

In the case of pH, it is expected that pH values should not be lower than the stipulated trigger value, which is 7.3. Values recorded for these monitoring periods for the three sites revealed that pH median values were above trigger values (Figure 4.17). The same can be observed considering summer, winter comparison, thus corroborating a significant concern for the presence of high pH values (Figure 4.18).

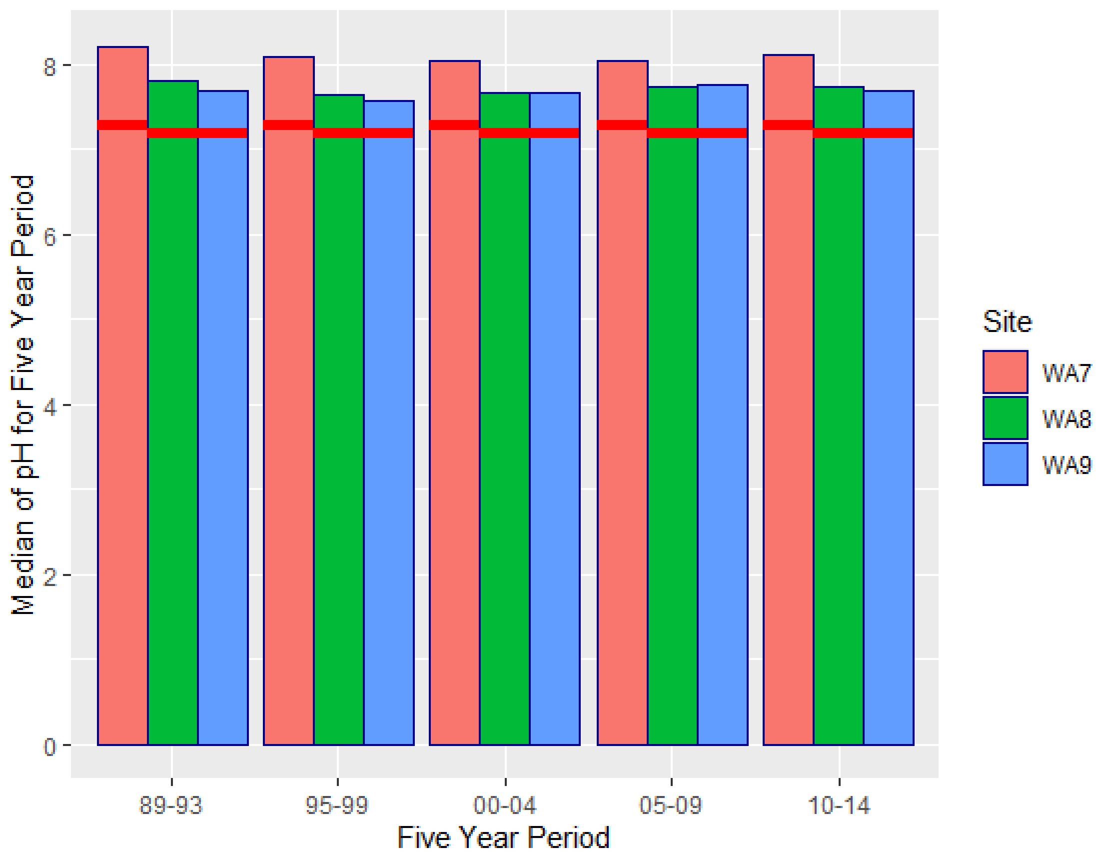


Figure 4.17: pH Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.
*The red lines represent the ANZECC trigger value for pH

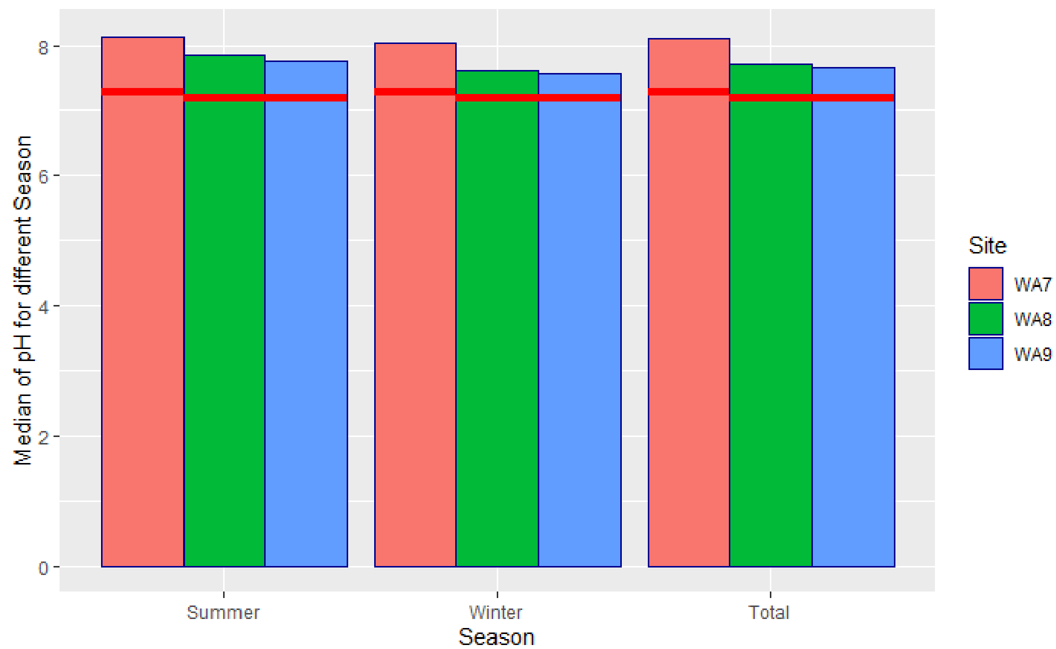


Figure 4.18: pH Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons. *The red lines represent the ANZECC trigger value for pH

4.2.8 Turbidity (TURB)

For turbidity, WA8, and WA9 (Figure 4.19) showed similar trends. Initially, values recorded showed reduced amount below trigger values, but these values since increased over time above trigger value. Nevertheless, in WA7(Figure 4.19), a slightly different pattern occurred. Slightly elevated values were recorded recently, while elevated values were measured between 1994-1999 & 2000-2004 with the highest value recorded between 2000-2004. Seasonality revealed that both overall median and winter values for turbidity exceeded trigger values (Figure 4.20).

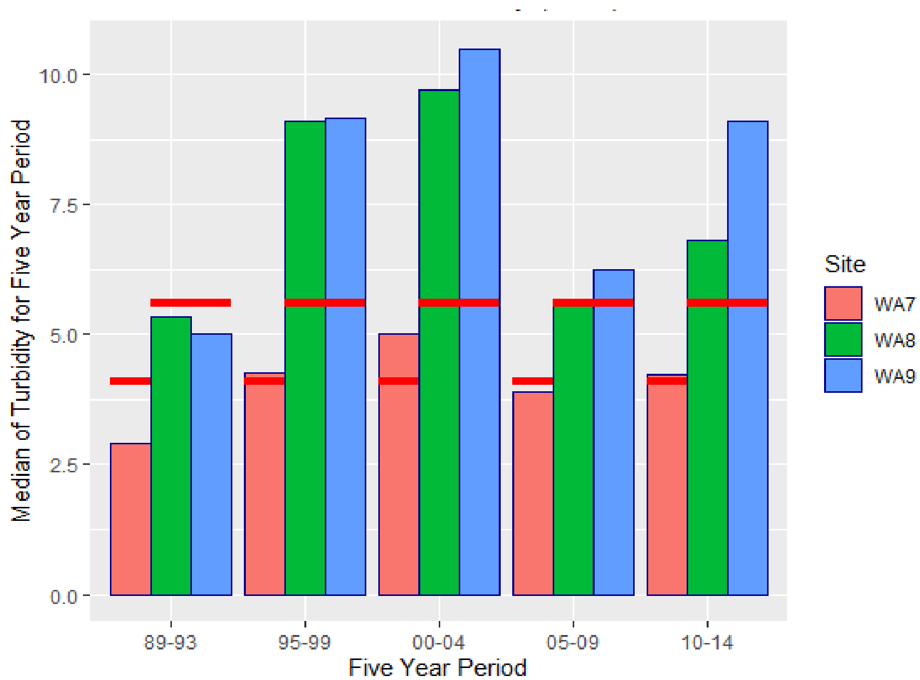


Figure 4.19: Turbidity Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for turbidity

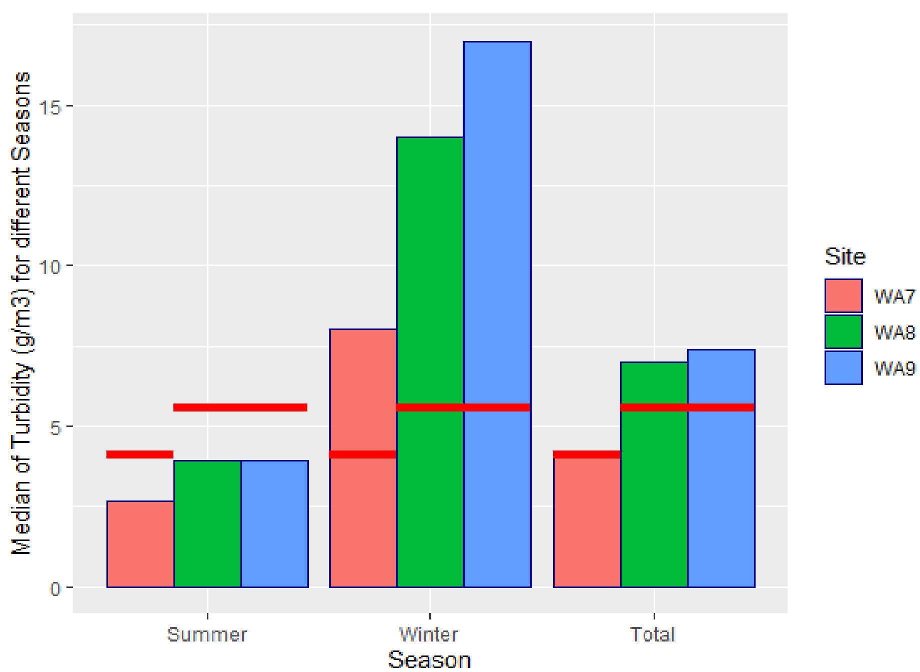


Figure 4.20: Turbidity Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for turbidity

4.2.9 Water Clarity (CLAR)

WA7 had a good water clarity overall compared to WA8 & WA9 (Figure 4.21). Water clarity values measured in WA7 exceeded the expectations of trigger values; whereas, WA8 and WA9 have poor water clarity and are not meeting the expectation, except WA8 in 2010-2014.

The seasonality comparison showed that most of the exceeded values were apparently during the summer periods (Figure 4.22), while winter period had poor water quality for all three sites.

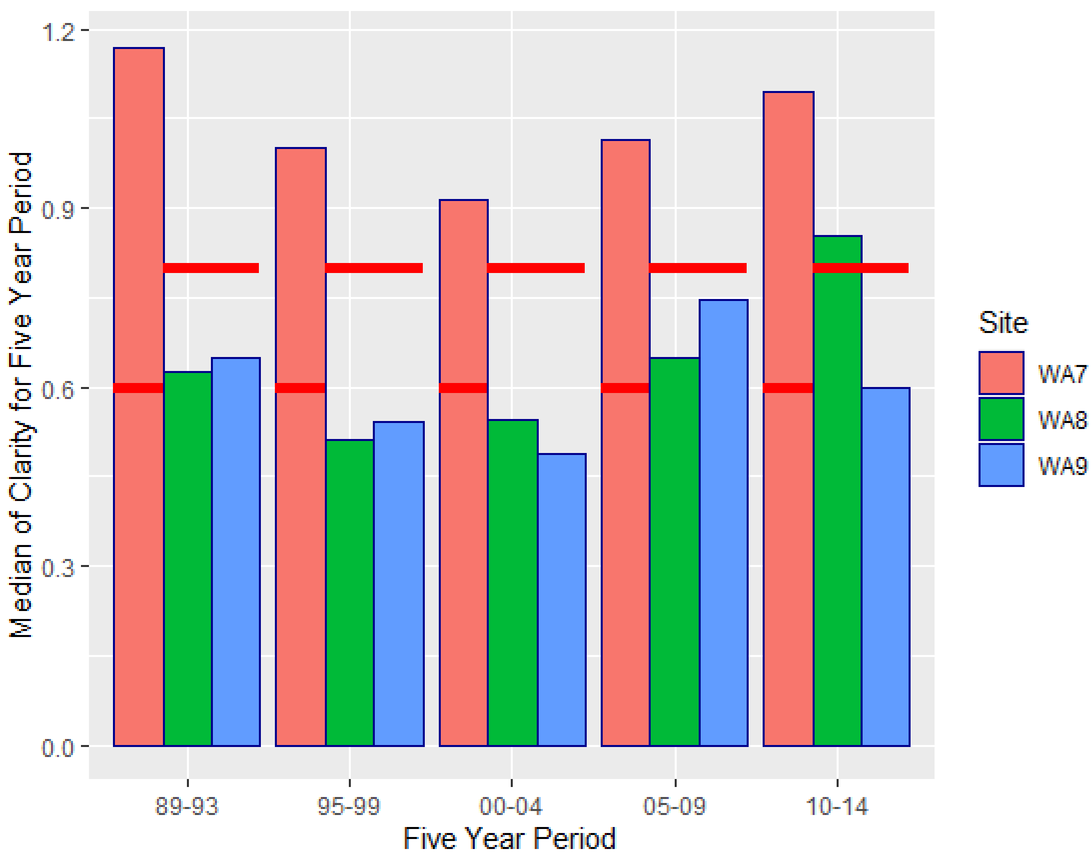


Figure 4.21: Water Clarity Patterns for Manawatu NRWQN Monitoring Sites for 1989-2014.

*The red lines represent the ANZECC trigger value for water clarity

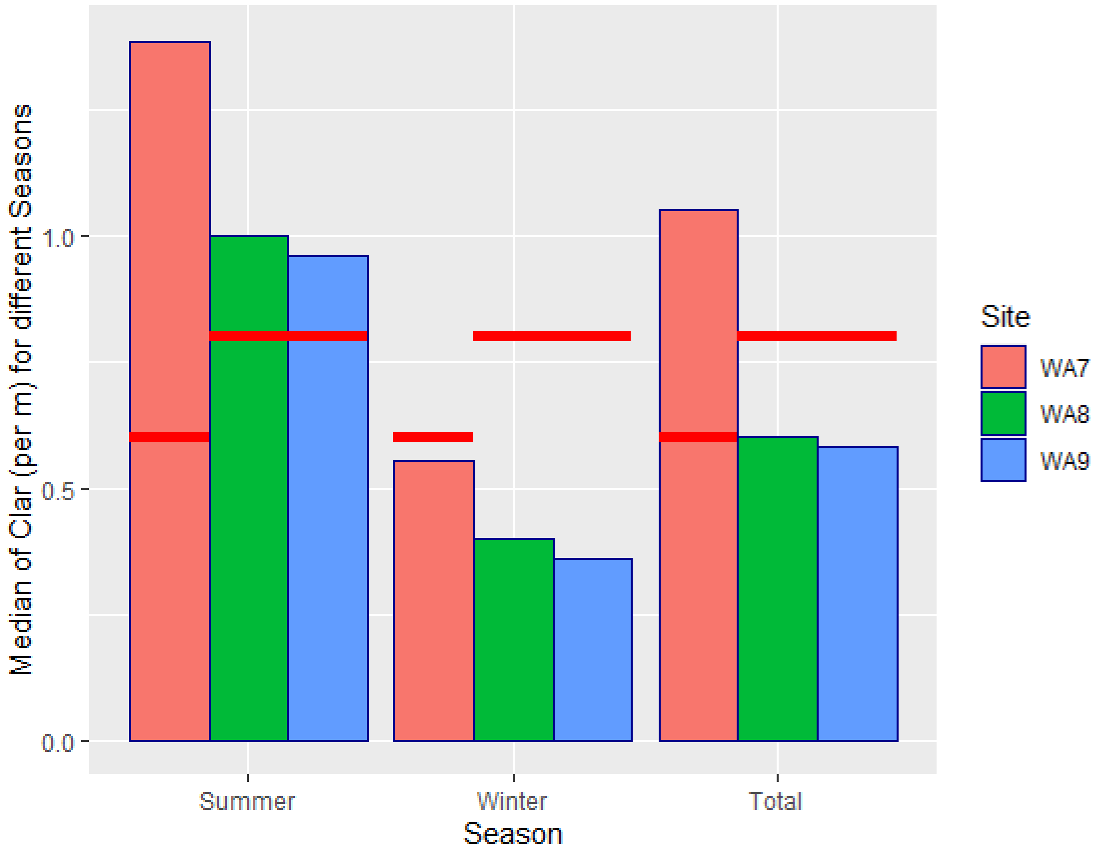


Figure 4.22: Water Clarity Patterns for Manawatu NRWQN Monitoring Sites for Different Seasons.

*The red lines represent the ANZECC trigger value for water clarity

4.3 Summary Statistics and Temporal Changes in Selected Water Quality Variables

To observe the extent and significance of the temporal changes in water quality variables for the Manawatu Catchment, an independent sample test (Kruskal-Wallis) was conducted for the difference in the median across stratified years for each station. Results showed no statistically significant difference except for DRP, pH, and DO% for WA7 (Figures 4.23 to 4.25). Specifically, after conducting the multiple comparison test for DO%, the variability ($p < 0.05$) occurred between 2005-2009 and 1989-1993 (Figure 4.23). In those years, the median values changed significantly from 104.5 to 99. In addition, the similar significant change was observed from between 2000-2004 and 1989-

1993 ($p < 0.05$), 2010 -2014-1989 to 1993 ($p < 0.05$) and 1995-1999 and 1989- 1993 ($p < 0.05$) respectively. More importantly, there was a reduction in DO from 104.55% to the current value of 99.70%, which is within the recommended trigger values.

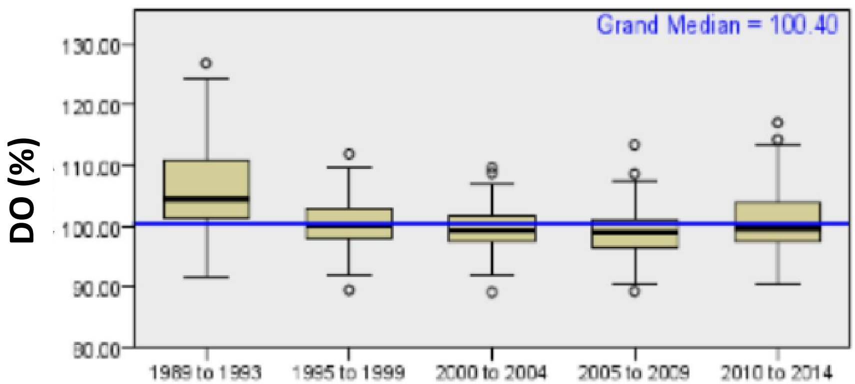


Figure 4.23: DO% Summary Statistics for WA7 Over 5-year Periods.

The pH values overtime showed statistically significant difference ($p < 0.05$) as well (Figure 4.24). The difference was observed to emanate from 2000-2004 and 2010-2014 ($p < 0.05$), 2005-2009 and 1989-1993 ($p < 0.05$) and 1995-1999 and 1989-1993 ($p < 0.05$) and 2010-2014 and 1989-1993 ($p < 0.05$) respectively. The changes in these values between the early and the current values was 8.22 to 8.10 which was within the recommended values for New Zealand rivers.

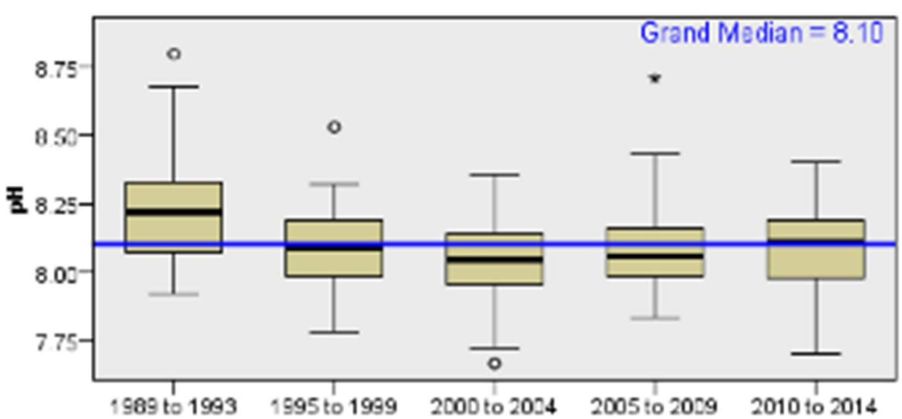


Figure 4.24: pH Summary Statistics for WA7 Sites Over 5-year Periods.

Lastly, for WA7, DRP was another variable that showed statistical significance (Figure 4.25). From the boxplot, it was observed that the major difference was from 1989-1993 and 2010-2014 ($p < 0.05$), 1989-1993 and 1995-1999 ($p < 0.05$) and 1989-1993 and 2000-2004 ($p < 0.05$). The median value changed from 5 to 10.45.

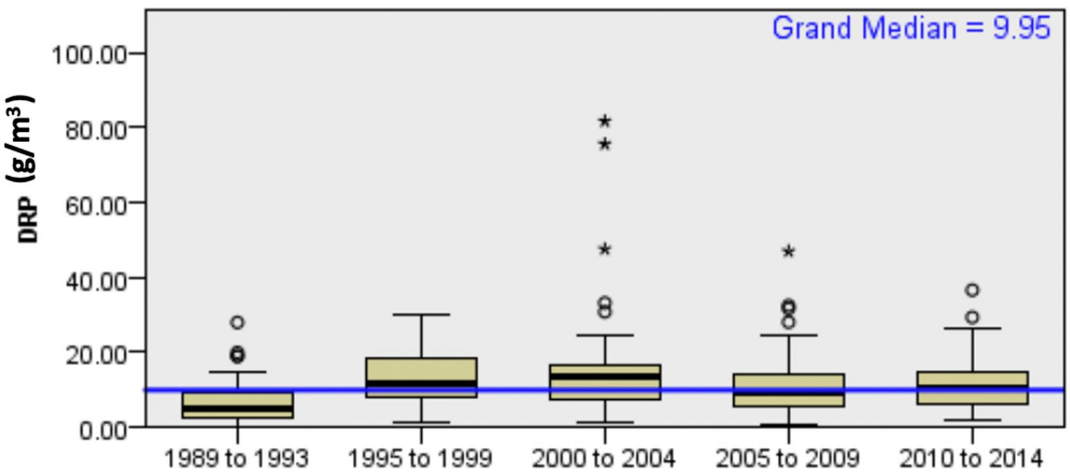


Figure 4.25: DRP Summary Statistics for WA7 Sites Over 5-year Periods.

For WA8, five water quality parameters showed significant differences. These included DO%, pH, NO_3, TN, and DRP. For DO% values in WA8 (Figures 4.26 to 4.31), the difference as observed between 2000-2004 and 1989-1993 ($p < 0.05$) and 1995-1999 and 1989-1993 ($p < 0.05$). The median values recorded at those years were 47.0 g/m^3 to 98.75 g/m^3 and 104.70 g/m^3 to 99.75 g/m^3, respectively (Figure 4.26).

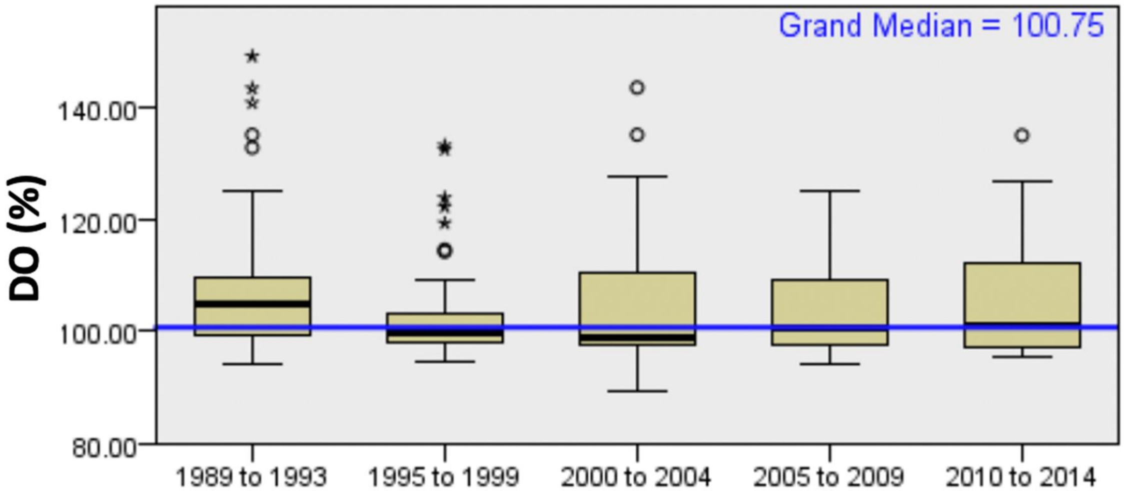


Figure 4.26: DO% Summary Statistics for WA8 Sites Over 5-year Periods.

The pH values also show significant difference with the difference occurring between 1995-1999 and 1989-1993 ($p < 0.05$) and 2000-2004 and 1989-1993 ($p < 0.05$) with median values of 7.64 to 7.82 and 7.64 to 7.63 respectively (Figure 4.27). Notably, these values did not exceed the stipulated values despite the variability.

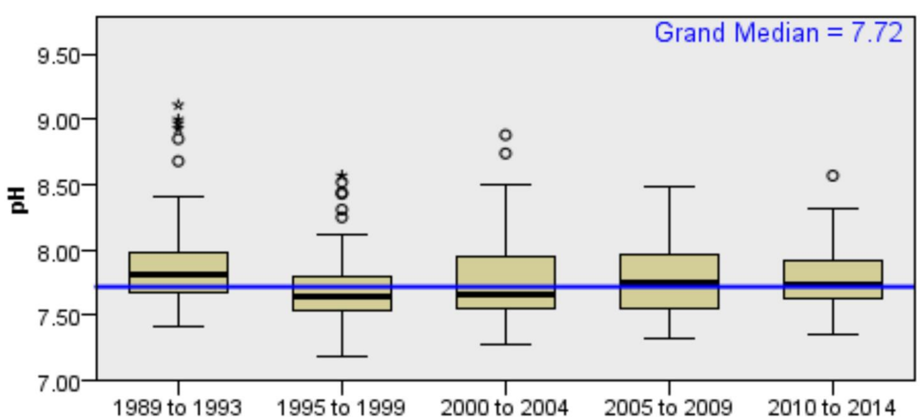


Figure 4.27: pH Summary Statistics for WA8 Sites Over 5-year Periods.

For NO_3, the major contributor to the significant difference measured was from median values recorded between 2010-2014 and 2000-2004 ($p < 0.05$). At these years, median values dropped from 686 g/m^3 to 387.50 g/m^3, which was below the trigger values (Figure 4.28).

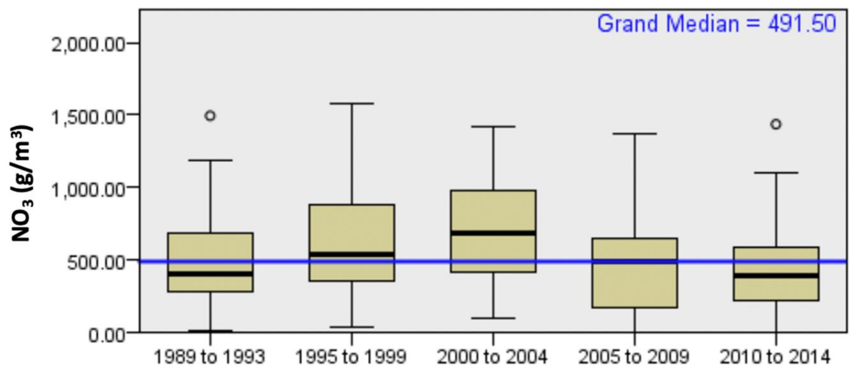


Figure 4.28: NO_3 Summary Statistics for WA8 Sites Over 5-year Periods.

The TN values recorded showed statistical significance across grouped years for WA8 (Figure 4.29). The posthoc multiple comparison test revealed that the difference was from 1989 -- 1993 and 2000 -- 2004 ($p < 0.05$), 2010 -- 2014 and 2000 -- 2004 ($p < 0.05$) and 2005 -- 2009 and 2000 -- 2004 ($p < 0.05$). During these years, the median values changed from 627.5 g/m^3 to 1061.50 g/m^3, 1061.50 g/m^3 to 629.50 g/m^3, 780 g/m^3 to 1,061.50 g/m^3. These values and the difference recorded revealed that irrespective of the reduction from 2004, values were significantly above the trigger value.

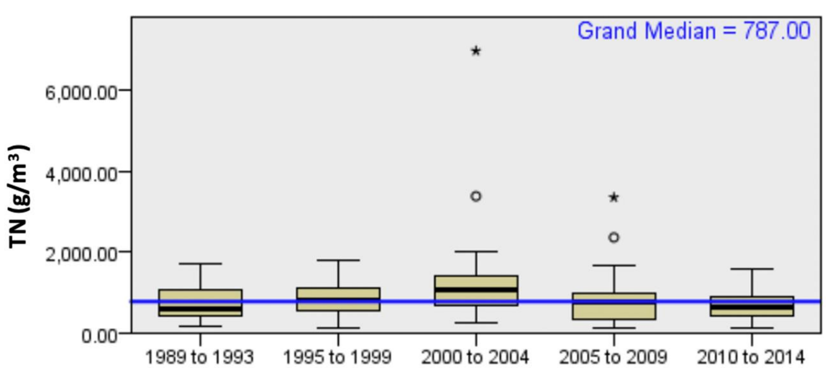


Figure 4.29: TN Summary Statistics for WA8 Sites Over 5-year Periods.

The DRP values revealed statistical differences as well for this site (Figure 4.30). The difference occurring at 2005 -- 2009 and 1995 -- 1999 ($p < 0.05$), 1989 -- 1993 and 1995 -- 1999 ($p < 0.05$), 1989 -- 1993 and 2000 -- 2004 ($p < 0.05$). The reveals that the median values from 1989 did not significantly change in 2014 (8 – 10.9 g/m^3).

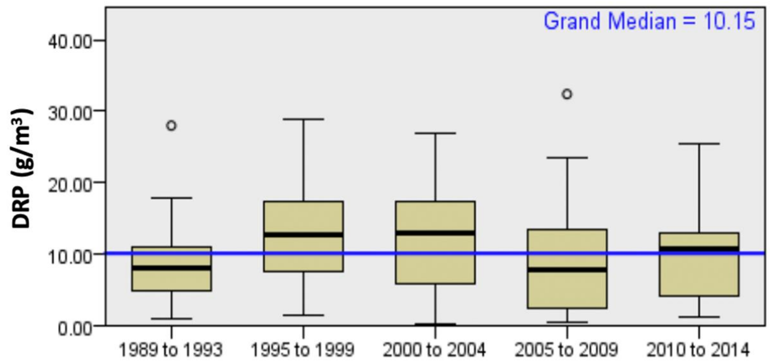


Figure 4.30: DRP Summary Statistics for WA8 Sites Over 5-year Periods for 25 years

The result from the WA9 site showed DO%, DO ppm, pH, NO3, TN, DRP, and TP showed a statistical significance difference (Figures 4.31 to 4.34). However, the posthoc test was not significant for DO% ($p = 0.11$) and DO ppm ($p = 0.031$), probably due to almost the pairwise comparison testing. For pH, the statistical difference measured was between 1995 -- 1999 and 2005 -- 2009 ($p < 0.05$), having median values of 7.58 to 7.76 (Figure 4.31).

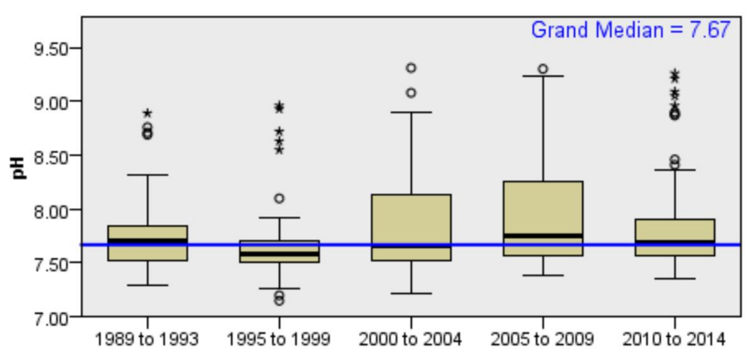


Figure 4.31: pH Summary Statistics for WA9 Sites Over 5-year Periods

For NO_3, the statistical difference were observed from 2010 -- 2014 and 1995 -- 1999 ($p < 0.05$), 2010 -- 2014 and 2000 -- 2004 ($p < 0.05$), 1989 -- 1993 and 2000 -- 2004 ($p < 0.05$), and 2005 -- 2009 and 2000 -- 2004 ($p < 0.05$). The values during the periods were 421 g/m^3 to 606 g/m^3, 421 g/m^3 to 716.50 g/m^3, 432.50 g/m^3 to 716.50 g/m^3 and 432 g/m^3 to 716.50 g/m^3 respectively (Figure 4.32).

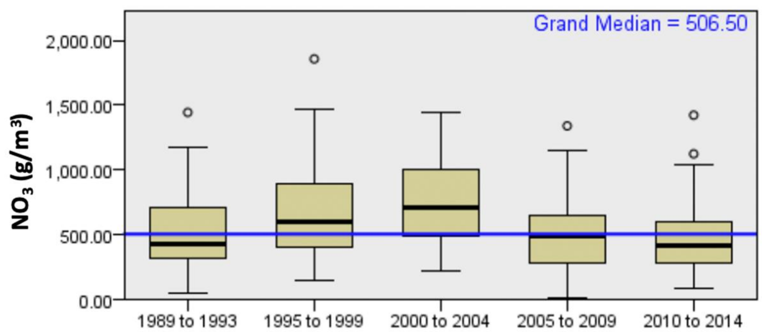


Figure 4.32: NO_3 Summary Statistics for WA9 Sites Over 5-year Periods

Similarly, TN observed showed statistical significance with the difference noticeable during 2010 -- 2014 and 2000 – 2004 ($p < 0.05$) and 2005 -- 2009 and 2000 -- 2004 with median values at 758.50 g/m^3 to 1,149.50 g/m^3 and from 863 g/m^3 to 1,49.50 g/m^3. These values recorded implies that there is no statistical difference between the earliest and current TN values (Figure 4.33).

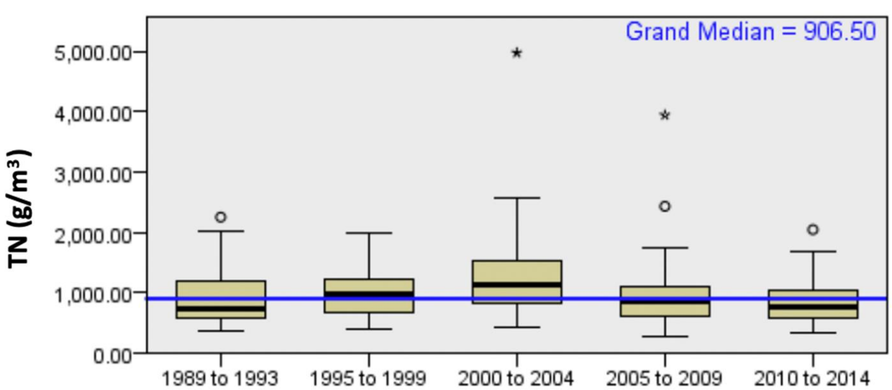


Figure 4.33: TN Summary Statistics for WA9 Sites Over 5-year Periods

DRP values recorded showed statistical significance, with the difference predominant within 2010-2014 and 2000-2004 ($p < 0.05$), 2010-2014 and 1995-1999 ($p < 0.05$), 2010–2014 and 1989-1993 ($p < 0.05$), 2005-2009 and 2000-2004 ($p < 0.05$), 2005-2009 and 1995-1999 ($p < 0.05$), 2005-2009 and 1989-1993 ($p < 0.05$), and 2000-2004 and 1989 -1993 ($p < 0.05$). Importantly noting, current trend values revealed that DRP values recorded a decrease from 39.80 g/m^3 to 18.80 g/m^3 which is slightly above 2-fold reduction yet values higher than the trigger values indicating a water resource concern.

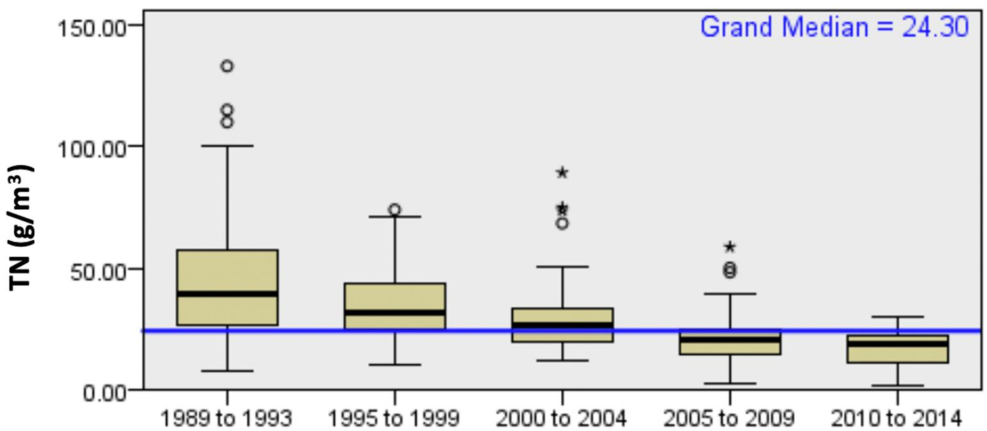


Figure 4.34: DRP Summary Statistics for WA9 Sites Over 5-year Periods

4.4 Correlation Matrix for the Different Sites

A correlation matrix is a technique generally used to identify relationships among a set of variables. A significant relationship reveals a potential pattern over time between variables, while a non-significant relationship indicates that linear relationships are not likely. To eliminate subjectivity among variables, this study adopted two significant values (α= 0.05 and 0.01). There were several relationships significant at both the 95% and 99% confidence interval, even though many seemed weak. To reduce the number of relationships observed, only spearman correlation values of (r) $\geq$ 0.75 were reported (Table 4.4). WA7, situated at the upstream of the Manawatu River, revealed that flow had a strong-positive and significant association with nutrient pollutants (NO_3, TN, and TP at 1% level). Turbidity had a strong but negative correlation with other physical parameters such as clarity and EC at a 1% level. This relationship suggests that nutrients are introduced into the river from the surrounding land, through runoff or mass weathering and are likely to remain undisturbed. Clarity showed an inverse relationship with TN, TP, and turbidity, but the reverse was the EC case. This relationship suggests that the prolonged influx of pollutants into the river can obstruct river water clarity. Turbidity showed a strong and positive correlation with TP & TN. Generally, soil matter has been reported as the sink for pollutants on land and finds its way in rivers and streams through sediments. Therefore, this study agrees with other findings that suggest a significantly high affinity between phosphorus and sediments. Also, a strong positive relationship was observed between DRP & TP as well as TN and NO3, suggesting that the pairs emanate from the same non-point sources. At the same time, DO reduce at elevated temperature by the observed relationship between them. For site WA8 (Table 4.5), DO% showed a positive and robust correlation with pH and negative correlation with turbidity and TP at a 1% level of significance. Flow showed a consistent relationship with TP & TN, EC, turbidity, and clarity, as reported from the WA7 site.

Again, clarity was inversely correlated with Turbidity and TP but proportional in relationship with EC. DO% showed strong negative relationships with turbidity & TP but positively correlated with pH. For the downstream (WA9), the site showed a few strong statistical relationships based on the research cut-off points (Table 4.6). Turbidity increased with the flow, while EC and clarity decreased at high flow conditions. Similarly, Turbidity increase was associated with a decrease in clarity and EC to suggest that elevated measurement of EC is likely to be from metallic salts instead of organic pollutants. It revealed that NH_4 and TN entered the river from the same point as they showed strong positive statistically significant relationships at the 1% level.

Table 4.4: Spearman's Correlation Coefficient for Site WA7

	Temp	DO%	DOppm	Flow	Clar	Turb	pH	EC	NH4	NO3	TN	DRP	TP	Abs
Temp	1.000													
DO%	0.103	1.000												
DOppm	**-.868**	**.344**	1.000											
Flow	**-.568**	**-.331**	**.359**	1.000										
Clar	**.395**	**.412**	**-.156**	**-.854**	1.000									
Turb	**-.425**	**-.413**	**.189**	**.867**	**-.923**	1.000								
pH	**.390**	**.621**	-0.064	**-.637**	**.639**	**-.634**	1.000							
EC	**.414**	**.126**	**-.321**	**-.784**	**.754**	**-.726**	**.483**	1.000						
NH4	0.062	**-.408**	**-.232**	**.324**	**-.447**	**.407**	**-.373**	**-.236**	1.000					
NO3	**-.643**	**-.246**	**.467**	**.758**	**-.622**	**.617**	**-.620**	**-.500**	**.296**	1.000				
TN	**-.595**	**-.347**	**.379**	**.855**	**-.756**	**.753**	**-.654**	**-.605**	**.419**	**.918**	1.000			
DRP	**-.205**	**-.402**	0.002	**.590**	**-.630**	**.660**	**-.572**	**-.621**	**.435**	**.448**	**.564**	1.000		
TP	**-.291**	**-.497**	0.028	**.758**	**-.841**	**.864**	**-.666**	**-.675**	**.473**	**.524**	**.679**	**.799**	1.000	.
Abs	**-.282**	**-.235**	**.135***	**.733**	**-.720**	**.729**	**-.468**	**-.643**	**.317**	**.472**	**.615**	**.584**	**.704**	1.000

bold and underline Correlation Coefficient Significant at a Magnitude of 0.01 and bold Correlation Coefficient both at 0.05 (both at 2-tailed)

Table 4.5: Spearman's Correlation Coefficient for Site WA8

	Temp	**DO%**	**DOppm**	**Flow**	**Clar**	**Turb**	**pH**	**EC**	**NH4**	**NO3**	**TN**	**DRP**	**TP**	**Abs**
Temp	1.000													
DO%	**.487**	1.000												
DOppm	**-.589**	**.306**	1.000											
Flow	**-.608**	**-.732**	0.001	1.000										
Clar	**.478**	**.743**	**.134**	**-.887**	1.000									
Turb	**-.521**	**-.761**	**-.118**	**.898**	**-.974**	1.000								
pH	**.511**	**.790**	**.156**	**-.744**	**.692**	**-.717**	1.000							
EC	**.376**	**.640**	**.151**	**-.796**	**.791**	**-.797**	**.664**	1.000						
NH4	**-.399**	**-.621**	-0.081	**.670**	**-.700**	**.682**	**-.607**	**-.527**	1.000					
NO3	**-.679**	**-.515**	**.236**	**.591**	**-.437**	**.455**	**-.576**	**-.233**	**.455**	1.000				
TN	**-.672**	**-.659**	**.126**	**.791**	**-.680**	**.693**	**-.679**	**-.453**	**.632**	**.869**	1.000			
DRP	**-.469**	**-.702**	**-.136**	**.686**	**-.701**	**.719**	**-.639**	**-.603**	**.679**	**.533**	**.661**	1.000		
TP	**-.480**	**-.764**	**-.166**	**.865**	**-.952**	**.954**	**-.703**	**-.755**	**.711**	**.449**	**.692**	**.787**	1.000	
Abs	**-.166**	-0.041	0.111	0.058	-0.069	0.089	-0.064	0.004	0.055	**.157**	**.138***	**.123***	0.1	1.000

bold and underline Correlation Coefficient Significant at a Magnitude of 0.01 and bold Correlation Coefficient both at 0.05 (both at 2-tailed)

Table 4.6: Spearman's Correlation Coefficient for Site WA9

	Temp	DO%	DOppm	Flow	Clar	Turb	pH	EC	NH4	NO3	TN	DRP	TP	Abs
Temp	1.000													
DO%	**.421**	1.000												
DOppm	**-.257**	**.618**	1.000											
Flow	**-.603**	**-.672**	**-.253**	1.000										
Clar	**.486**	**.714**	**.362**	**-.877**	1.000									
Turb	**-.530**	**-.726**	**-.344**	**.879**	**-.952**	1.000								
pH	**.487**	**.828**	**.493**	**-.720**	**.703**	**-.710**	1.000							
EC	**.401**	**.627**	**.351**	**-.780**	**.783**	**-.802**	**.659**	1.000						
NH4	**-.158**	**-.195**	**-.245**	-0.014	-0.038	0.089	**-.212**	0.009	1.000					
NO3	**-.654**	**-.432**	-0.01	**.528**	**-.378**	**.391**	**-.545**	**-.162**	**.213**	1.000				
TN	**-.665**	**-.561**	-0.097	**.708**	**-.613**	**.624**	**-.633**	**-.352**	**.218**	**.860**	1.000			
DRP	0.112	-0.074	**-.284**	-0.095	0.013	-0.06	-0.028	0.071	**.130**[*]	0.029	0.031	1.000		
TP	**-.182**	**-.451**	**-.348**	**.559**	**-.691**	**.645**	**-.410**	**-.492**	-0.032	0.089	**.388**	**.447**	1.000	
Abs	**-.168**	-0.085	0.049	**.134**	-0.066	0.088	-0.036	-0.054	0.028	**.218**	**.218**	-0.061	-0.019	1.000

[bold and underline] Correlation Coefficient Significant at a Magnitude of 0.01 and [bold] Correlation Coefficient both at 0.05 (both at 2-taile

4.5 Application of PCA in Source Identification of Water Quality Variables

Before the PCA/FA analysis, the Bartlett test for sample adequacy was determined, and the result revealed sample adequacy of 0.848, 0.868, and 0.697 at a significance level of <0.001 for WA7, WA8, and WA9 respectively (Table 4.7). Furthermore, conducting PCA/FA required that all the data sets was normalized. Normalization is to ensure unbiased extraction, followed by wrong hypotheses or assumptions that are introduced from different variable units, which is unavoidable in water quality data. To this end, this study implemented the center-log-ratio (Clr) transformation (Blake *et al*., 2016), which was originally developed by Aitcluson (1986). PCA is a widely used statistical process implored to shrink large dataset into several factors assumed to be the cause of variability in a system. According to Jaiswal *et al*., (2019), it re-aligns a group of datasets such that new matrices formed revealed the maximum variability in a system, without alteration to the basic information in the dataset (Jankowska *et al*., 2017). After applying the above methods, sites WA7, WA8, and WA9 produced four, four, and six principal components (PCs) (Table 4.8), which explained 88%, 93%, and 96% variabilities, respectively. Specifically, WA7 had PC 1, PC 2, PC 3, and PC 4 explaining 56.8%, 16.7%, 9.6%, and 5.4% of the variability with significantly high loadings in Turbidity, EC, TP and Abs in PC1. Also, PC 2 accounted for high loading in NO3 and TN, while PC 3 and PC 4 accounted for high loadings NH_4 and DRP, respectively. Communality values (i.e. proportion of common variance) showed the extent to which each component accounted for each variable and reported in Table 4.9. The values showed that the variabilities of each variable were well captured with values greater than 0.8, implying that only 20% or less for each variable were left unexplained. For WA8, this study initially selected five components, same as the number of components extracted from the EPA–PMF Model for that site but had none of the variables in the fifth component having a loading of ≥ ± 0.75 cut-off criterion for reporting dominance.

Therefore, four components were selected to circumvent this, and it explained 89.1% of the variance. For WA8, PC 1, PC 2, PC 3 and PC 4 explained 59.2%, 15.1%, 9.1% and 5.62% respectively. The communalities for each variable reported in Table 4.6 were over 85% except for DRP (75%). PC 1 accounted for the presence of turbidity, EC, TP, and Abs. PC 2 identified NO3 and TN, while PC 3 and PC 4 identified high loadings for NH4 and DO. For site WA9, six components were extracted and explained 95.7% of the variability. PC 1, PC 2, PC 3, PC 4, PC 5 and PC 6 explained 45%, 18%, 14.5%, 9.3%, 5.5% and 3.6% respectively with communalities of over 90% apart from Abs (85%). PC 1 showed high positive loadings for turbidity, absorbance, and high negative loadings with EC. The negative loadings implied that most of the variable (EC) were below the mean values. In this case, the -ve sign is ignored and concentrates on the loadings. For PC 2, positive loadings were observed for NO3 and TN, while PC 3, PC 4, PC 5, and PC 6 identified strong loadings for TP, DRP, NH4, and DO.

Table 4.7: Kaiser-Meyer-Olkin (KMO) and Bartlett's Test

Site		WA7	WA8	WA9
KMO	The measure of sampling adequacy	0.848	0.868	0.697
	Sig.	0.000	0.000	0.000

Table 4.8: Principal Component Extraction for Three Sites after Varimax Rotation and Kaiser Normalization

	WA7				WA8				WA9					
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC5	PC6
DO	-.120	.569-	-.695	-.188	-.114	.067	-.059	**.982**	-.240	-.066	-.086	-.233	-.197	**.915**
Turb	**.887**	.267	.187	.146	**.831**	.294	.378	-.056	**.784**	.319	.450	-.087	.057	-.115
Abs	**.844**	.248	.092	-.185	**.861**	.264	.233	-.087	**.826**	.169	.340	.022	-.011	-.142
EC	**-.847**	-.206	.099	.068	**-.909**	-.130	-.019	.086	**-.962**	-.023	-.013	-.017	-.034	**.123**
NH4	.305	.288	**.831**	.149	.347	.295	**.854**	-.081	.024	.212	.018	.068	**.959**	-.171
NO3	.203	**.923**	.048	.194	.102	**.952**	.081	.105	.055	**.966**	-.070	.068	.147	-.085
TN	.504	**.785**	.125	**.844**	.371	**.797**	.333	.078	.281	**.859**	.348	.031	.138	.007
DRP	.444	.199	.169	.223	.483	.640	.252	-.201	-.018	.069	.125	**.965**	.067	-.196
TP	**.857**	.155	.269	.180	**.808**	.236	.407	-.087	.496	.117	**.793**	.250	.014	-.103

Bold Values Represent Selected Contributory Parameters of Concern

Table 4.9: Communalities for the Various Sites Based on Principal Component Extraction

Parameter	Initial	Extraction (WA7)	Extraction (WA8)	Extraction (WA9)
DO_ppm	1.00	0.86	0.98	0.99
TURB	1.00	0.92	0.92	0.94
EC	1.00	0.80	0.85	0.94
NH4	1.00	0.87	0.94	0.99
NO3	1.00	0.92	0.93	0.97
TN	1.00	0.92	0.89	0.96
DRP	1.00	0.98	0.75	0.99
TP	1.00	0.88	0.88	0.96
Abs	1.00	0.81	0.87	0.85

4.6 Source Identification using Positive Matrix Factorization Method

To interpret pollution sources, the PMF method was conducted using EPA.PMF 5.0 software package. The receptor modeling technique was carried out according to the required output expected from a combination of Base Model Displacement, Base Model Bootstrapping, and Base Model BS-DISP methods, respectively described (EPA, 2014). These techniques were conducted by try and error, usually by selecting several factors in sequence and ensuring all modeling conditions were met with minimum error and optimal R^2 selected manually. Figures 4.35 to 4.37 shows the result from the extraction and modeling process called the factor profile measured as a percentage (small red boxes). Four factors were generated for site WA7 (Figure 4.35) which included DRP (100%), NH4 (79.1%), Absorbance (45.3%) for factor 1, TN (59.3%) and NO3 (84%) for Factor 2, Turbidity (83.9%) and TP (58.9%) for factor 3 while DO (59.2%) and EC (73.1%) were observed in factor 4. For WA8 (Figure 4.36), factor 1 was dominated by NH4 (85.6%), factor 2 identified DRP (78.8%) and Absorbance (36.1%), factor 3 had EC (72.7%) and DO (62.1%), factor 4 had NO3 (73.5%) and TN (48.9%), and factor 5 identified Turbidity (84.2%). Finally, for WA9 (Figure 4.37), six factors were extracted. Factor 1 identified NH4 (86.6%), factor 2 DO (61.4%) and Absorbance (42.4%), factor 3 DRP (80.4%), factor 4 had Turbidity (85.5%) and TP (39.4%), factor 5 showed NO3 (75.4%) and TN (46.4%) while factor 6 revealed TP (32.2%).

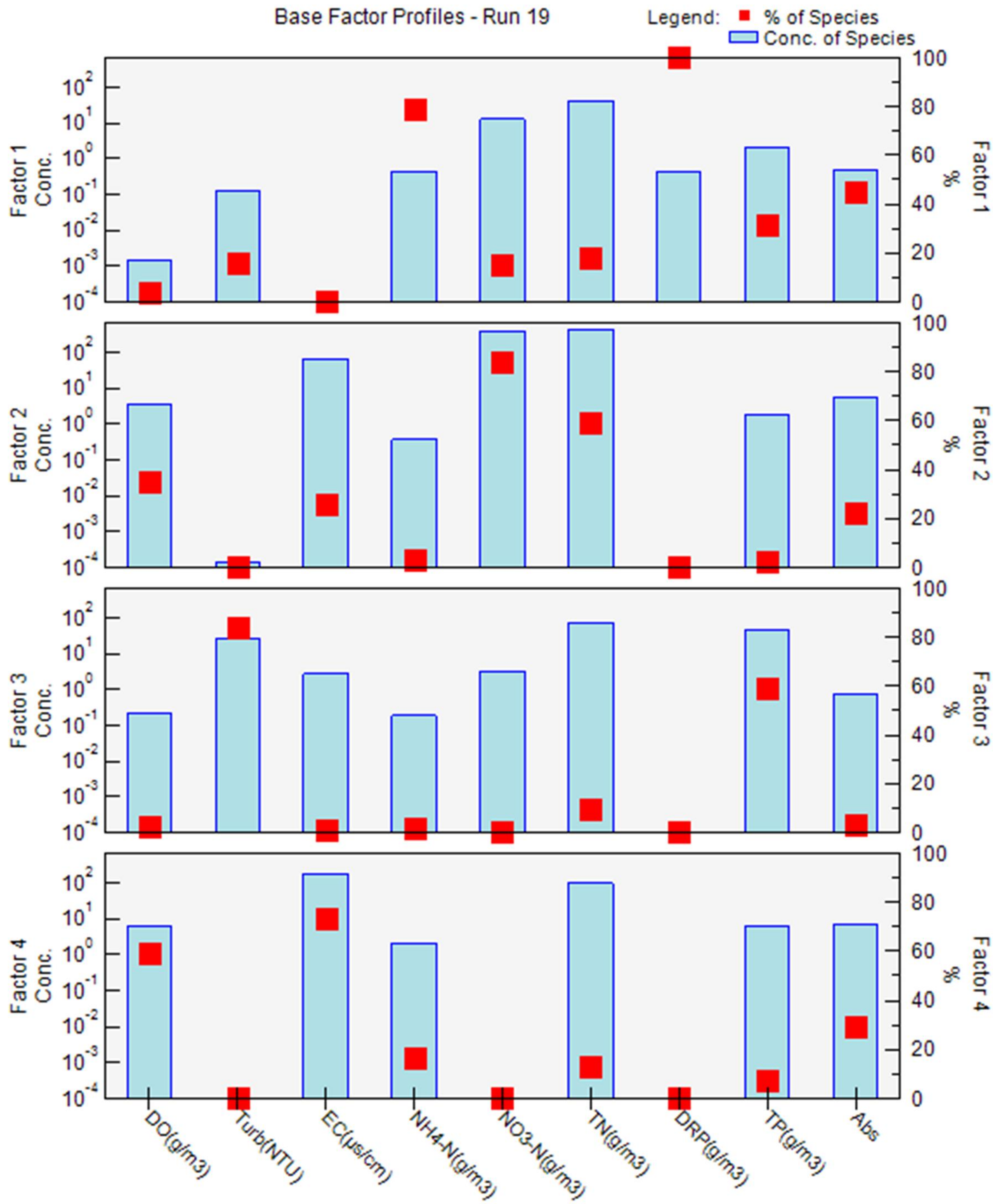


Figure 4.35: Profile Concentrations for WA7 Sites Using PMF

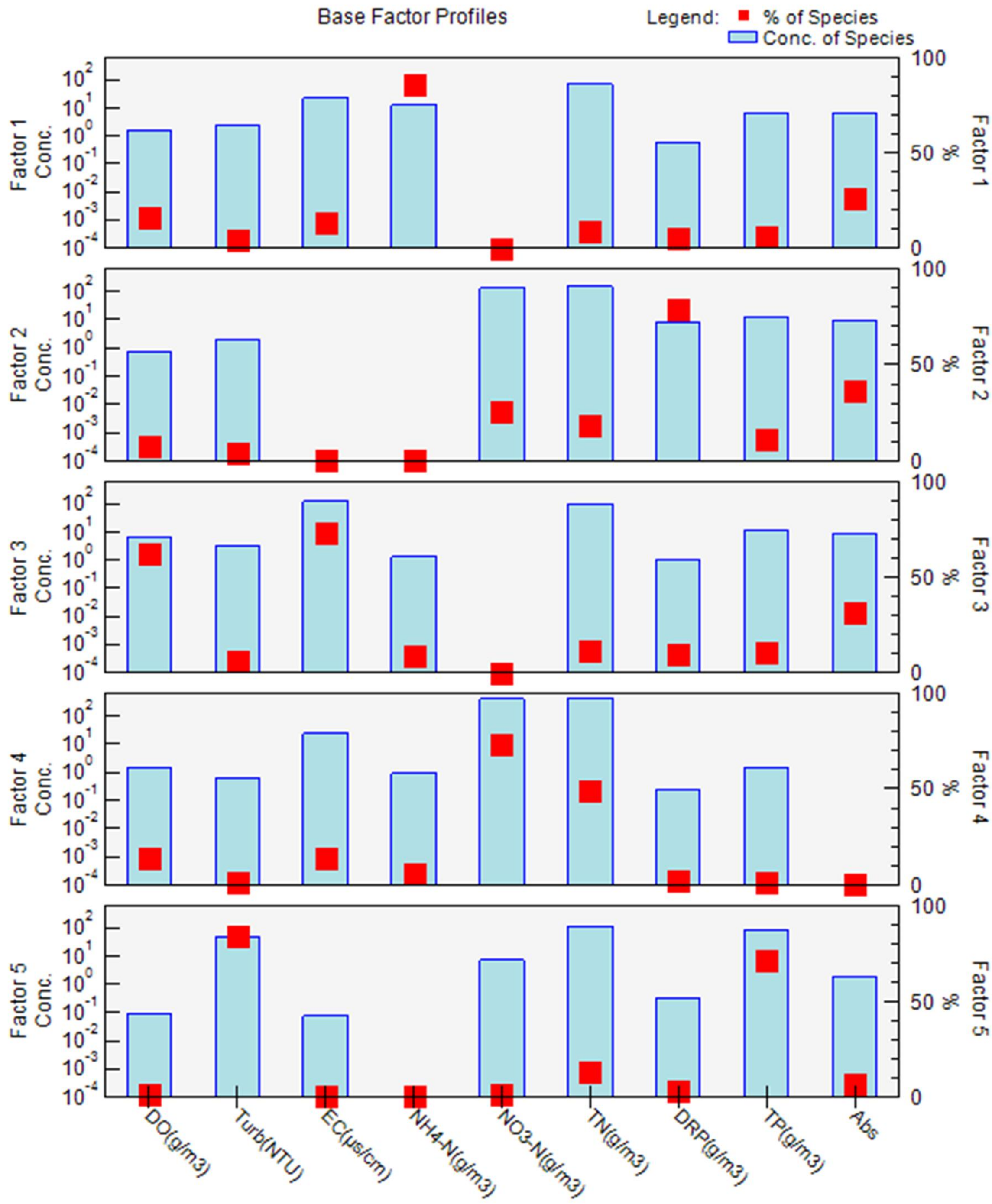


Figure 4.36: Profile Concentrations for WA8 Sites Using PMF

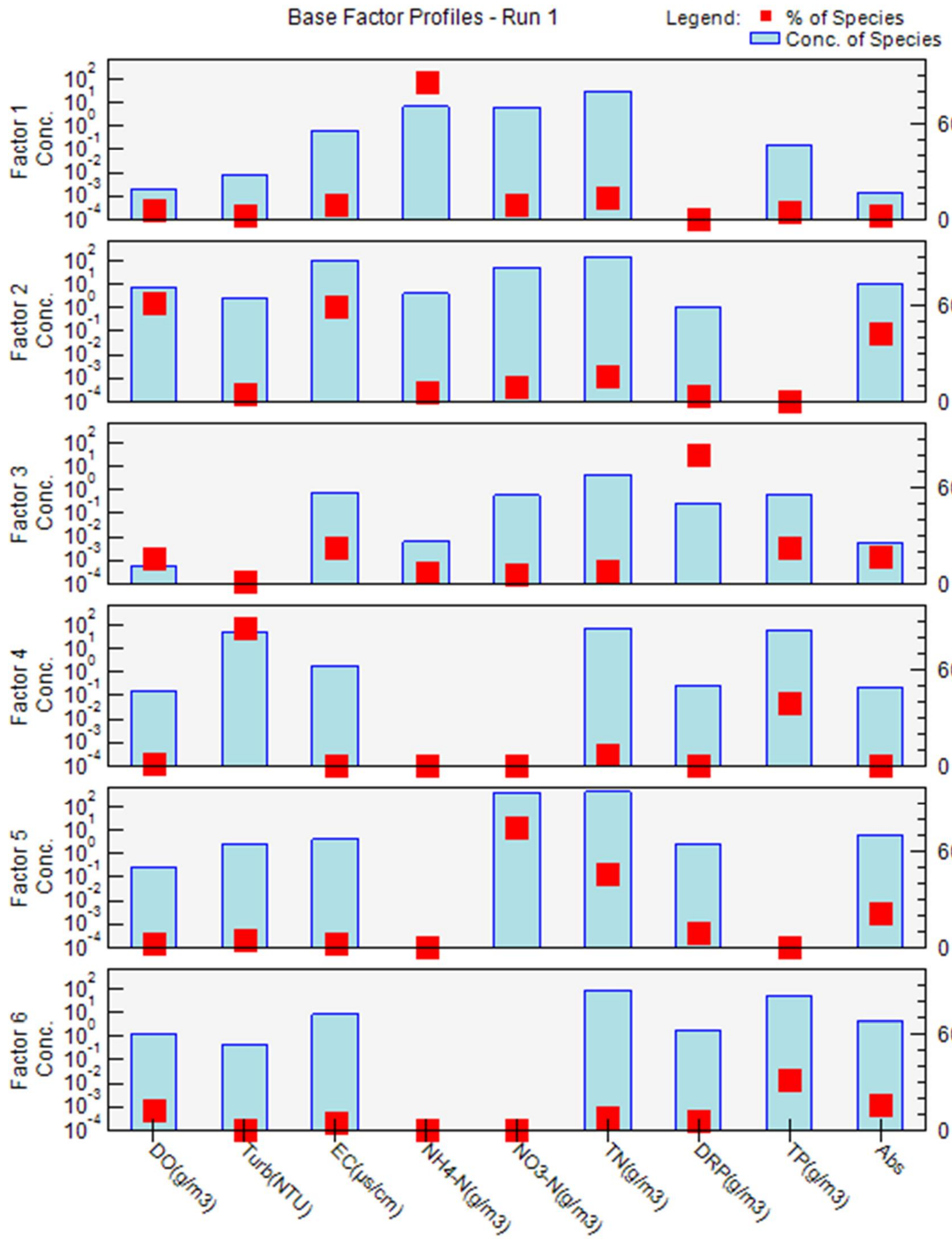


Figure 4.37: Profile Concentrations for WA9 Sites Using PMF

4.7 Model Performance of PMF for Manawatu Watershed

The model output from PMF modelling for the pollutants measured at different sites are shown in Appendices A-C. The Figures (Appendices A-C) extracted from the PMF model generally showed very good performance in modelling the trends and explaining the variability of each variable. The R^2 produced showed that with the exception of DO, NH4 and Abs, other variables were well predicted for WA7 in the order DO (0.15) <Abs (0.45) < NH4 (0.62) < EC (0.76) < DRP (0.84)< Turbidity (0.96) < TP (0.98) < TN (0.98) < NO3 (0.99). For WA8, R^2 values for each variable was in the order: DO (0.23) < Absorbance (0.54) < EC (0.84) < TP (0.94) < DRP (0.99) < NO_3-N (0.99) < NH_4-N (0.99) < TN (0.98) < Turbidity (0.93). For WA9 site, R^2 values were in the order Abs (0.05) < DO (0.78) < EC (0.80) < TN (0.97) < TP (0.98) < Turbidity (0.98) < DRP (0.99) < NO_3-N (0.99) < NH_4-N (0.99).

5. DISCUSSION

5.1 Land Connectivity and Effects on Water Quality

The rivers within the Manawatu catchment generally had poor water quality, with median nutrient values above ANZECC trigger values. For TP, all three stations had 5-year median values above the ANZECC threshold, with the highest TP values measured in WA9. Thus, baseline phosphorus concentrations reveal a legacy of catchment sources that go beyond just inputs from storm events. The rainfall plots show that periods of high rainfall do not correspond to high TP values. Although high TP values were observed in the three stations in 2004, the rainfall pattern overall suggests that in-channel erosion is more likely to be the source of TP pollution. From the land-use analyses (Figure 4.2), it showed that high-producing grassland (66%) is the dominant land-use class. However, connectivity analyses showed that a large amount of TP would have been introduced through watershed from the upstream (WA7) than any other monitoring sites. This reason for this was because connectivity analyses showed that a large area of high-producing grassland was connected to the flood plain. Several studies in the literature have shown that high-producing grassland is a significant source of TP among other nutrients (Julian *et al*. 2017; Snelder *et al*., 2017; Larned *et al*., 2019). The seasonality effect shows that TP values were higher than standard in both summer and winter for all three stations except for WA9 in the summer. This also underscores the fact that there is no direct relationship between the rainfall pattern with TP recorded. TP values may have been continuously introduced but gradually from other sources rather than directly from the watershed. The gradual release of TP might have been influenced either by in-channel erosion or the presence of riparian buffers. The presence of in-channel erosion or riparian buffers can limit the runoff rate and reduce the concentration of pollutants into the river. A similar pattern was also observed for DRP, NH4, turbidity, TN, NO_3. The trends observed suggest that the release of these pollutants was after a storm event. From the rainfall graphs, spikes were observed in 1995, 2004, and 2011. The storm events in 2004 and 2011 were similar in magnitude but did not release the same amount of pollutants of these years. The reason may be because of riparian buffers as well as scaled back fertilizer application over-time. This finding corroborates the study of Abbott *et al.*, (2017) that found despite the landslides occurring in the Manawatu catchment, minimal suspended solids (SS) are transported into the river given that a small fraction of LU/LC is connected to the river.

Similar rising trends in NH_4, NO_3, TN were observed for all three sites, but a different pattern was observed for NH_4. The similarity for WA7 & WA8 for NO_3 & TN suggests that both sites were significantly contributing to NO_3 & TN pollution. However, for NH_4 disproportionate amount of NH_4 was observed among sites. Higher values of NH_4 was observed in WA9 than any other site (WA7 & WA8). The reason for this can be attributed to the presence of urban settlements that produce a large amount of waste rich in NH4.

5.2 Water Quality Assessment

Data analysis conducted with variables for over 25 years showed remarkable insights into the pollution status in the Manawatu catchment. Results for all sites clearly showed the pollution varied over time (Figures 4.3 to 4.22). and in most cases, above ANZECC trigger values. High pollution (sediment and nutrients) was measured between the 2000-2004 period in all three sites resulting from significant increased rainfall compared to other years (see sections 4.3.1 to 4.3.11).

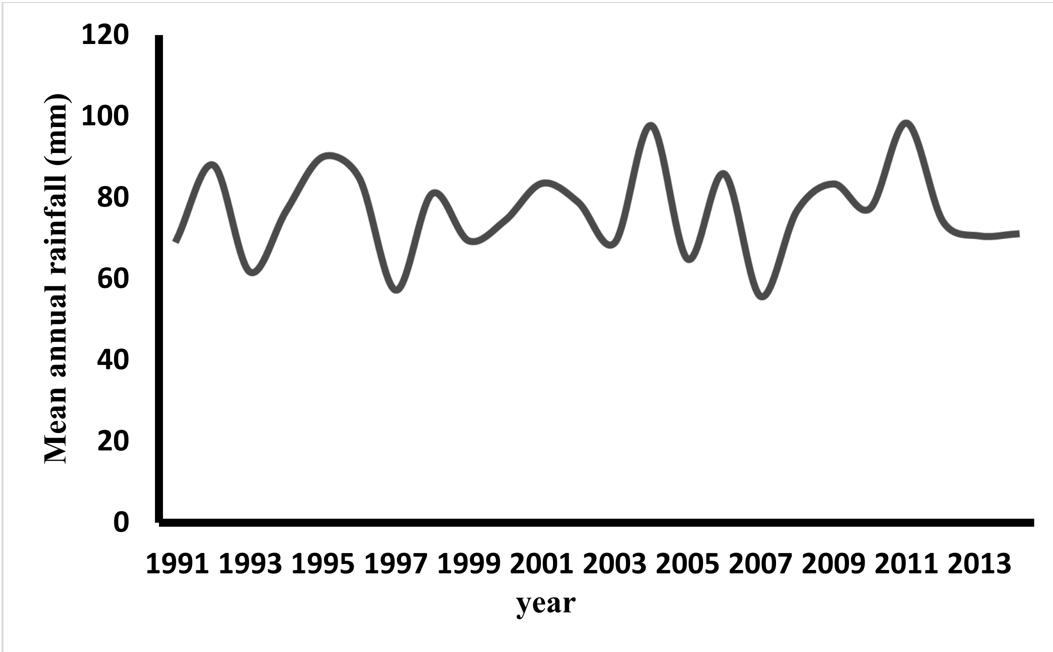


Figure 5.1: Mean Annual Rainfall for Palmerston North in Manawatu Catchment

These findings were observed sharply and were revealed by the post-hoc test of medians, which showed a statistical difference in nutrients concentration. The increase in nutrients has been attributed to the extreme rainfall event that occurred in the catchment between 2000-2004 (Figure 5.1). According to Dymond *et al.*, 2006 and Fuller 2007, the rainfall of that year was significantly elevated in February 2004. It was responsible for flushing a high amount of sediments and nutrients into the river, especially in 2004 and 2011. It was recorded during that period that the lower North Island experienced a massive storm with over 20 hours of rainfall (Fuller, 2007). Abbott *et al*. (2016) reported that a significant storm event could produce an exceptional amount of sediments, especially in the loose and hilly terrain of the Manawatu watershed. The significant increase in nutrients and sediments during the 2000-2004-year period only showed that a large amount of eroded soil was deposited, which transported these pollutants.

Consequently, these findings are corroborated by the study of Larned *et al*., (2016), and Kamarinas *et al*., (2016) that revealed the water quality in NZ was poor, and will continue to show a degrading trend due to periodical influx of nutrients that have accumulated in the soil for up to 50 years.

PC1 for WA7 (Table 4.8), showed turbidity, Electrical conductivity, total phosphorus, and absorbance as significant pollutants. From previous studies, turbidity is the result of soil erosion and the runoff process (Kemker, 2014; Salem *et al*., 2019; Memon *et al*., 2014; Shrestha & Kazama, 2007). However, more likely these pollutants from PC1 in WA7 were from in-channel sources. In Manawatu River catchment, in-channel sources emanate from flood plains that trap sediments and nutrients over time and releases them during rainfall events. Electrical Conductivity present can also be a marker for the influence of mass weathering effect on water quality (Ogwueleka, 2015), while high loadings in TP represent the action from fertilizer being applied on intensive agricultural areas (Salem *et al*., 2019; Cruz *et al*., 2019). Lastly, high loadings in absorbance (Abs) can represent the presence of high dissolved organic matter comprising largely of humic substance (Reynolds, 2002; Dignae *et al*., 2000). Therefore, PC 1 for WA7 likely represents a combination of soil or mass weathering and agricultural pollution. PC 2 showed high loadings from NO3 and TN (Table 4.8). Fukasawa (2005) reported that the presence of these nutrients is indicative of fertilizer application rich in nitrogen. Although Cruz *et al*. (2019) reported that TP and NO3-N entered the Siriri River in Brazil, the source of this pollution was different. However, from the correlation matrix developed, TP was correlated with turbidity and TN, which suggests that they emanated from the same source. As we established earlier, turbidity likely came from soil erosion. Therefore, NO_3 & TN are nutrients deposited on the soil around the river. It can be suggested that PC 2 was attributed to agricultural pollution, suggesting that agricultural pollution could be widespread and a significant source of pollution in the Manawatu watershed.

PC 3 identified NH4, while PC 4 showed the presence of DRP (Table 4.8). Woldeab *et al*. (2019) reported that the presence of TN, DRP, and NO3- were prevalent and significantly higher in vegetated and agricultural areas. The presence of NH3-N (NH4) can be attributed to the presence of liquid manure from livestock within the watershed. Therefore, since DRP was correlated with TP, with DRP a constituent of TP, it can serve as an indicator for natural pollution source from soil erosion. Dymond *et al*. (2016) mentioned that the soil material in Manawatu is rich in phosphorus. With this nutrient identified in both PC 1 and PC 4, it suggests that TP presence is a more diffuse pollution source. Therefore, the least variable principal component (PC4) is more from a natural component. Therefore, PC 3 may be attributed to livestock pollution as well as the draining of fertilizers applied in the agricultural fields, while PC 4 represents a natural pollution source. These findings can be supported by the relationship developed with the watershed connectivity analysis between land use and floodplains. Table 4.1 shows that for WA7, large areas of high producing grassland (73.5 km^2) are connected to the river. This process makes it very likely for agricultural pollution to enter the flood plain quickly in a significant amount.

Similarly, contributions from Kamarinas *et al*., (2016) revealed that high producing grassland and plantation forest produces a large amount of sediments. Darius (2005) and Croke & Hairsine (2006) also reported that a significant amount of sediment and nutrients entered rivers from a plantation forest with the nutrients applied during replanting to improve plant growth. Therefore, these findings support the report obtained from our site investigation and conform to our conclusions.

For WA8, in PC 1 (Table 4.8), similar trends from WA7 were observed as they showed similar combinations of variables. Therefore, PC 1 probably originated from both soil erosion and agricultural pollution sources, while PC 2 is likely an effect of agricultural pollution alone (Table 4.8). Consequently, PC 3 accounted for livestock pollution, while PC 4 identified the presence of DO, which accounted for abiotic conditions. Interestingly, loading in DO suggests its less variable and imply that DO is constant, the reason why it was never less than triggers values in all three sites. Its sufficiency connotes a significantly good environmental quality for aquatic life, which leads to good aquatic health (Mallya, 2007).

A significant increase in the pollution would be observed in WA8 as an area of connected plantation forest and high producing grassland increased. Similarly, PC(s) for WA8 suggest that the watershed is polluted with both soil erosion and agriculture pollution. This finding is supported with the study of Julian *et al*., (2017) that reported that large amounts of NOx leaking away into most rivers in NZ has increased since 1989, despite the reduction in fertilizer application since the early 80s and consistent with turbidity and nutrient observed in large amounts in a lowland river.

Despite the establishment of high turbidity and nutrients associated with lowland rivers, WA9 showed a little variance based on the result obtained from the PCs (Table 4.8). Specifically, PC(s) revealed strong loading in turbidity and fewer loadings in nutrients. The strong loading identified by turbidity, absorbance, and EC may suggest that these three markers assumed to be from soil or bank erosion from urban areas. The reason for this assertion stemmed from the fact that this component did not include the presence of nutrients. Presence of NO_3 and TN in site WA9 maybe from runoff of domestic sewage from the wastewater treatment plant or urban areas. One of the attributes of this site is that it had a wastewater treatment plant installed for the treatment of waste from both industrial and domestic sources. This finding is supported by the report of Alves *et al*. (2018), who earlier reported the presence of organic matter alone in water could be attributed in no small amount of domestic sewage and industrial wastewater that could have been treated by traditional methods. Hulya and Thagal (2008) also reported that a high amount of nutrients within an urban area is likely by the action from treated wastewater. Pollution with nutrients seems likely as the downstream site had a wastewater treatment plant installed. PC 3, PC 4 & PC 5 accounted for the presence of nutrients. Again, based on this result, it is observed and more likely that phosphorus enters the river from two different sources through the pollutant varied over time. Since PC 3 showed more variability than PC 4, it can be said that PC 3 stems from the influence of agricultural areas.

In contrast, PC 4 accounts for the natural deposition of phosphorus entering the river during soil erosion or a landslide. Therefore, the presence of TP in PC 4 represents pollution from natural sources. NH_4 in PC 5 can enter the river through discharge from domestic sewage and may not naturally be found except in an oxygen-rich environment. Therefore, having large variability in NO_3 and TN within this site, it is somewhat safe to suggest that NH_4 came from aerobic pollution of domestic or livestock waste. This pollution is due to the constant appearance of DO in PC 6. This component was earlier classified as a natural occurrence of an abiotic condition. Whereas for WA7, PMF identified high loading in NH4, DRP, TP, and absorbance in Factor 1 (Figure 4.35). The presence of NH4, DRP, and TP is attributed to the effect of agricultural land uses resulting from fertilizer application and animal waste (Dils *et al*., 1999). Factors 2 showed high loadings in NO_3, TN, and DO (Figure 4.35).

Similarly, this can be attributed to the presence of sufficient oxygen, which can play a significant role in the oxidation of nutrients entering the river from fertilizer application and a source for degradation. Therefore, it is no surprise to find NH_4 in factor 1, which could be oxidation by-product for NO_3 and TN. Dale *et al*. (2007) reported that nutrients such as TN enter the river system at non-point sources from fertilizers applied on agricultural land, suburban lawns, and soils containing these nutrients. Factor 3 identified turbidity and TP. This factor is related to soil erosion. This conclusion is corroborated with the findings of Hulya & Hayal, (2008) and Paule *et al*., (2014) that suggested that runoff from agricultural areas are usually a source of TP and turbidity. Factor 4 is described as a physiochemical source. For WA8, high loadings in TP and turbidity are attributed to soil erosion or mass weathering, represented in Factor 1(Figure 4.36). Factor 3 was classified as agricultural pollution. Shreatha and Kazama (2007) reported that nitrogen compounds were found from the Fuji River because of the application of nitrogenous fertilizer applied around agricultural lands within the river.

Similar findings were reported by Kazama and Yoneyam (2002). Factor 2 is termed a physiochemical source due to the presence of EC & DO. Factor 4 can be described as pollution from livestock and agricultural waste. In WA9, NH4 was dominant and was likely released from domestic sewage (Figure 4.36). From the literature mentioned earlier, studies have shown that NH_4 can be released from several sources. However, these sources depend on the typical land use or anthropogenic activities associated with pollution sites. However, a high percentage of NH4 can be attributed to runoff from industrial wastewater treatment plants or domestic sewage. These findings agree with the findings of Gholizadeh *et al*. (2016) that identified the presence of ammonical-N to emanate from an industrial or domestic source. The high presence of DRP in factor 2 in WA9 indicated the presence of nutrients from agricultural catchments.

It is important to note that WA9 is a larger watershed encompassing WA8 and WA7. Therefore, WA8 and WA7 empty into WA9 with more agricultural practices occurring in WA7 and WA8, the reason for a high DRP. The high presence of TP and turbidity in factor 3 be attributed to mass weathering pollution, which had remained one of the characteristics of lowland catchment. EC and DO in factor 4 represent physicochemical source pollution. In contrast, factors 5 and 6 are the signatures for the identification of organic and agricultural pollution sources from the presence of absorbance and nutrients. These findings are supported by the results from the watershed connectivity model developed. Tables 4.1-4.3 revealed a reduction in the LU/LC of plantation forest and high-producing grassland within this watershed, which has shown to be a conduit for transporting pollutants into the river. Julian *et al*. (2007) reported that high grassland increased nutrients in significant rivers in NZ and further mentioned that high grassland showed no significant decreased over the years, indicating that the pollution trend may proportionally increase or remain the same. The observation from this study will likely be skewed to that assumption as elevated concentrations of nutrients (TN, NH4 -N, TP, DRP) and sediment loads were recorded across New Zealand. These were due to cattle, deer's, or Dairy Cows (Buck *et al*., 2004; Davies-Colley *et al*., 2004; Mc Dowell, 2008). Julian *et al*. (2017) further support this as sheep stock rate was higher in the uplands experiencing steep slopes in New Zealand. As more livestock gather, intensive grazing of grasses and their movement can expose the soil to erosion.

Consequently, between the early 1990s and 2012, dairy cattle were increased by a factor of 2, which made P- fertilizers and N- fertilizers application to significantly increase to meet feed demand for dairy cattle (Stats NZ, 2015). Additionally, when lactating dairy cows consume pastures grown by P and N- based fertilizers, approximately 0.8 and 0.6 of the total tons of P and N fertilizers are deposited on the soil as animal waste (Monaghan *et al*., 2007). According to Ledgard (2001), these values remain underestimated as different dairy pastures are likely to assimilate an extra amount of atmospheric N. increase in pasture grazing, strip grazing, and cropping/harvest. These were identified as the root cause of soil catchment exposure to erosion, which is a useful practice in NZ (Julian *et al*. 2017). These findings support the findings from our study as more nutrients and sediment loads were a characteristic of sites or catchment within the Manawatu area having a large area with plantation forest (PF) and high producing grassland connected to the flood plain.

Interestingly, nutrient-rich sediments were released into rivers after precipitation. A study conducted by Abell *et al*. (2010) on 101 National lakes showed that high-producing grassland increased the mean TP and TN concentration. A similar study was carried out by Ozkundakci *et al*., (2014) that revealed high grassland also increased with nutrients in 25 national lakes

5.3 Water Management Application

The purpose of this study was to assess the pollution status of three longitudinal sites within the Manawatu River watershed using multivariate statistics and the PMF model using EPA PMF 5.0 package. Generally, from the study, multiple lines of evidence suggested point, natural, domestic, and agricultural sources contributed to pollution. These had an adverse implication on the poor water quality characteristic of the river by increasing contamination level above threshold or trigger values. The study and previous studies in the literature revealed that most rivers had better water clarity, which was the same only for upland rivers in this study. The good water clarity widely observed in WA7 only suggest the combined effects of both minimum soil erosion, and inclusion of riparian buffers or wetland within the catchment has created a natural renewable water supply. From the findings of this study, this concludes that there is a return – flow and reduced consumptive use. Generally, both precipitation and return flow conditions contribute nutrients and soil matter into the river.

Since river pollution is both a localized and watershed-scale environmental issue based on the different land use actions taking place within a watershed or catchment, it is evident that water resource management practice within Manawatu River catchment should be based off on the report of this study. First, improving the properties of agricultural soils and its terrain by utilizing less nutrient and retaining nutrients for a long time can improve the consumptive use of agricultural areas. This process can reduce the amount of natural renewable water supply entering the river, reducing the flood and contamination levels of a densely polluted agricultural field into the Manawatu River. Another recommendation will be reducing water withdrawal within the river to properly dilution the contaminants that diffuse into the river from the watershed. Jeppesen *et al.* (2005) and Hilt *et al*. (2018) identified that many water bodies showed no improvement in nutrient concentration after pollution reduced due to the overloading of nutrients previously from surrounding agricultural lands. This can be appropriately guided by understanding the assimilation capacity of the Manawatu River. The assimilation capacity refers to the amount of waste that a river can accept to help cushion the effects of contamination without feeling or being stressed by pollution. This process is vital because agriculture practice is majorly responsible for a large amount of water in rivers. Therefore, this may be one of the reasons for increased pollution at the intermediate site. With intensive agricultural practice less likely to slow down, as the central government of NZ has urged various stakeholders to double agricultural products by 2025 (MBIE, 2015), this will become worse except some other measures just itemized are considered. Lastly, this study also concludes that since WA7 & WA8 had similar inferences based on the statistical and modeling technique used, the intermediate site (WA8) can be used as a reference site having to possess the worst condition with the top site (WA7). A sampling at WA7 can be minimized for monies to free up the implementation of other pressing water resources management strategies that are peculiar to the watershed.

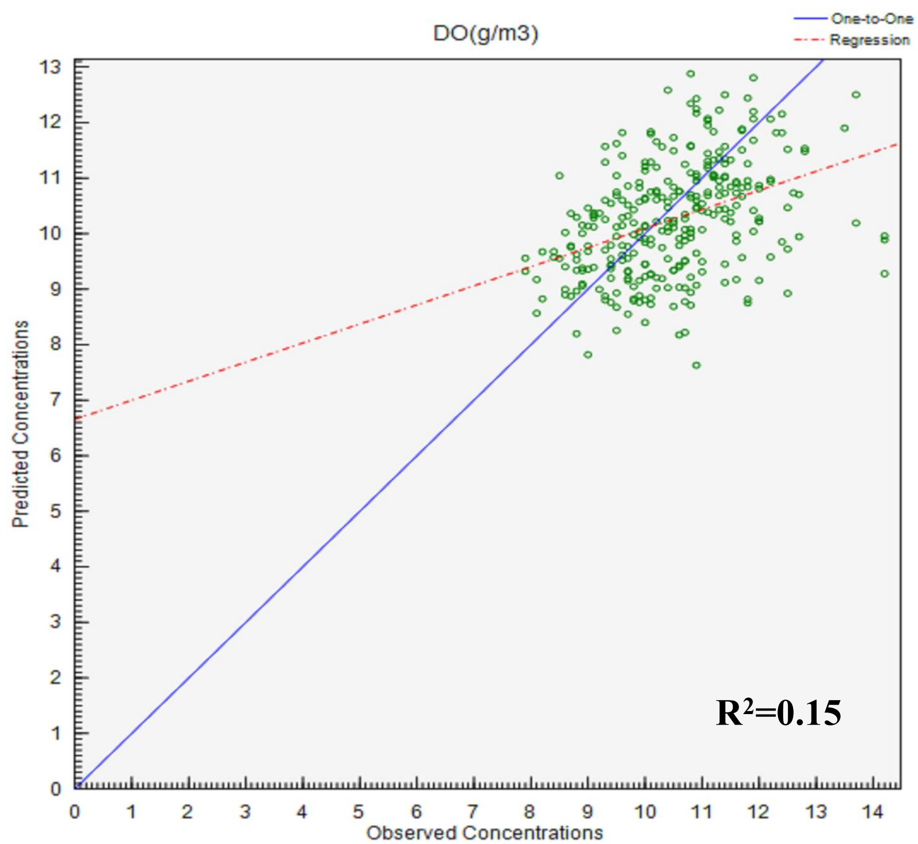
6. CONCLUSION

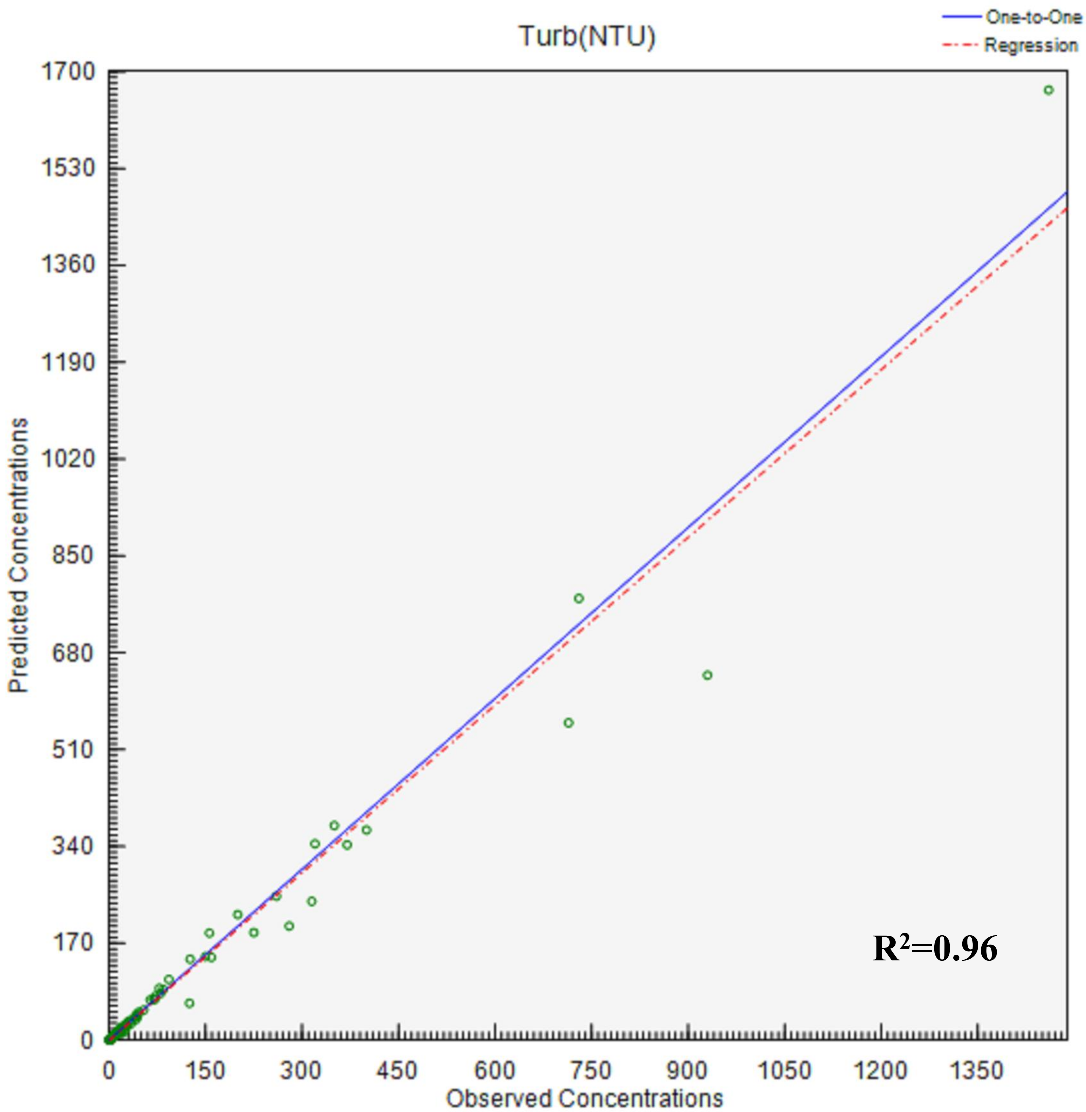
The purpose of this study was to identify pollutants and their sources within the Manawatu catchment by using multivariate statistical methods to assess relationships between LULC and water quality. Land use analyses showed that high-producing grassland was a dominant pollution source in all sites, while the meaningful existence of urban coverage increased pollution at the downstream section (WA9) especially for NH_4. Connectivity studies revealed that 73.4% of the entire catchment were dominated by high-producing grassland and 43.3% were directly connected to streams via runoff. The principal component analysis identified domestic, natural, and agricultural activities as pollution sources, with domestic pollution sources more identifiable in the downstream section of Manawatu catchment. The connectivity also showed the role of LULC in water quality as more high-producing grassland areas contributing to increased pollution and remain so when other LULC combine. However, this study revealed that nutrients such as TP, TN showed declining trends in concentration for all three sites yet median values exceeded trigger values. NH_4 also declined significantly for WA8 but in elevated condition at WA7 & WA9, whereas NO_3 declined below trigger values overtime in lowland rivers and remained of poor quality in the upland sub-catchment. However, declining trends of pollutant concentration are such that one may worry at the its very slow or insignificant rate. Introducing or improving the retention capacities of wetlands or riparian buffers will be a viable solution for the Manawatu Catchment. Overall, PMF revealed point, natural, and agricultural sources contributed close to 86%, 32%, and 75%, respectively in the downstream section of the river. At the intermediate sub-catchment, point, and agricultural sources contributed up to 100%, and 78% respectively, while soil or bank erosion contributed 84%. For the upstream section of sub-catchment, agricultural pollution, and soil erosion were both 84% each. Future work within the Manawatu River catchment should consider developing reaeration models to provide insight on assimilatory capacity and determine the health risk associated with the use of Manawatu River for farming. Lastly, this study shows the need for constant and continuous water quality monitoring for not only evaluating water quality variables but also being a useful means to evaluate the effectiveness of current wetland or riparian buffers already in place.

APPENDIX SECTION

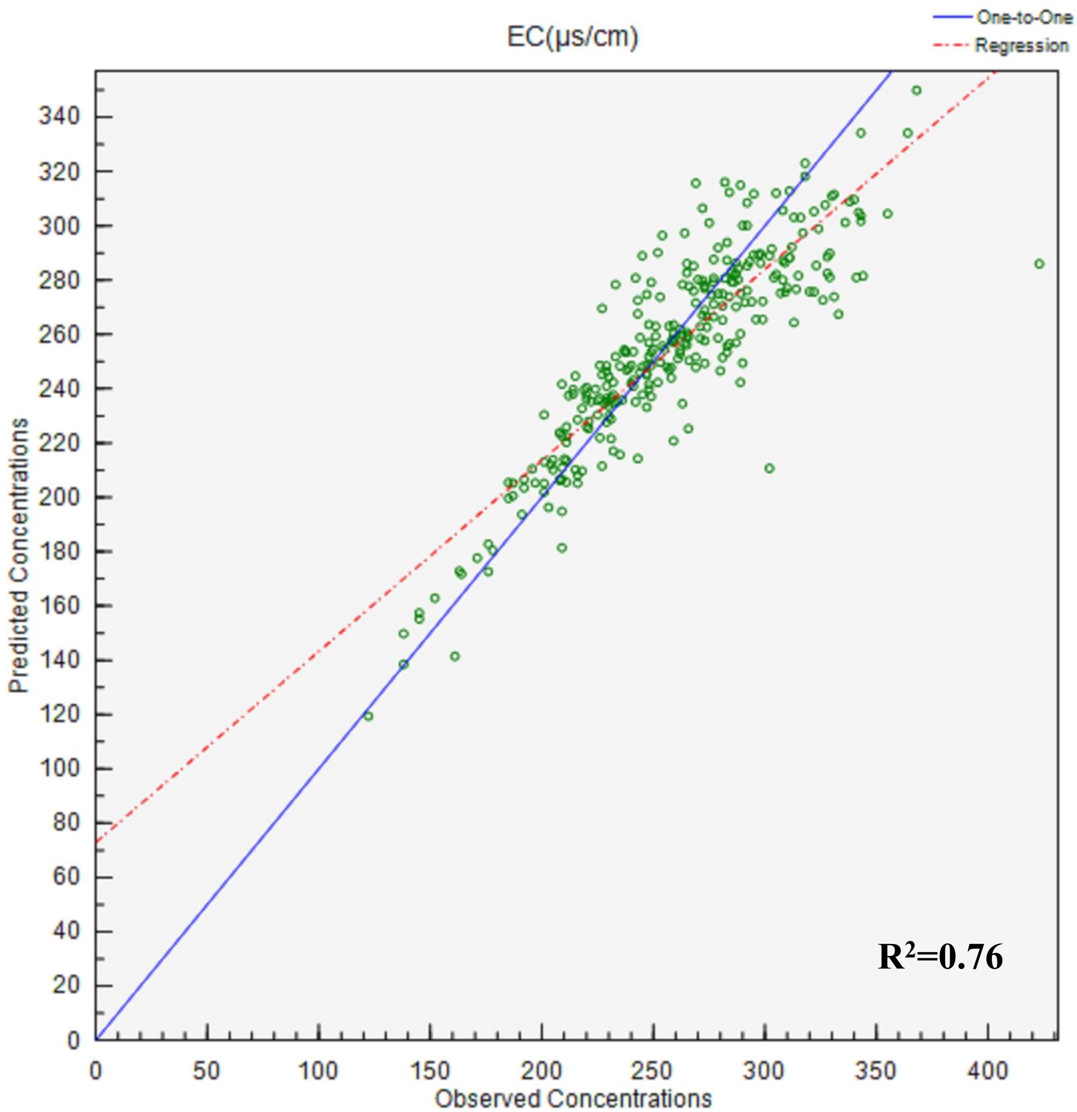
APPENDIX A

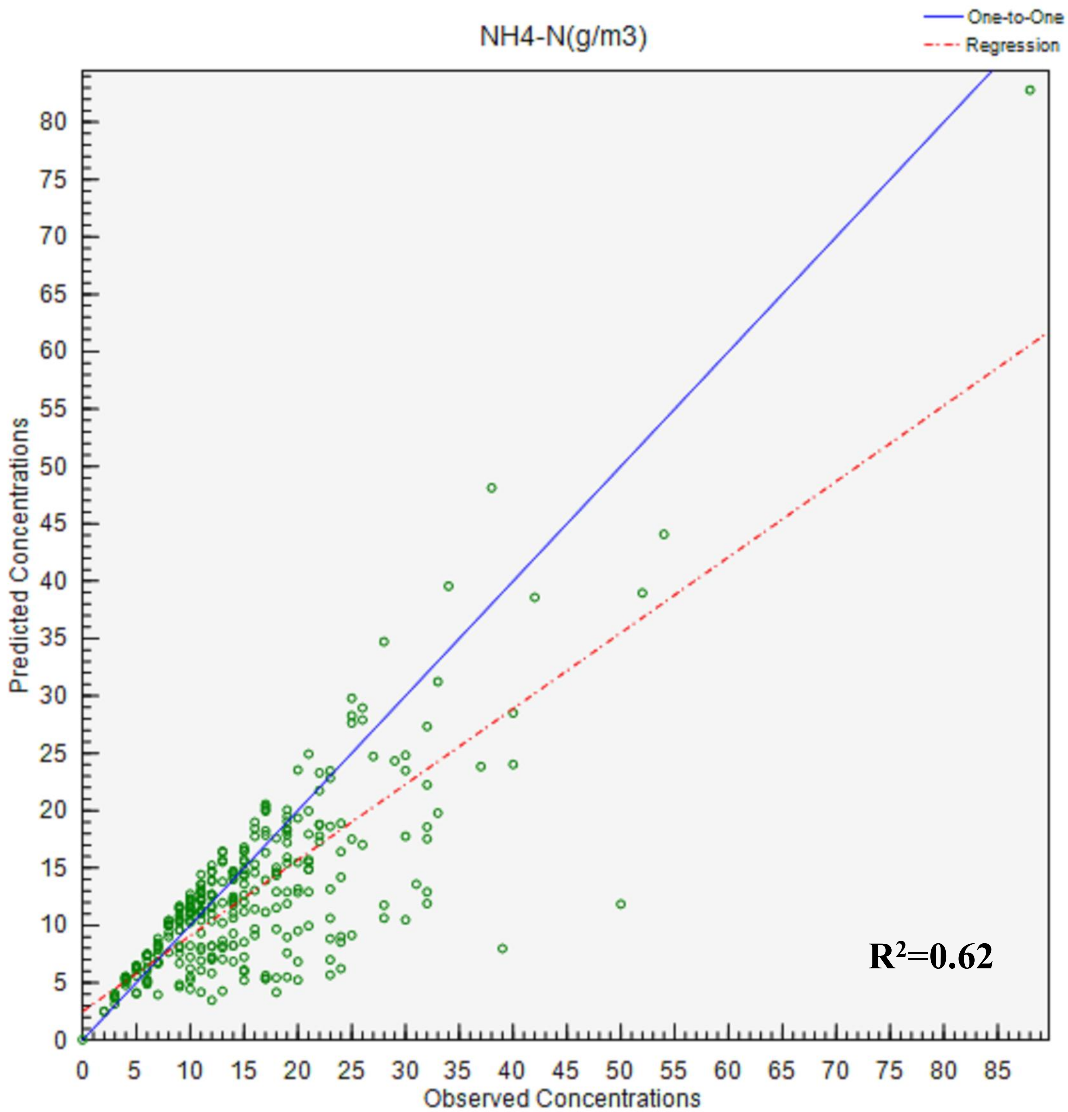
REGRESSION PLOT fOR SITE WA7 (UPSTREAM) in the MANAWATU CATCHMENT

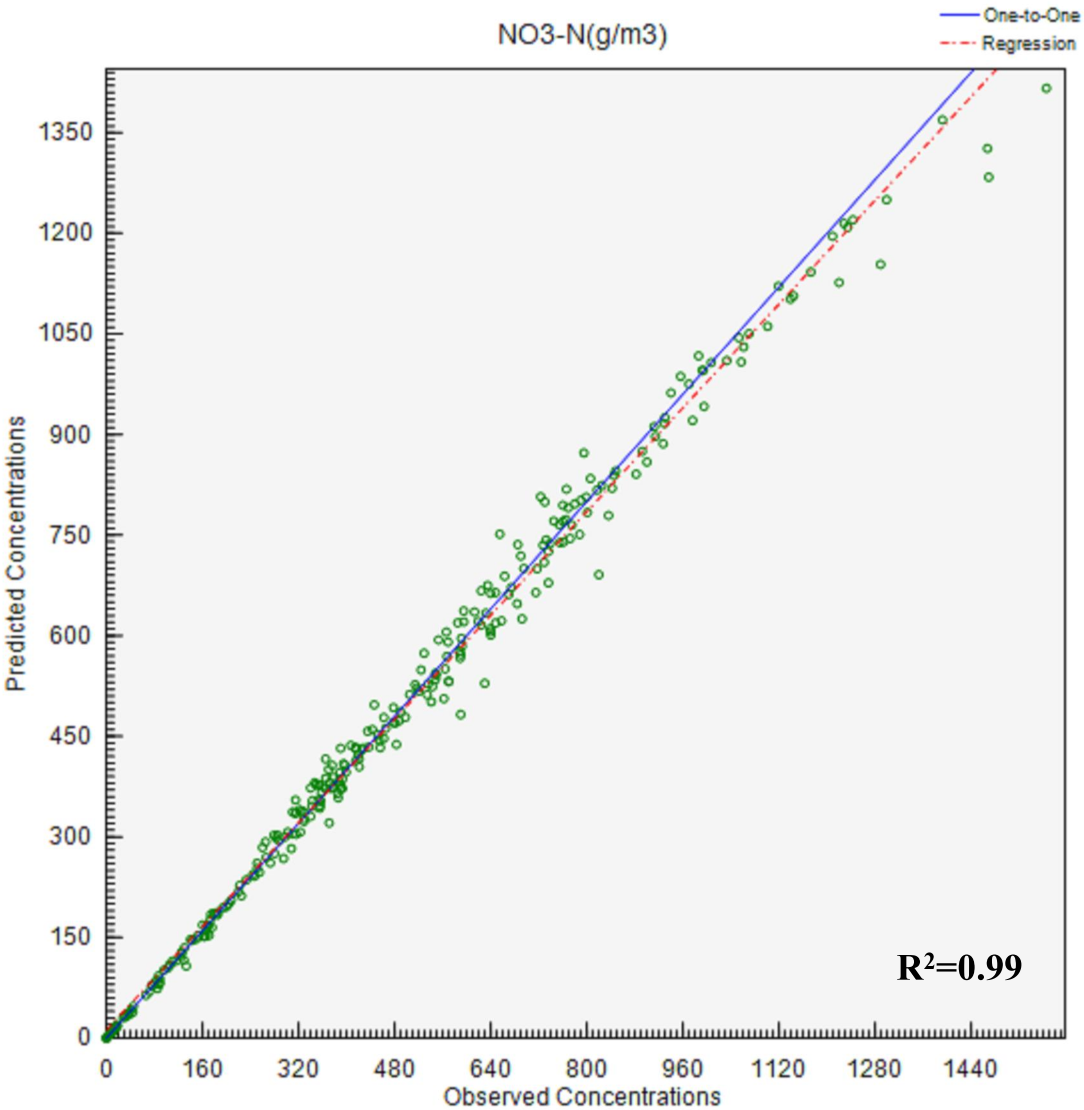


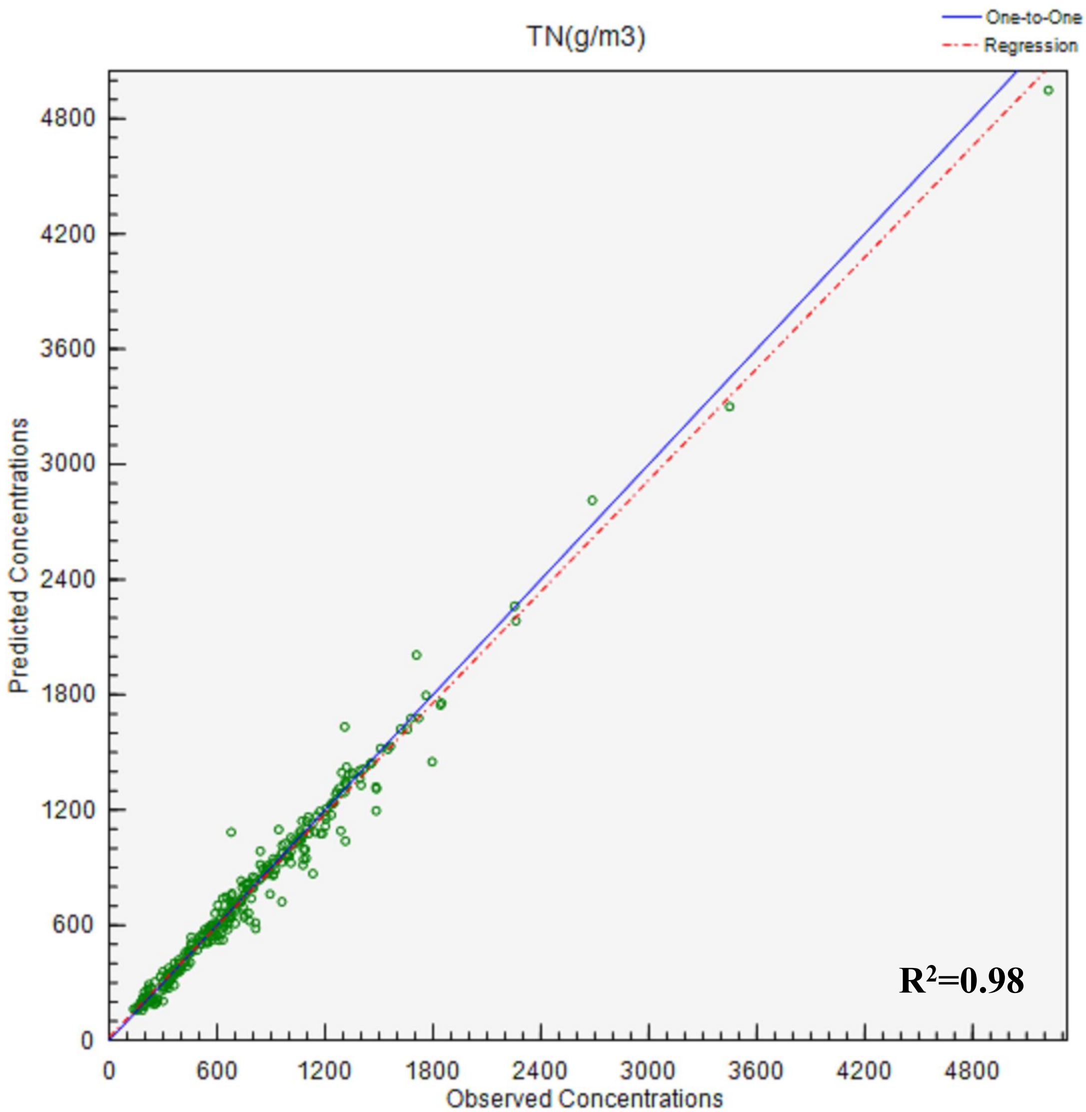


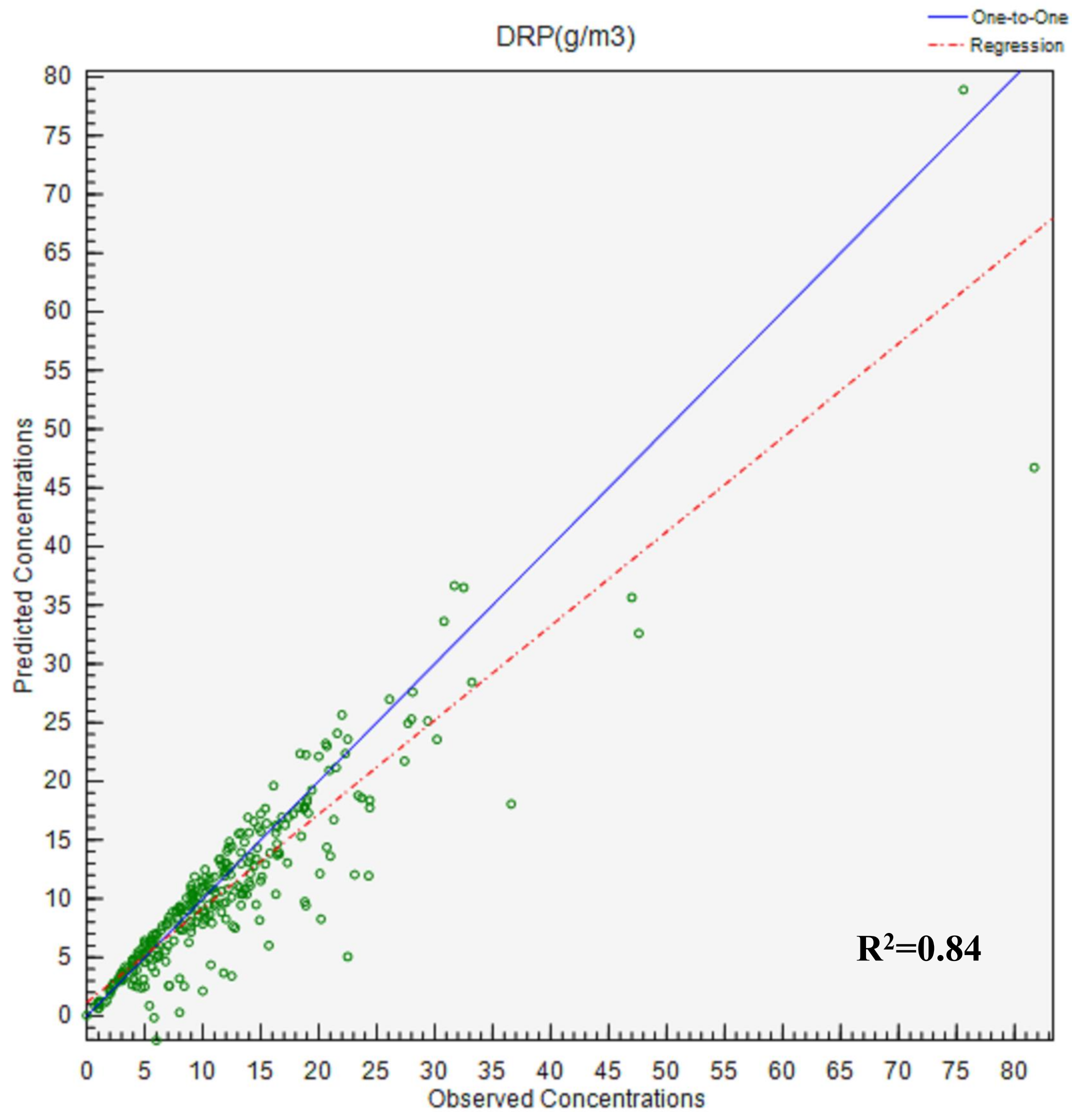
Turb(NTU)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
170
340
510
680
850
1020
1190
1360
1530
1700
0
150
300
450
600
750
900
1050
1200
1350
R²=0.96

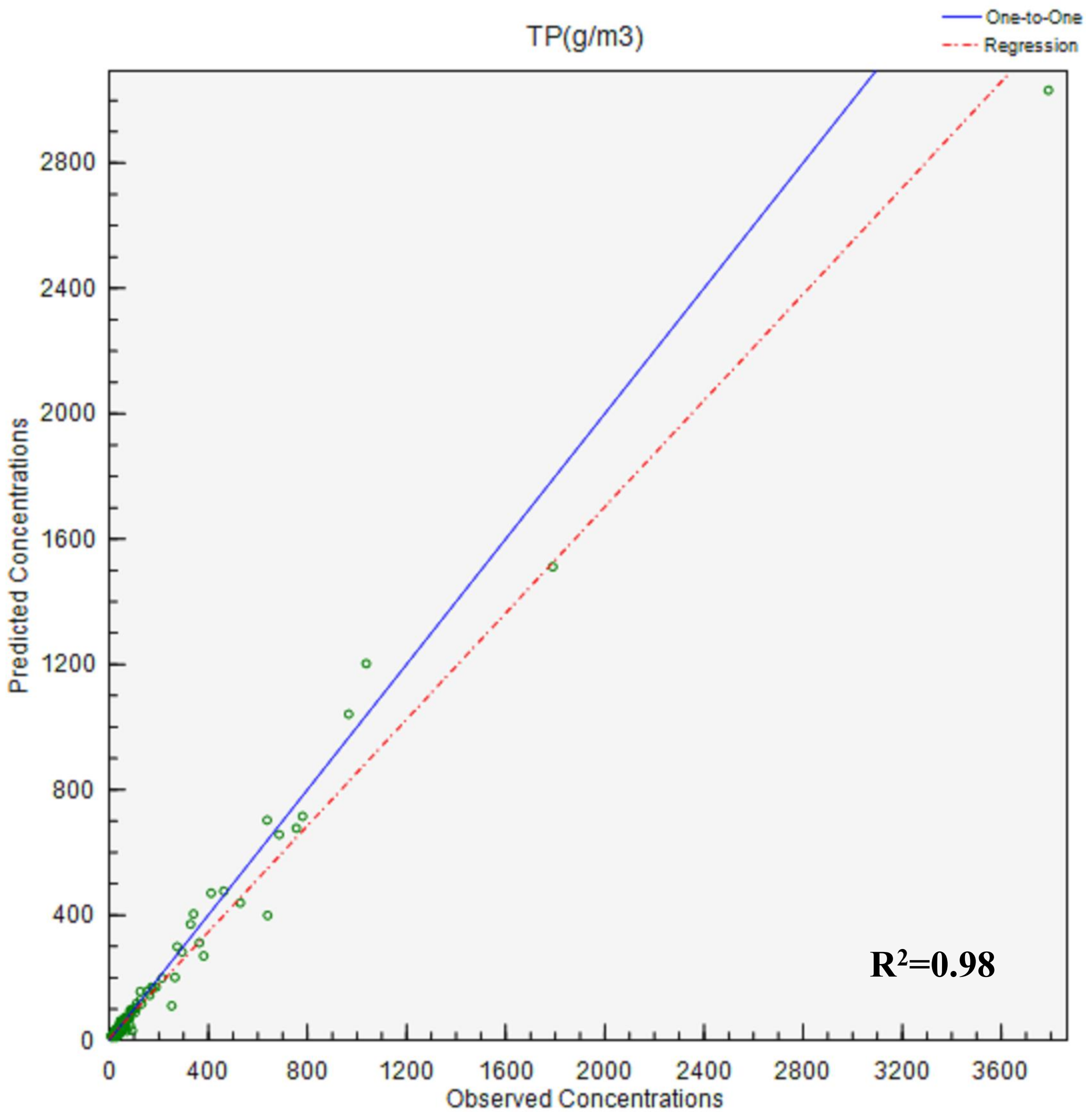

EC(µs/cm)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.76
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
0
50
100
150
200
250
300
350
400


NH4-N(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
R2=0.62

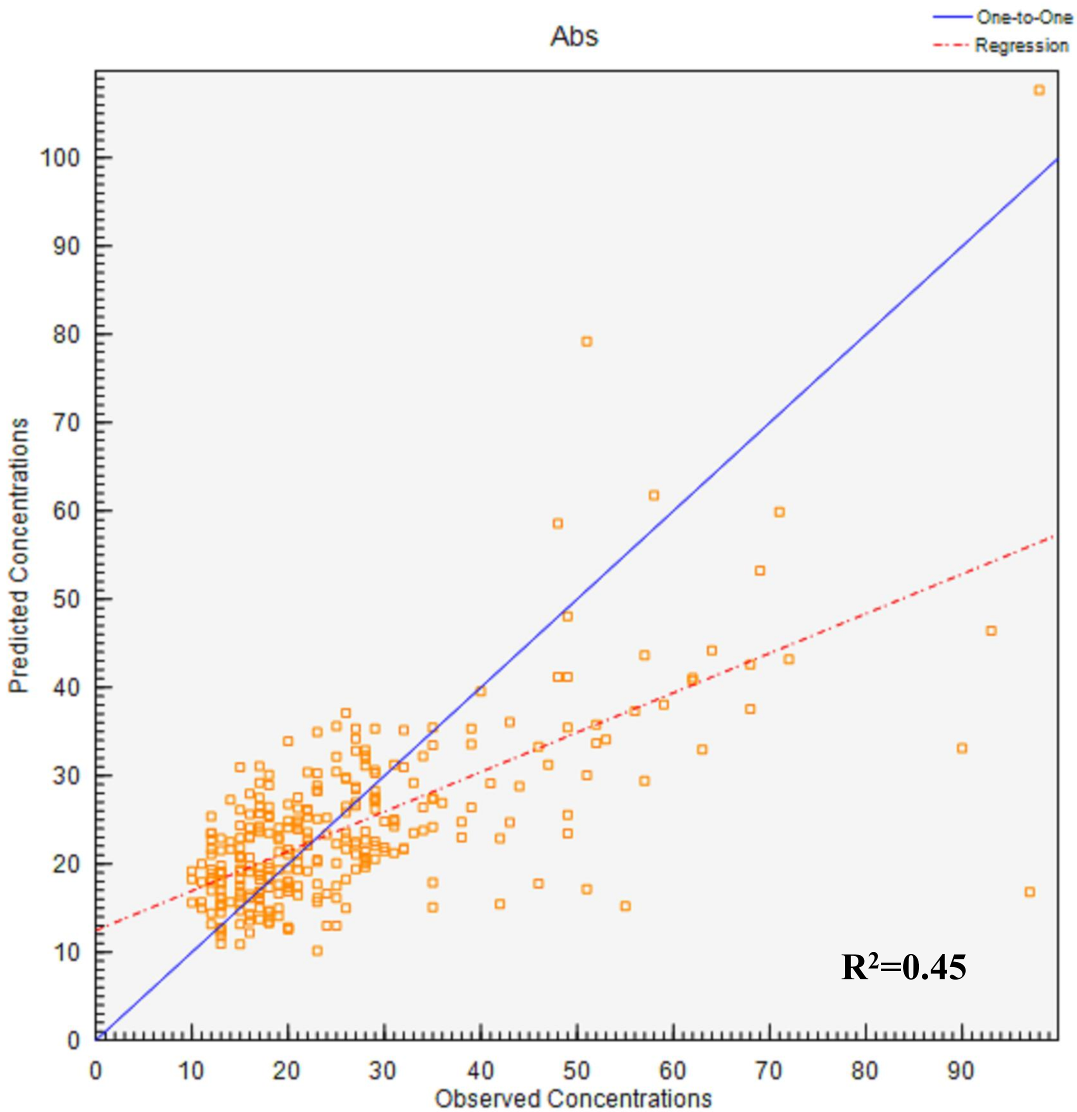

NO3-N(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
150
300
450
600
750
900
1050
1200
1350
0
160
320
480
640
800
960
1120
1280
1440
R²=0.99


TN(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
600
1200
1800
2400
3000
3600
4200
4800
R2=0.98


DRP(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.84
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80

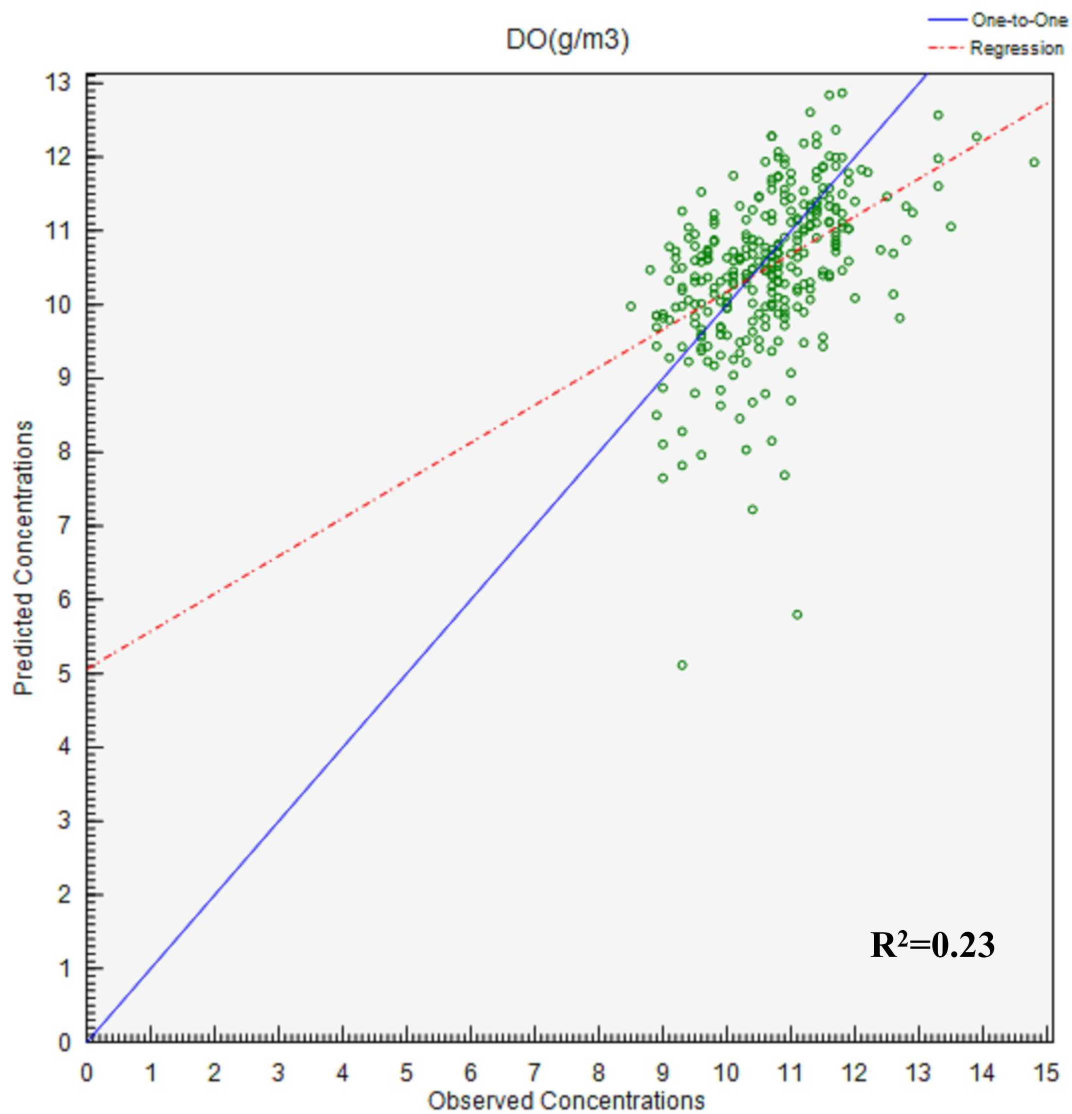


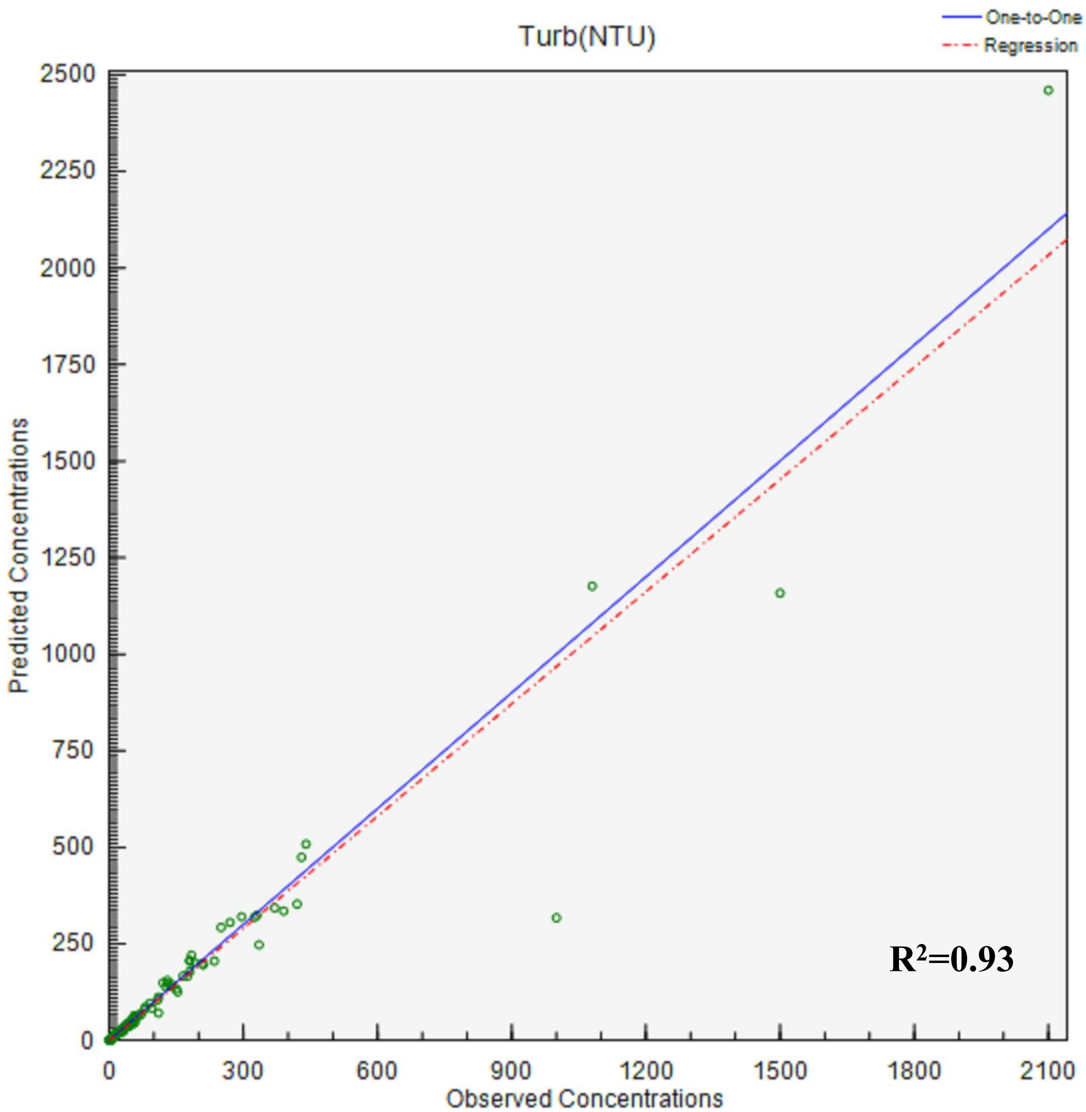
TP(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
400
800
1200
1600
2000
2400
2800
3200
3600
R²=0.98

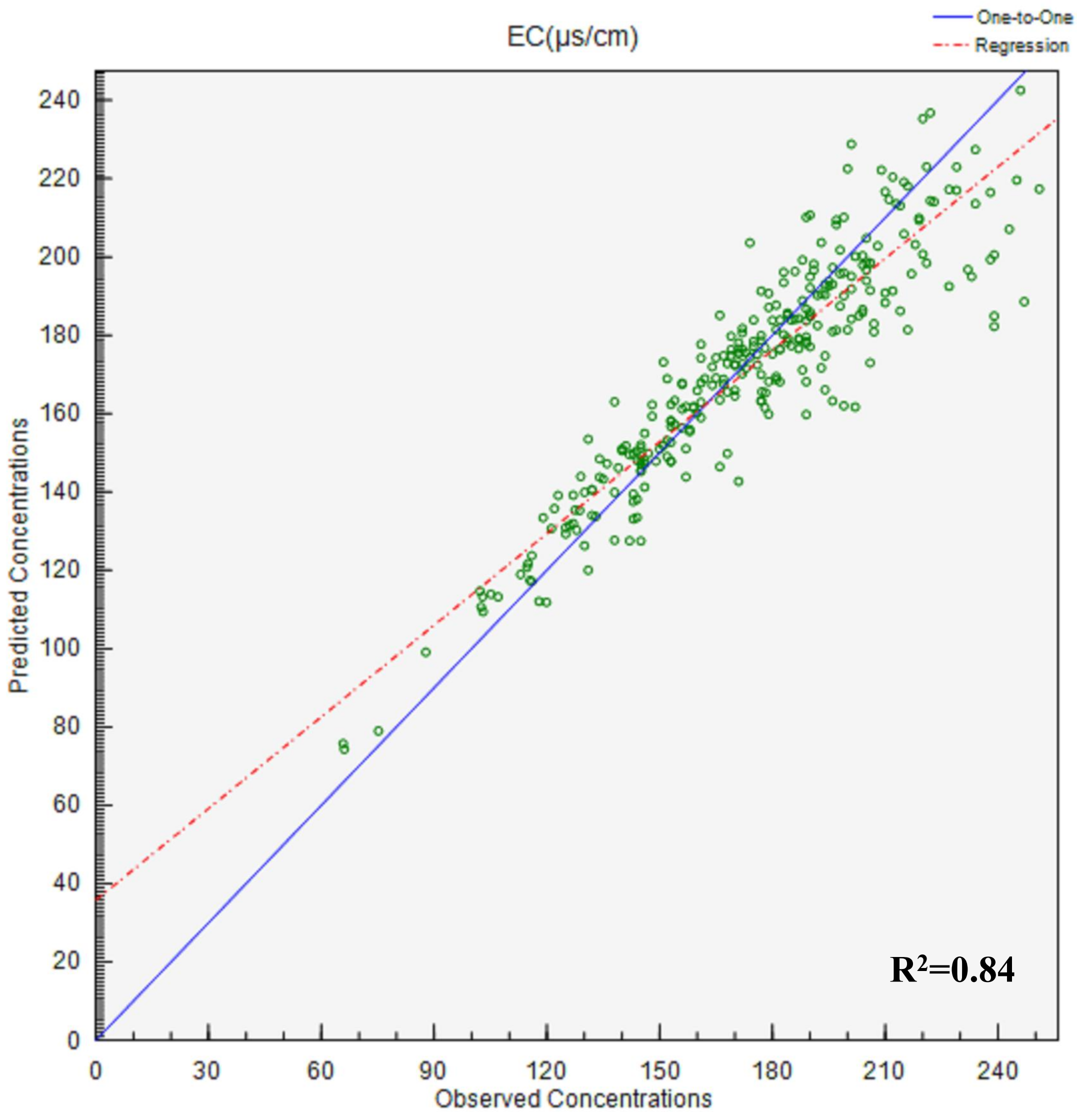

Abs
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.45
0
10
20
30
40
50
60
70
80
90
100

APPENDIX B

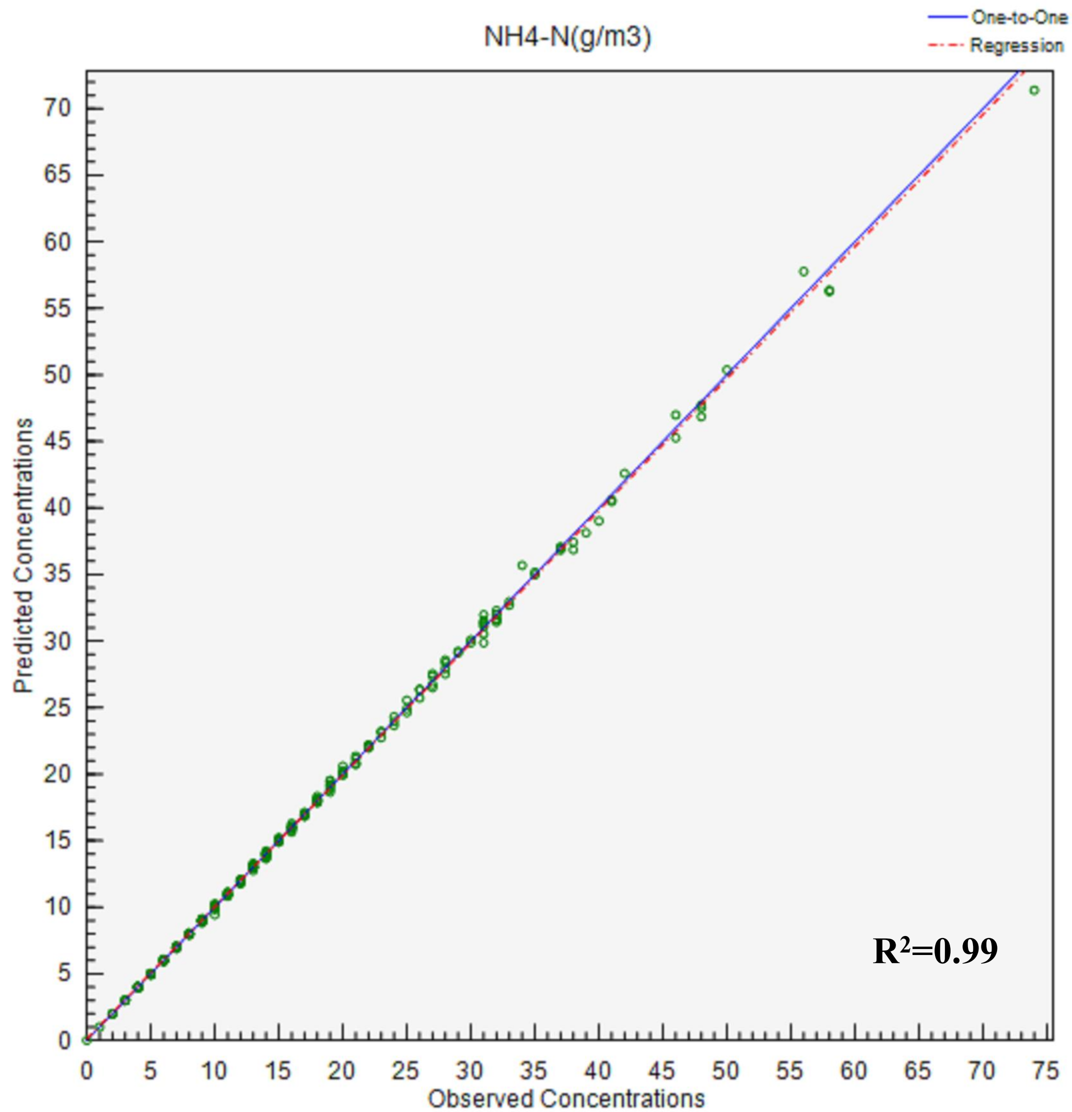
REGRESSION PLOT fOR SITE WA8 (INTERMEDIATE) in the MANAWATU CATCHMENT

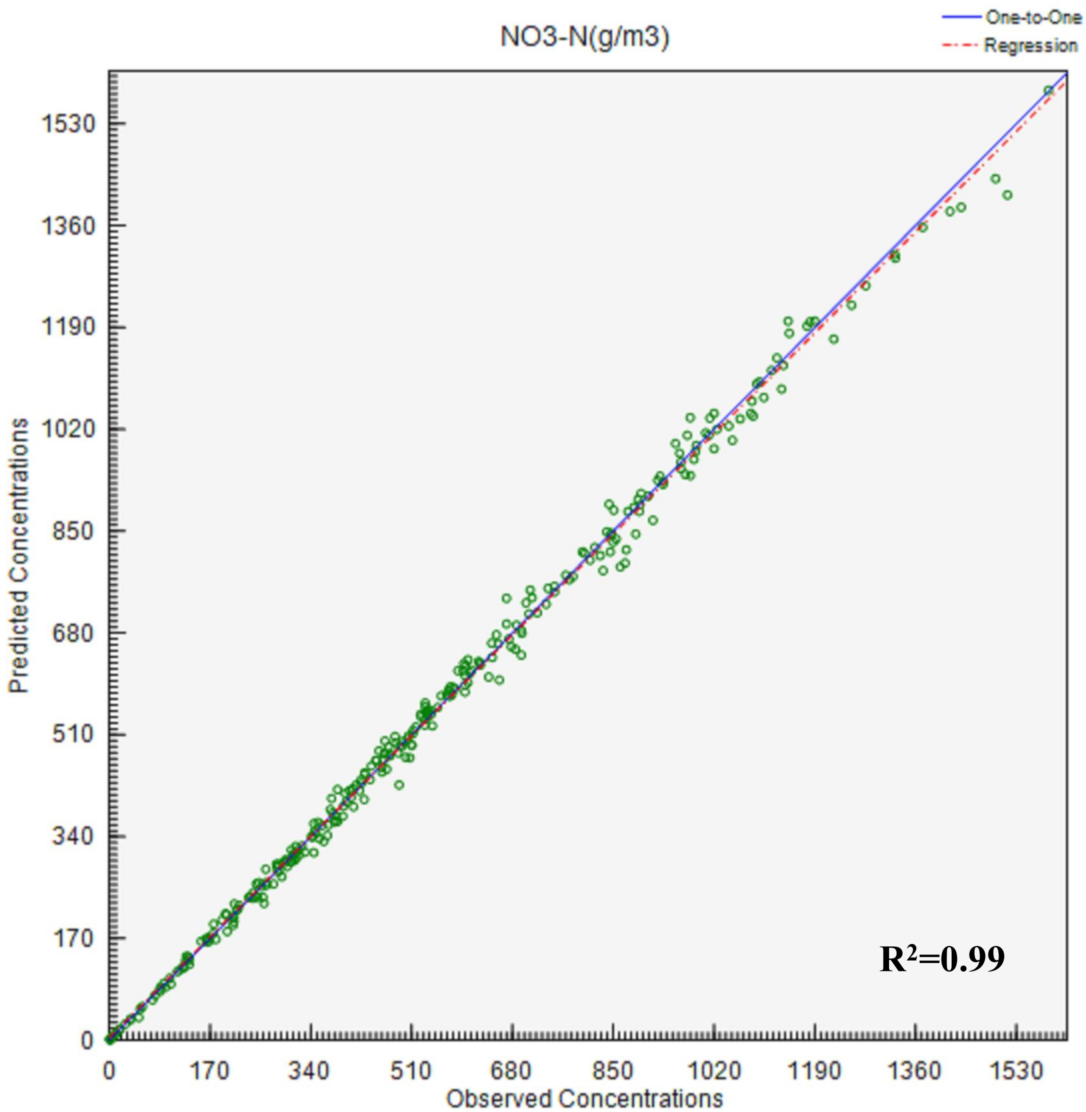


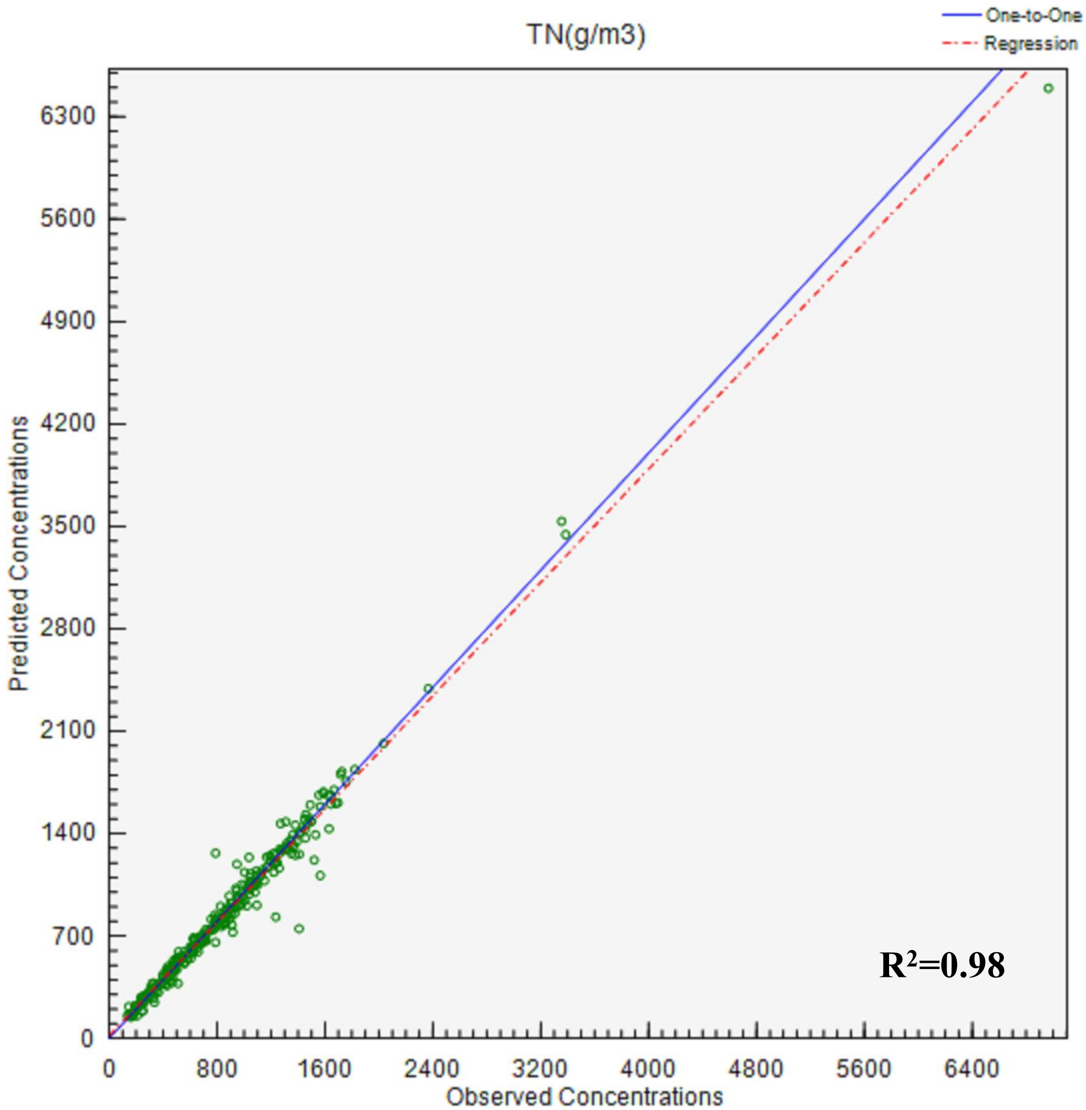

Turb(NTU)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0
300
600
900
1200
1500
1800
2100
R²=0.93

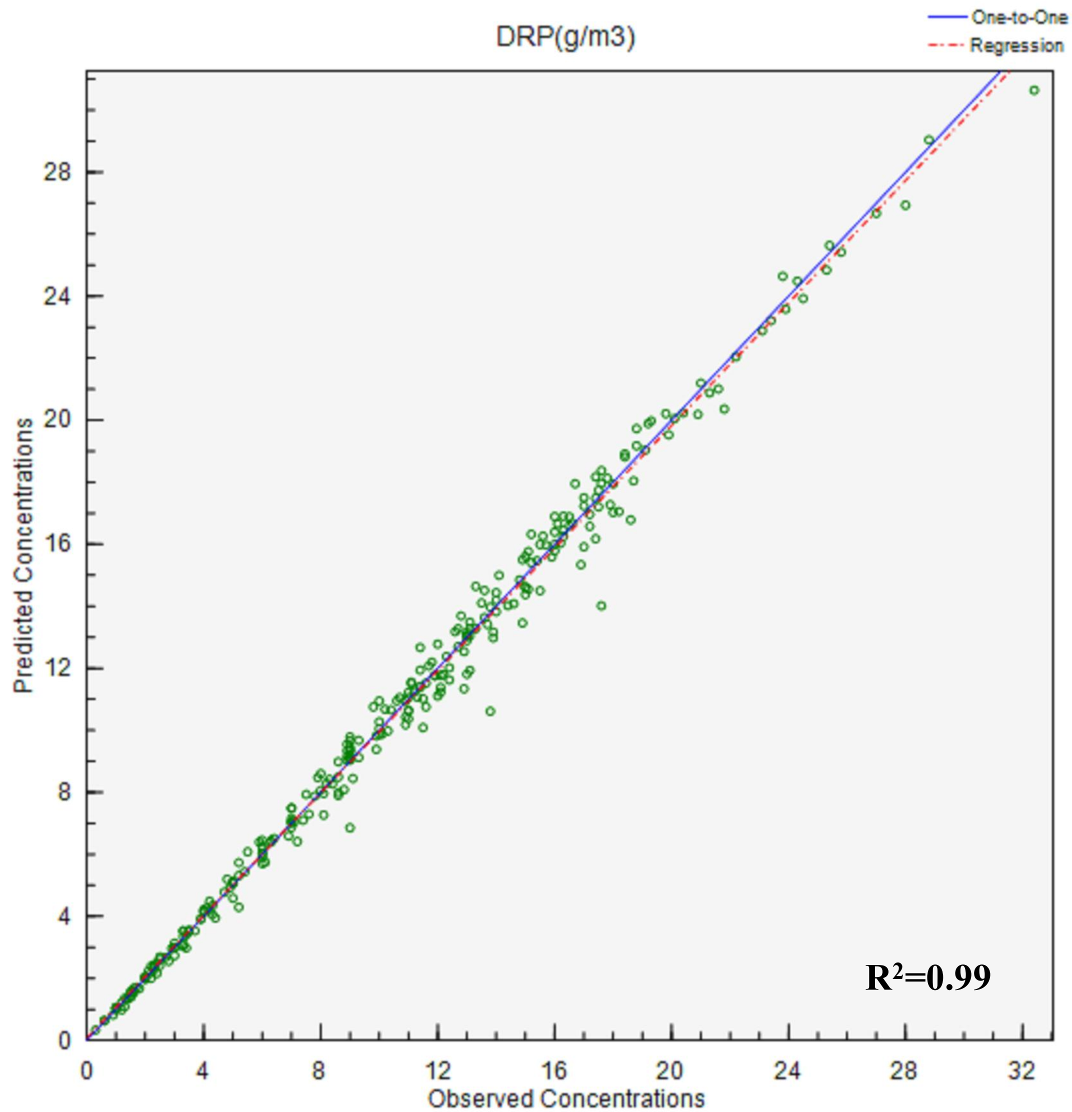


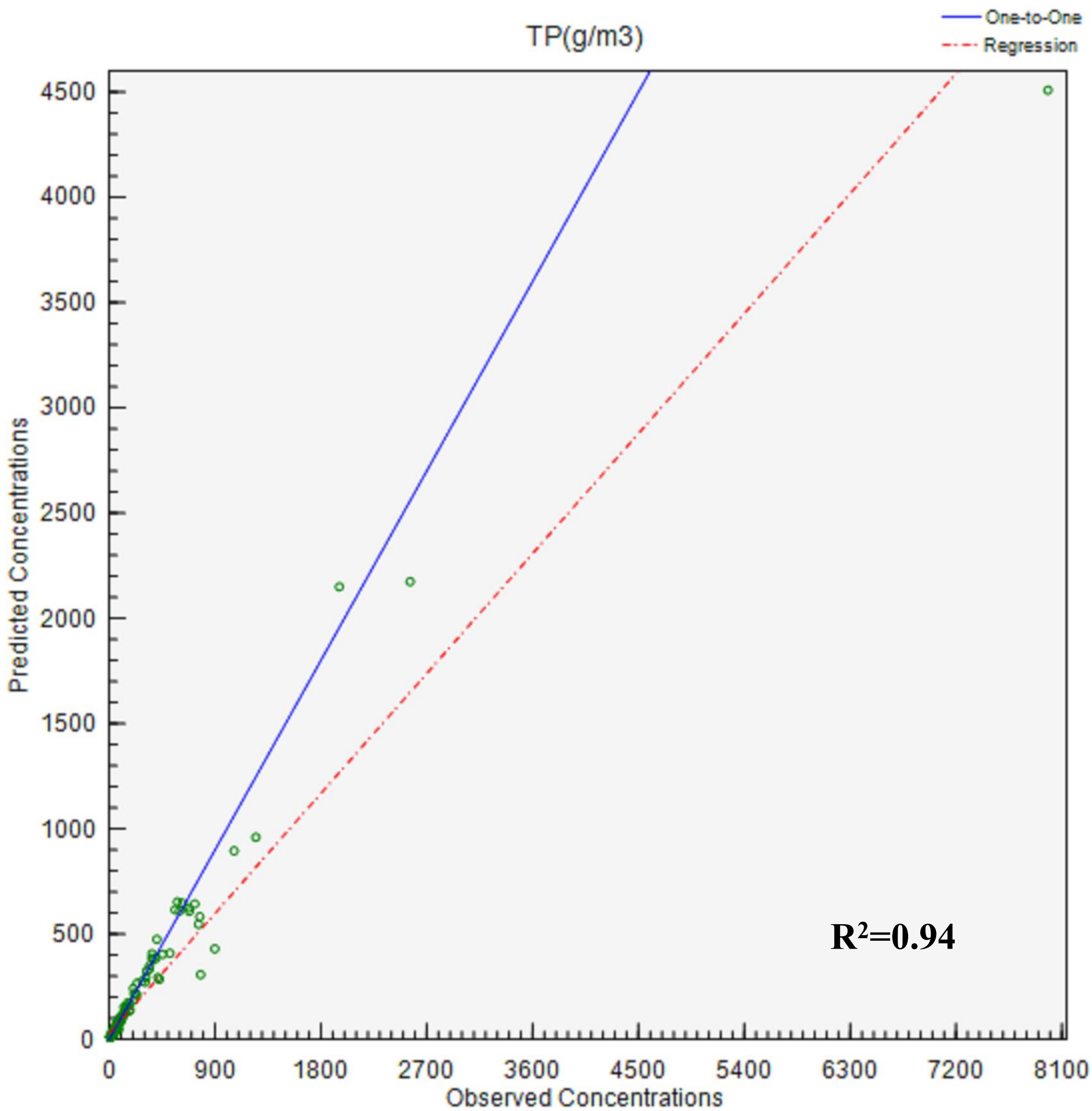
EC(µs/cm)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
20
40
60
80
100
120
140
160
180
200
220
240
0
30
60
90
120
150
180
210
240
R²=0.84

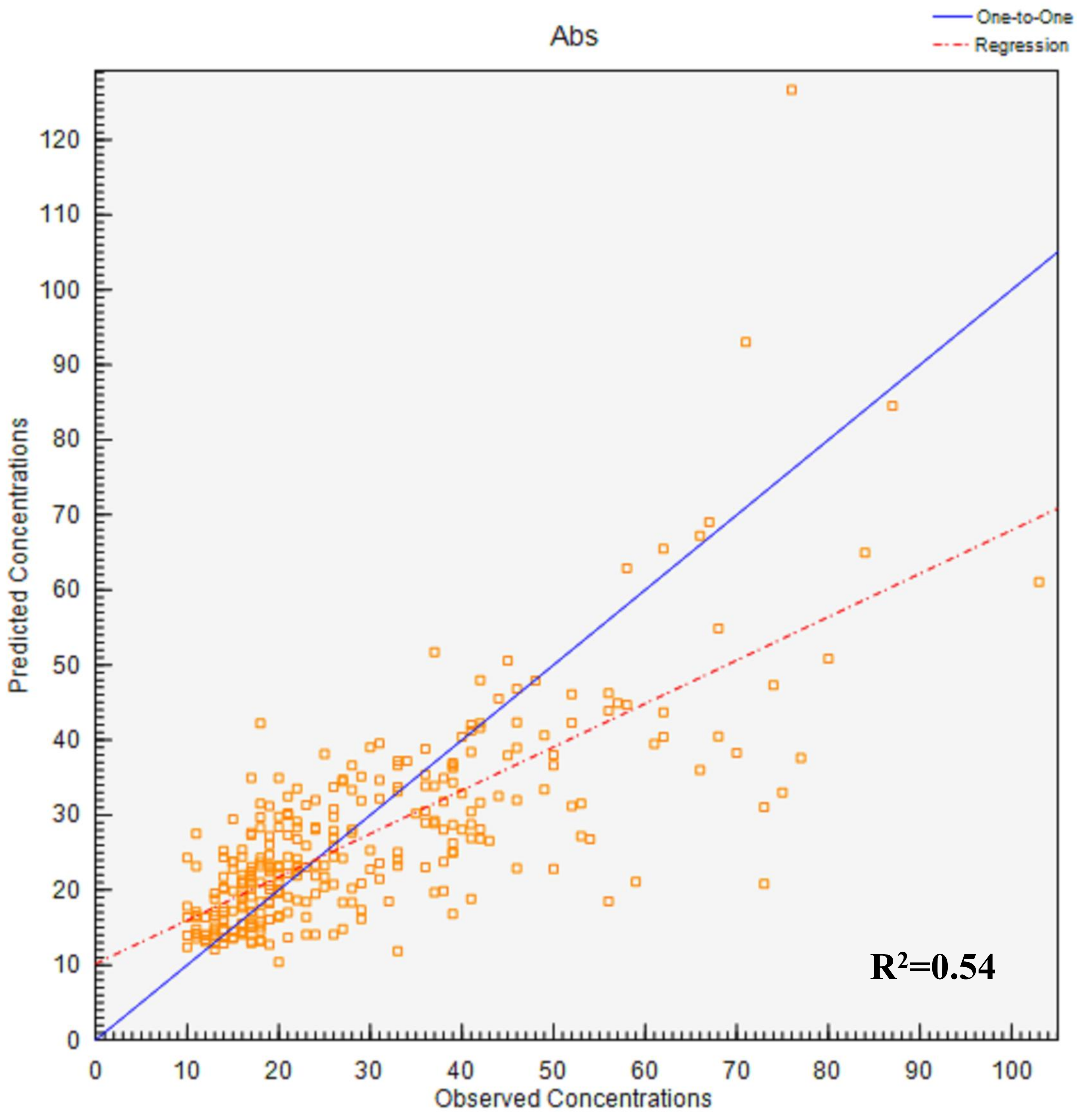

NH4-N(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.99


NO3-N(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
170
340
510
680
850
1020
1190
1360
1530
R²=0.99


TN(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.98
0
700
1400
2100
2800
3500
4200
4900
5600
6300
0
800
1600
2400
3200
4000
4800
5600
6400

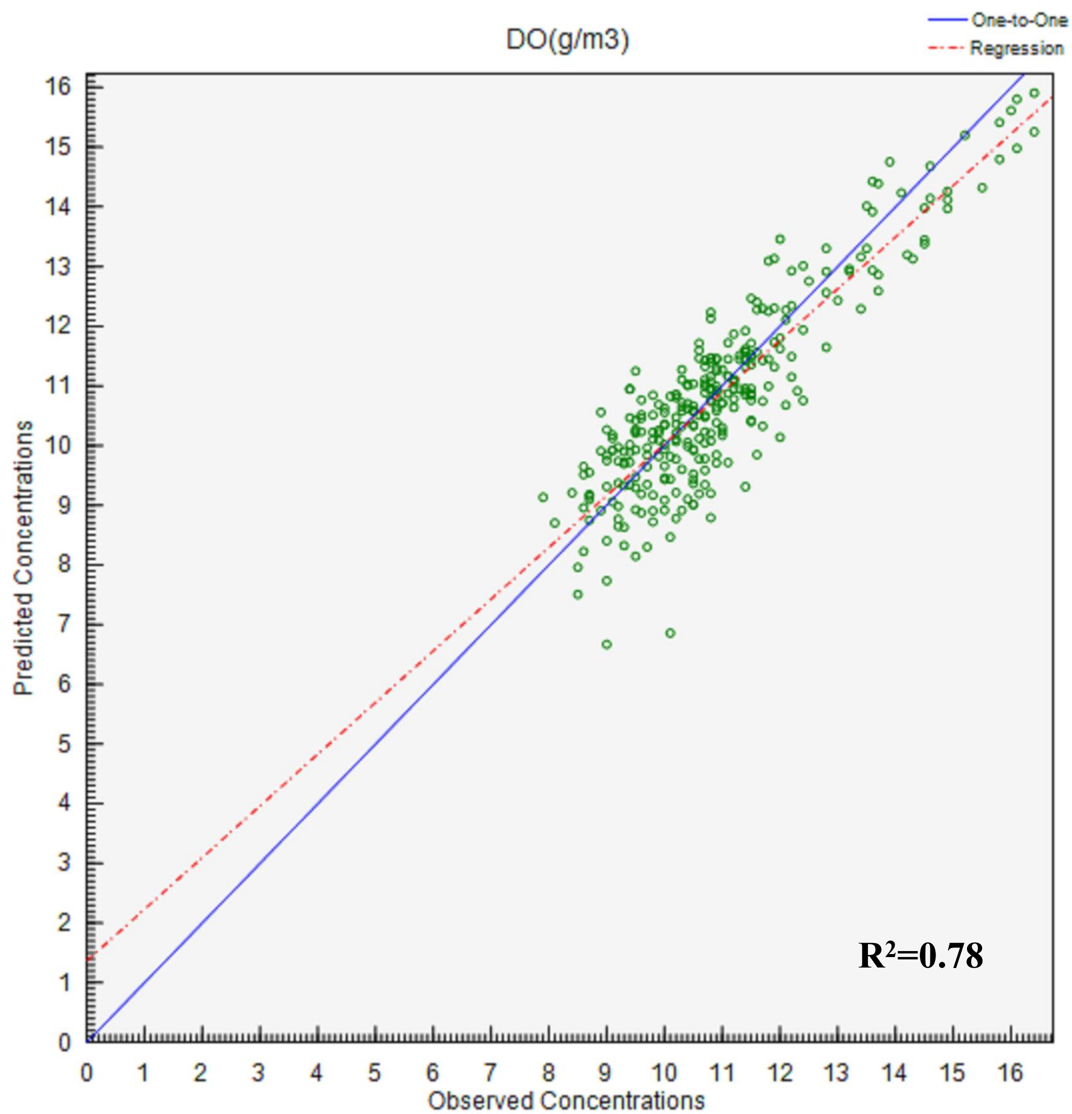

DRP(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
4
8
12
16
20
24
28
32
R²=0.99

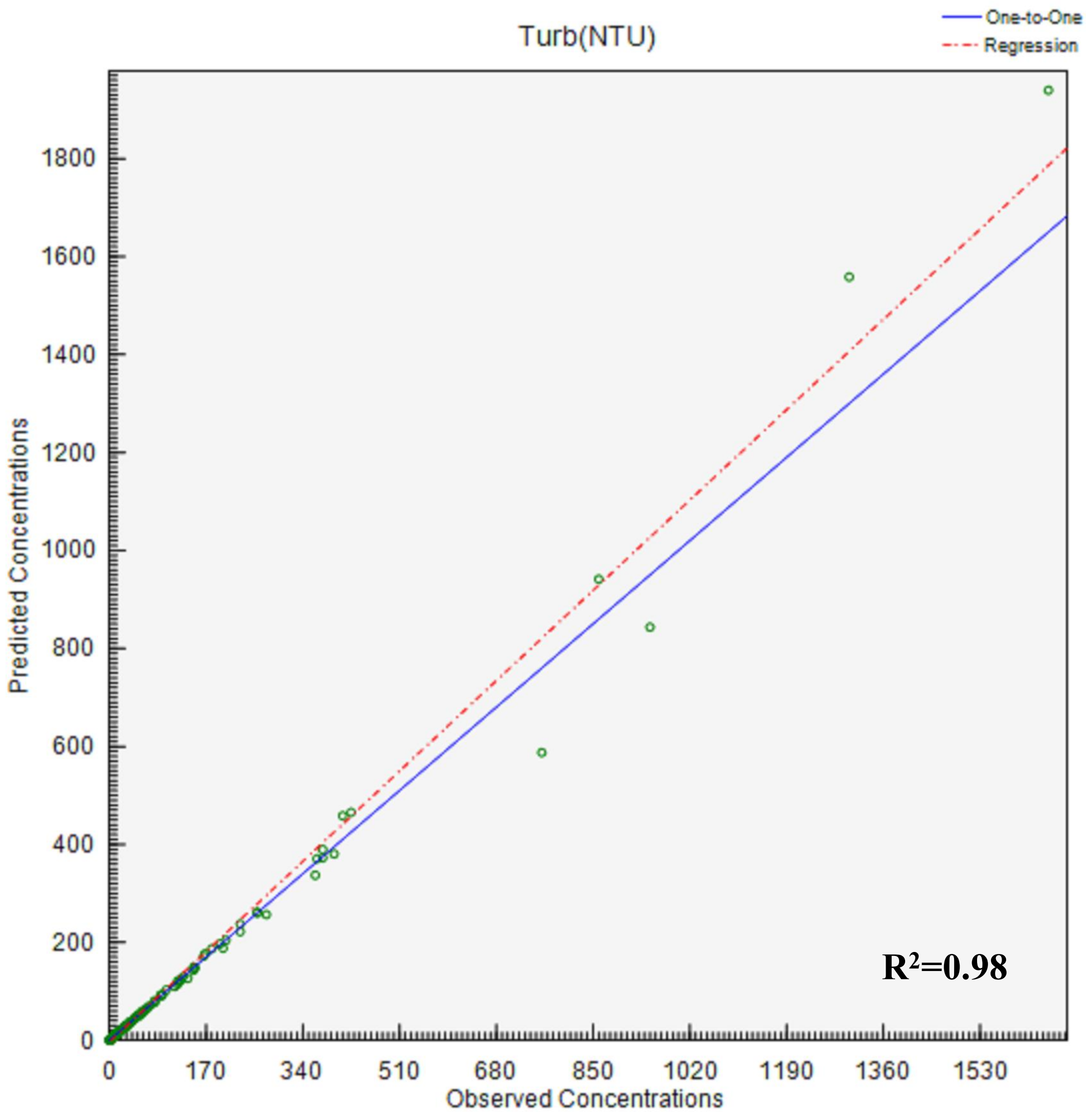

TP(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
500
1000
1500
2000
2500
3000
3500
4000
4500
0
900
1800
2700
3600
4500
5400
6300
7200
8100
R²=0.94

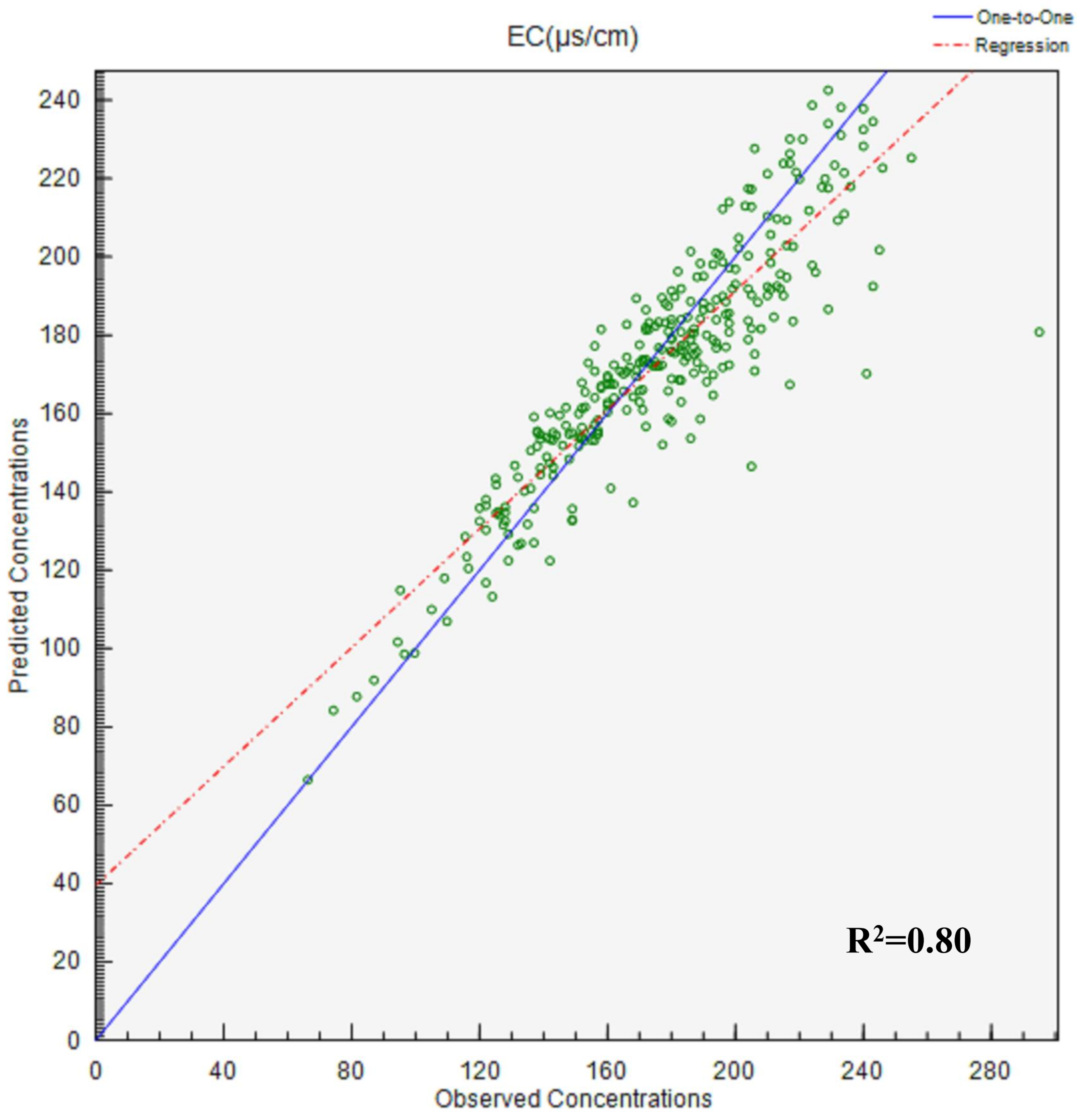

Abs
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.54
0
10
20
30
40
50
60
70
80
90
100
110
120

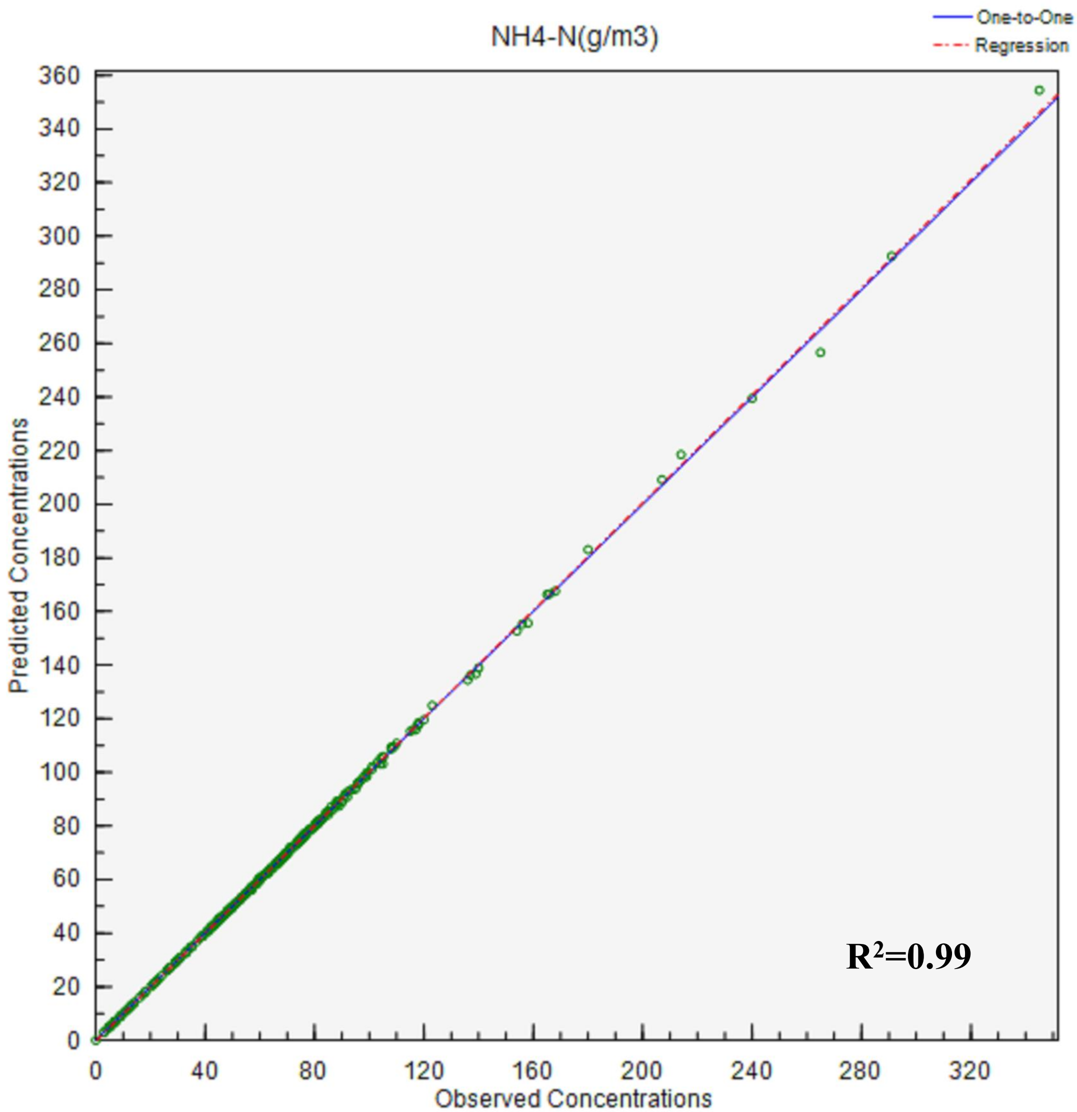
APPENDIX C

REGRESSION PLOT fOR SITE WA9 (DOWN STREAM) in the MANAWATU CATCHMENT

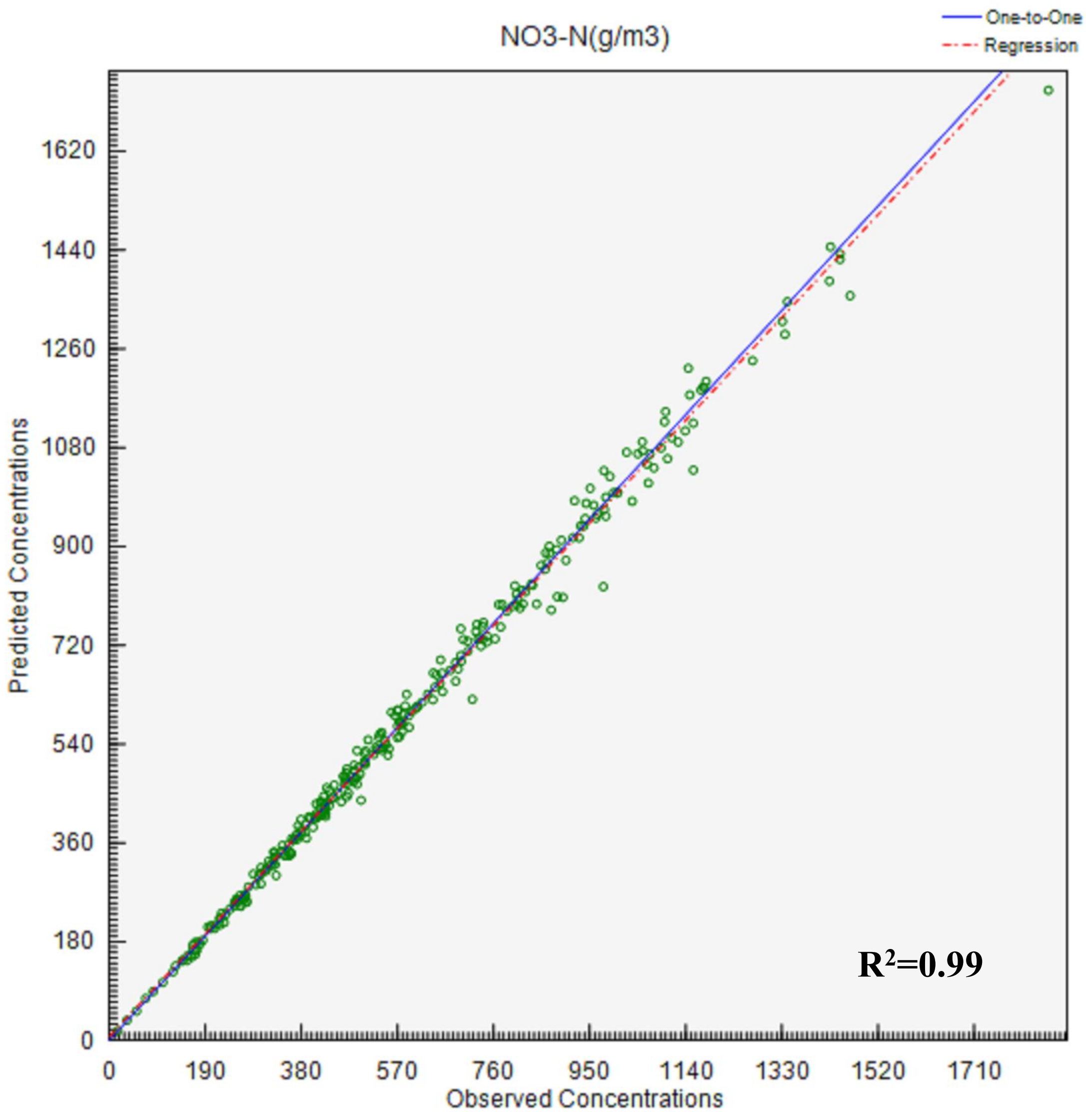


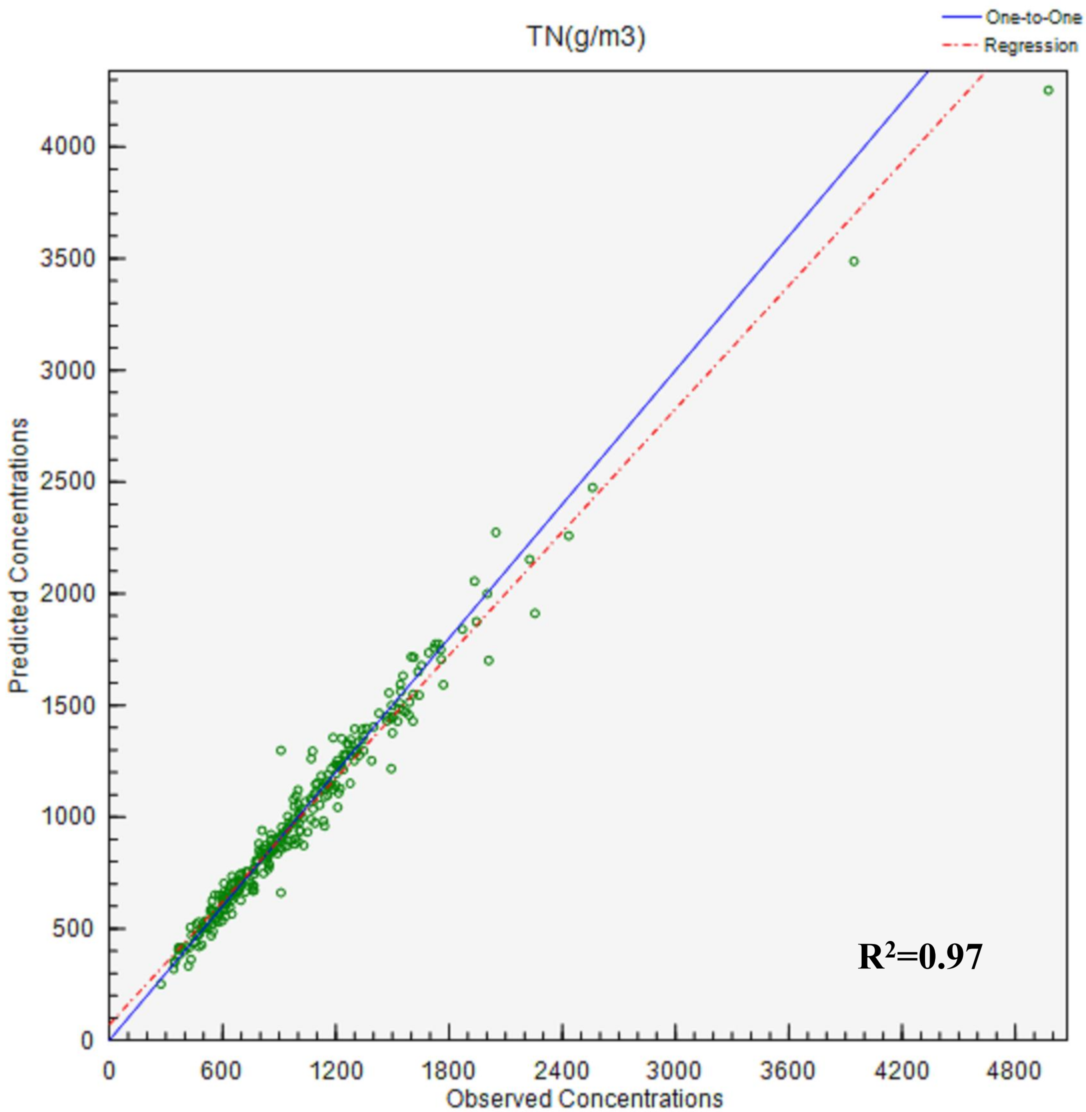

Turb(NTU)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
200
400
600
800
1000
1200
1400
1600
1800
0
170
340
510
680
850
1020
1190
1360
1530
R²=0.98

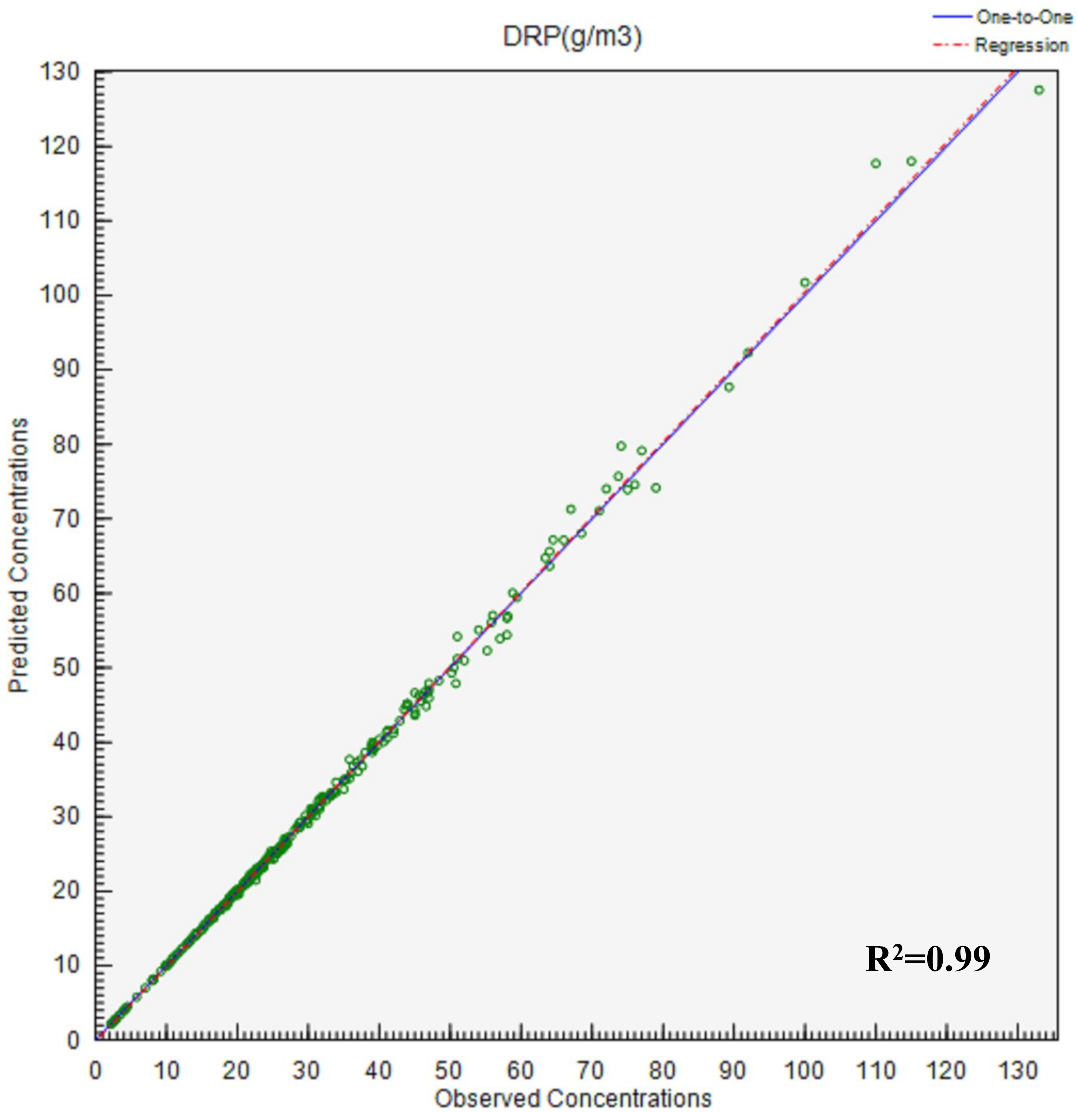

EC(µs/cm)
One-to-One
Regression
240
220
200
180
160
140
120
100
80
60
40
20
0
Predicted Concentrations
R²=0.80
0
40
80
120
160
200
240
280
Observed Concentrations



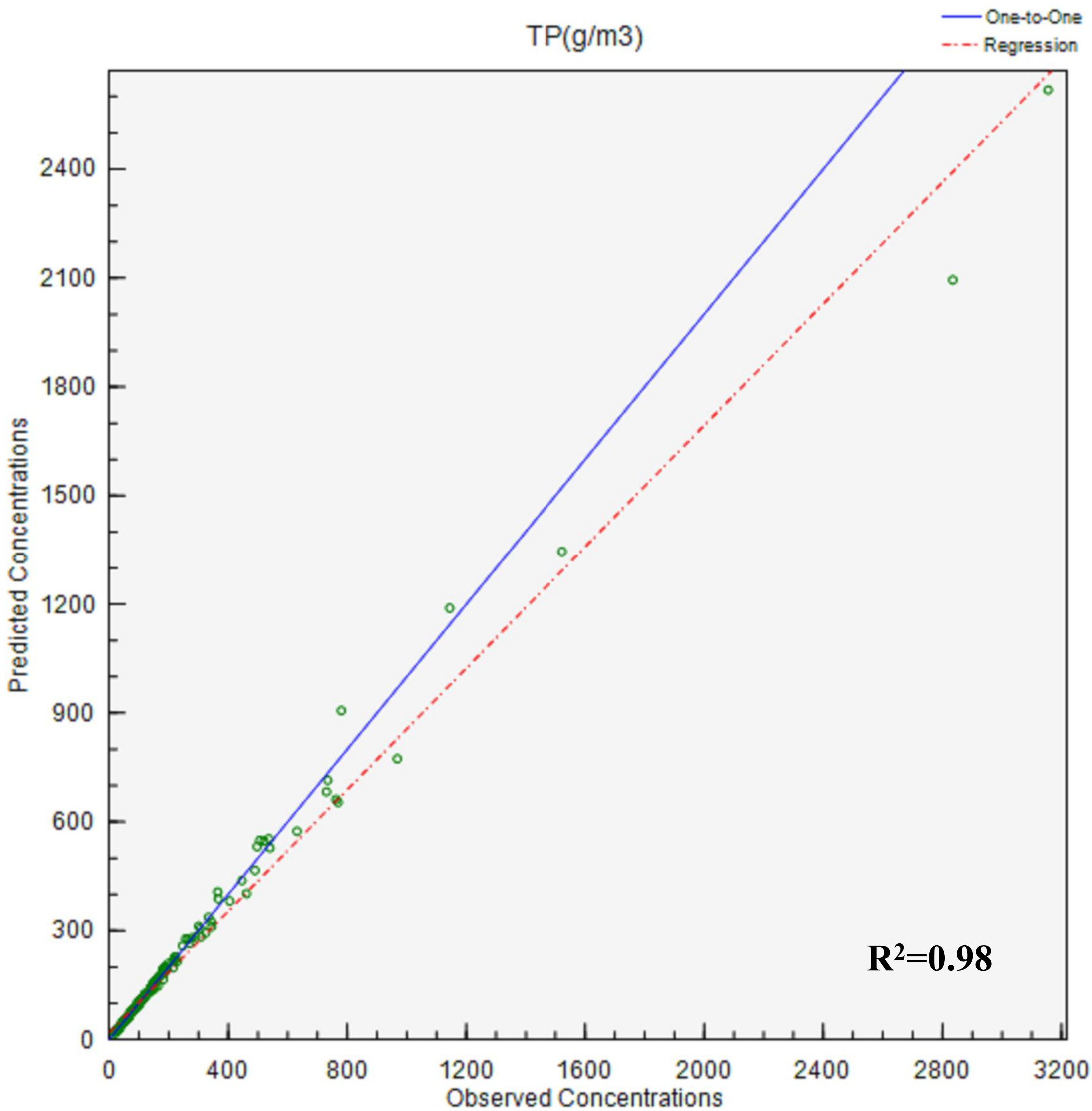
NH4-N(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R2=0.99


NO3-N(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
180
360
540
720
900
1080
1260
1440
1620
0
190
380
570
760
950
1140
1330
1520
1710
R2=0.99

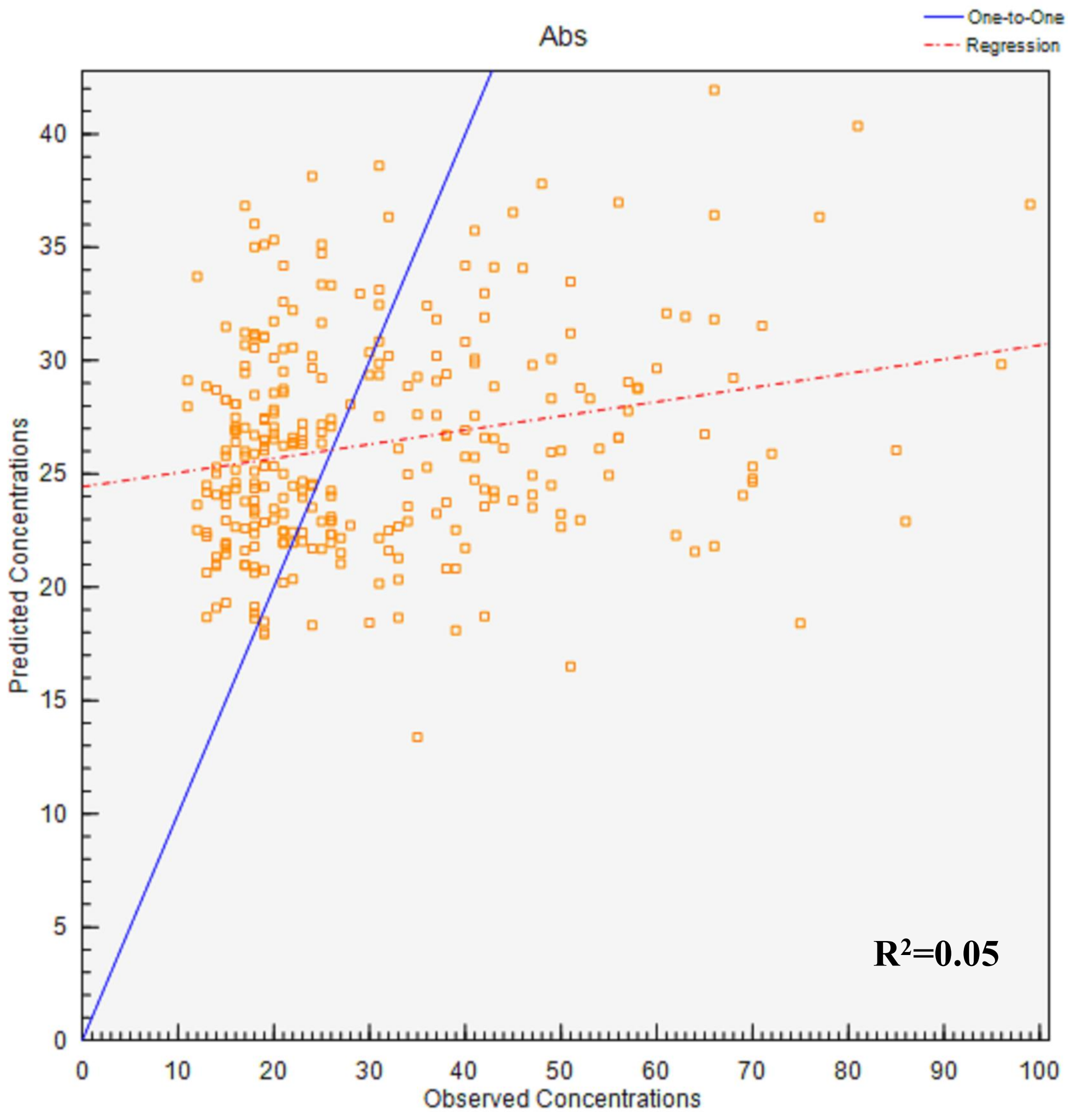

TN(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
R²=0.97



DRP(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
10
20
30
40
50
60
70
80
90
100
110
120
130
R²=0.99



TP(g/m3)
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
300
600
900
1200
1500
1800
2100
2400
0
400
800
1200
1600
2000
2400
2800
3200
R2=0.98


Abs
One-to-One
Regression
Predicted Concentrations
Observed Concentrations
0
5
10
15
20
25
30
35
40
0
10
20
30
40
50
60
70
80
90
100
R²=0.05

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