A Critical Examination of Chemical Extremes in Freshwater Systems

By

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Abstract

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The objectives of this thesis are to explore and identify: 1) the causative factors for extreme endpoints in freshwater chemistry, specifically eutrophication and acidification, and 2) the convergence of anthropogenic pollution, watershed composition and climate effects that could contribute to the occurrence of freshwater chemical extremes. Eutrophication is reviewed as a well-studied water quality issue that remains relevant as a management challenge. Extra focus is given to acidification, quantified as a decrease in acid neutralizing capacity (ANC), because it has a strong influence on physical properties such as nutrient (i.e., phosphorus, nitrogen) resuspension that can potentially leading to chemical extremes.

Data from lakes in the western Great Lakes region are examined with respect to effects of acid inputs on in-lake ANC and pH response. Although drainage systems are discussed, special attention is paid to softwater seepage lakes as being the most sensitive with regards to acidification risk. The challenges of using data-intensive mass balance models in lakes with intermittent sampling histories lead to development of a simpler model for estimating open-water ANC in data-sparse locations. Acid input sources are compared as combinations of area-weighted charge balances using publicly available data from long term monitoring programs. Weighted data combinations are then analyzed using maximum likelihood methods suitable for use with observational data. The final model correctly predicted low ANC events (ANC < 25 µeq L^{-1}) 20 out of 24 times (R^2 = 0.50 adjusted for small sample size; 168 observations), but underestimates the severity of the lowest extremes.

Three factors stand out as being strongly related to acidification risk during the open water season: 1) volume of snowmelt, 2) in-lake ANC following spring turnover, and 3) pulsed runoff from associated wetland soils following drought and re-wetting events. Recommendations for future research focus on quantifying acid and nutrient content in pulsed runoff events and their impacts on freshwater systems given antecedent conditions in both lakes and connected wetlands.

Keywords: acid neutralizing capacity, acidification, eutrophication, lake, nutrients, wetland

Table of Contents

List of Figures

List of Tables

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'Things work out best for those who make the best of the way things work out' *John Wooden*

1. General introduction

1.1 Background and objectives

Freshwater systems are in trouble. Stresses on their availability and quality are evident, even as human demand for clean water is projected to rise (Bates *et al*., 2008). Although extremes in ecological systems are presumed as an intermittent but unsurprising occurrence (Doak *et al.*, 2008), the frequency of water chemistry extremes is on the rise and strongly linked to increased intensity of the hydrologic cycle (Towler *et al*., 2010). Two such extremes that have challenged freshwater systems are eutrophication and acidification; factors contributing to their occurrence must be identified to improve forecasting. This is especially true in cases where remediation efforts have failed to produced expected management outcomes, or when conditions commonly linked to pollution occur in areas where anthropogenic pollution is negligible.

Eutrophication is a well-studied phenomenon. Despite a long history of research, it remains a persistent challenge affecting many surface water systems. The negative effects of eutrophication, primarily linked to anthropogenic oversupply of the nutrients phosphorus and nitrogen, can be strongly affected by the chemistry of the water column (Carpenter, 2005). Phosphorus can be resuspended from lake sediments under conditions of low oxygen and low pH causing internal eutrophication; this process can be accelerated in acidification of iron-rich waters, since the formation of iron sulfides under reducing conditions will liberate phosphorus previously bound to iron (Smolders *et al*., 2006).

As with eutrophication, acidification is also a long-standing problem, and occurs when acid neutralizing capacity (ANC) is insufficient to buffer acid inputs (Likens and Bormann, 1974). In the USA, legislation has been in place for several decades to counteract the impacts of increased acidity, especially from anthropogenic sources (Clean Air Act, 1963). Despite advances in reducing pollutant emissions and decreased atmospheric deposition, not all lakes expected to recover from acidification have done so (Stoddard *et al*., 2003).

Acidity in freshwater is often linked to atmospheric deposition of strong mineral acids (*i.e*., the acid anions sulfate (SO_4^{2-}) and nitrate (NO_3^-) as the dominant input source). However, watershed sources of acid inputs have also been noted under specific conditions. A manipulated wetland study in Wales showed good agreement between measured acidity under conditions of artificial drought and from subsequent years of natural drought (Hughes *et al*., 1997). Research from poorly buffered lakes in Ontario suggested that large acid inputs can also occur as pulsed flow to lakes from associated wetlands following cycles of drought and re-wetting (Yan *et al*., 1996; Devito *et al*., 1999; Warren *et al*., 2001; Eimers *et al*., 2007). Acid sources in pulsed runoff have been linked to loads accumulated from historic anthropogenic deposition (Yan *et al*., 1996). However, historic pollution inputs are not requisite; acid pulses have also been linked to drought and re-wetting cycles from wetlands in the Experimental Lakes Area in Ontario, an area of extremely low anthropogenic pollution (Bayley *et al*., 1992).

Although surface water responses to external inputs are often related to qualities distinct to regional features (*e.g*., landforms, precipitation, and topography; Swanson *et al*., 1988) and hydrological position (*e.g*. seepage or drainage lake; Kratz *et al*., 1997), the effects of specific watershed features like wetlands can supersede those of landscape position (Canham *et al*., 2004). When runoff potential is high enough to generate flow (Tromp-van Meerveld and McDonnell, 2006), acid inputs from wetland runoff pulses can overwhelm the buffering capacity of connected freshwater systems. Re-wetting of dried wetland soils can also increase the extractable phosphorus pool (Olde Venterink *et al*., 2002), indicating that pulses from wetlands may transport much more than acid equivalents.

The central objective of this thesis is to characterize factors (*i.e*. watershed components, anthropogenic effects and climate conditions) that lead to eutrophication in freshwater systems, and to both identify and quantify contributions of these same factors to acidification risk in lakes of the western Great Lakes region with low inherent buffering capacity. To meet these objectives, the process of eutrophication and its effects on freshwater systems are extensively reviewed (Chapter 2). Factors contributing to acid events in lakes, equivalent to low in-lake ANC, are discussed with respect to both seepage and drainage systems, with seepage lakes identified as the most sensitive to acidification (Chapter 3). The effects of acidification risk factors including inherent lake chemistry, water budgets and wetlands (*i.e*. drought and re-wetting cycles) are quantified through development of a model to predict low ANC in seepage lakes (Chapter 4). Results of this work will assist in identifying the likelihood of chemical extremes given available data. Future validation will assist in prevention of extremes in freshwater through forecasting.

1.2 Thesis structure

This thesis comprises five chapters. Chapter 1 (current) presents background information and study objectives. Chapters 2-4 are manuscripts that are either published (Chapter 2) or intended for publication (Chapters 3 and 4). Chapter 5 summarizes key findings and offers recommendations for further study.

Chapter 2 explores eutrophication in terms of ecosystem nutrient transport and cycling, using lakes as representative indicators of cumulative upstream effects. Special attention is given to natural (*e.g.*, fire, drought) and anthropogenic (*e.g.*, pollution, sedimentation) events that can cause or enhance eutrophication, and how climate change may exacerbate these effects. Conditions where increased nutrient loads do not result in eutrophication are also considered. Two case studies are presented to compare morphometric and limnological differences.

Chapter 3 compares water chemistry data from two western Great Lake areas where acidification events have occurred in spite of low regional acid deposition. Factors contributing to in-lake acid events are discussed, with reference to contributing effects from soil characteristics, lake chemistry, connected wetlands, and drought events. The relationship between ANC and pH is evaluated in cases where acid inputs may be strongly influenced by metal acid species.

Chapter 4 develops a model for predicting open-water ANC where insufficient data exist to calibrate existing mass balance models. Factors contributing to low in-lake ANC discussed in Chapter 3 are used as the basis for weighting inputs following drying events in associated wetlands. Potential components of the lake ANC model are calculated using an area-weighted charge balance approach combined with variable runoff inputs. Acid input components are evaluated using likelihood methods, and those that best fit available data are used in a simple linear regression.

Chapter 5 concludes by summarizing key findings in light of the theme consistently linked to freshwater chemical extremes: drought. Future work is suggested with a focus on the combined impacts of variable snowmelt (volume and timing), the occurrence and frequency of drought (evapotranspiration greater than precipitation), and potential effects on lake acidity and nutrient status.

2. Eutrophication of freshwater systems

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2.0 Abstract

Eutrophication is defined as an increase in nutrient input to surface waters to the extent of over enrichment, with a corresponding increase in primary productivity and related negative effects. Eutrophication is widely recognized as a serious, primarily human-caused (anthropogenic) environmental issue. The process of nutrient transport is explored starting with water as both a molecule and substance, and its passage over and through the landscape to aquatic systems. Two primary nutrient cycles, phosphorus (P) and nitrogen (N), are discussed with focus on anthropogenic perturbations and their cumulative effects. Consideration is given to states of ecological succession, natural and cultural eutrophication, fire, drought, and instances where increased nutrient loading does not result in eutrophication. Nutrient concentrations and ratios (N:P) are reviewed for their effects on phytoplankton growth and potential for cyanobacteria, capable of toxin production, to dominate phytoplankton communities. Two case studies are presented to contrast the impacts of point and non-point source pollution. Lake and watershed features are discussed in the context of aquatic system response following nutrient input, and speed of recovery after commencement of mitigation efforts. Watershed management examples are presented, as well as topics for future research.

Keywords: Algae, cyanobacteria, eutrophication, lake, nutrient, nitrogen, phosphorus, stream, wetland

2.1 Introduction

Since the advent of modern ecology in the 20th century, increasing attention has been paid to surface water ecosystems, especially lakes as downstream indicators of cumulative upstream point and diffuse-source impacts. One result of collective nutrient inputs is eutrophication, which can be severe enough to be evident at coarse visual levels as the 'greening' of lakes and streams (Schindler, 1974; Edmondson, 1991). Eutrophication has been varyingly defined as an increase in the production of organic matter (Nixon, 1995), enrichment with inorganic plant nutrients (Lawrence *et al.*, 1998), or more specifically phosphorus and nitrogen overenrichment leading to excessive plant, algal and cyanobacterial growth and anoxic events (Carpenter, 2005). Although eutrophication occurs naturally in some systems, its current frequency and intensity in freshwater is cause for immediate concern.

While considered a renewable resource, the global allocation of freshwater is restricted by proportional availability (Figure 2.1). Demands for clean sources are increasing while accessibility, quality and supplies of freshwater are limited; escalated occurrences of eutrophication are applying additional pressure on a strained resource. Nutrient flow on a global scale has more than doubled for nitrogen and more than tripled for phosphorus relative to pre-industrial estimates (Cassara, 2008). This is concurrent with increases in harmful algal blooms and associated detrimental effects on aquatic food webs, commercial fisheries, public health, recreation and tourism (Hoagland *et al.*, 2002). To appreciate eutrophication as a serious environmental hazard, it is worthwhile to examine the mechanisms and causes for its occurrence in freshwater.

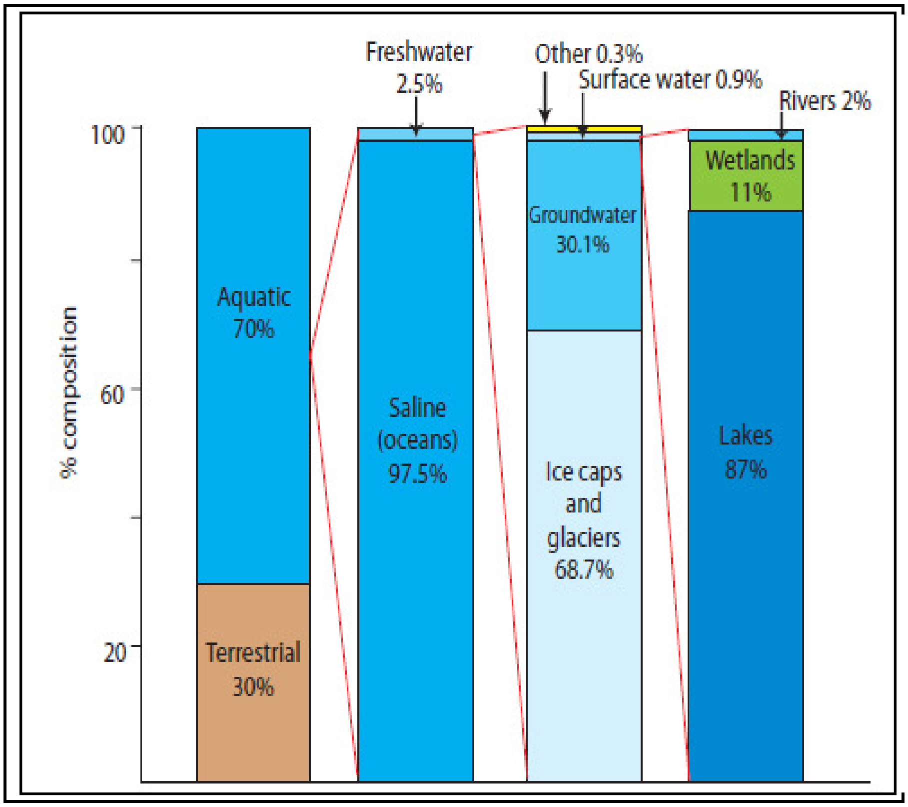

Figure 2.1. Global water resources as percentages of available water fractions. The 'other' category refers to water locked in biological structures, soil moisture, permafrost, *etc*. Adapted from values in: Babkin, V.I. and Klige, R.K. (2003). The hydrosphere. *In* World Water Resources at the Beginning of the Twenty-first Century. (Shiklomanov, I.A. and Rodda, J.C., Eds.) Cambridge University Press, New York, New York, USA. 25 pp.

Importance and structure of water

Water is the most common substance known to occur naturally in all three physical states: gas, liquid, and solid. Water molecules are composed of two hydrogen atoms bonded to one oxygen atom in a 3-dimensional triangular (tetrahedral) configuration (Figure 2.2). The smaller, positively charged hydrogen ions are repelled both by each other and by the larger, negatively charged oxygen ion. This spatial arrangement yields a polarized molecule with an overall charge gradient ranging from one slightly negative to one slightly positive region (a dipole, since there are only two oppositely charged regions). Polar compounds like water are subject to additional intermolecular connections in fluid and solid states, such as hydrogen bonding and van der Waals forces. The combination of these forces and the molecular structure of water both result in the unique properties of water to expand during freezing, and reach maximum density at about 4°C. It is also amphoteric, meaning it can act as either a proton donor (acid) or acceptor (base), and is often referred to as a universal solvent for its ability to dissolve numerous substances. The fundamental characteristics of water make it an essential component of geochemical weathering.

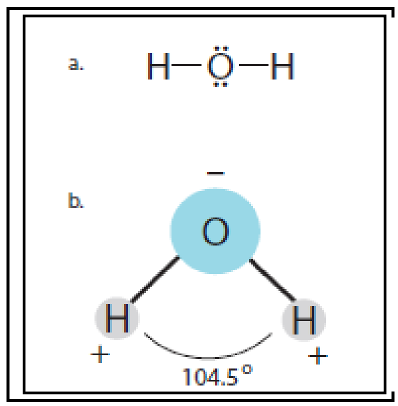

Figure 2.2. Lewis diagram of electron pairs and water molecule configuration. The electron pairs (a) force the hydrogen atoms into a characteristic configuration (b), creating a charge difference across the water molecule.

Movement over and through land

Beginning with precipitation (*e.g.*, rain, snow, sleet, hail), water is deposited on the landscape and becomes a component of the weathering process (Figure 2.3). Unless it is experiencing a force greater than that of gravity, water migrates from relatively high elevations to relatively low points on the landscape, transporting and dissolving substances in its progress. There are a number of things that will naturally affect the movement of water along established hydrologic pathways. These include:

- Freezing and thawing of water and soils
- Spatial and temporal precipitation patterns

- Watershed slope
- Area and type of wetlands
- Soil depth to bedrock or other impermeable surface
- Soil type
- Vegetation community composition, senescence or combustion
- Flow modifications (*e.g.*, beaver activity, hydroelectric dams, urbanization, wetland conversion, withdrawals for agricultural, municipal and industrial uses)

All of these attributes combine to shape the quantity and quality of water entering aquatic ecosystems from the surrounding land. As water proceeds over and through the landscape, its movement is one of the primary means of nutrient relocation from terrestrial sources to aquatic systems. Collection corridors for flowing water are termed lotic systems, and refer to rivers and streams that may be permanent or ephemeral (temporary). Although water is rarely static, points of accumulation do occur on the landscape (*e.g.*, lakes, ponds, wetlands) and are termed lentic systems.

Implications for overloading the system

Nutrients begin as minerals located in rock, soil, organic matter or as airborne particles. Through the processes of mechanical and chemical weathering, decomposition (physical, chemical and biological), mineralization and atmospheric deposition, nutrients are transformed into more biologically available, water soluble components. The unique assembly of water and its passage over and through the landscape transports chemically accessible nutrients to aquatic organisms, which benefit directly. When nutrient delivery is increased through anthropogenic effects, inputs to surface water systems result in disproportionate amounts of easily incorporated chemicals relative to what would occur naturally. The function and structure of aquatic systems which developed in concert with the terrestrial environment is disrupted by the resulting nutrient imbalance.

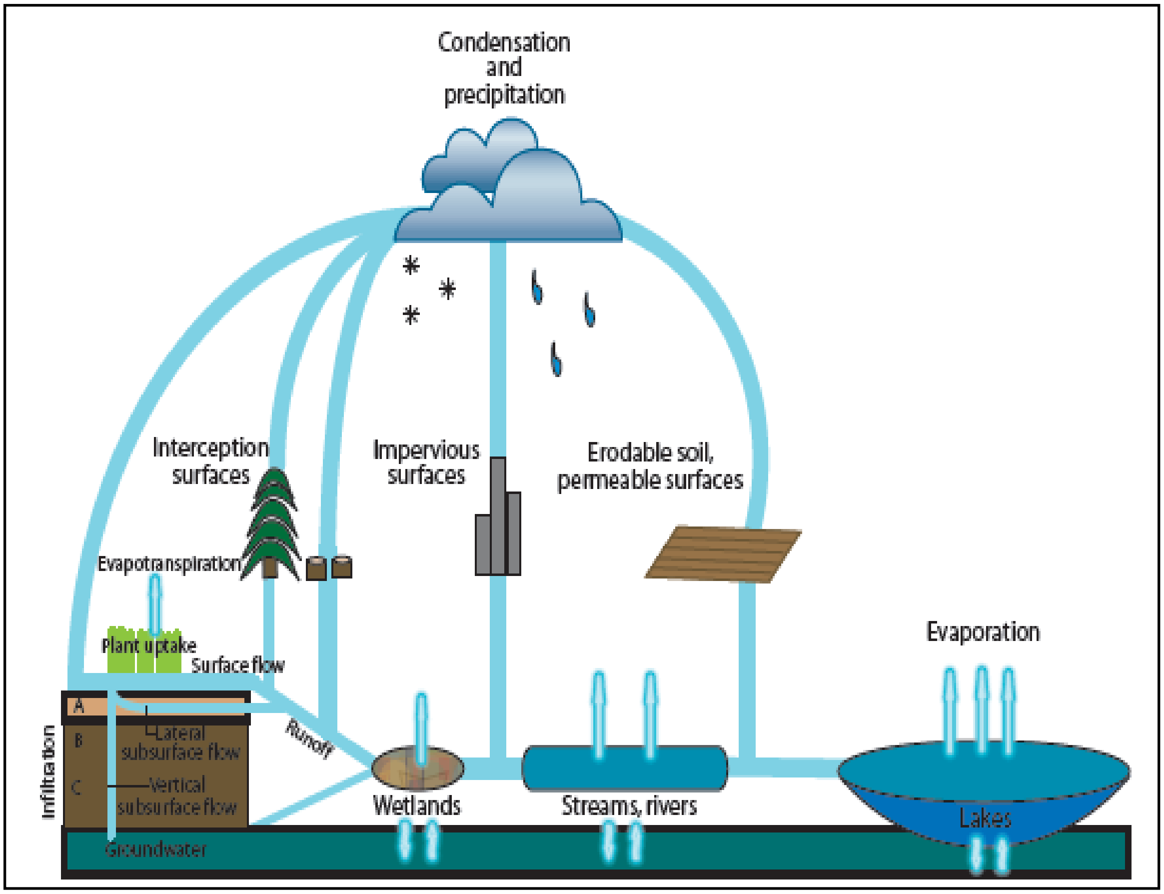

Figure 2.3. Diagram of generalized movement of water at the landscape scale. Climate influences precipitation volumes, and not all precipitation reaches aquatic systems as runoff. Conversion of precipitation to run-off is affected by factors that can increase (*e.g.,* impervious surfaces, forest canopy removal, wetland conversion) or decrease (*e.g.,* migration to deep groundwater through permeable soils, plant uptake, temporary storage, evaporation, evapotranspiration) water movement across the landscape. These same factors can affect nutrient concentrations within the runoff.

Nutrient cycles in aquatic ecosystems

In general, a nutrient is any substance required for growth and development that an organism cannot produce itself. However, the discussion of nutrients relative to aquatic systems usually relates to phosphorus and nitrogen, since their abundance can create the most problems in surface waters. The division between macro- and micronutrient categories is often a matter of perspective: silica is not an important constituent for many mid-summer phytoplankton (photosynthetic algae and cyanobacteria), but is vital for diatoms that tend to dominate algal communities in early spring. For many organisms, compounds required for growth and maintenance are obtained externally and environmental availability limits growth of both individuals and populations. However, organisms such as cyanobacteria are able to meet at least part of their nutrient needs through chemical conversions that take place internally, often under specific external conditions. Eutrophication works to the advantage of these species in particular, and often to the detriment to other organisms in the aquatic community.

What makes nutrient availability so pivotal rests on the theory of the limiting factor, or the Law of the Minimum. Usually attributed to Justus von Liebig, a gifted chemist, researcher and teacher who popularized the term, it was originally proposed by Karl Sprengel, a German botanist working in the field of agriculture (van der Ploeg *et al.*, 1999). Sprengel noted that it was not availability of all nutrients that affected plant growth, but the amount of the least available nutrient relative to need that determined crop yield (Jungk, 2009). Traditional considerations placed nitrogen, followed by phosphorus as limiting primary production in terrestrial, estuarine, and marine systems, while the reverse order was applied to freshwater systems. Phosphorus is still often considered the primary nutrient on which management should focus in limiting the eutrophication of freshwater environments (Schindler *et al.*, 2008), although nitrogen has been seen as limiting in lakes when levels of phosphorus were very high (Downing and McCauley, 1992). Additional analyses also suggest that both nitrogen and phosphorus are often equivalently limiting, and coincident enrichment creates a positive and synergistic response regardless of system location (Elser *et al.*, 2007; Lewis and Wurtsbaugh, 2008). When limiting nutrients are supplied in excess, increased growth occurs relative to unenriched areas and the taxonomic diversity of communities that grow in response can change.

2.2 Phosphorus

The name phosphorus is derived from Greek and roughly means 'bearer of light', although in Latin it translates as Lucifer and has been called the devil's element (Emsley, 2000). The discovery of phosphorus is credited to Hennig Brandt who in 1669 isolated a compound from his own urine in his search for the philosopher's stone (the mythical substance capable of turning base metals into gold). The material with the greenish glow gave its name to the wrongly assigned process by which it was thought to emit light: phosphorescence (re-emission of light after surface excitation) instead of the correct chemiluminescence (glowing as a result of a cold chemical reaction). Phosphorus is a critical element in all known forms of life. Although toxic when ingested in certain forms and biologically unavailable in others, phosphorus bound as phosphate (PO_4-P) is water soluble and a necessary and vital component of many biological structures (*e.g.*, nucleic acids, proteins, ATP, cell membranes) and processes (*e.g.*, phosphorylation and photosynthesis).

Phosphorus is never found naturally as a free element owing to its extreme reactivity. It can exist in several allotropes (chemical forms), the most common of which are white and red phosphorus. Although white phosphorus was used industrially for many years, its instability under ambient conditions (*i.e.,* when exposed to air), toxic vapours and debilitating human health effects from chronic exposure lead to its replacement by the far more stable red phosphorus under the Berne Convention of 1906 (Emsley, 2000). With no significant atmospheric component in the phosphorus cycle (Figure 2.4), all sources originate from phosphate rock, which occurs as an apatite (Table 2.1) of either sedimentary or igneous origins. The natural phosphorus cycle is quite slow owing to the inherently low solubility of many phosphorus-containing compounds. However, phosphorus is a strong adsorber and adheres tenaciously to the charged surfaces of many soil particles, particularly fine-grained clays and silts. Transmission of adsorbed phosphorus to aquatic ecosystems is enhanced by watershed activities that alter forest

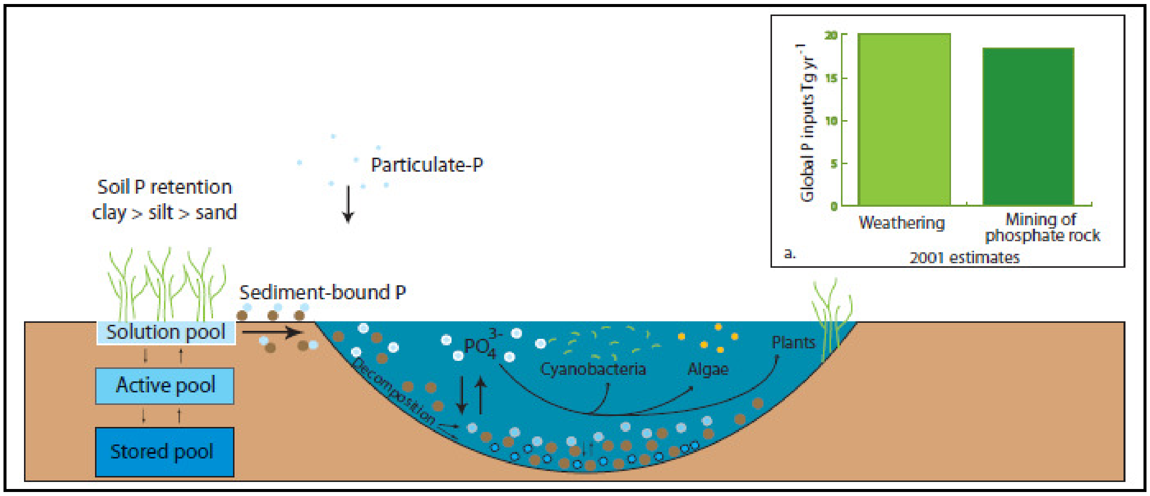

Figure 2.4. Illustration of a simplified phosphorus cycle for a lake catchment. Much of the phosphorus that reaches surface water systems is transported adsorbed to particles in the soil solution pool. Similar storage fractions exist in lake sediments, where phosphorus concentrations in the water column are affected by pH and oxygen-dependent sediment-water interactions. The inset graph shows phosphorus inputs to the global phosphorus cycle at the maximum range of estimated global P inputs from natural sources compared to anthropogenic inputs. Humans have roughly doubled the amount of phosphorus in circulation, even when compared to the higher end of natural input estimates. [a]Adapted from values in Bennet, E.M, Carpenter, S.R. and Caraco, N.F. (2001). Human impacts on erodable phosphorus and

vegetation species composition and cover, disturb or expose soil, and increase overland or shallow subsurface flow, which enhances erosion (Sims *et al.*, 1998). Once transported to aquatic systems, phosphorus undergoes chemical processes that result in increased amounts of more biologically available forms relative to other fractions present (Table 2.2). Anthropogenic activity can supercharge this cycle by delivering increased amounts of P directly to aquatic systems, thereby circumventing natural weathering processes. This occurs through movement of soluble, accessible P (*e.g.*, chemical fertilizer, sewage, mining fines), the delivery of which can be exacerbated by watershed activities that increase transport rates.

Table 2.1. Phosphate (PO_4) mineral composition and the four primary apatite functional groups (R). Fluoroapatite is by far the most common. The crystal structure of all apatites is based on a double repeating unit, represented by the chemical formula being divisible by two.

Common name	*Chemical formula*
Primary structure	$Ca_{10}(PO_4)_6(R)_2$
Fluorapatite	- F
Hydroxyapatite	- OH
Chlorapatite	- Cl
Bromapatite	- Br

Table 2.2. Common analytical fractions of phosphorus. Organic and inorganic forms may co-occur in each fraction, and filtration is meant to separate soluble and insoluble contributions to the measure of total phosphorus. Concentrations in freshwater generally follow a gradient of [TP] > [TDP] > [SRP]. Phosphorus concentrations in surface water samples are often measured in µg L^{-1} (parts per billion) of phosphate or moles L^{-1} of phosphorus.

Analytical fraction	*Abbreviation*	*Fraction and analytical separation*
Total Phosphorus	TP	All phosphorus dissolved or suspended in the water sample; analyzed from unfiltered water following digestion
Total Dissolved Phosphorus or Total Soluble Phosphorus	TDP or TSP	Phosphorus analyzed from water after filtration through a 0.45 µm membrane filter and following digestion; the method is standardized to represent dissolved phosphorus, although fine particulates may be present in the filtrate
Soluble Reactive Phosphorus	SRP	Dissolved, biologically available phosphorus remaining in water filtered through a 45 µm membrane filter and analyzed within 12-24 hours of sample collection
Particulate Phosphorus	Part-P	All suspended and colloidal undissolved phosphorus, often determined by difference (TP – TDP)

2.3 Nitrogen

Unlike phosphorous, nitrogen occurs most commonly as an extremely stable atmospheric gas, dinitrogen (N_2). Dinitrogen gas comprises approximately 78% of our breathable atmosphere and is remarkably unreactive due to the strength of the triple bond. It was first identified as a separable and non-combusting component of air in 1772 by Scottish physician Daniel Rutherford, who called it noxious or fixed air. Although it can be difficult to create other compounds from elemental nitrogen, converting nitrogen-containing molecules back to N_2 gas is comparatively easy and often results in large, sometimes uncontrollable energy releases. Nitrogen also occurs naturally in the form of solid minerals of ammonium salts, and as potassium nitrate, otherwise called saltpetre and known to alchemists since at least the Middle Ages. Purified nitrogen compounds, especially nitrate (NO_3-N), have two primary uses: as effective fertilizers, and as a main constituent of gunpowder and other incendiary devices (Leigh, 2004). Bat feces, or guano, is also an excellent and inexpensive source of crude nitrates. Like phosphorus, nitrogen is an essential nutrient and a key component of many crucial biological structures (*e.g.,* amino and nucleic acids, neurotransmitters).

Since the primary form of nitrogen is as a stable atmospheric gas, natural systems must rely on processes that can break the triple bond since neither plants nor animals can directly access molecular N_2. Lightening strikes and volcanic activity produce localized amounts of bioavailable nitrogen that are dispersed with precipitation, a process known as atmospheric fixation. However, the naturally occurring main source of chemically accessible nitrogen is through direct bacterial fixation, the anaerobic process of converting N_2 gas directly to bioavailable forms. Once the triple bond is broken, nitrogen compensates for its nonreactive elemental state by a high propensity to combine with a seemingly endless number of ions and functional groups, only a small number of which are routinely analyzed (Table 2.3). The nitrogen cycle (Figure

2.5) is a complex chemical tangle relative to that of phosphorus because of the strong atmospheric component. In addition to being vital nutrients, nitrogenous components are also important terminal electron acceptors for certain anaerobic forms of respiration. The chief constituents of the nitrogen cycle are bacteria and their ability to produce reactive forms of nitrogen, including ammonium, NH_4-N, and the far more water soluble nitrate, NO_3-N (Figure 2.6). It is the propensity for nitrogen to occur as a stable, biologically inaccessible gas that traditionally made it a limiting nutrient, especially with sufficient phosphorus sources.

From the years 1890 to 1990, anthropogenic inputs of reactive nitrogen to the global cycle increased almost nine times relative to preindustrial levels; primary sources include production of nitrogen-fixing crops (*e.g.,* legumes, rice), extraction and combustion of fossil fuels, and the use of synthetic fertilizers (Galloway *et al.*, 2003). In 1903 and1909 respectively, the Birkeland-Eyde and Haber-Bosch processes industrialized nitrogen fixation, with the latter (Figure 2.7) globally established in the 1950s as the primary method (Smil, 2001). What cyanobacteria and other nitrogen-fixing bacteria had been doing for billions of years prior, humans chemically engineered, and atmospheric nitrogen was converted into a commercially available product. Coincident with the synthesis of chemical fertilizers was the increase in use of fossil fuels and associated reactive nitrogen contributions. High rates of atmospheric nitrogen deposition have been implicated in causing conditions of nitrogen saturation (Aber *et al*., 1989), where chronic nitrogen inputs to forested ecosystems alters nitrogen cycling. Continuous nitrogen loading increases both nitrate losses in runoff and nitrogenous gas losses to the atmosphere, and decreases the ecosystem's ability to retain nitrogen, one side effect of which is increased nutrient input to receiving waters. Although food production created excess reactive nitrogen on purpose, the energy industry created it by accident (Galloway *et*. *al*, 2003). In just over 100 years, the nitrogen cycle was short-circuited and supercharged with remarkable human efficiency.

Table 2.3. Common analytical fractions of nitrogen. Fractions are based primarily on separation of organic and inorganic forms in dissolved and undissolved fractions. Surface water concentrations are often measured in μg L^{-1} (parts per billion) of the compound or moles L^{-1} nitrogen.

Analytical fraction	*Abbreviation*	*Fraction and analytical separation*
Total Nitrogen	TN	All nitrogen present within an unfiltered sample of water
Total Kjedahl Nitrogen	TKN	All organic forms of nitrogen, both dissolved and undissolved, plus ammonia present in an unfiltered sample of water
Ammonia-N	NH_3-N	A fraction of dissolved inorganic nitrogen often referred to as simply 'ammonia' although most methods measure NH_3-N + NH_4-N, whose relative
Ammonium-N	NH_4-N	concentrations in surface waters are pH and temperature dependent; traditionally determined from an unfiltered sample, although many analytical instruments now require filtration
Nitrate	NO_3-N	A fraction of dissolved inorganic nitrogen and the conjugate base of nitric acid; analyzed from water filtered through a 0.45 μm membrane filter
Nitrite	NO_2-N	A fraction of dissolved inorganic nitrogen and the conjugate base of nitrous acid; analyzed from water filtered through a 0.45 μm membrane filter
Nitrate + Nitrite	NO_x	In practice, nitrate and nitrite are often measured together from surface water samples, since nitrite concentrations in the presence of oxygen are very small; analyzed from water filtered through a 0.45 μm membrane filter
Dissolved Inorganic Nitrogen	DIN	(NH_3-N + NH_4^+-N) + NOx
Dissolved Organic Nitrogen	DON	TN – DIN

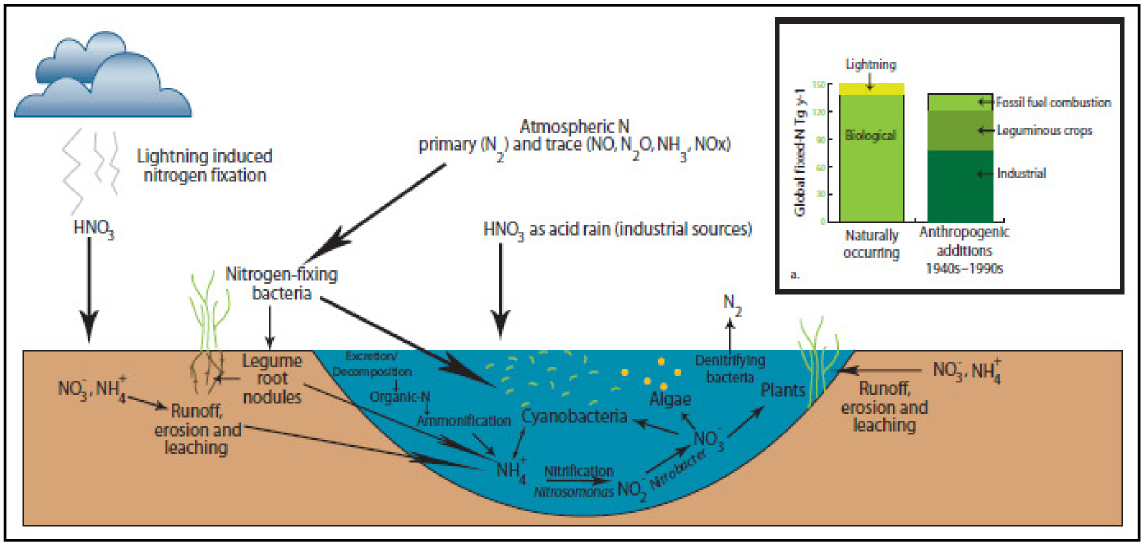

Figure 2.5. Illustration of a simplified nitrogen cycle. Nitrogen reaches aquatic systems dissolved (NO_3-N) in water and adsorbed (NH_4-N) to particles moving in overland or shallow subsurface flow, or by direct fixation (of N_2) and deposition (of HNO_3). Although equilibrium occurs between ammonia (NH_3-N) and ammonium (NH_4-N) species, the latter is the dominant form present in most soil and freshwater systems and is the one represented here. Nitrogen cycling is driven by the activity of bacteria and fungi and is far more complex than what is depicted here. The inset graph shows nitrogen at maximum ranges from natural sources compared to anthropogenic inputs. As with phosphorus, humans have roughly doubled the amount of nitrogen in circulation even when compared to the higher end of natural input estimates. [a]Adapted from values in Vitousek *et al*. (1997).

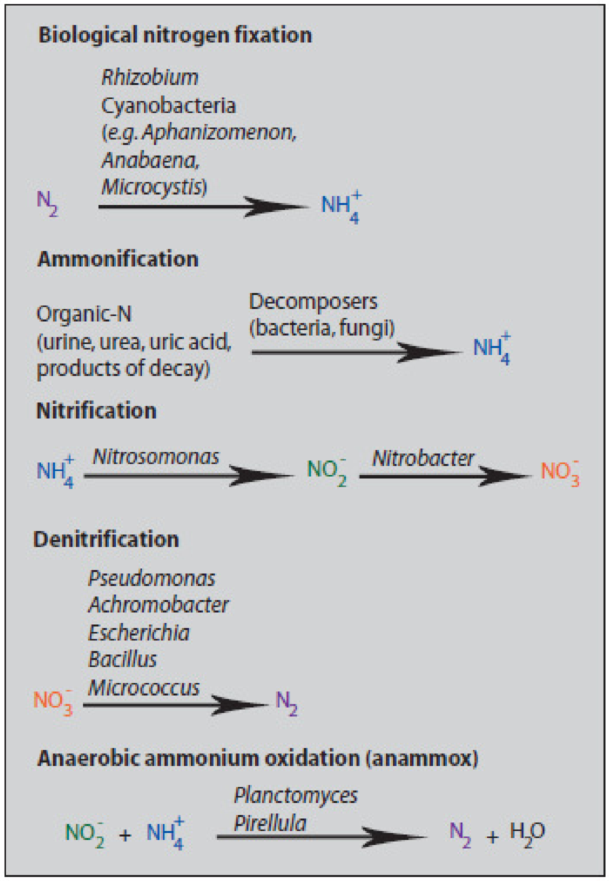

Figure 2.6. Schematic of nitrogen chemistry as a consequence of bacterial and fungal activity. While some processes are strictly aerobic, such as oxidation reactions that produce NO_3^-, others (*e.g.*, denitrification, anammox) are results of facultative anaerobes, which can function with or without the presence of oxygen. Adapted from equations in Wetzel (2001).

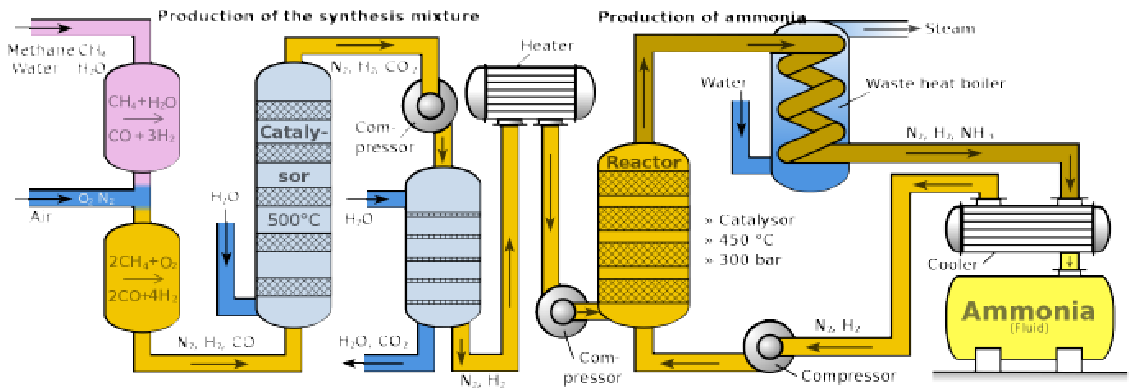

Figure 2.7. Schematic of the Haber-Bosch process of industrial fixation as the anthropogenic alternative to biological fixation. The process is named after Fritz Haber, who developed the chemistry, and Carl Bosch, who scaled the method for industrial production. Both men later won Nobel Prizes for their efforts, and presumably credited the invaluable assistance of Robert Le Rossignol, who developed and built the requisite high-pressure system.

2.4 Aquatic ecosystem structure

Nutrient input patterns

For aquatic systems, nutrient concentrations are measured from samples collected to address two primary input patterns:

- Point-source impacts from localized inputs (*e.g.,* sewage outfalls), where paired samples are usually collected upstream and downstream of the pollution source
- Nonpoint or diffuse impacts from unconfined sources (*e.g.,* surficial runoff from disturbed soils, atmospheric deposition), where samples are collected all along the channel (time and funds permitting), or frequently at the most downstream point of the area of interest to represent cumulative watershed effect

Nonpoint nutrient inputs are by far the more difficult of the two processes to measure and control, since transport is unconstrained by location and dependent upon geomorphology, level of watershed disturbance and surface and subsurface hydrology. Preventing or limiting eutrophication in aquatic systems has focussed heavily on function and properties of the riparian zone, the area immediately adjacent to the channel bank or margin. Riparian zones are transitional areas that mark the interface between aquatic and terrestrial ecosystems, characterized by saturated soils and hydrophilic vegetation. They are often left as intact buffers to mitigate eutrophication impacts from overland and shallow subsurface nitrogen and phosphorus inputs into both lentic and lotic systems. Riparian zone effectiveness in reducing nutrient loading is highly variable between locations, and even within lengths along the same system. Removal of nitrogen from runoff prior to stream input is best achieved by riparian buffers of at least 50 m, since subsurface removal appears to be a more effective mediator of excess nitrogen, and both herbaceous and forest-herbaceous riparian buffers are more effective at nitrogen conversion processes when wider (Mayer *et al*., 2006). Riparian buffers that retain persistent nitrogen inputs from agricultural sources may themselves become sources of forms of atmospheric nitrogen such as nitrous oxide (N_2O), an important greenhouse gas. This potentially trades prevention of aquatic nitrogen enrichment for an environmental impact of a different sort (Hefting *et al*., 2002).

Lotic systems

Rivers, streams, brooks and any other moving surface water constitute lotic systems. The classic assumption of flowing waters is that they do not experience the extreme, deleterious effects of eutrophication as do lakes, since any added nutrients or anoxia-inducing organic carbon loads are constantly aerated and moved downstream. Most flowing surface water is heterotrophic (Hynes, 1975; Dodds, 2006), meaning carbon is obtained from the surrounding landscape, or sources outside the stream channel (allochthonous), instead of within the water body itself (autochthonous). Hynes (1975) stated 'the fertility of the valley rules that of the stream', meaning that it is the surrounding watershed, or all land draining into the stream, that defines its chemical character. The River Continuum Concept (Vannote *et al*., 1980; Minshall *et al*., 1985) stressed that lotic systems integrate physical gradients as they move through the landscape, linking processes upstream with those downstream. There are few effects in lotic systems that do not translate themselves somewhere else down the channel.

Trophic status (Table 2.4), or the measure of primary productivity relative to total phosphorus levels, has long been determined for lakes (Carlson, 1977) but the process has only recently been studied in lotic systems. Primary productivity is the amount of photosynthetic biomass obtained at a given time from a known volume of water, the most common equivalent measure of which is chlorophyll *a* (or chl*a* in μg L^{-1}). For flowing waters, trophic level has been proposed as a ratio of heterotrophic to autotrophic state. Respectively, these two states are determined by metabolic activity at night (oxygen demand for aerobic respiration) and gross primary production (accumulation of photosynthate mass) during daylight hours (Dodds, 2006). Regional stream trophic states provide a baseline for comparison between determined reference systems and lotic systems potentially affected by increased nutrient loading.

Table 2.4. Trophic status of inland waters based on concentrations of epilimnetic total phosphorus (TP) and maximum chlorophyll *a* (chl*a)* and transparency as measured by Secchi disk depth. Trophic Index (TI) is calculated using the three previous measurements as correlates. Note that as phosphorus and chlorophyll concentrations increase, transparency of the water decreases.

Trophic Status	*TP (μg L^{-1})[a]*	*Maximum chla (μg L^{-1})[b]*	*Secchi depth (m)[c]*	*TI[c]*
Oligotrophic	< 5	< 8	> 8 - 4	< 30 – 40
Oligomesotrophic	5 – 10	occasionally > 8	---	---
Mesotrophic	10 – 30	8 – 25	4 – 2	40 – 50
Eutrophic	30 – 100	26 – 75	2 – 0.5	50 – 70
Hypereutrophic	> 100	> 75	0.5 – < 0.25	70 – 100+

Sources: [a]Vollenweider, R. (1970); [b]Mitchell and Prepas (1990); [c]Carlson (1977).

Determining stream order

Lotic systems constitute a network of surface water channels on the landscape that humans, with a propensity for classification, have divided into ranked orders. Channels are hierarchically categorized based on their Horton-Strahler number, a reflection of branching complexity (Figure 2.8). The index ranges from first order, for a small, headwater system with no tributaries, up to twelfth order at the mouth of the Amazon River. Approximately 80% of global lotic systems are first or second order (Waugh, 2002). Stream order is important when determining the effects of eutrophication on flowing water, since order is a reflection of both position in the landscape and size. For example, headwater streams are often small and respond rapidly to landscape perturbations (*e.g.*, intense storms, flooding, fire, tree removal) relative to large, higher order systems, which reflect more collective effects.

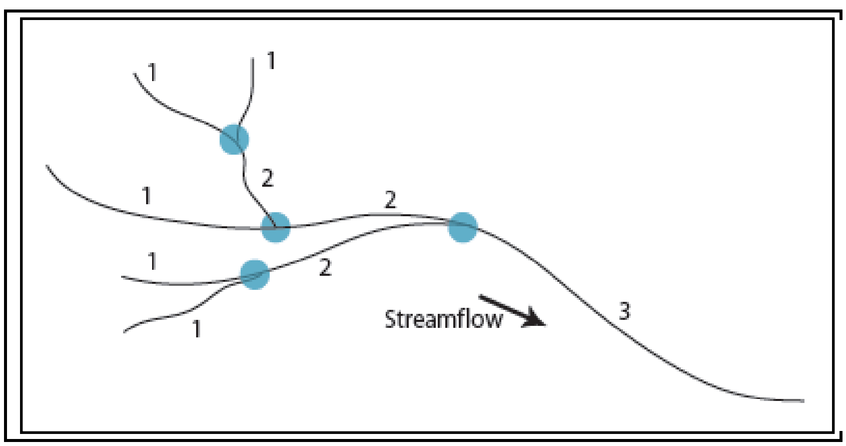

Figure 2.8. Stream order determination using the Horton-Strahler method. Streams are numbered based on branching hierarchy. Stream order only rises for downstream reaches after the confluence of identically ordered upstream systems. Reaches downstream of differently ordered stream confluences default to the stream with the highest order. Adapted from Brooks *et al*., 2003).

Runoff, discharge and loading rates

Relating a nutrient concentration to the landscape requires determining watershed area, runoff and discharge. A watershed consists of all land area surrounding a water body of interest where surface and shallow subsurface flow converge to a single point (Figure 2.9). Runoff is the precipitation within the watershed that reaches the channel as a contribution to flow, minus amounts lost to interception (*e.g.*, soil wetting), evaporation, (*i.e.,* from soil, open water, leaf surfaces), transpiration (as a by-product of plant respiration), and landscape sinks (*i.e.,* localized points of accumulation with slow or nonexistent outflow, deep seepage to underground storage). Discharge is a measure of the rate of water volume flowing past a set location at a known point in time. Channel width, depth and velocity are measured at regular intervals across a linear stretch of water (*i.e.,* not at a bend in the river) to calculate discharge. Both discharge and runoff are used in conjunction to estimate loading rates. In general, areal loading rates are a product of nutrient concentrations and volume of discharge over a specified

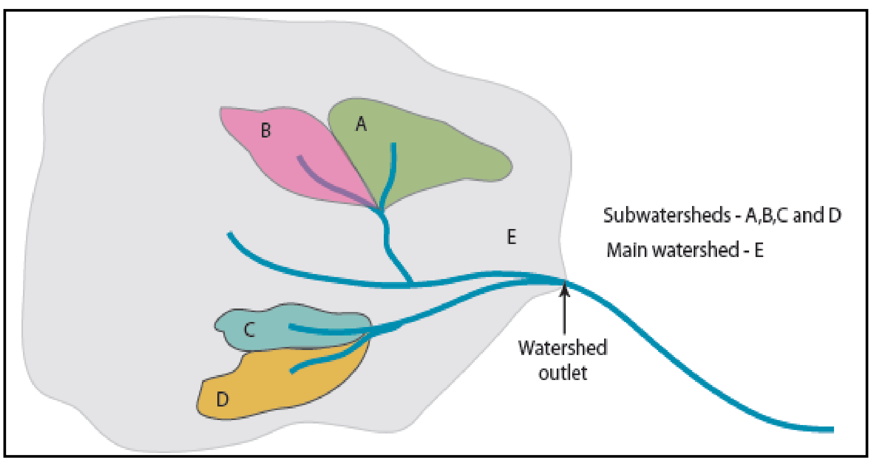

Figure 2.9. Illustration of watershed delineations relative to landscape position. Watersheds by definition converge to a single point. Small watersheds become part of larger watersheds as the point of reference moves downstream. The watersheds of downstream aquatic systems can quickly become very large as they incorporate the watersheds of all smaller systems flowing into them.

length of time divided by watershed area. Loading rates can change in response to season (*e.g.,* decrease in nutrient release during periods of rapid plant growth, freezing in temperate systems), natural events (*e.g.,* flooding, fire) or anthropogenic effects (*e.g.,* agriculture, wetland conversion).

Wetlands

Regardless of the variation in form (Table 2.5), wetlands are all defined by permanently or seasonally saturated hydric soils overlying a water table at or near ground level, characteristic hydrophilic plant cover and oftentimes high biological diversity. Wetlands provide a crossing point between terrestrial and aquatic systems, naturally different from each yet essential to both (Mitsch and Gosselink, 2007). The importance of wetlands in aquatic systems is being increasingly recognized as disproportionate to their areal presence on the landscape, which is especially true in lower latitudes (Krecek and Haig, 2006). Although globally protected in policy by the Ramsar Convention of 1971, wetlands and particularly headwater wetlands, have come under steady pressure in the face of continued urban development, agricultural expansion and forest harvesting practices. Wetlands provide regions in aquatic networks that function as:

- Landscape filters via chemical deposition and binding
- Areas that reduce surface water flow force
- Collection basins for flood moderation in periods of high flow
- Groundwater recharge zones

Additionally, wetland sediments can provide important adsorption sites for transported phosphorus, and increased surface area, oxic/anoxic zones and bacterial availability for enhanced nitrogen cycling. Wetlands themselves are also important sources of colored dissolved organic carbon, the presence of which can provide some short-term protection from the effects of increased nutrients. Although wetlands act as natural filters for adsorbed chemicals, particularly phosphorus, binding sites within the sediments can become exhausted with excess inputs. Rises in water levels (*i.e.*, with storm events or snowmelt) can result in wetland discharge events that release nutrients to connected downstream systems. Wetlands can act as sinks during drier periods, or as sources of nutrients and other chemical constituents during times of increased water movement and landscape connectivity.

Lentic systems

Lakes differ from wetland ecosystems in that they are more permanent water bodies which may or may not be separated from direct contact with the water table, and which have or seasonally develop identifiable stratifications based on depth, light penetration, temperature, horizontal limits of plant growth (Figure 2.10) and trophic status (see Table 2.4). Concentrations of dissolved oxygen and salts can also be factors in stratification of the water column. The intersection of adequate light availability, temperature and nutrient levels are the main factors which interact to create optimal conditions for green growth in lakes. When the control of nutrient limitation is removed, photosynthetic production can escalate dramatically.

When dissolved or adsorbed nutrients reach a lake their transport paths often diverge. Sediment bound fractions will either settle quickly, sink slowly, or remain suspended as colloidal fractions, depending on sediment size and density. Dissolved fractions are subject to vertical and horizontal circulation patterns characteristic of the lake system, and more immediately available for uptake and use. As with wetlands, lakes can be both sinks and sources of accessible nutrients.

Table 2.5. The five major wetland classes of the Candian Wetland Classification system with associated characteristics.

Wetland Class	*pH range*	*Location*	*Hydrology*	*Dominant vegetation*
Bog	3 – 5	arctic and subarctic regions, in areas of little to no relief	receives only ombrotrophic (mineral poor) precipitation as water inputs; no runoff, little or no connection to groundwater	> 40 cm peat accumulation; primarily *Sphagnum* moss, some willow (*Salix*), tamarack (*Larix*) and black spruce (*Picea mariana*)
Fen	5 – 8	arctic and subarctic regions, in depression basins	connected to groundwater, slow internal drainage; precipitation and moderate runoff as additional inputs	> 40 cm peat accumulation; sedges (*Carex, Cyperus*), wildflowers, cedar (*Thuja*), tamarack and shrubs; little to no *Sphagnum* moss
Swamp	~ 7.2	temperate to tropical regions, associated with streams, rivers or lakes	groundwater a primary input; may or may not be seasonally or annually flooded; may experience repeated flood ‘pulses’	trees and shrubs, predominantly dense coniferous or deciduous forests; not always immediately recognized as a wetland, especially during dry periods
Marsh	7 – 8	may be freshwater (primarily inland) or saltwater (primarily coastal)	water inputs as groundwater, precipitation and runoff; can be important groundwater recharge areas	reeds, rushes (*Typha*, *Phragmites*), grasses, sedges; also broad leafed and floating aquatic plants
Shallow Open Wetland	Similar to lakes and dependent on soils, bedrock and mode of origin	transitional form between lake and marsh; many locations	characterized by > 75% open water; water column continually unstratified; water inputs from groundwater, precipitation, runoff and other water bodies	depth < 2 m; distinguished from lakes by at or near continuous submergent vegetation, such as milfoils (*Millefolium*); also duckweed (*Lemna*); emergent vegetation restricted to perimeters

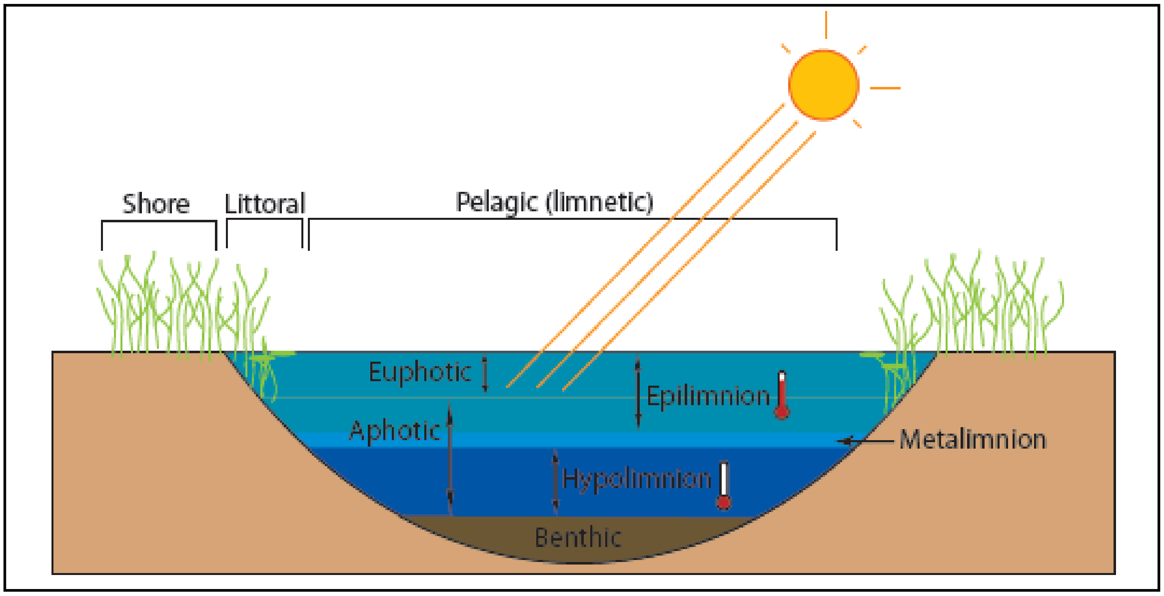

Figure 2.10. Lake zones delineated on the basis of physical location (littoral, pelagic, benthic), light availability (euphotic, aphotic) and temperature (epilimnion, hypolimnion). Although lower limits of the euphotic and epilimnetic zones may sometimes occur at the same depth, this is not always the case.

Temperature and mixing

Because of its inherent physical properties, water stratifies in response to temperature gradients within the water column. Cooler, denser water settles at the bottom, forming the hypolimnion, while a warmer, less dense layer remains at the surface, comprising the epilimnion; in between these two layers is a narrow region where the water temperature drops rapidly when measured from top to bottom (the metalimnion, or thermocline). Lakes will destratify and the water column will undergo mixing (turnover) with seasonal or wind effects that circulate the water (Figure 2.11). If turnover occurs once per year, the lake is said to be monomictic, and two turnovers per year classify a lentic system as dimictic. Lakes that only weakly stratify in warm conditions, such as shallow water systems, can undergo repeated mixing events and are said to be polymictic. Lakes that have multiple basins of varying depths which experience mixing in only parts of the lake (*i.e.*, shallower regions) are meromictic. In tropical and subtropical regions, meromictic conditions prevail in very deep lakes which can remain

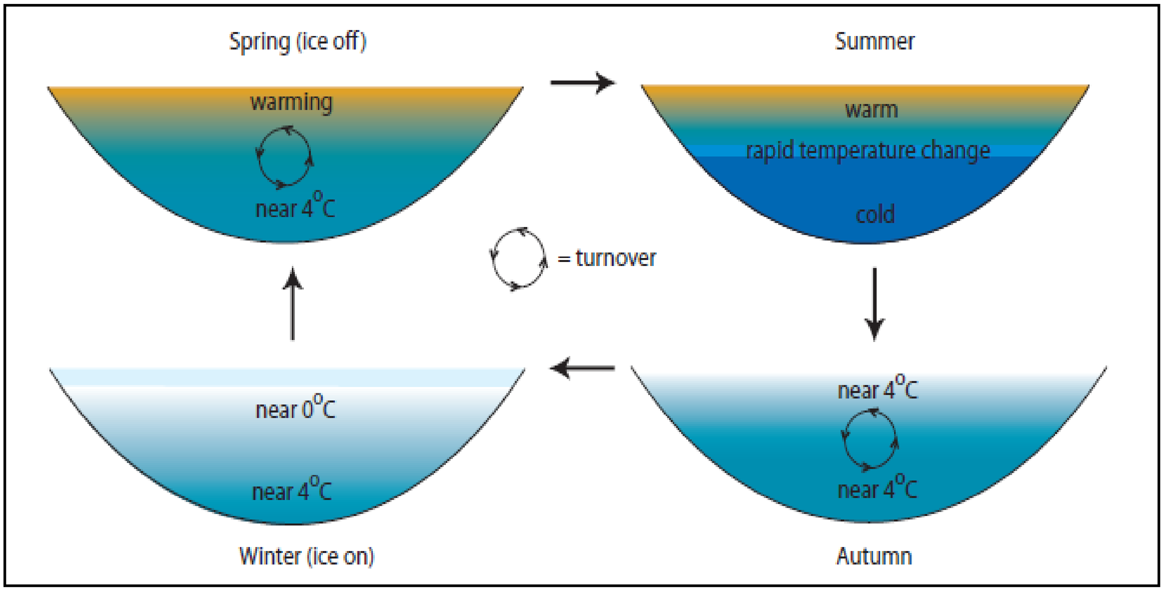

Figure 2.11. Diagram of seasonal stratification and mixing events in temperate lakes. Shallow temperate lakes can mix and re-stratify repeatedly over summer months, while the hypolimnion in deeper lakes remains isolated until turnover events. The hypolimnion in very deep temperate lakes may not mix completely. At lower latitudes, deeper lakes trend towards depicted summer conditions year-round, with shallow lakes subject to destratification from moderate cooling and wind events. The hypolimnion in very deep subtropical and tropical lakes may rarely mix. Adapted from figures in Mitchell and Prepas (1990).

persistently stratified in unfailingly warm temperatures, thermally isolating the colder hypolimnion.

In general, a metalimnion does not form in water that has cooled to the point of ice formation. In lakes which form ice during winter, gradual water density and temperature gradients will exist under ice relative to depth, with cooler, denser water located at the lake bottom. Temperatures at the surface can rise even while under ice cover, especially if low snow conditions permit increased light penetration and winter phytoplankton blooms; by late winter lakes may exhibit chemical stratification in dissolved oxygen (DO) profiles near bottom sediments (Babin and Prepas, 1985). This is especially true in lakes with a high surface area to volume ratio and having only weakly developed or shallow hypolimntic zones in open water months. By late winter, DO concentrations in deep water may be at or near zero as oxygen is consumed by chemical processes at the sediment-water interface, and by organisms that routinely overwinter in benthic regions. The resulting anoxic conditions and changes in hydrogen ion activity (pH) over the bottom sediments create a reducing environment conducive to liberating metal bound and soil adsorbed P fractions (Figure 2.12). The increased soluble P is circulated to surface waters in the spring after ice cover recedes and the seasonal rise in air temperatures results in lake water turnover. Shallow, polymictic systems are more susceptible to internal nutrient cycling regardless of location, due to their vertical compression and propensity for sediment and chemical resuspension.

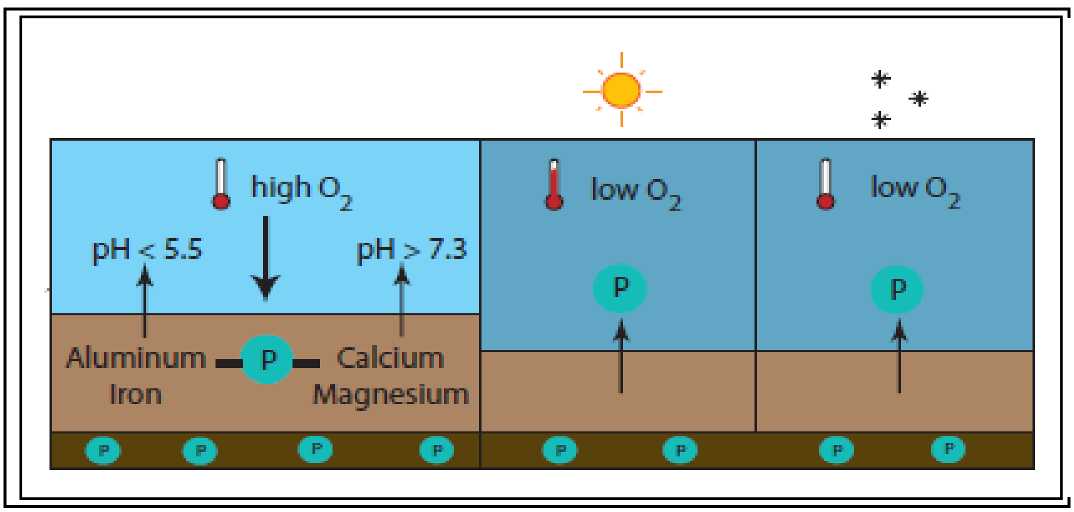

Figure 2.12. Diagram of conditions leading to phosphorus resuspension from bottom sediments. Release is affected by oxygen concentration and pH. Phosphorus will preferentially bind to many metals and form precipitates, but will return to the solution pool under reducing conditions, or if pH reaches acidic or alkaline levels. Low oxygen levels can occur in warm water, which is unable to maintain high dissolved oxygen concentration, but can also occur in cold water where oxygen has been depleted by consumption. Migration of phosphorus to the stored pool occurs with increased sedimentation and isolation from the water column.

Light, turbidity and primary productivity

The majority of primary productivity in lakes is photosynthetic growth, which by definition requires sunlight. Concentrations of chl*a* (µg $L^{-}1$) are used to represent primary productivity, although it should be noted that not all photosynthetic pigments are restricted to being chlorophylls. Since chl*a* is measured from a known volume of filtered water, this can include any green growth suspended in the water column in addition to phytoplankton, such as small pieces of macrophytes (rooted aquatic vegetation) or zooplankton (microscopic animals) that have eaten green matter.

Primary productivity can be limited by conditions that constrain the depth of the euphotic zone, such as high turbidity. Turbidity is a measure of water column transparency which quantifies suspended material. The simplest method of measure is one which has changed little since its invention in 1865 by Father Pietro Angelo Secchi. Taking a Secchi depth involves lowering a 20 cm disk with alternating white and black quadrants over the shady side of a boat, ideally between 9 a.m. and 3 p.m. The midpoint between the depth at which the disk first disappears on the way towards the lake bottom and reappears on the way up is the Secchi depth. Multiplying this value by two gives roughly the depth of the lower limit of the euphotic zone (Lind, 1985; also see Figure 2.10). Turbidity can also be measured using a light meter, or with a collected water sample and a nephelometer. Each method relies on the same mechanism, which measures turbidity as equivalent to the amount of light reflected off of particles suspended in the water. Despite variation in results between users, Secchi depth is almost always collected as a contributing measurement to determining trophic index, since it is easy to take and the equipment rarely malfunctions even in the hands of the most inexperienced operator.

Turbidity is a major factor affecting primary productivity in that it affects light penetration into the water column. High turbidity can be caused by suspended sediments and inorganic particles, or by an active bloom itself. In this manner, certain species of phytoplankton that are unable to regulate their buoyancy and move to sunlight at the lake surface are self-limited in large blooms which decrease light penetration and reduce euphotic zone depth. However, shallow lakes can exhibit alternate stable states over a wide range of nutrient concentrations, of either macrophyte-dominated transparent conditions or phytoplankton-dominated turbid conditions. Turbidity measurements used to determine trophic status would not always accurately reflect primary productivity or related nutrient concentrations in bi-stable shallow water systems (Scheffer *et al*., 1993).

Seasonally in temperate regions and year-round in polar regions, light penetration into the water column is also attenuated both by ice and snow cover, with primary productivity in temperate lakes usually at annual lows during winter months. Subtropical and tropical systems have no such limitations, and primary productivity in these regions is most often a function of nutrient availability, turbidity and wind mixing.

Nutrient ratios and phytoplankton dynamics

The relative concentrations of requisite elements to each other have been used as an index of bloom dominance in lentic systems since Redfield (1934) determined the ratio of C:N:P for marine phytoplankton was 106:16:1, now suggested as an average stoichiometric ratio instead of an optimum (Klausmeier *et al*., 2004). In freshwater systems, ratios of epilimnetic nitrogen to phosphorus are often used to predict phytoplankton species dominance. Ratios of N:P that are approximately 16 are considered optimal for phytoplankton production in general. Ratios of N:P > 20 are defined as phosphorus limited and favouring green algae, and N:P < 10 are considered nitrogen limited, favouring cyanobacteria (Bulgakov and Levich, 1999). The composition of nutrient sources has also been suggested as playing a strong role in lake total nitrogen (TN) to total phosphorus (TP) ratios, where trophic status corresponded with TN:TP ratios. High TN:TP ratios (*i.e.*, low TP concentrations) are found in oligotrophic lakes, where natural systems release much less phosphorus than nitrogen in runoff, and moderate TN:TP values corresponded to mesotrophic lakes with runoff from a larger variety of more fertile sources. Extremely low TN:TP values (*i.e.*, very high TP concentrations) have been related to eutrophic systems whose ratios approximated that of sewage (Downing and McCauley, 1992). Although all blooms are seen as degradations in water quality, cyanobacteria have the potential to release potent toxins upon death and decay of the active bloom and are regarded in even lower favour than algal blooms. Eutrophication is often followed by shifts in phytoplankton assemblages towards cyanobacteria which are well suited to exploiting phosphorus rich environments and outcompeting algal species (Steinberg and Hartman, 1988).

2.5 Eutrophication

Ecological succession versus eutrophication

When an increase in nutrients occurs from either point-sources or diffuse entry and increases primary productivity, quantified as chlorophyll *a* (chl*a*) in µg L^{-1}, and causes a shift in trophic status, an aquatic system is said to be experiencing eutrophication. The distinction is important. Seasonal or otherwise intermittent nutrient increases may incur discrete bloom events, but a shift in trophic status requires nutrient inputs at a higher, sustained level. A resulting change in ecological functioning is indicative of true eutrophication.

With ecological succession, changes in trophic status are usually measured on longer time scales *i.e.,* in the order of hundreds or thousands of years, although catastrophic events like landslides or forest fires can accelerate this progression. Traditional succession theory classifies most surface water forms as intermittent features on the landscape. Younger systems begin as oligotrophic (nutrient-poor) water bodies that gradually experience sedimentation over time; the accumulated sediments fill the water body, physically changing shape, depth and volume, and also altering it chemically through solution-dissolution processes at the sediment-water interface (Sawyer, 1966). This implies that existing aquatic systems are positioned as points on a temporal gradient that will naturally converge to eutrophication. Accelerating successional processes causes problems that can prove extremely difficult to reverse. Response to external conditions has been proposed as system dependent, relating loss of resilience to rate of ecosystem perturbation. Systems with low inherent capacity to change may experience dramatic shifts in structure and function relative to systems with greater elasticity to either stochastic or persistent events (Scheffer *et*. *al*, 2001). Even relatively constant aquatic systems can experience catastrophic change in the face of introduced and unrelenting pressures.

Natural eutrophication

Natural eutrophication has been separated from ecological succession to differentiate their relative time scales. While succession occurs over long periods, eutrophication as a result of either rapid increases in nutrient inflow rates or in-system concentration of nutrients does occur naturally in the form of:

- Landslides
- Mass wasting events (*e.g.*, sediment deposition from flooding, beaver dam breaks)
- Seasonal drought
- Precipitation events following fire

The classification of drought-induced natural eutrophication becomes complicated beyond seasonal limits, when long-term trends of human-caused climate effects are considered and exceed estimated thresholds of what can be called natural.

Cultural eutrophication

Hasler (1947) defined the term cultural eutrophication as an increase in the rate and intensity of harmful algal blooms occurring as a direct result of human-caused nutrient loading. Eutrophication from human-caused effects is often related to post-industrial era impacts. However in North America recent paleolimnological work suggests even prehistoric humans altered the trophic status of a lake through runoff from nearby permanent settlements and agricultural activities (Ekdahl *et. al*, 2004). Cultural eutrophication has accompanied major milestones in human advancement, including:

- Modernized agricultural practices (*e.g*., fertilizer use, manure inputs, pesticides bound to organophosphate adjuvants)
- Population growth
- Industrial activity (*e.g.,* synthetic fertilizer production, fossil fuel extraction and combustion, forest clearcutting, agricultural practices)
- Introduction of the flush toilet and centralized sewage treatment
- Use of phosphate-containing cleaning agents (*e.g*., detergents, degreasers)
- Urbanization and associated increases in impermeable surfaces (*e.g*., concrete, asphalt, rooftops)
- Remote resource access and associated road construction
- Wetland conversion and failure to protect sensitive areas

Anthropogenic pursuits have altered biogeochemical pathways for nitrogen and phosphorus in dramatic fashion. That human activities are supplying an excess of biologically available nutrients to aquatic systems is clear; how we will mitigate cumulative effects from disparate sources is less so.

2.6 Conditions that affect eutrophication

There are naturally occurring situations that can limit or exacerbate the effects of eutrophication, with some being more seasonal and less persistent than others. Mechanisms include light limitation, precipitation and extremes in water chemistry that either limit phytoplankton growth in the presence of nutrients, or affect internal nutrient cycling from the water column to the sediment layer.

Dissolved organic carbon

Carbon is the chemical foundation of all known life and in elemental form exists as stable, tetravalent allotropes of single carbon atoms combined with four hydrogen atoms. Although required for growth and development, carbon is not usually considered a limiting resource since it is readily available in both terrestrial and aquatic systems, and has a significant atmospheric component in its cycle. Dissolved organic carbon (DOC) is receiving increased research attention for its ability to absorb ultraviolet (µv) radiation, specifically photosynthetically active radiation (PAR). Since PAR is a requisite for photosynthesis in rooted aquatic plants (macrophytes), phytoplankton (microscopic plants and single-celled organisms) and cyanobacteria, a decrease in the depth to which light can penetrate water bodies can potentially limit primary production. However, not all DOC is created in the same manner nor in the same locations, and the source can affect the structure. Forms of DOC originate as the products of decay or waste matter and can be divided into either colored (CDOC) or uncolored DOC. The latter includes soluble fats, proteins and carbohydrates that have no appreciable light absorbing capabilities and are often from autochthonous sources. Occurrence of CDOC is primarily a result of plant constituents (*e.g.,* cellulose, lignins, tannins) that decompose and create complexes of humin, and humic and fulvic acids (Table 6), frequently from allochthonous sources such as wetlands (Williamson *et al.*, 1999; Wetzel, 2001). Light attenuation due to CDOC exhibits seasonal variation in surface water, and effects are primarily restricted to the spring season in temperate regions. Solar radiation eventually decomposes colored complexes into simpler forms of uncolored DOC through photodecay, or photobleaching (Molot and Dillon, 1997;

Osborn *et al*., 2001), which then no longer inhibits light penetration into the water column.

Table 2.6. Dissolved organic carbon (DOC) and constituents of uncolored and colored (CDOC) fractions, with fractionation solubilities for CDOC.

DOC Fraction	*Constituents*	*Solubility*
Uncolored DOC	Decayed plant debris, polysaccharides, lignins, proteins	---
CDOC	Humin	Insoluble in acids and alkalis
	Humic acid	Insoluble in acid Soluble in alkalis
	Fulvic acid	Soluble in acids and alkalis

Source: Sparks, D.L. (2003). Environmental soil chemistry, 2nd Edition. Academic Press, San Diego, USA. 352 pp.

Salinity

A saline freshwater lake may sound like a contradiction in terms, but in arid and semi-arid regions hydrologic processes can occur which concentrate freshwater and result in extremely high total dissolved solid (TDS) concentrations (Table 2.7). Saline lakes occur in landlocked systems where net water losses (evaporation, transpiration) have exceeded net water inputs (precipitation, runoff, groundwater) for long enough that TDS concentrations exceed 500 mg L^{-1} (Mitchell and Prepas, 1990). Saline lakes exhibit unique flora and fauna and often low biodiversity, reflecting adaptations not present in most freshwater species for surviving high solute environments. There are instances of saline lakes receiving high nutrient inputs, given their co-occurrence with agricultural operations in grassland and prairie environments, or with indigenous animal populations in desert and polar environments. Despite high levels of total P (0.15–24 mg L^{-1}), some saline lakes fail to exhibit classic symptoms of eutrophication and instead show low primary productivity from limiting levels of iron (Evans and Prepas, 1997), although naturally eutrophic conditions have been observed in Antarctic lakes surrounded by a large penguin rookery (Bell and Laybourn-Parry, 1999). The hypersaline Great Salt Lake, Utah, exhibited increased chl*a* levels following experimental nutrient enrichment only when salinity levels were low enough for cyanobacteria to exist in the lake (≤ 70 mg L^{-1} for this system) (Marcarelli *et al.*, 2006). Overall, salinity levels in aquatic systems need to be very high for nutrient inputs not to increase chl*a* production, and high salinity in itself does not appear to reduce dissolved nitrogen and P concentrations.

Table 2.7. Salinity levels and corresponding total dissolved solid (TDS) concentrations.

Classification	*TDS ($mg \cdot L^{-1}$)*
freshwater	< 500[a]
slightly saline	500 – 1000[a]
moderately saline	1000 - 5000[a]
saline	> 5000[a]
ocean water	~ 35 000[b]

Sources: [a]Mitchell and Prepas (1990);[b]Office of Naval Research (http://www.onr.nav.mil/)

Fire

Effects of fire on aquatic nutrient enrichment relate to the size (area burned) and intensity (vertical heat transfer) of the fire itself. Nitrogenous compounds volatilize fairly easily (200°C) and are often lost to the atmosphere in proportion to combusted organic matter. Phosphorous compounds have higher heats of volatilization (> 500°C) and are more likely to be transported as particulates in ash during the fire, or in the first rainy season post-fire during wind erosion and runoff events (Debano and Conrad, 1978; Boerner, 1982). Water quality in five Iowa, USA streams degraded following fire. Although NO_3^--N concentrations were higher in burned streams compared to reference streams, the negative effects on water quality were mostly related to increases in fine sediment transport and particulate organic matter. Stream periphyton (algae and bacteria growing on submerged aquatic surfaces) decreased following fire, possibly as a result of increase turbidity and light limitation (Minshall *et al.*, 2001). Boreal subarctic headwater peatland lakes subject to fire experienced increases in P and inorganic nitrogen fractions, but no associated increase in chl*a*. This was also related to light limitation as a result of concurrent increases in DOC concentrations (McEachern *et al.*, 2000). Ranalli (2004) summarized that measureable water quality effects following fire were likely if:

- Receiving waters were oligotrophic or mesotrophic
- The residence time of the water body was short relative to the length of time nutrient concentrations remain elevated in runoff
- The watershed had steep slopes
- Soil cation-exchange capacity was low or nonexistent

Drought

Drought is a regular component of ecosystems in many regions, and considerations of its impacts have largely considered biotic survival during low flow periods. Overland transport of dissolved and adsorbed nutrients is limited or nonexistent in drought conditions, and water inputs are restricted to those available from groundwater or direct precipitation. Drought accompanied by elevated temperatures may reduce water levels through evaporation. In a simulated summer drought, denitrification increased with drought severity and ammonium concentrations were severely decreased (Dowrick *et al.*, 1998). Such a scenario would favour cyanobacterial dominance in phytoplankton communities since phosphorus, with no significant atmospheric component in its cycle, would increase in relative concentration in tandem with N depletion and further decrease the N:P ratio.

2.7 Two case studies in eutrophication

The rate and magnitude of recovery from eutrophication can be highly variable. Response to nitrogen and phosphorus input control measures range from rapid return to pre-impact conditions, to chronic effects of nutrient overenrichment. Hysteresis, or the lagging of the response following the impact, means eutrophication effects will persist in certain systems long after control measures have been put in place. This may require more consistent defence of management methods in the face of what appears to be maximum effort but minimal results. The following case studies provide examples of different nutrient input sources, aquatic system responses and mitigation efforts undertaken in reaction to instances of cultural eutrophication (Table 2.8).

Table 2.8. Physical parameters of Lake Washington, USA and Taihu Lake, China. The range for residence times and flushing coefficients for Taihu Lake reflect the numerous bays and variable water movement and storage patterns across this lake. Note that flushing coefficients are the inverse of residence time.

Water Body	[a]*Lake Washington, USA*	[b]*Taihu Lake, China*
Current Trophic Status	Mesotrophic	
Watershed Area (km^2)	1270	36500
Surface Area (km^2)	88	2428
Max. Depth (m)	65	2.6
Mean Depth (m)	33	1.9
Volume (m^3)	3.0	4.3
Residence Time (yr)	[c]2.4	[e]0.3-12.8
Flushing Coefficient (yr^{-1})	[d]0.4	[e]0.08 - 3.1

Sources: [a]Edmondson (1991); [b]Xu, H., Yang, L.Z., Zhao, G.M., Jiao, J.G., Yin, S.X. and Liu, Z.P. (2009). Anthropogenic impact on surface water quality in Taihu Lake region, China. *Pedosphere* **19** 765-778; [c]International Lake Environment Committee-World Lake Database http://wldb.ilec.or.jp/ Accessed January 2011. [d]Major Lakes Monitoring-King County Water and Land Resources Division http://green.kingcounty.gov/ Accessed April 2011. [e]Hu, L., Hu, W., Zhai, S. and Wu, H. (2010). Effects on water quality following water transfer in Lake Taihu, China. *Ecological Engineering* **36** 471-481.

A point-source impacted deep water lake

Lake Washington (Figure 2.13) remains a classic case of point-source pollution and recovery, and a story that reflects both committed individuals and the inherent characteristics of the lake itself. Lake Washington is situated in a heavily populated metropolitan area including the city of Seattle and neighbouring smaller cities in the state of Washington, USA. The Cedar and Sammamish Rivers are the primary inlets (90% of inflow), with only a few secondary inlets contributing an additional 10% of inflow. The original outlet was the Black River, which emptied into Puget Sound on the Pacific Ocean. However, the Black River was by-passed with the opening of the Lake Washington Ship Canal in 1917, which dropped the lake level approximately 3 m, permanently separated the two water bodies and dried out the river (Crowley, 1999). Currently, the sole outlet remains the Lake Washington Ship Canal, which also discharges into Puget Sound.

Figure 2.13. Aerial image of Lake Washington, USA. Siegmund, W. (2006). Lake Washington, Interstate 90, Lacey V. Murrow Memorial Bridge, Seattle, Washington, USA. Permission for use granted under the GNU Free Documentation License, version 1.2 or later. The view from this vantage point shows the heavy settlement around Lake Washington's shoreline.

Beginning in the mid-1800s, Lake Washington began receiving sewage inputs from surrounding communities, including the then fledgling city of Seattle. In 1922, there were 30 sewage outfalls from Seattle draining into the lake, despite it being the city's source of drinking water, and despite a typhoid outbreak in 1907. Sewage from the west side of the lake was diverted to Puget Sound after completion of infrastructure in 1936 (Edmondson, 1991). In 1933, prior to full completion of the sewer diversion, the lake was already characterized as being in good condition, with low nutrient concentrations and high annual deep water dissolved oxygen (DO) concentrations (Scheffer and Robinson, 1939).

Despite the efforts at sewage diversion in 1936, from the 1940s to the 1950s eleven additional secondary sewage treatment plants were in operation and discharging to Lake Washington. By 1963, the lake was significantly polluted and experiencing large and frequent summer algal blooms with accompanying decreased water clarity and increased chl*a* concentrations. Death and subsequent decay of the blooms released noxious odours and decreased deep water DO concentrations, severely hampering sport fishing and other recreational activities. By the 1960s, the trophic status of Lake Washington had degraded from mesotrophic to eutrophic (Edmondson, 1991). Concerted action from the community to improve the water quality in the lake was aided tremendously by the research and support of the late W.T. Edmondson, and in 1958 a public vote resulted in sewerage upgrades that diverted sewage flow away from the lake for a second time. Construction commenced in 1963 and after completion in 1968 the water quality rapidly improved. By 1975, the water once again had returned to mesotrophic conditions, with high mid-summer transparency, low nutrient levels (17 $\mu g\ L^{-1}$ P) and low phytoplankton abundance (Edmondson, 1977).

Lake Washington’s remediation has much to do with its physical characteristics (see Table 8). The lake is long and thin, with limited amounts of shallow areas, and only two defined inflows of water with low P concentrations. The reasonably small residence time (2.4 yr) means water in the lake is replaced by inflow in fewer than three years. The lake is fairly deep, and sediment bound nutrients that reach the bottom are unlikely to be repeatedly resuspended into the water column; P losses to sediments have been estimated at 49% of annual inputs (Edmondson, 1991). As Edmondson recognized, Lake Washington was an excellent candidate for rapid recovery once the identifiable problem of point-source sewage input was rectified. It should be noted, however, that the lake's improvement came at the expense of Puget Sound as the alternate receiving body for continued sewage discharge, which translates more into relocation than remediation.

A non-point source impacted shallow water lake

Shallow water lakes are recognized as dynamic, polymictic systems driven by sediment-water interactions that make them susceptible to long term chronic eutrophication effects (Scheffer, 2004). Taihu Lake is one such example (see Table 2.8). Located approximately 100 km west of Shanghai, Taihu (Figure 2.14) is the third largest freshwater lake in China, positioned in the lower regions of the Yangtze River delta in one of the fastest developing areas of the country. The lake is situated in an area of low relief and its watershed receives loading from agriculture, industry and a human population at one of the highest densities in the world at nearly 1000 people km^{-2} (Chang, 1987). For these reasons, sediment loading and anthropogenic effects are major concerns for lakes in the region. The lake is a key drinking water source for many of the surrounding inhabitants and home to important fisheries for eel, crabs and carp.

Although the ratio of watershed area to surface area is similar between Lake Washington and Taihu Lake (14.4 and 15.0 respectively), depth and flow patterns are considerably different between the two lakes. The range of flushing rates for Taihu Lake reflects its complex bathymetric characteristics. The lake receives inputs from an estimated 172 surface inflows, some of which can reverse flow in drier months. Water retention times are variable between major bays, with shorter residence times in the south and east portions of the lake relative to those in the north, particularly Meiliang Bay (Qin *et al*., 2007). Taihu Lake's large surface area is also susceptible to wave formation and wind mixing, which readily resuspend bottom sediments. In the 1980s, Taihu Lake began experiencing noticeable cyanobacterial blooms along its north end. In 2001, the presence of cyanotoxins was confirmed from samples collected in one of the lake's bays (Shen *et al.*, 2003). In 2006 the lake experienced an enormous bloom dominated by cyanobacteria, which covered two thirds of the lake surface and left millions of residents without drinking water.

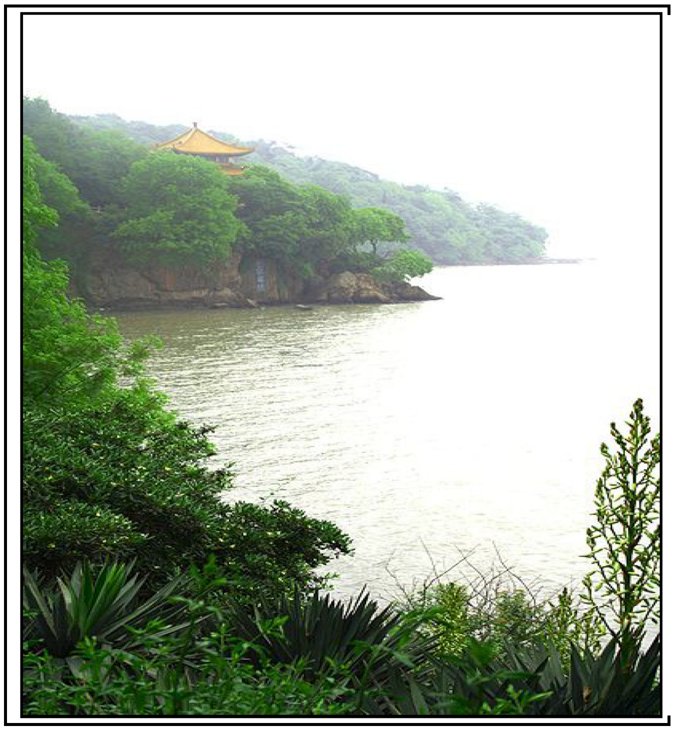

Figure 2.14. Image of Taihu Lake taken on 6 May, 2006 showing an unnamed bay with light green water characteristic of an eutrophication event. Unnamed source. (2007). Released to the public domain 5 June, 2007. In May of the following year, a massive cyanobacterial bloom prevented at least two million people from accessing their main source of freshwater. Information from: Kahn, J. 13 October, 2007. Part 3: In China, a lake's champion imperils himself. The New York Times, Asia Pacific.

Given Taihu Lake's large surface area, shallow depth and soft littoral sediments, hysteresis is a significant factor affecting system recovery. Superficial lake sediments are subject to wind mixing, which induces frequent resuspension of internal nutrients (Qin *et al.*, 2004). Mechanisms responsible for macrophyte dominance in a clear water stable-state (Scheffer *et al.*, 1993) are being explored as remediation possibilities (Qin *et al.*, 2003), while effective nutrient management plans continue in their development. Bulk water transfer to several heavily eutrophied bays has met with only limited success. Reductions in total P concentrations were noted, but only weak declines in total N and chl*a* concentrations were evident (Hu *et al.*, 2010). It is highly likely that multiple, concurrent treatments will be required for successful remediation. The size, complex geometry, variable water retention times and numerous inputs into Taihu Lake render it an unlikely candidate for matching the rapid rehabilitation of Lake Washington.

2.8 Future opportunities

The key to effective eutrophication control is balance between nutrient input and ecosystem demands, and recognizing when anthropogenic impacts require an equivalent effort in control and remediation. Although eutrophication can and does occur naturally, human-caused instances are increasing in number and intensity as remediation methods lag behind intensified inputs. There are many prospects for eutrophication control in systems where nutrient limitations and internal cycling processes have been removed or disrupted by human activities.

Management

Since all forms of P originate as mined or weathered minerals, sources are finite, and predictions have been forecast for the occurrence of peak phosphorus, the point at which resource depletion is matched by production capacity. After this point resource availability decreases, resource quality declines and finished product price increases dramatically, reflecting the growing difficulties in extraction and production. The Hubbert Linearization curve (1974) predicted the case of peak oil in the 1970s; applying the same principles for phosphorus has resulted in predictions for peak phosphorus ranging from 1989 (Dréy and Anderson, 2007) to roughly 2030 (Cordell *et al.*, 2009).

When the peak will occur is secondary to the certainty that it will occur. Alternatives may be found for oil, but elemental phosphorus is irreplaceable. However, phosphorus can be reclaimed and research opportunities require focus on increased efficiency of use, *in situ* retention and greater recapture and reuse, all of which can also reduce the effects of eutrophication. Efforts include:

- Manure capture and urban mining (use of human sewage) for both direct fertilization and purified fertilizer production
- Human population control to reduce agricultural pressure
- Improvements in sanitation, including low water-use systems ranging from in-house to large municipal applications
- Use of green water (soil water) *vs*. blue water (surface and groundwater) for global resource and food production; this relates more to tailoring renewable products to local growing conditions than to the amount of water required to grow the crop, and limits the risk of eutrophication from anthropogenic drought

Alleviating eutrophication effects in situ has involved the use of established methods, such as hypolimnetic withdrawal (Nürnberg, 1987), hypolimnetic oxygenation (Prepas and Burke, 1997), or phosphorus precipitation following addition of calcium carbonate and lime (Prepas *et al*., 1990), all of which reduce nutrient concentrations from the dissolved pool. The pivotal example of Experimental Lake 227 (Schindler, 1974) led to the restriction of phosphate use in many detergents, an important watershed-level control measure. However, in Canada, as an example, measures to address additional sources such as automatic dishwasher detergents have only been put in place as recently as 2010 (Government of Canada, 2009), industrial sources of phosphate have not been well addressed, and agricultural and municipal runoff remain important contributors (Table 2.9). These sorts of persistent, nonpoint nutrient inputs require additional characterization and preventive options relative to the more easily addressed point-source impacts. Future research and special consideration will also be required for sensitive areas like shallow lakes, wetlands and headwater systems. As natural nutrient conversion factories and early warning indicators of cumulative effects, these systems will need to function at full force for both detection and mitigation of eutrophication.

Table 2.9. Approximate phosphorus contributions from major sources to Canadian surface waters.[a]

Source		*Phosphorus load*
Municipal waste, sewers and septic systems	14.3%	*53% Human waste* *11% Household cleaners and detergents* *36% Commercial and industrial sources*
Industry	2.9%	
Agriculture	82.1%	
Aquaculture	0.70%	

[a]Adapted from values in: Chambers, P.A., Guy, M., Roberts, E.S., Charlton, M.N., Kent, R., Gagnon, C., Grove, G. and Foster, N. (2001). Nutrients and their impacts on the Canadian environment. Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada.

Monitoring

Long term datasets can improve predictability by providing a solid base of accumulated information against which to test ecological modelling scenarios. Accumulated monitoring data also allow for the identification of trends and risk factors, where planning knowledge could minimize costly reclamations. Changes in trophic status represent a regime shift. These shifts may be preceded by an increase in variability discernable from levels inherent in ecological systems. Simulations suggest that higher standard deviations in summer epilimnetic P concentrations could precede a shift to eutrophic conditions by about a decade (Carpenter and Brock, 2006). Long term monitoring data can provide validation for these types of predictive models that have the potential to sound the alarm before the effect is noticed.

Remote sensing is increasing in ecological applications as resource extraction moves farther from urban centres and personnel, time and funding for direct ecosystem sampling may be untenable. Identifying and monitoring sensitive and responsive critical areas, such as wetlands and headwater streams, will help in targeting prevention and mitigation efforts. Critical zones can be used as indicators of excess nutrient transport prior to downstream cumulative effects. As well, much remains unknown about phytoplankton community shifts in response to eutrophication. Ongoing analyses of phytoplankton community structure in Lake Washington and its response to nutrient inputs and subsequent control would not be possible without long-term ecological monitoring.

2.9 Conclusion

Improvement in trophic status is possible, although the case studies suggest some systems will exhibit prolonged response to eutrophication and require continued and determined management efforts. The detrimental effects of eutrophication are large and will continue to grow unless the influx of excess nutrients can be reduced, retained or redirected away from vulnerable surface waters. As Bill Bryson (2005) writes regarding species extinctions, humans are '…so remarkably careless about looking after things'. Unfortunately, the same can be said for our attention to the functioning of many aquatic systems. In pursuit of food, shelter and water, we have maximized the first two at the expense of the last one, over-fertilizing and choking valuable freshwater resources in the process. Management, monitoring and sustained efforts will be required to reverse the trend.

2.10 Acknowledgments

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3. Effectiveness of current U.S. critical limits in protecting sensitive lakes against acidification

3.0 Abstract

Critical limits are reference points against which the effects of accumulated acid loading are evaluated. In the U.S., the minimum screening criterion below which no damage due to acidification is expected is currently recommended as an acid neutralizing capacity (ANC) of 25 µeq L^{-1}. Screening criteria are applied to all freshwater systems, including those located in Class 1 areas with special provisions for protection. Two sets of lakes in U.S. Forest Service Class 1 areas of the western Great Lakes are compared to assess the suitability of these criteria as critical limits for ANC in guarding against acidification: seven lakes in northwestern Wisconsin (Chequamegon-Nicolet National Forest), and five lakes in northeastern Minnesota (Superior National Forest). In spite of overall low wet acid deposition between 1984-2011 in both areas, midsummer ANC below 25 µeq L^{-1} has been frequently measured in both lake sets, with ANC from one lake reaching -77 µeq L^{-1}. Hydrology and sources of acidity for each lake set are discussed with respect to effects on open water ANC. For sensitive lakes, vulnerability to low ANC events is predicted to increase in years when above normal snowmelt is followed by a dry open water season. Calculating allowable cumulative acid loading using the current guideline limit of 25 µeq L^{-1} does not protect lakes during coincident periodic acidification events generated by climatic conditions. Based on the lowest recorded ANC, a higher critical limit of 127 µeq L^{-1} is recommended.

3.1 Introduction

In the early 1990's federal land managers (FLMs) in the US were tasked with identifying and quantifying the impacts of air quality related values (AQRVs) in Class I protected areas (*e.g.*, Adams *et al.*, 1991; Peterson *et al.*, 1992a; Peterson *et al.*, 1992b); Class 1 areas were designated as such to protect the integrity of selected ecosystems. Although visibility is the only AQRV specifically noted in the Clean Air Act (CAA) (Clean Air Act, 1963), additional AQRVs commonly identified by FLMs include impacts on flora, fauna, odor, soil, and water. Uncertainty as to where to place minimum AQRV thresholds persists, especially for surface water; the US is currently still without a formal regulatory agreement for critical buffering limits to prevent acidification in aquatic systems. Inclusion of coincident effects of seasonality and weather on AQRV metrics are also lacking, especially in the context of sensitive lakes.

A keystone to the CAA is the requirement of a permit for new major sources of air pollution to obtain a Prevention of Significant Deterioration (PSD) permit. If the new source has the potential to negatively affect any Class I area, its impacts are closely examined as part of the permitting process due to the Act's mandate to 'preserve, protect, and enhance' (Clean Air Act, 1963). The challenge with PSD permits is the automatic designation of baseline conditions at the time of application. The identification of baseline conditions based solely on the timing of permit submittal is at best a weakly informed reference point against which to gauge the CAA requirements of no negative effects.

At the 1990 U.S. Forest Service Eastern Region meeting, FLMs worked to established critical limits for lake acid neutralizing capacity (ANC). A lower ANC limit of 25 μeq L^{-1} with pH > 5.5 was set as the point above which no significant damage was expected to biological components of freshwater systems; chronic effects were expected after prolonged exposure to ANC 0 – 10 μeq L^{-1}, and acute effects when ANC < 0 μeq L^{-1} (Figure 3.1; Adams *et al*., 1991). This approach implies that:

- critical loads calculated using a green line limit of in-lake ANC of at least 25 μeq L^{-1} should provide consistent protection against acidification and low pH
- in-lake ANC should never fall below 0 μeq L^{-1}

Despite reductions of important air pollution constituents (e.g. sulfate (SO_4^{2-}), nitrate (NO_3^-)), the return of water quality to pre-industrial estimates, as a benchmark of complete remediation, has not occurred consistently in Class 1 regions of the US (Stoddard *et al*., 2003). For effective management, it is essential to qualify the factors that constitute an impaired system. This includes distinguishing why recovery has been inconsistent, and identifying the conditions linked to low ANC events in some

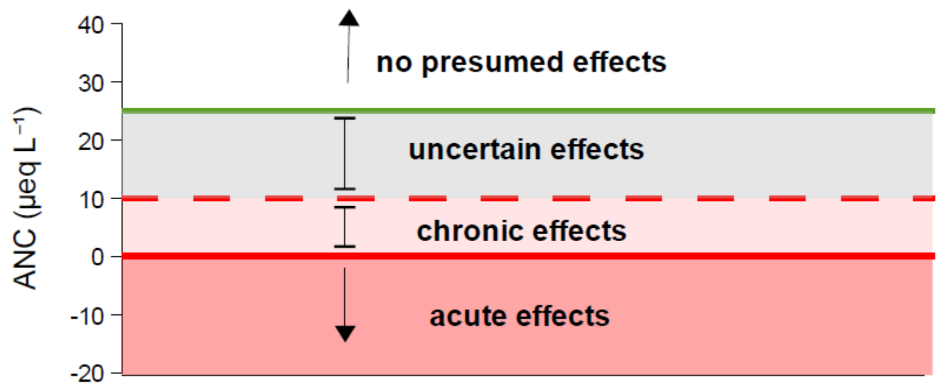


Figure 3.1. Schematic of green line (ANC 25 µeq L^{-1}), chronic red line (ANC 10 µeq L^{-1}) and acute red line (ANC 0 µeq L^{-1}) with expected in-lake effects. Adapted from screening criteria established in Adams *et al*. (1991).

freshwater systems, using weakly-buffered lakes as specific examples. This will allow FLMs to determine: 1) if critical loads calculated using a critical limit ANC of 25 µeq L^{-1} are sufficient for protection of ecological integrity, or expected ecosystem services, and 2) when the negative effects of any increased pollution will be most severe. To this end, low ANC events from two sets of lakes are compared with respect to differences in hydrology (seepage *vs* drainage lakes) and climatic conditions (temperature and precipitation).

ANC and pH

As a measure of buffering capacity, ANC is a balance between contributions from carbonate buffering, pH, organic acids and acidic metal species (*e.g*. aluminum) (Eqn 1; Stumm and Morgan (1981)).

$$ANC = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [R^-] - [H^+] - 3[Al^{3-}]\ 2[Al(OH)^{2+}] - [Al(OH)_2^+] \qquad (1)$$

where:

$[OH^-] + 2[CO_3^{2-}] + [HCO_3^-] - [H^+]$= carbonate alkalinity,

$[R^-]$ = anions of organic acids (*i.e*. buffering from the strong conjugate base), and

$-\log [H^+]$ = pH

In natural systems, pH is in equilibrium with both carbonate alkalinity and weak organic acids, the latter usually quantified as concentrations of dissolved organic carbon (DOC). Increases in either CO_2 or DOC will have an effect on pH, but will have no direct effect on ANC (Figure 3.2); very high DOC lakes may have naturally low pH without having concurrently low ANC. (Stumm and Morgan, 1981). Lake ANC-pH relationships are thus variable and system dependent, although reasonable synchrony may exist between lakes in the same region (Baines *et al*., 2000). Large decreases to ANC can occur when additions of strong mineral acids or acid metal species increase beyond the available buffering capacity.

Acidity from increased mineral acid inputs will result in a decrease in pH. Carbonate alkalinity in an open system (*e.g.*, freshwater lakes exposed to air) can neutralize added bases but not added mineral acids unless a source of base cations and contributions from $CO_{2(g)}$ are available (Burau and Zasoski, 2002). In lakes with base-rich landscape parent material, such as limestone, various base cations (e.g. Ca^{2+}, Mg^{2+}) bound to CO_3^{2-} are present in watersheds. However, soils in the Great Lakes region are generally acidic (Shacklette and Boerngen, 1984) and acidic soils have low carbonate buffering potential; estimates of base cation availability from weathering origins are low, and uncertainty in weathering estimates can be high (Kolka *et al*., 1996; Li and McNulty, 2007). Low inherent base cation inventory can become further depleted in acidified soils, leaving little remaining buffering capacity for water moving from terrestrial to aquatic systems (Fernandez *et al*., 2003). Although there are some calcareous soils, from a management perspective an extremely low buffering capacity can be expected in runoff from most western Great Lakes watersheds.

Turnover events cycle high ANC water throughout the water column following production and accumulation of ANC from reducing bacteria in hypoxic lake sediments. Spring ANC sets the baseline conditions for lakes in temperate regions, especially those with weak landscape sources of ANC or no buffering inputs from groundwater; in these

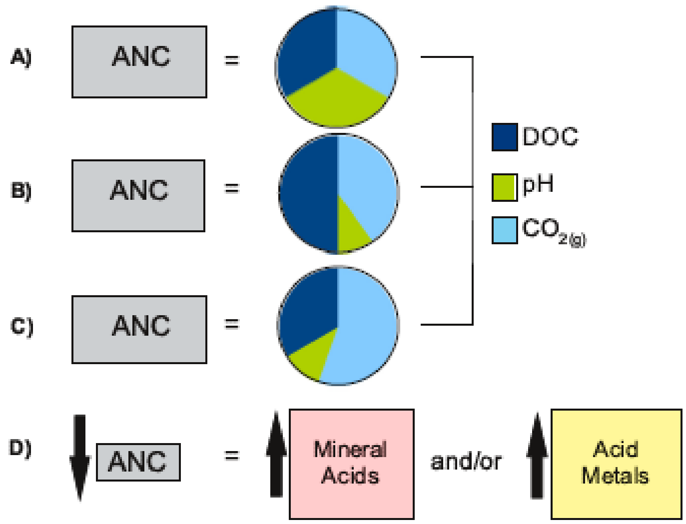


Figure 3.2. Schematic of factors affecting ANC in freshwater systems open to the atmosphere. Organic acids are represented by dissolved organic carbon (DOC), which are in equilibrium with pH and atmospheric $CO_{2(g)}$(A). Increases in either DOC (B) or $CO_{2(g)}$ (C) have no appreciable effect on in-lake ANC. However, increases in strong mineral acids (*i.e.*, SO_4^{2-}, NO_3^-), either alone or in combination with metal acid species (e.g. Fe^{2+}, Al^{3+}) (D), will decrease ANC. In systems with low carbonate alkalinity, the decrease in ANC can be extreme.

cases, internal ANC production followed by spring turnover is the primary source of epilimnetic ANC (Schindler, 1986; Schindler *et al*., 1986; Giblin *et al*., 1990). Systems with good connections to groundwater have higher ANC than those relying solely on internal production. In situations of prolonged drought, however, groundwater links can uncouple and leave previously well buffered systems susceptible to acidification (Webster *et al*., 1990; Webster and Brezonik, 1995). For lakes reliant on internal ANC, increased thermal stability is also a threat to the effectiveness of spring turnover. High air temperatures can result in intensive thermal stratification that lowers the thermocline and increases epilimnetic volume (Jankowski *et al*., 2006). These conditions can result in weak or incomplete turnover events that fail to effectively replenish epilimnetic ANC from internal sources.

Sources of acid inputs

Inputs of strong mineral acids or acid metal species can enter aquatic systems and lower ANC incrementally or rapidly, depending on a combination of both lake ANC levels and acid input concentration at the time of delivery. Acidification from atmospheric pollution can occur through both wet and dry deposition of strong acids (*e.g.*, SO_4^{2-}, NO_3^-). Although wet deposition chemical constituents are routinely measured at long-term collection points as part of the National Atmospheric Deposition Program (NADP) (Lamb and Bowersox, 2000), dry deposition is not; quantification of dry deposition inputs is notoriously difficult to extrapolate over wide areas beyond local measurements (Wesely and Hicks, 2000). Although throughfall is a reasonable proxy for total deposition, *i.e*. wet plus dry deposition (Butler and Likens, 1995), it is not measured consistently at NADP sites and is generally collected beneath tree canopies (Lamb and Bowersox, 2000). Even though acid deposition overall has decreased steadily throughout the U.S. following CAA legislation and subsequent amendments (Lynch *et al*., 2000) (Figure 3.3), wet deposition of SO_4^{2-} and NO_3^- linked to anthropogenic sources still occurs.

Acidity can also be generated when previously reduced strong mineral acids are oxidized from normally saturated soils following drought. Yan *et al*. (1996) reported a large mineral acid pulse to Swan Lake, Ontario, after a two year drought was followed by a very wet year. The extreme acidity of the pulse was linked to high stores of SO_4^{2-} in sediments from historical deposition originating in nearby smelters. Near Dorset, Ontario, Canada high annual SO_4^{2-} runoff to lakes from associated wetlands was also noted following very dry summers, where wetlands shifted to being a source of acid export rather than a sink (Devito *et al*.,1999); this occurred despite Dorset being in an area of lower acid deposition relative to Sudbury, Ontario, an area of smelting activity (Keller *et al*., 2003). Following three successive years of below normal precipitation and a subsequent summer drought and re-wetting episode, stream transport of SO_4^{2-}

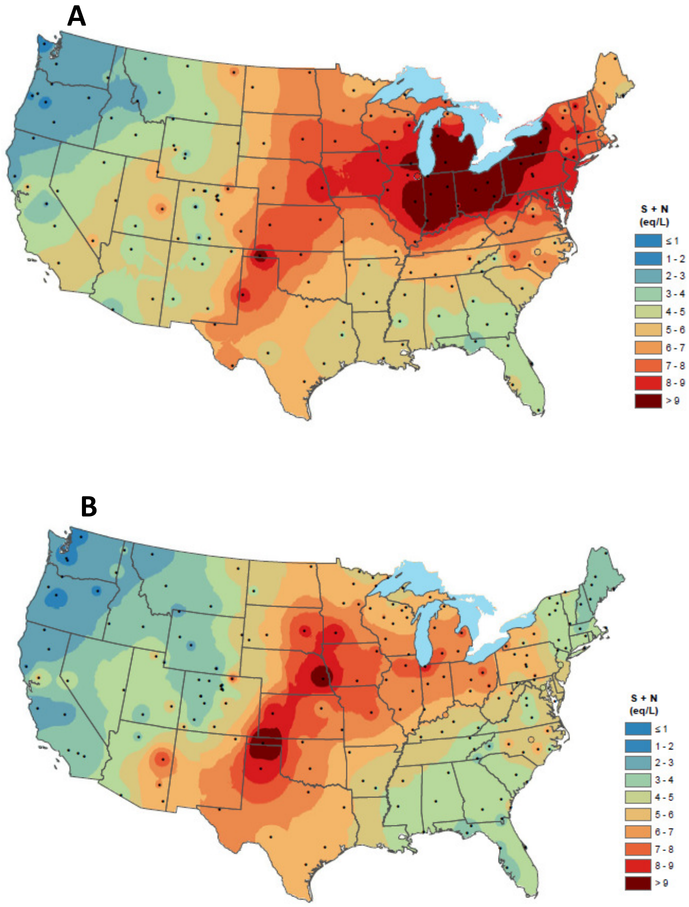


Figure 3.3. Annual precipitation weighted wet deposition SO_4^{2-} and NO_3^- (eq L^{-1}) isopleth maps for the conterminous U.S. for A) 1994 and B) 2011 (NADP, 2014). Black dots represent NADP sample sites.

equated to a 614% increase in export from a temperate swamp system near Hamilton, Ontario (Warren *et al.*, 2001). The ability of wetlands to retain acidity is compromised when water levels drop and hydric soils are exposed to air.

Inputs of acidic metal species will also decrease ANC. However, decreases in pH may not be evident in water samples due to the high variability of in pH response when hydrolysed acid metals are strongly represented as components of ANC. Inputs of acid metal species can lower ANC dramatically without apparent decreases in pH. Relationships for ANC and pH in lakes should be used with caution as high variability is to be expected when metal acid species figure strongly, and in-lake ANC is inherently low.

Two metals commonly linked to increases in surface water acidity are ions of iron (Fe) and aluminum (Al). Reduced forms of each can be found in hypoxic wetland water, depending on local soil types; oxidative events such as the drawdown and exposure to air of normally submerged soils can both decrease pH while concurrently increasing the solubility of available metals (Reddy and DeLaune, 2008). High acid metal inputs during subsequent rain events can decrease the ANC of lakes below that expected from contributions of mineral acids alone; this is evident in areas such as the Adirondack Mountains, where soil Al content is naturally high and deposition-acidified terrestrial runoff transports solubilized Al to aquatic systems (Driscoll and Postek, 1995; Driscoll *et al*., 2003).

Hydrology effects

In general, inland lake systems are either one of two basic hydrology types: drainage or seepage. Water inputs to seepage lakes consist of direct precipitation and limited runoff from the landscape. Seepage lakes may or may not be well-connected to groundwater. Drainage lakes receive water inputs through direct precipitation and landscape runoff, may or may not be connected to groundwater, may or may not have an inflow, and always posses an outflow (Brooks *et al*., 1997). The land-locked nature of seepage lakes renders them more susceptible to concentration and dilution effects when wide ranges in precipitation inputs and losses to evapotranspiration occur; this can also occur in drainage lakes during dry periods when lake levels drop below the outflow. Seepage lakes with limited or no connection to groundwater are often naturally acidic and very sensitive to further acidification (Shaw *et al*., 2004). Early open water season ANC will be heavily influenced by snowmelt in seepage systems.

3.2 Lake comparisons

Lakes in the western Great Lakes region historically received low levels of acid deposition (Figure 3.3). Despite low acid deposition inputs, temporal depressions in ANC have been recorded at lakes in Class I areas in both Minnesota and Wisconsin (Figure 3.4), and monitoring efforts of U.S. Forest Service staff have captured events of ANC < 0 µeq L^{-1} from each lake set (Figure 3.5). Seven seepage lakes in the Rainbow Lake Wilderness (RLW) area inside the Chequamegon-Nicolet National Forest, Bayfield County, WI, have been sampled intermittently from 1984-2011. In northeastern Minnesota, five lakes in the Superior National Forest (SNF) have been sampled from 2008-2011. The SNF lakes include both drainage and seepage systems located over three counties (Table 3.1).

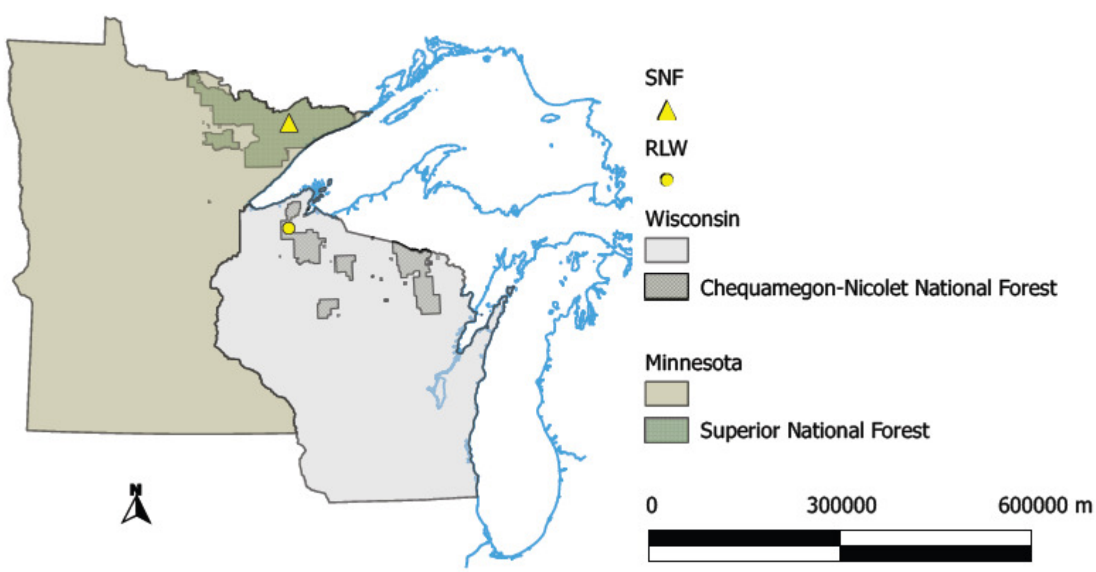
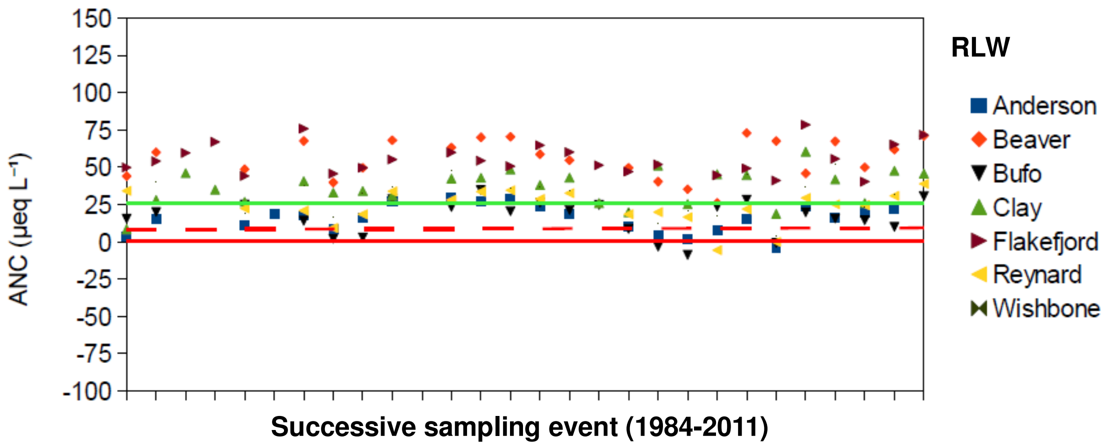


Figure 3.4. Map of the western Great Lakes region showing general lake set locations in the Superior National Forest (SNF) and Rainbow Lakes Wilderness (RLW) area. Icons for both SNF and RLW also represent points to where precipitation data were interpolated. Map created using Quantum GIS v. 1.7, Wroclaw edition using shapefiles from the Great Lakes Information Network (2013), the United States Census Bureau (2013) and the USDA Forest Service (2014).



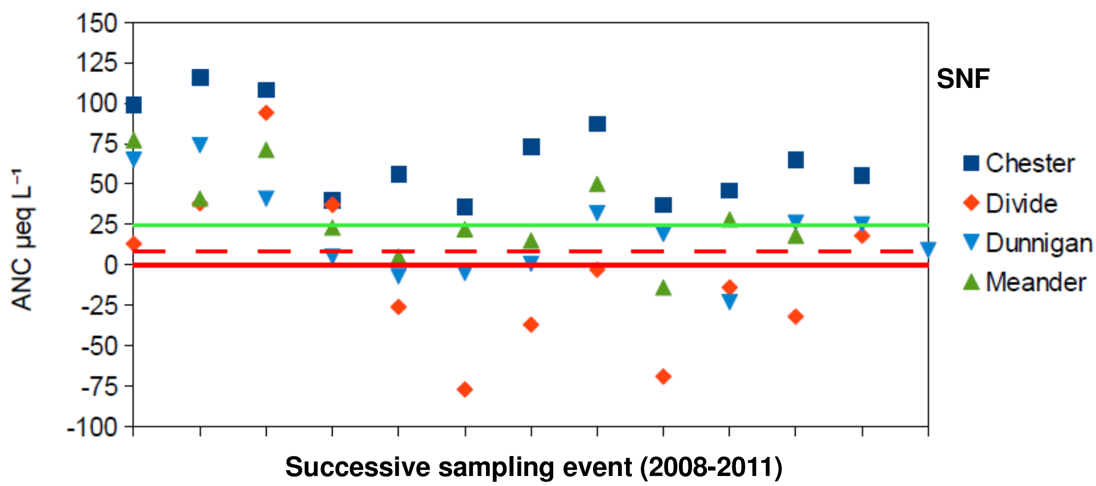


Figure 3.5. Plot of measured ANC (µeq L^{-1}) for seven RLW lakes (NW Wisconsin) and four SNF lakes (NE Minnesota). All seven RLW systems are seepage lakes. The SNF lakes are comprised of two drainage (Chester, Meander) and two seepage (Divide, Dunnigan) systems. Samples were collected over different time frames for RLW (1984-2011) and SNF (2008-2011). Each tic mark on the x-axis represents a unique sampling event. Green, dashed red and solid red lines correspond to in-lake ANC limits presented in Figure 3.1.

Table 3.1. Minnesota lake locations, major drainage basin and hydrology. All lakes are managed as part of the Superior National Forest.

Lake	*County*	*Drainage basin*	*Hydrology*
Chester	Cook	Lake Superior	drainage
Crooked	Cook	Rainy River	drainage
Divide	Lake	Lake Superior	seepage
Dunnigan	Lake	Rainy River	seepage
Meander	St. Louis	Rainy River	drainage

Both lake sets are located in areas of similarly low overall relief, although local elevation differences around the SNF lakes can be more extreme due to the regional peneplain (Ojakangas and Matsch, 1982). Surrounding the RLW lakes are sandy soils overlaying thick deposits of glacial outwash. Upland Spodsols with low silicate clay content dominate the RLW lakes, interrupted by open and forested peatland Histosol soils in low slope (0-3%) areas (USDA-NRCS, 2006). Sandy glacial outwash also occurs throughout the SNF area with thin soils and exposed bedrock, as the forest is situated on the southern limits of the Canadian Shield (Ojakangas and Matsch, 1982; Minnesota Geological Survey, 2006). Soils in the SNF region are primarily sandy or loamy sand Inceptisols, interspersed with wet Inceptisols (aquepts) and Histosols associated with peatlands and wet forests (Minnesota Geological Survey, 2006; MDNR, 2014). Northeastern Minnesota is also home to large iron ore deposits, the two nearest the sampled lakes being the Mesabi and Vermillion ranges (MDNR, 1998).

In temperate systems, runoff can be separated into snowmelt plus any additional runoff events that take place throughout the frost-free period. Although use of a fixed water year is common when calculating water budgets, monthly time steps provide a more explicit measure of hydrologic inputs. This is especially relevant where seepage lakes are concerned, as they lack outflows and are strongly affected by available water inputs and evaporative loss.

To determine a simple water budget for each lake set, evapotranspiration was calculated using the method of Valiantzas (2006), suitable for areas without recorded wind speed. The frost-free season was calculated as the number of days from the last spring frost to the first autumn frost using air temperature data from the nearest National Climatic Data Center: station GHCND:USC00472240, Drummond, WI for RLW lakes, and station GHCND:USC00213417, Gunflint Lake, MN for SNF lakes. Precipitation data were interpolated to the centroid of the minimum bounding box for RLW lakes (46.4035 latitude, -91.1948 longitude), and to the point of minimum distance between all lake centroids for the SNF lakes (47.8965 latitude, -91.2405) using the Parameter-elevation Regressions on Independent Slopes Model (PRISM Climate Group, 2012).

For sample periods during which the lowest ANCs were recorded, evapotranspiration exceeded precipitation for much of the open water season, dramatically so for the SNF lakes (Figure 3.6). This suggests that the lakes, as well as any associated wetlands, were experiencing drought conditions for at least a portion of the frost-free season.

Effects of lake type are evident within the SNF lake region; the two SNF lakes with the lowest measured ANC are the only two seepage systems, Divide and Dunnigan (Figure 3.5). Of interest is that the low ANC occurred during very dry periods, when evapotranspiration consistently equalled or exceeded precipitation (Figure 3.6). Barring other inputs, chemical constituents in seepage lakes should become more concentrated when evaporative demand increases, yet Divide Lake reached measured ANC well below the minimum guideline level of 0 μeq L^{-1}. All other lakes show similar patterns in ANC for systems within both lake sets (Figure 3.5). This implies that the lakes in each set are responding similarly to a common factor within their respective regions despite differences in chemistry between lakes. Considering the possible sources of acidity already discussed, pulsed input from oxidized wetland soils is suggested as the acid input source, with differences in the magnitude of response related to ANC inherent to individual lakes and hydrology type. This is similar to pulsed acid inputs recorded in other, weakly buffered temperate lakes, synchronous with drought and subsequent re-wetting events of associated wetland soils (Warren *et al.*, 2001; Eimers *et al.*, 2007).

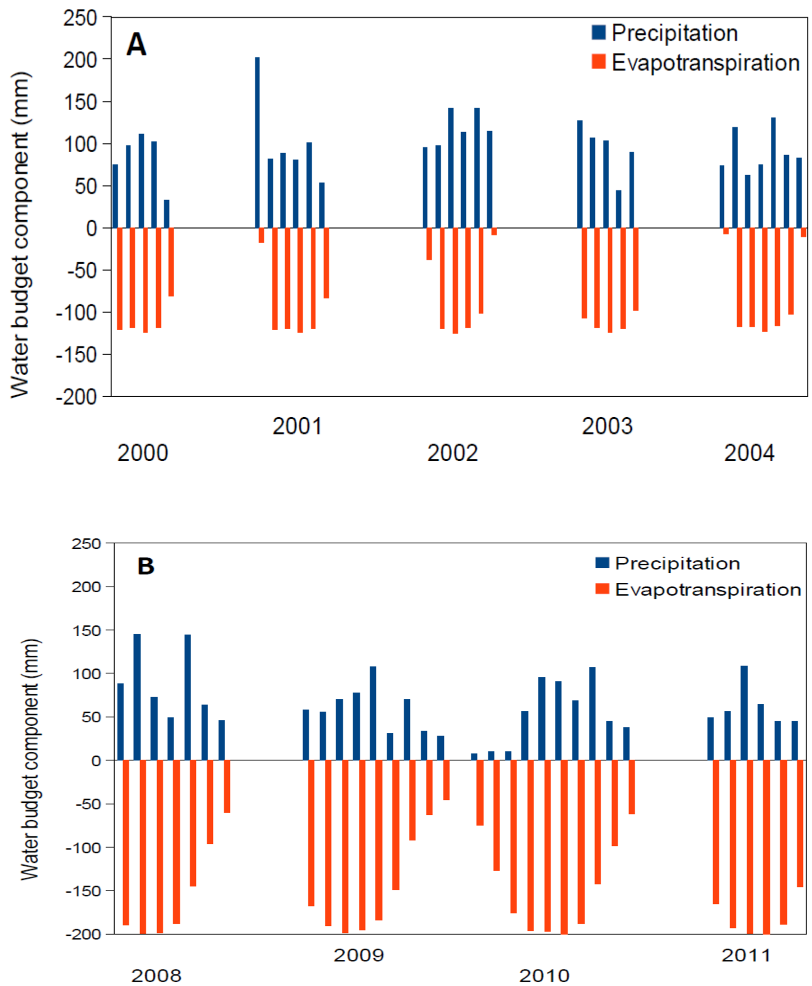


Figure 3.6. Plots of precipitation and evapotranspiration for the A) RLW (2000-2004) and B) SNF (2008-2011) regions from open water months during successive sample years. Years displayed for RLW lakes were those sampled during the most recent drought conditions. Aquatic systems experience drought stress when water loss due to ET (orange bars) exceeds available P (blue bars).

Sum of monthly normal precipitation (mean monthly precipitation 1981-2001) for all frost months was divided by sum of PRISM-interpolated monthly precipitation for the same period of frost months to arrive at a unitless winter precipitation ratio (WPR). As a representation of the volumetric effects of snowmelt in seepage lakes, the WPR for sampled years per lake set (as in Figure 3.6) was then multiplied by a fixed value of 25 μeq L^{-1}, the current green line limit, to compare dilution effects between lake sets. Years of high snow have a clear impact on ANC (Figure 3.7). For seepage lakes from both sets, higher than normal snowmelt followed by a very dry open water period precede summer months with the lowest recorded ANC.

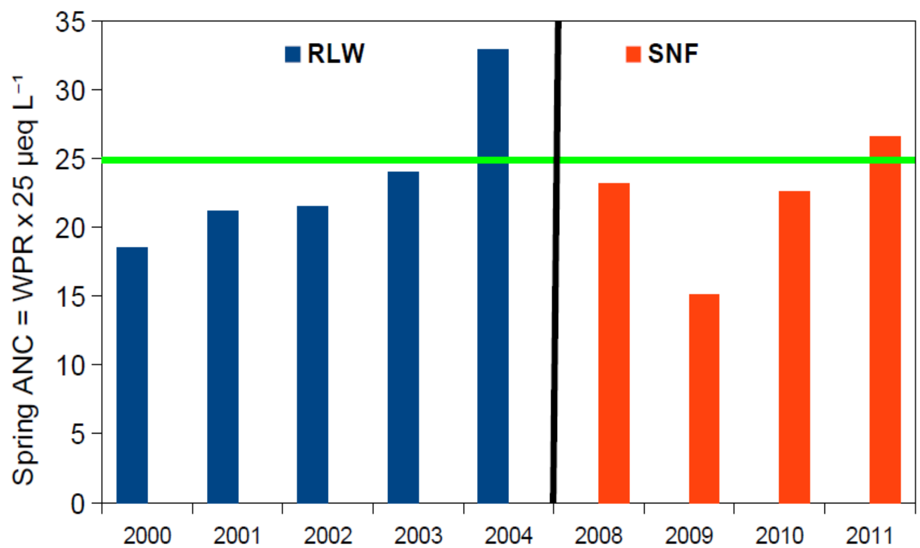


Figure 3.7. Demonstration plot of the effect of snowmelt volume on spring ANC using values estimated by multiplying the winter precipitation ratio (WPR) by a fixed ANC of 25 μeq L^{-1}.(green line equivalent to that presented in Figure 3.1). Years of low snowmelt such as 2004 (RLW) and 2011 (SNF) would result in higher spring ANC, while the opposite is evident for high snowmelt years.

Plots of ANC and pH over time for one seepage lake from each region are presented in Figure 3.8 (A and B). The plots show that these lakes often have low pH, regardless of ANC. Samples from Divide Lake show pH measurements do not always track well with those of ANC. Where pH is much lower than ANC, organic acid inputs are implicated. Where ANC is much lower than pH, such as the extremely low ANC recorded in Divide Lake (Figure 3.8B), the difference could be attributed to acidity resulting from inputs of metal species, reflecting the iron content that is generally high in these soils. Regardless of mechanism, when ANC and pH are both low, and in the face of low atmospheric deposition, runoff from previously dried wetland soils is the most likely acid input source.

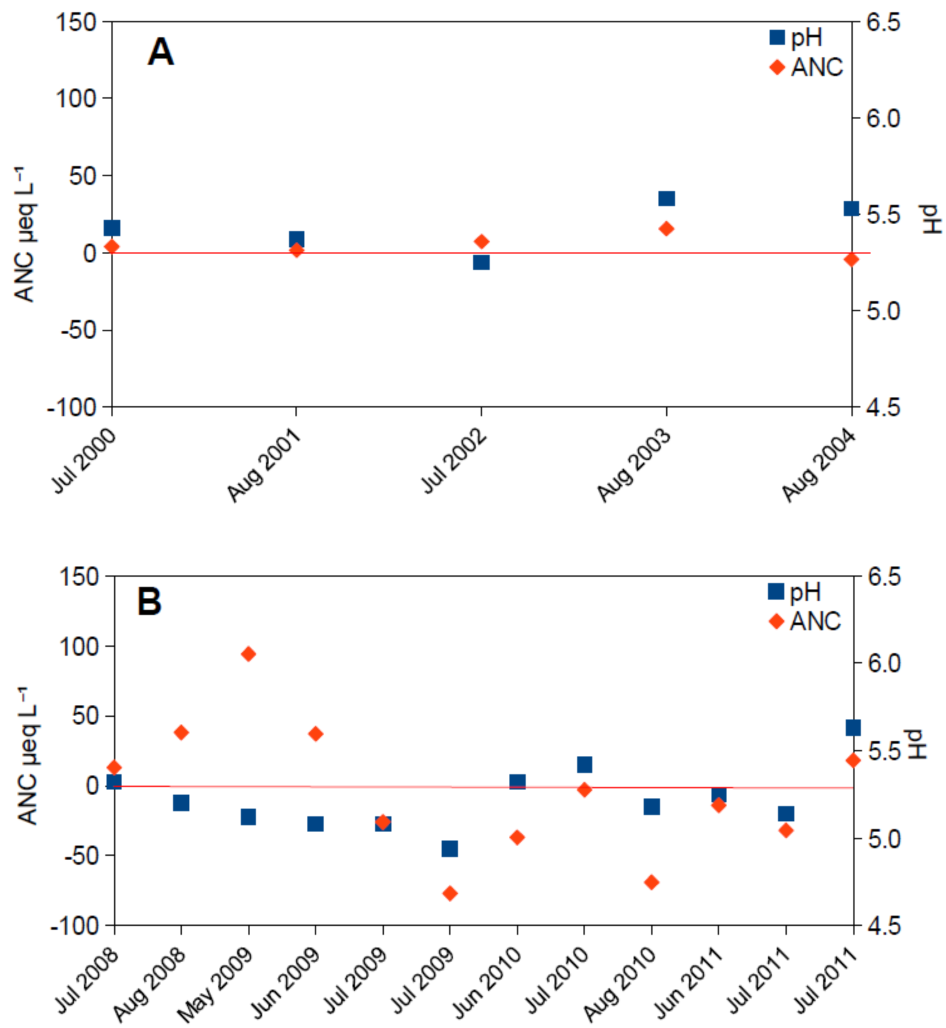


Figure 3.8. Plots of pH and ANC (µeq L^{-1}) over successive sampling events expressed as equal intervals for two of the most sensitive lakes per region: A) Anderson Lake (RLW) and B) Divide Lake (SNF). Data ranges correspond to those presented in Figure 3.6. Solid red line corresponds to red line presented in Figure 3.1 (0 µeq L^{-1} ANC).

Data from both lake sets show that current guideline limits are inappropriate against which to calculate loading amounts for SO_4^{2-} and NO_3^-. Ideally, loading amounts should be reduced to mitigate the lowest recorded ANC for lakes in a given an airshed (Figure 3.9). For Divide Lake (SNF), average in-lake ANC for 2008 was 25.5 µeq L^{-1} for which current guideline limits would suffice. However, for 2009-2011, mean ANC was 7, -36 and -9 µeq L^{-1}, respectively, with the lowest measured ANC at -77 µeq L^{-1} in 2009. The critical limit under these conditions would have to be adjusted upward from 25 µeq L^{-1} to 127 µeq L^{-1} so that acid inputs from atmospheric deposition will not contribute to further acid stress. However, this assumes that all acid deposition in a given watershed will reach the lake as acid inputs. A better estimate of the likelihood of acid inputs to lake systems would allow this number to be refined.

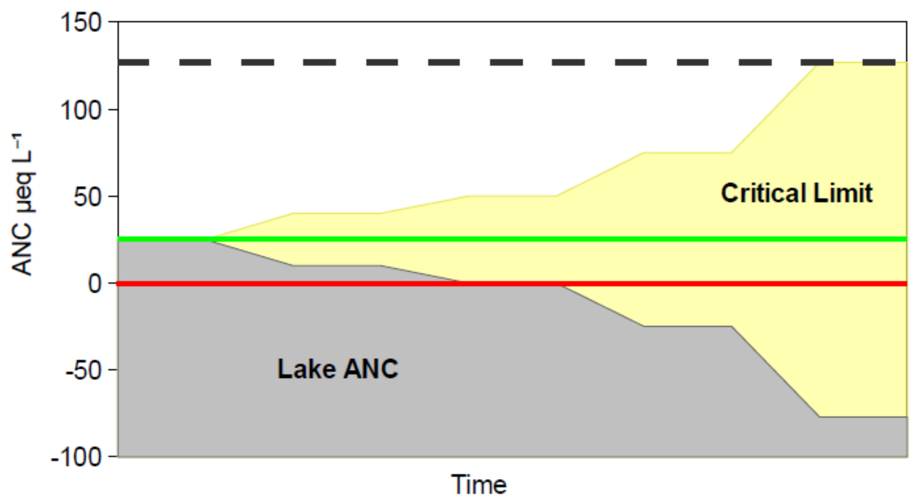


Figure 3.9. Representative plot of critical limit modifications relative to decreasing in-lake ANC over an open water period. Allowable loads calculated using the current green line limit are only effective when lake ANC is at least 25 µeq L^{-1} for the entire open water period. Limits against which to calculate loading rates should be high enough to provide a factor of safety against episodic low ANC events, especially those below the red line (0 µeq L^{-1}). The point of lowest ANC is -77 µeq L^{-1}, reported from Divide Lake (SNF) in 2009; a proposed critical limit is set to accommodate this lowest measured value (black dashed line). Green line (25 µeq L^{-1}) is the same as that described in Figure 3.1.

3.3 Conclusion

For temperate freshwater systems, when critical loads are to accommodate dynamic conditions they become target loads (Pardo, 2010) and must be rapidly adjustable. However, this is not feasible for many pollutants. Loading sources that cannot be rapidly adjusted must have limits set to accommodate the lowest anticipated ANC for lakes in Class I areas. The target of 127 μeq L^{-1} is suggested to incorporate the lowest recorded ANC proportional to the green line value of 25 μeq L^{-1}, above which freshwater systems are assumed not negatively impacted (Figure 3.1). Likelihood of occurrence for extremely low in-lake ANC will factor into final management recommendations, although data collected over a longer time frame is required to better estimate or model the frequency of low ANC events.

For seepage lakes, response to acid inputs will be strongly impacted by dilution effects of snowmelt in spring ANC. In drainage lakes, high snowmelt will have little effect on in-lake ANC following spring turnover, but low snowmelt volumes may have a concentrating effect on spring ANC if outflow ceases. In either seepage or drainage lakes, extensive summer drying of hydrologically connected saturated soils (*e.g.*, wetlands, exposed littoral sediments) will increase oxidation products, resulting in an accumulation of strong mineral acids, as well as acid metal species where present. Subsequent re-wetting of connected wetlands will rapidly transport ANC depleting inputs to associated lakes. The effects of ANC depletion from mineral acids and oxidized acid metal species in wetlands will be most profound in lakes where buffering sources are already weak (internal ANC sources dominate or low carbonate substrates exist) or become weakened (through dilution effects, a deep thermocline, or drought effects). The frequency of low ANC events will increase if rising temperatures simultaneously decrease the effectiveness of spring turnover to seasonally restore epilimnetic ANC, while also increasing the propensity of drought; excessive drying followed by runoff events will shift saturated soils such as wetlands from sinks to sources of acid inputs.

3.4 Acknowledgments

This work was funded by Lakehead University graduate student scholarships and a NSERC PGS-D awarded to N. Serediak. The authors sincerely thank staff in Region 9 of the USDA Forest Service, specifically Trent Wickman, Dale Higgins, and Jim Barrott for immense help with supplying data, constructive edits, and keen interest.

4. Development of a simple model for estimating acid neutralizing capacity in northern Wisconsin seepage lakes

4.0 Abstract

Quantifying acid inputs aids the management decision to set critical loading limits for poorly buffered lake systems. The challenge of predicting acid neutralizing capacity (ANC) in many small seepage lakes stems from difficulty in characterizing acid inputs and a lack of the data required to calibrate dynamic mass balance models. The ability to integrate data from other monitoring sources can improve modelling efforts in predicting the ANC of seepage lakes in data sparse areas. Available in-lake data from seven seepage lakes in northern Wisconsin, USA, in combination with public domain monitoring data were used to develop pattern matches to in-lake ANC based on area weighted charge balances. Charge balance combinations that incorporated area weighted input from saturated soils following dry periods worked best. All trajectory matches were evaluated using maximum likelihood methods; the charge balance combinations that best fit available data were then used as x-values in simple linear regression. Likelihood results from linear regression had an $R^2_{adj} = 0.49$ between observed and expected values, with slope = 1. Our results suggest that northern Wisconsin seepage lakes rely on internal ANC production for buffering and are vulnerable to acidification from: 1) direct deposition when dilution effects are high, and 2) associated wetlands when dry periods are followed by precipitation sufficient to generate runoff.

4.1 Introduction

Freshwater lakes acidify when the buffering capacity of the lake water can no longer neutralize acid inputs. Complete absence of buffering capacity occurs when acid neutralizing capacity (ANC) is exhausted, and protection for aquatic ecosystems usually requires system-specific ANC targets greater than zero. In freshwater systems, critical loads (CLs) are often established using ANC as a chemical point of reference (Galloway and Dillon, 1983; Pardo, 2010). The classic definition of a CL is '...the highest level of pollutant deposition which a system can tolerate below which no damage occurs, within the limits of current knowledge.' (Nilsson and Grennfelt, 1988). Although the United States is still without a formal CL agreement, interim guideline values for freshwater ANC limits that specify acidification thresholds are in place (Table 4.1). Despite legislation and amendments that have yielded decreased atmospheric sulfate deposition (Stoddard *et al.*, 1999; Lynch *et al.*, 2000), many freshwater systems have shown little to no recovery in either ANC or pH (Webster and Brezonik, 1995; Jeffries *et al*., 2003; Eimers *et al*., 2007).

Table 4.1. Interim in-lake limits (critical thresholds) for freshwater surface systems (Adams *et al*., 1991); deposition should not decrease freshwater chemistry below these levels. Note that 1 µeq L^{-1}= 50 µg L^{-1} $CaCO_3$.

ANC	*Color code*	*as mg* L^{-1} *$CaCO_3$*	*Impact on aquatic biota*
25 µeq L^{-1}	Green line value	1.25	Not apparent
10 µeq L^{-1}	Chronic red line value	0.5	Chronic effects after prolonged exposure
0 µeq L^{-1} and pH ≤ 5.5	Episodic red line value	0	Acute effects, especially for fish at susceptible life stages (*e.g*. fry)

A challenge in setting CL limits for freshwater lakes is the inherent difficulty in predicting lake ANC in response to acid input. Modelling acidification as ANC response requires an understanding of inputs in terms of both content and pattern, and the biochemical acid neutralizing processes within the lake and its watershed. However, input patterns in certain systems have proven difficult to define; the timing of acidification events in poorly buffered, soft-water seepage lakes has been a particular challenge to characterize. Episodic acidification has been identified as originating from natural sources such as wetlands, complicated by effects of climate and local hydrology (Eilers and Bernet, 1997; Webster *et. al*., 1993; Devito *et. al*., 1999). Acidification can be dominated by deposition, watershed or organic acid inputs (Baker *et. al*., 1991), requiring the identification of all significant input sources as contributing factors. Pollution risk from both energy development and agricultural sectors increases the need to better describe why and how seepage lakes acidify and whether or not the processes that contribute to decreasing ANC are predictable.

Although multiple models exist with which to calculate CL targets to prevent acidification, *e.g.*, MAGIC (Cosby *et al.*, 2001), SMB (Sverdrup and De Vries, 1994), data requirements are often onerously high to support estimation of multiple parameters. These requirements for predictive modelling seemingly preclude estimation of acid input patterns and ANC for lake systems that have not been intensively sampled. Prediction, however, is important to provide a basis for acidification management strategies, as seepage lakes represent the majority of Wisconsin's 15,074 documented lakes (Wisconsin DNR, 2009). Where detailed time series data are absent for in-lake measurements, long term, publicly available data products can be used to complement sparse, local records.

The objectives of this research were: 1) to develop spatially weighted combinations of acid inputs using interpolated long term monitoring data and use these inputs in a charge balance approach to estimate lake ANC concentration, 2) to evaluate combinations of weighted acid inputs best supported by in-lake ANC data, 3) to develop a statistically based model for lake ANC concentration estimation during frost-free months using weighted combinations, and 4) to suggest possible reasons for the inconsistency of low lake ANC concentration in some northern seepage lakes despite steady decreases in the acidity of wet deposition inputs.

4.2 Methods

Data and site description

The Rainbow Lakes Wilderness (RLW) area (Figure 4.1) is a 2585 ha parcel of land in the Chequamegon-Nicolet National Forest in Bayfield County, Wisconsin, USA. It is located in a designated Class I area under provision 162(a) of the Clean Air Act, meaning development within the airshed is not permitted to significantly reduce air quality (Clean Air Act, 1963). Seven lakes in the RLW area have been intermittently monitored by US Forest Service staff beginning in 1984. Except for one suite of samples from late

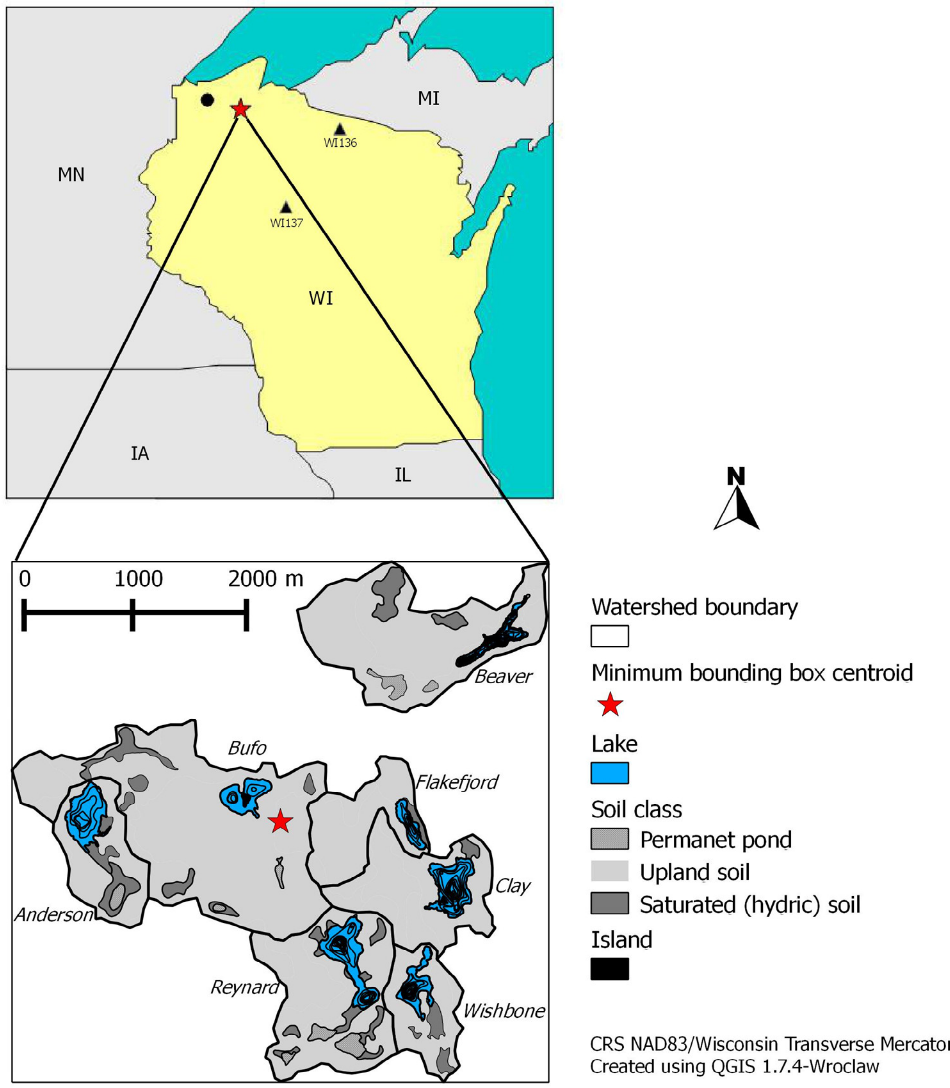


Figure 4.1. Location of the Rainbow Lakes Wilderness (RLW) area, northwestern Wisconsin, US. The minimum bounding box including all seven watersheds is outlined in black in the fly-out and the centroid is the red star. Black triangles in the upper map mark the nearest NADP-NTN stations WI37 (Spooner) and WI36 (Trout Lake), while the black circle denotes the NOAA climate station GHCND:USC00472240 (Drummond, WI).

winter in 1984, all other samples were collected during the open water period. Monitoring data include color, pH, ANC and dominant ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}) although data were not collected to the same detail and frequency in every year. The most complete data record was that of ANC, for which data inventory included 168 observations from 1984 to 2011. Values for in-lake ANC (µeq L^{-1}) were determined using a Gran titration on unfiltered water (USGS, 2008). Since the equivalence point is extrapolated from curve data collected prior to reaching a measured endpoint, ANC may reach negative values. Gran titrations are recommended for samples with low anticipated buffering capacity and when there are contributions to ANC from mineral acids, organic acids or other non-carbonate sources (USGS, 2008).

The RLW lakes are small seepage lakes isolated from groundwater and currently unaffected by development, allowing only non-motorized recreational use. Remnants of an old railway bed and former logging roads persist in the area and are now used as hiking trails. The flat to gently rolling topography was formed by Pleistocene glaciation, characterized by deposition of stratified sand and gravel interspersed with numerous small lakes and peat depressions. One exploratory drill hole near the center of the RLW area penetrated just under 182 m of glacial outwash without reaching an aquifer (Cannon *et al*., 1981); as such, lakes in the region are not well connected to groundwater. Upland soils dominate the lake watersheds, typically Spodsols, which are sandy soils with low clay content and very high infiltration capacity; soils in low lying areas are primarily Histosols, which have high organic content and are frequently saturated (USDA-NRCS, 2006). Canopy cover has recovered remarkably since intensive logging and forest fires decimated forest vegetation in the early 1900's. Following logging removal of white pine (*Pinus strobus*), forest cover has regenerated to a deciduous-dominated mix including sugar maple (*Acer saccharum*), aspen (*Populus* spp.), red maple (*Acer rubrum*), basswood (*Tilia* spp.), oak (*Quercus* spp.), hickory (*Carya* spp.) interspersed with coniferous species such as red pine (*Pinus resinosa*), northern white cedar (*Thuja occidentalis*), white pine, jack pine (*Pinus banksiana*), spruce (*Picea* spp.), and balsam fir (*Abies balsamea*) (Haugen *et al*., 1998).

Geographic information

A geographic information system (GIS) was constructed using Quantum GIS (QGIS) (Quantum GIS, 2012). Lake bathymetry was digitized from scanned copies of the State of Wisconsin Lake Survey Series contour maps directly into GoogleEarth™, exported to QGIS as KML files and projected to NAD 1983 Wisconsin Transverse Mercator. The GIS layers for soils, vegetation and elevation were obtained from various sources through the USDA-NRCS Geospatial Data Gateway. The assembled GIS was used to calculate areas and volumes of relevant geophysical features (Table 4.2); calculated values were then used as deposition weighting factors for interpolated precipitation data. Although a digital elevation model was available, the low relief and hummocky terrain of the RLW area challenged the software's ability to reliably determine watershed area. As such, all watersheds were delineated by Mr. Dale Higgins, USDA Forest Service Hydrologist with the Chequamegon-Nicolet National Forest.

Table 4.2. Physical features of the Rainbow Lakes Wilderness (RLW) systems. Saturated soils were totalled from all hydric soils plus small, permanent ponds for each watershed area. Total upland soil is 100 minus percentage of saturated soil.

Lake	*Perimeter (m)*	*Surface Area (m^2)*	*Volume (m^3)*	*Maximum Depth (m)*	*Watershed Area (m)*	*Saturated Soil (%)*
Anderson	2435	129000	1636000	12.2	1638000	29.7
Beaver	2452	69600	683000	11.9	686000	8.0
Bufo	1557	82000	427000	11.9	429000	6.6
Clay	2092	130000	1850000	13.7	1852000	3.0
Flakefjord	1197	42000	294000	6.1	296000	6.0
Reynard	2511	143400	1277000	13.7	1279000	6.4
Wishbone	2330	70500	662000	12.2	664000	14.5

Charge balances

Although carbonate alkalinity is often equated with buffering capacity, the Acid Neutralizing Capacity (ANC) is a more explicit measurement of the total buffering capacity of a water body. The ANC value incorporates carbonate alkalinity, the buffering contributions of weak organic and inorganic acids (*i.e*. their conjugate bases) and the acidic effects of metal species (Eq. 1).

$$\begin{aligned}ANC = (&[\text{Carbonate alkalinity}] + \\ &[\text{Conjugate base of weak organic and inorganic acids}]) - \\ &([H^+] + [\text{Acidic metal ions}])\end{aligned} \quad (1)$$

Using a charge balance approach, ANC can also be defined as the difference between the cations of strong bases and the anions of strong acids (Stumm and Morgan, 1981). With this method, a charge balance in units of microequivalents per liter ($\mu eq\ L^{-1}$) was used to calculate the difference between atmospheric wet deposition inputs of strong acid anions and strong base cations as a proxy of ANC atmospheric input and its contribution to the overall buffering capacity of a lake (Eq. 2) :

$$ANC = (2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+]) - (2[SO_4^{2-}] + [NO_3^-] + [Cl^-]), \text{ or} \quad (2)$$
$$ANC = [\text{strong base cations}] – [\text{strong acid anions}]$$

Ions in Eq. 2 are routinely reported following chemical analysis of wet deposition collected as part of the National Atmospheric Deposition Program (NADP) (Lamb and Bowersox, 2000). Ion deposition inputs (eq/L) were weighted by area to the watershed as a whole as well as to subwatershed areas (*i.e*. lakes, upland soils and saturated soils) by using interpolated precipitation estimates (mm subsequently converted to m), multiplied by respective area (m^2), then multiplied by 1000 (1 m^3 = 1000 L) to calculate area weighted deposition inputs. Final balances were converted to $\mu eq\ L^{-1}$ relative to estimated total lake volume for direct comparison with in-lake measurements.

Standard NADP measurements do not include dry deposition, which is notoriously difficult to quantify. Although important as a terrestrial input, contributions of dry deposition are not a large portion of total atmospheric inputs to lakes, especially when lake surface area is small and uncertainty in determination is high (Wesely and Hicks, 2000). However, the following approach is recognized as a biased underestimate of potential acid inputs when unmeasured dry deposition is a large fraction of total deposition, especially in terrestrial zones that are connected to lakes.

Component combinations and area-weighted charge balances

Since temperate lake systems are defined by seasons that affect both input patterns and internal lake dynamics, in-lake ANC was assumed to be heavily influenced by time of year and resultant effects on physical and biological processes. Charge balances formulated with input from various spatial components began with the full watershed and progressed through sub-watershed component combinations (Table 4.3). For each input combination, component weighted charge balances were added to equal a single-value estimate of total acid equivalents reaching the lake as a proxy for in-lake ANC (Eq. 3):

$$ANC_{Estimated} = ANC_{m-1} - (ANC_{Component\ 1} + ANC_{Component2} + \ldots)_m, \qquad (3)$$

where:

$ANC_{Estimated}$ = estimated current month ANC for each lake resulting from the spatially weighted charge balance,

ANC_{m-1} = ANC of the lake from the month prior, and

$(ANC_{Component} + \ldots)_m$ = sum of area-weighted input charge balances for the current month from specified components

Each calculated input charge balance was weighted to a component area identified by GIS polygon to represent different spatial scales: entire watershed, upland soil, lake surface area, and saturated soil. Charge balance inputs from snow meltwater were assumed to occur in one pulse in the first frost-free month of each water year, and were compared using three different area weighting components: entire watershed area, lake surface area alone, and area of saturated soil plus lake surface area. For the start of each water year, lake spring turnover was assumed complete and weighted input components were subtracted from the estimated spring ANC value (see next section). For each subsequent open water month, the ANC input (positive or negative, based upon charge balance calculations for that month) was subtracted from the ANC of the month prior. Fall turnover was assumed to occur during the final month of the open water season; as such, at the end of each open water period the ANC value was returned to the spring ANC value calculated for that particular year.

Table 4.3. Descriptions of component combinations (CCs) examined using simulated annealing in the likelihood package (RStudio v. 0.97.551). All components are precipitation weighted wet deposition charge balances (eq L^{-1}) multiplied by GIS polygon area (m^2) and converted to µeq L^{-1}. Combinations were selected to represent inputs based on spatial extent (*e.g.*, complete watershed, lake surface, saturated soils) and time (*i.e.*, frozen or frost-free period).

CC	*Balance components (all units in* µeq L^{-1}*)*
1	Spring ANC – (watershed snowmelt) – (watershed frost-free runoff)
2	Spring ANC – (watershed snowmelt)
3	Spring ANC – (lake snowmelt) – (frost-free deposition to lake)
4	Spring ANC – (lake and saturated soil snowmelt) – (frost-free deposition to lake)
5	Spring ANC – (lake and saturated soil snowmelt) – (frost-free deposition to lake) – (frost-free runoff from saturated soils weighted by organic acid estimate)
6	as CC 5 but with runoff from saturated soils only occurring once an estimated spill threshold reached
7	as CC 5 but saturated soil runoff also includes estimate of acidity from drought-induced oxidation
8	as CC 5 but saturated soil runoff only includes estimate of acidity from drought-induced oxidation
9	as CC 5 but with an estimate of seasonal carryover of oxidation acidity when a dry autumn is followed by a dry winter

Saturated soils in two of the study watersheds (Beaver and Bufo) were more distant from the lake edge than was typical for the other lakes (Figure 4.1). For these two lakes, a distance decay weighting was used as in Canham *et*. *al*. (2004) to accommodate reduction of pulse impacts from the longer flowpath. Acid inputs were multiplied by the inverse of the shortest line length (m) between the two nearest edges of saturated soil and lake surface polygons. For Bufo Lake, the saturated soils appeared to be linked in an arc; as such, only the nearest leading edge of the closest polygon was used to calculate the weighting measure.

Hydrology and water chemistry

The RLW area is situated in a region of only sparse local gauges. Neither precipitation volume nor deposition chemistry is locally monitored. Hence, these inputs were interpolated from publicly available data collected by national networks. Chemical deposition data were obtained by open-access download through the National Trends Network, a component of the NADP (NADP, 2011), from the two nearest long term monitoring stations, WI136 and WI137 (Figure 4.1). Because wet deposition chemistry at NADP sites exists as precipitation-weighted values (Lamb and Bowersox, 2000), an estimate of local RLW precipitation was needed to appropriately weight the data. Using the GIS, the centroid of the minimum bounding box surrounding the watersheds for all seven lakes was determined. Precipitation volumes for the RLW area were then interpolated to the centroid (46.40354 latitude, -91.19487 longitude) using the Parameter-elevation Regressions on Independent Slopes Model, or PRISM (PRISM Climate Group, 2012). For the RLW lakes, interpolation to an area centroid and not to each individual lake was considered acceptable given the resolution of the GIS data and lake proximity. Since lake level elevation measurements were unavailable over the entire period of record, lake volume was estimated as a single value using the contour interval method described in Taube (2000) and in (Eq.4):

$$V = 1/3\ H\ (A_1 + A_2 + (A_1 \times A_2)^{1/2}), \quad (4)$$

where:

V = volume,

H = difference in depth between two successive depth contours,

A_1 = area of the lake within the outer contour,

A_2 = area of the lake within the inner contour

Spring ANC was determined as a fixed value for each individual lake. Mean ANC calculated using all ANC measurements per lake over the period of record was used as an estimate of spring ANC for each lake, respectively (Table 4.4). Stoddard (1987) reported on alkalinity dynamics in a small, high alpine lake with rapid spring flushing due to snowmelt and concurrent loss of ANC due to dilution. While seepage lakes do not flush in this manner, melting snow (or lack of snow) was recognized as an important component in the water budget. To compensate for annual spring dilution and concentration effects from variable snowmelt, the estimated spring ANC for each lake was multiplied by a winter precipitation ratio each year (WPR). The WPR was calculated by adding monthly normal precipitation from all months during the frozen period (mm); this value was then divided by the total PRISM-interpolated precipitation (mm) over the same period of frozen months to arrive at a unitless ratio of maximum snowmelt contribution to lake volume per water year. In years with low snow, the WPR was greater than 1 and spring ANC was higher than average, while the opposite was true for wet years. For each water year, spring ANC was reset to the average ANC for each lake, then multiplied by the WPR to represent an assumed annual spring turnover.

Potential buffering capacity from mineral weathering of RLW soils is low given their high sand content. As well, input of buffering capacity from the watershed to the lake is only meaningful when 1) contact time between precipitation and land area is sufficient to generate mineral dissolution products and 2) flow reaches the lake. The hydrology of the RLW lakes is such that little surface runoff is likely to occur during frost-free months from the sandy upland soils that comprise the majority of RLW lake watersheds (USDA-

NRCS, 2006).

Table 4.4. Descriptive statistics for ANC (μeq L^{-1}) in the RLW lakes for all samples collected per lake over the entire period of record (1984-2011). Abbreviations represent standard deviation (sd) and coefficient of variation (cv).

Lake	*Maximum*	*Minimum*	*Mean*	*sd*	*cv*
Anderson	35.9	-4.3	16.5	10.0	60.3
Beaver	72.9	26.1	55.7	13.2	23.6
Bufo	34.6	-8.8	16.6	11.5	69.6
Clay	60.3	8.4	36.5	11.8	32.3
Flakefjord	78.5	40.3	55.5	10.4	18.8
Reynard	38.8	-5.6	23.5	11.2	47.7
Wishbone	51.8	4.1	29.8	12.5	41.8

Evaporation and transpiration (or evapotranspiration, ET) represent the major components of water loss in seepage systems. A simplified Penman equation (Eq. 5; Valiantzas, 2006) was used to estimate ET, weighted to surface area by cover type (Table 4.5) in the RLW area:

$$ET = 0.051\,(1-\alpha)R_S\,(T_{mean}+95)^{1/2} - 2.4(R_S\,R_A^{-1})^2 + 0.75(T_{mean}+20)(1-(RH\;100^{-1})), \quad (5)$$

where:

ET = MJ m^{-2} day^{-1} and 1 MJ m^{-2} day^{-1} = 0.408 mm/day,

α = albedo, the fraction of light reflected from a surface

$R_S = 0.5(R_A)$ = incoming solar radiation in MJ m^{-2} day^{-1},

$R_A = 3N\sin(0.131N) - 0.95\Phi$ = extraterrestrial radiation in MJ m^{-2} day^{-1},

$T_{mean} = 0.5(T_{max}+T_{min})$ = mean temperature in ^{o}C,

T_{max} = maximum temperature per selected time frame (e.g., daily, monthly, yearly),

T_{min} = minimum temperature per selected time frame,

$N = 4\Phi\sin(0.53i - 1.65) + 12$, $i = 1,...,12$ to represent daylight hours,

Φ = latitude in radians (RLW Area centroid = 0.8099 rad), RH = 200 - (T_{mean} - $T_{dewpoint}$) = relative humidity in %,

$T_{dewpoint}$ = dewpoint temperature in ^{o}C

Temperature (maximum and minimum), dewpoint data and 30-year normals (temperature and precipitation) were also downloaded from the PRISM site and interpolated to the RLW centroid. From the GIS, most saturated soils identified were vegetated and were interspersed with areas of open water; the value for grassland (α = 0.23; Ahrens, 2003) was therefore used as a compromise to reflect the generally higher proportion of ground level vegetation cover per saturated soil polygon.

Table 4.5. Percent composition for five cover classes comprising the terrestrial portion of the RLW watersheds, not including the lake surface. Open category refers to areas of mixed low vegetation, occasionally with visible water corresponding to areas of saturated (hydric) soil. Pond refers to areas of shallow, standing water with < 25% vegetation cover. Category headings correspond to those of the National Land Cover Dataset map 5516 (Wisconsin) (NLCD, 2006).

			Cover composition (%)		
Lake	*Pond*	*Open*	*Deciduous*	*Coniferous*	*Mixed wood*
Anderson	3.5	19.5	77.0	0.0	0.0
Beaver	2.2	2.7	69.0	26.1	0.0
Bufo	0.0	8.3	86.7	5.0	0.0
Clay	0.0	2.0	94.0	4.0	0.0
Flakefjord	0.0	2.5	86.6	10.9	0.0
Reynard	5.6	3.9	88.0	0.0	2.5
Wishbone	0.0	8.0	88.1	3.9	0.0

A range of albedo values have been determined for snow types related to age of snowpack, from old snow (0.40) to new snow (0.95) (Ahrens, 2003). However this level of detail was unavailable for the study lakes. As such an average albedo value of 0.68 was used for all estimates of ET from snow as a compromise between the almost doubled ET if the albedo for old snow was consistently used, compared to low or zero calculated ET using the albedo for new snow. Snow cover was assumed for the four months of December to March inclusive. Volumetric input from snowmelt was assumed to occur in one pulse during the first frost-free month following winter. Rather than use a fixed water year, annual water budgets were divided into frozen and frost-free periods. The number of frost-free days were determined using NOAA National Climatic Data Centre data from climate station number GHCND:USC00472240 (Figure 4.1) located at Drummond, WI, in operation over the period 1970-2005. Frost-free days were counted starting from the last frost in spring to first frost in autumn, with frost defined as maximum temperatures at or below -1^{o} C to avoid any difficulties classifying near zero measurements. Where data were unavailable, values from the two years previous and two years subsequent to the data gap were averaged to provide an estimate, with the exception that 2006-2011 values were conservatively estimated as an average of the final four years of the recorded data range prior to station closure.

Because saturated soils in the region occur in areas of low slope (0-3%), both direct runoff and fill-and-spill approachs (Spence and Woo, 2003; Tromp-van Meerveld and McDonnell, 2006) were used to characterize runoff events; balances were tested comparing runoff from saturated soils as the most likely source areas with (fill-and-spill) or without (direct) a runoff threshold value. Even extremely dry conditions do not lower water levels more than approximately 30 cm in hydric soils due to increases in water tension (USDA-NRCS, 2012). As such, thresholds were estimated over a range of 0-30 cm in 5 cm increments with 20 cm providing a reasonable fit as a maximum while still permitting runoff to occur. Spill thresholds of 0 cm and 20 cm were then used to calculate the cumulative water volume (CWV, m^3) available for runoff in monthly increments. For modelling purposes, runoff in frost-free months was assumed to be complete when either the spill threshold was reached, or when CWV was positive (no threshold). For each month CWV was calculated by subtracting area-weighted ET from precipitation. During frozen months, CWV was restricted to either zero or positive values, since evaporative water loss from frozen soil with depleted or otherwise absent snow cover was assumed negligible. No such restrictions were imposed during frost-free months and positive CWV values represented potential runoff; zero or negative values represented either no runoff or dry conditions, respectively.

Spring ANC for the RLW lakes was assumed to be predominantly influenced by biochemical processes occurring within the lake. This was deemed acceptable for two reasons: first, the lakes are situated in a landscape with weak or non-existent terrestrial sources of ANC external to the lake and second, despite the lack of watershed sources positive ANC values are measurable in the lake. One suite of lake chemistry samples taken prior to the end of the frost-free period show not only detectable ANC, but some of the highest levels per lake (Figure 4.2). As such, ANC production was assumed to be biological in origin (*e.g.*, sulfate or nitrate reducing bacteria producing bicarbonate limited only by substrate availability). This is similar for systems measured in Canada (Cook *et al.*, 1986) where the bulk of the ANC was produced in-lake in several systems. Although models exist with which to estimate spring ANC from internal loading following turnover (Kelly *et al.*, 1987; Baker and Brezonik, 1988) they require more data than were available.

No in-lake information was available for nutrients in terms of concentration, uptake or production. Effects of nitrate inputs were assumed to be a worst-case estimate (*i.e.*, no uptake), and 'ANC neutral' in the following year. Although the chemistry of nitrate suggests including inputs as a buffering effect when consumed as a nutrient, no information was available in this regard. As such, nitrate was included in the direct deposition charge balance as a weak conjugate base of strong acid, but was assumed to provide no buffering as a result of biological uptake.

Acid inputs (*i.e.*, ANC depleting inputs) from saturated soils represented a large unknown. Values from the peatland acidity budget developed by Wood (1989) were used to estimate acid equivalents under three scenarios: export of organic acids with and without a spill threshold and export of acidity generated from oxidation events (*i.e.*, drought). For organic acids, Wood (1989) found no differences in equivalent concentrations between open water months after runoff volume corrections. Although color has been used as a proxy to estimate DOC (Molot and Dillon, 1997), it was not routinely available in the lake chemistry data set and not available from wetlands. Export of organic acids was therefore estimated at 20 μeq L^{-1} (Wood, 1989) and multiplied by wetland runoff volume to estimate inputs to each lake.

Following dry summers, Devito *et. al*. (1999) noted high annual SO_4^{2-} in wetland runoff to central Ontario lakes; high SO_4^{2-} exports following periods of drought and rewetting events have also been recorded in wetland-connected streams (Eimers *et al*., 2003; Eimers *et al*., 2007). Wood (1989) provided an areal estimate of acidity from oxidation of saturated soil of 16.3 μeq m^{-2}. To estimate the area of dried hydric soil for each RLW lake, a ratio was used when CWV was a loss (*i.e*., a negative value) per month for the open water season (Eq. 6); the estimate of dried soil was then multiplied by the areal oxidation acidity value (Eq. 7). The estimate of acidity from oxidation was included in monthly balances over the frost-free period only when CWV in subsequent months was positive. No threshold value was applied to oxidation weighted runoff estimates since doing so removed them from the balance *i.e*., applying a threshold for oxidation products did not ever result in a positive CWV high enough to equal flow greater than threshold. To assess potential carryover effects when CWV was negative in the last frost-free month of the previous autumn, for one combination this value was carried forward as a start value for the next open-water season. In all other component combinations, no starting deficit was assumed.

$$DSS = -1(-CWV) \times SSA \times (SSV)^{-1} \qquad (6)$$

where:

DSS = dried saturated (hydric) soil in m^2,

CWV = negative cumulative water volume in m^3,

SSA = total saturated soil area in m^2,

SSV = total saturated soil volume at threshold in m^3

$$OA\ (\mu eq) = DSS \times 16.3\ (\mu eq\ m^{-2}) \qquad (7)$$

where:

OA = oxidative acidity in μeq

Galloway (1995) warned of time-delayed effects of ammonium on ANC based upon uptake or nitrification, as acidity is generated when ammonium is consumed directly as a nutrient, or when nitrification occurs. Under conditions where plant growth or nitrate reducing bacterial activity is limited, nitrate uptake would be insufficient to balance generated acidity. The most likely scenario for an accumulation of acid following nitrification was assumed to be drought, as uptake of nitrate for growth is limited when water is limited. Although model combinations weighting saturated soil acidity from nitrogen components were tested and were moderately successful in three lakes, nutrients are rarely, if ever, exported from ombrotrophic peatlands in large amounts except in snowmelt (Verry, 1997). As such, these data are not presented here.

Statistics

Both public domain and available in-lake data were used to establish trajectory matches between balances of different components (*i.e.*, input formulations) and measured lake ANC values. This method of comparison incorporated both process (ecological) and observation (analytical) error. For comparisons of trajectory matches, no parameters were estimated beyond standard deviation and maximum likelihood methods were used since they work well with ecological data, accommodate autocorrelation, and permit user-defined distributions. All statistical analyses were completed using RStudio v. 0.97.551. Likelihood methods require identifying a suitable probability density function for y-values; distribution and variance of lake ANC data were examined using tests for normality (Shapiro-Wilks test) and homogeneity of variance (Bartlett's test), respectively. Data points were examined for removal as outliers using a maximum Cook's distance of 0.5. Evaluation of best matches between calculated *vs* measured ANC were made using the likelihood package with a normal probability density function. From the balance combinations that provided the best trajectory fit to the available ANC data, two additional parameters were estimated as coefficients in standard linear regressions of the form $y = ax + b$. The Durbin-Watson test in the forecast package was used to test residuals for autocorrelation in the final model.

4.3 Results

Over the entire monitoring period, some of the lowest lake ANC occurred during periods of the lowest recorded wet deposition acid inputs and the highest in-lake averages occurred during periods of the highest recorded wet deposition acid inputs (Figure 4.2). Although variable over time, the seven lakes showed reasonable between-lake synchrony of ANC within individual sample years (Figure 4.3). In-lake ANC data were found to be normally distributed (Shapiro-Wilks normality test $W = 0.99$, $p = 0.15$) with homogeneous variance (Bartlett's test $K = 2.38$, $p = 0.86$ with 6 d.f.). Results of all trajectory match comparisons between component combinations (CC 1 - 9) indicate the best trajectory match (CC 8) incorporated snowmelt from the lake and saturated soils, direct deposition to the lake, and frost-free saturated soil runoff weighted by acidity from oxidation (Table 4.6). Trajectory matches with the poorest fit were those incorporating the watershed as a whole (CC 1,2) and those including estimates of acidity from direct runoff of organic acids from saturated soils (CC 5) (Table 4.6).

Restricting organic acid weighted runoff from saturated soil with a threshold value essentially collapsed CC 6 to that of CC 4 even when an optimal threshold value was chosen. As such, CC 6 was not considered as a separate model candidate. The regressions compared using the best fit trajectory matches (CC 3, 4, and 8) showed only marginal differences between each of the three linear models and all were significant at $p < 0.001$ (Table 4.7). Since maximum likelihood results are only comparable between model runs using identical data sets, all data points were

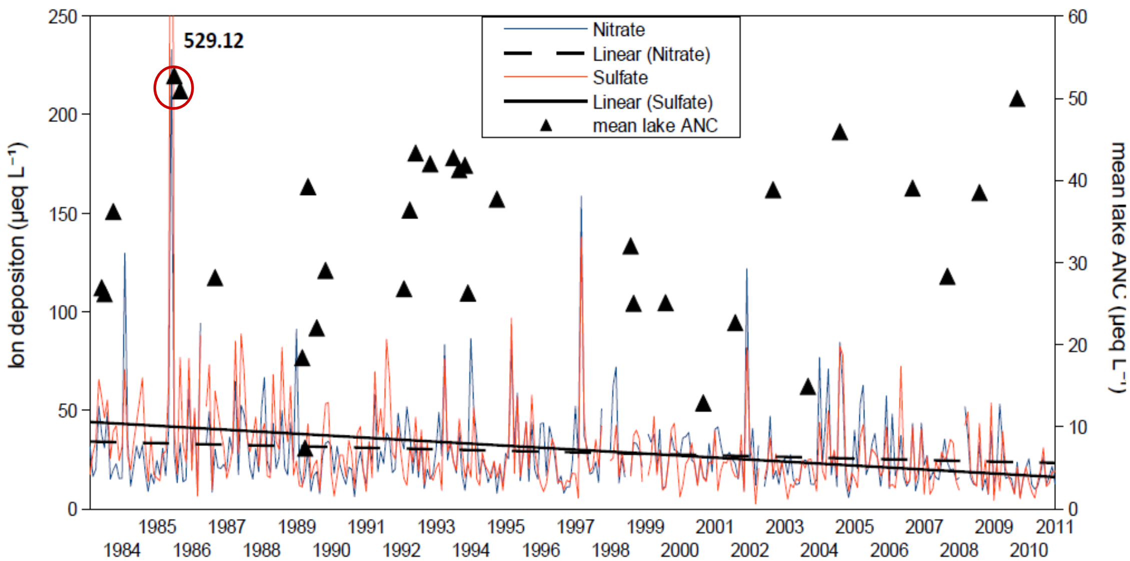


Figure 4.2. Time plot of SO_4^{2-} and NO_3^- interpolated wet deposition to the RLW area, including trend lines and points of mean lake ANC. Value for one extremely high SO_4^{2-} measurement listed to right of truncated peak. Highest measured in-lake ANC values (red circle) occurred during years of highest recorded mineral acid wet deposition. Decreased inputs of SO_4^{2-} and NO_3^- wet deposition to the RLW systems have not translated into consistently increased buffering capacity as in-lake ANC on an annual basis. Values for mean ANC (µeq L^{-1}) are averages from all seven lakes by sample year.

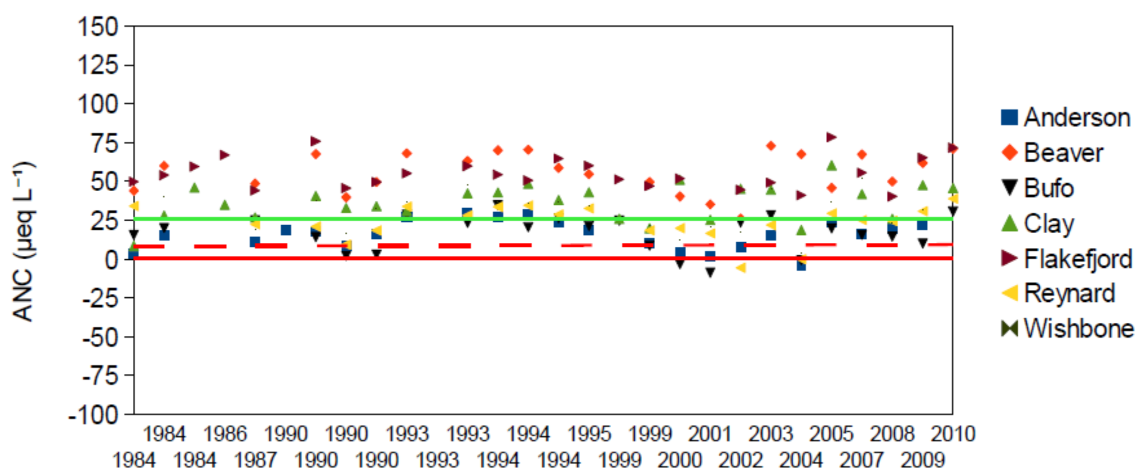


Figure 4.3. Plot of ANC (µeq L^{-1}) per lake showing ranges in variation between lakes over sample years. Although not constant, relative ANC concentration is very similar between lakes. Note that the x-axis is not a true time series; years are displayed at equal intervals in order of successive sampling event. Horizontal lines represent current CL guideline values below which deposition effects are presumed chronic (dashed red line) or acute (solid red line). Values above the solid green line are presumed to have no negative effect (Adams *et al.*, 1991).

Table 4.6. Results of all trajectory matches using component combinations listed in Table 4.3. For these comparisons, slope corresponds to the best fit line between observed and expected values passing through the origin. Since no intercept was estimated for CCs at this stage, negative values for R^2_{adj} occurred since comparisons were made between observed data and unfitted models. Best CC matches to in-lake ANC are bolded. Abbreviations stand for maximum likelihood estimator (MLE) and Akaike Information Criterion corrected for small sample sizes (AIC_{corr}).

CC	*MLE*	AIC_{corr}	*sd (of MLE)*	R^2_{adj}	*slope*
1	-911.1	1824	54.84	-7.27	0.18
2	-842.2	1686	36.39	-2.64	0.55
3	**-700.3**	**1403**	**15.63**	**0.33**	**0.86**
4	**-703.1**	**1408**	**15.90**	**0.30**	**0.88**
5	-950.5	1903	69.31	-12.21	0.20
6	**-705.0**	**1412**	**16.08**	**0.30**	**0.89**
7	-951.3	1905	69.66	-12.34	0.18
8	**-706.3**	**1415**	**16.20**	**0.28**	**0.95**
9	-951.5	1905	69.74	-12.34	0.17

used in each analysis (*i.e.*, each model was evaluated against all 168 discrete measurements of in-lake ANC). No measured values had a Cook's distance greater than 0.5, thus no data were removed as outliers. Residuals showed no remaining autocorrelation from Durbin-Watson tests (forecast package) for linear models using CC 3 (DW = 1.79, p = 0.14), CC 4 (DW = 1.74, p = 0.08) and CC 8 (DW = 1.82, p = 0.23)(Figure 4.4). A plot of observed versus expected ANC for the model incorporating CC 8 is shown (Figure 4.5). The model did not predict acute ANC but did predict green line violations 20 out of 24 times (83% efficiency) in the RLW lake with the lowest average ANC (Figure 4.6).

Table 4.7. Results of the three linear models of the form y = *a*x + *b*, evaluated using likelihood methods. All models were good candidates with no statistical differences. Of the three, the model incorporating CC 8 included the most acid input components in the area-weighted charge balance and came closest to approximating low ANC events.

CC	*Intercept (a)*	*Coefficient (b)*	*MLE*	*AIC_{corr}*	*sd (of MLE)*	*R^2_{adj}*	*slope*
3	10.00	0.65	-677.99	1362.14	13.70	0.48	1.00
4	11.60	0.63	-679.56	1265.24	13.73	0.47	1.00
8	14.61	0.63	-676.38	1361.00	13.59	0.49	1.00

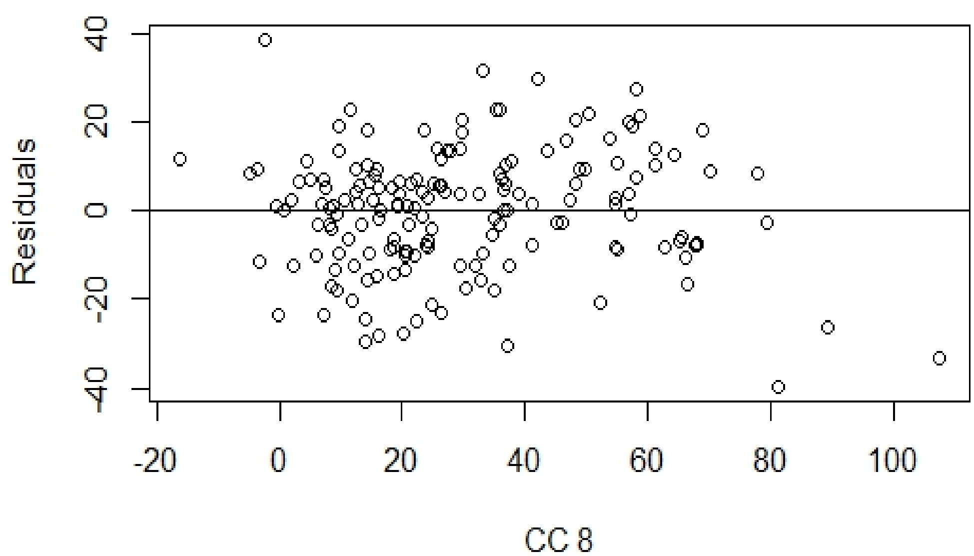


Figure 4.4. Residuals of the simple regression using the best component combination (CC 8). The residuals show no strong patterning supporting the use of a linear model; contrasts with CCs 3 and 4 show very similar patterns. Values below the line on the right side of the plot suggest that this model as it stands overestimates extremely low values of in-lake ANC.

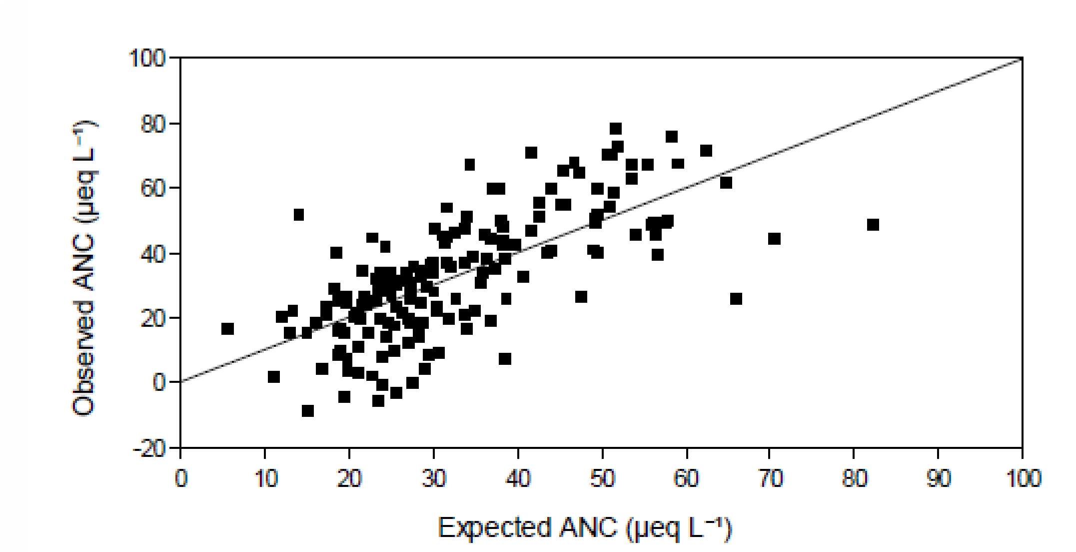


Figure 4.5. Plot of observed versus expected values of in-lake ANC (µeq L^{-1}) for the third linear model incorporating the best trajectory match of CC 8.

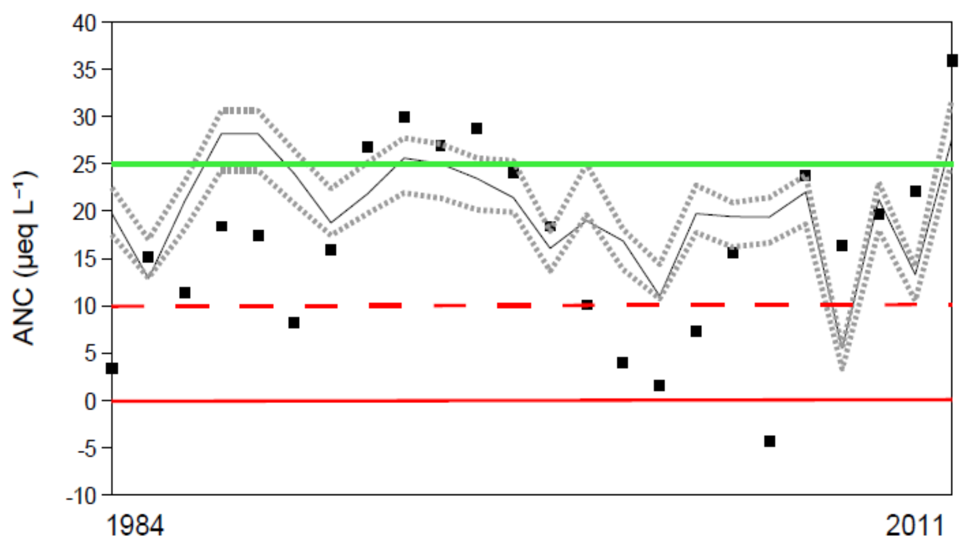


Figure 4.6. Plot of fitted model values from the best component combination (CC 8) for Anderson Lake. The x-axis is not a true time series and data are presented at equal intervals over the period of record to compress graph size. Solid black squares are measured Anderson in-lake ANC, while the black line is the fitted model output. Dashed grey lines equal upper and lower support intervals (analogous to confidence intervals). Colored lines are current CL guideline limits as per Table 4.1 (Adams *et al.*, 1991).

4.4 Discussion

Our results confirm that for sensitive seepage lakes, publicly available long-term monitoring data can be combined effectively with limited in-lake data to estimate lake ANC during the frost-free period. Area-weighted charge balances provide a good trajectory match to measured ANC when the best component combination is incorporated. Statistical assessment of weighted charge balances identify pulsed runoff from connected wetlands as the watershed component that most improves model fit to the lowest in-lake ANC. This suggests that the area of hydric soil dried and oxidized prior to runoff events is an important indicator of acid input potential. Component combinations in the final linear model also supports the assertion of Canham *et al*. (2004) that wetlands are 'well-plumbed' with respect to runoff, although our results suggest that this is not as direct runoff. Even in low-slope wetland areas, the best model fit is obtained when P – ET is required to be greater than a spill threshold for runoff to occur. Performance of the fitted model suggests that long term monitoring products can be used to estimate ANC during frost-free months. Prediction of extreme events may be further improved with better empirical measurements of acid inputs from oxidized wetland soils.

Effects of acid input pulses from oxidation (drying) events have also been recorded from other similarly weakly buffered systems in North America, although in areas of higher mineral acid deposition relative to RLW (Devito *et al*., 1999; Jefferies *et al*., 2002). Jefferies *et al*. (2002) have suggested that wetlands may be sinks for accumulated acid inputs that subsequently become sources following drying of saturated soils. Eimers *et al*. (2003) measured high SO_4^{2-} in streams draining wetlands following drying and re-wetting cycles, which was not mirrored in upland runoff, and Aherne *et al*. (2008) have suggested that recovery from acidification is hampered by climate effects, with SO_4^{2-} export increasing following drought events. Our results support the view that wetlands can be an intermittent source of acidity to freshwater systems, and that dramatic increases in wetland runoff acidity are strongly related to antecedent climatic and hydrologic conditions. These results also suggest inclusion of an extra source of watershed acidity in addition to those proposed by Baker *et al.* (1991): where no mine waste or naturally occurring high acid soils exist, pulsed runoff from oxidized wetland soils following periods of excessive drying can also depress lake ANC when subsequent precipitation rapidly transports strong acid oxidation products to receiving water.

Dilution effects, especially from snowmelt, can also leave seepage systems vulnerable to acidification from direct deposition. Comparisons of SO_4^{2-}:base cation concentration ratios (after Baker *et al.*, 1991) from available in-lake ion data suggest that RLW lakes are largely watershed dominated (*i.e.*, acid inputs from watershed sources via runoff) but can also be intermittently deposition dominated (*i.e.*, acid inputs from direct deposition to lake). During times of large spring snowmelt events, dilution effects greatly decrease spring ANC, increasing the susceptibility to wet deposition mediated acidification over the open water season. However, after incorporating dilution effects using a snowmelt precipitation ratio, the lowest measured in-lake ANC did not occur in years of high snowmelt from the RLW watersheds. As well, direct deposition to the lake surface is the primary means of acid input to RLW lakes during the open water months, but represents a small proportion of total acid inputs. Thus, acidification from direct deposition is not implicated at current levels of SO_4^{2-} and NO_3^- wet deposition. However, it should be noted that very high snowmelt volumes can result in open water spring ANC being lower than current guideline limits based on dilution effects alone.

The use of a water year defined by frozen and frost-free periods instead of a fixed length is recommended, as it greatly improved trajectory matches and model fit compared to the use of rigid annual measures. However, not enough information was available to allow all modeling factors to vary in a similar manner; runoff spill thresholds were fixed, and static weighting values were used for spring ANC, wetland organic acids, and acid equivalents released from dried hydric soils. Better empirical measures of currently fixed values could improve estimates of lake ANC by 1) better predicting runoff occurrence following drought and re-wetting events, 2) beginning open water monthly ANC balances from a more informed position, and 3) refining the wetland runoff oxidation weighting factor to prevent underestimation of acid input potential and improve estimates of acute ANC (< 10 µeq L^{-1}).

4.5 Conclusion

In summary, area-weighted charge balances using long-term monitoring data are effective in estimating low ANC at chronic levels (< 25 µeq L^{-1}) in data sparse areas. Results of component combinations suggest that poorly buffered northern Wisconsin seepage lakes are most vulnerable to acidification when:

- dilution effects from snowmelt are high
- spring ANC is low (internally mediated)
- oxidation products are rapidly flushed into the lake following drying events in wetland soils (drought mediated)

The prospect of critical convergences in wetland area, hydrologic state, deposition and drought effects must be considered singly and in combination when determining CLs. Periods of drought should be incorporated as an acidification risk factor for weakly buffered systems when wetlands are present in the watershed.

4.6 Acknowledgments

This work was funded by Lakehead University graduate student scholarships and a NSERC PGS-D awarded to N. Serediak. The authors sincerely thank staff in Region 9 of the USDA Forest Service, specifically Dale Higgins for delineating above and beyond the call of duty and clarifying many points. Special thanks are extended to Janice Burke for gracious and constructive editing.

5. General conclusions

Results of this thesis research support the contention that climate effects and related hydrologic impacts are strong regulators of freshwater chemistry that can lead to deleterious extremes even in low pollution areas. Both direct (*e.g.*, sewage outfalls) and indirect (*e.g.*, non-point source) inputs of anthropogenic pollution are linked to extremely poor water quality. Input from pulsed wetland runoff is also an important driver of acidification in sensitive seepage lakes of the western Great Lakes region, where inputs from connected wetland soils following drought and re-wetting cycles provided a better fit to available in-lake ANC data. Drought intensity and frequency, as well as the proportion of annual rainfall occurring from heavy precipitation events are projected to increase with global climate change in high latitude areas (Kundzewicz *et al.*, 2008). This suggests that extremes in water chemistry driven by hydrologic effects will also increase in both frequency and intensity, resulting in further indirect degradations of water quality from rising temperatures. Temperate systems may be at increased risk for water quality deterioration from climate impacts, since the earlier onset of spring means a longer open water season, and higher temperatures mean increased potential for evaporative loss and wetland drought.

Winter precipitation is also forecast to shift from snow to more rain in many continental regions (Kundzewicz *et al.*, 2008). This could shift the timing of nutrient delivery, specifically NO_3^-, from later to earlier in spring (Casson *et al.*, 2012). The impacts of drought described in Chapter 3 imply that anthropogenic inputs are at risk of having proportionally large negative effects during weather extremes; the critical limit for calculating acid loads requires a much higher margin of safety when high snowmelt volume, drought effects (*e.g.*, increased oxidation in hydric soils) and frost-free season runoff pulses from watershed wetlands are included as risk factors.

Effects of hysteresis are important and relative to type and intensity of chemical extreme. Shallow, freshwater lakes such as Taihu Lake (Chapter 2) are highly susceptible to resuspension of nutrients from bottom sediments when water levels drop further due to drought. Hysteresis has a strongly negative impact when freshwater systems have historical burdens of nutrient loading that can equate to an almost continuous oversupply to the water column. Poorly buffered seepage lakes are susceptible to acidification during pulsed runoff events following drying periods (Chapters 3, 4). Similar historical loads of strong mineral acids were implicated in acid pulses from some Ontario lakes (Yan *et al.*, 1996); extreme acidification could result in a complete absence of hysteresis and an inability to achieve the same ecological function following recovery.

Limited data availability for model development in Chapter 4 necessitated using all data in a single linear regression. However, regression with splines may be a better choice in systems where longer in-lake monitoring records are available, as acidification extremes could be better estimated using regressions that are joined at threshold points and calibrated over different ranges of response. Additionally, crucial spring ANC measurements and model weighting factors for wetland runoff (*e.g.*, acid equivalents) are weakly informed. More detail is needed on re-wetting event runoff pulses from oxidized hydric soils, specifically:

1. effects of drought timing and severity on the chemistry of pulsed wetland runoff
2. likelihood of runoff from wetlands to connected surface water systems
3. effects of early, weak or nonexistent spring turnover on lake buffering capacity to pulsed runoff inputs
4. quantification of runoff constituents, especially nutrients and total acid inputs (strong mineral acids and acid metal species)
5. downstream impacts of pulsed runoff inputs in drainage systems

A dynamic approach to determining water years for hydrologic budgets is recommended. Chapter 4 demonstrates that using a fixed water year is inappropriate when pulsed runoff inputs from dried wetlands are the primary source of acidification risk. Length of the frost-free season has a strong effect on estimates of evapotranspiration, which in turn affects antecedent moisture for consecutive frost-free months. The implication for the term 'seasonal' is that it is a length of time of a fixed and know period (Hyndman and Athanasopoulos, 2013). However, a decomposition of PRISM-interpolated precipitation data (1969-2012) using the stl function in the forecast package (RStudio v. 0.97.551) shows that the seasonal component can change over time (Figure 5.1). These changes must be reflected in water budgets for high latitude areas; the use of a fixed water year fails to incorporate differences in seasonality that are highly relevant to temperate regions.

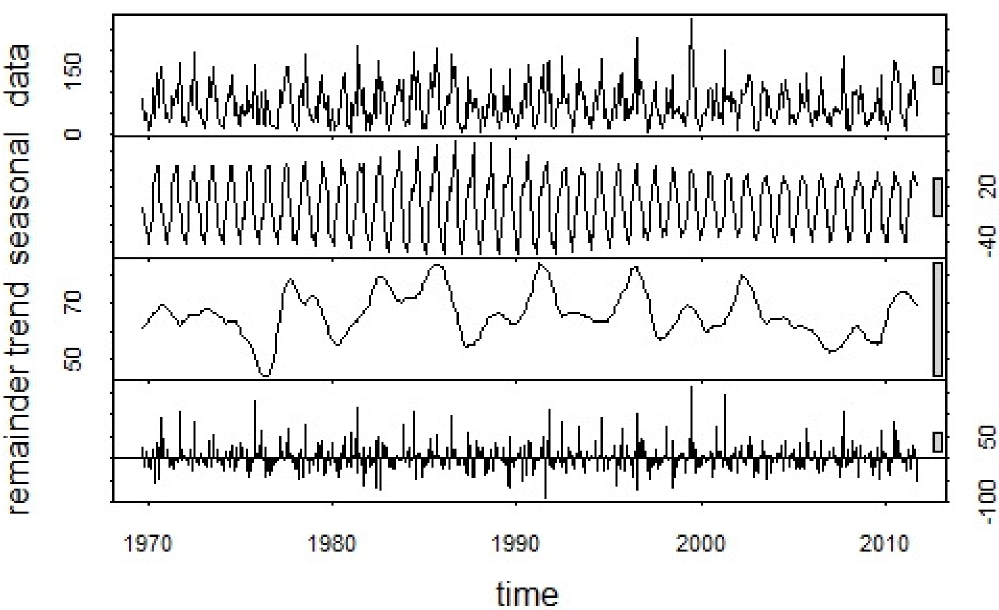


Figure 5.1 Multipart graph of seasonal and trend time series decomposition using loess for PRISM precipitation (mm) interpolated to the centroid of the Rainbow Lakes Wilderness (RLW) area. The bottom three graphs are additive components of the raw precipitation data in the top graph. Grey bars of bottom three plots represent increases in scale relative to grey bar of raw data in top graph. Contributions of trend are minor compared to those of season.

Further improvements in predicting extreme chemical events in freshwater systems are required to improve management practices in limiting direct and indirect negative anthropogenic effects on water quality. Increased long term monitoring is strongly recommended to increase the forecasting potential of chemical extremes relative to hydrology type, specifically: 1) potential transport of point and non-point source inputs from upstream to downstream locations in drainage systems, and 2) localized acidification risks, especially in weakly buffered seepage lakes, or in drainage systems where outflow has ceased.

6. Works cited

Adams, M.B., Nichols, D.S., Federer, C.A., Jensen, K.F. and Parrott, H. (1991). Screening procedure to evaluate effects of air pollution on Eastern Region wildernesses cited as Class 1 air quality areas. General Technical Report NE-151. 33 pp.

Aber, J.D., Nadelhoffer, K.J., Steudler, P. and Melillo, J.M. 1989. Nitrogen saturation in northern forest ecosystems. *BioScience* **39:** 378-386.

Aherne, J., Futter, M.N. and Dillon, P.J. (2008). The impacts of future climate change and sulphur emission reductions on acidification recovery at Plastic Lake, Ontario. *Hydrology and Earth Systems Science* **12**: 383-392.

Ahrens, C.D. (2003). Meteorology today: an introduction to weather, climate, and the environment. Seventh edition, Thomson Brooks/Cole. 624 pp.

Babin, J. and Prepas, E.E. (1985). Modelling winter oxygen depletion rates in ice-covered temperate zone lakes in Canada. *Canadian Journal of Fisheries and Aquatic Sciences*. **42:** 239-249.

Bulgakov, N.G. and Levich, A.P. (1999). The nitrogen:phosphorus ratio as a factor regulating phytoplankton community structure:nutrient ratios. *Archiv für Hydrobiologie* **146:** 3-22.

Baines, S. B., Webster, K.E., Kratz, T.K., Carpenter, S.R. and Magnuson, J.J. (2000). Synchronous behaviour of temperature, calcium, and chlorophyll in lakes of northern Wisconsin. *Ecology* **81**: 815-825.

Baker, L.A. and Brezonik, P.L. (1988). Dynamic model of in-lake alkalinity generation. *Water Resources Research* **24**: 65-74.

Baker, L.A., Herlihy, A.T., Kaufmann, P.R. And Eilers, J. M. (1991). Acidic lakes and streams in the United States: the role of acidic deposition. *Science* **252:** 1151-1154.

Bayley, S.E., Schindler, D.W., Parker, B.R., Stainton, M.P. and Beaty, K.G. (1992). Effects of forest fire and drought on acidity of a base-poor boreal forest stream: similarities between climatic warming and acid precipitation. *Biogeochemistry* **17**: 191-204.

Bell, E.M. and Laybourn-Parry, J. (1999). The plankton community of a young, eutrophic, Antarctic saline lake. *Polar Biology* **22:** 248-253.

Boerner, R.E.J. (1982). Fire and nutrient cycling in temperate ecosystems. *BioScience* **32:** 187-192.

Brooks, K.N., DeBano, L. and Gregerson, H.M. (1997). Hydrology and the management of watersheds, 2nd revised edition. Iowa State Press. 502 pp.

Bryson, B. (2005). A short history of nearly everything, illustrated edition. Anchor Canada Limited. 624 pp.

Brooks, K.N., Ffolliott, P.F., Gregersen, H.M., and DeBano, L.F. (2003). Hydrology and the management of watersheds. Third edition. Blackwell Publishing, Iowa State Press, Ames, Iowa, USA, 574 pp.

Burau, R.G. and Zasoski, R.J. (2002). Soil and water chemistry. University of California Davis SSC 102 124 pp. Retrieved from http://lawr.ucdavis.edu/

Butler, T.J. and Likens, G.E. (1995). A direct comparison of throughfall plus stemflow to estimates of dry and total deposition for sulfur and nitrogen. *Atmospheric Environment* **29**: 1253-1265.

Canham, C.D., Pace, L.M., Papaik, M.J., Primack, A.G., Roy, K.M., Maranger, R.J., Curran, R.P. and Spada, D.M. (2004). A spatially explicit watershed-scale analysis of dissolved organic carbon in Adirondack lakes. *Ecological Applications* **14**: 839-854.

Cannon, W.F., Cameron, C.C., Grosz, A.E., Dunn Jr, M.L., Gazdik, G.C.,and Hill, J.J. (1981). Mineral resources of the Rainbow Lakes Wilderness Area and the Flynn Lake Wilderness Study Area, Bayfield County, Wisconsin. Geological Survey Bulletin 1511. United States Geological Survey Report. 30 pp.

Carlson, R.E. (1977). A trophic state index for lakes. *Limnology and Oceanography* **22:** 361-369.

Carpenter, S.R. (2005). Eutrophication of aquatic ecosystems: bistability and soil phosphorus. *Proceedings of the National Academy of Sciences of the U.S.A.* **102:** 10002-10005.

Carpenter, S.R. and Brock, W.A. (2006). Rising variance: a leading indicator of ecological transition. *Ecology Letters* **9:** 311-318.

Cassara, A. (2008). Measuring eutrophication on a global scale. World Resources Institute, EarthTrends. http://earthtrends.wri.org/updates/node/278 Accessed October 2010.

Casson, N.J., Eimers, M.C. and Watmough, S.A. (2012). Impact of winter warming on the timing of nutrient export from forested catchments. *Hydrological Processes* **26**: 2546 – 2554.

Chang, W.Y.B. (1987). Large lakes of China. *Journal of Great Lakes Research* **13:** 235-249.

Clean Air Act. (1963). The Clean Air Act of 1963. P.L. 88-206. Amended 1967 (P.L. 90-148), 1970 (P.L. 91-604), 1977 (P.L. 95-95) and 1990 (P.L. 101-549).

Cook, R.B., Kelly, C.A., Schindler, D.W. and Turner, M.A. (1986). Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. *Limnology and Oceanography* **31**: 134-148.

Cordell, D., Drangert, J-O., and White, S. (2009). The story of phosphorus: global food security and food for thought. *Global Environmental Change* **19:** 292-305.

Cosby, B.J., Ferrier, R.C., Jenkins, A. And Wright, R.F. (2001). Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrology and Earth Systems Sciences Discussion* **5**: 499-518.

Crowley, W. (1999). Lake Washington Ship Canal. Essay 1444, Historylink.org http://www.historylink.org/. Accessed November 2010.

Debano, L.F. and Conrad, C.E. (1978). The effect of fire on nutrients in a chaparral ecosystem. *Ecology* **59:** 489-97.

Devito, K.J., Hill, A.R. and Dillon, P.J. (1999). Episodic sulphate export from wetlands in acidified headwater catchments: predictions at the landscape scale. *Biogeochemistry* **44**: 187-203.

Dodds, W.K. (2006). Eutrophication and trophic state in rivers and streams. Limnology and Oceanography **51:** 671-680.

Downing, J.A. and McCauley, E. (1992). The nitrogen:phosphorus relationship in lakes. *Limnology and Oceanography* **37:** 936-945.

Dowrick, D.J., Hughes, S., Freeman, C., Lock, M.A., Reynolds, B. and Hudson, J.A. (1998). Nitrous oxide emissions from a gully mire in mid-Wales, UK, under simulated summer drought. *Biogeochemistry* **44:** 151-162.

Dréy, P. and Anderson, B. (2007). Peak phosphorus. Energy Bulletin. http://www.greb.ca/GREB/Publications_files/Peakphosphorus.pdf Accessed January 2011.

Driscoll, C.T. and Postek, K.M. (1995). The chemistry of aluminum in surface waters. In The environmental chemistry of aluminum, 2nd edition., Sposito, G. ed. CRC Press, Boca Raton, FL. 480 pp.

Driscoll, C.T., Driscoll, K.M., Roy, K.M. and Mitchell, M.J. (2003). Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environmental Science and Technology* **37**: 2013-2042.

Eaton, A.E.,. Clesceri, L.S., Rice, E.W and Greenberg, Arnold E. (Eds). 2005. Standard methods for the examination of water and wastewater (centennial edition). American Public Health Association, American Water Works Association and Water Environment Federation joint publication.

Edmondson, W.T. (1977). Trophic equilibrium of Lake Washington. US-Environmental Protection Agency Report 600/3-77-087. August 1977. 35 pp, 3 figures, 3 tables.

Edmondson, W. T. (1991). The uses of ecology: Lake Washington and beyond. University of Washington Press, USA. 372 pp.

Eilers, J.M. And Bernet, J.A. (1997). Temporal trends and spatial patterns in acid-base chemistry for selected Minnesota lakes. Minnesota Pollution Control Agency report. 101 pp. plus appendices.

Eimers, M.C., Dillon, P.J., Schiff, S.L. and Jeffries, D.S. (2003). The effects of drying and re-wetting and increased temperature on sulphate release from upland and wetland minerals. *Soil Biology & Biogeochemistry* **35**: 1663-1673.

Eimers, M.C., Watmough, S.A., Buttle, J.M. and Dillon, P.J. (2007). Drought-induced sulphate release from a wetland in south-central Ontario. *Environmental Monitoring and Assessment* **127**: 399-407.

Ekdahl, E.J., Teranes, J.L., Guilderson, T.P., Turton, C.L., McAndrews, J.H., Wittcop, C.A., and Stoermer, E.F. (2004). Prehistorical record of cultural eutrophication from Crawford Lake, Canada. *Geology* **32:** 745-748.

Elser, J.J., Bracken, M.E.S., Cleland, E., Gruner, D.S., Harpole, W.S., Hillebrand, H., Ngai, T., Seabloom, E.W., Shurin, J.B., and Smith, J.E. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters* **10:** 1135-1142.

Emsley, J. (2000). The 13^{th} element: the sordid tale of murder, fire, and phosphorus. John Wiley & Sons. New York, Chichester, England. 327 pp.

Evans, J.C. and Prepas, E.E. (1997). Relative importance of iron and molybdenum in restricting phytoplankton biomass in high phosphorus saline lakes. *Limnology and Oceanography* **42:** 461-472.

Fernandez, I.J., Rustad, L.E., Norton, S.A., Kahl, J.S. and Cosby, B.J. (2003). Experimental acidification causes soil base-cation depletion at the Bear Brook watershed in Maine. *Soil Science Society of America Journal* **67**: 1909-1919.

Galloway, J.N. (1995). Acid deposition: perspectives in time and space. *Water, Air and Soil Pollution* **85**: 15-24.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., and Cosby, B.J. (2003). The nitrogen cascade. *Biogeochemistry* **53:** 341-356.

Galloway, J. N., & Dillon, P. J. (1983). Effects of acid deposition: the importance of nitrogen. *Statens Naturvaardsverk*.

Giblin, A.E., Likens, G.E., White, D. and Howarth, R.W. (1990). Sulfur storage and alkalinity generation in New England lake sediments. *Limnology and Oceanography* **35**: 852-869.

Government of Canada. (2009). Regulations amending the phosphorus concentration regulations. *Canada Gazette* **143:** http://www.canadagazette.gc.ca/ Accessed February 2011.

Great Lakes Information Network. (2013). Great Lakes shoreline shapefile. Retrieved March 2014 from gis.glin.net/

Hasler, A.D. (1947). Eutrophication of lakes by domestic drainage. *Ecology* **28:** 383-395.

Haugen, D.E., Freeman, P.C. And Theisen, M.A. (1998). The forest resources of the Chequamegon-Nicolet National Forest. U.S. Forest Service Resource Bulletin NC-194. 60 pp.

Hefting, M.M., Bobbink, R. and de Caluwe, H. (2002). Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *Journal of Environmental Quality* **32:** 1194-1203.

Hoagland, P., Anderson, D.M., Kaoru, Y., and White, A.W. (2002). The economic effects of harmful algal blooms in the United States: estimates, assessment issues, and information needs. *Estuaries* **25:** 819-837.

Hu, L, Hu, W., Zhai, S. and Wu, H. (2010). Effects on water quality following water transfer in Lake Taihu, China. *Ecological Engineering* **36:** 471-481.

Hubbert, M.K. (1974). U.S. energy reserves, a review as of 1972; A background paper prepared at the request of Henry M. Jackson, Chairman, Committee on Interior and Insular Affairs, United States Senate, Pursuant to Senate Resolution 45, A National

Fuels and Energy Policy Study: Serial No. 93-40 (92-75), Part 1. U.S. Government Printing Office, Washington, USA. 186 pp.

Hughes, S., Reynolds, B., Hudson, J.A. and Freeman, C. (1997). Effects of summer drought on peat soil solution chemistry in an acid gully mire. *Hydrology and Earth System Sciences* **1**: 661-669.

Hynes, H.B.N. (1975). The stream and its valley. *Verhandlungen des Internationalen Verein Limnologie* **19:** 1-15.

Hyndman, R.J. and Athanasopoulos, G. (2013) *Forecasting: principles and practice***.** Online textbook. http://otexts.org/fpp/. First accessed March, 2013.

IPCC Secretariat. (2008). Climate change and water. Bates, B.C., Kundzewicz, Z.W., Wu, S. and Palutikof, J.P. *Eds*. Technical Paper VI. 210 pp.

Jankowski, T.J., Livingstone, D.M., Bührer, H., Forster, R. and Niederhauser, P. (2006). Consequences of the 2003 European heat wave for lake temperature profiles, thermal stability and hypolimnetic oxygen depletion: Implications for a warmer world. *Limnology and Oceaongraphy* **51**: 815-819.

Jeffries, D.S., Semkin, R.G., Beall, F.D. And Franklyn, J. (2002). Temporal trends in water chemistry in the Turkey Lakes watershed, Ontario, Canada, 1982-1999. *Water, Air and Soil Pollution* **2**: 5-22

Jeffries, D.S., Clair, T.A., Couture, S., Dillon, P.J., Dupont, J., Keller, W. and Weeber, R. (2003). Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition. *AMBIO* **32**: 176-182.

Jungk, A. (2009), Carl Sprengel—The founder of agricultural chemistry: A re-appraisal commemorating the 150th anniversary of his death. *Journal of Plant Nutrition and Soil Science* **172:** 633-636.

Kelly, C.A., Rudd, J.W.M., Hesslein, R.H., Schindler, D.W., Dillon, P.J., Driscoll, C.T., Gherini, S.A. And Hecky, R.E. (1987). Prediction of biological acid neutralization in acid-sensitive lakes. *Biogeochemistry* **3**: 129-140.

Keller, W., Heneberry, J.H. and Dixit, S.S. (2003). Decreased acid deposition and the chemical recovery of Killarney, Ontario, lakes. *AMBIO* **32**: 183-189.

Klausmeier, C.A., Litchman, E., Daufresne, T. and Levin, S.A. (2004). Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature* **429:** 171-174.

Kolka, R.K., Grigal, D.F. and Nater, E.A. (1996). Forest soil mineral weathering rates: use of multiple approaches. *Geoderma* **73**: 1-22.

Krecek, J. and Haig, M. (2006). Headwater wetlands. *In* Environmental Role of Wetlands in Headwaters. Springer, the Netherlands. pp. 1-6.

Kundzewicz, Z.W., Mata, L.J., Arnell, N.W., D�ll, P., Jimenez, B., Miller, K., Oki, T., Şen, Z. and Shiklomanov, I. (2008). The implications of projected climate change for freshwater resources and their management. *Hydrological Sciences Journal* **53**: 3-10.

Lamb, D. And Bowersox, V. (2000). The national atmospheric deposition program: an overview. *Atmospheric Environment* **34**: 1661-1663.

Lawrence, E., Jackson, A.R.W. and Jackson, J.M. (1998). Eutrophication. *In* Longman Dictionary of Environmental Science. Addison Wesley Longman Limited. London, England. pp. 144-145.

Leigh, G.J. (2004). The word's greatest fix: a history of nitrogen and agriculture. Oxford University Press. Oxford, New York, USA. 256 pp.

Lewis, W.M. and Wurtsbaugh, W.A. (2008). Control of lacustrine phytoplankton by nutrients: erosion of the phosphorus paradigm. *International Review of Hydrobiology* **93:** 446-465.

Li, H. and McNulty, S.G. (2007). Uncertainty analysis on simple mass balance model to calculate critical loads for soil acidity. *Environmental Pollution* **149**: 315-326.

Lind, O.T. (1985). Handbook of common methods in limnology, second edition. Kendall Hunt Publishing Co., Dubuque, Iowa, USA. 199 pp.

Lynch, J.A., Bowersox, V.C. and Grimm, J.W. (2000). Acid rain in Eastern United States. *Environmental Science and Technology* **34**: 940-949.

Marcarelli, A.M., Wurtsbaugh, W.A. and Griset, O. (2006). Salinity controls phytoplankton response to nutrient enrichment in the Great Salt Lake, Utah, USA. *Canadian Journal of Fisheries and Aquatic Sciences* **63:** 2236-2248.

Mayer, P.M., Reynolds, S.K., McCutchen, M.D. and Canfield, T.J. (2006). Meta-analysis of nitrogen removal in riparian buffers. *Journal of Environmental Quality* **36:** 1172-1180.

McEachern, P., Prepas, E.E., Gibson, J.J. and Dinsmore, W.P. (2000). Forest fire induced impacts on phosphorus, nitrogen and chlorophyll a concentrations in boreal subarctic lakes of northern Alberta. *Canadian Journal of Fisheries and Aquatic Sciences* **57:** 73-81.

Minnesota Department of Natural Resources (MDNR). (2014). Ecological classification system – northern Superior uplands section. Retrieved March 2014 from dnr.state.mn.us/

Minnesota Department of Natural Resources (MDNR). (1998). Mineral industries of Minnesota including regions of known but undeveloped resources. [map]. Retrieved March 2014 from dnr.state.mn.us/

Minnesota Geological Survey (2006). Geology of Minnesota dominant soil type. [map]. Retrieved February 2014 from mngs.umn.edu/

Minshall, G.W., Brock, J.T., Andrews, D.A. and Robinson, C.T. (2001). Water quality, substratum and biotic responses of five central Idaho (USA) streams during the first year following the Mortar Creek Fire. *International Journal of Wildland Fire* **10:** 185-199.

Minshall, G.W., Cummins, K.W., Peterson, R.C., Cushing, C.E., Bruns, D.A., Sedell, J.R. and Vannote, R.L. (1985). Developments in stream ecosystem theory. *Canadian Journal of Fisheries and Aquatic Sciences* **42:** 1045-1055.

Mitchell, P. and Prepas, E.E. (1990). Atlas of Alberta Lakes. University of Alberta Press, Edmonton, Alberta, Canada. 690 pp.

Mitsch, W.J., and Gosselink, J.G. (2007). Wetlands, 4th Edition. John Wiley & Sons, New York, New York, U.S.A. 600 pp.

Molot, L.A. and Dillon, P.J. (1997). Photolytic regulation of dissolved organic carbon in northern lakes. *Global Biogeochemical Cycles* **11:** 357-365.

National Atmospheric Deposition Program (NRSP-3). 2011. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820. http://nadp.sws.uiuc.edu/

National Atmospheric Deposition Program (NADP). 2014. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820. [maps]. Retrieved February 2014 from http://nadp.sws.uiuc.edu/

National Climatic Data Center: National Oceanic and Atmospheric Administration, Climate Data Online, http://www.ncdc.noaa.gov/. Created September 2012.

National Wetlands Working Group. 1997. The Canadian Wetland Classification System, 2nd Edition. Warner, B.G. and Rubec, C.D.A. (ed). Wetlands Research Centre, University of Waterloo, Waterloo, Ontario, Canada. 9 pp.

Nilsson, J. and Grennfelt, P., eds. (1988). Critical loads for sulphur and nitrogen. *Miljörapport* 1988:15. Nordic council of Ministers, Copenhagen. Report. 418 pp.

Nixon, S.W. (1995). Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia* **41:** 199-219.

Nürnberg, G.K. (1987). Hypolimnetic withdrawal as lake restoration technique. *Journal of Environmental Engineering* **113:** 1006-1017.

Ojakangas, R.W. and Matsch, C.L. (1982). Minnesota's geology. University of Minneapolis Press, Minneapolis, MN. 268 pp.

Olde Venterink, H., Davidsson, T.E., Kiehl, K. and Leonardson, L. (2002). Impact of drying and re-wetting on N, P and K dynamics in a wetland soil. *Plant and Soil* **243**: 119-130.

Osborn, C.L., Morris, D.P., Thorn, K.A., and Moeller, R.E. (2001). Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation. *Biogeochemistry* **54:** 251-278.

Pardo, L. H. (2010). Approaches for estimating critical loads of nitrogen and sulfur deposition for forest ecosystems on US Federal lands. General Technical Report NRS-71. Newtown Square, PA: USDA, Forest Service, Northern Research Station. 25 pp.

Peterson, D.L., Schmoldt, D.L., Eilers, J.M., Fisher, R.W. and Doty, R.D. (1992a). Guidelines for evaluating air pollution impacts on Class 1 wilderness areas in California. General Technical Report PSW-GTR-136. 34 pp.

Peterson, J., Schmoldt, D., Peterson, D., Eilers, J. Fisher, R. and Bachman, R. (1992b). Guidelines for evaluating air pollution impacts on Class 1 wilderness areas in the Pacific Northwest. General Technical Report PNW-GTR-299. 83 pp.

Prepas. E.E. and Burke, J.M. (1997). Effects of hypolimnetic oxygenation on water quality in Amisk Lake, Alberta, a deep eutrophic lake with high internal phosphorus loading rates. *Canadian Journal of Fisheries and Aquatic Sciences* **54:** 2111-2120.

Prepas, E.E., Murphy, T.P., Crosby, J.M., Walty, D.T., Lim, J.T., Babin, J., and Chambers, P.A. (1990). Reduction of phosphorus and chlorophyll *a* concentrations following $CaCO_3$ and $Ca(OH)_2$ additions to hypereutrophic Figure Eight Lake, Alberta. *Environmental Science and Technology* **24:** 1252-1258.

PRISM Climate Group (2012). Oregon State University, prism.oregonstate.edu/. Created September 2012.

Quantum Geographic Information System version 1.7.4-Wroclaw. (2012). Quantum GIS Development Team, Open Source Geospatial Foundation Project. qgis.osgeo.org/. Licensed under the GNU General Public License. First accessed April 2012 and relentlessly thereafter.

Qin, B., Hu, W., Gao, G., Luo, L. and Zhang, J. (2004). Dynamics of sediment resuspension and the conceptual schema of nutrient release in the large shallow Lake Taihu, China. *Chinese Science Bulletin* **49:** 54-64.

Qin, B., Song, Y. and Gao, G. (2003). The role of pheriphytes in the shift between macrophyte and phytoplankton dominated systems in a shallow, eutrophic lake (Lake

Taihu, China). Science *in China Series C: Life Sciences*. **49:** 597-602.
Qin, B., Xu, P., Wu, Q., Luo, L. and Zhang, Y. (2007). Environmental issues of Lake Taihu, China. *Hydrobiologia* **581:** 3-14.

Reddy, K.R. And DeLaune, R.D. (2008). Biogeochemistry of wetlands: science and applications. CRC Press, Boca Raton, FL. 774 pp.

Redfield, A.C. (1934). On the proportions of organic derivations in sea water and their relation to the composition of plankton. *In* James Johnstone Memorial Volume (R.J. Daniel, Ed.). University Press of Liverpool, pp. 177-192.

Rinalli, A.J. (2004). A summary of the scientific literature on the effects of fire on the concentration of nutrients in surface waters. U.S. Department of the interior U.S. Geological Survey 1849 C. Street, NW Washington, DC. Report, 27 pp.

RStudio statistical software environment, version 0.97.328 (2009-2012). RStudio, Inc. Licensed under version 3 of the GNU Affero General Public License. First accessed on a dark night long ago.

Spence, C. and Woo, M. (2003). Hydrology of subarctic Canadian shield: soil-filled valleys. *Journal of Hydrology* **279**: 151-166.

Sawyer, C.N. (1966). Basic concepts of eutrophication. *Journal of the Water Pollution Control Federation* **38:** 737-744.

Scheffer, M. (2004). Ecology of shallow lakes. Kluwer Academic Publishers, Norwell, Massechusetts, USA. 374 pp.

Scheffer, M., Carpenter, S., Foley, J.A., Folke, C., and Walker, B. (2001). Catastrophic shifts in ecosystems. *Nature* **413:** 591-596.

Scheffer, M., Hosper, S.H., Meijer, M-L., Moss, B. and Jeppesen, E. (1993). Alternative equilibria in shallow lakes. *Trends in Ecology and Evolution* **8:** 275-279.

Scheffer, V.B. and Robinson, R.J. (1939). A limnological study of Lake Washington. *Ecological Monographs* **9:** 95-143.

Schindler, D. W. (1974). Eutrophication and recovery in experimental lakes: implications for lake management. *Science* **184:** 897-89.

Schindler, D.W. (1986). The significance of in-lake production of alkalinity. *Water, Air, and Soil Pollution* **30**: 941-944.

Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M.J., Beaty, K.G., Lyng, M. and Kasian, S.E.M. (2008). Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences* **105:** 11254-11258.

Schindler, D.W., Turner, M.A., Stainton, M.P. and Linsey, G.A. (1986). Natural sources of acid neutralizing capacity in low alkalinity lakes of the Precambrian Shield. *Science* **232**: 844-847.

Shacklette, H.T. and Boerngen, J. G. (1984). Element concentrations in soils and other surficial materials of the conterminous United States. U.S. Geological Survey Professional Paper 1270. 63 pp.

Shaw, B., Mechenich, C. and Klessig, L. (2004). Understanding lake data. USDA-University of Wisconsin Extension RP-03/2004. 20 pp.

Shen, P.P., Shi, Q., Hua, Z.C., Kong, F.X., Wang, Z.G., Zhuang, S.X. and Chen, D.C. (2003). Analysis of microcystins in cyanobacteria blooms and surface water samples from Meiliang Bay, Taihu Lake, China. *Environment International* **29:** 641-647.

Sims, J.T., Simard, R.R. and Joern, B.C. (1998). Phosphorus loss in agricultural drainage: historical perspective and current research. *Journal of Environmental Quality* **27:** 277-293.

Smil, V. (2001). Enriching the earth: Fritz Haber, Carl Bosch and the transformation of world food production. The MIT Press. Cambridge, Massachusetts, USA 338 pp.

Smolders, A.J.P., Lamers, L.P.M., Lucassen, E.C.H.E.T., Van Der Velde, G. and Roelofs, J.G.M. (2006). Internal eutrophication: how it works and what to do about it – a review. *Chemistry and Ecology* **22**: 93-111.

Steinberg, C.E.W. and Hartmann, H.M. (1988). Planktonic bloom-forming cyanobacteria and the eutrophication of lakes and rivers. *Freshwater Biology* **20:** 279-287.

Stoddard, J.L. (1987). Alkalinity dynamics in an unacidified alpine lake, Sierra Nevada, California. *Limnology and Oceanography* **32**: 825-839.

Stoddard, J.L., Jeffries, D.S., Lükewille, Clair, T.A., Dillon, P.J., Driscoll, C.T., Forslus, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., van Dam, H., Webster, K.E., Wieting, J. and Wilander, A. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* **401**: 575-578.

Stoddard, J.L, Kahl, J.S., Deviney, F.A., DeWalle, D.R., Driscoll, C.T., Herlihy, A.T., Kellog, J.H., Murdoch, P.S., Webb, J.R. and Webster, K.E. (2003). Response of surface water chemistry to the Clean Air Act Amendments of 1990. Report. EPA 620/R-03 1. 78 pp.

Stumm, W. and Morgan, J.J. (1981). Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. Second edition. Wiley, New York. 780 pp.

Sverdrup, H. and De Vries, W. (1994). Calculating critical loads for acidity with the simple mass balance method. *Water, Air, and Soil Pollution* **72**: 143-162.

Taube, Clarence M. (2000). Instructions for winter lake mapping. Chapter 12 *In* Schneider, James C. (ed). (2000). Manual of fisheries survey methods II: with periodic updates. Michigan Department of Natural Resources, Fisheries Special Report 25, Ann Arbor.

Tromp-van Meerveld, H.J. and McDonnell, J.J. (2006). Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. Water Resources Research **42:** (2).

Towler, E., Rajagopalan, B., Gilleland, E., Summer, R.S., Yates, D. And Katz, R.W. (2010). Modeling hydrologic and water quality extremes in a changing climate: a statistical approach based on extreme value theory. *Water Resources Research* **46**: 1-11.

United States Census Bureau. (2013). TIGER/Line© shapefiles. Retrieved March 2014 from census.gov/

United States Department of Agricultura-Natural Resources Conservation Service (USDA-NRCS). (2006). *Web soil survey – Bayfield County*. Retrieved April 2012 from websoilsurvey.nrcs.usda.gov/

USDA Forest Service. (2014). National Forest boundaries shapefile. Retrieved March 2014 from fsgeodata.fs.fed.us/

United States Geological Survey (USGS). (2008). National field manual for the collection of water-quality data (TWRI Book 9). Retrieved September 2012 from water.usgs.gov/

Valiantzas, J.D. (2006). Simplified versions for the Penman evaporation equation using routine weather data. *Journal of Hydrology* **331**: 690-702.

van der Ploeg, R.R., Böhm. W. and Kirkham, M.B. (1999). On the origin of the theory of mineral nutrition of plants and the Law of the Minimum. *Soil Science Society of America Journal* **63:** 1055-106.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R. and Cushing, C.E. (1980). The River Continuum Concept. *Canadian Journal of Fisheries and Aquatic Sciences* **37:** 130-137.

Verry, E.S. (1997). Hydrological processes of natural, northern forested wetlands. *In* Northern Forested Wetlands Ecology and Management, Trettin, C.C., Jurgensen, M.F., Grigal, D.F., Gale, M.R. and Jeglum, J..K., eds. CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida. 246 pp.

Vollenweider, R. (1970). Scientific fundamentals of the eutrophication of lakes and flowing water, with particular reference to nitrogen and phosphorus as factors responsible in eutrophication. OECD Publications, Paris, France.

Warren, F.J., Waddington, J.M., Bourbonniere, R.A. and Day, S.M. (2001). Effect of drought on hydrology and sulphate dynamics in a temperate swamp. Hydrological Processes **15**: 3133-3150.

Waugh, D. (2002). Geography, an integrated approach (3rd ed.). Nelson Thornes Ltd. Gloucestershire, United Kingdom. 656 pp.

Webster, K.E. and Brezonik, P.L. (1995). Climate confounds detection of chemical trends related to acid deposition in upper Midwest lakes in the USA. *Water, Air, and Soil Pollution* **85**: 1575-1580.

Webster, K.L., Brezonik, P.L. and Holdhusen, B.J. (1993). Temporal trends in low alkalinity lakes of the Upper Midwest (1983-1989). *Water, Air, and Soil Pollution* **67**: 397-414.

Webster, K.E., Newell, A.D., Baker, L.A. and Brezonik, P.L. (1990). Climatically induced rapid acidification of a softwater seepage lake. *Nature* **347**: 374-376.

Wesely, M.L. and Hicks, B.B. (2000). A review of the current status of knowledge on dry deposition. *Atmospheric Environment* **34**: 2261-2282.

Wetzel, R.G. (2001). Limnology, lake and river ecosystems (3rd ed.) Academic Press. San Diego, California, USA. 1006 pp.

Williamson, C.E., Morris, D.P., Pace, M.L., Olson. O.G. (1999). Dissolved organic carbon and nutrients as regulators of lake ecosystems: resurrection of a more integrated paradigm. *Limnology and Oceanography* **44:** 795-803.

Wisconsin Department of Natural Resources (DNR). (2009). *Wisconsin DNR lakes*. Retrieved February 2012 from dnr.wi.gov/

Wright, F.E. (2010). Flow diagram for the production of ammonia. Image. Permission for use granted under the GNU Free Documentation License, version 1.2 or later.

Wood, J.A. (1989). Peatland acidity budgets and the effects of acid deposition. Ecological Applications Research Division, Sustainable Development, Environment Canada. 34 pp.

Yan, N.D., Keller, W., Scully, N.M., Lean, D.R.S. and Dillon, P.J. (1996). Increased UV-B penetration in a lake owing to drought-induced acidification. *Nature* 381: 141-143.

Zumdahl, S.S. (1993). Chemistry. Houghton Mifflin publishers, Boston, USA. 1211 pp.

Appendix I - *Glossary*

Absorption – incorporation of dissolved material inside another substance or structure (*e.g*. water droplet or cell)

Acid neutralizing capacity – the ability of water to buffer against incoming acid inputs

Adsorption – adhesion of atoms, ions or molecules (*e.g*. gas, liquid, dissolved solid, biomolecule) to a surface

Allotrope – different molecular forms of the same chemical element (*e.g*. graphite and diamond are allotropes of carbon)

Anaerobic – a condition indicating the absence of oxygen as an electron acceptor; also termed anoxic

Anthropogenic – an environmental effect or condition resulting from human activities

Apatite – a group of calcium phosphate minerals most commonly bound to a hydroxyl (OH^-) or halide ion (often F^- or Cl^-) and the main source of phosphorus required by photosynthetic organisms

Chlorophyll *a* – abbreviated chl*a*, from the Greek roots meaning 'green' (chloro) and 'leaf' (phyllo); an inner-sphere chelate found as a photosynthetic pigment in many primary producers and often measured as an indicator of phytoplankton biomass; though not all phytoplankton use chl*a* as the main electron donor in photosynthesis, it is the one most commonly encountered

Critical load – the quantitative amount of a pollutant that a sensitive target can tolerate without permanent, deleterious effects

Critical limit – an established point of reference below which no harm is expected to a target system from pollution inputs

Direct deposition – an input of precipitation falling directly onto a surface, *e.g*., a lake or wetland, in contrast to indirect inputs, *e.g*., runoff from the landscape to a lake

Hydrology – the study of water and its forms, cycling, movement, distribution and quantity

Hydrophilic – the condition of a molecule or substance being attracted to and tending to be dissolved by water

Maximum likelihood – a method of estimating the parameters of a statistical model given the distribution of the data

Photosynthesis – a redox reaction which converts carbon dioxide (CO_2) and water (H_2O) into carbohydrates (general formula CH_2O) and oxygen (O_2) following excitation by ultraviolet light

Primary productivity – biomass production primarily as a result of photosynthesis, usually measured as a mass per unit area or per volume of water

Appendix II – *sample R code*

Maximum likelihood estimation using the likelihood package

Adapted from code graciously provided by Dr. Charles Canham, Likelihood Methods in Ecology course, April 2-6, 2012, Cary Institute of Ecosystem Studies.

```
######################################################################
#
#      Simple linear regression with RLW data
#
######################################################################

# load the simulated annealing library
library(likelihood)

#set working directory
setwd("~/Critical Load/Data files/CSVs and anneal results/RLW the good stuff")

# load the RLW datafile
alldata <- read.csv("Filename.csv",header=T)

# display list of variables in the data file
str(alldata)

#display first few rows of the data file
head(alldata)

#omit any cells that are NA or missing values
attach(alldata)
data = na.omit(data.frame(alldata))
detach(alldata)


###########################################################
#
#    PDFs
#
##########################################################

# define a normal PDF
my.dnorm <- function(x,mean,sd) {dnorm(x,mean,sd,log=T)}
```

```
#######################################################
#
#    Alternate scientific models
#
#######################################################

# define a basic linear model
linear.model1 = function(a,b,X1) { a + b*X1 }

linear.model2 = function(a,b,X2) { a + b*X2 }

linear.model3 = function(a,b,X3) { a + b*X3 }

#########################################################
##
## SETTING UP ANNEAL
##    The "anneal" function in the likelihood package requires:
##    1. a scientific "model"
##    2. a pdf to use to calculate likelihood
##    3. a list of the parameters to estimate (par), with initial starting values
##    4. a list of the variables in the model (var)
##
##    In addition, you can define the upper and lower limits for the
##      range to search for each parameter (par_lo and par_hi)
##
###########################################################

## You'll typically have to set up separate "par" and "var" lists for each model
##  (at least in cases where the variables and parameters differ among the models

## Set up par and var for the simple linear regression model
##    NOTE: par will include both the parameters of the scientific model
##    plus any parameters needed for the PDF...
par<-list(a = 1, b = 1, sd = 1, s = 1)

var <- list(X1 = "Balance3", X2 = "Balance4", X3 = "Balance8")
# you're telling anneal what variables in the dataset to plug in as X1, X2, etc.

## Set bounds and initial search ranges within which to search for parameters
##   NOTE: the s and sd parameters have to be greater than zero (algebraically)
par_lo<-list(a = -1000, b = -100, sd = 0.00001, s = 0.00001)
par_hi<-list(a = 1000, b = 100, sd = 10000, s = 10000)

## Specify the dependent variable, and name it using whatever
```

```
##    argument name is used in the pdf ("x" in the normal.pdf function above)
var$x<-"ObsANCueqL"

## predicted value in your PDF should be given the reserved name "predicted"
##   Anneal will use your scientific model and your data and calculate the
##   predicted value for each observation and store it internally in an object
##   called "predicted"
var$mean<-"predicted"

## Have it calculate log likelihood
var$log<-TRUE

##  now call the annealing algorithm, choosing which model to use
results<-
anneal(linear.modelNumber,par,var,data,par_lo,par_hi,my.dnorm,"ObsANCueqL",
  hessian = F, max_iter=5000)

## display some of the results in the console
results$best_pars;
results$max_likeli;
results$aic_corr;
results$slope;
results$R2

## now write the results to a file...
write_results(results,"Filename.txt")
```

stl decomposition using the forecast package and code adapted from Hyndman and Athanasopoulos (2013)

```
# time series decomposition using the forecast package
library(fpp)

#set working directory
setwd("~/Critical Load/Data files/CSVs and anneal results/RLW the good stuff")

# load the RLW datafile
# scan function expects only data; do not include time references (i.e. year, month,
day)
precip <- scan("RLWinterpolatedprecip.csv", skip=1)

head(precip)

# convert to a time series
```

```
# this is where data are correlated to time; specify as start(year,month)
precip.ts = ts(precip, start=c(1969,10), frequency=12)

# double-check it's really a time series with a single column of values
str(precip.ts)

# decomposed trend-seasonal-remainder plot for interpolated RLW precipitation
precip.tsdecomp = stl(precip.ts, t.window=25, s.window=15, robust=TRUE)
plot(precip.tsdecomp)
```