# Assessing the Role of Phosphorus as a Source Water and Treatment Vulnerability Indicator:

# Implications for Planning, Management and Operations

by

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# **Author's Declaration**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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### **Abstract**

Source water protection (SWP) refers to the pressing global need to address the combination of issues affecting water supply and treatment: water quality, water quantity and timing of availability. Although SWP has been increasingly advocated by drinking water professionals, tools to relate upstream land-use impacts to downstream water treatability are lacking. Treatment water quality metrics can seldom be used to decouple the cumulative water quality impacts of natural and anthropogenic land-use disturbances; moreover, some changes in source water quality that potentially compromise the effectiveness of treatment are not reflected by changes in magnitude of these treatment water quality metrics. This underscores the need for an effective vulnerability indicator: a metric for monitoring and assessing the susceptibility of a system to harm arising from source water quality changes. In this research, a proof-of-concept approach was used to evaluate phosphorus as an indicator for linking source water and treatment vulnerabilities in a forested watershed in Alberta, Canada.

Relationships between phosphorus and various water quality parameters were assessed using historical Elbow River discharge and Glenmore Reservoir water quality data from 2000 to 2010 to elucidate source water vulnerabilities. The results showed that allochthonous inputs from the Elbow River were the primary drivers of source water quality in the reservoir during significant hydrological events. Autochthonous processes such as dilution and deposition of allochthonous inputs in reservoir bottom sediments buffered water quality changes within the reservoir. Carbon:nitrogen:phosphorus (C:N:P) nutrient ratios observed in the reservoir were indicative of severe-to-moderate phosphorus-limitation for primary production. Although total phosphorus (TP) concentrations reached threshold levels for supporting mesotrophic to eutrophic conditions, primary production was limited. Consistently low reservoir chlorophyll-a levels and low dissolved phosphorus concentrations suggest that drinking water treatment impacts are unlikely to be confounded by the presence of algal matter.

The impacts of source water quality changes to drinking water treatability were inferred using historical source water quality data and treatment performance metrics at the Glenmore Water Treatment Plant (WTP) using forward-stepwise multiple linear regression. Raw water TP and total organic carbon (TOC) concentrations explained 78.8% of the coagulant dose variation used in coagulation and flocculation processes (n = 22). Additional plant water quality data and treatment

performance metrics were collected in 2012 to confirm these observations. Plant raw water UV-absorbance at 254 nm (UVA<sub>254</sub>) and TP concentrations described 98.3% of the alum coagulant dose variation used in the newly-installed Actiflo© ballasted-sand flocculation process (n = 26). SUVA and TP together explained 91.2% of the polymer dose variation (n = 26). The inclusion of TP as a significant predictor of coagulant and polymer doses, coupled with a review of literature, suggest that TP is a more sensitive indicator of waterborne particle concentrations present in the raw water than turbidity. Accordingly, TP may play a role in the critical drinking water treatment processes of coagulation, flocculation and clarification which has direct implications for process optimization, chemical coagulant costs, sludge production and impacts to subsequent treatment processes.

Scenario building based on anticipated land-uses and impacts from catastrophic landscape disturbances using the coagulant regression models was used to explicitly link potential source water quality impacts to drinking water treatability. The innovative approach of estimating land-use TP loading, steady state reservoir TP concentrations and coagulant dosing requirements at the WTP provides a framework that enables the development and coordination of land-use planning, reservoir management and drinking water treatment operations strategies respectively. Total phosphorus provides a common vulnerability metric relevant to both land-use and water managers for developing and assessing integrated land-use management and SWP strategies.

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# **Table of Contents**

List of Figures	viii
List of Tables	ix
Chapter 1: Introduction	1
1.1 Research motivation	1
1.2 Objectives	3
1.3 Thesis organization	4
Chapter 2: Literature review	5
2.1 Phosphorus as a source water and treatment vulnerability indicator	5
2.2 Water quality characterization for drinking water treatment	8
2.3 Conventional drinking water treatment processes	12
2.3.1.1 Pre-oxidation	12
2.3.1.2 Coagulation & flocculation	13
2.3.1.3 Filtration	17
2.3.1.4 Disinfection	18
2.3.1.5 Distribution system	19
2.4 Phosphorus as a water quality indicator	19
2.4.1.1 Phosphorus source	20
2.4.1.2 Phosphorus transport	25
2.4.1.3 Phosphorus fate in lacustrine/reservoir systems	26
2.4.2 Factors affecting source/transport/fate of phosphorus in freshwater and engineered treatment	
systems	28
2.4.2.1 Phosphorus response to hydrological events	28
2.4.2.2 Phosphorus adsorption to fine-grained sediments	29
2.4.2.3 Phosphorus-metal complexation/precipitation and adsorption	30
2.4.2.4 Primary productivity	33
2.4.2.5 Co-leaching with organic solutes in soils	36
2.4.3 Implications of landscape disturbances to drinking water treatment in forested watersheds	38
Chapter 3: Methods	40
3.1 Research approach	40
3.1.1 Watershed description	40
3.1.2 Glenmore Reservoir	43
3.1.3 Glenmore Water Treatment Plant	45
3.1.4 Watershed planning in Alberta, Canada	48
3.1.4.1 Environmental indicators for Bow River Basin monitoring	49
3.1.4.2 Phosphorus as an environmental indicator in the WSMP	50
3.2 Data analysis	50
3.3 Statistical methods	53
3.3.1 Evaluation of spatial and seasonal characteristics of source water quality	
3.3.2 Correlations between source water quality parameters	
3.3.3 Correlations between reservoir and treatment plant raw water quality	54

3.3.4 Multiple linear regression with treatment metrics	55
Chapter 4: Results and discussion	57
4.1 Source water quality characterization	57
4.2 Spatial and temporal water quality trends (2000-2010)	57
4.3 Source water vulnerability assessment using historical data (2000-2010)	60
4.3.1 Phosphorus relationships with significant hydrological events	60
4.3.2 Phosphorus and suspended sediment relationships	64
4.3.3 Primary production	66
4.4 Relationship between reservoir and plant raw water quality	69
4.5 Phosphorus as a treatment vulnerability indicator	70
4.5.1 Coagulation and flocculation	70
4.5.2 Chemical oxidation	82
4.5.3 Filtration	83
4.5.4 Disinfection by-products	84
Chapter 5: Implications for watershed planning, reservoir management and treatment operations	87
5.1 Phosphorus as a source water and treatment vulnerability indicator	87
5.1.1 Implementation within Watershed Management Plans	88
5.1.1.1 Urban development (growth) scenario	89
5.1.1.2 Catastrophic landscape disturbance scenario	92
Chapter 6: Conclusions and implications	94
6.1 Conclusions	94
6.1.1 Phosphorus as a source water vulnerability indicator	94
6.1.2 Phosphorus as a treatment vulnerability indicator	95
6.2 Implications for planning, management and operations	96
References	97
Appendix A: Glenmore WTP water quality sampling (2012)	123
Appendix B: Elbow River & Glenmore Reservoir water quality, by location (2000-2010)	125
Appendix C: Glenmore Reservoir spatial water quality analysis (2000-2010)	134
Appendix D : Glenmore Reservoir water quality data, by month (2000-2010)	139
Appendix E : Glenmore WTP water quality data (2012)	148
Appendix F: SPSS multiple linear regression summaries.	151

# **List of Figures**

Figure 2.1 Phosphorus: a potential water quality indicator for linking source water and treatment
vulnerabilities
Figure 2.2 Typical process train for surface water treatment using conventional treatment
Figure 3.1 Elbow River watershed
Figure 3.2 Bathymetry, shoreline features and compartments in the Glenmore Reservoir44
Figure 3.3 Glenmore WTP Process Flow Diagram
Figure 3.4 Conceptual map of research approach
Figure 4.1 Elbow River discharge phosphorus concentrations (2000-2010)
Figure 4.2 Glenmore Reservoir phosphorus concentrations (2000-2010)
Figure 4.3 Relationship between river discharge at Weaselhead bridge and TP (2000-2010)
Figure 4.4 Relationship between Elbow River discharge at Weaselhead bridge and Glenmore Reservoir
TP (2000-2010)63
Figure 4.5 Relationship between Elbow River discharge TSS and TP (2000-2010)
Figure 4.6 Relationship between Glenmore Reservoir turbidity and TP (2000-2010)
Figure 4.7 Nutrient conditions, productivity in Glenmore Reservoir (2000-2010)
Figure 4.8 Relationships between Glenmore Reservoir phosphorus concentrations and chlorophyll-a
(2000-2010)
Figure 4.9 Relationship between alum dose and raw water quality parameters (2012):76
Figure 4.10 Relationship between raw water SUVA and DOC removal by Actiflo© at Glenmore WTP
(2012)79
Figure 4.11 Relationship between polymer dose and raw water quality parameters (2012):81
Figure 5.1 Relationship between mean reservoir TP concentration and predicted mean alum dose91
Figure 5.2 Historical monthly mean discharge (1967-1977)
Figure 5.3 Relationship between extrapolated landscape disturbance reservoir TP concentrations and
predicted mean alum dose

# **List of Tables**

Table 2.1 Key water quality thresholds associated with surface water treatment process select	ion and
design (MWH, 2012)	8
Table 2.2 Common water quality parameters for drinking water treatment	10
Table 2.3 Pre-oxidation effects: speculative mechanisms	15
Table 2.4 Selection of commonly used coagulants	17
Table 2.5 Empirical watershed TP yield coefficients	21
Table 2.6 Summary of post-fire exports of phosphorus in catchment-scale forested watersheds	23
Table 2.7 Factors affecting source, transport and fate of phosphorus in aquatic systems: implicat	ions for
source water and treatment	29
Table 2.8 Reported Carbon:Phosphorus molar ratios in freshwater lentic systems	35
Table 2.9 Documented algal and/or primary productivity impacts of phosphorus on drinkin	g water
treatment processes	36
Table 2.10 Land-use water quality impacts	38
Table 2.11 Impact of land-use change on water parameters, by basin size	39
Table 3.1 Characteristics of Elbow River Watershed	40
Table 3.2 Characteristics of Glenmore Reservoir	45
Table 3.3 Water quality objectives in the Elbow River	50
Table 3.4 Elbow River discharge, Glenmore Reservoir water quality parameters (2000-2010)	51
Table 3.5 Glenmore WTP raw water quality data (2000-2010)	53
Table 3.6 Available treatment process performance metrics at the Glenmore WTP	53
Table 4.1 Reservoir water quality summary statistics (2000-2010)	59
Table 4.2 Simple linear models of corresponding water quality parameters (2000-2010)	69
Table 4.3 Summary of coagulant dose regression models (2000-2010)	71
Table 4.4 Summary of alum coagulant dose regression models (2012)	72
Table 4.5 Estimated particle and NOM charge demand	
Table 4.6 Summary of polymer dose regression models (2012)	79
Table 4.7 Summary of pre-treatment chlorine dose regression models (2012)	83
Table 4.8 Summary of filter run-time regression models (2000-2010)	84
Table 4.9 Summary of TTHM regression models (2000-2010)	85
Table 4.10 Summary of HAA regression models (2000-2010)	85
Table 5.1 Estimated and projected mean annual phosphorus yields	91
Table 5.2 Vollenweider estimate of Reservoir TP concentrations based on land-use TP yields	91
Table A.1 Schedule of water quality analyses (2012)	124
Table C.1 Kruskal-Wallis tests for water quality spatial differences by month (2000-2010)	135
Table C.2 Kruskal-Wallis tests for water quality differences attributable to depth, by month	137
Table C.3 Water quality parameters exhibiting variability due to sample depth	138
Table E.1 Phosphorus concentrations at Glenmore WTP	
Table E.2 Turbidity at Glenmore WTP	
Table E.3 Organic carbon concentrations at Glenmore WTP	149
Table E.4 pH at Glenmore WTP	149

Table E.5 Raw water conductivity at Glenmore WTP	149
Table E.6 Raw water color at Glenmore WTP	. 150
Table E.7 Raw water Specific Ultraviolet Absorbance at Glenmore WTP	. 150
Table E.8 Raw water UVA <sub>254</sub> at Glenmore WTP	. 150
Table E.9 Raw water metal concentrations at Glenmore WTP	. 150
Table E.10 Coagulant (alum dose, mg/L) at Glenmore WTP	. 150
Table E.11 Polymer dose (mg/L) at Glenmore WTP	. 150
Table E.12 Pre-treatment chlorine dose (mg/L) at Glenmore WTP	150

## **Chapter 1: Introduction**

### 1.1 Research motivation

Since 2008, source water protection (SWP) has been identified as a top priority by North American drinking water treatment professionals (Runge & Mann, 2008; Mann & Runge, 2010; Murphy, 2012). This likely is related to the pressing global need to address a combination of issues that directly affect and potentially threaten drinking water supply and treatment: water quality, water quantity and timing of availability (Emelko, Silins, Bladon & Stone, 2011). The quality and quantity of water supplies generally reflect dominant upstream land uses (Arbuckle & Downing, 2001; Carpenter *et al.*, 1998; Crosbie & Chow-Fraser, 1999). Although SWP has been increasingly advocated by drinking water professionals (Postel & Thompson, 2005), tools to relate upstream land-use impacts to downstream water treatability are lacking (Emelko *et al.*, 2011). Water quality metrics and analysis tools can seldom be used to decouple the cumulative water quality impacts of various natural and anthropogenic disturbances (Schindler, 2001); moreover, some changes in source water quality that potentially compromise the efficacy of drinking water treatment processes are not always discernable with commonly utilized water quality metrics (Emelko *et al.*, 2011).

Forested watersheds typically provide high quality source water; however, a wide range of natural and anthropogenic landscape disturbances have the potential to substantially deteriorate source water quality in these environments (Delpla, Jung, Baures, Clement & Thomas, 2009). While some efforts to mitigate or minimize landscape disturbances in critical drinking watersheds exist (Anderson & Hoover, 1975 Gullick, 2003), inappropriate land-use planning practices also may exacerbate disturbance impacts and further deteriorate water quality, thereby impacting downstream water uses (Frederick, 1993). For example, water quality may deteriorate beyond key thresholds, thereby requiring some water users to incur additional drinking water treatment costs that may include the need for extensive infrastructure upgrades (Clark & Morand, 1981; Emelko *et al.*, 2011; Goodrich, Adams, Lykins & Clark, 1992). In some circumstances, the marginal cost of treatment for the continued provision of safe drinking water may substantially exceed the costs of appropriate land-use management and planning.

The ultimate goal of drinking water treatment is to produce chemically and microbiologically-safe drinking water by removal of solids and/or natural organic matter and subsequent disinfection (MWH,

2012). Turbidity arising from waterborne solids and natural organic matter influences disinfection efficiency and acts as a potential carrier of pathogens and other contaminants (LeChevallier & Au, 2004; LeChevallier, Evans & Seidler, 1981). Natural organic matter (NOM), which includes a suite of organic compounds generated by biological processes both in a water body (autochthonous material) and in the surrounding watershed (allochthonous material) along with anthropogenic organic compounds (Crouè, Korshin & Benjamin, 2000), has numerous impacts on water treatment. Specifically, it 1) impedes flocculation/coagulation processes (Chow *et al.*, 1999), 2) shields pathogens from disinfection (Geldreich, 1989), 3) drives oxidant demand (Gallard & von Gunten, 2002), 4) acts as a precursor for disinfection by-product (DBP) formation (Becher, 1999; Matsuda *et al.*, 1992; Peters, Young & Perry, 1980), 5) provides potential carbon sources for bacterial regrowth in distribution systems (Escobar, Randall & Taylor, 2001; Huck, 1990; Miettinen, Vartiainen & Martikainen, 1997), and 6) potentially degrades finished water quality aesthetics (Gopal, Tripathy, Bersillon & Dubey, 2007; Guo & Ma, 2011). Accordingly, knowledge of the source and character of turbidity and NOM informs and often defines treatment process selection and design. It also informs appropriate source water protection measures.

Water resource planning and management activities have been extensively conducted at the watershed scale to enable the coordination of landscape activities and their impacts on downstream water uses (Loucks, 1998; Weber & Hufschmidt, 1963). Nonetheless, a continued challenge to this coordination is the lack of vulnerability metrics relevant for both land-use and water managers. Land-use impacts on key water quality parameters pertinent to drinking water treatment (i.e. turbidity and NOM loading) often are indiscernible at the scales at which typical planning and management activities are undertaken (Food and Agriculture Organization [FAO], 2001). At large spatial scales, the relationships between landscape activities and water quality impacts are confounded by the cumulative effects of multiple stressors (Reid, 1993).

To better enable an integrated approach to SWP, a vulnerability indicator that links landscape activity and water treatability is desirable. Ideally, such an indicator would be easy and inexpensive to analyze while reflecting water quality degradation associated with landscape activity and indicating the relative treatability of source waters for potable water production. Nutrients (and specifically phosphorus) represent a potential source water and treatment vulnerability indicator.

Land-use impacts on nutrient concentrations in source waters have been generally discernable at watershed-scales (FAO, 2001). Catchment exports of nutrients are strongly associated with land use and population density (e.g. Carpenter *et al.*, 1998) and a broad range of best management practices have been developed and implemented to reduce land-use impacts on nutrient export to receiving waters. Moreover, nutrients are often associated with turbidity and NOM in source waters. In particular, phosphorus is commonly sediment-associated, engages in complexation-precipitation and adsorption-desorption reactions with metals and is usually the limiting nutrient for primary production in freshwater systems. Phosphorus also is easily measured using standardized analytical methods. However, as phosphorus does not drive drinking water treatment process design, it has seldom been investigated for characterizing drinking water treatment vulnerabilities.

This thesis evaluates and demonstrates the potential role of phosphorus as both an indicator of source water vulnerability and drinking water treatability. A case study investigating a forested watershed located in Alberta, Canada is used as a proof-of-concept demonstration of the potential application of this water quality metric as a source water and treatment vulnerability indicator. The completed assessment presented herein explicitly links upstream landscape impacts on water quality to downstream drinking water treatability. The framework enables the development of improved landuse planning and reservoir management strategies and could serve as a template for subsequent modification and application to a broader range of water uses to better inform integrated SWP and water management.

# 1.2 Objectives

The overall goal of this research was to examine phosphorus as a source water and treatment vulnerability indicator to connect upstream land-use disturbances in a watershed to downstream drinking water treatability impacts. Specific objectives of the research in support of this goal were:

- 1. To develop a conceptual model linking source water quality impacts and drinking water treatment processes through a literature review of the potential factors and mechanisms affecting the source, fate and transport of phosphorus.
- 2. To evaluate phosphorus as a source water vulnerability indicator and evaluate the potential links between phosphorus and drinking water treatability.

3. To discuss potential implications of phosphorus as a source water and treatment vulnerability indicator for land-use planning, reservoir management and treatment operations.

## 1.3 Thesis organization

This thesis is organized in the following manner:

- Chapter 2 provides a brief literature review of phosphorus source, transport and fate in aquatic systems and its implications to drinking water treatability;
- Chapter 3 describes the research approach and methods used herein;
- Chapter 4 presents the source and treated water quality data and WTP operational data from the Elbow River discharge, Glenmore Reservoir and Glenmore Water Treatment Plant (WTP);
- Chapter 5 provides an evaluation of phosphorus as a potential source water and treatment vulnerability indicator and implications for watershed planning, reservoir management and treatment operations; and
- Chapter 6 provides conclusions and recommendations for further research.

## **Chapter 2: Literature review**

# 2.1 Phosphorus as a source water and treatment vulnerability indicator

Vulnerability can be defined as the "susceptibility to harm from exposure to stresses associated with environmental change...and from the absence of capacity to adapt" (Adger, 2006) whereas vulnerability indicators are metrics used to monitor and assess the extent of susceptibility. Therefore, phosphorus can be considered a source vulnerability indicator for freshwater systems: increased phosphorus loading to a water source often results from land-use changes (Rast & Lee, 1978; Reckhow & Chapra, 1983) and its abundance in receiving freshwaters is indicative of heightened susceptibility to eutrophication (Schindler, 1977). This can lead to augmented ecosystem structure and dynamics, increases in source water turbidity, more organic matter build-up in bottom sediments and loss of oxygen in the water column (Canadian Council of Ministers of the Environment [CCME], 2004). Anoxic conditions at the sediment-water interface arising from decomposing organic matter further promotes the release of sediment- and organic-bound phosphorus back into the water column (Correll, 1998), exacerbating the problem of eutrophication (CCME, 2004). An increase in river discharge and reservoir phosphorus concentrations is also suggestive of increased sediment loading that has long-term implications for reservoir capacity (e.g. Hollingshead, Yaremko & Neill, 1973) as phosphorus is commonly associated with particulate contaminants (e.g. metals and NOM) (e.g. Blake et al., 2010; Meybeck, 1982).

Water quality parameters such as turbidity, dissolved organic carbon and colour play a significant role in the selection, design and optimization of treatment processes (MWH, 2012); however, they are poor source water vulnerability indicators as they cannot be relied upon quantitatively to monitor or assess environmental changes at the watershed scale (FAO, 2001). Moreover, some changes in source water quality (e.g. source or character) have a substantial impact on treatment efficacy, yet cannot be reflected by changes in the magnitude of these water quality parameters. In this research, phosphorus is hypothesized to be a good drinking water treatment vulnerability indicator in addition to its known, extensive use as a source water vulnerability indicator (Figure 2.1). Historically, phosphorus has not been considered a treatment vulnerability indicator because of a lack of 1) apparent impact on treatment processes and 2) risk to public health (CCME, 2004).

The purpose of this review of literature is to develop a conceptual model linking source water quality impacts to drinking water treatment processes (Figure 2.1). First, an overview of water quality impacts to conventional drinking water treatment processes is described (Figure 2.1 "A"). Second, factors affecting the source, fate and transport of phosphorus that can be used to infer source water quality changes are examined to elucidate potential drinking water treatment implications (Figure 2.1 "B"). Finally, factors of direct relevance to source waters derived from forested watersheds are highlighted to explore the implications for land-use planning, reservoir management and treatment operations (Figure 2.1 "C").

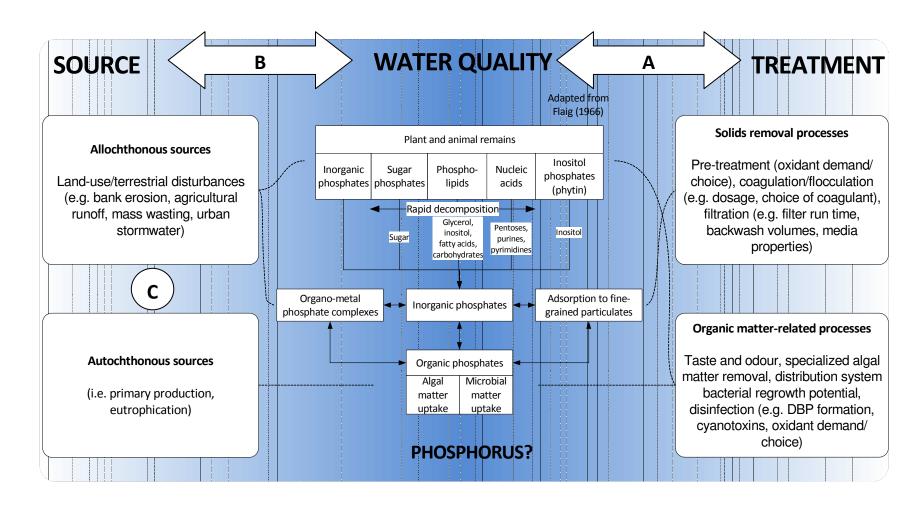


Figure 2.1 Phosphorus: a potential water quality indicator for linking source water and treatment vulnerabilities

## 2.2 Water quality characterization for drinking water treatment

The goal of drinking water treatment is to achieve water quality that meets established goals or standards through the removal of waterborne chemicals (e.g. inorganic ions, dissolved organics), solids (e.g. colloids, silt) and biological matter (e.g. bacteria, protozoa) (MWH, 2012). Source water quality is a critical determinant in the selection, design and optimization of drinking water treatment processes (MWH, 2012); water quality-based threshold values and ranges form the basis for water treatment process selection and design (Table 2.1). Some source water quality changes (i.e. changes in contaminant character) that substantially impact drinking water treatment needs are not reflected by changes in the magnitude of these water quality parameters (Table 2.2), however (Emelko *et al.*, 2011). The need for understanding such shifts in source water quality has led to the development of various technologies and approaches for further characterization of some aspects of water quality, especially those that drive surface water treatment process selection and design (e.g. turbidity, DOC) (Bridgeman, Bieroza & Baker, 2011; Emelko *et al.*, 2011; Sharp, Jarvis, Parsons & Jefferson, 2006).

Table 2.1 Key water quality thresholds associated with surface water treatment process selection and design (MWH, 2012)

Process	Turbidity (NTU)	Color (color units)	Dissolved Organic Carbon (mg/L)	
Conventional	High > 20 NTU	High > 20 c.u.	High > 4 mg/L	
Direct/inline filtration	Low ≤15 NTU	Moderate-low ≤ 20 c.u.	Low < 4 mg/L	
Microfiltration	Low ≤10 NTU	Moderate-low ≤10 c.u.	Low < 4 mg/L	

Turbidity is an indirect measure of a water matrix's particulate and dissolved constituents based on the ability of these constituents to scatter light (American Public Health Association [APHA], 2006). Although turbidity is not a direct measurement of these constituents, it has been extensively used in dictating the type and extent of drinking water treatment required prior to disinfection as it can be continuously monitored. The constituents comprising turbidity can interfere with disinfection, be a source of pathogens and also shield pathogens from disinfection (LeChevallier, Evans & Seidler, 1981). It is one of the least expensive and more effective methods for extrapolating suspended solids concentrations in the water (Gippel, 1995; Marttila & Kløve, 2012 Packman, Comings & Booth, 1999; Sidle & Campbell, 1985) and is not bound by the size-exclusion basis of Total Suspended Solids (TSS) analytical methods. However, water temperature, shape, size and mineral composition of particles (Clifford, Richards, Brown & Lane, 1995; Gippel, 1995) and water color imparted by

dissolved solids (Malcolm, 1985) may confound turbidity's overall relationship with TSS and/or ability to reflect the abundance of suspended and colloidal particles in the water matrix. Further analysis of turbidity has been limited to size distribution techniques such as particle size analysis through dynamic light scattering (Seaman & Bertsch, 1997; Urban & Schurtenberger, 1998) and optical imaging (Xu, 2001), or characterized as other aggregate aquatic properties such as surface charge and zeta-potential. While the latter properties provide additional insight for optimization of some treatment processes, they provide little insight pertaining to the sources from which or processes because of which the suspended particulate matter originated.

Dissolved organic carbon (DOC) comprises the majority of NOM measured as total organic carbon (TOC) in natural freshwater systems (Schlesinger & Melack, 1981; Wetzel & Rich, 1973). In drinking water treatment, organic solutes are generally more difficult to remove than their particulate counterparts and act as precursors of disinfection-by-products, increase oxidant demand, induce flocculation inefficiencies, promote bacterial re-growth in drinking water distribution systems and may degrade potable water aesthetics (taste/odour) (e.g. Matilainen, Vepsäläinen & Sillanpää, 2010). Natural organic matter (NOM) characterization approaches are limited by the diversity and labile nature of NOM, resulting in the lack of standard analytical methods that yield reproducible results (Guo & Ma, 2011; Leenher, 1985; Matilainen et al., 2011; Owen et al., 1995). In the last few decades, there has been an overwhelming focus on NOM characterization techniques. Specific UV-absorbance at 254 nm (SUVA) has been a common approach for attempting to predict NOM removal during drinking water treament based on carbon aromaticity in water samples (Traina, Novak & Smeck, 1990; Weishaar et al., 2003), SUVA values > 4 indicate mainly hydrophobic NOM forms and higher aromaticity, whereas SUVA values < 3 indicate mainly hydrophilic materials (Edzwald and Tobiason, 1999). NOM compounds consisting of light-absorbing chemical structures (e.g. aromatic rings) have been deemed to be more reactive and therefore more likely to act as precursors for regulated DBPs (Reckhow, Singer & Malcolm, 1990; Singer, 1999).

*Table 2.2 Common water quality parameters for drinking water treatment* (adapted from Edzwald, Becker & Wattier, 1985)

Water Quality	Measurement	Advantages	Disadvantages				
Parameter Solids/organic matter removal							
Turbidity	Measure of relative clarity of water; indirect surrogate measure of suspended particles; turbidity character determines chemical disinfectant demand and DBP formation potential <sup>1</sup> ; traditional parameter to measure water treatment plant performance		Non-specific; optical measurement may not be reflective of TSS or colloidal content; character of turbidity unknown				
Color	Surrogate measure of humic matter; secondary standard of 15 Pt-Co units; no standard instrumental method of measurement; traditional aesthetic parameter	Online, continuous monitoring available; easy to measure	Non-specific				
тос	Collective measure of (particulate and dissolved fractions) organic matter	DOC comprises the majority of TOC; key driver of coagulant dose and	Non-specific; aggregate measure unable to capture character of NOM				
DOC Primary driver of coagulant dosage and performance; collective measure of dissolved organic matter		aggregate measure of magnitude of organic matter present					
UV-absorbance at 254 nm (UVA <sub>254</sub> )	UV-absorbance of a water sample at a given wavelength (typically 254 nm); measure of the aromatic content of a sample	Provides some indication of TTHM formation; easy to monitor	Little relevance to unregulated DBPs; not a good surrogate measure of DOC removal for processes that selectively remove non-aromatic fractions				
Specific UV absorbance (SUVA)  UVA <sub>254</sub> normalized by DOC; surrogate measure for estimating proportion of dissolved aromatic content		Estimates relative contribution of aromatic vs. hydrophilic content of organic matter; easy to monitor	Unable to provide information about reactivity of DOC derived from different types of source materials				
Disinfection Efficac	у	1	I.,				
Total Trihalomethanes (TTHM), Haloacetic acid (HAA) formation potential	Indirect measure of THM and HAA precursors; no standard on precursors; some standards on THMs formed	Indication of maximum THM and HAA formation	No standards on precursors and/or unregulated DBPs				
Coliforms	Indicator of the presence of microorganisms and the effectiveness of disinfection. May be used with other microbiological indicators for fecal contamination ( <i>E. coli, Enteroccocci</i> ).	Rapid presence/absence tests available	Irrelevant to solids and natural organic matter removal from the raw water				

Water colour has been loosely associated as a surrogate measure of NOM. It has been used to discern the contribution of humic and fulvic acids present in the water matrix (Frimmel, 1998; Hem & Efraimsen, 2001; Hongve, Riise & Kristiansen, 2004; Volk, Dundore, Schiermann & LeChevallier, 2002). Recent development of easy operation, high sample throughput and high sensitivity fluorescence spectroscopic, chromatographic and mass-spectrometric methods (Jaffe et al., 2004; Fellman, Hood & Spencer, 2010; Matilainen et al., 2011) has resulted in increased use of these methods to measure average optical and/or mass properties of NOM samples. However, these approaches must be used cautiously to infer the composition and reactivity of NOM. Variable reactivity of NOM species has been observed for samples exhibiting similar average properties using these methods (Weishaar et al., 2003). Some methods, such as fluorescence spectrophotometry, are also easily influenced by environmental factors such as temperature, oxygen concentration, extreme pH, spectral interference or metal quenching and only may be indicative of the small fluorescent fraction of the organic matter present (Fellman et al., 2010). Additional applicability studies of novel NOM characterization methods in freshwater environments are still necessary as these techniques have been applied predominantly in marine and coastal environments (Hudson, Baker & Reynolds, 2007).

Ecological and biogeochemical approaches to characterize source water have provided some useful insights into the source and character of NOM. Algal-dominated systems have exhibited fulvic acid properties consistently different from those in systems dominated by organic inputs from plants and soils (Malcolm, 1990; McKnight & Aiken, 1998). Using carbon isotope signatures ( $\delta^{13}$ C values), fulvic acids from plant/soil-derived organic carbon sources typically contained less  $^{13}$ C than other colloidal organic materials (Schiff *et al.*, 1990). The absence of nitrogen and presence of aromatic rings in lignaceous material, an important constituent of wood/plant detritus, has also led to the speculation that systems with terrestrially-dominated (allochthonous) inputs of organic matter have characteristically higher C:N atomic ratios (Hecky, Campbell & Hendzel, 1993; Wetzel, 1975) and higher aromatic carbon to aliphatic carbon ratios (McKnight & Aiken, 1998). Carbon-14 ( $^{14}$ C) dating has also been used to evaluate organic carbon age, which may allude to the organic carbon source but requires system-specific interpretation (Malcolm, 1990; Stevenson 1985; Thurman, 1985). These methods and approaches require extensive data collection and validation of source-character relationships and are therefore impractical for source water characterization.

## 2.3 Conventional drinking water treatment processes

Conventional treatment, direct filtration, in-line filtration and membrane filtration are four types of drinking water treatment process trains used for drinking water treatment (MWH, 2012). In Canada, conventional water treatment plants (Figure 2.2) are the most widespread type of treatment infrastructure used for surface water treatment (Statistics Canada, 2013). When mechanical mixers are employed in conventional treatment, their hydraulic stability generally affords more operational flexibility than other treatment processes (MWH, 2012).

Conventional treatment process trains include coagulation, flocculation, clarification (typically sedimentation), granular media filtration and disinfection (MWH, 2012). Since the discovery of DBP formation from chlorination processes, pre-treatment chlorination/pre-oxidation has been less widely employed as part of the conventional treatment process configuration (Matilainen *et al.*, 2010). The following sections describe the contribution of each process to produce safe drinking water and highlights how source water quality changes may impact its effectiveness and/or efficiency. Additional detail is available in *Water Treatment: Principles and Design* (MWH, 2012).

#### 2.3.1.1 Pre-oxidation

Pre-oxidation of raw water has been used to enhance the performance of subsequent particle separation processes in drinking water treatment (Jekel, 1998; MWH, 2012). This is achieved by the oxidization of organic compounds, inhibition of algal/biofilm growth, elimination of phenols (thereby controlling odors) and co-precipitation of heavy metal ions (Ma & Liu, 2002; MWH, 2012). Often, low oxidant doses have aided the removal of turbidity whereas higher doses have increased residual turbidity (e.g. Reckhow, Singer & Trussell, 1986). Its effectiveness has been particularly evident in organic/algal rich raw waters at low dosages (Jekel, 1998). However, since the discovery of DBP formation from chlorination processes, chlorine has been less widely-applied as a pretreatment oxidant (Matilainen *et al.*, 2010), especially when high concentrations of DBP precursors are still present. Ozonation has become the preferred alternative to chlorination prior to coagulation. Despite the potential for less DBP formation, the effectiveness of ozonation as a pre-treatment process to coagulation and flocculation is highly sensitive to the source water quality and in particular NOM characteristics (Liu, Cheng & Wang, 2009; Liu, Wang, Wang, Tang & Yang, 2007). The implications of pre-oxidation for subsequent treatment unit processes have been widely

inconsistent in the literature due to the lability, diversity and reactivity of NOM (Table 2.3). Some treatment systems reconfigured to incorporate pre-oxidation once DBP precursors have been removed post-coagulation have demonstrated enhanced DOC and UV-absorbance at 254 nm  $(UVA_{254})$  removal by 5-32% and 8-33% respectively (Uyguner, Bekbolet & Selcuk, 2007).

### 2.3.1.2 Coagulation & flocculation

Coagulation and flocculation processes promote the separation of colloidal and suspended solids present in the raw water. Coagulation involves introducing a hydrolyzing chemical (e.g. alum, iron salts or organic polymers) to the water matrix, which induces the destabilization of small suspended and colloidal particulate matter by counteracting the repulsive forces between particles as induced by their surface charges. Flocculation is the physical process by which destabilized particles collide and aggregate to form larger flocs. Depending on the orientation and composition of the flocs, they may subsequently be removed by gravity sedimentation, flotation and/or filtration (e.g. Chowdhury, Roberson & Owen, 1997; Montgomery, 1992). Compression of the electrical double layer, adsorption and charge neutralization, adsorption and interparticle bridging and enmeshment in precipitates are mechanisms for achieving particle destabilization; several mechanisms are often exploited simultaneously during coagulation and flocculation processes (Letterman, Amirtharajah & O'Melia, 1999).

Coagulant selection and optimization depends on the concentration and types of particles/NOM present in the source water, water temperature and overall water quality. Waterborne particles generally possess negative surface charges which are typically imparted in four ways: isomorphous replacement (crystal imperfections), structural imperfections (broken bonds on crystal edge of clay and mineral particles), carboxylic acid groups from NOM when pH is greater than ~5 and ionization of inorganic groups on particulate surfaces (Stumm & Morgan, 1996). Humic acids comprise the majority of dissolved NOM in natural waters and impart negative surface charges when adsorbed to surfaces of other particles (Thurman, 1985). Though inorganic particles may also impart negative charges, NOM contributes to the overwhelming majority of the negative surface charges of suspended particles present in surface water supplies (Edzwald, 1993; Shin, Spinette & O'Melia, 2008). Accordingly, NOM is usually regarded a primary driver of coagulant dose. This relationship has been extensively employed in the control of coagulant dosing since the 1960's (Bean *et al.*, 1964).

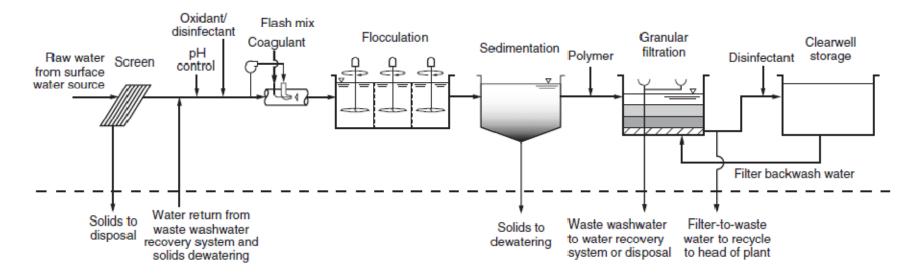


Figure 2.2 Typical process train for surface water treatment using conventional treatment (Source: MWH, 2012)

Table 2.3 Pre-oxidation effects: speculative mechanisms (adapted from Jekel, 1998)

Mechanism	Description	Net effect	Literature Cited
Organo-metal- complex formation	Oxidation and precipitation or release of metal cations through oxidation of organic matter; hydrolyzation into precipitates	+ effect on coagulation/ sedimentation/ filtration	Felix-Filho, 1985; Reckhow et al., 1986.
Precipitation of calcium salts	Formation of carboxylic acids that form insoluble Ca-salts under sufficiently high Ca conc. at high ozone/chemical doses	+ effect on coagulation/ sedimentation/ filtration	Becker & O'Melia, 1996; Edwards & Benjamin, 1992; Maier, 1984
Polymerization reactions of organic radicals	Combinations of organic radicals (from oxidation or ozonation) to form dimers of higher molecular weight	? organic radicals form higher molecular weight, but below those of coagulating properties	Farvardin & Collins, 1989; Grasso & Weber, 1988; Jekel & Beulker, 1992
Algal matter aggregation	Enhancement of interparticle flocculation and particle filtration via interaction of extracellular organic matter on algal cell surfaces	- if EOM broken down by overdosing (impairs coagulation)	Betzer et al., 1980; Hoyer et al., 1987; Jekel & Reicherter, 1987; Montiel & Welte, 1998; Plummer & Edzwald, 1998
Inorganic particle stabilization	Reduced adsorbability of DOM; adsorption of high molecular weight NOM to inorganic particles reduced via increased electrical charge or steric effect	- for keeping organic matter intact for aggregation and removal	Chandrakanth & Amy, 1996; Gibbs, 1983; Jekel, 1985, 1986 a,b
Reduced metal- organic complex solubility	Sweep coagulation at insufficient metal doses increases metal solubility of metal-organic compounds formed under neutral-pH flocculation	- enhanced oxidation preferentially forms soluble complexes, especially if in- adequate metal cations	Edwards & Benjamin, 1992; Jekel, 1986; Singer, 1990.

The average surface charge of particles can be characterized as the zeta-potential through the measurement of the average particle velocity induced when a potential difference is applied across a capillary cell containing a sample. The surface charge of particles has been reported to be between -15 to -25 mV for many particles in natural waters (Bean, Campbell, Anspach, Ockershausen & Peterman, 1964) However, this aggregate surrogate metric of surface charge cannot be used to discern surface charges attributed to inorganic particles and NOM; this insight can be used to inform coagulant selection and optimization. Colloid surface area is mechanistically the best surrogate measure of inorganic particle surface charge; however, its measurement is impractical and standard suspended solids measurements would underestimate colloid surface area as some colloids may pass through most filters. Therefore, turbidity has been deemed the best available method of quantifying colloid concentrations as colloids are on the order of wavelength of visible light and will scatter

incident visible light (MWH, 2012). The use of SUVA to further optimize coagulant dosing also has been suggested because it is indicative of organic matter composition which may influence coagulation efficacy (Edzwald & Kaminski, 2009).

Coagulation and flocculation processes are also impacted by the ionic strength, type of counterions present, pH and alkalinity. An increase in ionic strength reduces the energy barrier that must be overcome to reduce electrostatic repulsion between particles by compressing their electrical double layer thicknesses and allow for rapid flocculation. According to the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory, the ionic concentration required to compress the electrical double layer to the point where flocculation can occur is inversely proportional to the sixth power of the charges present on the counterions in solution, assuming that the electrolytes do not adsorb or precipitate (MWH, 2012). A change in pH induced by the addition of the coagulant may also precipitate metal hydroxides that allow for increased inter-particle collisions. The optimal pH range for metal precipitate formation differs depending on the coagulant used. Typically, source waters with low alkalinity need to be amended with bicarbonates to buffer pH changes. It has been recognized that TOC removal by flocculation becomes more challenging with increasing alkalinity (Bratby, 2006). The addition of coagulant consumes alkalinity and reduces pH; pH depression to 5.5 to 6.5 where optimal TOC removal is achieved may be difficult in higher alkalinity waters (Bratby, 2006).

Table 2.4 below provides a summary of the characteristics of the most commonly used coagulants. Metal salts may also complex with various ligands (e.g.  $SO_4^{2-}$ ,NOM,  $F^-$ ,  $PO_4^{3-}$ ) to form soluble and insoluble products, influencing coagulant dosing (Jenkins, Ferguson & Menar, 1971; Stumm & O'Melia, 1968). As the prediction of optimal coagulant conditions based on water quality is complex and poorly understood, operators have largely relied on the results of bench scale jar tests to inform optimal coagulation conditions (Kawamura, 1996; MWH, 2012). The relative roles of NOM and particles in coagulation processes have been quantitatively documented as empirical stoichiometric relationships using controlled batch jar-test experiments (Black, Singley & Whitle, 1963; Edzwald & Van Benschoten, 1990; O'Melia, Becker & Au, 1999; Shin *et al.*, 2008; Stumm & O'Melia, 1968).

Table 2.4 Selection of commonly used coagulants (Source: MWH, 2012)

Water	Coagulant				
Quality	Alum (III) Fe (III)		PACI		
Parameter					
Turbidity	Sweep floc (large	Sweep floc will be required	Medium-basicity (40-50%)		
	aggregates of aluminum	for low turbidity waters	are suitable for waters with		
	hydroxide or ferric		low turbidity		
	hydroxide) will be required				
	for low turbidity waters				
Alkalinity	High alkalinity values make p	oH adjustment more difficult.	n/a		
	Insufficient alkalinity results	in the formation of soluble			
	aluminum species. Alkalinity	impact using Fe < Al.			
pН	Optimum pH range	Optimum pH range is from	PACl are less sensitive and		
	between 5.5 and 7.7 but	5 to 8.5 or more	are used over a wide pH		
	fluctuates seasonally;	luctuates seasonally;			
	higher pH corresponds with				
	algal growth, thereby				
	affecting coagulant dose				
NOM	Removal of NOM increases	Removal of NOM increases	Removals up to 20% has		
	as pH is reduced; up to	as pH is reduced; up to	been achieved.		
	70% removal has been	80% removal has been			
	achieved	achieved			
Temperature	Affects solubility products; fl	n/a			
	tends to be weaker				
Mixing	Hydrolysis reactions very fas	t; mixing time should be less	Initial blending time less		
	than 1 s and preferably less th	nan 0.5 s.	critical		

### 2.3.1.3 Filtration

Filtration is primarily employed in drinking water treatment to remove solids from the water matrix. Conventional treatment trains employs rapid dual media filtration: Filters typically comprise of a bed of granular material that is uniform in size and are operated at a high hydraulic loading rate with low head loss, with void spaces between granular media larger than particles being removed (MWH, 2012). Filtration relies on a combination of physico-chemical mechanisms other than straining (i.e. removal of particles by size exclusion) for the removal of particulate matter in the water matrix (e.g. Amirtharajah, 1988; Ives, 1982). Effective coagulation pre-treatment is most often critical for effective filtration; particles must be properly destabilized as filter media grains also carry a negative surface charge. Depth penetration into filters is used to maximize particle retention capacity while minimizing particle breakthrough and head loss.

A typical filter run cycle in a conventional drinking water treatment plant lasts from 1 to 4 days and its effectiveness for particle removal can be described using a breakthrough curve. The period during

which substantial particle breakthrough may occur after backwash is known as filter ripening. After the filter media is acclimatized, particle breakthrough reaches a pseudo-steady state and is put into operation. The end of the filter run can be triggered in one of three ways: 1) if the filter's capacity to remove additional particles is exhausted and particle breakthrough is observed in the filter effluent, 2) if terminal head loss is reached or 3) based on a convenient operational schedule for plant operators. At this time, water flow is reversed (sometimes with air scour) to detach particles and regenerate the filtration media.

### 2.3.1.4 Disinfection

Disinfection is used in drinking water treatment to inactivate pathogenic microorganisms. Inactivation is achieved by destruction or impairment of cellular structures, altering the cell permeability or the protoplasm of microorganisms. Chemical agents commonly used include chlorine, chloramines, ozone and chlorine dioxide; UV radiation is the most common non-chemical means of drinking water disinfection (MWH, 2012). Disinfection is typically applied at the end of treatment to minimize the potential for DBP formation and maintain an adequate residual to deter pathogen re-growth in the distribution system.

The presence of solids and/or organic matter in the water matrix leftover from pre-treatment processes highly influence disinfection efficacy through consuming oxidant demand, providing particle shielding of pathogens and acting as potential precursors of DBPs through reacting with the oxidant. Accordingly, the objective of minimizing DBP formation conflicts with the objective of maximizing disinfection to reduce risk of waterborne pathogenic organisms. The identification and verification of reaction mechanisms with NOM have not been well elucidated due to the complexity and diversity of NOM in natural waters, even though higher concentrations of NOM have generally implied increase in the formation of DBPs (MWH, 2012). Various empirical relationships have been developed for predicting DBP formation and are reviewed in Amy, Chadik, Chowdhury (1987) and Sadiq & Rodriguez (2004). Most relationships have been expressed as log-log multiple linear regression models or as multiple nonlinear regression models, linking DBP concentrations as a function of TOC or DOC, UVA<sub>254</sub>, pH, water temperature, concentration of bromide ions, chlorine dose and reaction time of residual chlorine.

Other DBPs have been identified and some of them have been deemed a higher health risk than trihalomethanes [THMs] and haloacetic acids [HAAs]. However, as THMs and HAAs are the two most prominent groups of chlorination DBPs found in drinking water (FPTCDW, 2008; 2009), these are the ones that are currently regulated. The removal of DBP precursors through pre-treatment processes has been deemed the best way to reduce THMs, HAAs and other DBPs concurrently (FPTCDW, 2008; 2009).

### 2.3.1.5 Distribution system

Drinking water is delivered to customers through the distribution system. Distribution systems comprising of cast iron, galvanized steel and copper pipes are often faced with the challenge of corrosion. These pipes are typically lined with a bitumastic seal coat, cement mortar, or both to reduce corrosion and/or lead release (MWH, 2012). Different aspects of corrosion are typically reported on in the literature, ranging from pipe degradation (weight loss, oxygen consumption or corrosion current), scale formation (head loss or scale deposition), and by-product release (color, staining, customer complaints, iron/lead concentrations). Residual phosphorus concentrations in the finished water have been used as a corrosion inhibitor (e.g. Edwards & McNeill, 2002), although the presence of phosphorus has also been associated with the problem of microbial regrowth (Miettinen et al., 1997).

# 2.4 Phosphorus as a water quality indicator

Phosphorus (P) is an essential nutrient for health and productivity in aquatic ecosystems. It is an essential component of nucleic acids and intermediary metabolites in all life forms (Correll, 1998). It is often cited as the limiting mineral nutrient for primary productivity in freshwater lacustrine ecosystems (Hecky & Kilham, 1988; Schindler, 1974; 1977; Smith & Shapiro, 1981). Phosphorus rarely occurs in its pure elemental form; it is typically transported from terrestrial landscapes to aquatic systems as a mixture of labile particulate and soluble forms (e.g. orthophosphate, pyrophosphate, organic phosphate esters, phosphodiesters and organic phosphonates) (Correll, 1998).

Particulate and soluble forms of phosphorus are operationally discerned at a limit of 0.45 microns ( $\mu$ m); however, most phosphorus species passing through a 0.45  $\mu$ m filter are associated with a continuum of colloids and particles greater than 0.01  $\mu$ m as opposed to existing in a strictly dissolved form (Haygarth & Jarvis, 1997; Haygarth & Sharpley, 2000). Phosphorus can also be classified based

on its inorganic or organic speciation. Inorganic phosphorus is most stable in soils as mineral complexes (e.g. aluminum, iron, calcium phosphates) and may exist as orthophosphates adsorbed to soil particles with high surface areas (e.g. clays). Organic phosphorus may be assimilated as part of plant, animal, algae and microorganisms and their remains (Flaig, 1966) or may be found in the organic matter coatings of soil particles (Frossard, Brossard & Metherell, 1995; Ryden, Syers & Harris, 1973). An overview of the literature relevant to phosphorus source, transport and fate in aquatic systems as relevant to the present research is summarized in the following sections; comprehensive reviews on phosphorus biogeochemical cycling of phosphorus in aquatic systems have been extensively documented elsewhere (e.g. Correll, 1998; Reddy, Kadlec, Flaig & Gale, 1999; Withers & Jarvie, 2008).

### 2.4.1.1 Phosphorus source

Increased anthropogenic development has exacerbated natural climatological pressures, contributing to the increased frequency and magnitude of land disturbances (Schindler & Donahue, 2006). Land disturbances attributed to more intensive land-uses generally accelerate mobilization and downstream transport of nutrients. Several studies have documented increased aquatic phosphorus concentrations following forest harvesting in organic soil layers (Evans, Prepas, Devito & Kotak, 2000; McColl, 1978; Stevens, Hornung & Hughes, 1989; Yanai, 1991), potentially via increased water yield/runoff, decomposition of litter, soil erosion and decreased plant phosphorus uptake (Bosch & Hewlett, 1982; Devito & Dillon, 1993; Fredriksen, Moore & Norris, 1975; Nicolson, Foster & Morrison, 1982). Cleared forested watersheds have exhibited nutrient losses double those of re-established forests (Chanasyk, Whitson, Mapfumo, Burke & Prepas, 2003; Dillon & Kirchner, 1975; Wetzel, 2001). The majority of terrestrial phosphorus exports to aquatic environments from these landscapes generally occur during significant hydrological events, with the majority of phosphorus transported with a first flush effect (i.e. higher concentrations of pollutants at the beginning of runoff events) (e.g. Deletic, 1998; Lee & Bang, 2000; Pacini & Gächter, 1999).

Increased recreational demands also have indirect impacts on natural nutrients cycles: poor fisheries and fish habitat management have led to widespread declines of fish species (Carpenter *et al.*, 1998; Post, Sullivan, Cox, Lester & Walters, 2002), causing a "trophic cascade" and potentially promoting nutrient retention as algal biomass in lakes (Carpenter & Kitchell, 1996; Carpenter, Kitchell & Hodgson, 1985). Conversion to pastures, feedlots, croplands and urban areas result in even greater

nutrient export to downstream aquatic environments (Wetzel, 2001), as can be estimated by empirical TP yield coefficients (Table 2.5). Additional empirical TP yield coefficients have been derived from various land-uses and are summarized by Jede (2006).

Table 2.5 Empirical watershed TP yield coefficients (Reckhow & Chapra, 1983; Rast & Lee, 1978)

Land Use	Reckhow & Chapra, 1983 mg m <sup>-2</sup> yr <sup>-1</sup> (kg ha <sup>-1</sup> yr <sup>-1</sup> )	Rast & Lee, 1978 mg m <sup>-2</sup> yr <sup>-1</sup> (kg ha <sup>-1</sup> yr <sup>-1</sup> )
Forest	10 (0.10)	2-45 (0.02-0.45)
Precipitation	20 (0.20)	15-60 (0.15-0.60)
Agriculture/rural	50 (0.50)	10-300 (0.10-3.00)
Urban	100 (1.00)	50-500 (0.50-5.00)
Dry fall	80 (0.80)	-
Septic-tank drain fields	-	0.3-1.8 kg cap <sup>-1</sup> yr <sup>-1</sup>

In forested watersheds, wildfires pose the greatest catastrophic landscape disturbance threat to source water regions and accordingly the greatest disruption to nutrient biogeochemical processes (e.g. Pinel-Alloul *et al.*, 2002; Shakesby & Doerr, 2006; Silins *et al.*, 2009; Smith, Sheridan, Lane, Nyman & Haydon, 2011; Townsend & Douglas, 2004). Antecedent land/forest management practices play essential roles in mitigating wildfire impacts through controlling the extent and magnitude of the fire disturbance, which subsequently influences the mobilization and export of nutrients to aquatic systems. For example, long periods of successful fire suppression in watersheds with frequent natural fires have increased small tree density, resulting in an unnatural accumulation of ground fuels (e.g. Miller & Urban, 2000; Parsons & DeBenedetti, 1979; Stephens *et al.*, 2009). Under these conditions, forests are also susceptible to large-scale insect infestations, disease outbreaks and heightened risk of fire, which have well-documented impacts on water quality and availability via changes to hydrological processes (Diiwu, Silins, Bladon & Anderson, 2008; Emelko *et al.*, 2011).

Nutrient biogeochemical cycles in wildfire-impacted watersheds have been documented to be substantially affected. Burned soils tend to be coarser, more hydrophobic, easily eroded and have low infiltration rates (Chanasyk *et al.*, 2003). While phosphorus losses through volatilisation (T<sub>volatilization</sub> > 550 °C) (Hernandez, Garcia & Reinhardt, 1997; Murphy *et al.*, 2006; Raison, 1979) or leaching are relatively insignificant (Certini, 2005), fire increases the bioavailability of organic phosphorus through conversion to orthophosphates (Cade-Menun, Berch, Preston & Lavkulich, 2000; Chambers & Attiwill, 1994; Serrasolsas & Khanna, 1995). This effect is compounded by fire-induced change of typically acidic Boreal forest soil pH (Allen, Swenson, Querejeta, Egerton-Warburton & Treseder, 2003; Prescott, Maynard & Laiho, 2000) towards the peak phosphorus bioavailability pH of 6.5

(Sharpley, 2000), although soluble phosphorus concentrations are buffered by soils. Cations oxidized by fire are more soluble and available to bind soluble phosphorus and precipitate as organo-metal-phosphate complexes (Chanasyk *et al.*, 2003). Accordingly, phosphorus losses in wildfire-impacted forested watersheds are more strongly linked to erosional processes (Allin, Stone, Silins, Emelko & Collins, 2012; Chanasyk *et al.*, 2003).

Significant phosphorus loadings to surface waters during run-off events have been consistently observed in fire-impacted forested catchments (Certini, 2005; Smith *et al.*, 2011), despite a wide range of phosphorus yields reported (Table 2.6). In a southern Alberta watershed similar in size and geography to the Elbow River watershed, Allin *et al.* (2012) reported significant increases of baseline TP concentrations in both burned and burned, salvaged-logged watersheds, the majority of which was observed as particulate phosphorus. No recovery of sediment and phosphorus yields had been observed nine (9) years post-disturbance. This underscores the potentially lasting implications of wildfire to water quality in forested watersheds, such as those in Alberta.

Table 2.6 Summary of post-fire exports of phosphorus in catchment-scale forested watersheds (adapted from Smith et al., 2011)

Reference	Location	Vegetation	Sampling Regime	Catchment area (km²)	P form	First year export (kg ha <sup>-1</sup> year <sup>-1</sup> ) after wildfire (multiple increases over pre-fire or unburned control)
Bayley <i>et al.</i> , 1992	North-west Ontario, Canada	Boreal pine forest	Weekly (ice-free period, May–October)	0.12, 0.56, 1.7	TP	0.03–0.13 (1.4x)d
McEachern et al., 2000	Caribou Mountains Northern Alberta, Canada	Subarctic Boreal forest peatland- conifer forests	Monthly (ice-free period, late June - late August,	0.326, 82.08	TP TDP SRP	0.28-0.94 (1.3x-4.3x) 0.14-0.62 (1.7x-7.5x) 0.07-0.39 (3.2-17.3x) <sup>#</sup>
Lane <i>et al.</i> , 2008	East Kiewa River, NE Victoria, Australia	Wet Eucalyptus forest	Weekly–fortnightly and storm events	1.36, 2.44	TP	1.67 (4-5x)
Blake <i>et al.</i> , 2010	Blue Mountains, near Sydney, Australia	Dry Eucalyptus forest	n/a	0.89	PP	0.49
Prepas <i>et al.</i> , 2003	Central Alberta, Canada	Mixed species boreal forest	Pre-fire: 2_ daily Post-fire: 1–2 times weekly and storm events	248	PP TP	0.04 (1.5x) 0.06(1.3x)
Townsend & Douglas, 2004	Kakadu National Park, Northern Australia	Tropical savannah, open dry Eucalyptus forest	Every 3 days and storm events	6.6	TP	0.03 (1.8x)
Mast & Clow, 2008	Glacier National Park, NW Montana	Subalpine coniferous forest	2x weekly (during snowmelt) to monthly	96.4	TP	0.03 (0.3x)

Table 2.6 Summary of post-fire exports of phosphorus in catchment-scale forested watersheds (continued)

Reference	Location	Vegetation	Sampling Regime	Catchment area (km²)	P form	First year export (kg ha <sup>-1</sup> year <sup>-1</sup> ) after wildfire (multiple increases over pre-fire or unburned control)
Sheridan et al., 2007	(a) Ovens River (b) Tambo River-1 (c)Dargo River (d) Tambo River-2 (e) Mitta Mitta River (f) Kiewa River Victoria, SE Australia	Dry and wet Eucalyptus forests, subalpine woodland	Pre-fire: monthly Post-fire: fixed interval and storm events	(a) 495 (b) 523 (c) 676 (d) 895 (e) 1533 (f) 1655	TP	(a) 1.1 (9x) (b) 0.6 (431x) (c) 0.41 (10x) (d) 0.26 (30x) (e) 3.2 (37x) (f) 0.13 (1x)
Burke <i>et al.</i> , 2005	Boreal Plain, Canada	Boreal forest	Pre-fire: once-twice daily Post-fire: weekly and storm events	247, 150, 130, 165	PP DP	3.7 x increase (max 18x) Similar increase, but not significant
Silins et al., 2008; Bladon et al., 2008; Allin et al., 2012	Rocky Mountain region, SW Alberta, Canada	Montane to subalpine coniferous forests	Snowmelt (10–14 days), winter (1–2 monthly) and storm events	3.6, 7.1, 8.2	TP PP	8x/12x TP concentrations in burned, salvage logged watersheds than reference respectively particulate P comprised most of TP, coupled P and sediment interactions likely implicated in slow recovery of P production (especially in salvage logged watersheds)

<sup>#</sup> based on hand calculations - mean burned yields compared to reference yields

### 2.4.1.2 Phosphorus transport

Surface runoff is the principle pathway for phosphorus mobilization and transport from landscapes to streams and rivers (Correll, 1998). Phosphorus concentrations in streams generally increase with peak discharge but decrease with increasing discharge frequency and duration (Burke, Heathwaite & Preedy, 2004). The majority of phosphorus in surface waters originate from overland surface flows rather than from groundwater due to its binding capacity to most soils and sediments as phosphates (Correll, 1998). Accordingly, phosphorus loading to receiving surface waters is strongly related to land use, population density, soils, vegetation and precipitation patterns (Carpenter *et al.*, 1998). Waterlogged, anoxic environments and surface soils saturated with phosphorus after extended overfertilization are two atypical environmental conditions through which subsurface contributions of phosphorus may be substantial (Mozaffari & Sims, 1994). Macropores and drainage tiles also provide preferential pathways through which phosphorus is transported to aquatic systems, especially during significant hydrological events (Macrae, 2004; Macrae, English, Schiff & Stone, 2007; Vidon & Cuadra, 2011).

A widely accepted phosphorus mobilization and transport model to aquatic systems developed by Haygarth and Jarvis (1999) includes three sequential processes: 1) solubilisation (leaching), 2) physical detachment and 3) direct (incidental) transfer of recent phosphorus amendments (e.g. excess nutrient application on agricultural lands). Solubilisation occurs through distinct mechanisms: Inorganic phosphorus is released as geological media are weathered (Black, 1967) while organic phosphorus originates from hydrolysis of organic matter by phosphatase (Turner & Haygarth, 2002). Plant uptake and soil phosphorus levels limit the proportion of soluble phosphates exported to freshwater systems (Burke *et al.*, 2004); however, under artificially enhanced soil phosphorus concentrations (e.g. manure application, wildfire), equilibrium soluble phosphorus concentrations may be increased due to saturation of available soil sorption sites (Sims *et al.*, 2000).

Physical detachment involves the transport of terrestrial particulate phosphorus forms, usually by erosion of particles and colloids from soils (Burke *et al.*, 2004; Chanasyk *et al.*, 2003). Highly mobile colloid contributions have been found in subsurface pathways (Kretzschmar, Borkove, Grolimund & Elimelech, 1999) with strong affinity with inorganic phosphorus; however, size fractions, source and loading of colloidal transfer have not been well elucidated. A substantial proportion of colloidal organic phosphorus in soil suspensions is biologically assimilated in bacteria (Kretzschmar *et al.*,

1999), which may be physically detached and transported under elevated nutrient/carbon concentrations in the soil (Johnson & Logan, 1996; McCarthy & Zachara, 1989). Favourable environmental conditions for transport typically occur in springtime when colloidal organic phosphorus in leachate and soil biological activity are at their highest (Turner, 2000; Turner & Haygarth, 2002).

Various models have been proposed to explain phosphorus transport in aquatic environments. Froelich (1988) suggested that phosphorus containing compounds are subject to the "phosphate buffer mechanism", a reversible two step-process regulating phosphorus transport in solution or with sediments (i.e. natural clay particles): 1) fast kinetic (minutes to hours) adsorption/desorption to and from surfaces, 2) slow kinetic (days to months) solid-state diffusion into interior of particles. This mechanistic model has been loosely linked to ecological models to explain biological processes in streams. The nutrient spiralling model describes the continual assimilation and mineralization of nutrients along the stream's length (Fisher, 1977; Meyer & Likens, 1979; Newbold, Elwood, O'Neill & Winkle, 1981; Webster & Patten, 1979) and has become the dominant approach for describing downstream propagation of nutrients as linked to aquatic ecosystems (Ensign & Doyle, 2006). The river continuum concept elaborates on the nutrient spiralling model and suggests that these nutrient cycles are exhibited longitudinally as a continuous gradient, where energy loss is minimized by biological communities through approaching equilibrium with nutrient and dynamic physical conditions of the stream (Vannote, Minshall, Cummins, Sedell & Cushing, 1980). There is also considerable consensus regarding the ability of headwaters to regulate the downstream delivery of phosphorus within the river channel (reviewed in Withers & Jarvie, 2008). Despite these unifying concepts, these concepts still require additional research for application in larger ( > third order) rivers (Ensign & Doyle, 2006), especially to quantify and assess the relative importance (magnitude) of ecological processes so that management options can be effectively designed and implemented (Jarvie, Neal & Withers, 2006; Stutter, Langan & Cooper, 2008; Withers & Jarvie, 2008).

## 2.4.1.3 Phosphorus fate in lacustrine/reservoir systems

Upon entering lacustrine/reservoir environments, phosphorus compounds may be retained via autochthonous biological assimilation and/or deposition into bottom sediments. The sediments may act as a temporary phosphorus sink which regulate aqueous phase inorganic phosphorus concentrations (i.e. orthophosphates) at the sediment phosphorus-equilibrium concentration. These

bottom sediments, given sufficient perturbations (e.g. bioturbation, significant hydrological events), may become re-suspended in the water column and exported from the system, or may become geologically deposited. Anoxic conditions may also induce a biogeochemical equilibrium shift to release inorganic orthophosphates from both particulate and organic forms of phosphorus (reviewed in Correll, 1998). The high rates of biological assimilation of orthophosphate promotes an increased potential for lake/reservoir eutrophication (reviewed in Correll, 1998; Burke *et al.*, 2004).

The ecological significance of inorganic phosphorus to eutrophication and its fate in receiving aquatic systems has been extensively researched and corroborated in limnology (Burke *et al.*, 2004; Heckrath, Brookes, Poulton & Goulding, 1995). Total Phosphorus (TP) and orthophosphates are used as key predictors of autochthonous primary production and eutrophication. Numerous empirical steady-state nutrient concentration and nutrient-algal models have been developed for predicting steady-state lacustrine/reservoir productivity and trophic states (e.g.; Ahlgren *et al.*, 1988; Nürnberg, 1984; Vollenweider, 1970; Watson, McCauley & Downing, 1992). Existing empirical nutrient-algal models seldom portray temporal variability of phosphorus concentrations, speciation and algocoenosis (Munn & Prepas, 1986) due to the complexity of environmental factors and biogeochemical cycling. Trophic state indices (TSIs, amongst which the Carlson TSI has been the most extensively used for freshwater systems) as determined by TP concentrations have therefore represented the maximum *potential* trophic state attainable and may be less reflective of actualized primary productivity (Carlson, 1977).

# 2.4.2 Factors affecting source/transport/fate of phosphorus in freshwater and engineered treatment systems

Phosphorus is not regarded as a direct threat to drinking water treatment processes. Bartenhagen et al. (1994) reported interference in coagulation-flocculation processes of drinking water treatment plants when phosphate levels exceeded 1.0 mg/L; however, natural phosphorus levels in the majority of Canadian freshwater systems are generally below this threshold (CCME, 2004). Indirectly, sufficient phosphorus in source waters may lead to eutrophication, which has well-documented impacts on treatment (see Section 2.4.2.4). Phosphate impacts on coagulation by adsorption to aluminum hydroxide during drinking water treatment were also assessed at bench-scale (Pommerenk & Schafran, 2005). Phosphates were nearly completely removed from solution across a wide pH range and were observed to lower surface charge and shift the isoelectric point of the metal precipitate during coagulation (Pommerenk & Schafran, 2005). The lack of additional evidence implicating phosphorus in drinking water treatment processes or direct health threats in the absence of algae has diminished the impetus for investigating its use as a treatment vulnerability indicator. Five factors affecting the source, transport and fate of phosphorus were identified that supported the potential use of phosphorus as a source water and treatment vulnerability indicator through the literature review (Table 2.7). An assessment of these factors may be used to infer the dominant pathways and processes affecting source water quality and their implications for drinking water treatment.

### 2.4.2.1 Phosphorus response to hydrological events

Landscape disturbance alone generally does not result in surface water quality deterioration within a watershed. The occurrence of significant hydrological events over relatively large geographical areas is typically required for the mobilization and transport of pathogens, sediments, organic matter and nutrients to be observable at the catchment outlet (e.g. Grimes, 1980; 1982). Hydrological events have been largely been regarded as *pathways* for phosphorus transport (e.g. overland flow, subsurface flow, etc.). However, the impacts of rainfall intensity, duration and the interval between rainfall events may also augment the occurrence of other processes acting on phosphorus (as described in the subsequent sections 2.4.2.2 to 2.4.2.5) (Haygarth, Heathwaite, Jarvis & Harrod, 1999; McDowell, Sharpley, Kleinman & Gburek, 2002). Accordingly, hydrological events are critical to the source, fate and transport of phosphorus.

Table 2.7 Factors affecting source, transport and fate of phosphorus in aquatic systems: implications for source water and treatment

_	implications for source water	
Factor	Source Implications	Treatment Implications
Significant	Significant hydrological events usually	Allochthonous/autochthonous contributions
hydrological	result in increased rates of erosion and	of organic matter has been associated with
events	sediment transport to water bodies.	organic matter of varying biodegradability,
	Source water quality may become	which has implications for DBP formation
	dominated by allochthonous processes.	
Adsorption	Significant hydrological events result in	Phosphorus may act as an indicator of fine-
to fine-	increased rates of erosion and sediment	grained particulate matter ("solids" fraction
grained	transport to water bodies. P is often	of turbidity), which would affect processes
particulate	adsorbed to these sediments. These	related to particulate matter removal; long-
matter	sediments increase turbidity (during or	term implications for organics and/or algae
	immediately after hydrological events);	removal.
	and engage in natural coagulation/	
	flocculation processes. Long-term	
	implications include increase in P	
	equilibrium concentration, reduction of	
	reservoir depth/capacity and potential for	
	eutrophication.	
Metal	Lock up of P, reduce short-term	Metal cations, organic solutes and
precipitation,	bioavailability and primary productivity	phosphorus hydrolyze into insoluble
adsorption	unless released; precipitation, adsorption	precipitates, particularly when oxidized and
and	and complexation affect natural	affect particle removal efficacy; corrosion
complexation	coagulation/flocculation processes.	inhibitor in distribution system.
Limiting	If limiting nutrient in the aquatic system,	Algal-related impacts to treatment
nutrient for	increase in concentrations may lead to	(summarized in
primary	eutrophication (increased primary	Table 2.9); may affect biological filtration;
production	autochthonous production).	microbial growth in distribution systems.
Co-leaching	Preferential leaching of P with specific	The ability to discern organic matter source
with organic	fractions organic matter has been	and character may be used to optimize
solutes	observed in soils; accordingly P may be	organic-related properties/treatment
	used to discern upstream (allochthonous)	processes.
	organic matter exports (soils, decaying	
	matter) and/or agricultural run-off vs. in-	
	reservoir (autochthonous) organic matter.	

## 2.4.2.2 Phosphorus adsorption to fine-grained sediments

The majority of phosphorus in stream flow are transported in particulate form (Blake *et al.*, 2010; Burke *et al.*, 2004). In a review of river transport budgets, Meybeck (1982) estimated that 95% of phosphorus naturally transported by rivers is in particulate form. Higher TP concentrations (2 to 8.9 times greater than that present in watershed soils) have been attributed to selective erosion of fine sediments and/or deposition of coarse sediments in transport (Avnimelech & McHenry, 1984; Duffy, Schreiber, McClurkin & McDowell, 1978). Even in agricultural watersheds where dissolved

phosphorus species are more prevalent in soils, the abundance of fine-grained sediments in the receiving water body allows for the potential adsorption and subsequent transport of phosphorus in the particulate form.

In rivers where sediment transport is high, a significant proportion of TP loading can be sedimentassociated (Ballantine, Walling & Leeks, 2009; Logan, 1987; Logan, Oloya & Yaksich, 1979; Stone & English, 1993), which may have significant implications for long-term reservoir productivity and/or capacity. A substantial proportion of these fine-grained sediments, consisting of silt and clay sized materials, are colloidal in nature and may remain in suspension for extended periods in receiving water bodies (Armstrong, Perry & Flatness, 1979; DePinto, Young & Martin, 1981; Lick, 1982), contributing to raw water turbidity (Grayson, Finlayson, Gippel & Hart, 1996). Phosphorus sorption to sediments increases with reduction in sediment particle size, particularly with finegrained sediment fractions (< 63 µm) (Armstrong et al., 1979; Stone & English, 1993; Stone & Mudroch, 1989; Stone & Saunderson, 1992) with high aluminum and organic matter content (Meyer, 1979). Fine-grained sediments are accordingly considered the most geochemically active and important in nutrient transport (Allen, 1986; Peart & Walling, 1982; Stone & Mudroch, 1989). In receiving water bodies, sediment-associated phosphorus may become deposited in bottom sediments. Increased salinity, anion competition of sorption sites and anoxic conditions promotes the desorption of phosphorus from sediments as orthophosphates to support primary production (Cuker, Gama & Burkholder, 1990; Heath & Francko, 1988; Thomas & Munawar, 1985).

### 2.4.2.3 Phosphorus-metal complexation/precipitation and adsorption

Phosphorus-metal interactions have been widely reported in both soil and aquatic systems. A comprehensive review of phosphorus speciation in soil, water and sediments was provided in Holtan, Kamp-Nielsen & Stuanes (1988). In phosphorus-saturated soils, a large proportion of the TP is preferentially exported in the colloidal form (Hens & Merckx, 2001). Orthophosphate readily adsorbs to colloidal aluminum, iron and manganese through chemisorption in acidic soils and calcium minerals in neutral or alkaline soils (Certini, 2005; Hall Jr., Bernhardt & Likens, 2002; Meyer, 1979). Clays, oxides, organics to which phosphorus may be bound are displaced across soil horizons by percolation and accumulate in the subsoil as illuvium (Fanning & Fanning, 1989; Soil Science Glossary Terms Committee, 2008). Low ionic strength, high pH and high monovalent to divalent

cation ratios have generally been observed to enhance mobilization of humic substances and iron-phosphate colloidal complexes from soils (Thurman, 1985; Tipping & Ohnstad, 1984).

In the pH range typically observed in most natural soils, phosphorus occurs predominantly as HPO<sub>4</sub>-<sup>2</sup> ions in soil solutions (Hinsinger, 2001; Lindsay, 1979). These ions act as inorganic ligands in soil solution with strong affinity for ion pair or complex formation with metal cations (e.g. calcium, magnesium, iron and aluminum) and organic ligands (Lindsay, 1979). The prevalence of specific metal compounds and their association with phosphorus is mediated by pH, cation and organic ligand availability (Hinsinger, 2001). The solubility of the iron and aluminum phosphates formed increase proportionally with pH, whereas the solubility of calcium phosphates decrease, except at pH values above 8.0 (Hinsinger, 2001; Lindsay, 1979). Accordingly, metal and/or phosphorus compounds may be mobilized and introduced into freshwater environments in various forms based on antecedent hydrological regime and soil conditions.

The solubility of phosphates in aquatic systems are regulated through aluminum, iron and calcium complex formation in precipitation-dissolution reactions at aerobic conditions (Hosomi, Okada & Sudo, 1981; Hosomi & Sudo, 1986; Stumm & Morgan, 1996) or adsorption-desorption to magnesium silicates (Smith & Hwang, 1978), aluminum oxides (Huang, 1977) and calcites (Freeman & Rowell, 1981). At anaerobic conditions, aluminum phosphates and iron phosphates are released to the water column as solutes from sediments (Joh, 1983). Colloidal aluminum oxyhydroxides have been observed to be less sensitive to redox changes, however (Joh, 1983). The solubility of these complexes is highly dependent on pH and other major competitor ions (specifically aluminum, iron and calcium ions) present in the water matrix. Colloidal aluminum hydroxides generally out-compete ferric hydroxides for orthophosphate adsorption and play a major role in suppressing the release of orthophosphate in the water column and the burial of phosphorus in the sediment (Kopáček, Borovec, Hejzlar & Porcal, 2001). Studies of alum-treated eutrophic lakes show that long-term removal of phosphorus can result from in-lake cycling due to binding with colloidal aluminum hydroxides (Rydin, Huster & Welche, 2000). In natural waters, excessive dissolved phosphorus species also readily bind to high molecular mass organic matter (e.g. humic acids) in the presence of metal oxides and precipitate as organo-metal-phosphate complexes (Busman, Lamb, Randall, Rehm & Schmitt, 2009; Dolfing, Chardon & Japenga, 1999; Hens & Merckx, 2001; Zhang & Zhang, 2010). However, organic anions have also been observed to block sorption sites on positive cation mineral surfaces, thereby reducing phosphorus adsorption (Holtan et al., 1988; Sample, Soper,& Racz, 1980).

The net contribution of precipitation and adsorption reactions to phosphorus speciation may be confounded by the prevalence of iron and aluminum hydrous oxides and relative phosphate concentrations in the water matrix. At high pH, oxides possess a negative surface charge. Phosphate sorbs to these oxides by ligand exchange with aquo-, hydroxyl-, or ol-groups (Berkheiser, Street, Rao & Yuan, 1980; Sample et al., 1980). This has different impacts on the suspended particles and/or the water matrix. Ligand exchange with aquo- groups increases negative charge of particle surfaces but does not alter the concentration of hydroxyl ions in solution; ligand exchange with hydroxyl groups does not impact surface charge but releases hydroxyl ions into solution. The presence of ionizable phosphate groups (amongst others such as carboxyl and amino groups) contributes to the overall surface charge density of the resultant flocs and water matrix pH (Berkheiser et al., 1980; Sample et al., 1980). At the former conditions, phosphates have been observed to be completely removed from solution across a wide pH range (Pommerenk & Schafran, 2005). Sufficient phosphate concentrations have been shown to lower the surface charge of pure aluminum hydroxide and lower the isoelectric point (pH<sub>iep</sub>) of aluminum hydroxide during drinking water coagulation at bench-scale (Pommerenk & Schafran, 2005). The shift of the aluminum hydroxide pH<sub>iep</sub> implies the formation of inner-sphere complexes (i.e. adsorption to surfaces by forces other than electric potential [e.g. covalent bonding]) (Pommerenk & Schafran, 2005). Any change in water matrix pH will change the chemical equilibrium and the rate of precipitation reactions, which can dominate in highly concentrated phosphorus suspensions in which fast-sorption sites have been exhausted (Sample et al., 1980).

The chemical precipitation of phosphorus using divalent or trivalent metals salts has been employed extensively in coagulation-flocculation during drinking water treatment and nutrient removal and recovery in wastewater treatment. Iron and aluminum are commonly added as chlorides or sulphates to induce phosphorus precipitation, while calcium carbonate has been used to remove phosphorus as calcium phosphate precipitates (Morse, Brett, Guy & Lester, 1998). The formation of phosphorus-metal precipitates increases colloid contact opportunities and density of colloidal particles, aiding flocculation and promoting sedimentation of particles from the water matrix. Metal-phosphate complexation and sorption reactions have also been exploited in drinking water distribution systems. Specifically, phosphate corrosion inhibitors have been used extensively in distribution systems since the early 1900s (Edwards & McNeill, 2002). Orthophosphates have been dosed (typically at a dose of approximately 1 mg/L) in these environments to inhibit the release of lead in distribution systems by

reducing metal corrosion rates (e.g. Trussell & Wagner, 1996; Edwards & McNeill, 2002; Schock & Sandvig, 2009; Volk, Dundore, Schiermann & LeChevallier, 2000). Although recent studies (e.g. Zhang & Andrews, 2011) have reported effects of phosphate-based corrosion inhibitors on disinfectant stability and DBP formation, the available research has been largely inconclusive about the mechanisms and relative efficacy of various phosphate inhibitors (McNeill & Edwards, 2001; Edwards & McNeill, 2002).

#### 2.4.2.4 Primary productivity

Phosphorus, nitrogen and carbon are essential nutrients for health and productivity in aquatic ecosystems. Whereas aquatic sources of carbon and nitrogen are augmented by solution from the atmosphere, phosphorus is generally only available geochemically. Accordingly, phosphorus is usually the limiting nutrient constraining maximum algal metabolic rate and growth in freshwater systems (Schindler, 1977). It is an essential constituent of cell protoplasm and is critical for enzymatic and energy transport functions in living cells (Reynolds, 1984). A freshwater system's nutrient profile as described by its carbon: nitrogen: phosphorus (C:N:P) stoichiometric relationship provides an indication of nutrient availability for primary production; an empirically-derived C:N:P atomic ratio of 106:16:1 reflects minimum nutrient requirements to sustain algal growth (Redfield, 1958).

The interpretation of nutrient ratios has varied widely beyond using them to determine the extent to which phosphorus limits primary production. Carbon to phosphorus (C:P) stoichiometric relationships (Table 2.8) have been used to explain ecological interactions between organic matter and phosphorus in freshwater systems. However, most studies have shown higher variability and higher ratios for particulate matter found in lakes than in marine systems (Blomqvist, Gunnars & Elmgren, 2004; Hecky, Campbell & Hendzel, 1993), presumably because of low salinity and varying degrees of oxic environments in freshwater bodies (Caraco, Cole & Likens, 1990). Moreover, it is difficult to generalize study outcomes as there are no standardized conventions for C:P ratio reporting (e.g. total, particulate or dissolved fractions of carbon or phosphorus are measured).

It has been argued that higher C:P ratios, particularly given longer hydraulic residence times ( > 6 months), reflect increased contributions of autochthonous organic matter formation in a source water versus organic matter derived from allochthonous processes (Hecky *et al.*, 1993); however, the

contrary has also been observed (e.g. Arvola, Kankaala, Tulonen & Ojala, 1996; Meili, 1992). If allochthonous sources comprise the majority of particles in lake waters, signals from underlying autochthonous processes and/or composition may be masked, particularly where detritus present has similar composition to living cells in systems with rapid turnover (Harris, 1986). The interpretation of C:P ratios in freshwater evidently requires the establishment of system-specific criteria to guide the discernment of autochthonous and allochthonous organic matter contributions (Hecky *et al.*, 1993).

Algae, cyanobacteria and their metabolites (e.g. microcystins) are health threats in drinking water (i.e. potentially carcinogenic, detrimental to neurological systems and/or act as precursors to regulated and unregulated DBPs). Recent studies have shown that algal organic matter is a major contributor to nitrogenous DBPs (e.g. haloacetonitriles [HAN] and halonitromethanes) (Bond, Huang, Templton & Graham, 2011; Fang, Yang, Ma, Shang & Zhao, 2010) which are potentially more carcinogenic than currently regulated DBPs (THMs and HAAs) (Lui, Hong, Zheng & Liang, 2012; Richardson, Plewa, Wagner, Schoeny & DeMarini, 2007). In additional to health risks, algae also pose several treatment challenges (Table 2.9) which have been widely documented in the treatment literature.

Throughout drinking water treatment, the presence of biologically available phosphorus also supports the growth/re-growth of microbial populations. While this may be desired in biofiltration systems where bacteria/biofilms are used to facilitate redox reactions that breakdown contaminants, the growth of undesirable pathogen bacteria may also be supported. Bio-available organic carbon and phosphorus have both been observed to significantly regulate microbial growth in drinking water; phosphate concentrations up to  $10 \mu g/L$  have been observed to increase microbial growth in distribution systems (Miettinen *et al.*, 1997).

Table 2.8 Reported Carbon: Phosphorus molar ratios in freshwater lentic systems

Reference	Location	Sampling Regime	C:P ratios (molar)
Arvola et al., 1996	Lake Paajarvi,	Spring, Summer, Autumn lake	Spring 3004:1
	Finland. Boreal	water	Summer 1793:1
	oligomesotrophic lake		Autumn 2033:1
Dillon & Molot, 1997	Central Ontario. 20	Long term averages, DOC:TP	1292:1 to 1845:1
	lakes within	ratio	Acidified lake: 3230:1
	undisturbed, forested		
	watersheds.		
Elser et al., 1995	Canadian Shield	Weekly means of C:N:P ratios	Phytoplankton: 29.0:1
	Lakes	of bacteria & phytoplankton	Bacteria:
		for 16 week period. May-	36.9:1
		September, 1992	
Gächter & Bloesch,	Lake Lucerne,	Seston collected by sediment	Epilimnion: > 274:1
1985	Constance & Hallwil,	traps at lower border of	Stratification:
	Switzerland. (varying	epilimnion of lakes	253:1 - 1726:1
	dystrophy)		Turnover:
	1 0		165:1 - 840:1
Guildford & Hecky,	Marine and	Particulate atomic ratios on	Extreme nutrient
2000	freshwaters	basis of nutrient deficiency	deficiency: 258:1
			Moderate nutrient
			deficiency: 129-258:1
			No deficiency:
			< 129:1
Hecky et al., 1993	Temperate freshwater	Particulate matter of lakes	306:1
	lakes (ELA), Canada	(mean), epilimnion	
		concentrations	326:1
		Residence time < 3 months	412:1
		Residence time > 6 months	
Hochstädter, 2000	Lake Constance,	2x a week in situ	180:1 - 460:1
, , , , , , , , , , , , , , , , , , , ,	Switzerland. Large,	measurements of seston <sup>1</sup> ,	Bacteria 50:1-130:1
	deep, mesotrophic	April-December, 1995	Phytoplankton 180:1-
	,		500:1
			Zooplankton:
			124:115
Kopáček et al., 2004	Central Europe.	Annual averages	Seston (epilimnion):
	Acidified,		822:1
	mesotrophic water		Seston (hypolimnion):
	bodies ("simplified"		342:1
	ecosystem)		
Meili, 1992	18 Swedish forest	2 year period unusually	350:1 (autochthonous)
	lakes (varying	variable hydrologic conditions	2000:1
	dystrophy)		(allochthonous)
Ulén, 1978	Swedish lakes		Seston 253:1

defined as particles ( > 0.2 um including zooplankton)
mass ratios = molar ratios x 12/31

Table 2.9 Documented algal and/or primary productivity impacts of phosphorus on drinking water treatment processes

Process	Impacts	Sample Literature
Pre-treatment (oxidation)	Increased DBP production	Yoo et al., 1995; Petruševski, B. 1996; Her et al. 2004; Lee et al. 2001; Chen & Yeh, 2005; Henderson et al. 2008; Plummer & Edzwald, 2001
Coagulation/ flocculation	Increase coagulant demand via increased DOC concentrations; charge density and specific surface area Increased microcystins/algal metabolites through cell lysis Increased turbidity	Bernhardt, 1984; Bernhardt et al., 1991; James and Fawell, 1991; Velzeboer et al., 1995; Chow et al, 1998; Henderson et al., 2006; Henderson et al., 2008; Miller & Yates, 2006.
	Decrease coagulant demand via enhancement of interparticle flocculation and particle filtration via interaction of extracellular organic matter on algal cell surfaces (over-dosing breaks down this matter and impairs coagulation)	Betzer et al., 1980; Jekel & Reicherter, 1987; Hoyer et al., 1987; Montiel & Welt'e, 1998; Plummer & Edzwald, 2002; Ghernaout, Ghernaout & Saiba, 2010
Sedimentation	Increased sludge production Increased buoyant flocs/change in flocs properties	Walsby & Xypolyta 1977; Choi et al. 2006; Joh et al, 2011
Filtration	Shortened filter run times, increased backwash volumes	Bernhardt et al., 1991; Yun et al., 2002; Joh et al., 2011
	Impact on biological filtration – assimilable organic carbon (AOC) production potentially changing biofilm properties	Lauderdale <i>et al.</i> , 2012; Li <i>et al.</i> , 2010; Jang, Choi, Ro & Ka, 2012
Disinfection	Increased DBP production, microcystins	Hoehn <i>et al.</i> , 1980, Plummer & Edzwald, 2001; Fang <i>et al.</i> , 2010. Also refer to pretreatment
Finished water	Taste and odour	Suffet, 1995; Smith et al., 2002
	Microbial/biofilm regrowth	Miettinen <i>et al.</i> , 1997; Lehtola <i>et al.</i> , 2002; Sathasivan & Ohgaki, 1999

## 2.4.2.5 Co-leaching with organic solutes in soils

Organic matter can alter the sorption of phosphate to particulate matter either through direct sorption (often in association with metal cations as described in the previous section) or as a competitor for sorption sites on inorganic particles (Sample *et al.*, 1980). Our understanding of the influence of

organic matter on phosphate sorption is poor (Holtan *et al.*, 1988) given the limited availability of laboratory studies confirming organic phosphorus mobilization and transport mechanisms (Hens & Merckx, 2001; Kalbitz, Solinger, Park, Michalzik & Matzner, 2000; Williams & Edwards, 1993). The regulation of phosphorus transport by the presence of organic matter and/or other colloidal particles in maize-grown and sandy soils receiving manure applications has been observed in column studies (Chardon *et al.*, 1997; Toor, Condron, Di, Cameron & Cade-Menun, 2003). Co-leaching of phosphorus with organic solutes usually occurs when the sorption capacity of soils approaches saturation (Koopmans, Chardon & McDowell, 2007; Novak, Watts, Hunt & Stone, 2000; Schoumans & Groenendijk, 2000).

Phosphorus co-leaching with fulvic acids and hydrophobic neutral organic matter has been demonstrated in several studies as a dominant transport mechanism in terrestrial forest soils at acidic conditions (Broberg & Persson, 1988; Cronan & Aiken, 1985; Jones, Shaw & De Haan, 1993; Qualls & Haines, 1991); however, other organic solute fractions have been reported to be leached with phosphorus to varying degrees. Dissolved organic phosphorus has been associated with hydrophilic humic acid and hydrophilic neutral fractions (Qualls & Haines, 1991). In another study, Makarov & Leoshkina (2009) reported significantly less phosphorus in the fulvic acid fraction of organic solutes. The few generalizations that can be made regarding phosphorus-organic solute association are likely attributable to the complex source, character and biogeochemical interactions of organic matter (Chardon *et al.*, 1997; Turner, 2000).

Phosphorus's association with specific fractions of DOC may provide additional insight to the source and character of the DOC present, enhancing our ability to make effective drinking water treatment design and optimization decisions because both influence raw water treatability (MWH, 2012). Larger, hydrophobic molecules drive coagulant dose as they tend to be more easily removed by coagulation (Amy *et al.*, 1987; Amy, Sierka, Bedessem, Price & Tan, 1992) compared to smaller, hydrophilic molecules (Boyer, Singer & Aiken, 2008; Cheng & Chi, 2003; Lee & Westerhoff, 2006; Lui *et al.*, 2012). Regulated DBPs are generally associated with hydrophobic acid and higher molecular weight fractions of natural organic matter (Hua & Reckhow, 2007; Song, Orr, Hong & Karanfil, 2009); however, smaller hydrophilic organic molecules less effectively removed by coagulation-flocculation have also been associated with the formation of dihaloacetic acid and other emerging DBPs of concern during disinfection (Hua & Reckhow, 2007; Zhao, Gu, Li, Li & Leung, 2009).

## 2.4.3 Implications of landscape disturbances to drinking water treatment in forested watersheds

Approximately two-thirds of all water supplies in North America originate from forested watersheds (Stein et al., 2005). Water quality in these watersheds generally reflect the dominant land uses (Table 2.10) (Arbuckle & Downing, 2001; Carpenter, et al., 1998; Crosbie & Chow-Fraser, 1999). Resource extraction (forestry, petrochemical extraction), rural/urban development and climate changeassociated natural disturbances (e.g., wildfires, insect infestations such as Mountain Pine Beetle) pose well-documented threats to source water quality in these watersheds. These threats have significant implications for aquatic ecosystem health and drinking source water supplies and treatment (Emelko et al., 2011; Kurz et al., 2008; Schindler & Donahue, 2006). Even undisturbed forested watersheds may not necessarily produce high quality water consistently for all uses, despite their buffering capacity for water quality changes through natural infiltration processes (Anderson, Hoover & Reinhart, 1976; Neary, Ice & Jackson, 2009; Smith et al., 2011). While traditional SWP strategies have focused on minimizing or eliminating anthropogenic threats to preserve source water quality (e.g. logging bans), these strategies are often ineffective against natural disturbances like wildfire and may even exacerbate source water quality impacts arising from such disturbances (e.g. due to fuel load build-up) (Emelko et al., 2011). This underscores the pressing need for the development and implementation of SWP strategies that integrate forest and water management to mitigate impacts to water users.

Table 2.10 Land-use water quality impacts (adapted from Brown & Binkley, 1994)

Land use	Water Quality Impacts
Urban	Household chemical products, pet wastes, yard applications, industrial chemicals, transportation by-products, construction-displaced sediments
Agricultural	Soil tillage, fertilizer, pesticide applications, irrigation water, animal concentrations
Resource extraction (e.g. mining)	Heavy/toxic metals, acidification, increased rates of erosion
Forests, rangelands	Nutrients, oxygen-demanding organic material, suspended sediments, toxics (if pesticides present), metals

Contemporary forest management practices have evolved to incorporate new understanding of natural successional patterns, transient ecological states and hydrological response after catastrophic events (Bolstad & Swank, 1997; Smith *et al.*, 2011; Paysen, Narog & Cohen, 1998; National Research Council, 2008). Physical and chemical water quality from catastrophic events have been

observed to have longer lasting impacts to than previously expected. Catastrophic land disturbances in forested watersheds such as wildfires and insect infestations increase sediment concentrations and export (Moody, Martin & Cannon, 2008; Silins *et al.*, 2009), organic matter (Evans, Monteith & Cooper, 2005; Hughes, Reynolds & Roberts, 1990; Neal *et al.*, 1998;), nutrients (Bladon *et al.*, 2008; Mast & Clow, 2008; Silins *et al.*, *In review*) and trace metals (Kelly, Schindler, St. Louis & Donald, 2006). The resulting water quality impacts can pose tremendous challenges for water treatment plants.

The lack of a vulnerability indicator linking land-use impacts to source water quality and their downstream treatment implications presents a significant challenge for the development and implementation of effective SWP strategies. Land-use impacts on water quality are not always discernible based on an assessment of commonly utilized water quality metrics such as turbidity, dissolved organic carbon and colour (Table 2.11), despite their extensive use in drinking water treatment. Water quality changes are highly scale dependent, site specific and often require decoupling of complex biogeochemical and ecological processes (Reid, 1993; FAO, 2001; Buck, Niyogi & Townsend, 2004; Sebestyen *et al.*, 2008). Moreover, some source water quality changes that potentially compromise the effectiveness of treatment are not always reflected by a change in magnitude of these water quality parameters. A review of factors and mechanisms affecting the source, fate and transport of phosphorus in freshwater systems has revealed potential for phosphorus's utility as a source water <u>and</u> treatment vulnerability indicator. Accordingly, this research will evaluate the strength and significance of these factors and mechanisms to infer dominant processes influencing source water quality and their implications for treatment.

Table 2.11 Impact of land-use change on water parameters, by basin size (FAO, 2001)

	Basin Size (km²)						
Parameter	0.1	1	10	100	1000	10000	100000
Average/peak/base flow	X	X	X	X	0	0	0
Groundwater recharge	X	X	X	X	О	О	0
Sediment load	X	X	X	X	0	0	0
Nutrients	X	X	X	X	X	0	0
Organic matter	X	X	X	X	0	0	0
Pathogens	X	X	X	0	О	О	0
Salinity	X	X	X	X	X	X	X
Pesticides	X	X	X	X	X	X	X
Heavy metals	X	X	X	X	X	X	X
Thermal regime	X	Х	0	0	0	0	0

x = observable impact, o = impact not observable

## **Chapter 3: Methods**

## 3.1 Research approach

The overall goal of this research is to examine phosphorus as a source water and treatment vulnerability indicator to connect upstream land-use disturbances in a watershed to downstream drinking water treatability impacts. To achieve this goal, a proof-of-concept demonstration using water quality data (including phosphorus) collected from the Glenmore Reservoir and Glenmore WTP located within the Elbow River watershed in Alberta, Canada was used. The completed assessment presented herein explicitly links upstream landscape impacts on water quality to downstream drinking water treatability.

### 3.1.1 Watershed description

The headwaters of the Elbow River originate in the eastern slopes of the Rocky Mountains (Figure 3.1) The river flows approximately 120 km across landscapes that include alpine and subalpine forests, boreal foothills and aspen parkland (Mitchell & Prepas, 1991). The Elbow River has an average slope of 1% (Dixon, 2006). Characteristics of the Elbow River watershed are summarized in Table 3.1.

Table 3.1 Characteristics of Elbow River Watershed (adapted from Mitchell & Prepas, 1991)

Parameter	Value
Area (excluding reservoir) (km <sup>2</sup> )	1235.7 <sup>i</sup> , 1238 <sup>ii</sup>
Soil	Pleistocene glaciation: Glacial till and lacustrine deposits
	Alpine soils - poorly developed
	Boreal foothills: gray podzols
	Aspen parklands: black chernozemics, orthic gray luvisols, eutric
	brunisols
Bedrock geology	Porcupine Hills Formation (tertiary): sandstone, mudstone; nonmarine
	Upstream of confluence of Elbow/Little Elbow river: Palaeozoic origin
	(marine limestone & dolomite)
	Downstream of Hwy. 22, tertiary Paskapoo Formation: quartz, feldspar
	and a chert/calcareous matrix
Terrain	Rolling to mountainous
Dominant vegetation	Trembling aspen/fescue; trembling aspen/pine; pine/white spruce;
	heaths
Mean annual sunshine (h)	2314

<sup>&</sup>lt;sup>i</sup> Environment Canada, 2013

ii Wijesekara, et al., 2012

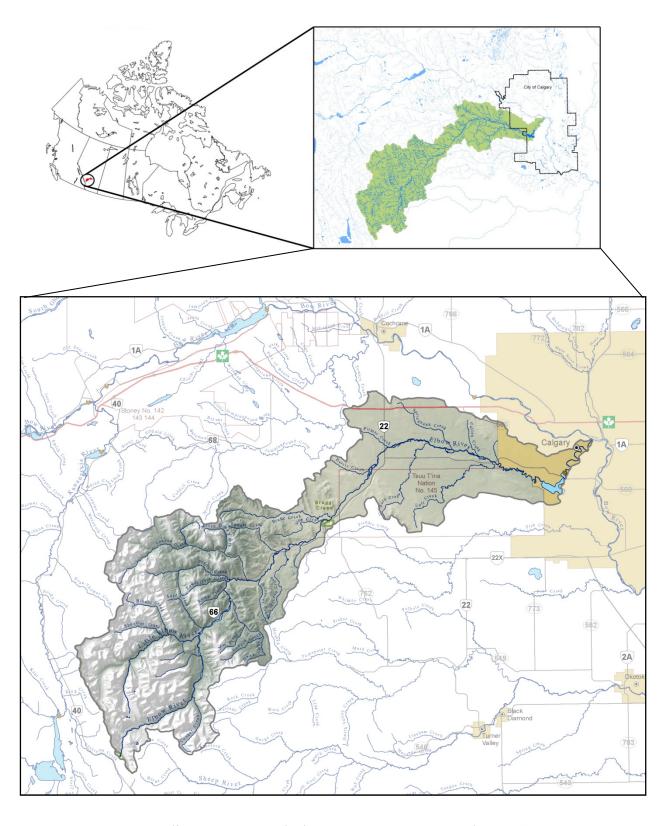


Figure 3.1 Elbow River watershed (Bow River Basin Council (BRBC), 2012)

The majority (63%) of the watershed is zoned as "Green Areas" (i.e. forest reserves), while the rest of the watershed is classified as "White Areas" (i.e. settled lands) for agriculture, urban residential development and recreational purposes (Elbow River Watershed Partnership, 2008). The watershed primarily has four municipal jurisdictions: Kananaskis Improvement District, Municipal District of Rocky View No. 44, Tsuu T'ina First Nation and the City of Calgary (Figure 3.1). In the City of Calgary's Municipal Development Plan (2010) and the Calgary Metropolitan Plan (2012), the provision of clean, affordable drinking water for its population was identified as a critical need to sustain desired socio-economic growth. In 2004, the City of Calgary (urban areas) comprised 2% of the watershed area. 13% and 22% of the watershed is under the jurisdiction of the Tsuu T'ina Nation and the Municipal District of Rocky View #44, respectively. The predominant land use (80%) in the Municipal District of Rocky View #44 is low-intensity agriculture followed by residential land use (16%) (Sosiak & Dixon, 2004).

An independent study by Marshall Macklin and Monaghan (1985) identified potential land use risks to the water supply. The water quality of both Elbow River and Glenmore Reservoir were deemed acceptable overall, but urbanization posed the most immediate ongoing anthropogenic threat. Sosiak and Dixon (2004) identified nonpoint source runoff from agriculture, recreation and residential developments in the upper watershed and urban runoff from Calgary conveyed through the storm sewer system (Environmental Management Associates (EMA), 1993) as two major sources influencing water quality in the Elbow River watershed. Significant increases in total dissolved phosphorus (TDP), fecal coliforms, total coliforms and turbidity were observed in the upper Elbow, although there was no evidence of adverse water quality impacts to the lower Elbow and the Glenmore Reservoir at the time of the study (Sosiak, 1999). Additional data were collected by the City of Calgary and Alberta Environment between 1999 and 2003 to describe spatial and temporal water quality trends and to elucidate factors contributing to water quality deterioration in the upper Elbow River, but insufficient data were available to explain the increasing trends for the aforementioned parameters (Sosiak & Dixon, 2006).

#### 3.1.2 Glenmore Reservoir

The Glenmore Reservoir is a manmade impoundment on the Elbow River in Alberta, Canada. It was constructed in 1932 and currently provides potable water to approximately half the population of City of Calgary (over half a million people) (Beers & Sosiak, 1993; North/South Consultants, Inc., 2007). Ten (10) storm water culverts empty directly into the Reservoir, nine (9) others discharge immediately upstream into the Elbow River (Jerome, 2013); however, the vast majority of inflows to the reservoir is derived from Elbow River discharges (Mitchell & Prepas, 1991) during May, June and July (Xiang, 2004). The Elbow River empties into the Glenmore Reservoir storing water from a cumulative watershed area of 1235.7 km² (Environment Canada, 2013). Morphological and flow characteristics of the reservoir are summarized in Table 3.2. A map of the Glenmore Reservoir is presented as Figure 3.2.

In recent years, the reservoir has shifted from eutrophic to oligotrophic conditions. In 1984, Marshall, Macklin, Monaghan Ltd. classified the reservoir as slightly eutrophic based on 1982-83 data using the Vollenweider eutrophication model, while Hargesheimer and Lewis (1988) classified it as bordering on mesotrophic. In the 2007 North/South Consultant's *Aquatic Ecosystem Health in Alberta* report, the Glenmore Reservoir was classified as oligotrophic, based on measured nutrient and dissolved oxygen levels. The latest classification suggests that the reservoir and water treatment plant are likely to be less susceptible to the impacts of excessive primary production.

The reservoir has improved downstream water quality at the confluence of the Elbow and Bow Rivers because it is a sink for TSS and sediment-associated phosphorus (North/South Consultants, Inc., 2007). Nonetheless, the high levels of benthic algal biomass observed immediately below the reservoir, which are indicative of eutrophic conditions, have been of increasing concern in recent years (North/South Consultants, Inc., 2007). Increasing occurrences of algal blooms below the reservoir are an indication of the potential long-term consequences of water quality deterioration within the reservoir (Dixon, Hardisty, McCauley & Hargesheimer, 1993; Watson, McCauley, Hardisty, Hargesheimer & Dixon, 1996; Watson, Satchwill & McCauley, 2001).

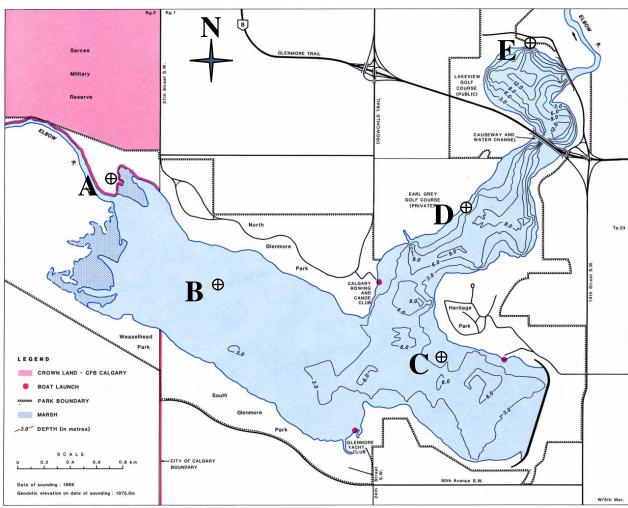


Figure 3.2 Bathymetry, shoreline features and compartments in the Glenmore Reservoir. A. Weaselhead Bridge B. Weaselhead C. Heritage Cove D. Mid-Lake E. Head Pond/Screen House (Glenmore WTP treatment plant intake) (City of Calgary 1983, Bathymetry Source n.d.)

Table 3.2 Characteristics of Glenmore Reservoir (Updated from Mitchell & Prepas, 1993)

Parameter	Value
Control Structures	Dam and 1-km dyke on southeast bay
Elevation (m)	1073.5
Full supply level (FSL) (m)	1076.9
Volume at FSL (m <sup>3</sup> )	$23.4 \times 10^6$ , 17.6 x $10^{6}$ a
Surface area at FSL (km <sup>2</sup> )	3.84
Maximum drawdown (1976-1987) (m)	5.38
Mean annual drawdown (1976-1987) (m)	3.48
Maximum depth at FSL (m)	21.1
Mean depth at FSL (m)	6.1, 7.4 <sup>a</sup>
Shoreline length at FSL (km)	15.5
Lake length at FSL on NE-SW axis (km)	4.5
Lake length at FSL on NW-SE axis (km)	4.75
Mean annual lake evaporation (mm)	712
Mean annual precipitation (mm)	426
Mean residence time (yr)	$0.07, 0.11^a$
Mean annual inflow (m <sup>3</sup> /yr)	299 x 10 <sup>6</sup> , 271 x 10 <sup>6 a</sup>
Annual withdrawal for Calgary water supply (1987) (m <sup>3</sup> )	101.8 x 10 <sup>6</sup>
Mean annual outflow to the Elbow River (1908-1986) (m <sup>3</sup> )	$258.0 \times 10^6$

a (Dixon, 2011)

#### 3.1.3 Glenmore Water Treatment Plant

The Glenmore WTP is located due north of the Head Pond compartment of the Glenmore Reservoir. A schematic of the WTP is presented in Figure 3.3. It was originally constructed in 1933 and expanded in 1957 and 1965. Between 2000 and 2010, conventional treatment was employed. Since May 18th, 2011, a new pre-treatment facility employing Actiflo© (ballasted-sand flocculation) was commissioned to meet projected needs to 2021 (City of Calgary, n.d.). This upgrade was commissioned to address extreme turbidity events encountered during annual spring freshet. The compact system introduces microsand and to coagulant for seeding floc formation and encourages rapid settling to remove turbidity and organic matter. With four Actiflo© clarifier units in operation, the Glenmore WTP has a maximum capacity of 400,000 m³/day. The addition of two more units in 2011 have increased plant capacity to 950,000 m³/day. Other operational changes and upgrades included:

• the shift of pre-treatment chlorine dose from application at the raw header to immediately prior to filtration for the reduction of DBP formation,

- the installation of a sodium bi-sulfate system to replace sulphur dioxide gas used for dechlorination,
- the installation of a potassium permanganate and powdered activated carbon system before pre-treatment as an alternative to chlorine for chemical oxidation to control taste and odour,
- the upgrade of filters with air scour to enhance backwash and filter performance,
- the commissioning of an enhanced residuals treatment facility to reduce waste streams,
- the commission a clearwell for additional primary disinfection contact time; and
- the implementation of a filter-to-waste recycle system to reduce backwash water discharge to the environment. (City of Calgary, n.d.)

Changing source water quality impacts on treatment at the Glenmore WTP have been documented. Lewis and Seidner (1993) noted increased chlorine demand and DBP production, in the late 1980s and early 1990s. Algal blooms of increasing intensity have been observed prior to 2000 in the reservoir (Dixon *et al.*, 1993; Watson *et al.*, 1996, 2001). In the early 1990's, a three year study found a positive association between the presence of phytoplankton in the reservoir and taste and odour events, which coincided with increased consumer complaints about taste and odour in the treated water (Hardisty, 1994).

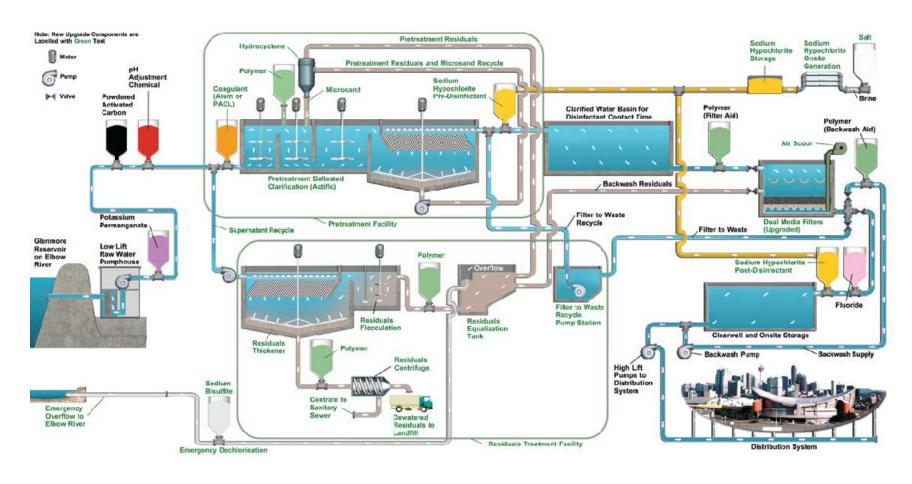


Figure 3.3 Glenmore WTP Process Flow Diagram (City of Calgary, n.d.)

#### 3.1.4 Watershed planning in Alberta, Canada

The Province of Alberta has initiated a number of province-wide policy adaptations across several departments and boards relating to land and water use impacts on sustainable development through the Land Use Framework (2008a) and the Water for Life Strategy (2008b). An essential strategy of the Land Use Framework involves the alignment of land-use policies with natural resource values at a regional (watershed) basis to achieve long-term economic, environmental and social goals. It complements the Water for Life Strategy, which provides the fundamental basis for water management and planning in Alberta. The Strategy is promulgated within the legislative framework established by the Water Act (2012) and the Framework for Water Management Planning (2001).

Water for Life (2008b) establishes a hierarchy of three partnerships: the Alberta Water Council (AWC), Watershed Planning and Advisory Councils (WPAC) and Watershed Stewardship Groups (WSG). The three nested scales of partnership provide a range of strategic, tactical and operational levels for water management and planning. WPACs are established for major river basins through the Water Act and are tasked with the creation of water and watershed management plans. These plans are advisory documents that have "no [legislative] authority beyond compelling decision-makers to consider [them] in their decision-making" (Alberta Water Council, 2008).

Water Management Plans (WMPs)<sup>1</sup> developed under the *Water Act* (2012) provide guidance and recommendations regarding "water conservation and management, setting clear and strategic directions regarding how water should be managed". WMPs may be integrated as part of Watershed Management Plans (WSMPs), which more comprehensively address integrated watershed issues. *The Bow River Basin Watershed Management Plan* (2012) and the *Elbow River Basin Water Management Plan* (2008) were developed by the Bow River Basin Council (BRBC) and Elbow River Watershed Partnership respectively to provide guidance and recommendations within the Elbow River watershed upstream of the Glenmore Reservoir. Developed in alignment with the goals of the *Land Use Framework* and the *Water for Life Strategy*, these plans establish the watershed values around which SWP policies are developed.

<sup>&</sup>lt;sup>1</sup> <u>Approved</u> Water Management Plans must be considered by the Director for making license and approval decisions, Water Management Plans are optionally considered.

#### 3.1.4.1 Environmental indicators for Bow River Basin monitoring

The purpose of a WSMP is to address cumulative impacts of land uses on various downstream water uses. Environmental indicators are employed as part of WSMPs to "measure, monitor and evaluate watershed conditions as part of an iterative, adaptive environmental performance management system" (Bow River Basin Council (BRBC), 2012). Water quality parameters are selected to establish objectives, targets and warning levels based on reach-specific environmental outcomes. An objective is a water quality indicator value set at which a desired environmental outcome may be achieved. Targets are indicator values that would reflect the most desirable environmental conditions and warning levels are usually indicative of detrimental environmental impacts. These thresholds are determined based on existing guidelines, scientific literature, reach specific tools, intended water uses and/or historical data-based percentiles (Forrest & Kobryn, 2007).

The water quality indicators pertinent to the "Elbow River Central" reach containing the Glenmore Reservoir have been predominantly determined based on ecosystem health. Total ammonia, nitrates, TOC, total coliforms and Giardia are the only parameters explicitly specified to address municipal drinking water treatment challenges. A target threshold of 0.04 mg total ammonia per litre was established because chlorine demand during drinking water treatment would reach unacceptable levels at higher ammonia concentrations. Total coliforms counts above 20,000 per 100 mL affect "the ability of a treatment plant to remove contaminants if pre-disinfection is present" (BRBC, 2012). TOC concentrations above 3.0 mg/L increase coagulant and chlorine demands substantially (BRBC, 2012); accordingly, a water quality target of 3.0 mg/L and objective of 5.0 mg/L were established for base flow conditions. An objective value of 0.267 mg nitrate /L was established for the Elbow River as it corresponded with the stimulation of excessive algal growth affecting municipal water supplies in the Bow River, a river adjoining with the Elbow River downstream of the Glenmore Reservoir (Sosiak & Dixon, 2004). Dissolved oxygen and water temperature objectives were established for the protection of cold-water fish species. 10% of water quality objectives established in federal drinking water guidelines were adopted for pesticides and degradation products due to insufficient data regarding the prevalence and risk associated with these compounds.

#### 3.1.4.2 Phosphorus as an environmental indicator in the WSMP

A water quality objective for TP was not recommended in the WSMP (Table 3.3), as TP in this reach of the Elbow River was predominantly particulate and therefore not bio-available for primary production. Total dissolved phosphorus was considered a better water quality indicator of the threat of excessive primary production. The 90th percentile (1993-2006) of TDP historical data (0.009 mg TDP /L) (Sosiak & Dixon, 2004) was used as the water quality objective. A proposed metric of 150 mg/m<sup>3</sup> chlorophyll-*a* for the open water season was established to prevent adverse impacts arising from stimulation of excessive algal growth (BRBC, 2012).

Table 3.3 Water quality objectives in the Elbow River (Source: BRBC, 2012)

Proposed Indicator	WQOs, Warning Levels and Targets	Baseline Water Quality (Median, Percentiles) mg/L	Rationale
Total Phosphorus	WQO: No recommendation for TP. TDP deemed better WQO for this reach.     TARGET: Eliminate levels that cause nuisance aquatic plant growth.	Open Water Weaselhead 1993-2006 Monthly 0.011 (0.089) 90	<ul> <li>TP objectives were not originally provided in Phase One. Where this occurred, the agreement was to use Alberta Surface Water Quality Guidelines (0.05 mg/L)</li> <li>TP in this reach is predominantly particulate phosphorus which can increase above this level without concurrent algae production. For this reason, TDP deemed better indicator for this reach.</li> </ul>
Total Dissolved Phosphorus	• WQO: 0.009 mg/L TDP • TARGET: Eliminate levels that cause nuisance aquatic plant growth.	Open Water Weaselhead 1993-2006 Monthly 0.002 (0.009) 90	• Based on 90th percentile (1993-2006) for all available data from Mar. to Nov. at the Elbow River at Weaselhead.

## 3.2 Data analysis

The evaluation of phosphorus as a source water and treatment vulnerability indicator was undertaken using the approach summarized in Figure 3.4. The City of Calgary and Alberta Environment and Sustainable Resource Development (AESRD) have compiled a data set between 2000 and 2010 (herein referred to as "historical water quality data") during ice-free months on either a bi-weekly or monthly basis to document water quality changes in the Elbow River discharge and the Glenmore Reservoir. These water quality data (n > 73, depending on the water quality parameter analyzed)

were collected in the Elbow River discharge at the Weaselhead Bridge and within the Glenmore Reservoir in four major reservoir compartments: 1) Elbow River, 2) Weaselhead, 3) Heritage Cove, 4) Mid-Lake and 5) Head Pond/Screen House (Figure 3.2). Samples were collected from multiple sampling locations within each reservoir compartment and were pooled when differences between sampling locations were not statistically significant. Each sampling event generally encompassed the measurement of *in-situ* physical parameters including water temperature, dissolved oxygen and conductivity. Grab samples were obtained for pH, TOC, nutrients and other chemical parameters (Table 3.4).

An assessment of phosphorus correlations with various water quality parameters was conducted using historical Elbow River inflow and Glenmore Reservoir water quality data to elucidate potential source water quality vulnerabilities (denoted "1" in Figure 3.4). Specifically, the response of phosphorus (total phosphorus [TP] and total dissolved phosphorus [TDP]) to hydrological events, and the relative abundance of these forms of phosphorus in the Elbow River inflow and in the Glenmore Reservoir were investigated to infer the influence of allochthonous inputs to the reservoir. Phosphorus transport mechanisms into the reservoir from the inflow was also inferred through exploring the correlations between reservoir TP and turbidity as well as Elbow River inflow TP and total suspended solids concentrations respectively. Nutrient ratios (C:N:P), reservoir chlorophyll-a concentrations and Carlson's trophic state indices (TSI) were used to evaluate the ecological significance of phosphorus to autochthonous primary production in this system (Carlson, 1977 - Equations 1, 2).

$$TSI (chlorophyll \ a) = 10 \left(6 - \frac{2.04 - 0.68lnChl}{ln2}\right)$$
 Equation 1
$$TSI (TP) = 10 \left(6 - \frac{ln\frac{48}{TP}}{ln2}\right)$$
 Equation 2

Table 3.4 Elbow River discharge, Glenmore Reservoir water quality parameters (2000-2010)

Physical Parameters	Chemical Parameters				
Colour (CU/Pt-Co)	Ammonia, ammonium (mg/L)	Potassium (mg/L)			
Conductivity (µS/cm)	Calcium (mg/L)	Silica (mg/L)			
Temperature (°C)	Carbon (TOC,DOC, mg/L)	Sodium (mg/L)			
Turbidity (NTU)	Chlorine (mg/L)	Sulphate (mg/L)			
	Dissolved oxygen (mg/L, % sat.)	Nitrogen (nitrate, nitrite, total Kjeldahl			
	Extracted chlorophyll-a (µg/L)	nitrogen, total nitrogen, mg/L)			
	Fluoride (mg/L)	Phosphorus (TP, TDP, mg/L)			
	Magnesium (mg/L)	Total alkalinity (mg/L)			
	pН	Total hardness (mg/L)			

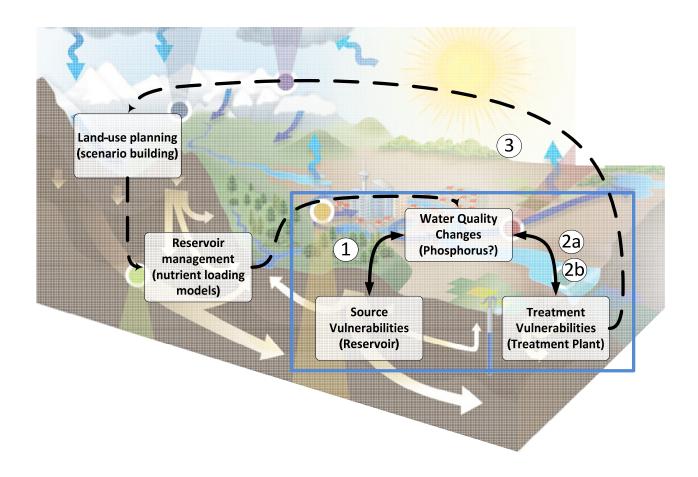


Figure 3.4 Conceptual map of research approach

Source water quality conditions compromising the effectiveness of drinking water treatment were inferred using available historical source water and plant raw water quality data (Table 3.5), and treatment performance metrics (

Table 3.6) using forward-stepwise multiple linear regression (denoted "2a" in Figure 3.4). The developed regression models provided an initial examination of the relationship between process performance and source water quality (including TP and TDP) changes; however, changes in water quality occur throughout the treatment process and thereby may influence treatment process performance. Accordingly, an additional plant water quality data and treatment performance metrics collection program was initiated as part of this research. Forty (n = 40) samples were collected between April and December 2012. Water quality parameters (water turbidity, TOC/DOC, temperature, pH, conductivity, color, zeta potential, UV absorbance and metal concentrations) were collected at five locations throughout the WTP (sequentially from raw water intake): raw water,

clarified water, clarified water post-chlorination (i.e. filter influent), filter effluent and finished water (Appendix A). Multiple linear regression was conducted using these data (denoted "2b" in Figure 3.4) to verify relationships observed from the historical data and to elucidate additional relationships between water quality changes and treatment performance.

The potential impacts of source water quality changes to drinking water treatment processes were subsequently extrapolated using regression models where phosphorus was found to be implicated (denoted "3" in Figure 3.4). Phosphorus loading calculated using land-use nutrient export coefficients was used in reservoir loading models to estimate steady state source water phosphorus concentrations. Treatment performance impacts were then extrapolated based on the estimated reservoir phosphorus concentrations.

Table 3.5 Glenmore WTP raw water quality data (2000-2010)

							1			
Monitoring	Alkalinity	Color 460	Conductivity	Fluoride	Giardia/ Cryptosporidi um	Heavy Metals (As, Pb, Cd)	pH/Temp	TOC	Turbidity	$\mathrm{UVA}_{254}$
Manual	✓	1		1	1	1		✓	1	<b>✓</b>
Continuous			✓				✓		1	

Table 3.6 Available treatment process performance metrics at the Glenmore WTP

<b>Treatment Process</b>	Performance metrics
Coagulation & Flocculation	Coagulant, polymer dose
Chemical oxidation	Chlorine dose
Filtration	Filter run time
Disinfection	TTHM, HAA formation

#### 3.3 Statistical methods

All statistical analyses were conducted using SPSS 17.0 for Windows. Values less than method detection limits were replaced with half the detection limit value (Ellis & Gilbert, 1980), as this simple method works well when there are relatively few of these values in the data (Smith, Silver & Harnly, 2006). In both historical and supplemental data sets, values below detection limits generally comprised less than 5% of all values collected for water quality parameters evaluated with multiple linear regression. Accordingly, more intensive statistical methods (e.g. simulating values by sampling

from hypothetical distributions or imputing values from known covariates) were not conducted for this research. Units of water quality parameters are reported as mg/L unless otherwise indicated.

# 3.3.1 Evaluation of spatial and seasonal characteristics of source water quality

Box plots were constructed to explore the spatial (Appendix B) and temporal variability (Appendix D) of water quality parameters in the Elbow River discharge and in the Glenmore Reservoir. Non-parametric Kruskal-Wallis tests with Bonferroni correction were utilized to evaluate differences in water quality parameters between sampling locations within the same reservoir compartment and between reservoir compartments (Appendix C). A significance level of 0.05 was used for all statistical analyses.

### 3.3.2 Correlations between source water quality parameters

Spearman's rho correlation coefficients were calculated to screen for statistically significant moderate to strong discharge and reservoir inter-parameter correlations ( $\alpha=0.05$ ,  $\rho\geq0.40$ ). Spearman's rho is calculated as the linear correlation coefficient of the ranked data for large samples (n>20) and rank approximations (Helsel & Hirsch, 2002). This provides an unbiased indication of monotonic trends exhibited by two variables while eliminating effects of nonlinearity and extreme values. Observations for various parameters were not temporally consistent and therefore time series analysis was not appropriate to determine spatial aspect of water quality fluctuations in different sampling locations within the reservoir (Legendre & Legendre, 2012). Potential factors affecting phosphorus source, transport and fate were inferred based on its relationships with relevant water quality parameters, which were elucidated using simple linear regression. Regression analyses were conducted using log-transformed water quality variables to satisfy the normality assumption.

# 3.3.3 Correlations between reservoir and treatment plant raw water quality

An assumption implicit to drawing inferences about how source water quality changes impact treatment performance is the ability of the reservoir source water quality to be adequately reflective of raw water quality at the treatment plant intake. Accordingly, reservoir water quality and the plant

raw water quality were compared through box plot construction and simple linear regression to evaluate the similarity between reservoir and treatment plant intake raw water quality. The arithmetic mean of reservoir samples collected on the same day was calculated and paired with the corresponding on-line water quality data recorded at the plant raw water intake. The most consistently available water quality parameters (pH, TOC, temperature and turbidity) in both the reservoir and the plant were compared.

## 3.3.4 Multiple linear regression with treatment metrics

Multiple linear regression was selected to infer the source water quality conditions that compromise the effectiveness of drinking water treatment. It was selected to maximize the use of a relatively small data set (n < 30) while assessing multiple potential explanatory water quality parameters. Data recorded while the treatment system was not in operation (as indicated by a flow rate of 0 L/s through the plant) were removed from analyses. Water quality and treatment performance data were log-transformed to meet the normality of residuals assumption for multiple linear regression (Harvey, E., personal comm., 2013). Water quality data were excluded list-wise by date, occluding the consideration of all water quality parameters exhibiting log-linear relationships with treatment performance parameters. Where data availability permitted, additional water quality parameters exhibiting significant log-linear relationships (based on Pearson's correlation coefficients and visual confirmation using matrix scatter plots) were also considered.

A forward stepwise multiple linear regression procedure using ordinary least squares was applied to determine significant predictors of treatment performance metrics. Where k represents the number of predictors used in a multiple linear regression model, at least 10 times k data points should be available: models violating this rule of thumb were omitted (Harvey, E., personal comm., 2013). The goal of this regression analysis was to determine whether phosphorus contributed to the variability of any treatment performance metrics as well as, or better than other water quality parameters. Adjusted coefficient of determination (Adjusted-R<sup>2</sup>) values were reported to allow for comparison of relative fit between models containing different number of predictors. Residual plots and the Durbin-Watson statistic were used to verify that autocorrelation of residuals did not confound the multiple linear regression relationships. Variance inflation factors (VIF) were also used to assess the potential collinearity between predictors.

Online plant raw water quality parameters (conductivity, temperature, TOC, turbidity) and TP were considered for all regression models. Plant raw water UVA<sub>254</sub> greatly limited the data available for modeling using the historical water quality data set as it was not consistently available and therefore was not considered in all regression models. As a measure of significant hydrological events, Elbow River inflow into the Glenmore Reservoir was noted to be strongly correlated with most treatment performance metrics. Accordingly, it was used as a seasonal indicator variable to adjust for potential issues of autocorrelation, where appropriate.

The plant process treatability models developed were validated using an independent data set collected during the confirmatory sampling period between April and December 2012. Forty (40) additional samples were collected at five (5) locations within the treatment plant to assess the source and fate of phosphorus and confirm its relevance to drinking water treatment processes. It should be recognized that the supplemental data set was collected at substantially different operational conditions: Actiflo© (ballasted-sand flocculation) replaced conventional flocculation in the treatment process since 2010; while pre-treatment chlorination was applied immediately prior to filtration instead of at the raw water header.

## **Chapter 4: Results and discussion**

## 4.1 Source water quality characterization

Spatial and temporal patterns in Elbow River discharge and Glenmore Reservoir water quality data were characterized to better understand source water quality conditions influencing water quality in the Glenmore Reservoir and drinking water treatment impacts. Previous studies have reported spatial and temporal water quality patterns in the reservoir (Hargesheimer & Lewis, 1988), long-term water quality changes due to upstream sources (Dixon, 2006) and in-reservoir algal blooms that cause taste and odour problems in the drinking water of Calgary (Hardisty, 1994; Satchwill, Watson & Dixon, 2007). Few studies have examined the dominant drivers of water quality change within the Glenmore Reservoir. These drivers include changes in the relative contributions of autochthonous and allochthonous matter and land-use planning practices and reservoir management strategies. Increased knowledge of these drivers is necessary to understand water quality changes in the reservoir and that lead to drinking water treatment challenges.

Spatial and temporal water quality patterns in the Elbow River and Glenmore Reservoir between 2000 and 2010 are presented in Section 4.2. Section 4.3 examines the relationships between phosphorus and source water quality changes within the Elbow River inflow and Glenmore Reservoir. Section 4.4 presents a statistical comparison of reservoir and plant water quality. Section 4.4 assesses how changes in source water quality influence water treatment processes.

### 4.2 Spatial and temporal water quality trends (2000-2010)

Water quality in the Elbow River inflow and each compartment of the reservoir were compared using box plots (Appendix B) and statistically evaluated using Kruskal-Wallis tests (Appendix C). For the majority of water quality parameters (i.e. chlorine, DOC, dissolved oxygen, chlorophyll-*a*, fluoride, potassium, magnesium, sodium, nitrite, silica, sulphate, TDP, total Kjeldahl nitrogen) examined, there was no significant difference (p > 0.05) between the inflow of the Elbow River and any of the compartments in the Glenmore Reservoir. Of the remaining water quality parameters exhibiting spatial heterogeneity (i.e. color, conductivity, temperature, turbidity, ammonia, ammonium, calcium, nitrate, pH, total alkalinity, total hardness, TP, TOC), only six (6) parameters (color, temperature, ammonia, total alkalinity, calcium, nitrates) were significantly different in the Weaselhead compartment of the reservoir during more than one month (p < 0.05). Calcium, nitrates and total

alkalinity were significantly different in September between reservoir compartments: the slight peak in nitrates in Mid-Lake during September supports the hypothesis that fertilizer and stormwater runoff from the adjacent golf course and subdivisions may be a contributing factor (City of Calgary, 2010b).

Water quality trends in the reservoir are generally consistent with previous literature. Hardisty (1993) reported that the Glenmore Reservoir behaves as one homogenous basin and water quality within the basin was horizontally well-mixed. Mixing in reservoirs is enhanced given increased turbulence, decreased residence time and shallower depths (Imboden & Wüest, 1995). She proposed that the presence and persistence of algal blooms in the reservoir is related to the processes that influence phytoplankton ecology at the reservoir basin scale (Hardisty, 1993). In contrast, this study noted some seasonal differences in physical and chemical water quality characteristics between the Weaselhead compartment of the reservoir (including the Elbow River inflow to the reservoir) and the rest of the reservoir. Riverine inflows dissipate along the axis of the reservoir with changes in basin width and depth (Kennedy & Walker, 1990). The substantial sedimentation and deposition of particles within the shallow (1 to 3 m deep) Weaselhead compartment of the reservoir leads to a localized decrease in water depth, which may have accentuated the difference in reservoir morphological characteristics and in water quality characteristics between the lotic and lentic regions of the reservoir. The gradual decrease in reservoir depth also reduces the retention time of the Glenmore Reservoir (~1 month) (Mitchell & Prepas, 1991), potentially leading to reservoir water quality characteristics that are increasingly related to allochthonous contributions from the Elbow River.

Chemical and suspended particulate stratification are generally negligible in reservoirs; stratification is usually dependent on temperature variation (Imboden & Wüest, 1995). Vertical thermal stratification does not often occur in the Glenmore Reservoir (Mitchell & Prepas, 1991). Some weak thermal stratification events have occurred for a few days in the summer near the causeway (Dixon, 2011). In the present study, significantly different temperatures in the reservoir compartments were observed during September, indicating thermal stratification. During this period, differences in temperature coincide with changes that occur for other water quality parameters (ammonia, total alkalinity, calcium and nitrate). Vertical density differences and density differences between river inflows and reservoir water strata arising from thermal stratification induce density flows which may influence water quality distribution in thermally stratified reservoirs (Kennedy & Walker, 1990). As

chemical and suspended particulate stratification was otherwise generally not evident in the Glenmore Reservoir, reservoir water quality data downstream of the Weaselhead compartment were aggregated for subsequent data analyses (herein referred to as the "reservoir water quality") (Table 4.1). All units were measured in milligrams per litre (mg/L) unless otherwise indicated.

Table 4.1 Reservoir water quality summary statistics (2000-2010)

	n	Minimum	Maximum	Median	Mean	Standard Error of Mean	Standard Deviation
Ammonia	170	0.005	0.106	0.010	0.015	0.001	0.013
Ammonium	176	0.005	0.106	0.010	0.014	0.001	0.014
Calcium	123	41.04	69.39	52.75	53.58	0.61	6.75
Chlorophyll-a	144	0.16	7.05	1.37	1.65	0.11	1.26
Color (Color Units)	179	1.0	29.9	2.4	3.6	0.33	4.4
Conductivity (µS/cm)	174	128.6	489.6	359.6	373.3	3.71	49.0
Dissolved Oxygen Concentration (% saturation)	164	72.4	142.0	96.9	97.6	0.87	11.2
Dissolved Oxygen Concentration	166	7.09	15.9	9.5	9.8	0.13	1.73
DOC	73	0.65	5.46	1.88	2.07	0.10	0.8
Fluoride	125	0.18	0.64	0.25	0.25	0.004	0.045
Magnesium	123	10.138	21.640	15.868	15.843	0.179	1.986
Nitrate	177	0.001	0.268	0.026	0.047	0.004	0.049
Nitrate + Nitrite	177	0.001	0.286	0.026	0.048	0.004	0.050
Nitrite	177	0.001	0.022	0.001	0.002	0.000	0.003
pН	173	7.33	8.75	8.18	8.13	1	-
Potassium	123	0.534	4.122	0.933	1.024	0.039	0.435
Silica	129	2.525	6.122	4.143	4.063	0.054	0.618
Sodium	123	1.625	9.866	3.790	4.233	0.141	1.567
Sulphate	125	23.287	76.005	55.017	54.926	0.973	10.876
Temperature (°C)	173	0.16	21.3	11.76	10.56	0.50	6.62
TOC	170	0.71	8.32	1.82	2.11	0.08	1.021
Total Alkalinity	125	120.0	185.7	143.3	148.1	1.425	15.9
Total Dissolved Phosphorus	176	0.001	0.044	0.002	0.003	0.000	0.004
Total Hardness	125	165.5	322.2	203.1	213.0	2.898	32.40
Total Kjeldahl Nitrogen	112	0.025	0.760	0.175	0.211	0.012	0.131
Total Nitrogen	112	0.007	0.896	0.206	0.251	0.014	0.149
Total Phosphorus	178	0.001	0.372	0.007	0.012	0.002	0.030
Turbidity (NTU)	178	0.35	162.0	1.674	4.958	1.132	15.1

Units in mg/L unless otherwise specified

Seasonal variation of reservoir water quality data (2000-2010) was characterized using box plots (Appendix D). The period of greatest change in reservoir water quality occurred from April to June. For example, the highest turbidity and monthly mean organic carbon (total and dissolved) levels were observed in May and June, respectively. In contrast, the highest monthly means for most other water quality parameters occurred during April. The simultaneous deterioration of multiple water quality parameters within the reservoir with periods of increased precipitation and run-off events suggests that water quality are predominantly driven by the effect of the Elbow River inflow during these periods. Some years are characterized by two lagged regional run-off events that include a local snowmelt and a second, larger run-off event attributed to snowmelt in the basin headwaters at higher elevations (Mielke, L. personal communication, 2012). Despite some expected differences in water quality in these two hydrological events, the sparsely distributed historical water quality data were insufficient to observe differences between these two hydrological events.

# 4.3 Source water vulnerability assessment using historical data (2000-2010)

Relationships between phosphorus and water indicators (quality and quantity) were examined to determine key drivers that influence changes in source water quality to the reservoir. Specifically, these relationships were used to infer the relationships between allochthonous and autochthonous sources and their potential impacts to source water quality. These inferred relationships provide a context in which to interpret causes for water treatment challenges.

## 4.3.1 Phosphorus relationships with significant hydrological events

Monthly variation in the phosphorus concentrations in the Elbow River inflow and Glenmore reservoir are presented in Figure 4.1 and 4.2. Particulate phosphorus comprises the majority of monthly phosphorus concentrations in the Elbow River (Figure 4.1). The majority of phosphorus was transported to the Glenmore Reservoir during high flow events in spring (April, May and June) in the particulate form. Elbow River TP concentrations increased with peak discharge (R<sup>2</sup>=0.419, p<0.001, Figure 4.3), but are generally lower at higher discharges in the summer (July, August, September) and the fall (October, November, December) compared to spring hydrological events. Reservoir TDP was not significantly correlated with Elbow River discharge (p=0.79).

Elbow River discharge was used as an indicator of significant hydrological disturbance in the watershed. However, it is difficult to infer allochthonous and autochthonous impacts to reservoir water quality deterioration based on changes in discharge alone as discharge can dilute contaminant concentrations or increase contaminant loads (e.g. bank erosion). Accordingly, the relationships between Elbow River discharge and TP in both the discharge and the reservoir were compared (Figure 4.4). Reservoir water quality was driven by allochthonous contributions of sediment-associated phosphorous, especially during spring run-off. The observed increase in TP concentration is apparent in both the river inflow and the reservoir. Conversely, reservoir water quality is likely more related to processes within the reservoir in the autumn; reservoir TP concentrations decreased despite a positive correlation between Elbow River TP and discharge during these months. This suggests either a dilution effect or removal of TP in the reservoir due to sedimentation and deposition or precipitation mechanisms.

High reservoir TP concentrations despite relatively low Elbow River discharges in April (extreme values denoted in Figure 4.4) are indicative of a first flush effect of allochthonous TP into the reservoir. These results are consistent with the observations that solid-phase contaminant concentrations generally increase with peak discharge but decrease with increasing discharge frequency and duration (Burke, Heathwaite & Preedy, 2004). The transport of up to 80% of phosphorus adsorbed to sediment has been observed during the first storm event of the season to receiving water bodies (Riemersma, Little, Ontkean & Moskal-Hébert, 2006). The extreme values observed in the present study contributed to the reduction to the overall significance of the relationship between reservoir TP and Elbow River inflow during spring months.

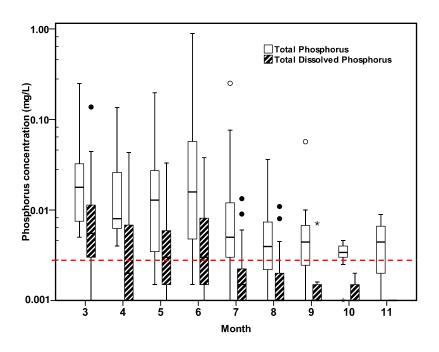


Figure 4.1 Elbow River discharge phosphorus concentrations  $(2000-2010)^2$  (MDL = 0.002 mg/L)

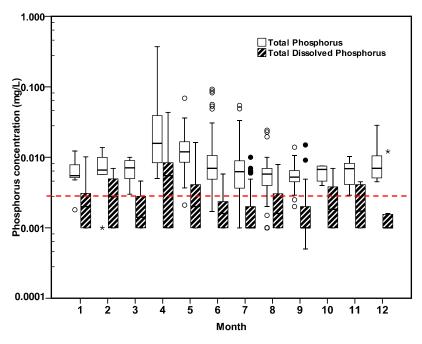


Figure 4.2 Glenmore Reservoir phosphorus concentrations  $(2000-2010)^2(MDL = 0.002 \text{ mg/L})$ 

<sup>2</sup> MDL = Method Detection Limit. Multiple MDL were observed between 2000-2010. Dashed line indicates highest MDL used. Values below MDL were treated as half the detection limit in the construction of these box plots.

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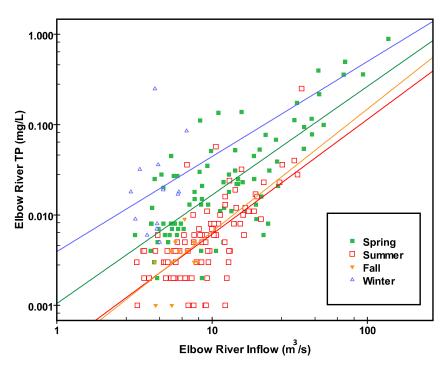


Figure 4.3 Relationship between river discharge at Weaselhead bridge and TP (2000-2010) (spring  $R^2$ =0.59, p<0.001; summer  $R^2$ =0.46, p<0.001; fall  $R^2$ =0.21, p<0.001; winter  $R^2$ =0.06, p<0.001)

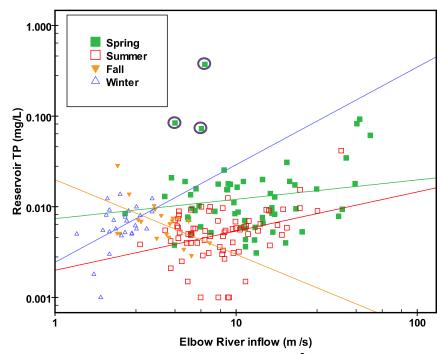


Figure 4.4 Relationship between Elbow River discharge at Weaselhead bridge and Glenmore Reservoir TP (2000-2010). Data enclosed in purple circles denote extreme values. (spring  $R^2$ =0.03, p<0.001; summer  $R^2$ =0.11, p<0.001; fall  $R^2$ =0.28, p<0.001; winter  $R^2$ =0.19, p<0.001)

# 4.3.2 Phosphorus and suspended sediment relationships

The relationship between phosphorus and sediment was explored by examining 1) the proportion of phosphorus in particulate and dissolved forms (Figures 4.1 & 4.2), 2) Elbow River TSS and TP data and 3) Glenmore Reservoir turbidity and TP data. Based on an analysis of historical water quality data (2000-2010), approximately 92% of the annual phosphorus load in the Elbow River consists of particulate phosphorus. Total dissolved phosphorus represented 7.7  $\% \pm 3.3\%$  (mean  $\pm$  standard error of the mean) of the flow-weighted annual phosphorus loading to the reservoir. These proportions are consistent with other estimates of phosphorus fluxes in many rivers of the world (Meybeck, 1982). Levels of TSS in the Elbow River inflow were positively correlated with TP ( $R^2 = 0.852$ , p < 0.001, Figure 4.5). Previous literature on sediment P relationships in the Elbow River indicate that the majority of the phosphorus transported in the Elbow River is particulate (Beers & Sosiak, 1993), the majority of annual sediment transport to the reservoir occurs during spring runoff between the end of May and beginning of June (Hollingshead et al., 1973; Hudson, 1983) and the annual sediment loading to the reservoir is 138 t/km<sup>2</sup> which is attributed to river reaches between Bragg Creek and the Glenmore Reservoir (compared to 11-34 t/km<sup>2</sup> upstream of Bragg Creek) (Beers & Sosiak, 1993). Present sediment loads in the Elbow river have increased by a factor of 1.6 from that (84 t/km<sup>2</sup>/year) reported by Hollingshead et al. (1973) and continued deposition of sediment presents a significant challenge for reservoir management by reducing reservoir capacity.

Beers & Sosiak (1993) reported that bedrock and vegetated river banks in the upper reaches of the Elbow River did not represent significant sediment sources compared to agriculturally intensified lower reaches of the river. However, Sosiak & Dixon (2006) reported evidence of significant bank erosion in the upper Elbow River when runoff rates are high during snowmelt. A recent study estimated that the source of over 85% of the TSS loading to the Bow River (which adjoins with the Elbow River downstream of the Glenmore Reservoir) is from the stormwater system of the City of Calgary (Golder Associates Limited, 2007). The same study also reported that less than 10% of TP loads were derived from the same TSS loading. Additional studies are required to determine whether the stormwater contributions to the reservoir have similar water quality impacts. However, it can be speculated that there is significant potential for phosphorus transport and/or storage associated with the abundance of TSS loading to the reservoir (Ballantine *et al.*, 2009; Logan, 1987; Logan *et al.*, 1979; Stone & English, 1993).

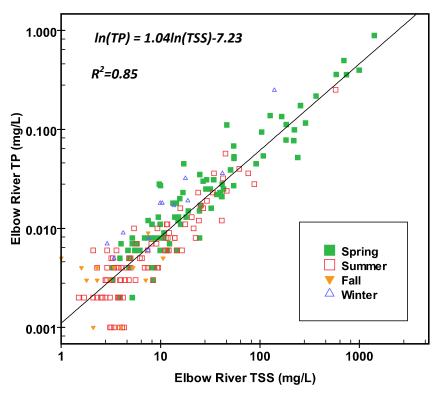


Figure 4.5 Relationship between Elbow River discharge TSS and TP (2000-2010)

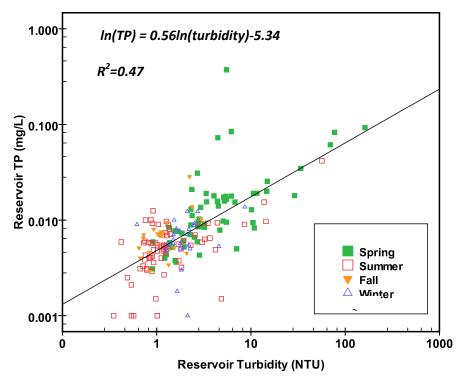


Figure 4.6 Relationship between Glenmore Reservoir turbidity and TP (2000-2010)

A combination of Elbow River discharge TSS concentrations, discharge and reservoir turbidity values were used to infer the potential association of phosphorus to particulate matter  $< 63 \,\mu m$  within the reservoir. A significant log-linear relationship was observed between turbidity and TP concentration in the reservoir ( $R^2 = 0.467$ , p < 0.001, Figure 4.6). While phosphorus in the Elbow River inflow was predominantly in particulate form, a greater fraction of phosphorus species in the reservoir was in the dissolved phase. During periods of high river discharge, the proportion of particulate phosphorus present within the reservoir increased but it was comparatively lower than in the Elbow River inflow. The reduction of the portion of particulate phosphorus in the reservoir is most likely related to deposition processes in the reservoir.

## 4.3.3 Primary production

Phosphorus is the limiting nutrient in most freshwater aquatic systems (Hecky & Kilham, 1988; Schindler, 1974; 1977; Smith & Shapiro, 1981). In the Glenmore Reservoir, median reservoir nutrient mass ratios (C:P, C:N, N:P) were 297:1, 9:1, and 29:1 respectively (Figure 4.7 A,B). Reservoir C:P ratios were lowest in April and highest during the summer months, when primary production was highest. This observation supports the conceptual model proposed by Hecky *et al.* (1993) that higher C:P ratios represent increased autochthonous primary production.

Chlorophyll-*a* is an indicator of phytoplankton biomass and therefore a surrogate measure of the overall primary production in aquatic systems (Wetzel, 2001). Although chlorophyll-*a* was not measured in the Elbow River inflow, it has been reported that allochthonous upstream sources of phytoplankton biomass were not significant contributors to the phytoplankton biomass observed in the reservoir and that any observed algal production occurred within the reservoir (Hardisty, 1993). Chlorophyll-*a* concentrations within each reservoir compartment were consistently low (Figure 4.7 C) and generally reflect oligotrophic to mesotrophic conditions between 2000 and 2010 (Figure 4.7 D). This observation is consistent with the low biomass and organic content typically present in the Glenmore Reservoir (Satchwill, 2001).

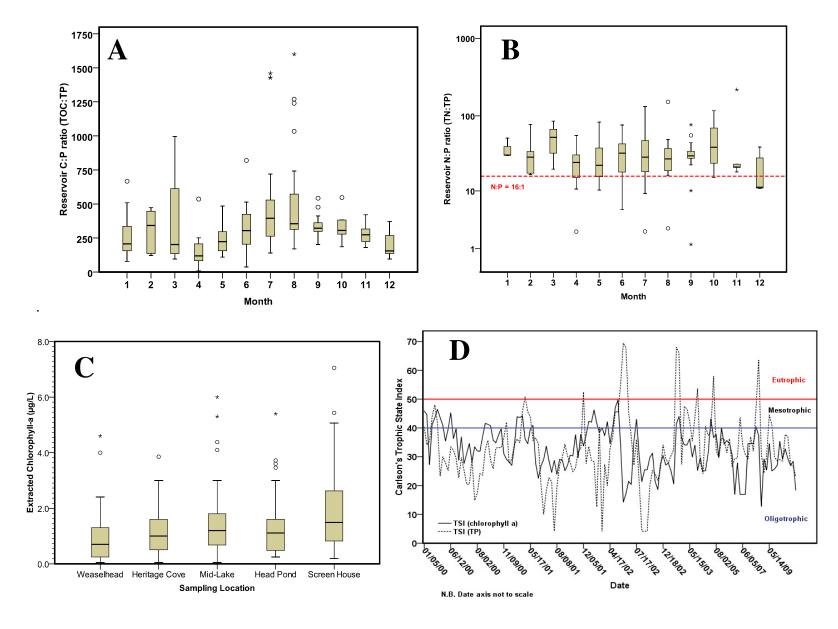


Figure 4.7 Nutrient conditions, productivity in Glenmore Reservoir (2000-2010): A. TOC:TP, B. TN:TP, C. Chlorophyll-a D.Carlson's TSI

The *Bow Basin Watershed Management Plan* (2012) reported that TP is a poor indicator of primary production in the Bow River basin. Carlson's TSI based on TP concentrations (Figure 4.7 D) occasionally exceeded 50 (indicative of eutrophic conditions) but TSI values remained consistently less than 50 when determined based on reservoir chlorophyll-a concentrations. Between 2002 and 2003, there were only two instances when Carlson's TSI (based on TP concentrations) was eutrophic and only one period where the chlorophyll-a concentration approached eutrophic conditions (June 2002). The TSIs were typically lower than those determined by TP. Total phosphorus was not significantly correlated with chlorophyll-a ( $R^2 = 0.026$ , P = 0.058), whereas TDP was significantly correlated with chlorophyll-a ( $R^2 = 0.155$ , P < 0.001) (Figure 4.8). Both these findings suggest that either a limited amount of the phosphorus was bio-available or primary production was limited by other factors (e.g. availability of other micronutrients/light) or a combination thereof.

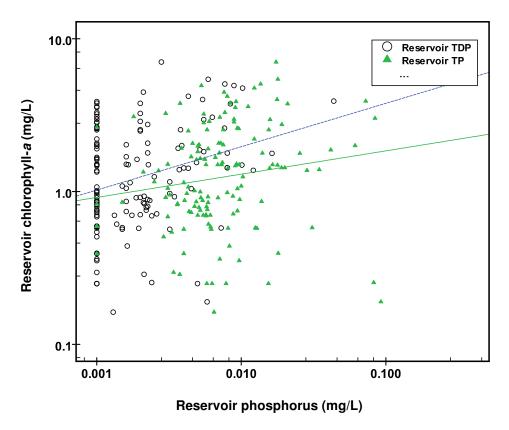


Figure 4.8 Relationships between Glenmore Reservoir phosphorus concentrations and chlorophyll-a (2000-2010):  $TP(\triangle, R^2 = 0.026, P = 0.058)$  &  $TDP(\bigcirc, R^2 = 0.155, P < 0.001)$ 

Several environmental factors may affect the role of phosphorus in primary production in the Glenmore Reservoir. Firstly, particulate phosphorus is the predominant form of phosphorus transported to the reservoir. This form of phosphorus may deposit on the bottom of the reservoir. In

some lacustrine environments, phosphorus release from bottom sediments has been comparable to external loading (Ishikawa & Nishimura, 1989; Wang, Hondzo, Wilson & Stauffer, 2001). In the Glenmore Reservoir, the well-oxygenated Weaselhead compartment may reduce the desorption of phosphorus from deposited sediments to the water column (Hollingshead *et al.*, 1973). The low hydraulic retention time (~1 month) in the reservoir may also suppress the release of bio-available dissolved phosphorus species into the water column through sustaining well-oxygenated conditions at the sediment-water interface. The well-established wetlands in the Weaselhead region of the reservoir may also play an essential ecological role in regulating reservoir primary productivity. Speciation of phosphorus forms leaving wetland areas could be vastly different could be vastly different from the inflow but more research is required to examine this process in detail.

# 4.4 Relationship between reservoir and plant raw water quality

Selected water quality parameters in the reservoir and plant intake were used to assess the degree to which reservoir water quality changes were reflected and representative of raw water quality at the plant intake (box plots are presented in Appendix B). The high correlation between water quality parameters with corresponding measurements at the plant intake was observed (Table 4.2). While pH values were generally conserved, slight reductions in TOC and turbidity in the reservoir were observed in the plant raw water intake. Plant raw water temperatures were generally higher than those observed in the reservoir. Overall, the water quality conditions in the reservoir can be assumed to be representative of raw water quality conditions at the plant intake.

Table 4.2 Simple linear models of corresponding water quality parameters (2000-2010)

Parameter	Linear model	95% confidence interval for slope		$\mathbb{R}^2$	p-value
		Lower	Upper		
рН	$pH_{plant} = 1.00 pH_{reservoir}$	0.99	1.01	0.99	< 0.001
TOC	$TOC_{plant} = 0.77 TOC_{reservoir} + 0.11$	0.48	1.06	0.37	< 0.001
Temperature	$Temp_{plant} = 1.05 Temp_{reservoir}$	1.04	1.07	0.99	< 0.001
Turbidity	Turbidity <sub>plant</sub> = $0.93$ Turbidity <sub>reservoir</sub> - $1.03$	0.87	1.00	0.94	< 0.001

# 4.5 Phosphorus as a treatment vulnerability indicator

Compared to the abundance of literature investigating phosphorus mobility and cycling in natural aquatic systems, there is a paucity of research on the effects of phosphorus on drinking water treatability. Investigations of the impact of phosphorus on drinking water treatability have been limited. They include situations where there is 1) excessive primary production at the source, 2) a desire to support biological filtration, 3) microbial growth in the distribution system and 4) possible interference of coagulant and floculation processes (Pommerenk & Schafran, 2005) at phosphate levels above 1.0 mg/L (Bartenhagen *et al.*, 1984).

Phosphorus and several physical and chemical water quality parameters typically used as indicators of drinking water treatment performance were evaluated to investigate if phosphorus (as TP or TDP) provided additional insight regarding source water treatability. Based on the source vulnerability assessment presented in Section 4.3, low chlorophyll-*a* concentrations and reservoir trophic states indicative of oligotrophic-mesotrophic conditions suggested that algae (primary production) did not affect source water quality during the study period. These data also suggest that the well-known impacts of phosphorus to treatment processes through algal matter and/or algal by-product formation did not confound the analysis of phosphorus impacts to treatability.

A statistical investigation of the relationship between phosphorus and various process-specific performance metrics (conventional water quality parameters used to assess treatment performance) was conducted (Appendix F). Oxidation chlorine dose, coagulant/polymer dosing, filter run time and DBP concentrations were selected as process-specific metrics of chemical oxidation, coagulation/flocculation, filtration and disinfection process performance respectively.

# 4.5.1 Coagulation and flocculation

Coagulation and flocculation processes at the Glenmore WTP commenced with the addition of alum (February 2008 - December 2010) or polyaluminum chloride (PACl) (December 2002 - January 2008). Data were pooled because insufficient data were available to develop alum and PACl regression models separately. Only water quality parameters exhibiting a linear relationship with coagulant dose were considered for forward stepwise multiple linear regression. Accordingly, pH was not considered as a potential predictor despite its known impacts on coagulant dose (alum in

particular). All multiple linear regression models and regression coefficients of inputted parameters derived from the historical data set were statistically significant (Table 4.3, p < 0.05).

Table 4.3 Summary of coagulant dose regression models (2000-2010)

Regression model*	Regression parameter	Parameter coefficients	Standard errors	t-value	p-value	R <sup>2</sup> /Adj. R <sup>2</sup>	p-value
ln(East	k	6.443	0.658	9.790	< 0.001		
coagulant)	ln(TP)	0.792	0.129	6.161	< 0.001	0.788/0.766	< 0.001
[n = 22]	ln(TOC)	0.363	0.128	2.837	0.011		
ln(East	k	-10.033	6.689	-1.50	0.151		
coagulant)	ln(TP)	0.616	0.181	3.405	0.003	0.583/0.536	< 0.001
$[n = 21]^{**}$	ln(Alk.)	3.165	1.278	2.477	0.023		
ln(West	k	2.178	0.133	16.35	< 0.001		
coagulant)	ln(TOC)	1.112	0.182	6.117	< 0.001	0.581/0.565	< 0.001
[n = 29]							

<sup>\*</sup> water quality parameters considered: plant raw water - conductivity, temperature, TOC, turbidity; reservoir raw water - TP, total alkalinity, color.

Coagulant requirements<sup>3</sup> in the east treatment train were different from the west treatment train as treatment trains were not simultaneously in operation and were therefore subjected to different water quality conditions. Total phosphorus and TOC explained most of the coagulant dose variability ( $R^2 = 0.788$ , p < 0.001) in the east treatment train. An extreme value attributed to the floods of July 2005 influenced the east treatment train coagulant dose regression models substantially. After removing this extreme value from the regression model, TP and total alkalinity together explained 0.583 of the variability of the east treatment train coagulant dose. In the west treatment train, TOC was the primary predictor variable of coagulant dose ( $R^2 = 0.581$ , p < 0.001).

Additional data collection in 2012 confirmed the utility of TP as a treatment vulnerability indicator for coagulation and flocculation processes, even though a change in process configuration occurred with the implementation of the Actiflo© process. Actiflo© uses alum as a coagulant to destabilize particles and a polymer to induce particle bridging to enable rapid flocs formation (Blumenschein, Latker & Banerjee, 2006). Sand is introduced subsequently to increase flocs density of flocs and promote rapid removal by sedimentation. Since the implementation of Actiflo©, one coagulant dose has been recorded for both treatment trains. Simple log-linear regressions of raw water TP, DOC,

<sup>\*\*</sup> July 5th, 2005 extreme value omitted from regression analyses

<sup>&</sup>lt;sup>3</sup> Coagulant requirements were assumed to be optimized. "Coagulant" refers to both alum and polyaluminum chloride (PACl).

UVA<sub>254</sub>, turbidity, SUVA and zeta potential with alum dose revealed that each parameter independently explained 0.956, 0.918, 0.895, 0.839, 0.761 and 0.747 of the variability of alum dose respectively (Figure 4.9). The combination of UVA<sub>254</sub> and TP contributed most to the variability of alum dosing ( $R^2 = 0.983$ , p < 0.001) (Table 4.4). A VIF of 12 was estimated in this model, suggesting the potential for multi-collinearity. When considering factors affecting the variance of regression coefficients, the limited sample size (n = 26) may have inflated this statistic (O'Brien, 2007). Moreover, VIF compares the effects of the proportion of variance shared between an independent variable and other independent variables to the condition that none of the variance of an independent variable is shared with other independent variables (O'Brien, 2007). In contrast to a controlled experiment designed to minimize correlation between independent variables, this condition is unlikely to occur given the empirical approach taken in this research (O'Brien, 2007).

Table 4.4 Summary of alum coagulant dose regression models (2012)

Regression model*	Regression parameter	Parameter coefficient	Standard errors	t-value	p-value	R <sup>2</sup> /Adj. R <sup>2</sup>	p-value
In (Aluma dosa)	k	6.923	0.118	58.749	< 0.001		
$ \ln(\text{Alum dose}) \\ [n = 26] $	ln(UVA <sub>254</sub> )	0.753	0.124	6.082	< 0.001	0.983/0.981	< 0.001
$[\Pi = 20]$	ln(TP)	0.339	0.074	4.602	< 0.001		

<sup>\*</sup> water quality parameters considered: conductivity, TOC, DOC, UVA, SUVA, turbidity; TP

Coagulation using metal salts is achieved primarily through enmeshment with metal salt precipitates or charge neutralization of negatively charged waterborne particles (Duan & Gregory, 2003). These mechanisms are influenced by pH, alkalinity, the concentration and character of waterborne particles and NOM (MWH, 2012; Pernitsky & Edzwald, 2006). When low particle concentrations are present in the raw water, coagulant is dosed such that the solubility product constant for the metal salt is exceeded to induce precipitation of metal hydroxides. These precipitates increase particle contact opportunities and entrap waterborne particles; this type of coagulation is known as precipitation and enmeshment or sweep floc (Packham, 1965; Stumm & O'Melia, 1968). Coagulant dosing requirements for sweep floc (in the absence of NOM) are dependent on particle concentrations and independent of the character of the particles present (Packman, 1962; MWH, 2012). At higher particle concentrations, coagulant may be dosed at soluble levels to form cationic hydrolysis products, which destabilize particles through charge neutralization of colloids. Most waterborne particles carry a negative surface charge as the water matrix pH typically exceeds the isoelectric point (pH<sub>iep</sub>) of the majority of particles. Optimized coagulation by charge neutralization is generally achieved by increasing coagulant dose proportionally with particulate surface area concentrations (MWH, 2012),

a surrogate measure for the overall surface charge of particles and natural organic matter. Charge reversal and particle restabilization may occur if the charge demand is exceeded through coagulant addition. Suboptimal coagulant dosing results in excess chemical coagulant costs, increased sludge production and potential deleterious impacts to subsequent treatment processes.

The overall charge demand can be used to estimate the coagulant dose required for achieving particle destabilization through charge neutralization. The simplifying assumption that NOM charge demand (~10 µeq/mg C at pH 7 [Thurman, 1985]) is typically higher than that of particles (~0.1 µeq/mg suspended solids [Pernitsky & Edzwald, 2006]) in water can be used to estimate the overall particle charge demand. Based on average raw water quality parameters measured at the Glenmore WTP in 2012, the NOM charge demand is estimated to be approximately 10 times greater than the relatively insignificant particle charge demand (Table 4.5). During spring run-off in July 2012, turbidity and TOC reached 100 NTU and 5.7 mg/L respectively. The particle charge demand, as estimated using the method by Pernitzky & Edzwald (2006), contributed to more than a third of the total estimated charge demand despite an increase in NOM concentrations. This change in the relative contribution of particle concentrations in the source water during significant hydrological events underscores that both sweep floc and charge neutralization mechanisms may be required at different times for optimizing coagulation flocculation strategies in this system.

Table 4.5 Estimated particle and NOM charge demand

Water quality	pН	Alkalinity (mg/L CaCO <sub>3</sub> )	TP (mg/L)	Turbidity (NTU)	TOC (mg/L)	UVA <sub>254</sub> (cm <sup>-1</sup> )	SUVA (m <sup>-1</sup> /mg/L)	Estimated particle <sup>b</sup> ,NOM <sup>c</sup> charge (µeq/L)
"average" raw water (2012)	8.3	152.7	0.025	4.958	2.51	0.039	2.427 20% humics <sup>a</sup>	Particles: 0.5 NOM: 5.0
"run-off" raw water (July 2012)	8.3	149.6	0.104	99.985	5.70	0.149	4.117 30% humics <sup>a</sup>	Particles: 10 NOM: 17.1

a Humic content estimated from average SUVA: % aromaticity = 6.52SUVA + 3.63 (Weishaar et al., 2003)

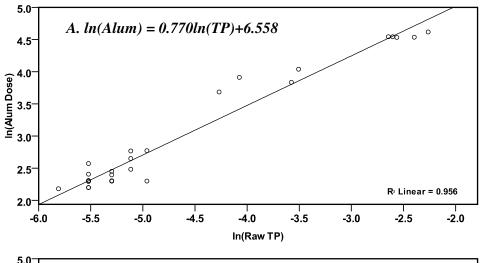
Although turbidity is the most common water quality metric used for optimizing coagulation and flocculation, the regression analyses presented herein indicated that TP was a better predictor for optimizing coagulation and flocculation processes when alum coagulant was used at the Glenmore

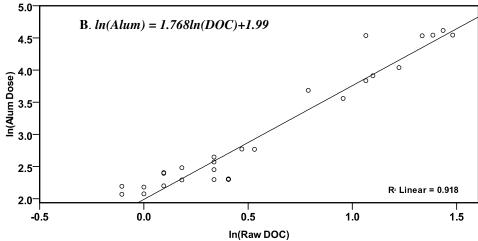
b Estimate of charge demand due to particles calculated from average turbidity data using an assumed relationship of 1 NTU = 1 mg/L suspended solids and assuming  $0.1 \,\mu\text{eq/L}$  negative charge per unit concentration of suspended solids

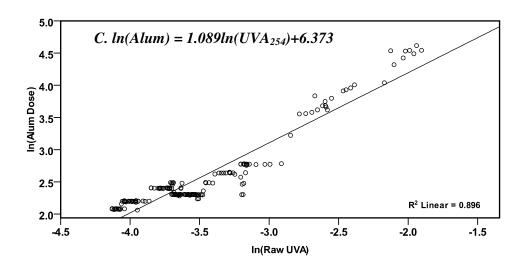
c Estimate of charge demand due to NOM calculated from average TOC data multiplied by the estimated % humic content from the SUVA column, and assuming  $10 \mu eq/L$  negative charge per unit concentration of humic TOC.

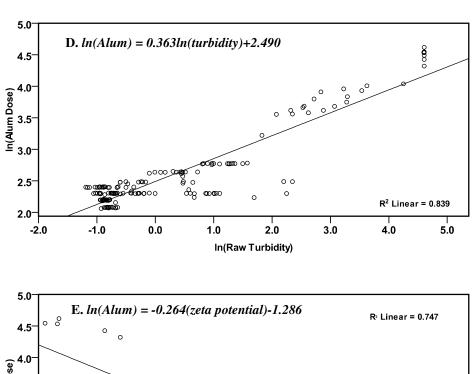
Water Treatment Plant. The relationship between turbidity and waterborne particle concentrations is influenced by the ability of particulate and dissolved constituents present within a water matrix to scatter light (APHA, 2006). This relationship may be further confounded by water temperature, shape, size and mineral composition of particles (Clifford, Richards, Brown & Lane, 1995; Gippel, 1995) and water color imparted by dissolved solids and organic matter (Malcolm, 1985). Based on the strong association of TP with fine-grained sediments in the source water, TP is a mass-based indicator of waterborne particle concentrations. Low TP concentrations in the source water indicate low particle concentrations and the need for sweep floc coagulation; conversely, high TP concentrations are indicative of higher particle concentrations and increased overall particle charge demand. The latter case may necessitate coagulation by charge neutralization for optimal coagulant dosing strategies.

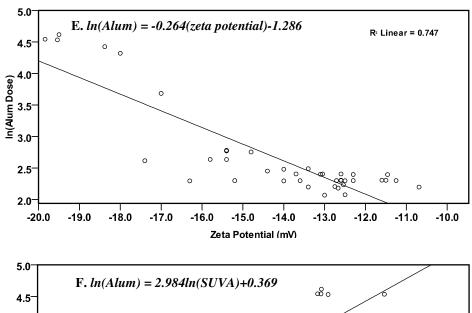
Moreover, phosphorus has also been observed to influence metal complexation and precipitation reactions. A study by Bartenhagen et al. (1994) as cited by the US EPA (2012) observed interference of drinking water coagulation and flocculation processes at phosphate levels above 1.0 PO<sub>4</sub><sup>3-</sup> mg/L. At bench-scale, orthophosphate at sufficiently high concentrations (9.5 mg PO<sub>4</sub><sup>3</sup>/L or 3.1 mg P/L) has been shown to lower the pHiep of pure aluminum hydroxide precipitate by adsorption to the surface of the precipitate and formation of inner-sphere complexes (Pommerenk & Schafran, 2005). Phosphorus, in the form of multivalent anions (e.g.  $H_2PO_4^{-}$ ,  $HPO_4^{-2}$ ,  $PO_4^{-3}$ ), imparts additional surface charge on particles or increases hydroxyl ion concentrations in the water matrix (Berkheiser et al., 1980; Sample et al., 1980). Above the pH<sub>iep</sub>, phosphorus may form more negatively charged surface complexes on particle surfaces, resulting in electrostatic repulsion between particles and impairment of settable floc (Pommerenk & Schafran, 2005). At lower pH values (pH 5.5 - 7.7) favouring the formation of aluminum phosphate precipitate, the presence of phosphorus improved coagulation and flocculation efficacy by potentially increasing inter-particle contact opportunities (Jenkins et al., 1971; Stumm & O'Melia, 1968). While phosphorus concentrations in this system and most unpolluted environmental waters are typically below the levels at which effects on coagulation and flocculation have been observed, the inclusion of TP in the regression models suggests that both the association of phosphorus with fine grained sediments and metal complexationprecipitation/adsorption-desorption mechanisms may impact coagulation/flocculation processes at even lower phosphorus concentrations.











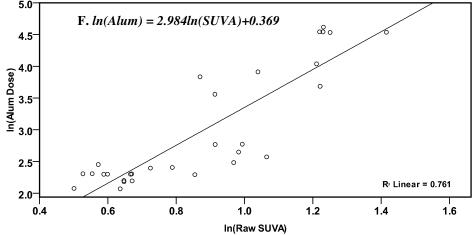


Figure 4.9 Relationship between alum dose and raw water quality parameters (2012):

A. Total phosphorus B. dissolved organic carbon C. UVA<sub>254</sub>

D. turbidity E. zeta potential F. SUVA

The incorporation of organic matter-related parameters (TOC and UVA<sub>254</sub>) and alkalinity into coagulant regression models is consistent with their well-documented roles in coagulation and flocculation processes. In environmental waters, natural organic matter is predominantly negatively charged and its abundance (as captured by TOC or DOC) drives coagulant dosing (Edzwald, 1993; Shin *et al.*, 2008). Coagulation and flocculation processes preferentially remove hydrophobic organic carbons (Binnie, Kimber & Smethhurst, 2002; Bratby, 2006). Hydrophobic organic carbon species contain high levels of aromatic and phenolic content, whereas hydrophilic organic carbon species contain high levels of aliphatic content (Edzwald, 1993; Aiken, McKnight, Thorn & Thurman, 1995; Leenheer & Croué, 2003). The inclusion of UVA<sub>254</sub> as a predictor of alum dose is indicative of the role of aromatic organic carbon content in coagulation and flocculation processes.

The effectiveness of coagulants are also sensitive to changes in pH and alkalinity (MWH, 2012). The optimum pH range for alum as a coagulant is between 5.5 and 7.7 (MWH, 2012). The non-linear relationship between pH and coagulant dose precluded the use of pH in the multiple linear regression models; however, alkalinity and coagulant dose were linearly correlated. Alkalinity is a reasonable predictor of coagulant dose because alkalinity is consumed as coagulants are added, reducing the overall pH of the water matrix and thereby influences the effectiveness of the coagulant used (MWH, 2012; Pernitsky & Edzwld, 2006). Moreover, sufficient alkalinity is required for aluminum species precipitation when using alum (MWH, 2012).

SUVA is an average measure of the proportion of aromatic/hydrophobic content of DOC in a water sample (Traina *et al.*, 1990; Weishaar *et al.*, 2003) and is therefore associated with the reactivity of NOM with alum (Edzwald, 1993; Edzwald & Tobiason, 1999; Weishaar *et al.*, 2003). DOC removal by coagulation and flocculation processes has been shown to be ineffective at low SUVA levels, which are indicative of a high proportion of hydrophilic organic matter (Archer & Singer, 2006; Edzwald & Van Benschoten, 1990; Reckhow, Boss, Bexbaura, Hesse & McKnight, 1992). Current guidance for compliance with DBP regulations exempt water agencies from the use of enhanced coagulation if average SUVA values for either raw or treated water are less than 2.0 L mg<sup>-1</sup>m<sup>-1</sup>. In the present study, higher SUVA values were generally associated with greater DOC removal; however, substantial DOC removal was also observed when SUVA values were below 2.0 L mg<sup>-1</sup>m<sup>-1</sup> (Figure 4.10). This observation is consistent with the weaker correlation between SUVA and alum dose (R<sup>2</sup> = 0.761) compared to UVA<sub>254</sub> and alum dose (R<sup>2</sup> = 0.896) and suggests that factors independent of organic matter aromaticity/hydrophobicity may influence coagulation and flocculation efficacy. This

is consistent with previous observations reported that coagulant demand is controlled by presence of dissolved NOM (Edzwald, 1993; Edzwald, Becker & Wattier, 1985; Pernitsky & Edzwald, 2006; Shorney, 1999), except when very high particle concentrations are present (Pernitsky & Edzwald, 2006; Shin *et al.*, 2008).

Polymers are introduced to bridge coagulated particles in the Actiflo© system, once particles are sufficiently destabilized with coagulant addition. Cationic polymer molecules typically have long chains extending into the dispersed phase such that flocs adsorb to these positively charged "tails" to form larger aggregates (Dickinson & Eriksson, 1991; Gregory & Barany, 2011). In this system, measures pertaining to NOM (SUVA, UVA<sub>254</sub>) were the strongest predictors of polymer (Magnafloc ® LT22S manufactured by BASF SE) dose, together explaining 0.928 of its variability (Table 4.6); however, the VIF of 15.7 indicates that the predictors are collinear, given that UVA<sub>254</sub> and DOC are strongly correlated.

Simple log-linear regressions of polymer dose (Magnafloc® LT22S) with raw water SUVA, UVA<sub>254</sub>, TP, DOC, zeta potential and turbidity with polymer dose yielded coefficients of determination of 0.854, 0.853, 0.804, 0.797, 0.778 and 0.744 respectively (Figure 4.11). SUVA was considered for the polymer dose regression models instead of DOC and UV<sub>254</sub>. In the subsequent multiple linear regression analysis, SUVA and TP together explained 91.2% of the variability of polymer dose (Table 4.6). SUVA and TP are likely to provide a better, unbiased estimate of polymer dose as these predictors are less likely to be collinear (VIF = 3).

Magnafloc® LT22S is a cationic polyelectrolyte commonly used as a flocculation aid. As these polymers are typically several times more expensive compared to inorganic metal coagulants, most coagulation and flocculation systems are designed to adequately destabilize colloidal particles and achieve charge neutralization prior to polymer addition for interparticle bridging. Accordingly, optimal polymer dose is proportional to particle concentration and collision frequency rather than the total surface charge of particles (Edzwald, Bottero, Ives & Klute, 1998; MWH, 2012).

In this study, the significant polymer regression model based on SUVA and TP suggests that a phase change of the hydrophobic proportion of organic matter during coagulation and flocculation may have occurred. It is possible that TP, as a surrogate measure of suspended particle concentrations, provides seeding particles or surfaces onto which hydrophobic organic compounds can undergo such a phase change. Organic matter adsorbed to these suspended particles interacts with hydrophobic

organic compounds more strongly than with hydrophilic organic compounds (Aiken *et al.*, 1985), resulting in the preferential precipitation and/or adsorption of hydrophobic organic compounds onto other particles (Edzwald, 1993). The long molecular chains of cationic polymer, which are generally much higher in molecular weight than coagulants, may directly neutralize the negative charges of organic matter present on the surfaces of these suspended particles while effectively bridging multiple particles to form larger flocs.

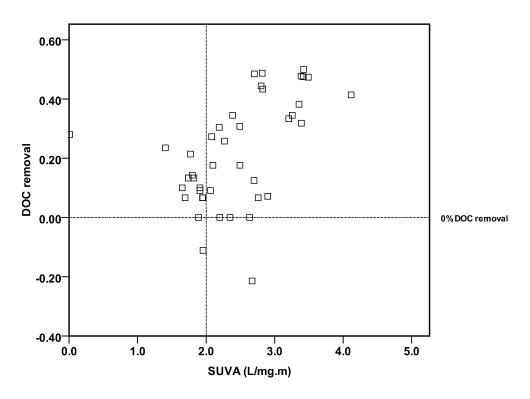
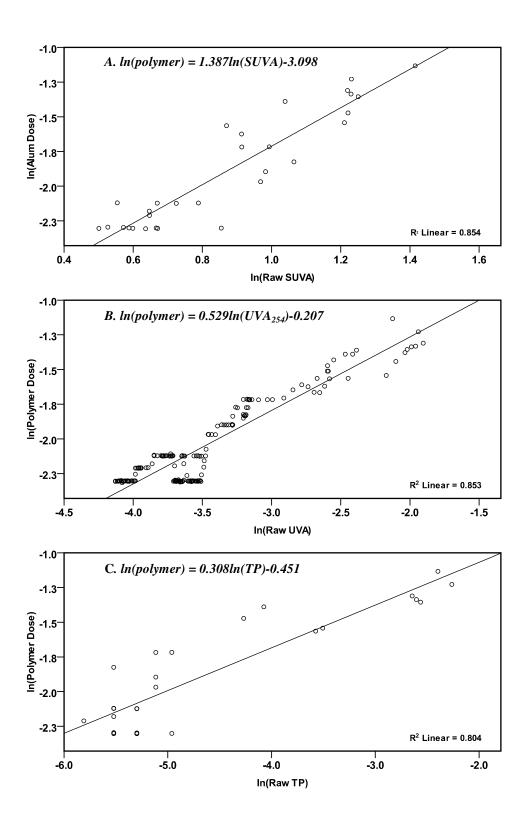


Figure 4.10 Relationship between raw water SUVA and DOC removal by Actiflo© at Glenmore WTP (2012)

Table 4.6 Summary of polymer dose regression models (2012)

Regression	Regression	Parameter	Standard	t-value	p-value	$R^2/Adj. R^2$	p-value
model*	parameter	coefficient	errors				
ln(Polymer	k	1.287	0.503	2.557	0.018		
dose)	$ln(UVA_{254})$	0.906	0.127	7.149	< 0.001	0.928/0.922	< 0.001
[n = 26]	ln(DOC)	-0.553	0.186	-2.963	0.007		
ln(Polymer	k	-1.971	0.297	-6.629	< 0.001		
dose)	ln(SUVA)	0.861	0.160	5.376	< 0.001	0.912/0.904	< 0.001
[n = 26]	ln(TP)	0.144	0.036	3.945	0.001		

<sup>\*</sup> water quality parameters considered: conductivity, TOC, DOC, UVA 254, SUVA, turbidity; TP, TDP



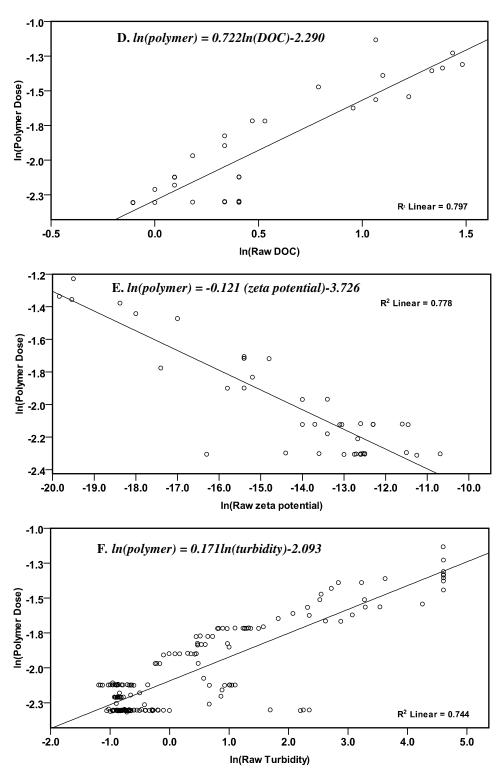


Figure 4.11 Relationship between polymer dose and raw water quality parameters (2012):

A. SUVA B. UVA<sub>254</sub> C. Total phosphorus

D. dissolved organic carbon E. zeta potential F. turbidity

#### 4.5.2 Chemical oxidation

The primary objective of chemical oxidation in the Glenmore WTP was to inhibit biofilm growth in the filters by maintaining a chlorine residual of 0.5 mg/L in the filter effluent (Mielke, L. personal communication, 2012). Between 2000 and 2008, chlorine gas (Cl<sub>2</sub>) was applied at the raw water header, prior to coagulation. This practice has been largely abandoned due to excessive DBP formation from chlorination processes, especially when high concentrations of DBP precursors (DOC) are present in raw water. Since 2008, on-site generation of liquid sodium hypochlorite (NaOCl) replaced chlorine gas to improve safety for employees. The point of sodium hypochlorite addition was also moved from the raw water header to a point immediately preceding filtration to minimize DBP formation and reduce chlorine dose. The final sodium hypochlorite dose was reported as the free chlorine concentration in solution.

Multiple linear regression analysis was not conducted using the 2000-2010 data for pre-treatment oxidation chlorine dose as the chlorine data were unavailable. Oxidation chlorine dose regression models were developed based on data collected in 2012. Only water quality parameters exhibiting linear relationships with chlorine dose were considered for multiple linear regression. The relationship exhibited between raw water TP and oxidation chlorine dose was significant ( $R^2 = 0.772$ , p < 0.001); however, TP did not account for additional variability unexplained by  $UVA_{254}$  and temperature (Table 4.7). Oxidation chlorine dose was best explained by the variability of UVA<sub>254</sub> and temperature in the raw water ( $R^2 = 0.941$ , p < 0.001). UVA<sub>254</sub> independently accounted for 86.1% of the variability in oxidation chlorine dose. This suggests that the hydrophobic/aromatic content of the dissolved organic matter is directly proportional to chlorine dose requirements at the conditions studied. The inclusion of temperature (a physical property of the water matrix) in the strongest regression model suggests that reaction kinetics may also play a significant role in driving pretreatment chlorine dose, consistent with the widely reported impact of temperature on chlorine reaction kinetics (reviewed in Amy et al., 1987; Chowdhury, Champagne & McLellan, 2009; Deborde & von Gunten, 2008). The relationship exhibited between raw water TP and oxidation chlorine dose was significant ( $R^2 = 0.772$ , p < 0.001); however, TP did not account for additional variability unexplained by UVA<sub>254</sub> and temperature.

Table 4.7 Summary of pre-treatment chlorine dose regression models (2012)

Regression	Regression	Parameter	Standard	t-value	p-value	R <sup>2</sup> /Adj. R <sup>2</sup>	p-value
model*	parameter	coefficient	errors				
ln(Cl <sub>2</sub> dose)	k	1.831	0.182	10.043	< 0.001	0.615/0.600	< 0.001
[n = 27]	ln(TDP)	0.202	0.032	6.322	< 0.001	0.013/0.000	< 0.001
$ln(Cl_2 dose)$	k	0.511	0.019	26.296	< 0.001	0.682/0.671	< 0.001
[n = 26]	ln(SUVA)	0.129	0.017	7.751	< 0.001	0.082/0.071	
ln(Cl <sub>2</sub> dose)	k	1.188	0.066	17.933	< 0.001	0.711/0.699	< 0.001
[n = 27]	ln(TP)	0.110	0.014	7.838	< 0.001	0.711/0.099	
ln(Cl <sub>2</sub> dose)	k	1.286	0.050	25.909	< 0.001	0.061/0.055	< 0.001
[n = 26]	$ln(UVA_{254})$	0.191	0.016	12.200	< 0.001	0.861/0.855	< 0.001
In(Cl. dosa)	k	1.043	0.054	1	< 0.001		
ln(Cl2 dose)  [n = 26]	ln(UVA <sub>254</sub> )	0.184	0.010	0.895	< 0.001	0.941/0.936	< 0.001
[11 – 20]	ln(Temp)	0.088	0.016	0.285	< 0.001		

<sup>\*</sup> water quality parameters considered: raw water conductivity, SUVA, UVA, temperature, TOC, DOC, turbidity, TP, TDP.

#### 4.5.3 Filtration

Twenty-four (24) gravity-fed conventional treatment (anthracite over sand) filters are in operation at the Glenmore WTP. Filter performance is highly reliant on the efficacy of preceding pre-treatment processes (as they impact influent physical, chemical and biological water properties), filter design and operating flow rates (MWH, 2012). Typical filter runs for rapid media filtration last between 1 to 4 days (MWH, 2012). Water quality deterioration and head loss build-up result in filter run termination and backwashing. At the Glenmore WTP, average filter run times were 41 hours prior to backwash. Filters were operated for up to 60 hours (February 2009) and as low as 19 hours (October 2005). Backwash was usually initiated prior to turbidity breakthrough and/or excessive head loss development so as to maintain consistent, staggered backwashing between filters.

Historical filter runtimes were regressed with water quality parameters to determine whether reservoir phosphorus (TP or TDP) concentrations would explain any of the variability of filtration performance amongst other water quality parameters exhibiting linear relationships with filtration runtime. Total phosphorus was weakly correlated with filter run time ( $R^2 = 0.102$ , p = 0.04). This finding was expected as pre-treatment processes (coagulation, flocculation, clarification) removed the majority of raw water TP present, as observed during the additional plant water quality sampling activities in 2012 (Appendix E).

Raw water UVA<sub>254</sub> and the natural logarithm of raw water TOC concentrations were the best predictors of filter run-time (Table 4.8). Despite the significance of raw water turbidity as a

parameter used to optimize filter operation, it was not the best predictor of filter run time. This alludes to the fact that in conventional treatment, most of the turbidity has been removed during pretreatment processes; the remaining particles present in the filter influent are typically not particles present in the raw water but amorphous and unstable precipitates of the coagulant used to form sweep flocs (O'Melia, 1985). The surfaces of these flocs may be coated with organic matter from the raw water, which likely comprises of higher hydrophobic/aromatic organic compounds (Aiken *et al.*, 1985). Accordingly, UVA<sub>254</sub> was the best raw water quality predictor of filter run time.

Table 4.8 Summary of filter run-time regression models (2000-2010)

Regression model*	Regression parameter	Parameter coefficient	Standard errors	t-value	p-value	R <sup>2</sup> /Adj. R <sup>2</sup>	p-value
Mean filter run	k	52.254	2.184	23.921	< 0.001		
time	UVA <sub>254</sub>	-1.790	0.524	-3.415	0.003	0.634/0.591	< 0.001
[n = 20]	ln(TOC)	-6.464	2.213	-2.921	0.010		

<sup>\*</sup> water quality parameters considered: plant raw water - conductivity, TOC, UV-absorbance; reservoir raw water - TP, color.

#### 4.5.4 Disinfection by-products

Regulated DBPs were monitored in the treated water semi-weekly for total trihalomethanes (TTHMs) and monthly for haloacetic acids (HAAs). TTHMs and HAAs were generally below Canadian Drinking Water Quality Guideline values of 100 and 80  $\mu$ g/L, respectively. However, there were several periods (June-July 2005 and May-June 2008) during which TTHM and HAA threshold values were exceeded. Mean monthly TTHMs and HAAs were highest in June (52.1  $\pm$  2.0 and 48.8  $\pm$  5.8  $\mu$ g/L respectively) and lowest in February (8.2  $\pm$  0.2 and 8.2  $\pm$ 0.8  $\mu$ g/L respectively).

Many empirical models have been developed to predict the occurrence of DBPs in drinking water (Sadiq & Rodriguez, 2004). These models have largely focused on operational conditions and aggregate water quality characteristics to predict the formation of DBPs. Available water quality parameters exhibiting a log-linear relationship with TTHM or HAA concentrations from 2000 to 2010 were considered in the forward regression analysis presented herein. Raw water TP was not a significant predictor of TTHM or HAA concentrations; this was anticipated as the filter effluent to which the disinfection chlorine dose is added typically contains very low concentrations of particulate matter.

TTHM concentrations were best predicted by temperature and TOC, the combination of which accounted for 94.5% of the variability of TTHM concentrations (Table 4.9). The regression was

repeated without reservoir water quality regressors as the residuals of the resulting ordinary least squares solution were not normally distributed. This simultaneously allowed for the incorporation of a larger sample data set. The residuals from the resultant model were normally distributed and homoscedastic; however, the residuals were positively auto-correlated (Durbin-Watson statistic = 0.747) despite the inclusion of two seasonal predictors (i.e. temperature and Elbow river discharge). Collinearity of predictors was not an issue in the models developed; the VIF for each predictor was consistently less than 5.

Table 4.9 Summary of TTHM regression models (2000-2010)

Regression model	Regression parameter	Parameter coefficient	Standard errors	t-value	p-value	R <sup>2</sup> /Adj. R <sup>2</sup>	p-value
1. (TTIIM)	k	1.778	0.112	5.816	< 0.001		
ln (TTHM) [n = 16]*	ln(T)	0.478	0.061	0.843	< 0.001	0.945/0.937	< 0.001
$[\Pi = 10]$	ln(TOC)	0.821	0.113	0.252	< 0.001		
	k	2.191	0.035	61.983	< 0.001		
1 (TTIDA)	ln(TOC)	0.515	0.023	22.572	< 0.001		
ln (TTHM) [n = 830] **	ln(T)	0.342	0.012	28.202	< 0.001	0.881/0.881	< 0.001
$[11 = 830]^{3/3}$	ln(Turbidity)	0.049	0.012	4.125	< 0.001		
	ln(Q)	0.071	0.023	3.124	0.002		

<sup>\*</sup> water quality parameters considered: plant raw water - conductivity, temperature (T), TOC, turbidity; reservoir raw water - TP, total alkalinity, color; Elbow River inflow (Q)

The reduced sampling requirements of HAAs have further limited the number of samples available for regression analysis with the TP data. Removing TP as a regressor, the forward regression procedure identified raw water temperature, TOC and turbidity to collectively account for 87.4% of the variation in HAA concentrations (Table 4.10). The VIF for each predictor was no greater than 2.5, suggesting that collinearity between predictors was not likely to have influenced the model. Residuals were normally distributed, homeoscedastic and did not exhibit significant autocorrelation.

Table 4.10 Summary of HAA regression models (2000-2010)

Regression Model	Regression parameter	Parameter coefficient	Standard errors	t-value	p-value	R <sup>2</sup> /Adj. R <sup>2</sup>	p-value
	k	2.357	0.056	42.161	< 0.001		
ln (HAA)	ln(T)	0.404	0.033	12.135	< 0.001	0.874/0.869	< 0.001
[n = 77]*	ln(TOC)	0.501	0.085	5.896	< 0.001	0.8/4/0.809	< 0.001
	ln(Turbidity)	0.111	0.041	2.707	0.008		

<sup>\*</sup> water quality parameters considered: plant raw water - total organic carbon (TOC), turbidity, temperature (T), Elbow River inflow(Q)

<sup>\*\*</sup> water quality parameters considered: plant raw water - conductivity, temperature (T), TOC, turbidity; Elbow River inflow (Q)

As previously noted for oxidation chlorine dose, the inclusion of temperature in these DBP models was not surprising as temperature is known to impact chlorine reaction kinetics (Deborde & von Gunten, 2008). The inclusion of TOC underscores its well-established role as a measure of DBP precursor concentrations. Despite the ability of raw water turbidity to contribute to both DBP multiple linear regression models, there is no mechanistic basis for it to directly impact DBP formation; the variance in raw water turbidity is likely much greater than that of any other metric of DBP precursors. Accordingly, it was able to explain additional variability not accounted for by other significant predictors.

# Chapter 5: Implications for watershed planning, reservoir management and treatment operations

# 5.1 Phosphorus as a source water and treatment vulnerability indicator

The decoupling of cumulative water quality impacts of various natural and anthropogenic disturbances can seldom be accomplished using water quality metrics and analysis tools (Schindler, 2001). Moreover, some changes in source water quality that potentially compromise the efficacy of drinking water treatment processes are not always discernible with commonly utilized water quality metrics (Emelko *et al.*, 2011). In this thesis, phosphorus was identified as a possible metric to link landscape activity with drinking water treatability.

The use of TP as a more sensitive indicator of waterborne particle concentrations present in the raw water than turbidity was supported given that the majority of TP was observed in the particulate form. TP is an exclusive indicator of waterborne particle concentrations in this system whereas turbidity, the conventional treatment metric used to estimate particle concentrations may be confounded by the presence of dissolved constituents. Accordingly, TP may play a role in the critical drinking water treatment processes of coagulation, flocculation and clarification which has direct implications for process optimization, chemical coagulant costs, sludge production and impacts to subsequent treatment processes. The statistically significant relationships reported herein, coupled with a review of literature, points to several mechanisms through which TP potentially plays a role in the critical drinking water treatment processes of coagulation, flocculation and clarification. These are:

- 1) Phosphorus readily adsorbs to fine-grained particulate matter ( $< 63 \mu m$ );
- 2) Phosphorus engages in complexation-precipitation reactions with dissolved metals and metal coagulants to increase waterborne particle concentrations; and
- 3) Phosphorus, in the form of multivalent anions, imparts additional surface charge on particles or increases hydroxyl ion concentrations in the water matrix.

Further studies are required to validate the contribution of these potential mechanisms in coagulation, flocculation and clarification.

#### 5.1.1 Implementation within Watershed Management Plans

Environmental indicators were employed by the *Bow River Basin Watershed Management Plan* (2012) and the *Elbow River Basin Water Management Plan* (2008) to "measure, monitor and evaluate watershed conditions as part of an iterative, adaptive environmental performance management system" (BRBC, 2012). The overall intent of using indicators is to address cumulative impacts of land uses on water uses. The water quality parameters incorporated within these plans as objectives, targets and warning levels were established to address issues of direct ecological impact (e.g. eutrophication management and prevention) as well as some technical and socio-economic impacts on other watershed uses (e.g. nuisance macrophytic growth impacting recreational uses). Given that drinking water treatment is a principal water use within the Elbow River Watershed, the suite of environmental indicators should also ideally capture the cumulative impacts of land-use on source water quality and drinking water treatment.

In this research, phosphorus (as TP and TDP) was evaluated as a source water and treatment vulnerability indicator. TDP was preferred over TP as an indicator for eutrophication management in the 2012 Elbow River Watershed Management Plan; however, this research demonstrated the applicability of TP as a treatment vulnerability indicator. TP is a mass-based indicator of waterborne particle concentrations that provides insight to the coagulation regime(s) (i.e. sweep floc, charge neutralization and enmeshment in precipitate mechanisms) used in this system and accordingly can be used to optimize the critical drinking water treatment processes of coagulation, flocculation and clarification. Suboptimal coagulant dosing results in excess costs associated with chemical coagulants, increased sludge production and deleterious impacts to subsequent treatment processes which may preclude the continued provision of safe drinking water.

The well-documented empirical relationships between landscape activity and nutrient exports can be used with the findings of the present research to explicitly link upstream landscape impacts on water quality to downstream drinking water treatability, ultimately enabling an integrated approach to SWP. Landscape activity empirical TP export coefficients were used to estimate TP loading to the receiving water body. Consequently, lake and reservoir nutrient models were used to estimate steady state TP concentrations present. Finally, the alum coagulant dosing regression models developed in this research were used to extrapolate the impact of source water quality changes to drinking water treatment, as reflected by change in TP concentrations in the source water.

The completed assessment provides a source-to-treatment framework that enables both land-use and water managers to evaluate the marginal cost of treatment for the continued provision of safe drinking water against the costs of implementing appropriate SWP strategies in the watershed. While traditional SWP strategies have focused on minimizing or eliminating anthropogenic threats to preserve source water quality (e.g. logging bans), these strategies are ineffective against natural disturbances like wildfire and may even exacerbate source water quality impacts arising from these disturbances (e.g. due to build-up of fuel loads) (Emelko et al., 2011). Accordingly, scenario building using regression models similar to the ones presented in this thesis may be used as a tool to inform the development of SWP strategies by assessing the relative trade-offs of present and future intended land and water uses in an integrated manner. Urban development pressures arising from population growth in the greater Calgary metropolitan area constitute the most imminent anthropogenic threat to source water (City of Calgary, 2005), whereas the most catastrophic natural source water threat in Canadian forested watersheds is arguably wildfire (Van Wagner, 1988). The best-fitted alum coagulant dosing model was used in both an urban growth scenario and a catastrophic wildfire scenario to demonstrate the application of this framework, which with subsequent validation and calibration could be used to inform SWP and integrated land and water management strategies.

#### 5.1.1.1 Urban development (growth) scenario

Despite urban areas comprising only 5.9% of the Elbow River watershed (Wijesekara et al., 2012), urban land use typically contributes most to water quality degradation (including TP inputs). Agricultural (16.7%), rangeland and parklands (6.2%) and forests (44%) comprise the majority of the Elbow River watershed area (Wijesekara et al., 2012). Wijesekara et al. (2012) reported clear-cut areas accounting for 1.8% of the watershed area as of 2010, with the remaining area consisting primarily of rock/impervious surfaces as part of the mountainous terrain to the west. For simplicity, best management practices were assumed for the clear-cut areas and embedded into forest "landuses" whereas agricultural, rangeland and parklands were aggregated as agricultural/rural land-uses. Based on a total watershed area of 1238 km2, the above land-use attributes and the use of the lowest phosphorus export coefficients (Reckhow & Chapra, 1983), the 2010 mean annual phosphorus yield was estimated to be 7,621 kg/yr (Table 5.1). The lowest phosphorus export coefficients were selected to provide a loading similar in magnitude to those presently observed; additional validation and calibration of these coefficients are outside the scope of this research.

Wijesekara *et al.* (2012) projected increases of 65%, 20% and 1% in urban, rangeland/parkland and agricultural land-uses respectively as well as decreases of 6% and 28% of evergreen and deciduous forests cover respectively. Discrepancies in the figures reported by Wijesekara *et al.* (2012) were assumed to be rounding errors, which was split evenly between forest, agricultural/rural and urban land-uses. These land-use changes are expected to increase the mean annual phosphorus yield to 10,351 kg/yr (36% increase from 2010). These phosphorus export yields could subsequently be used to estimate mean annual reservoir phosphorus concentrations using various empirical reservoir models. Many empirical models of varying complexity and applicability are available; however, the extensively-used Vollenweider phosphorus concentration prediction model (Vollenweider, 1970) was selected to demonstrate the application of one such model (Table 5.2).

The mean reservoir TP concentration in 2010 estimated using the empirical Vollenweider model was 0.0148 mg/L, which was almost double the mean observed concentration in 2010 ( $0.0067 \pm 0.0014 \text{ mg/L}$ ) (mean  $\pm$  standard error of mean) but generally consistent with the historical long-term mean concentration of  $0.0122 \pm 0.0023 \text{ mg/L}$ . This difference is likely attributable to the limited number of reservoir TP samples (n = 5) collected in 2010. Using the 2010 estimated TP concentration of 0.0148 mg/L, the estimated mean alum dose was 21.2 mg/L (Figure 5.1). The observed mean alum dose (10.9 mg/L) in 2010 falls within the 95% confidence interval of the estimated mean alum dose. The projected mean reservoir TP concentration in 2031 was estimated to be 0.020 mg/L; the corresponding projected mean alum dose is 23.4 mg/L.

The mean observed UVA<sub>254</sub> of 0.039 cm<sup>-1</sup> was assumed to be a constant to simplify the alum regression model in the absence of additional UV absorbance data. Additional verification and calibration of land-use phosphorus yield coefficients, reservoir TP concentration model and alum dose models are necessary to increase confidence in the alum coagulant dose estimates. Moreover, it is noted that these estimates have been made independent of any apparent impacts attributable to algae growth in the reservoir. Favourable conditions for eutrophication (e.g. low dissolved oxygen levels releasing bio-available phosphorus from reservoir bottom sediments) may substantially change the relationship between phosphorus and alum coagulant dosing.

Table 5.1 Estimated and projected mean annual phosphorus yields

	Phosphorus Yield	2010 (Es	stimated)	2031 (Projected)		
Land Use	Coefficient <sup>i</sup> (mg m <sup>-2</sup> yr <sup>-1</sup> )	Area <sup>ii</sup> (km²)	Yield (kg/y)	Area <sup>ii</sup> (km²)	Yield (kg/y)	
Forest	2	567.0	1,134	490.7	982	
Agriculture/rural	10	283.5	2,835	306.8	3068	
Urban	50	73.0	3,652	126.0	6301	
Montane	n/a	314.5	-	314.5	-	
TOTAL	-	1238	7,621	1238	10,351	

i. Reckhow and Chapra, 1983, lowest estimates ii. Wijesekara et al., 2012

Table 5.2 Vollenweider estimate of Reservoir TP concentrations based on land-use TP yields

Parameter	Equation	Glenmore Reservoir
Hydraulic retention time $(\tau)$	$\tau = V/Q$	0.07 y
Surface overflow rate (q <sub>s</sub> )	$q_{s} = z/\tau$	105.7 m/y
Areal phosphorus loading $(L_p)$	$L_p = \frac{P_{load}}{surface area}$	1984.7 mg/m <sup>2</sup> /y (estimated, 2010) 2695.5 mg/m <sup>2</sup> /y (projected, 2031)
Mean reservoir depth (Z)	measured	7.4 m/y
Predicted mean reservoir phosphorus concentration (P)	$P = \frac{L_p}{q_s} \left[ \frac{1}{1 + \sqrt{\frac{z}{q_s}}} \right]$	0.014 mg/L (estimated, 2010) 0.020 mg/L (projected, 2031)

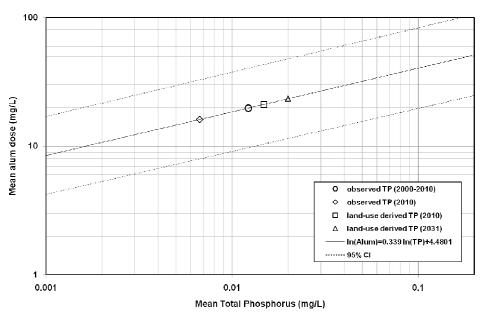


Figure 5.1 Relationship between mean reservoir TP concentration and predicted mean alum dose.  $ln(Alum\ dose) = 0.753\ ln\ (UVA_{254}) + 0.339\ ln\ (TP) + 6.923.\ UVA_{254} = 0.039\ cm^{-1}$ 

#### 5.1.1.2 Catastrophic landscape disturbance scenario

Approximately 96% of the annual average Elbow River discharge to the Glenmore Reservoir originates from the predominately forested landscapes upstream of Bragg Creek (Figure 5.2). In these landscapes, wildfires are arguably the most catastrophic natural source water threat (Van Wagner, 1988); the impacts of wildfire on source water quality (including nutrient exports) have been well-documented (Emelko *et al.*, 2011; Kurz *et al.*, 2008; Schindler & Donahue, 2006). In this research, wildfire impacts in the Elbow River Watershed were extrapolated based on impacts observed in a similar physiographic setting. The Oldman River Basin located south of the Elbow River Watershed has been subject to the impacts of the devastating Lost Creek Wildfire of 2003. The wildfire continues to have lasting implications on water quality/quantity, timing of availability and aquatic ecosystem health. Allin *et al.* (2012) reported first year post-fire mean TP concentrations of approximately 0.037 mg/L, approximately 8 times the TP concentration measured at a reference site not impacted by the wildfire. Up to 12 times the TP concentration was measured in a burned and salvaged logged site.

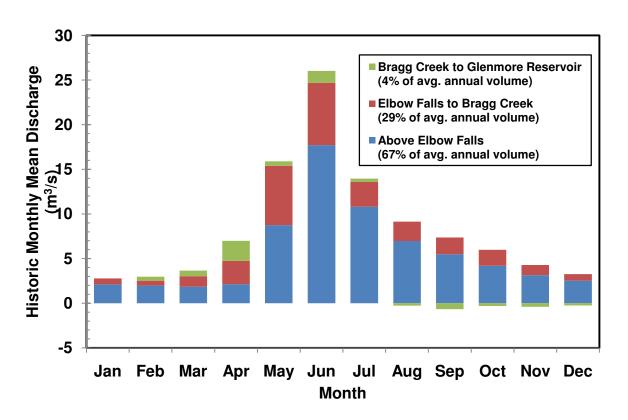


Figure 5.2 Historical monthly mean discharge (1967-1977)(Water Survey of Canada, 2010)

Figure 5.3 was generated based on simplifying assumptions that Glenmore Reservoir TP concentrations approach those observed in the Oldman River during extreme hydrological events and a constant assumed mean UVA<sub>254</sub> value of 0.039 cm<sup>-1</sup>. Using the approach used in the previous section, the expected Glenmore WTP mean alum coagulant dose could be determined based on the anticipated post-fire TP concentrations and UVA<sub>254</sub> values. This catastrophic scenario underscores the vulnerability of this source water to wildfire impacts. An eight-fold increase in source water TP concentrations alone (and accordingly waterborne particle concentrations) may double mean alum coagulant dosing requirements, while an increase in hydrophobicity of eroded wildfire-impacted soils (e.g. Doerr *et al.*, 2006; Sartz, 1953; Shakesby *et al.*, 1993; Robichaud & Brown, 1999) may also contribute to increased coagulant demand.

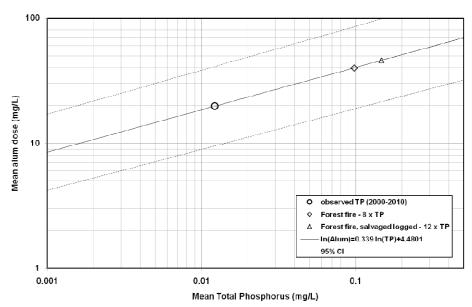


Figure 5.3 Relationship between extrapolated landscape disturbance reservoir TP concentrations and predicted mean alum dose.  $ln(Alum\ dose) = 0.753\ ln\ (UVA_{254}) + 0.339\ ln\ (TP) + 6.923.\ UVA_{254} = 0.039\ cm^{-1}$ 

# **Chapter 6: Conclusions and implications**

#### 6.1 Conclusions

The main purpose of this study was to evaluate phosphorus as a source water and treatment vulnerability indicator, to connect upstream landscape activities in a watershed to downstream drinking water treatability impacts. Based upon an analysis of the results from the present study, the following conclusions are drawn:

## 6.1.1 Phosphorus as a source water vulnerability indicator

- 1) Source water quality was not significantly different within the compartments of the Glenmore Reservoir downstream of the Weaselhead region and was assumed to be representative of raw water quality at the Glenmore WTP intake. Except for density flows which may occur during reservoir stratification for a few days each year, water quality changes generally occur at the reservoir scale. The investigation of the spatial and temporal variability of source water quality was necessary to discern impacts from upstream (allochthonous) and *in-situ* (autochthonous) sources and processes.
- 2) Phosphorus loading was predominantly transported from upstream sources by the Elbow River in particulate forms to the Glenmore Reservoir, during significant hydrological events such as spring runoff. Particulate forms of phosphorus represent the majority of phosphorus loads transported in river systems. These phosphorus forms contribute to increased source water turbidity and to reduced long-term reservoir capacity from the deposition of these particles in reservoir bottom sediments.
- 3) C:N:P nutrient ratios confirmed the role of phosphorus as the limiting nutrient for primary production in this source water; however, TP is a poor indicator of primary production in the watershed. Carlson's Trophic State Index derived from TP and chlorophyll-a concentrations in the reservoir are indicative of generally mesotrophic to oligotrophic conditions between 2000 and 2010. Consistently low chlorophyll-a levels observed during this period suggest that treatment impacts are unlikely to be confounded by the presence of algal matter. The deposition of particulate phosphorus on the bottom of the reservoir and a well-oxygenated sediment-water interface as maintained through low hydraulic retention times may suppress the release of bio-available dissolved phosphorus species into the water column. Reservoir TDP concentrations were significantly correlated with chlorophyll-a concentrations, supporting its current use as an indicator of primary productivity.

# 6.1.2 Phosphorus as a treatment vulnerability indicator

- 4) Coagulant requirements in drinking water coagulation and flocculation processes employed as part of a conventional treatment train at the Glenmore WTP were best described by TP and TOC in the east treatment train ( $R^2 = 0.788$ , p < 0.001) and TOC in the west treatment train ( $R^2 = 0.581$ , p < 0.001) between 2000 and 2010. After a change in process configuration with the implementation of ballasted-sand flocculation, alum coagulant dose variability was best described using UVA<sub>254</sub> and TP ( $R^2 = 0.983$ , p < 0.001). SUVA and TP together also explained the variability of polymer dose ( $R^2 = 0.912$ , p < 0.001). The inclusion of TP as a significant predictor of coagulant and polymer doses in this system, coupled with a review of literature, points to several mechanisms through which phosphorus acts as an indirect measure of the fraction of suspended particulate material (turbidity) when phosphorus is present predominantly in the particulate form. Accordingly, phosphorus potentially plays a role in the critical drinking water treatment processes of coagulation, flocculation and clarification. The mechanisms identified are:
  - i. Phosphorus readily adsorbs to fine-grained particulate matter ( $< 63 \mu m$ );
  - ii. Phosphorus engages in complexation-precipitation reactions with dissolved metals and metal coagulants to increase waterborne particle concentrations; and
  - iii. Phosphorus, in the form of multivalent anions, imparts additional surface charge on particles or increases hydroxyl ion concentrations in the water matrix.
- 5) The relationship between raw water TP and oxidation chlorine dose was significant ( $R^2 = 0.772$ , p < 0.001); however, TP did not account for additional variability not explained by the waterborne hydrophobic/aromatic content as reflected by UVA<sub>254</sub> and reaction kinetics as influenced by temperature at the conditions studied.
- 6) Low concentrations of raw water TP (~0.002 mg/L) remained in the influent to the conventional (anthracite over sand) filters. Accordingly, there were no theoretical bases for the use of TP as an indicator of treatment performance in post-clarification processes, despite the significant correlations observed.

# 6.2 Implications for planning, management and operations

- 7) This case-study investigating a forested watershed in Alberta, Canada was used as a proof-of-concept demonstration of phosphorus as a source water and treatment vulnerability indicator. Empirical models for TP loading and cycling in reservoirs were used to explicitly link upstream landscape impacts on water quality to downstream drinking water treatability. This framework enables the development and coordination of land-use planning, reservoir management and drinking water treatment operations strategies. Total phosphorus provides a common vulnerability metric relevant to both land-use and water managers through which land management and SWP strategies can be assessed.
- 8) TP is a mass-based indicator of waterborne particle concentrations that provides insight to the coagulation regime(s) used in this system (i.e. sweep floc, charge neutralization and enmeshment in precipitate mechanisms) and accordingly can be used to optimize coagulation, flocculation and clarification. The various mechanisms identified affecting the source, fate and transport of TP should be further examined to validate their respective roles in these processes. The optimization of these critical drinking water treatment processes results in cost-savings associated with chemical coagulants, reduced sludge production, improved solids/organics removal and ultimately, the continued provision of safe drinking water.

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Appendix A: Glenmore W1	ΓP water quality s	ampling (2012)
	123	

## Table A.1 Schedule of water quality analyses (2012)

1634 56 Av. SW, Calgary, AB T2P 2M5 Southern Rockies Watershed Project

## Glenmore Lab Testing Frequency (EVENT)

Parameters	Physical							Chemical											Biological		
Location	Color 460	Conductivity	ОЯР	Particle Count	рН/Тетр	75S	Turbidity	UV 254	Alkalinity	AI	Carbon, Dissolved Organic	Carbon, Total Organic	Fluoride	Free chlorine	неаvy Metals (As, Pb, Cd)	KMnO₄	Phosphorus, Soluble Reactive	Phosphorus, Total	TTHMs	Giardia/ Cryptosporidium	
Raw water	D	W			D	М	D	D	W	Т	D	D	М		T		D	D	Т	W	
PTFInfluent		MC			MC		MC														
Actiflo Clarified (whichever ones are in operation)		MC			MC		MC				D						D	D			
FTW recycle pump station					MC		MC				D			MC							
Clarified Water Basins (filter influent, post-pretreatment Cl-)					MC		MC				D			МС			D	D			
Filtration (filter effluent) - clearwell 57											D						D	D			
Finished water	D	W			D	М	D	D	W	Т	D	D	М	MC	T		D	D	Т		

## Glenmore Lab Testing Frequency (BASELINE)

Parameters	Physical Physical						Chemical												Biological		
Location	Color 460	Conductivity	ОКР	Particle Count	рН/Тетр	7.SS	Turbidity	UV 254	Alkalinity	4/	Carbon, Dissolved Organic	Carbon, Total Organic	Fluoride	Free chlorine	Heavy Metals (As, Pb, Cd)	KMnO₄	Phosphorus, Soluble Reactive	Phosphorus, Total	ттнмѕ	Giardia/ Cryptosporidium	
Raw water	W	W			W	М	D	Т	W		W	W	M		M		W	W	Т	W	
PTFInfluent	M	С	С		С																
Actiflo Clarified (whichever ones are in operation)		MC			MC		MC				W						W				
FTW recycle pump station		MC			MC		MC				W			MC							
Clarified Water Basins (filter influent, post-pretreatment Cl-)					MC		МС				W			MC			W				
Filtration (filter effluent) - clearwell 57					MC		МС				W						W				
Finished water	W	W			D	М	D	Т			W	Т	М	МС	М		W	W	Т		

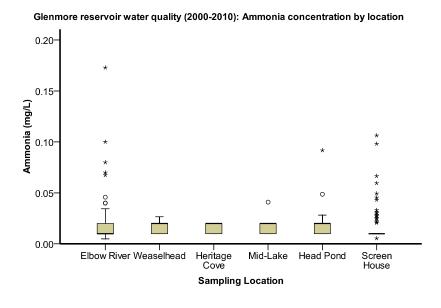
D = DAILY

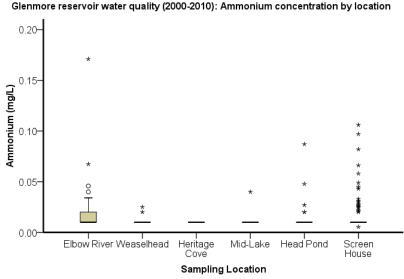
W = WEEKLY

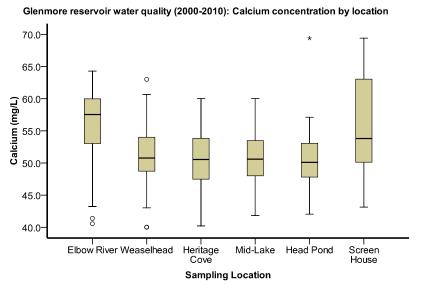
T = TWICE WEEKLY (MON AND THURS)

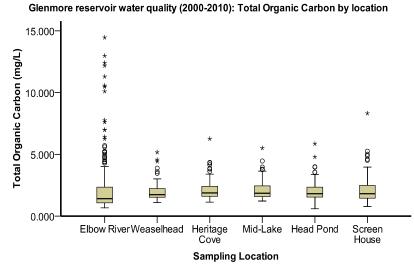
M = MONTHLY

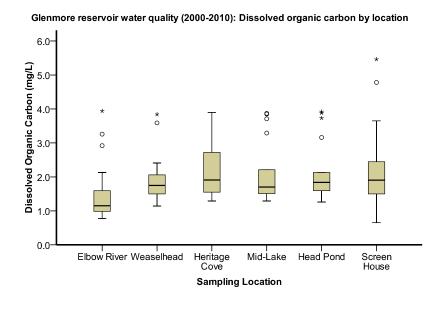
Appendix B: Elbow River & Glenmore Reservoir water quality, by location (2000-2010)

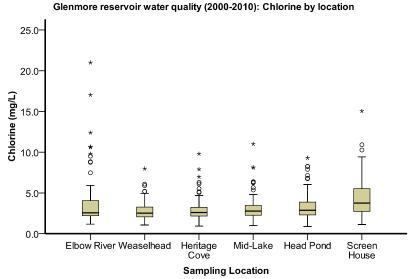


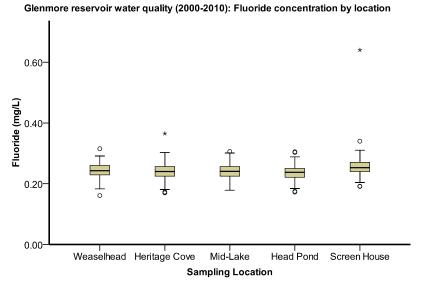


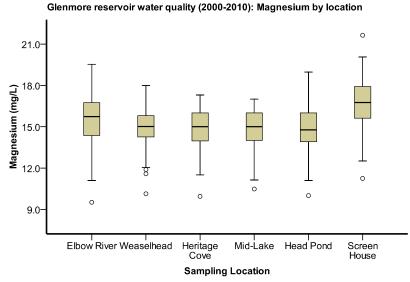


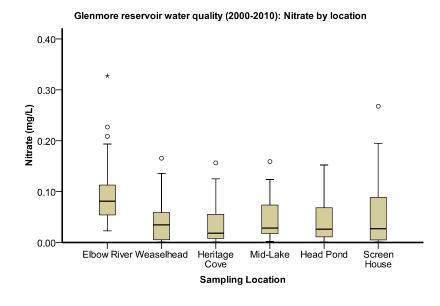


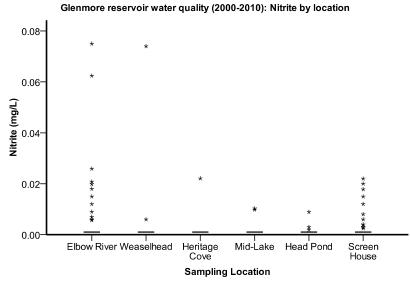


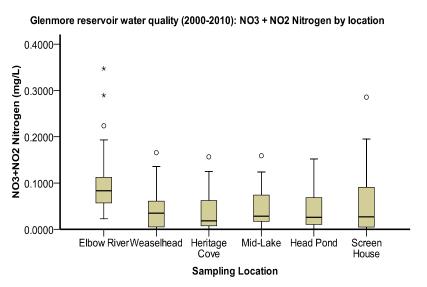


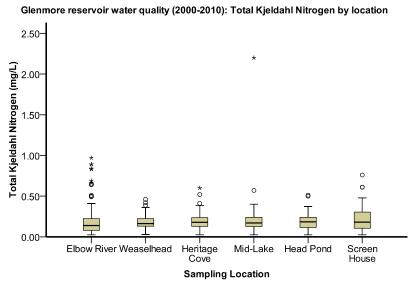


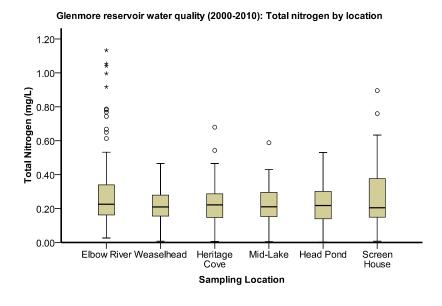


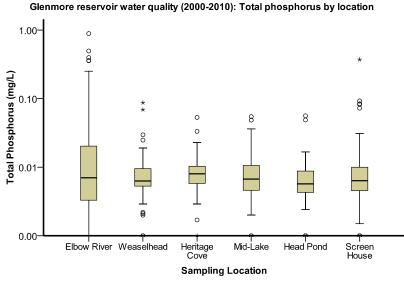


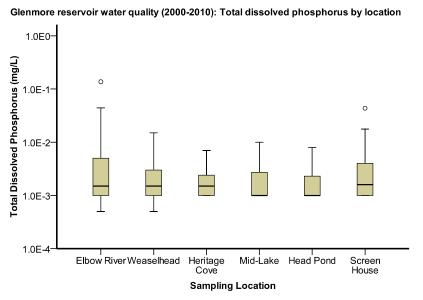


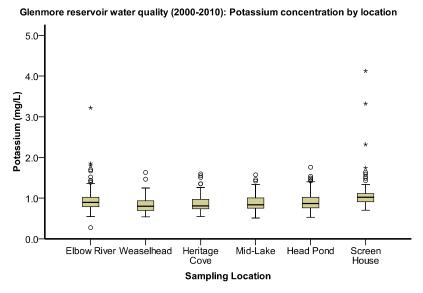


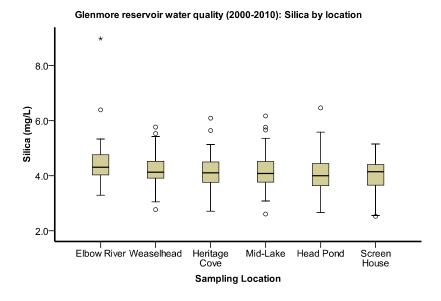


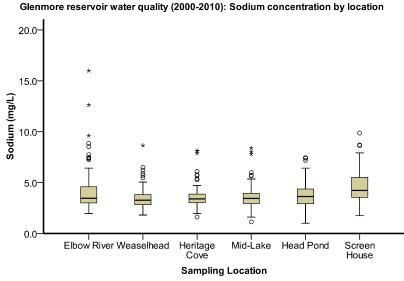


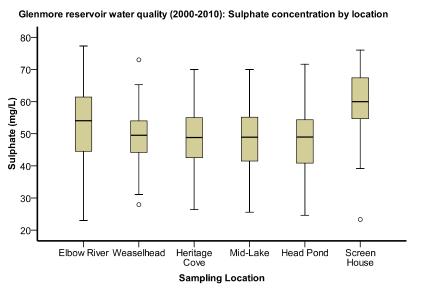


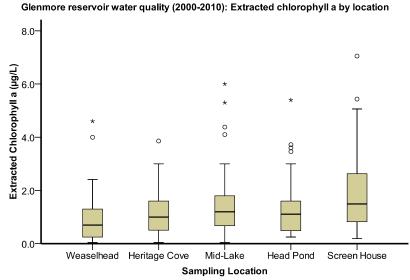


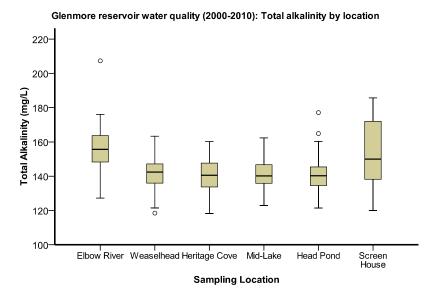


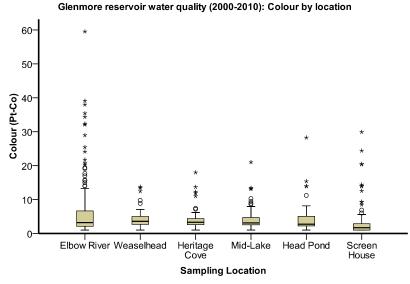


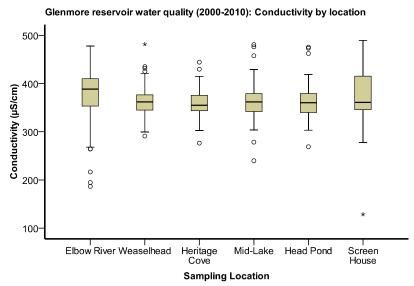


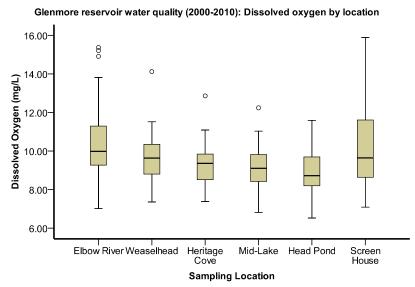


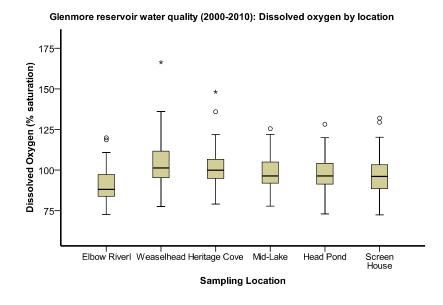


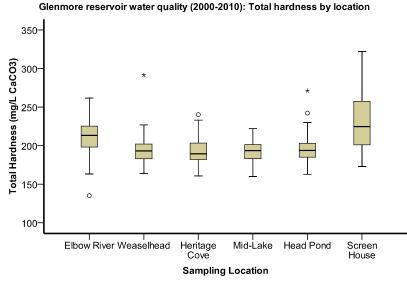


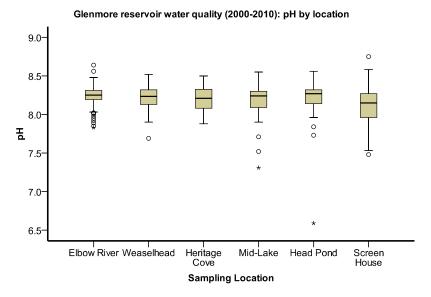


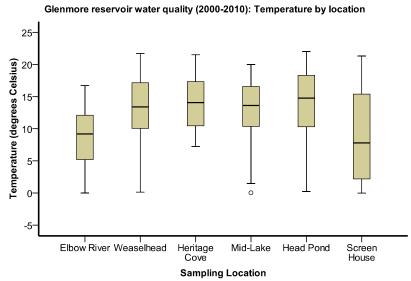


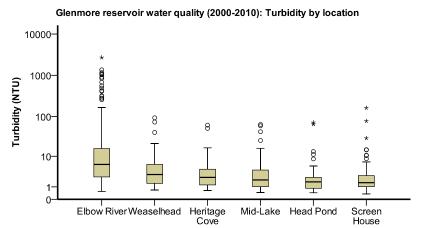












Sampling Location

Appendix C: Glenmore Reservoir spatial water quality analysis (2000-2010)

Table C.1 Kruskal-Wallis tests for water quality spatial differences by month (2000-2010)

Glenmore Reservoir

Weaselhead Bridge/Weaselhead Samples Excluded

Kruskal-Wallis Test Statistics<sup>a,b</sup>

Statistics = Asymp. Sig.

Statistics = Asymp. Sig.			Мо	onth		
	1	5	6	7	8	9
Ammonia	.568	.108	.048	.107	.018	.001
Ammonium	.521	.187	.392	.355	1.000	.682
Ca	.235	.050	.890	.287	.804	.001
Total Organic Carbon	.117	.245	.751	.715	.550	.949
Chlorine	.770	.436	.116	.783	.361	.318
Colour	.546	.971	.880	.007	.026	.399
Conductivity	.107	.020	.206	.983	.142	.012
Dissolved Oxygen-1	.135	.785	.386	.792	.036	.043
Dissolved Oxygen-2	.137	.490	.700	.741	.521	.915
FI	.132	.431	.313	.901	.551	.587
Mg	.770	.683	.923	.040	.732	.956
Na	.770	.737	.552	.474	.949	.598
Nitrate	.439	.948	.803	.202	.061	.000
Nitrite	.724	.162	.123	.564	.610	1.000
NO3+NO2 Nitrogen	.439	.813	.826	.209	.071	.000
Total Kjeldahl Nitrogen	.180	.164	.792	.301	.666	.585
Total Nitrogen	.180	.333	.763	.296	.743	.767
Total Phosphorus	.206	.075	.464	.299	.009	.135
Total Dissolved Phosphorus	.319	.021	.855	.703	.821	.981
рН	.025	.247	.765	.997	.607	.488
K	.380	.220	.100	.571	.257	1.000
Si	.134	.645	.009	.502	.522	.974
Sulphate	.380	.924	.138	.030	.396	.433
Total Alkalinity	1.000	.292	.297	.985	.201	.003
Total Hardness	.617	.424	.129	.271	.268	.218
Temperature (degrees Celsius)	.172	.204	.663	.289	.119	.001
Turbidity	.113	.231	.572	.077	.107	.175
Dissolved Organic Carbon		.994	.901	.987	.613	
Extracted Chlorophyll-a		.282	.727	.527	.456	.706

a. Kruskal Wallis Test

b. Grouping Variable: Site location Code

# Glenmore Reservoir Statistical Analyses for Water Quality Spatial Differences by Month (2000-2010) <u>Weaselhead Bridge/Weaselhead Samples Included</u> Kruskal-Wallis Test Statistics<sup>a,b,c</sup>

Statistics = Asymp, Sig.

Statistics = Asymp. Sig.					Мо	nth				
	1	3	4	5	6	7	8	9	10	11
Ammonia	.568	.008	.007	.104	.129	.244	.044	.001	.031	.002
Ammonium	.521	.008	.014	.050	.000	.000	.000	.008	.031	.002
Ca	.235	.006	.362	.024	.646	.000	.000	.000	.004	.014
Chlorine	.770	.239	.029	.008	.091	.920	.576	.374	.685	.086
Colour	.546	.003	.976	.992	.060	.004	.005	.191	.113	.050
Conductivity	.144	.000	.316	.207	.116	.005	.000	.000	.013	.008
Dissolved Organic			.655	.946	.873	.064	.051	.040	.053	
Carbon										
Dissolved Oxygen-1	.162	.009	.003	.001	.000	.041	.002	.003	.549	.038
Dissolved Oxygen-2	.164	.699	.269	.744	.588	.008	.003	.276	.143	
Extracted Chlorophyll-a				.115	.138	.050	.591	.442		
FI	.132			.341	.445	.958	.684	.704		
K	.380	.641	.122	.009	.122	.483	.022	.992	.745	.142
Mg	.770	.230	.191	.822	.299	.049	.199	.989	.088	.027
Na	.770	.205	.052	.223	.727	.587	.994	.694	.289	.014
Nitrate	.439	.247	.288	.002	.000	.000	.000	.000	.001	.008
Nitrite	.724	.659	.553	.211	.148	.432	.739	1.000	1.000	1.000
NO3+NO2 Nitrogen	.439	.280	.220	.001	.000	.000	.000	.000	.001	.008
рH	.034	.006	.000	.356	.788	.995	.277	.009	.157	.345
Si	.134	.127	.845	.203	.007	.075	.518	.994	.221	
Sulphate	.380	.480	.362	.730	.023	.018	.047	.540	.012	.014
Temperature (degrees	.176	.698	.616	.000	.000	.000	.000	.000	.007	.450
Celsius)										
Total Alkalinity	1.000	.002	.612	.035	.354	.000	.000	.000	.004	.014
Total Dissolved	.319	.014	.576	.006	.006	.330	.621	.717	.073	.116
Phosphorus										
Total Hardness	.617	.004	.052	.412	.271	.054	.000	.019	.007	.014
Total Kjeldahl Nitrogen	.180	.496	.290	.217	.700	.222	.069	.247	.255	.085
Total Nitrogen	.180	.734	.307	.544	.272	.505	.776	.833	.345	.462
Total Organic Carbon	.117	.297	.152	.356	.245	.001	.000	.002	.001	.014
Total Phosphorus	.206	.024	.152	.654	.216	.589	.006	.221	.004	.345
Turbidity	.113	.000	.045	.003	.000	.000	.000	.000	.001	.038

a. Kruskal Wallis Test

b. Grouping Variable: Site location Code

c. Only one non-empty group for December samples: no K-W tests in December

Table C.2 Kruskal-Wallis tests for water quality differences attributable to depth, by month (2000-2010)

# (2000-2010) Glenmore Reservoir Weaselhead Bridge/Weaselhead Samples Included Kruskal-Wallis Test Statistics<sup>a,b,c</sup>

Statistics = Asymp. Sig.

Statistics = Asymp. S	.g.					Month					
	1	2	3	4	5	6	7	8	9	10	11
Ammonia		1.000	.008	.013	.370	.649	.233	.010	.036	.031	.002
Ammonium		1.000	.008	.022	.281	.438	.037	.027	.213	.031	.002
Ca		.318	.006	.362	.141	.439	.023	.000	.004	.004	.014
Chlorine		.314	.239	.029	.011	.105	.459	.816	.257	.685	.086
Colour		.099	.003	.622	.324	.066	.186	.697	.090	.113	.050
Conductivity	.174	.283	.000	.228	.368	.344	.031	.000	.001	.013	.008
Dissolved Organic		.526		.655	.868	.417	.316	.467	.040	.053	
Carbon											
Diss. Oxygen	.192	.311	.009	.009	.059	.009	.058	.005	.032	.549	.038
(mg/L)	404	044	000	004	004	070	001	000	000	4.40	
Diss. Oxygen (%	.194	.311	.699	.384	.634	.673	.221	.098	.026	.143	
sat) Extracted		1.000		.275	.636	.232	.052	.444	.418		
Chlorophyll-a		1.000		.275	.030	.202	.032	.444	.410		
FI		.807			.131	.127	.604	.487	.542		
K		.598	.641	.122	.037	.613	.141	.341	.564	.745	.142
Mg		.807	.230	.191	.722	.152	.488	.324	.859	.088	.027
Na		.243	.205	.052	.074	.562	.095	.738	.424	.289	.014
Nitrate		.130	.247	.224	.037	.001	.002	.000	.000	.001	.008
Nitrite		.030	.659	.773	.109	.625	.777	.127	1.000	1.000	1.000
NO3+NO2 Nitrogen		.130	.280	.195	.019	.000	.001	.000	.000	.001	.008
рН	.048	.959	.006	.000	.378	.505	.125	.756	.030	.157	.345
Si		.879	.127	.845	.229	.040	.132	.785	.772	.221	
Sulphate		.314	.480	.362	.680	.021	.766	.451	.490	.012	.014
Temperature	.164	.211	.698	.874	.125	.000	.000	.000	.001	.007	.450
(degrees Celsius)											
Total Alkalinity		.308	.002	.612	.047	.850	.016	.003	.017	.004	.014
Total Dissolved		.376	.014	.229	.169	.001	.536	.246	.452	.073	.116
Phosphorus											
Total Hardness		.314	.004	.052	.274	.106	.101	.070	.127	.007	.014
Total Kjeldahl		.157	.496	.290	.466	.538	.479	.095	.259	.255	.085
Nitrogen		457	704	207	500	000	EE4	0.40	404	045	400
Total Nitrogen		.157	.734	.307	.592	.230	.551	.343	.461	.345	.462
Total Organic Carbon		.768	.297	.220	.426	.579	.032	.003	.014	.001	.014
Total Phosphorus		.207	.024	.194	.993	.394	.828	.608	.178	.004	.345
Turbidity		.311	.000	.133	.028	.000	.002	.000	.007	.004	.038
rurbiuity		.311	.000	. 133	.020	.000	.002	.000	.007	.001	.038

a. Kruskal Wallis Test

b. Grouping Variable: Sample Depth

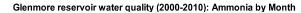
c. Only one non-empty group for December samples: no K-W tests in December

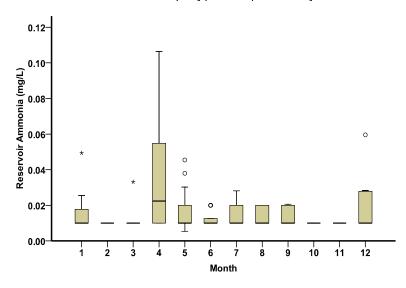
Table C.3 Water quality parameters exhibiting variability due to sample depth

Sampling locations	Physical parameters	Chemical parameters
Weaselhead samples included	Colour, conductivity, pH, total alkalinity, temperature, turbidity	Ammonia, ammonium, calcium, nitrate, TP, total dissolved phosphorus, total organic carbon
Weaselhead samples excluded	-	-

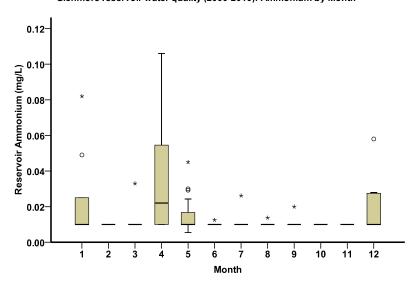
<sup>&</sup>lt;sup>1</sup> Site locations: Weaselhead bridge, Weaselhead, Heritage Cove, Mid-Lake, Head Pond, Screen House **bold face** indicates parameters significantly different for two or more months

Appendix D: Glenmore Reservoir water quality data, by month (2000-2010)

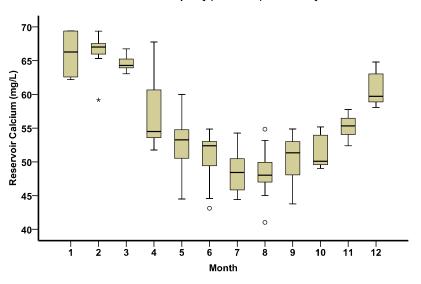




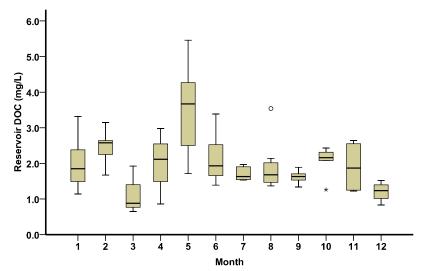
Glenmore reservoir water quality (2000-2010): Ammonium by Month

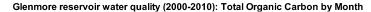


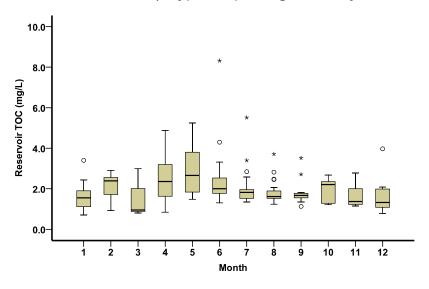
Glenmore reservoir water quality (2000-2010): Calcium by Month



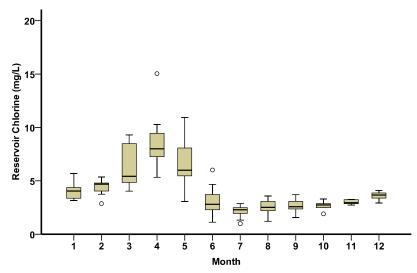
Glenmore reservoir water quality (2000-2010): DOC by Month



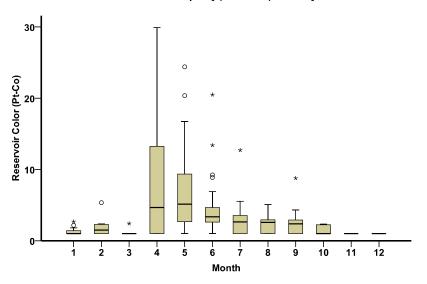




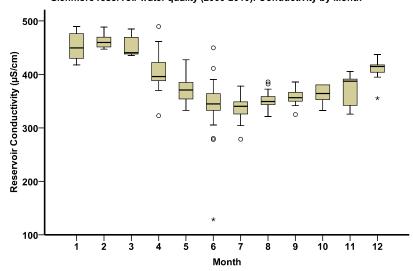
Glenmore reservoir water quality (2000-2010): Chlorine by Month



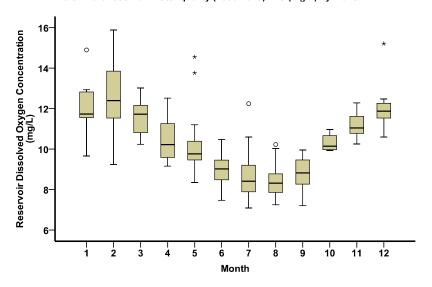
Glenmore reservoir water quality (2000-2010): Color by Month



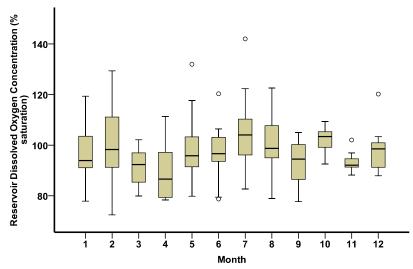
Glenmore reservoir water quality (2000-2010): Conductivity by Month



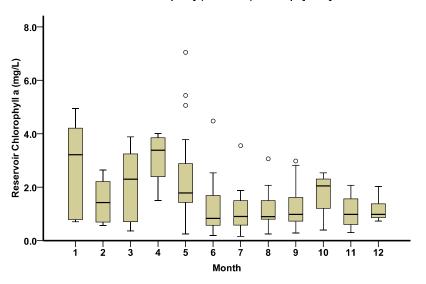
Glenmore reservoir water quality (2000-2010): DO (mg/L) by Month



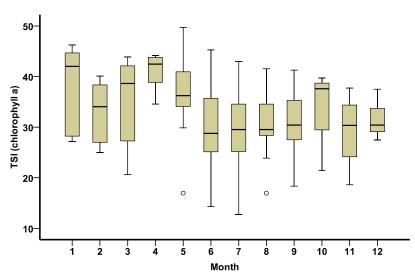
Glenmore reservoir water quality (2000-2010): DO (% sat.) by Month



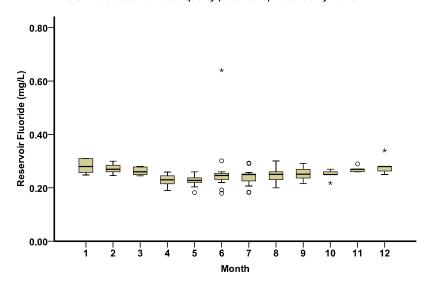
Glenmore reservoir water quality (2000-2010): Chlorophyll a by Month



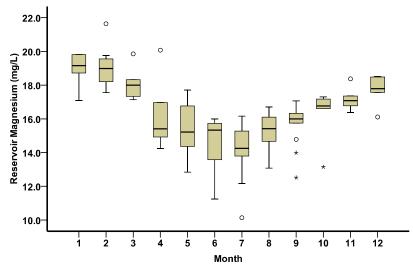
Glenmore reservoir water quality (2000-2010): TSI (chl. a) by Month



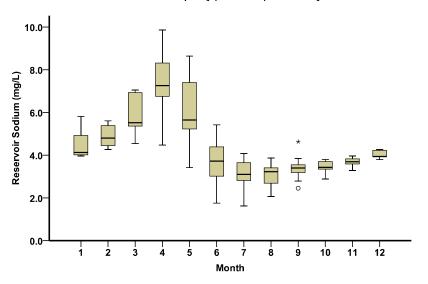




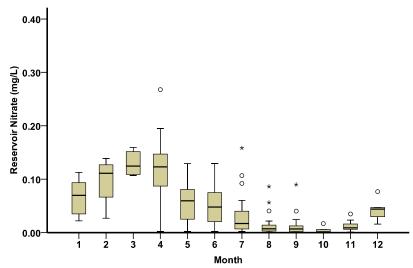
# Glenmore reservoir water quality (2000-2010): Magnesium by Month

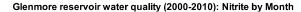


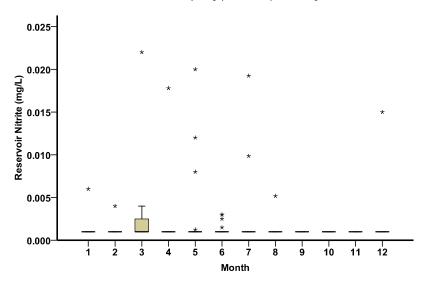
Glenmore reservoir water quality (2000-2010): Sodium by Month



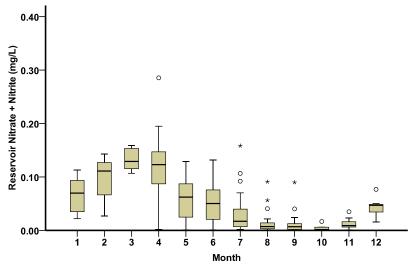
Glenmore reservoir water quality (2000-2010): Nitrate by Month



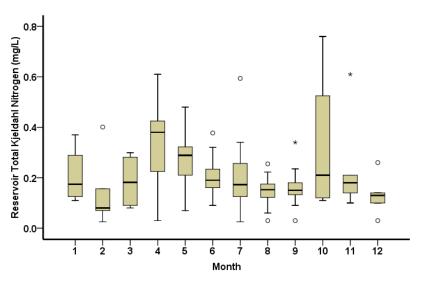




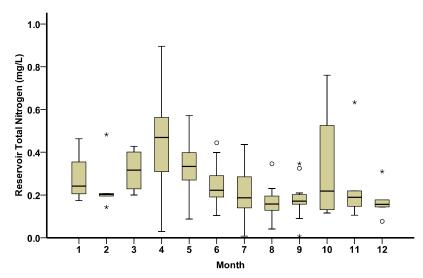
Glenmore reservoir water quality (2000-2010): NO3+NO2 by Month



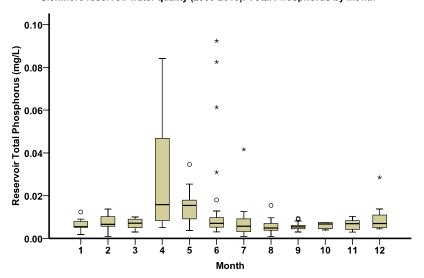
Glenmore reservoir water quality (2000-2010): TKN by Month



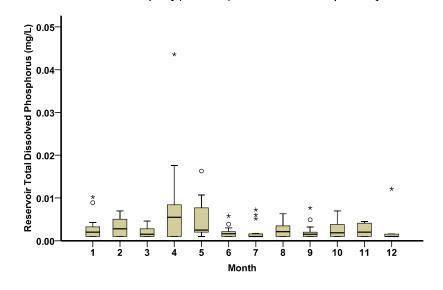
Glenmore reservoir water quality (2000-2010): Total Nitrogen by Month



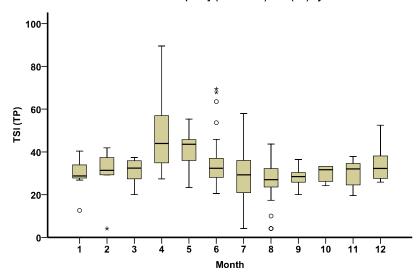




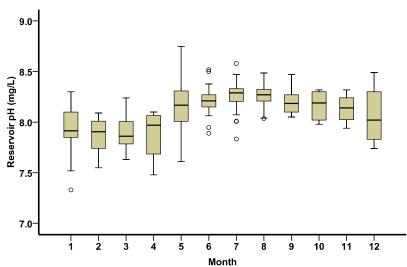
## Glenmore reservoir water quality (2000-2010): Total Dissolved Phosphorus by Month



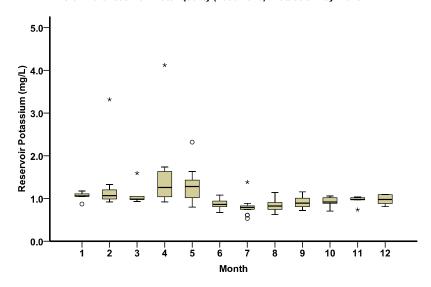
Glenmore reservoir water quality (2000-2010): TSI (TP) by Month



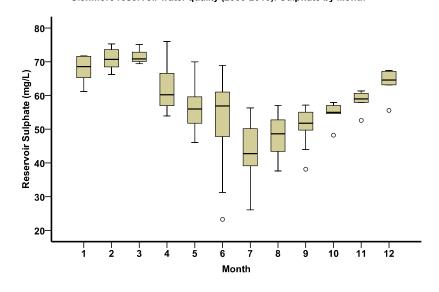
Glenmore reservoir water quality (2000-2010): pH by Month



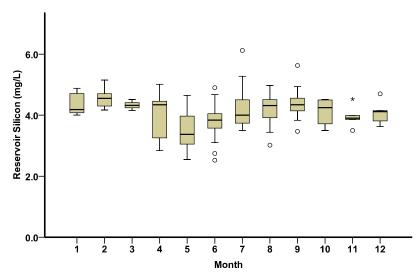
#### Glenmore reservoir water quality (2000-2010): Potassium by Month



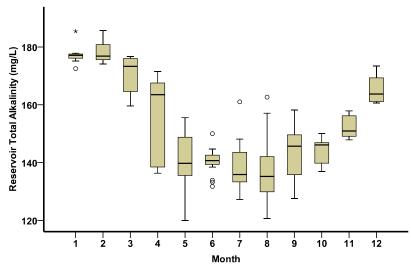
Glenmore reservoir water quality (2000-2010): Sulphate by Month

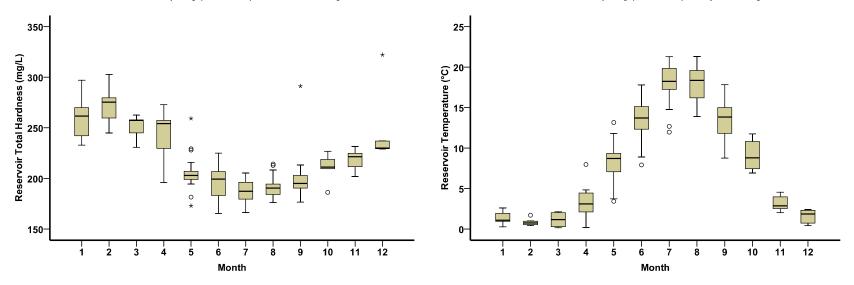


Glenmore reservoir water quality (2000-2010): Silicon by Month

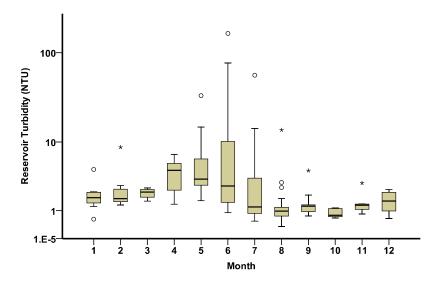


Glenmore reservoir water quality (2000-2010): Total Alkalinity by Month





Glenmore reservoir water quality (2000-2010): Turbidity by Month



Appendix E: Glenmore WTP water quality data (2012)

Table E.1 Phosphorus concentrations at Glenmore WTP

	Phosphorus (mg/L)				Me	ean	Std.
P			Minimum	Maximum Statistic		Std. Error	Deviation
	Raw TP	39	0.003	0.104	0.025	0.005	0.031
	Raw TDP	39	0.002	0.016	0.004	0.001	0.003
All	PTF effluent TP	40	0.002	0.007	0.003	0.000	0.001
₹	PTF effluent TDP	40	0.001	0.006	0.002	0.000	0.001
	Finished TP	40	0.001	0.006	0.002	0.000	0.001
	Finished TDP	40	0.001	0.006	0.002	0.000	0.001

Table E.2 Turbidity at Glenmore WTP

					Me	an	Std.
Tu	rbidity (NTU)	N	Minimum	Maximum	Statistic	Std. Error	Deviation
	Raw turbidity	254	0.304	99.985	8.677	1.405	22.389
All	PTF influent	249	0.400	142.360	9.809	1.609	25.385
▼	PTF effluent	254	0.372	3.283	1.013	0.034	0.541
	Finished	254	0.033	0.088	0.062	0.001	0.013

Table E.3 Organic carbon concentrations at Glenmore WTP

	Organic carbon				Me	an	Std.
	(mg/L)		Minimum	Maximum	Statistic	Std. Error	Deviation
	Raw TOC	42	1.000	5.700	2.507	0.200	1.299
	Raw DOC	42	0.900	4.400	2.167	0.161	1.041
	PTF effluent TOC	42	0.900	2.400	1.669	0.068	0.442
A	PTF effluent DOC	43	0.800	2.300	1.514	0.063	0.413
	Finished TOC	41	0.800	2.300	1.556	0.063	0.402
	Finished DOC	42	0.800	2.200	1.441	0.058	0.379

Table E.4 pH at Glenmore WTP

nII		-	Minimum	Mavimum	N	<b>Iean</b>	Std.
	pН	n	Minimum	Maximum	Statistic	Std. Error	Deviation
	Raw pH	254	7.768	8.638	8.285	-	-
All	PTF influent pH	254	6.992	8.170	7.548	-	-
·	PTF effluent pH	254	6.611	7.902	7.255	-	-

Table E.5 Raw water conductivity at Glenmore WTP

Conductivity				Me	ean	Std.	Median
(µs/cm)	n	Minimum	Minimum Maximum		Std. Error	Deviation	
All	254	204.8	526.4	397.6	3.0	47.1	381.809

## Table E.6 Raw water color at Glenmore WTP

				M	lean			
True Color	n	Minimum	Maximum	Statistic Std. Error		Std. Dev	Median	
True Color (CU)	9	1.000	9.100	3.789	.796	2.389	3.000	

Table E.7 Raw water Specific Ultraviolet Absorbance at Glenmore WTP

SUVA				M	ean		
(L mg <sup>-1</sup> m <sup>-1</sup> )	n	Minimum	Maximum	Statistic	Std. Error	Std. Deviation	Median
All	42	0.008	4.117	2.427	0.115	0.745	2.368

# Table E.8 Raw water UVA<sub>254</sub> at Glenmore WTP

UVA <sub>254</sub>	,	Minimum	Mavimum	N	Iean	Std.	Modion	
(cm <sup>-1</sup> )	n	Millimin	Maximum	Statistic Std. Error		Deviation	Median	
All	254	0.0002	0.149	0.039008	0.0017309	0.0275859	0.0283	

# Table E.9 Raw water metal concentrations at Glenmore WTP

				M	ean	Std.	
Metal	n	Minimum	Maximum	Statistic	Std. Error	Dev	Median
Aluminum (µg/L)	9	7.200	193.100	40.867	19.860	59.580	15.100
Calcium (mg/L)	9	48.000	69.000	55.000	2.147	6.442	54.000
Iron (µg/L)	9	15.000	134.400	44.989	12.754	38.263	25.000
Magnesium (mg/L)	9	12.000	19.000	16.000	.667	2.000	16.00

# Table E.10 Coagulant (alum dose, mg/L) at Glenmore WTP

				Mo	ean	Std.	
Alum Dose (mg/L)	n Minimum Maximun		Maximum	Statistic	Std. Error	<b>Deviation</b>	Median
All	254	7.848	101.172	20.527	1.192	19.003	11.998

# Table E.11 Polymer dose (mg/L) at Glenmore WTP

Polymer Dose				Me	ean	Std.	
(mg/L)	n	Minimum	nimum Maximum	Statistic	Std. Error	Deviation	Median
All	254	0.099	0.322	0.140	0.003	0.050	0.120

# Table E.12 Pre-treatment chlorine dose (mg/L) at Glenmore WTP

Chlorine dose				M	ean	Std.	
(mg/L)	n Minim	Minimum	m Maximum	Statistic	Std. Error	Deviation	Median
All	254	1.250	2.550	1.820	0.018	0.283	1.845

Appendix F: SPSS m	ultiple linear	regression sun	nmaries

# EAST COAGULANT DOSE (2000 - 2010)

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
In East Coagulant Dose (verified) (mg/L)	2.76305	.590695	22
TOC	1.9254	1.23072	22
Turbidity (0100)	4.6883	12.12248	22
Reservoir Color (Color Units)	3.7777651364E0	2.59160614675E0	22
Reservoir Total Phosphorus (mg/L)	.0090755909	.00789181557	22
Reservoir Nitrate (mg/L)	.0454931818	.03859588723	22
Reservoir TOC (mg/L)	2.0496590909E0	.91584767379	22

#### Variables Entered/Removed<sup>a</sup>

Model	Variables Entered	Variables Removed	Method
1	Reservoir TOC (mg/L)		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

#### Model Summary<sup>b</sup>

F					Change Statistics				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change
1	.899ª	.808	.798	.265326	.808	84.085	1	20	.000

a. Predictors: (Constant), Reservoir TOC (mg/L)

#### ANOVA<sup>b</sup>

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	5.919	1	5.919	84.085	.000 <sup>a</sup>
	Residual	1.408	20	.070		
	Total	7.327	21			

a. Predictors: (Constant), Reservoir TOC (mg/L)

#### Coefficients<sup>a</sup>

			dardized ficients	Standardize d Coefficients			Co	orrelations	6	Colline Statis	
Mode	el	В	Std. Error	Beta	t	Sig.	Zero- order	Partial	Part	Toleranc e	VIF
1	(Constant)	1.575	.141		11.139	.000					
	Reservoir TOC (mg/L)	.580	.063	.899	9.170	.000	.899	.899	.899	1.000	1.000

a. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

b. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

b. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

b. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

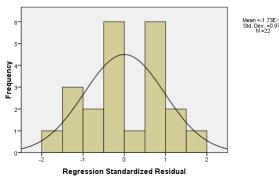
## Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	2.42122	4.77192	2.76305	.530919	22
Std. Predicted Value	644	3.784	.000	1.000	22
Standard Error of Predicted Value	.057	.226	.072	.036	22
Adjusted Predicted Value	2.40162	5.11238	2.77966	.594289	22
Residual	515594	.493950	.000000	.258931	22
Std. Residual	-1.943	1.862	.000	.976	22
Stud. Residual	-1.999	1.909	022	1.019	22
Deleted Residual	545864	.519218	016610	.291279	22
Stud. Deleted Residual	-2.179	2.057	026	1.055	22
Mahal. Distance	.000	14.317	.955	3.029	22
Cook's Distance	.000	1.132	.081	.237	22
Centered Leverage Value	.000	.682	.045	.144	22

a. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

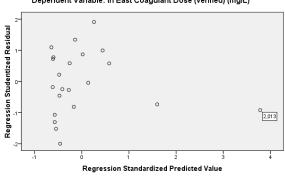
Histogram

Dependent Variable: In East Coagulant Dose (verified) (mg/L)



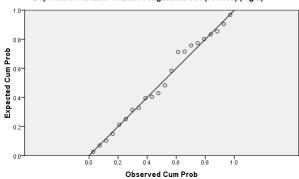
Scatterplot

Dependent Variable: In East Coagulant Dose (verified) (mg/L)



Normal P-P Plot of Regression Standardized Residual

Dependent Variable: In East Coagulant Dose (verified) (mg/L)



# EAST COAGULANT DOSE (2000 - 2010) - extreme value omitted

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
In East Coagulant Dose (verified) (mg/L)	2.67347	.425447	21
TOC	1.7777	1.04217	21
Turbidity (0100)	2.1501	2.34250	21
Reservoir Color (Color Units)	3.3532539524E0	1.69982305662E0	21
Reservoir Total Phosphorus (mg/L)	.0075268095	.00315978975	21
Reservoir Nitrate (mg/L)	.0401166667	.02993952063	21
Reservoir TOC (mg/L)	1.8846428571E0	.50169169175	21

#### Variables Entered/Removed<sup>a</sup>

Mod.	Variables Entered	Variables Removed	Method
1	Reservoir TOC (mg/L)		Forward (Criterion: Probability-of-F-to-enter < = .050)
2	Reservoir TP (mg/L)		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

#### Model Summary<sup>c</sup>

					Change Statistics				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change
1	.792ª	.628	.608	.266375	.628	32.019	1	19	.000
2	.867 <sup>b</sup>	.753	.725	.223096	.125	9.087	1	18	.007

- a. Predictors: (Constant), Reservoir TOC (mg/L)
- b. Predictors: (Constant), Reservoir TOC (mg/L), Reservoir Total Phosphorus (mg/L)
- c. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

#### **ANOVA<sup>c</sup>**

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	2.272	1	2.272	32.019	.000 <sup>a</sup>
	Residual	1.348	19	.071		
	Total	3.620	20			
2	Regression	2.724	2	1.362	27.367	.000°
	Residual	.896	18	.050		
	Total	3.620	20			

- a. Predictors: (Constant), Reservoir TOC (mg/L)
- b. Predictors: (Constant), Reservoir TOC (mg/L), Reservoir Total Phosphorus (mg/L)
- c. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

#### Coefficients<sup>a</sup>

		Unstand Coeffi	dardized cients	Standardize d Coefficients			Co	orrelation	S	Colline Statis	
Mod	lel	В	Std. Error	Beta	t	Sig.	Zero- order	Partial	Part	Toleranc e	VIF
1	(Constant)	1.407	.231		6.088	.000					
	Reservoir TOC (mg/L)	.672	.119	.792	5.659	.000	.792	.792	.792	1.000	1.000
2	(Constant)	1.258	.200		6.293	.000					
	Reservoir TOC (mg/L)	.545	.108	.642	5.043	.000	.792	.765	.591	.848	1.180
	Reservoir TP(mg/L)	51.693	17.149	.384	3.014	.007	.635	.579	.353	.848	1.180

a. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

#### Residuals Statistics<sup>a</sup>

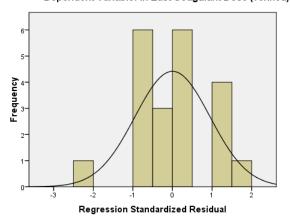
	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	2.29596	3.65707	2.67347	.369067	21
Std. Predicted Value	-1.023	2.665	.000	1.000	21
Standard Error of Predicted Value	.053	.173	.079	.031	21
Adjusted Predicted Value	2.32249	3.99576	2.68629	.412548	21
Residual	483351	.342935	.000000	.211648	21
Std. Residual	-2.167	1.537	.000	.949	21
Stud. Residual	-2.236	1.607	021	1.029	21
Deleted Residual	561446	.374906	012816	.258417	21
Stud. Deleted Residual	-2.557	1.688	029	1.085	21
Mahal. Distance	.181	11.112	1.905	2.722	21
Cook's Distance	.000	1.273	.091	.273	21
Centered Leverage Value	.009	.556	.095	.136	21

a. Dependent Variable: In East Coagulant Dose (verified) (mg/L)

#### Charts

#### Histogram

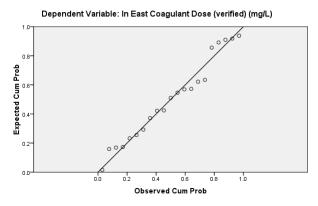
## Dependent Variable: In East Coagulant Dose (verified) (mg/L)

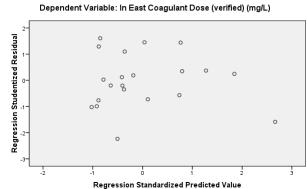


Mean =-2.64E-15 Std. Dev. =0.949 N =21

#### Normal P-P Plot of Regression Standardized Residual

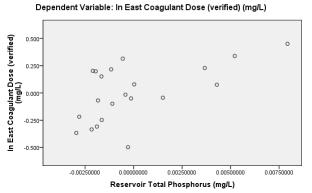
#### Scatterplot

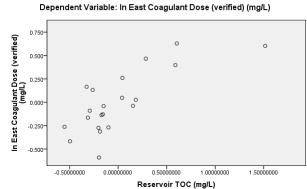




Partial Regression Plot

Partial Regression Plot





## WEST COAGULANT DOSE (2000 - 2010)

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
In West Coagulant Dose (verified) (mg/L)	2.77749	.737359	29
In(TOC)	.5390	.50545	29
In(Turbidity)	.5379	1.15800	29
In(Total Alkalinity)	5.025723	.0875293	29
In (Reservoir Total Phosphorus)	-4.6519678484E0	.63097103194	29

#### Variables Entered/Removeda

Model	Variables Entered	Variables Removed	Method
1	In(TOC)		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: In West Coagulant Dose (verified) (mg/L)

#### Model Summary<sup>b</sup>

		R			Change Statistics					
Model	R	Squa re	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change	Durbin- Watson
1	.762ª	.581	.565	.486156	.581	37.412	1	27	.000	.762

a. Predictors: (Constant), In(TOC)

#### ANOVA<sup>b</sup>

Model	Sum of Squares	df	Mean Square	F	Sig.
1 Regression	8.842	1	8.842	37.412	.000ª
Residual	6.381	27	.236		
Total	15.224	28			

a. Predictors: (Constant), In(TOC)

#### Coefficients<sup>a</sup>

		Unstandardi	Standardized Coefficients			
Model		В	Std. Error	Beta	t	Sig.
1	(Constant)	2.178	.133		16.350	.000
	In(TOC)	1.112	.182	.762	6.117	.000

a. Dependent Variable: In West Coagulant Dose (verified) (mg/L)

#### Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	.72254	4.93348	2.45769	.656860	1843
Std. Predicted Value	-3.657	3.837	569	1.169	1843
Standard Error of Predicted Value	.090	.364	.141	.050	1843
Adjusted Predicted Value	.72254	4.93348	2.45775	.656910	1843
Residual	-3.931410	3.251465	.133258	.643507	1843
Std. Residual	-8.087	6.688	.274	1.324	1843
Stud. Residual	-7.920	6.171	.257	1.262	1843
Deleted Residual	-3.931410	3.251465	.133206	.644031	1843
Stud. Deleted Residual	-7.920	6.171	.257	1.264	1843
Mahal. Distance	.000	9.446	1.438	1.604	1843
Cook's Distance	.000	38.703	.199	1.168	1841
Centered Leverage Value	.000	.326	.050	.055	1843

a. Dependent Variable: In West Coagulant Dose (verified) (mg/L)

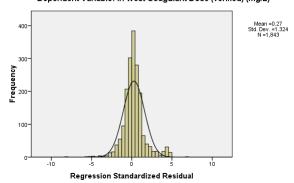
b. Dependent Variable: In West Coagulant Dose (verified) (mg/L)

b. Dependent Variable: In West Coagulant Dose (verified) (mg/L)

#### Charts

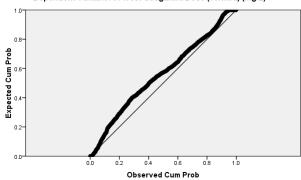
#### Histogram

## Dependent Variable: In West Coagulant Dose (verified) (mg/L)



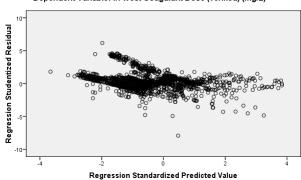
Normal P-P Plot of Regression Standardized Residual

Dependent Variable: In West Coagulant Dose (verified) (mg/L)



Scatterplot

Dependent Variable: In West Coagulant Dose (verified) (mg/L)



# **ALUM DOSE (2012)**

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
InClarifiedWBSouthAlumDose	3.047769	.9278816	26
InRawConductivity	5.893359	.0585235	26
InRawTOC	.774958	.5042501	26
InRawDOC	.611641	.4773450	26
InRawUVA	-3.091801	.7026908	26
InRawTurbidity	1.234226	2.1952129	26
InRawTP	-4.561519	1.1817600	26

#### Variables Entered/Removed<sup>a</sup>

Model	Variables Entered	Variables Removed	Method		
1	InRawUVA		Forward (Criterion: Probability-of-F-to-enter < = .050)		
2	InRawTP .		Forward (Criterion: Probability-of-F-to-enter < = .050)		
3	InRawConductivity		Forward (Criterion: Probability-of-F-to-enter < = .050)		

a. Dependent Variable: InClarifiedWBSouthAlumDose

## Model Summary<sup>d</sup>

						Change	Statistics		
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change
1	.984ª	.967	.966	.1712637	.967	709.828	1	24	.000
2	.991 <sup>b</sup>	.983	.981	.1262330	.016	21.177	1	23	.000
3	.994 <sup>c</sup>	.989	.987	.1040592	.006	11.846	1	22	.002

a. Predictors: (Constant), InRawUVA

# $\textbf{ANOVA}^{\text{d}}$

Mode	I	Sum of Squares	df	Mean Square	F	Sig.
1	Regression	20.820	1	20.820	709.828	.000ª
	Residual	.704	24	.029		
	Total	21.524	25			
2	Regression	21.158	2	10.579	663.881	.000 <sup>b</sup>
	Residual	.366	23	.016		
	Total	21.524	25			
3	Regression	21.286	3	7.095	655.254	.000°
	Residual	.238	22	.011		
	Total	21.524	25			

a. Predictors: (Constant), InRawUVA

b. Predictors: (Constant), InRawUVA, InRawTP

c. Predictors: (Constant), InRawUVA, InRawTP, InRawConductivity

 $d.\ Dependent\ Variable:\ In Clarified\ WBS outh Alum Dose$ 

b. Predictors: (Constant), InRawUVA, InRawTP

c. Predictors: (Constant), InRawUVA, InRawTP, InRawConductivity

 $d.\ Dependent\ Variable:\ In Clarified\ WBS outh Alum Dose$ 

Coefficients

				Standardized Coefficients		Sig.	Collinearity	Statistics
Mod	el	В	Std. Error	Beta	t		Tolerance	VIF
1	(Constant)	7.063	.154		45.743	.000	1.000	1.000
	InRawUVA	1.299	.049	.984	26.643	.000		
2	(Constant)	6.923	.118		58.749	.000		
	InRawUVA	.753	.124	.570	6.082	.000	0.084	11.883
	InRawTP	.339	.074	.432	4.602	.000	0.084	11.883
3	(Constant)	-10.519	5.069		-2.075	.050		
	InRawUVA	1.044	.133	.791	7.877	.000	0.050	20.041
	InRawTP	.304	.062	.387	4.943	.000	0.082	12.211
	InRawConductivity	3.085	.896	.195	3.442	.002	.157	6.355

a. Dependent Variable: InClarifiedWBSouthAlumDose

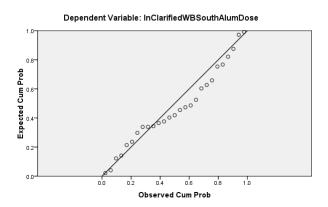
#### Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	1.982668	4.738124	3.023085	.9138593	27
Std. Predicted Value	-1.154	1.832	027	.990	27
Standard Error of Predicted Value	.027	.107	.042	.017	27
Adjusted Predicted Value	1.958712	4.773875	3.020845	.9130420	27
Residual	2116199	.2526340	0067478	.1019402	27
Std. Residual	-2.034	2.428	065	.980	27
Stud. Residual	-2.170	2.700	036	1.029	27
Deleted Residual	2410441	.3124652	0045071	.1191306	27
Stud. Deleted Residual	-2.392	3.226	017	1.116	27
Mahal. Distance	.668	12.423	3.238	2.740	27
Cook's Distance	.000	.442	.063	.117	27
Centered Leverage Value	.027	.478	.129	.107	27

a. Dependent Variable: InClarifiedWBSouthAlumDose

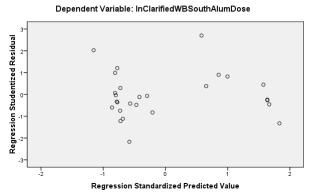
#### Charts

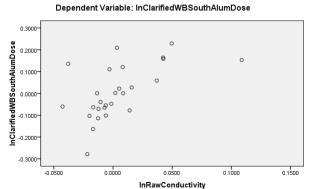
#### Normal P-P Plot of Regression Standardized Residual





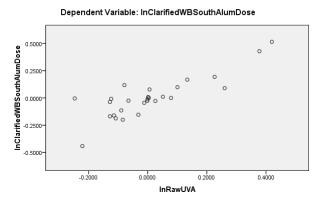
#### Partial Regression Plot

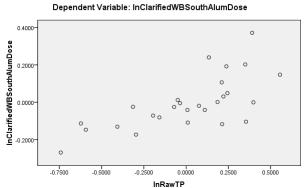




Partial Regression Plot

Partial Regression Plot





# ALUM DOSE (2012) \*SUVA considered instead

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
InClarifiedWBSouthAlumDose	3.047769	.9278816	26
InRawTP	-4.561519	1.1817600	26
InSUVA	.9017	.26924	26

#### Variables Entered/Removeda

Model	Variables Entered	Variables Removed	Method
1	InRawTP		Forward (Criterion: Probability-of-F-to-enter < = .050)
2	InSUVA		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: InClarifiedWBSouthAlumDose

# Model Summary<sup>c</sup>

-			Adjusted R	Std. Error of the	Change Statistics				
Model	R	R Square	Square		R Square Change	F Change	df1	df2	Sig. F Change
1	.978ª	.956	.954	.1995740	.956	516.402	1	24	.000
2	.984 <sup>b</sup>	.969	.966	.1715635	.013	9.477	1	23	.005

- a. Predictors: (Constant), InRawTP
- b. Predictors: (Constant), InRawTP, InSUVA
- $c.\ Dependent\ Variable: In Clarified WB South Alum Dose$

#### **ANOVA**<sup>c</sup>

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	20.568	1	20.568	516.402	.000ª
	Residual	.956	24	.040		
	Total	21.524	25			
2	Regression	20.847	2	10.424	354.133	.000 <sup>b</sup>
	Residual	.677	23	.029		
	Total	21.524	25			

- a. Predictors: (Constant), InRawTP
- b. Predictors: (Constant), InRawTP, InSUVA
- c. Dependent Variable: InClarifiedWBSouthAlumDose

#### Coefficients<sup>a</sup>

		Unstandard	zed Coefficients	Standardized Coefficients		
Mode	el	В	Std. Error	Beta	t	Sig.
1	(Constant)	6.549	.159		41.198	.000
	InRawTP	.768	.034	.978	22.724	.000
2	(Constant)	5.360	.410		13.087	.000
	InRawTP	.641	.050	.817	12.756	.000
	InSUVA	.679	.221	.197	3.078	.005

a. Dependent Variable: InClarifiedWBSouthAlumDose

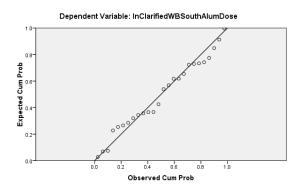
#### Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N					
Predicted Value	2.074830	4.784499	3.047769	.9131730	26					
Std. Predicted Value	-1.065	1.902	.000	1.000	26					
Standard Error of Predicted Value	.038	.087	.057	.012	26					
Adjusted Predicted Value	2.065034	4.843746	3.048669	.9177472	26					
Residual	3303089	.4586520	.0000000	.1645579	26					
Std. Residual	-1.925	2.673	.000	.959	26					
Stud. Residual	-2.014	2.741	002	1.012	26					

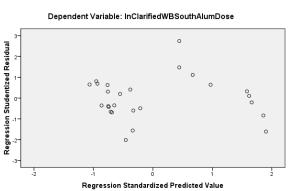
Deleted Residual	3613854	.4822223	0009000	.1834361	26
Stud. Deleted Residual	-2.170	3.267	.009	1.091	26
Mahal. Distance	.260	5.482	1.923	1.235	26
Cook's Distance	.001	.206	.038	.054	26
Centered Leverage Value	.010	.219	.077	.049	26

a. Dependent Variable: InClarifiedWBSouthAlumDose

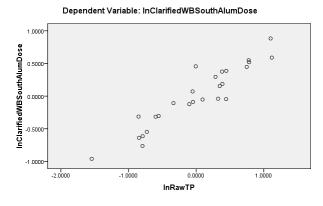
Normal P-P Plot of Regression Standardized Residual



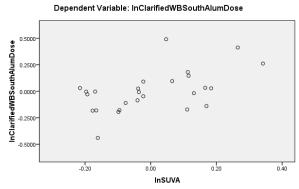
Scatterplot



Partial Regression Plot



Partial Regression Plot



# **POLYMER DOSE (2012)**

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
InClarifiedWBSouthPolyDose	-1.851313	.4016802	26
InRawDOC	.611641	.4773450	26
InRawTOC	.774958	.5042501	26
InRawTP	-4.561519	1.1817600	26
InRawTDP	-5.642686	.5921557	26
InRawConductivity	5.893359	.0585235	26
InRawTemp	2.517952	.4688768	26
InRawTOConline	.653029	.6087823	26
InRawUVA	-3.091801	.7026908	26
InRawTurbidity	1.234226	2.1952129	26

#### Variables Entered/Removed<sup>a</sup>

Model	Variables Entered	Variables Removed	Method
1	InRawUVA		Forward (Criterion: Probability-of-F-to-enter < = .050)
2	InRawDOC		Forward (Criterion: Probability-of-F-to-enter < = .050)
3	InRawConductivity		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: InClarifiedWBSouthPolyDose

#### Model Summary<sup>d</sup>

	,										
					Change Statistics						
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Cha nge		
1	.949ª	.901	.896	.1292413	.901	217.489	1	24	.000		
2	.963 <sup>b</sup>	.928	.922	.1123137	.027	8.780	1	23	.007		
3	.970°	.940	.932	.1048775	.012	4.377	1	22	.048		

- a. Predictors: (Constant), InRawUVA
- b. Predictors: (Constant), InRawUVA, InRawDOC
- c. Predictors: (Constant), InRawUVA, InRawDOC, InRawConductivity
- d. Dependent Variable: InClarifiedWBSouthPolyDose

#### $\mathbf{ANOVA}^{\mathtt{d}}$

						Sig.	
Model		Sum of Squares	df	Mean Square	F		
1	Regression	3.633	1	3.633	217.489	.000ª	
	Residual	.401	24	.017			
	Total	4.034	25				
2	Regression	3.744	2	1.872	148.384	.000 <sup>b</sup>	
	Residual	.290	23	.013			
	Total	4.034	25				
3	Regression	3.792	3	1.264	114.907	.000°	
	Residual	.242	22	.011			
	Total	4.034	25				

- a. Predictors: (Constant), InRawUVA
- b. Predictors: (Constant), InRawUVA, InRawDOC
- c. Predictors: (Constant), InRawUVA, InRawDOC, InRawConductivity
- d. Dependent Variable: InClarifiedWBSouthPolyDose

Coefficients<sup>a</sup>

			ndardized efficients	Standardized Coefficients				
Model		В	Std. Error	Beta	t	Sig.	Tolerance	VIF
1	(Constant)	174	.117		-1.494	.148		
	InRawUVA	.542	.037	.949	14.748	.000	1.000	1.000
2	(Constant)	1.287	.503		2.557	.018		
	InRawUVA	.906	.127	1.584	7.149	.000	0.064	15.705
	InRawDOC	553	.186	657	-2.963	.007	0.064	15.705
3	(Constant)	-9.451	5.154		-1.834	.080		
	InRawUVA	1.020	.130	1.785	7.826	.000	0.052	19.082
	InRawDOC	509	.175	605	-2.904	.008	0.063	15.926
	InRawConductivity	1.878	.898	.274	2.092	.048	0.159	6.271

a. Dependent Variable: InClarifiedWBSouthPolyDose

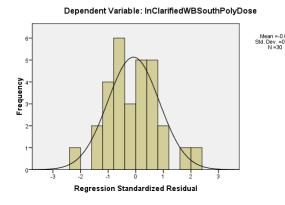
#### Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	-2.290415	-1.191625	-1.880674	.3794912	30
Std. Predicted Value	-1.128	1.694	075	.974	30
Standard Error of Predicted Value	.026	.090	.045	.015	30
Adjusted Predicted Value	-2.299807	-1.209159	-1.880507	.3800876	30
Residual	2242893	.2131211	0084341	.0978540	30
Std. Residual	-2.139	2.032	080	.933	30
Stud. Residual	-2.274	2.280	061	.977	30
Deleted Residual	2535506	.2683577	0086007	.1122694	30
Stud. Deleted Residual	-2.540	2.549	058	1.028	30
Mahal. Distance	.589	10.082	3.499	2.378	30
Cook's Distance	.000	.337	.048	.073	30
Centered Leverage Value	.024	.388	.138	.092	30

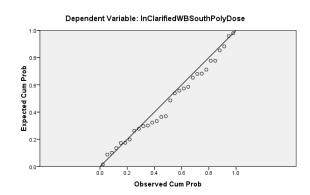
a. Dependent Variable: InClarifiedWBSouthPolyDose

#### Charts

Histogram

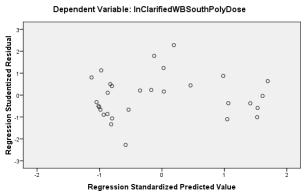


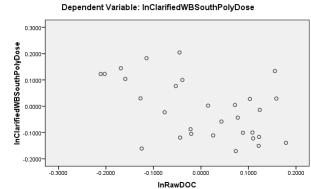
# Normal P-P Plot of Regression Standardized Residual



#### Scatterplot

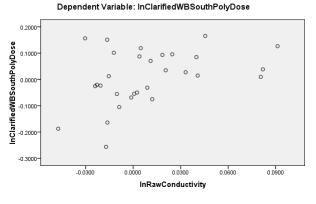
#### Partial Regression Plot

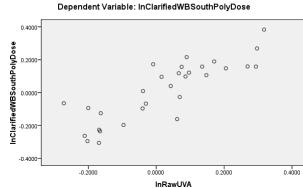




#### Partial Regression Plot

#### Partial Regression Plot





# **OXIDATION CHLORINE DOSE REGRESSION (2012)**

## **Descriptive Statistics**

	Mean	Std. Deviation	N
InSHFPrechlorine	.695010	.1447648	26
InRawDOC	.611641	.4773450	26
InRawTOC	.774958	.5042501	26
InRawTP	-4.561519	1.1817600	26
InRawTDP	-5.642686	.5921557	26
InRawConductivity	5.893359	.0585235	26
InRawTemp	2.517952	.4688768	26
InRawTOConline	.653029	.6087823	26
InRawUVA	-3.091801	.7026908	26
InRawTurbidity	1.234226	2.1952129	26

#### Variables Entered/Removed<sup>a</sup>

Model	Variables Entered	Variables Removed	Method
1	InRawUVA		Forward (Criterion: Probability-of-F-to-enter < = .050)
2	InRawTemp		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: InSHFPrechlorine

#### Model Summary<sup>c</sup>

			Adiusted R	Std. Error of the	Change Statistics					
Model	R	R Square	.,		R Square Change	F Change	df1	df2	Sig. F Change	
1	.928ª	.861	.855	.0550571	.861	148.838	1	24	.000	
2	.970 <sup>b</sup>	.941	.936	.0365371	.080	31.497	1	23	.000	

a. Predictors: (Constant), InRawUVA

b. Predictors: (Constant), InRawUVA, InRawTemp

c. Dependent Variable: InSHFPrechlorine

#### **ANOVA**<sup>c</sup>

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.451	1	.451	148.838	.000°
	Residual	.073	24	.003		
	Total	.524	25			
2	Regression	.493	2	.247	184.731	.000 <sup>b</sup>
	Residual	.031	23	.001		
	Total	.524	25			

a. Predictors: (Constant), InRawUVA

b. Predictors: (Constant), InRawUVA, InRawTemp

c. Dependent Variable: InSHFPrechlorine

#### Coefficients

				Standardized Coefficients			Toleran	
Model		В	Std. Error	Beta	t		ce	VIF
1	(Constant)	1.286	.050		25.909	.000		
	InRawUVA	.191	.016	.928	12.200	.000	1	1
2	(Constant)	1.043	.054		19.174	.000		
	InRawUVA	.184	.010	.895	17.602	.000	0.986	1.014
	InRawTemp	.088	.016	.285	5.612	.000	0.986	1.014

a. Dependent Variable: InSHFPrechlorine

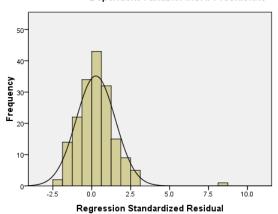
#### Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	.320414	.908060	.597222	.1589208	177
Std. Predicted Value	-2.667	1.517	696	1.131	177
Standard Error of Predicted Value	.009	.034	.015	.009	177
Adjusted Predicted Value	.320414	.908060	.597275	.1589033	177
Residual	0821411	.3136579	.0095918	.0458587	177
Std. Residual	-2.248	8.585	.263	1.255	177
Stud. Residual	-2.172	6.980	.183	1.096	177
Deleted Residual	0821411	.3136579	.0095382	.0462950	177
Stud. Deleted Residual	-2.172	6.980	.184	1.100	177
Mahal. Distance	.440	11.161	3.156	3.834	177
Cook's Distance	.000	1.449	.116	.259	176
Centered Leverage Value	.018	.434	.122	.148	177

a. Dependent Variable: InSHFPrechlorine

#### Histogram

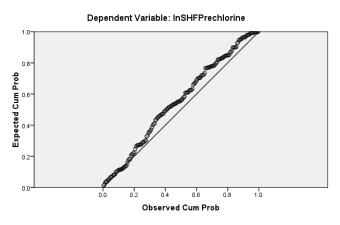
Dependent Variable: InSHFPrechlorine

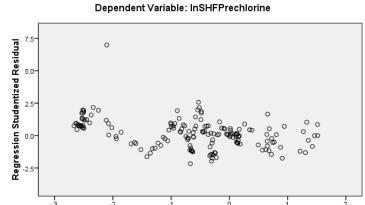


Mean =0.26 Std. Dev. =1.255 N =177

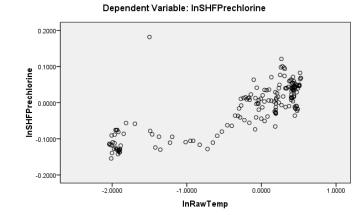
#### Scatterplot

Normal P-P Plot of Regression Standardized Residual



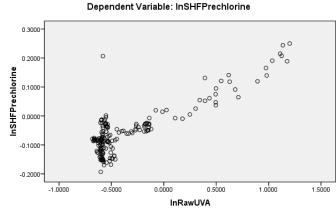


Partial Regression Plot



Partial Regression Plot

Regression Standardized Predicted Value



# **FILTER RUN TIME (2000-2010)**

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
Average Filter Run Time (h)	41.0333	4.65148	20
Conductivity_mean_mean	353.7912	27.40592	20
UVA_mean_mean	3.7412	1.37226	20
Temperature_mean_mean	14.4303	3.75072	20
In_TOC_R_mean	.6996	.32517	20
In_TP_R_mean	-4.8033	.65555	20
In_Color_R_mean	1.3386	.74982	20

#### Variables Entered/Removed<sup>a</sup>

Model	Variables Entered	Variables Removed	Method
1	UVA_mean_mean		Forward (Criterion: Probability-of-F-to-enter <= .050)
2	In_TOC_R_mean		Forward (Criterion: Probability-of-F-to-enter <= .050)

a. Dependent Variable: Average Filter Run Time (h)

#### Model Summary<sup>c</sup>

-		ř i	Ť		
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Durbin-Watson
1	.671ª	.450	.419	3.54470	
2	.796 <sup>b</sup>	.634	.591	2.97611	1.966

- a. Predictors: (Constant), UVA\_mean\_mean
- b. Predictors: (Constant), UVA\_mean\_mean, In\_TOC\_R\_mean
- c. Dependent Variable: Average Filter Run Time (h)

#### **ANOVA**<sup>c</sup>

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	184.920	1	184.920	14.717	.001 <sup>a</sup>
	Residual	226.169	18	12.565		
	Total	411.089	19			
2	Regression	260.515	2	130.258	14.706	.000 <sup>b</sup>
	Residual	150.573	17	8.857		
	Total	411.089	19			

- a. Predictors: (Constant), UVA\_mean\_mean
- b. Predictors: (Constant), UVA\_mean\_mean, In\_TOC\_R\_mean
- c. Dependent Variable: Average Filter Run Time (h)

#### Coefficients<sup>a</sup>

		Unstandardize	d Coefficients	Standardized Coefficients			Collinearity	Statistics
Model		В	Std. Error	Beta	t	Sig.	Tolerance	VIF
1	(Constant)	49.539	2.355		21.040	.000		
	UVA_mean_mean	-2.273	.593	671	-3.836	.001	1.000	1.000
2	(Constant)	52.254	2.184		23.921	.000		
	UVA_mean_mean	-1.790	.524	528	-3.415	.003	.901	1.110
	In_TOC_R_mean	-6.464	2.213	452	-2.921	.010	.901	1.110

a. Dependent Variable: Average Filter Run Time (h)

## Collinearity Diagnostics<sup>a</sup>

	Dimensio			Variance Proportions				
Model	n	Eigenvalue	Condition Index	(Constant)	UVA_mean_mean	In_TOC_R_mean		
1	1	1.942	1.000	.03	.03			
	2	.058	5.768	.97	.97			
2	1	2.836	1.000	.01	.01	.02		
	2	.106	5.170	.09	.22	.96		
	3	.058	7.008	.90	.76	.02		

a. Dependent Variable: Average Filter Run Time (h)

## Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	32.1954	45.6292	41.0333	3.70288	20
Std. Predicted Value	-2.387	1.241	.000	1.000	20
Standard Error of Predicted Value	.698	2.013	1.093	.376	20
Adjusted Predicted Value	32.1211	45.1705	40.9919	3.76954	20
Residual	-6.57186	3.59671	.00000	2.81512	20
Std. Residual	-2.208	1.209	.000	.946	20
Stud. Residual	-2.288	1.243	.006	1.000	20
Deleted Residual	-7.05624	3.86699	.04143	3.16688	20
Stud. Deleted Residual	-2.668	1.265	015	1.057	20
Mahal. Distance	.095	7.738	1.900	2.222	20
Cook's Distance	.000	.129	.042	.043	20
Centered Leverage Value	.005	.407	.100	.117	20

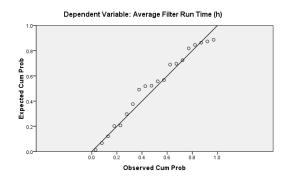
a. Dependent Variable: Average Filter Run Time (h)

#### Charts

Histogram

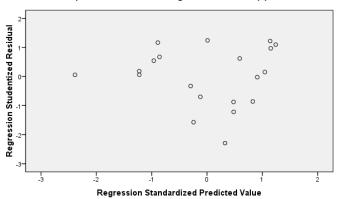
Dependent Variable: Average Filter Run Time (h)

Normal P-P Plot of Regression Standardized Residual



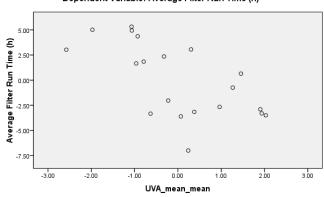
Scatterplot

Dependent Variable: Average Filter Run Time (h)



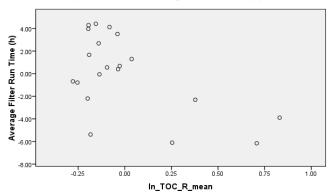
Partial Regression Plot

Dependent Variable: Average Filter Run Time (h)



Partial Regression Plot

Dependent Variable: Average Filter Run Time (h)



# TTHM (2000-2010)

#### **Descriptive Statistics**

	Moon	Ctd Deviation	N
	Mean	Std. Deviation	N
InTTHM	3.1088500	.73911476	830
In(InFlow)	2.1441	.78966	830
InTemp	1.648137	1.0661356	830
In(TOC)	.3391	.65917	830
In(Turbidity)	.5705	1.30521	830

#### Variables Entered/Removeda

Model	Variables Entered	Variables Removed	Method
1	In(TOC)		Forward (Criterion: Probability-of-F-to-enter < = .050)
2	InTemp		Forward (Criterion: Probability-of-F-to-enter < = .050)
3	In(Turbidity)		Forward (Criterion: Probability-of-F-to-enter < = .050)
4	In(InFlow)		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: InTTHM

#### Model Summary<sup>e</sup>

						Change Statistics				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change	Durbin- Watson
1	.820ª	.672	.672	.42361752	.672	1695.658	1	828	.000	
2	.935 <sup>b</sup>	.874	.873	.26317346	.202	1318.329	1	827	.000	
3	.938°	.880	.880	.25654109	.006	44.314	1	826	.000	
4	.939 <sup>a</sup>	.881	.881	.25519117	.001	9.762	1	825	.002	.613

a. Predictors: (Constant), In(TOC)

#### **ANOVA**e

Mode	I	Sum of Squares	df	Mean Square	F	Sig.
1	Regression	304.289	1	304.289	1695.658	.000ª
	Residual	148.586	828	.179		
	Total	452.875	829			
2	Regression	395.597	2	197.798	2855.870	.000 <sup>d</sup>
	Residual	57.278	827	.069		
	Total	452.875	829			
3	Regression	398.513	3	132.838	2018.401	.000°
	Residual	54.362	826	.066		
	Total	452.875	829		u.	
4	Regression	399.149	4	99.787	1532.299	.000°
	Residual	53.726	825	.065		
	Total	452.875	829			

a. Predictors: (Constant), In(TOC)

b. Predictors: (Constant), In(TOC), InTemp

c. Predictors: (Constant), In(TOC), InTemp, In(Turbidity)

d. Predictors: (Constant), In(TOC), InTemp, In(Turbidity), In(InFlow)

e. Dependent Variable: InTTHM

b. Predictors: (Constant), In(TOC), InTemp

c. Predictors: (Constant), In(TOC), InTemp, In(Turbidity)

 $<sup>\</sup>hbox{d. Predictors: (Constant), In(TOC), InTemp, In(Turbidity), In(InFlow)}\\$ 

e. Dependent Variable: InTTHM

Coefficients

		Unstandardized (	Coefficients	Standardized Coefficients		
Model		В	Std. Error	Beta	t	Sig.
1	(Constant)	2.797	.017		169.136	.000
	In(TOC)	.919	.022	.820	41.178	.000
2	(Constant)	2.305	.017		135.501	.000
	In(TOC)	.638	.016	.569	40.191	.000
	InTemp	.356	.010	.514	36.309	.000
3	(Constant)	2.288	.017		136.455	.000
	In(TOC)	.531	.022	.474	23.821	.000
	InTemp	.365	.010	.526	37.800	.000
	In(Turbidity)	.068	.010	.121	6.657	.000
4	(Constant)	2.191	.035		61.983	.000
	In(TOC)	.515	.023	.459	22.572	.000
	InTemp	.342	.012	.493	28.202	.000
	In(Turbidity)	.049	.012	.087	4.125	.000
	In(InFlow)	.071	.023	.076	3.124	.002

a. Dependent Variable: InTTHM

# Coefficient Correlations<sup>a</sup>

Model			In(TOC)	InTemp	In(Turbidity)	In(InFlow)
1	Correlations	In(TOC)	1.000			
	Covariances	In(TOC)	.000			
2	Correlations	In(TOC)	1.000	487		
		InTemp	487	1.000		
	Covariances	In(TOC)	.000	-7.596E-5		
		InTemp	-7.596E-5	9.639E-5		
3	Correlations	In(TOC)	1.000	430	720	
		InTemp	430	1.000	.132	
		In(Turbidity)	720	.132	1.000	
	Covariances	In(TOC)	.000	-9.259E-5	.000	
		InTemp	-9.259E-5	9.320E-5	1.304E-5	
		In(Turbidity)	.000	1.304E-5	.000	
4	Correlations	In(TOC)	1.000	190	481	232
		InTemp	190	1.000	.404	610
		In(Turbidity)	481	.404	1.000	515
		In(InFlow)	232	610	515	1.000
	Covariances	In(TOC)	.001	-5.255E-5	.000	.000
		InTemp	-5.255E-5	.000	5.827E-5	.000
		In(Turbidity)	.000	5.827E-5	.000	.000
		In(InFlow)	.000	.000	.000	.001

a. Dependent Variable: InTTHM

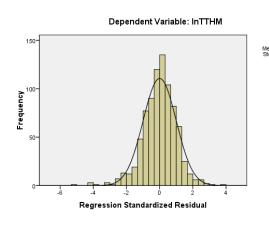
Residuals Statistics<sup>a</sup>

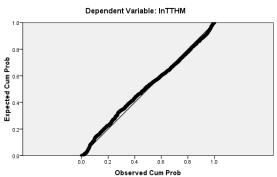
	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	1.7275754	4.8725328	3.1088500	.69388927	830
Std. Predicted Value	-1.991	2.542	.000	1.000	830
Standard Error of Predicted Value	.010	.059	.019	.006	830
Adjusted Predicted Value	1.7274102	4.8765006	3.1090819	.69406986	830
Residual	-1.30347610	1.00819945	.00000000	.25457476	830
Std. Residual	-5.108	3.951	.000	.998	830
Stud. Residual	-5.239	3.960	.000	1.002	830
Deleted Residual	-1.37149131	1.01296353	00023186	.25706198	830
Stud. Deleted Residual	-5.326	3.996	001	1.005	830
Mahal. Distance	.289	42.723	3.995	3.794	830
Cook's Distance	.000	.286	.002	.011	830
Centered Leverage Value	.000	.052	.005	.005	830

a. Dependent Variable: InTTHM

#### Charts

Histogram





Normal P-P Plot of Regression Standardized Residual

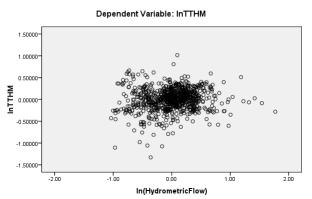
Scatterplot

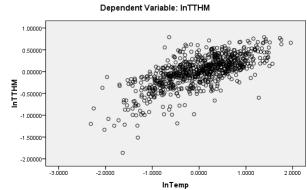
Dependent Variable: InTTHM

Regression Standardized Predicted Value

#### Partial Regression Plot

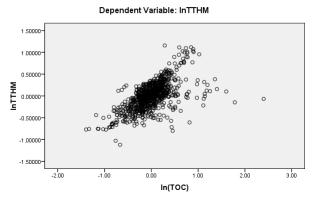
#### Partial Regression Plot

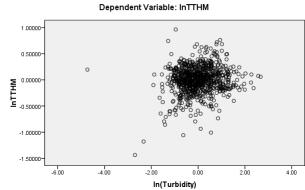




#### Partial Regression Plot

#### Partial Regression Plot





# HAA (2000-2010)

#### **Descriptive Statistics**

	Mean	Std. Deviation	N
InHAA	3.1117239	.71731076	77
In(InFlow)	2.0116	.62109	77
InTemp	1.584052	1.0865922	77
In(TOC)	.1786	.52337	77
In(Turbidity)	.2260	.92745	77

#### Variables Entered/Removeda

Model	Variables Entered	Variables Removed	Method
1	InTemp		Forward (Criterion: Probability-of-F-to-enter < = .050)
2	In(TOC)		Forward (Criterion: Probability-of-F-to-enter < = .050)
3	In(Turbidity)		Forward (Criterion: Probability-of-F-to-enter < = .050)

a. Dependent Variable: InHAA

#### Model Summary<sup>a</sup>

F						Change Statistics				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change	Durbin- Watson
1	.842ª	.709	.705	.38954445	.709	182.700	1	75	.000	
2	.928 <sup>b</sup>	.861	.858	.27067308	.152	81.341	1	74	.000	
3	.935°	.874	.869	.25979223	.013	7.328	1	73	.008	1.716

a. Predictors: (Constant), InTemp

b. Predictors: (Constant), InTemp, In(TOC)

c. Predictors: (Constant), InTemp, In(TOC), In(Turbidity)

d. Dependent Variable: InHAA

#### $\textbf{ANOVA}^{\text{d}}$

Mode		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	27.724	1	27.724	182.700	.000 <sup>a</sup>
	Residual	11.381	75	.152		
	Total	39.105	76			
2	Regression	33.683	2	16.842	229.875	.000 <sup>b</sup>
	Residual	5.422	74	.073	Į.	
	Total	39.105	76		Į.	
3	Regression	34.178	3	11.393	168.799	.000°
	Residual	4.927	73	.067		
	Total	39.105	76			

a. Predictors: (Constant), InTemp

b. Predictors: (Constant), InTemp, In(TOC)

c. Predictors: (Constant), InTemp, In(TOC), In(Turbidity)

d. Dependent Variable: InHAA

Coefficients<sup>a</sup>

		Unstandardized Coefficients		Standardized Coefficients		
Mode	I	В	Std. Error	Beta	t	Sig.
1	(Constant)	2.231	.079		28.305	.000
	InTemp	.556	.041	.842	13.517	.000
2	(Constant)	2.383	.057		41.585	.000
	InTemp	.388	.034	.587	11.363	.000
	In(TOC)	.639	.071	.466	9.019	.000
3	(Constant)	2.357	.056		42.161	.000
	InTemp	.404	.033	.612	12.135	.000
	In(TOC)	.501	.085	.365	5.896	.000
	In(Turbidity)	.111	.041	.144	2.707	.008

a. Dependent Variable: InHAA

## Coefficient Correlations<sup>a</sup>

Model			InTemp	In(TOC)	In(Turbidity)
1	Correlations	InTemp	1.000		
	Covariances	InTemp	.002		
2	Correlations	InTemp	1.000	546	
		In(TOC)	546	1.000	
	Covariances	InTemp	.001	001	
		In(TOC)	001	.005	
3	Correlations	InTemp	1.000	540	.184
		In(TOC)	540	1.000	600
		In(Turbidity)	.184	600	1.000
	Covariances	InTemp	.001	002	.000
		In(TOC)	002	.007	002
		In(Turbidity)	.000	002	.002

a. Dependent Variable: InHAA

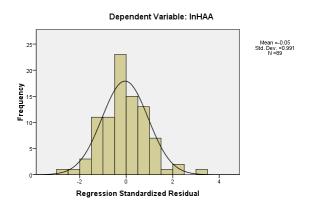
# Residuals Statistics<sup>a</sup>

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	1.8137146	4.6875105	3.0951077	.70298120	89
Std. Predicted Value	-1.936	2.350	025	1.048	89
Standard Error of Predicted Value	.031	.129	.058	.018	89
Adjusted Predicted Value	1.8137146	4.7727189	3.0972540	.70534744	89
Residual	69641471	.81105143	01309362	.25739891	89
Std. Residual	-2.681	3.122	050	.991	89
Stud. Residual	-2.537	3.232	051	1.010	89
Deleted Residual	69641471	.86934257	01523992	.27221188	89
Stud. Deleted Residual	-2.638	3.468	048	1.028	89
Mahal. Distance	.110	17.864	3.087	3.083	89
Cook's Distance	.000	.329	.020	.049	89
Centered Leverage Value	.001	.235	.041	.040	89

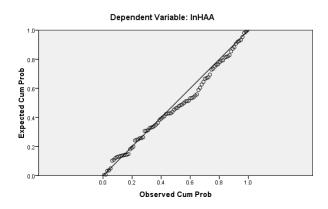
a. Dependent Variable: InHAA

#### Charts

#### Histogram



Normal P-P Plot of Regression Standardized Residual



Scatterplot

