Improving understanding of the chemical and biological nutrient removal mechanisms in existing wastewater lagoons

by

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Abstract

There are many rural communities in Manitoba using wastewater stabilization ponds to treat their sewage, but the nutrient removal process in these systems is not fully understood. The purpose of this thesis is to improve understanding of chemical and biological nutrient removal mechanisms of wastewater lagoon treatment and compare two different stabilization ponds – one aerated and one facultative. Surface samples were collected from lagoon cells and analysed. The windward and leeward sides of the ponds were sampled and the results were averaged. The facultative lagoon achieved overall ammonia-N removals similar to those of the aerated lagoon, and slightly lower orthophosphate removals. Nitrogen appears to be removed by ammonia volatilization; and assimilation into biomass. Phosphorus appears to be removed by assimilation into biomass; and precipitation at alkaline pH. When the Nitrogen to Phosphorus (N/P) ratio and ideal theoretical N/P ratio for cellular growth are compared there appears to be nitrogen limiting conditions in the secondary cells of both stabilization systems. There does not appear to be any significant advantage between aerated or facultative ponds; they will meet their ammonia discharge limits, but will require additional phosphorus treatment.

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Chapter 1: Introduction

1.1 Overview of Wastewater Stabilization Ponds

For more than 3000 years stabilization ponds have been used worldwide to treat wastewater (US EPA, 1983). The first recorded wastewater stabilization pond in the USA was constructed in Texas in 1901 (US EPA, 1983). Lagoons are a common treatment method in rural areas from tropical regions to arctic ones (US EPA, 1983). They are used because of the pathogen reduction, low energy costs, and ease of operation and maintenance (WHO, 2002). It can have the added benefit of providing irrigation for agriculture or a resource for aquaculture (WHO, 2002).

By definition wastewater stabilization ponds, or wastewater lagoons, are a human-made pond for wastewater treatment processes to occur; the terms pond and lagoon are often used interchangeably (Middlebrooks et al, 1982). They are often designed for lower flows than conventional municipal wastewater treatment plants (i.e. less than 7600 m^3/day) (Middlebrooks et al, 1982). One of the main disadvantages is the surface area required to build lagoons. This is one reason why they are more common in rural areas; space is readily available and there is lower population density.

Lagoons rely on natural processes to aid in wastewater treatment. Some ponds use natural photosynthetic oxygenation from algae and mixing effects from wind and turnover. Some ponds use mechanical mixing and aeration devices. They rely on a mixed microbial treatment approach with bacteria and algae generally responsible for treating the wastewater

(Weis et al, 2008). Consequently there tends to be an increase in algal solids in the effluent (CCME Report, 2006).

The wastewater stabilization ponds can achieve 80-95% biochemical oxygen demand, or BOD, removals with adequate retention times and temperatures; however, removals can be much lower with shorter retention times and low temperatures such as when ice covered (CCME Report, 2006). In colder climates ice cover results in anaerobic conditions, decreased organic removal, and less disinfection from sunlight (Townshend and Knoll, 1987). As a result colder climates often discharge lagoon effluent intermittently during warmer months (Middlebrooks et al, 1982).

An oxidation pond is one kind of wastewater stabilization pond. It is aerobic throughout and is usually less than 1 meter deep to encourage algae growth with higher temperatures and better light penetration (Larsdotter, 2006; US EPA, 1983). The aerobic conditions are supported by algal activity and surface mixing, natural or artificial. Due to the shape of the oxidation pond it may also be referred to as a raceway pond; another name is a high rate algal pond (Larsdotter, 2006) and they are almost completely aerobic (US EPA, 1983).

A facultative lagoon is another common pond. They are often anaerobic near the bottom where solids accumulate and aerobic near the surface from the photosynthetic effects of algae and mixing near the water surface (Middlebrooks et al, 1982). Facultative ponds are typically 1.2 – 2.5 meters deep (US EPA, 1983). Deeper facultative ponds have lower dissolved oxygen levels (US EPA, 1983).

Aerated partially mixed ponds use mechanical aeration. They are partially mixed because the mixing effects from aeration are not enough to maintain a suspension of all the

solids. There are still some solids deposited near the bottom of the pond. The partial mix system allows the growth of some algae because there is still enough light penetration. The ponds are typically 2 – 6 meters deep (US EPA, 1983). A partial mixed system is often followed by facultative ponds to allow for suspended solids to settle and anaerobically breakdown (von Sperling, 2007).

Another lagoon is the aerated completely mixed pond where there is enough mixing from aeration to keep all of the solids suspended. There is very little light penetration and algae are not usually a factor in treatment (US EPA, 1983). This type of pond is often designed like the activated sludge process, and like the partially mixed system is often followed by facultative ponds for the same reasons (US EPA, 1983). Aerated ponds reduce the area needed for treatment and evolved as mechanical aeration was added to over-loaded facultative ponds where there was no available space for expansion (US EPA, 1983).

The last kind of pond is an anaerobic pond. They are loaded so much with organics that there are virtually no aerobic conditions (US EPA, 1983). They are typically 2.5 – 5 meters deep (US EPA, 1983). Anaerobic ponds are not normally used for municipal waste, but rather industrial or agricultural waste (US EPA, 1983). As with mechanically aerated ponds this type of pond is normally the first pond in a series of ponds and reduces land requirements (US EPA, 1983).

After wastewater stabilization in the ponds there are a few common methods of discharge. One is a continuous discharge where the pond is designed for a non-stop unrestricted effluent discharge (Middlebrooks et al, 1982). Another is controlled, or intermittent, discharge where the pond is designed to contain the wastewater for 6 months to

2 years (Middlebrooks et al, 1982). The effluent is discharged when it is compatible with the receiving water. Often a long detention time minimizes the need for mechanical aeration (Middlebrooks et al, 1982). Lastly is a complete retention pond where evaporation and seepage are the mechanisms for release (Middlebrooks et al, 1982). There is no direct discharge to receiving waters. They usually require a large shallow pond to maximize the surface area for evaporation (CCME Report, 2006).

1.2 Factors Affecting Lagoon Performance

1.2.1 Environmental Effects

Environmental effects on lagoons can be many different things, like the amount and intensity of the light, or the wind speed. Lagoons are diverse systems where heterotrophic and autotrophic bacteria, algae, fungi and zooplankton work to treat the wastewater (Mbwele, 2006). Algae need light for photosynthesis to contribute to the treatment of wastewater. Facultative ponds can be divided into different regions as a result; biological activity takes place in the photic, heterotrophic and anaerobic regions (Crites and Tchobanoglous, 1998; Hosetti and Frost, 1998; Mara et al, 1992). Algae dominate the photic zone which is typically aerobic (Mbwele, 2006). As a result, light is an important factor in wastewater treatment when using wastewater stabilization ponds. In aerated lagoons there is typically less algal activity in the aerated sections.

Light varies throughout the day, by season and by latitude. In the summer there are longer days and a greater light intensity; in winter there are shorter days and reduced light intensity (Larsdotter et al. 2010). The impact of light in winter on the lagoon is also impacted

by the ice thickness and snow cover (Gu and Stefan, 1995). Thus the most active time of year for algae is during the summer when there is more light with a higher intensity.

Light intensity also varies by depth and the growth of algae near the surface can become limiting to light penetration (Larsdotter, 2006; Mbwele, 2006). Suspended solids, like algae, can shield the sunlight and natural light attenuation can decrease the effects (Bitton, 1999).

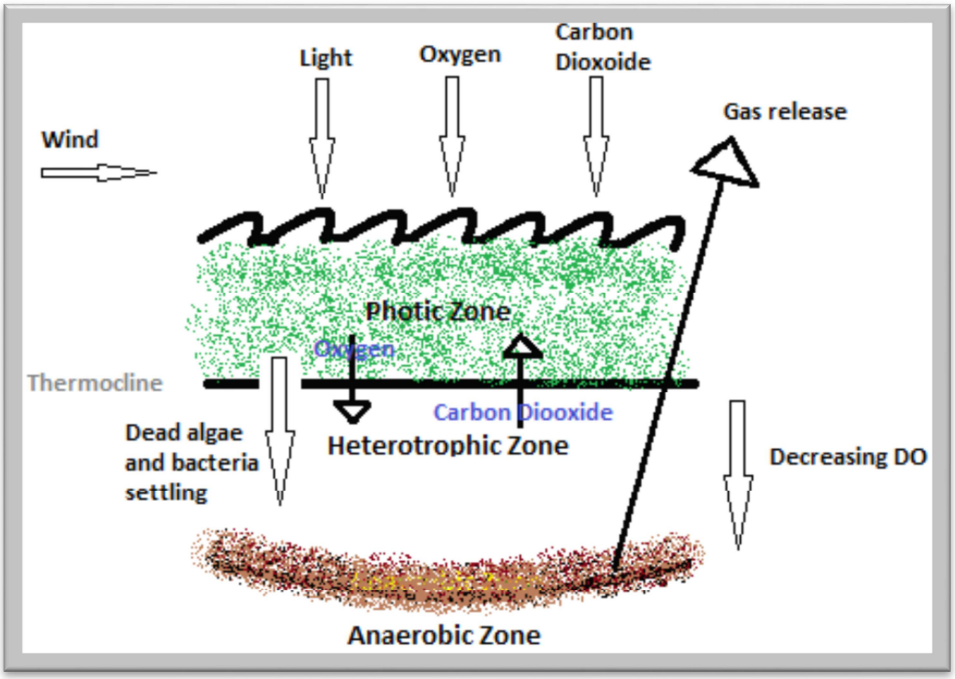


Figure 1: Representation of different zones in a stratified pond (adapted from Bitton, 1999).

Shielding can be compounded when ponds become stratified and algae concentrate in the photic zone (Mbwele, 2006) as seen in Figure 1. This zone is typically up to 50 cm in depth and is naturally aerated by algae in facultative ponds (Bitton, 1999). A thermocline tends to form in a stratified pond with warmer water above and cooler water below (Bitton, 1999). Below the thermocline is the heterotrophic zone which has decreasing oxygen content from the thermocline to the bottom of the pond and the anaerobic zone (Bitton, 1999). The greater UV light intensity near the surface also serves to inactivate viruses and bacteria (Bitton, 1999;

Silverman, 2013). UV-B light with a wavelength of 280 – 320 nm has a substantial effect on the destruction of coliform bacteria and short wavelength light does not penetrate very deeply into the ponds (Bitton, 1999). This selects for greater bacterial activity near the middle to bottom of the ponds where there is less light penetration.

There is also a diurnal effect from light. The changes in sunlight intensity throughout the day and night affect the temperature, pH and dissolved oxygen in the ponds (Kayombo et al, 2002). The radiation from sunlight causes an increase in temperature with the highest sunlight intensity resulting in a higher temperature in the pond (Tadesse et al, 2004). This generally occurs in the early afternoon (Tadesse et al, 2004).

The diurnal effect of light on pH and dissolved oxygen are related to photosynthesis. The sun's energy (photons) is used to power the creation of carbohydrates from carbon dioxide and water (energy from light is converted into biochemical energy through intermediaries ATP and NADPH) (Nir et al, 1997). Algae produce oxygen in the presence of sunlight as a by-product of photosynthesis. The oxygen produced is released from the algal cells resulting in an increase in the pond's dissolved oxygen. As carbon dioxide is consumed the pH becomes more alkaline because there is a reduction in the concentration of carbonic acid (Vaccari et al, 2006). The highest pH, and dissolved oxygen values are generally reached during the afternoon when light intensity is greatest (Kayombo et al, 2002). During the night there is the opposite effect, algae consume internal energy stores and dissolved oxygen from the water to oxidize glucose and produce carbon dioxide (Vaccari et al, 2006). The pH and dissolved oxygen concentration decreases through the night with the lowest values just before morning light (Tadesse et al, 2004).

Wind plays an important role in mixing and aerating the lagoons. During times with little wind the ponds tend to stratify, and are not completely mixed (Gu and Stefan, 1995; Mbwele, 2006; Tadesse et al, 2004). Wind speeds greater than 5 m/s (18 km/h) results in well mixed and stable wastewater lagoons (Badrot-Nico et al, 2010). During a couple of years monitoring wastewater ponds in Harris, Minnesota, USA, Gu and Stefan (1995) noted 45% of the time the ponds were completely mixed.

Air temperature and light can contribute to both stratification (Mbwele, 2006; Tadesse et al, 2004), and mixing (Gu and Stefan, 1995; Tadesse et al, 2004). During warm days with intense solar radiation, and minimal mixing effects from wind, the surface of the pond heats up and forms a thermocline (Gu and Stefan, 1995; Mbwele, 2006; Tadesse et al, 2004). There is warmer water near the surface, called the epilimnion, and cooler more dense water near the bottom of the pond, called the hypolimnion (Mbwele, 2006; Tadesse et al, 2004). Algae tend to stabilize near the surface during these times of stratification (Mbwele, 2006; Tadesse et al, 2004). According to Gu and Stefan (1995) this accounts for approximately 27% of the time between April and October in Harris, MN.

One direct effect of lagoon stratification is enhanced algae growth (Gu and Stefan, 1995). This is because there is less turbidity; when cells are well mixed debris and settled solids are stirred up and can limit light intensity by shading algae (Gu and Stefan, 1995). It also results in increased settling efficiency; when the pond is calm and stratified it allows suspended solids and debris to settle more effectively than if they are being mixed (Gu and Stefan, 1995). Aerated cells are partially or completely mixed continuously by mechanical devices (US EPA, 1983) making stratification unlikely in aerated lagoon cells.

Temperature contributes to mixing during lagoon turnover (Gu and Stefan, 1995; Tadesse et al, 2004). This turnover happens more often than in the spring and fall in shallow water bodies like lagoons. It can occur throughout the warmer months (in this case June to September), too. However, according to Middlebrooks et al (1982) the spring turnover has the greatest impact on lagoon treatment with spikes in BOD and TSS from the switch between anaerobic winter operation and open water operation.

At night the external temperature decreases and causes the upper layer of water in the pond to cool; when the temperature near the surface decreases below the temperature on the bottom, the pond will turnover (Gu and Stefan, 1995; Tadesse et al, 2004). Specifically what happens is the denser top layer of water will force the less dense lower layer of water to the surface mixing the pond in the process (Tadesse et al, 2004). Gu and Stefan (1995) show that this applied 28% of the time they were monitoring their lagoons. When wastewater lagoons are designed they are assumed to be completely mixed systems, but based on the results from Gu and Stephan (1995) they may only be completely mixed 59% of the time (45% complete mixed conditions plus one half of 28% when the cells turnover at night).

The other effect temperature has on lagoon performance is through reaction and growth rates (Tadesse et al, 2004). The temperature affects the breakdown of organic matter by selecting for certain species that consume it and influence their growth and death rates (Friedman and Shroeder, 1972). It also affects the nutrients available to these organisms (Friedman and Shroeder, 1972). Mayo and Noike (1996) found that heterotrophic bacteria population dynamics were not influenced by temperatures between 10 and 20˚C; however, at temperatures above 30˚C there was increased competition with the algal species *chlorella*

vulgaris, a single celled green algae, resulting in decreased heterotrophic growth. This means there are optimal temperatures for growth in the ponds for different species of microorganisms.

Also affected by temperature are the settled solids, or sludge. Marais (1974) found that fermentation almost stopped at temperatures less than 17˚C and was much more vigorous over 23˚C. In wastewater lagoons operated in colder climates the sludge accumulates in colder winter months and is fermented in the warmer summer months (Huray, 1977; Oswald, 1968). Clark et al (1970) found that aerated lagoons didn't accumulate as much sludge as facultative lagoons. An aerated lagoon in Alaska accumulated about 0.25 m^3 of sludge per year per 1000 people, and facultative lagoons in Canada and Alaska accumulated about 0.25 – 0.40 m^3 of sludge per year per 1000 people; the highest quantities were at the most northerly sites (Schneiter et al, 1983). Ideally there is a negligible net gain of solids throughout the year, where any sludge added during the colder months can be consumed during the warmer months (Schneiter et al, 1983).

Rockne and Brezonik (2006) found that in the late summer and early spring the rainfall was less than the loss from evaporation in the Harris, Minnesota lagoons. During the summer there was more rainfall than evaporative losses, but the contribution did not have a significant effect on the wastewater treatment process (Rockne and Brezonik, 2006). In Britain Whalley et al (2012) found that the rainfall was significant enough to be considered for storage capacity of the lagoon.

1.2.2 pH

Algal and bacterial effects are a significant contributor to changes in pH within wastewater stabilization ponds. Algae consume carbon dioxide causing an increase in pH (Pires et al, 2013; Tadesse et al, 2004). Fermentation of organic matter in wastewater ponds produces volatile fatty acids and carbon dioxide decreasing the pH (Bokil and Agrawal, 1977; Pires et al, 2013). As such there can be a pH gradient in ponds that are stratified with the pH at the surface higher than the pH at the bottom (Bokil and Agrawal, 1977; Tadesse et al, 2004). In practice wastewater stabilization ponds will not be stratified all the time due to mixing effects (Gu and Stefan, 1995).

Both carbon dioxide and dissociated bicarbonate ions are used in photosynthesis increasing the pH; phototrophic algae can use the carbon dioxide produced by bacterial oxidation more quickly than it can be made (Tadesse et al, 2004). Carbon dioxide becomes a limiting component and the need for more carbon is met by the consumption of bicarbonate ions (Borowitzka, 1998; Oswald, 1988; Tadesse et al, 2004). This use of bicarbonate ions when carbon dioxide is limiting creates a relationship between the pH and the alkalinity (Bokil and Agrawal, 1977; Tadesse et al, 2004). The consumption of bicarbonate by algae to produce carbon dioxide produces hydroxyl ions and increases the pH (Larsdotter, 2006; Tadesse et al, 2004). The alkalinity in a stratified pond is inversely related to the pH changes with depth. The alkalinity concentration is higher at the bottom and lower near the surface of the lagoon (Bokil and Agrawal, 1997).

A pH range of 7.5 – 8.5 is ideal for a number of algal species (Acien Fernandez et al, 2001; Christi, 2008; Marcel et al, 2003; Molina et al, 2001). Some algal species can still function

at pH values over 10 (Ogbonna et al, 2000). However, at a pH of greater than 10 algae growth can be inhibited (Qiang et al, 1996; Richmond and Cheng-Wu, 2001; Zhang and Richmond, 2003). pH values above 10 can negatively impact heterotrophic bacteria (Mayo and Noike, 1996). In lagoons, breakdown of organic matter is mainly completed by heterotrophic bacteria (Mbwele, 2006).

The pond pH can be used as a rough measure of what is happening within the wastewater lagoon. For example when more carbon dioxide is consumed by phototrophs than is produced by bacterial processes a pH greater than 8 is common (Kayombo et al, 2002). Conversely, a pH less than 8 indicates there is carbon dioxide remaining because it has not all been used in photosynthesis (Kayombo et al, 2002). This trend can be used as a quick measure of the amount of photosynthesis taking place in a pond at any given time when they are well mixed.

Based on all of this information a combination of mechanisms are responsible for pH changes and the effects they have in wastewater stabilization ponds. For example the pH decreases as a result of bacterial processes, but increases as a result of algal processes. The seasonal and diurnal changes in light can cause seasonal and diurnal changes in pH. The pH can have a significant effect on solubility of different molecules, or make a nutrient removal mechanism more, or less, likely to occur. It also can inhibit, or boost, the activity of some microorganisms depending on the acid or alkaline nature of the solution.

1.3 Organic Carbon and Nutrient Removal from Lagoons

1.3.1 Organic Carbon Removal

The main goal of the wastewater lagoon is stabilizing wastewater by removing carbonaceous matter (von Sperling, 2007). In a facultative pond there is waste stabilization occurring in suspension in the aerobic and facultative portion of the pond as well as within the settled solids anaerobically on the bottom of the pond (von Sperling, 2007). Bacteria are responsible for decomposition of organic matter (Mbwele, 2006; von Sperling, 2007). In the anaerobic zone at the bottom of the pond the sludge is made up of particulate BOD that has settled. It is broken down anaerobically producing among other things carbon dioxide and methane. Over time the only matter remaining will be non-biodegradable (von Sperling, 2007).

In the aerobic zone near the surface of a facultative pond there is soluble and colloidal (suspended particulate) organic matter. Dissolved oxygen is supplied by photosynthesis in algae and carbon dioxide is consumed. Conversely oxygen is consumed by bacteria as they aerobically breakdown the organic matter and produce carbon dioxide (von Sperling, 2007). Algae have an important function in facultative ponds because they constitute the majority of the biomass concentration in the pond (von Sperling, 2007).

Lastly in the middle between the surface layer and the bottom of the pond is the facultative zone which requires bacteria that can function in aerobic or anaerobic/anoxic conditions. They need to be able to stabilize the organic matter based on changing electron donors for respiration (von Sperling, 2007). Algae are inhibited in this middle depth of the pond because of light attenuation and suspended solids shading (von Sperling, 2007).

In a partially-mixed aerated lagoon the organic carbon is removed through a similar process to the facultative lagoon; however, aeration is supplied mechanically instead of by photosynthesis in algae. The partially-mixed system doesn't supply enough energy to keep the solids completely suspended and some still settle and degrade anaerobically (von Sperling, 2007). The complete-mix aerated lagoon requires substantially more energy and keeps all the solids in suspension to breakdown aerobically. They are oxidized by bacterial respiration like the aerobic zone of a facultative pond, but without the algae (von Sperling, 2007). These ponds require additional ponds in series to settle the solids (von Sperling, 2007).

1.3.2 Nitrogen Removal

Nitrogen is a nutrient required for cellular growth, but certain forms of it can also be a detriment to aquatic life. In wastewater the dominant forms of reactive nitrogen are ammonia and organic nitrogen; the two together are called total Kjeldahl nitrogen (Middlebrooks et al, 1982), and ammonia accounts for about 60-70% (Metcalf and Eddy, 2003). The other forms of reactive nitrogen in water are nitrite and nitrate; the four together are called total nitrogen (Metcalf and Eddy, 2003; Sawyer et al, 2003).

There are five main processes that can affect reactive nitrogen in the lagoon. The first process is ammonia lost to the atmosphere as gas (volatilization); the second is incorporation into cellular mass; the third is nitrification; the fourth is denitrification; and lastly is settling of mineralized particulate organic nitrogen (Middlebrooks et al, 1982).

Total ammonia-nitrogen is the combined total of un-ionized, or free, ammonia and ammonium in aqueous solutions; the equilibrium between these two is influenced by a number

of factors (CEQG-CCME, 2010; Griffiths, 2009; Metcalf and Eddy, 2003; Sawyer et al, 2003). The first factor to influence the equilibrium is the pH of the solution, and it has the largest impact (CEQG-CCME, 2010; Metcalf and Eddy, 2003; Sawyer et al, 2003). Temperature is also an important factor in this equilibrium (Griffiths, 2009; Middlebrooks et al, 1982) though not as significant a factor as pH (CEQG-CCME, 2010). Lastly is ionic strength, but this has a much less pronounced effect (CEQG-CCME, 2010).

A pH increase, or decrease, of 1 unit can cause a change by a factor of ten in the concentration of either free ammonia or ammonium (Environment Canada, 1999). At more alkaline pH there is a greater concentration of free ammonia and at a more neutral pH there is a greater concentration of ammonium; for example at a pH of 12 it is almost totally free ammonia, and at a pH of 7 it is almost totally ammonium (Griffiths, 2009; Korner et al, 2001; Sawyer et al, 2003).

An increase in temperature results in an increase in un-ionized ammonia and vice versa (CEQG-CCME, 2010). For example a 5˚C change in temperature may cause a 40% change in the concentrations of ammonia and ammonium (Environment Canada, 1999). Thus the temperature of the solution has an impact on the equilibrium of total ammonia-nitrogen, and can impact the toxicity. By waiting longer after the ice cover has melted it would allow for more ammonia treatment in the lagoon before discharge.

Some ammonia in lagoons is volatilized, or stripped to the atmosphere (Middlebrooks et al, 1982; Pires et al, 2013). Stratton (1968, 1969) demonstrated experimentally that ammonia rate constants, where it is stripped to the atmosphere, are directly related to the pH and temperature. As discussed earlier pH values of 10, or higher, are possible during algae growth

(Larsdotter, 2006). These times of greater algae growth that occur near midday, and during the summer, increase the pH and contribute to increased ammonia volatilization (Garcia et al, 2000; Riano et al, 2011). Lagoon wastewater treatment is aided by a more alkaline pH (Doran and Boyle, 1979; Mesple et al, 1996; Moutin et al, 1992; Nunez et al, 2001).

There are a number of articles that claim at higher pH ammonia volatilization is a major contributor to ammonia loss in wastewater stabilization ponds (Middlebrooks et al, 1982; Pano and Middlebrooks, 1982; Rockne and Brezonik, 2006; Shilton, 1996; Silva et al, 1995; Smith and Arab, 1998; Soares et al, 1996). However, there are some articles claiming ammonia volatilization plays a minimal role (Ferrara and Avci, 1982; Zimmo et al, 2003). To further complicate matters, Pano and Middlebrooks (1982) and Ferrara and Avci (1982) arrived at their conclusions based on an analysis of data collected from the same set of lagoons. Zimmo et al (2003) and Rockne and Brezonik (2006) were the only ones to do a nitrogen mass balance of the system.

Pano and Middlebrooks and Ferrara and Avci were analyzing data from different ponds, and both were using mathematical models to predict the mechanism of ammonia removal. The assumptions they made for their respective models were different and had much different outcomes. Ferrara and Avci were looking at the first cell in series which accounts for the greatest ammonia removals and Pano and Middlebrooks were analyzing the following cells. In the Zimmo et al (2003) article they were analyzing a continuous flow pilot scale duck weed and algae based lagoon system. In their algae based pond they found removals by ammonia volatilization of 7.4 – 37.4 mg-N per m^2 per day accounting for less than 1.5 % ammonia nitrogen removal; they found nitrification/denitrification was the main mechanism for nitrogen

removal. However, Rockne and Brezonik (2006) based their information on intermittent discharge wastewater stabilization ponds. They found ammonia volatilization played an important role in nitrogen removal particularly after ice-out when there was elevated pH and high total ammonia-N concentrations; this shifted the equilibrium to free ammonia and volatilization.

Assimilation of nitrogen into biomass is another contribution to the change of reactive nitrogen in the system (Middlebrooks et al, 1982; Ferrara and Avci, 1982; Rockne and Brezonik, 2006). After carbon, nitrogen is the next most important atom for cellular growth; algae can contain from 1% to more than 10% nitrogen (Becker, 1994; Tomaselli, 2004). Thus assimilation of nitrogen for cellular processes contributes to nitrogen removal from wastewater (Larsdotter et al, 2010), and bacteria and algae work cooperatively to break it down faster than if they did it independently (Weis et al, 2008).

Ammonium and nitrate are the two best nitrogen sources for assimilation into algae (Oliver and Ganf, 2000; von Sperling, 2007). Ammonium is the nitrogen source of choice for some algae; however, if there is limited supply different forms of nitrogen can be used (Bhaya et al, 2000). For example some cyanobacteria, or blue-green algae, can assimilate proteins, or in extremely limiting cases fix nitrogen from the atmosphere (Bhaya et al, 2000). However, many cyanobacteria cannot fix nitrogen in the presence of nitrate, ammonia or oxygen (Chorus and Bartram, 1999).

Aerobically ammonia can be oxidized to nitrite and then nitrate, through a biological process called nitrification. There are several sources that state this is not a significant process in lagoons (Middlebrooks et al, 1982; Pano and Middlebrooks, 1982; Rockne and Brezonik,

2006; Shilton, 1996; Silva et al, 1995; Smith and Arab, 1998; Soares et al, 1996). Conversely there are a couple of sources that believe it is a significant process in some lagoons (Ferrara and Avci, 1982; Zimmo et al, 2003). When cells are aerated there is greater likelihood of nitrification because it is an aerobic process. Mechanically aerated cells would have the potential for more nitrification because they are more consistently aerobic then facultative cells.

Under anaerobic conditions nitrate can be reduced to nitrite, nitric oxide then nitrous oxide and lastly returned to the atmosphere as nitrogen gas in a process called denitrification. Denitrification is unlikely in waste stabilization ponds with significant algae populations because they may produce enough oxygen to nearly saturate the water minimizing anaerobic conditions (Larsdotter et al, 2010; von Sperling, 2007). What this means is that anoxic conditions necessary for denitrification are inhibited by photosynthesis, as well as mechanical aeration, because of increases in the dissolved oxygen concentration. Rockne and Brezonik (2006) found denitrification did not play a significant role in facultative pond nitrogen removal based on very low nitrate concentrations detected.

Lastly at low pH values mineralization and adsorption to particulates can cause some forms of nitrogen to settle (Senzia et al, 2002). In mixed culture bacterial/algal systems low pH is less likely due to the higher pH resulting from photosynthesis of carbon dioxide and carbonate.

It is apparent there are several mechanisms for nitrogen removal from lagoons (e.g. volatilization, assimilation into biomass, nitrification, denitrification, and mineralization), but the proportion of nitrogen removed is likely different in each system.

1.3.3 Phosphorus Removal

Phosphorus is essential to the growth of organisms because it is used in cells to make phospholipids and nucleic acids (Larsdotter, 2006; Miyachi et al, 1964), and it is used in energy transfers with adenosine triphosphate, ATP. Algae are able to store phosphorus like bacteria as polyphosphate (Larsdotter, 2006; Powell et al, 2009; Powell et al, 2008, 2011b; Rao et al, 2011). The polyphosphate stored in the cells can be used during phosphorus limiting times (Eixler et al, 2006).

There are a number of different forms of phosphorus in the wastewater environment, and they can be affected by temperature and pH (Sawyer et al, 2003). Organic phosphorus, ortho- and poly-phosphate are the three main phosphorus types of importance (Mbwele, 2006; Metcalf and Eddy, 2003; Sawyer et al, 2003). Orthophosphates, also called dissolved or reactive phosphorus, dissociate in aqueous solutions. In an aquatic wastewater environment polyphosphate will eventually be hydrolyzed back to orthophosphate (Metcalf and Eddy, 2003). Organic phosphorus is contained within cells along with polyphosphate and when the cells breakdown the phosphorus is released (Brown and Shilton, 2014).

Precipitation of phosphorus is one mechanism of phosphorus removal in wastewater treatment, when algae are present (Doran and Boyle, 1979; Mesple et al, 1996; Moutin et al, 1992; Tam and Wong, 2000). When algae use carbon dioxide, or carbonate, for photosynthesis the resulting pH increase favours precipitation of phosphate salts (Larsdotter et al, 2007). When the pH is more alkaline phosphorus can be bound to cations and precipitate out of solution (Pires et al, 2013). Phosphorus removal by precipitation is strongly influenced by pH (Carlsson et al, 1997; Stumm and Morgan, 1981), temperature, cation and phosphorus

concentration (Song et al, 2002). This process could be used to minimize the necessity for chemical addition (alum or ferric) to precipitate phosphorus and the settled solids would be easier to salvage and use again (Brown and Shilton, 2014).

Calcium phosphates precipitate between pH 7 – 8.5 (Tuszynska et al, 2013), or higher (Picot et al, 2005; Puig et al, 2010; von Sperling, 2007). These calcium phosphate precipitates may also contain magnesium and calcite (Larsdotter et al, 2010). The pH is very important in precipitating these salts (Carlsson et al, 1997). It is important because the solubility of the salts decreases as the pH increases (Puig et al, 2010). However, the formation of phosphate precipitates is a difficult process to model (Carlsson et al, 1997). In a wastewater system there are too many variables with microorganism growth in the presence of organic and inorganic material at the same time and thermodynamically unstable forms of phosphate precipitates possible (Carlsson et al, 1997). Common phosphates thought to occur are: dicalcium phosphate $CaHPO_4$, octacalcium phosphate $Ca_8H_2(PO_4)_6$, tricalcium phosphate $Ca_3(PO_4)_2$, and hydroxyapatite $Ca_5OH(PO_4)_3$ (Carlsson et al, 1997).

Phosphorus is removed by assimilation into microorganisms such as algae and bacteria (Bitton, 1999; Brown and Shilton, 2014; Crites and Tchobanoglous, 1998; Larsdotter et al, 2010). Powell et al. (2006a) showed experimentally that phosphorus was being removed by algae and there was luxury phosphorus uptake. They used metal complexing agents to remove the possibility of loss by precipitation. Phosphorus uptake was most affected by the quantity of phosphate, concentration of light, and temperature (Boelee et al, 2012; Powell et al, 2006a). Longer hydraulic residence times also resulted in greater phosphorus removal by algae (Larsdotter, 2006; von Sperling, 2007).

Algae incorporate phosphorus in the form of inorganic orthophosphates (Becker, 1994). When there is more phosphate the algae will assimilate greater quantities (Aitchison and Butt, 1973; Markou et al, 2012; Powell et al, 2006b). It appeared as though some algal species removed more phosphorus at lower light intensities (Hessen et al, 2002; Markou et al, 2012; Martinez et al, 1999). However, this is contrary to what is expected (Brown and Shilton, 2014) because energy is required for phosphorus uptake and it is received through photosynthesis (Becker, 1994; Kaplan et al, 1986). It was discovered by Powell et al (2009) that this is because at higher light intensities the phosphorus is quickly stored, but also quickly used in cellular processes. Thus, when it was measured the algae exposed to lower light intensities still had more polyphosphate stored. The best environmental conditions for algae growth increases phosphorus uptake (Larsdotter, 2006).

A typical algal cell's composition can be represented by the empirical formula $C_{106}H_{181}O_{45}N_{16}P$ (Stumm and Morgan, 1981). A typical bacterial cell's atoms can be represented by the empirical formula $C_{60}H_{87}O_{23}N_{12}P$ (Metcalf and Eddy, 2003). These stoichiometric formulae demonstrate a ratio of 106 atoms of carbon to 16 atoms of nitrogen to one atom of phosphorus in algae (C:N:P 106:16:1), and 60 atoms of carbon to 12 atoms of nitrogen to one atom of phosphorus in bacteria (C:N:P 60:12:1). Wastewater treatment with algae may need to supplement nitrogen to ensure there are adequate materials for cellular growth (Boelee et al, 2012; Converti et al, 2009; Solovchenko et al, 2008), and to remove greater concentrations of phosphorus (Beuckels et al, 2015; Griffiths, 2009). In Griffiths' (2009) experiments urea and sodium nitrate ($NaNO_3$) worked well to increase the available nitrogen and remove additional phosphorus.

When increasing microorganism growth it may be necessary to include suspended solids removal. Algae cells can be 2 – 20 μm in diameter and can behave like a colloidal suspension making them difficult to settle (Wan et al, 2015). One method of lowering suspended solids is through chemical addition. Another is by auto- and bio-flocculation. Aquaculture and filtration are two additional techniques for lowering suspended solids. The addition of alum, lime, and ferric chloride are known to flocculate and settle solids and colloidal matter in wastewater treatment (US EPA, 1983), but because the nutrient recovery and reuse of their sludge is energy intensive (Brown and Shilton, 2014) they are not discussed further.

Autoflocculation is induced by increasing the pH of the solution often with the addition of sodium hydroxide (Barros et al, 2015). The increasing pH helps neutralize the cell wall allowing for a denser floc and enhanced settling (Barros et al, 2015). It also increases the precipitation of magnesium hydroxide, calcium hydroxide, calcium phosphates and other insoluble precipitates which adsorb to cellular matter as they settle (Barros et al, 2015). Autoflocculation is often followed by a sedimentation basin to settle the solids (Barros et al, 2015)

Bioflocculation is a similar process to autoflocculation, but is a biological method for settling suspended solids (Barros et al, 2015; Wan et al, 2015). Flocculation is aided by naturally released biopolymers, especially extracellular polymeric substances (predominantly made of polysaccharides and proteins), from bacteria and algae (Barros et al, 2015; Wan et al, 2015). Sometimes species known to help bioflocculation, such as *Pestalotiopsis* sp. KCTC 8637P or *Paenibacillus* sp., are introduced into the system to help settle suspended algae (Wan et al, 2015). This process encourages larger floc particles to form of bacterial-algal composition and

algal-algal composition with better settling characteristics (Wan et al, 2015). This process is usually followed by a sedimentation basin to allow the solids to settle (Barros et al, 2015; Wan et al, 2015).

Aquaculture is a method of generating food and other products from nutrient rich water and waste streams (US EPA, 1983). Some aquatic organisms can feed on algae and decrease the suspended solids, such as invertebrates (*Daphnia* – the water flea, *Artemia* – brine shrimp, and some bivalve mollusks) and certain species of fish (mostly from the carp family) (US EPA, 1983).

Lastly filtration, in particular intermittent sand filtration, is a common low maintenance method for removing solids from lagoons (US EPA, 1983). The two methods to set up the sand filters are single-stage or series (US EPA, 1983). The use of single-stage or series design depends on the polishing necessary for discharge (US EPA, 1983). The size of the sand is the most important factor to producing high quality effluent and generally a single-stage set up is sufficient to produce an effluent with less than 30 mg/L total suspended solids (US EPA, 1983).

Precipitated phosphorus adsorbed to particles, or assimilated into algal and bacterial cells can re-enter the water (Tuszynska et al, 2013). These settled solids, or sludge, can be affected by a myriad of conditions that contribute to the re-release of phosphorus into the wastewater system (Ann et al, 2000; Brown and Shilton, 2014; Gomez et al, 1999; Martens and Harris, 1970; Tuszynska et al, 2013). These conditions include the redox potential, dissolved oxygen, pH, temperature and molecular form of phosphorus (Linquist et al, 2011).

Slightly acidic conditions resulted in re-release of phosphorus from the sludge, and more alkaline conditions resulted in less available, more tightly bound, phosphorus (Peng et al, 2007;

Puig et al, 2010). A somewhat acidic environment may be found near the anaerobic zone at the bottom of the pond as by-product of fermentation. As a result it may be necessary to remove the settled biomass from the stabilization ponds to prevent the re-release of phosphorus from decaying cellular matter (Brown and Shilton, 2014). Algae cells have different properties than bacterial cells and the algal solids took several days to decay and release their nutrients (Powell et al, 2011a) which would allow adequate time for their removal.

Precipitation and assimilation into biomass are two effective methods of removing phosphorus from lagoons. A more alkaline pH could be encouraged to try and boost phosphate precipitation. If there is insufficient nitrogen for cellular processes supplemental nitrogen could be added to lagoons to increase phosphorus assimilation and uptake by microorganisms. This could increase microorganism growth, but also reduce levels of phosphorus in the final effluent. However, if additional growth is encouraged it might be necessary to implement a solids removal step to polish the final effluent before discharge. The re-dissolution of phosphates into the wastewater can sometimes be a problem in lagoons.

1.4 Wastewater Treatment and Discharge Regulations

Wastewater lagoons in Manitoba are licenced provincially by Manitoba Conservation and Water Stewardship. The Environmental Approvals Branch issues Licences under the Environment Act. Lagoons must also comply with the provincial directive Water Quality Standards, Objectives and Guidelines Regulation under the Water Protection Act (2011). Lastly they must also comply with the Federal Wastewater Systems Effluent Regulations under the Fisheries Act.

Under the Water Protection Act the Water Quality Standards, Objectives and Guidelines Regulation the communities of Niverville and Lorette (the two communities with lagoons monitored for this thesis) need to meet a 200 fecal coliform or *Escherichia coli* organisms/100 mL, 25 mg/L carbonaceous biochemical oxygen demand (CBOD), 25 mg/L biochemical oxygen demand (BOD), 25 mg/l total suspended sediments (TSS – excluding growing algae), and 1 mg/L phosphorus limit.

In the Federal Wastewater Systems Effluent Regulation under the Fisheries Act both communities need to meet the average effluent limit concentrations of: 25 mg/L CBOD; 25 mg/L TSS; 0.02 mg/L chlorine; and 1.25 mg/L un-ionized ammonia. The rural municipalities did not test for un-ionized ammonia before this year; neither community chlorinates their wastewater; and both stabilization pond systems have been able to meet the CBOD, BOD, and TSS regulations.

Their operating licence allows for intermittent discharges after June 15 and before November 1. This equates to a minimum of 227 days of storage capacity, and 228 days in leap years.

1.5 Scope of the thesis and objectives

To comply with the regulations for the operation of the wastewater treatment systems it is necessary to alter the way things have always been done. Over the period May 5, 2015 to November 9, 2015 this thesis examines the differences between the two types of lagoons; facultative (Niverville) and aerated (Lorette). It evaluates how the wastewater is treated in the lagoon system and if there is anything that can be done to limit the need for additional

treatment steps. Additional treatment steps, such as chemical precipitation, will be necessary if these lagoons are not in compliance with the discharge regulations.

In Manitoba there has been limited research into understanding the nutrient treatment mechanisms in lagoons. The scope of the thesis is to analyse the operation and treatment of the wastewater lagoons over the monitoring period. Then use this information to determine what is happening in the system and how to get the most from them.

For this thesis the lagoons were monitored from May 5, 2015 to November 9, 2015. The effectiveness of the two treatment methods are reviewed based on the information gathered during this timeframe. The data collected is also compared to the regulations they must comply with to determine what changes will need to be made, and if there are any areas for cost savings (i.e. using natural processes over chemical dosing to comply with regulations). Both communities have been able to successfully comply with licence CBOD, BOD, TSS and coliform limits for several years, but there is some uncertainty about their ability to treat nitrogen and phosphorus.

The research objective of this thesis is to improve understanding of chemical and biological nutrient removal mechanisms of existing wastewater lagoon treatment and compare two different stabilization ponds – one aerated and one facultative from a similar geographic region in Manitoba, Canada.

This can be separated into three main focuses:

1. The first is investigating what contributes to nitrogen and phosphorus removal from the wastewater stabilization ponds.
2. The second is a comparison of the two stabilization ponds to determine if one has any advantage over the other.
3. The third is determining whether the stabilization ponds will meet the changing effluent discharge requirements.

Chapter 2: Materials and Methods

2.1 Niverville Facultative Lagoon: process and operation

The wastewater lagoons used by the municipality of Niverville, Manitoba serve a community of approximately 5000 residents. An aerial photograph can be seen in Figure 2. The community is served by 6 lift stations that are called: Drover's Run, Arena Road, 3rd Avenue, 4th Street, Edelweiss and Claremont. The Claremont, 4th Street and Arena Road lift stations pump directly to the lagoon, and based on 2015 data account for about 35%, 62% and 3% of the flow respectively. The lagoon receives approximately 1400 m^3 per day. The lagoon also receives a small amount of wastewater hauled to the site from holding, and septic, tanks that wasn't quantified. The secondary wastewater stabilization ponds mature until they comply with regulatory requirements and can be discharged. The designated time period for discharge is from June 16 to October 31 of each year. The cells are designed to have a minimum 227 days of storage.

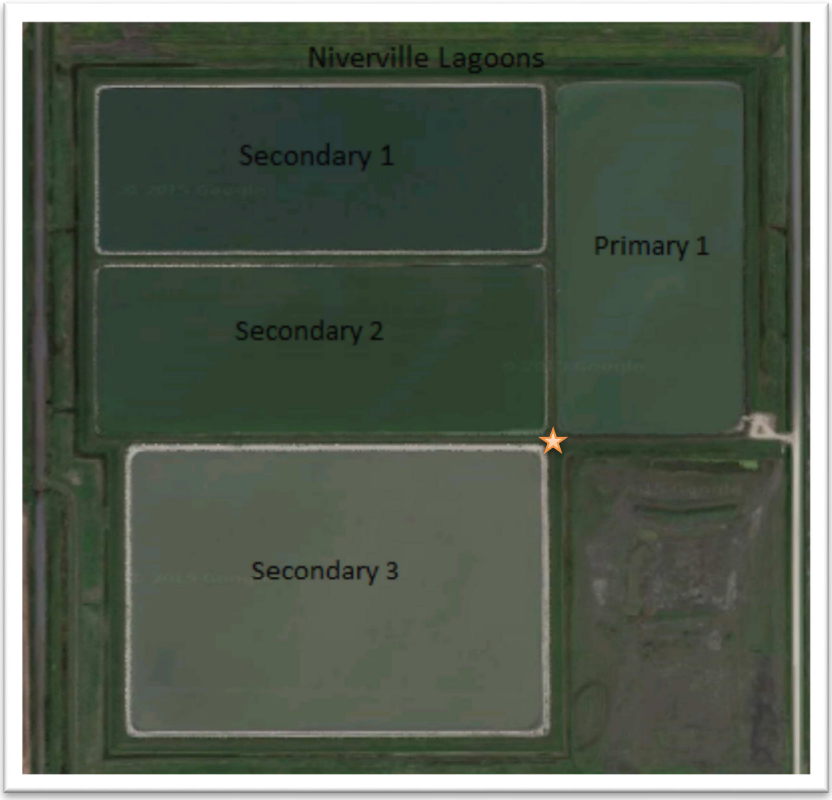


Figure 2: An overhead view of the Niverville Lagoon. The small star indicates the location of the rain gauge set up onsite (Google Maps, 2015a).

There are four purely facultative ponds. Each of the lagoon cells are rectangular in shape and have a flat bottom. The primary cell has earthen sides. The three secondary cells have stone rip-rap around all four sides. All of the lagoon cell sides are designed to have a slope of 4:1 (horizontal:vertical). The four lagoons have a maximum operating depth of 1.5 meters. It is necessary for them to maintain a minimum of 1 meter freeboard. The primary cell (primary 1) has a maximum capacity of approximately 110,000 m^3 (τ = 77 days); the north secondary cell (secondary 1) has a maximum capacity of approximately 128,000 m^3 (τ = 90 days); the middle secondary cell (secondary 2) has a maximum capacity of approximately 128,000 m^3 (τ = 90 days); and the south secondary cell (secondary 3) has a maximum capacity of approximately 208,000 m^3 (τ = 146 days).

Raw wastewater enters the primary cell through force-main piping to the center of the cell. There is generally one secondary cell connected in series at a time. The operation of the cells in 2014 and 2015 followed a similar pattern. The secondary cell 1 is filled during the late summer and fall (July/August to November) and then isolated for the winter. During this time period it goes through a freeze-thaw cycle and is discharged after June 15. The secondary cell 3 is used during the winter and early spring (November/December to April/May) and then isolated before discharge after June 15. The secondary cell 2 is empty through the winter and is used in the spring (April/May to July/August) while secondary cells 1 and 3 are isolated before they can be discharged. Secondary cell 2 is isolated in late summer (July/August) and discharged before November 1. This annual pattern is shown in Table 1 below.

Table 1: Representation of the annual pattern for lagoon cell operation in Niverville

<table>
<tr><th colspan="5">Niverville</th></tr>
<tr><th>Month</th><th>N-Primary 1</th><th>N-Secondary 1</th><th>N-Secondary 2</th><th>N-Secondary 3</th></tr>
<tr><td>January</td><td rowspan="12">online - active</td><td rowspan="6">isolated</td><td rowspan="4">offline - empty</td><td rowspan="4">online - active</td></tr>
<tr><td>February</td></tr>
<tr><td>March</td></tr>
<tr><td>April</td></tr>
<tr><td>May</td><td rowspan="3">online - active</td><td rowspan="2">isolated</td></tr>
<tr><td>June</td></tr>
<tr><td>July</td><td>discharge</td><td>discharge</td></tr>
<tr><td>August</td><td rowspan="4">online - active</td><td>isolated</td><td rowspan="3">offline - empty</td></tr>
<tr><td>September</td><td>discharge</td></tr>
<tr><td>October</td><td rowspan="2">offline - empty</td></tr>
<tr><td>November</td></tr>
<tr><td>December</td><td>isolated</td><td>online - active</td></tr>
</table>

The isolated secondary ponds must comply with regulatory guidelines before they can be discharged from the rear, west, of the cell into the Prefontaine Drain running along the Canadian Pacific Railway tracks. In 2015 they did not receive approval to discharge secondary

cells 1 and 3 until early July. The discharge commenced July 8, 2015. Secondary cell 2 was discharged starting September 30, 2015.

2.2 Lorette Aerated Lagoon: process and operation

The wastewater lagoons used by the Rural Municipality of Taché for the town of Lorette, Manitoba serve a community of almost 3000 residents. The community is served by one lift station. The lagoon receives approximately 600 m^3 per day and no hauled liquid wastewater. As in Niverville the cells are designed to have at least 227 days of storage capacity.

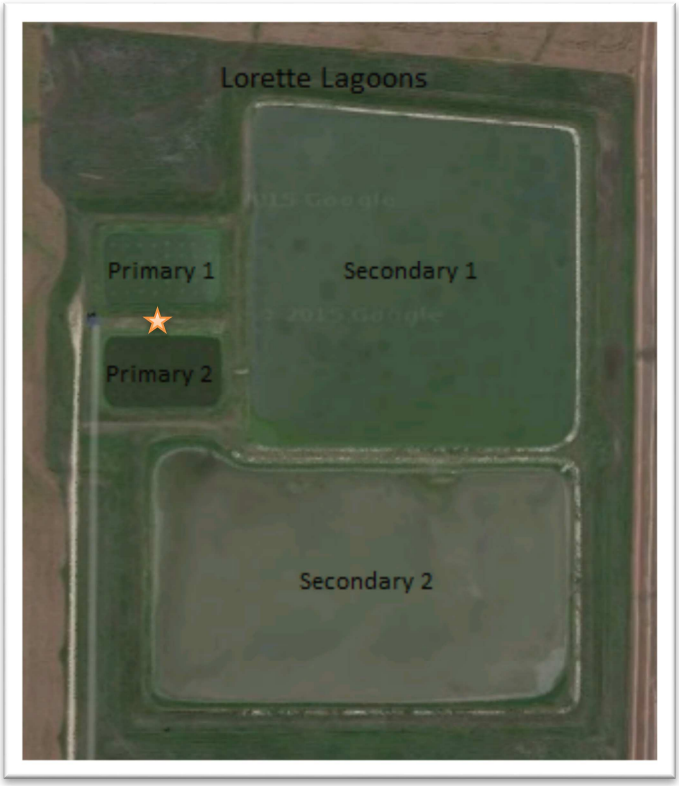


Figure 3: An overhead view of the Lorette Lagoon. The small star indicates the location of the rain gauge set up onsite (Google Maps, 2015b)

There are two primary aerated ponds and two unaerated secondary ponds. The primary cells have earthen sides, and the secondary cells have stone rip-rap around the north, east, and

south side. The west side of the secondary cells has earthen sides. The two primary cells (primary 1 and 2) are rectangular and have a flat bottom with submerged mechanical aerators. They have a maximum operating depth of 3.6 meters. The north secondary cell (secondary 1) is a not-quite-square polygon, and the south secondary cell (secondary 2) is almost rectangular. Both cells have a flat bottom, and a maximum depth of 1.5 meters. All four cells need to maintain 1 meter of freeboard. All of the lagoon cell sides are designed to have a slope of 4:1 (horizontal:vertical). The two primary cells have a capacity of just over 20,000 m^3 (τ = 33 days), the secondary cell 1, has an approximate capacity of 105,000 m^3 (τ = 176 days), and the secondary cell 2 has an approximate capacity of 108,000 m^3 (τ = 181 days).

Raw wastewater enters primary cell 1, through 300 mm forcemain piping in the north east corner of the cell. The wastewater flows into primary cell 2 in series before entering the secondary cells. The valves for all of the cells are open from November to April/May, and the flow equalizes throughout. In late May or early June the secondary cells are isolated and the primary cells are used for short-term storage during analysis and regulatory approval to discharge the secondary cells. In 2015 regulatory approval was received and secondary cell 1 was discharged June 18. Approval was not received to discharge secondary cell 2 until late October. This pattern is shown in Table 2.

The secondary cells in Lorette discharge to the rear, east, of the secondary cells and flow south into the Seine River Diversion.

Table 2: Representation of the annual pattern for lagoon cell operation in Lorette

<table>
<tr><th colspan="5">Lorette</th></tr>
<tr><td>Month</td><td>L-Primary 1</td><td>L-Primary 2</td><td>L-Secondary 1</td><td>L-Secondary 2</td></tr>
<tr><td>January</td><td rowspan="12">online - active</td><td rowspan="12">online - active</td><td colspan="2" rowspan="4">active - all valves open</td></tr>
<tr><td>February</td></tr>
<tr><td>March</td></tr>
<tr><td>April</td></tr>
<tr><td>May</td><td rowspan="4">isolated</td><td>isolated</td></tr>
<tr><td>June</td><td>discharge</td></tr>
<tr><td>July</td><td rowspan="3">online - active</td></tr>
<tr><td>August</td></tr>
<tr><td>September</td></tr>
<tr><td>October</td><td>discharge</td></tr>
<tr><td>November</td><td colspan="2" rowspan="2">active - all valves open</td></tr>
<tr><td>December</td></tr>
</table>

2.3 Raw wastewater characterization

A summary of the raw wastewater entering the lagoons in Niverville and Lorette is shown in Table 3. The samples were collected between 9:00 and 19:00 in Lorette, and between 10:00 and 20:00 in Niverville over 2 days. The samples were averaged to represent the concentration of the various parameters entering the lagoons daily. The samples were collected following hot dry weather and should be representative of the average dry weather wastewater concentration.

Table 3: A summary of average dry weather wastewater concentrations is shown for the major parameters analyzed in Niverville and Lorette.

Community	Flow (m3/d)	pH	sCOD (mg/L)	COD (mg/L)	NH3-N (mg/L)	PO_4-P (mg/L)	TSS (mg/L)	VSS (mg/L)
Niverville	1425	7.38	138.76	586.29	33.31	2.76	249	230
Std Dv	492	0.25	76.8	99.2	12.7	1.17	101	94
Lorette	597	7.44	258.29	569.87	35.68	4.01	263	243
Std Dv	89	0.16	51.4	119.5	7.2	0.79	69	68

The flow data is based on flow meter readings and pump run hours at the Niverville and Lorette lift stations. For the Lorette flow data there is a difference between the pump run hours and the flow meter. Based on information from the rural municipality staff the pump run hours are a better indicator of the flow received at the lagoon.

Niverville receives more than twice the average flow than Lorette. The soluble COD and phosphates are higher in Lorette than Niverville otherwise the concentrations of both wastewaters are similar. These communities are preparing to expand their wastewater stabilization ponds because of population growth. The raw wastewater information can be useful for future wastewater treatment expansion.

2.4 Lagoon Sampling Procedure

The lagoon cells in Lorette and Niverville were periodically sampled from the water surface using a 5 meter telescopic sample pole from May 5, 2015 to November 9, 2015. Samples were collected from the Lorette lagoon cells 6 times in May; 12 times in June; 8 times in July; 4 times in August; 5 times in September; 4 times in October; and 1 time in November. Samples were collected from the Niverville lagoon cells 6 times in May; 8 times in June; 12 times in July; 4 times in August; 5 times in September; 6 times in October; and 1 time in November. Generally the windward and leeward side of the lagoon cells were sampled, and the data was averaged for the cell. A 500 mL sample was collected from each location. Raw wastewater samples were taken from lift stations in both communities over 2 days following hot dry weather. Samples were collected between 9:00 – 19:00 in Lorette and 10:00 – 20:00 in Niverville over 2 days. The lift stations are approximately 15 meters below grade.

Samples were collected by lowering a container down from ground level to fill a 500 mL sample container used for all the samples collected.

The sample containers were stored in a cooler with cold packs after collection and during transportation. The containers were then transferred to a refrigerator in the Environmental Engineering Laboratory at the University of Manitoba where they were stored until analysis.

Photos were taken of the sample containers, and they were analyzed for pH, total ammonia-nitrogen, nitrate and nitrite, orthophosphate, chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), total suspended solids (TSS), and volatile suspended solids (VSS). The pH was measured in the field periodically to confirm the pH was representative when analyzed the following morning. Temperature was measured in the field when the samples were collected. The samples were periodically analyzed for total phosphorus. The samples were generally analyzed in the laboratory within 24 hours of their collection by post-doctoral and graduate students.

2.5 Analytical Methods

Rainfall was measured using a Springfield 120 mm rain gauge fixed to a fence post 1 meter off the ground. pH was measured in the lab, and in the field, using a Thermo model 230A pH meter. A glass Thermo alcohol filled -10 ˚C to 60 ˚C thermometer was used for field temperature measurement. A Thermo Scientific Orion 3 star DO meter and accompanying probe were used for field dissolved oxygen measurement.

Samples were also analysed by a Lachat Instruments flow injection analyser, or FIA, for ammonia, nitrate and nitrite, and orthophosphate. The ammonia was measured using the Berthelot reaction with the QuikChem® Method 10-107-06-1-I based on standard methods for the analysis of water and wastewater 4500 NH_3 H for FIA (Lachat Instruments, Loveland, CO). Nitrate and nitrite were measured using the cadmium reduction method with the QuikChem® Method 10-107-04-1-C based on standard methods 4500 NO_3-I for FIA (Lachat Instruments, Loveland, CO). Orthophosphate was measured using the ascorbic acid method with the QuikChem® Method 10-115-01-1-A based on standard methods 4500-P G (Lachat Instruments, Loveland, CO).

Total phosphorus was measured using the Hach® TNT 845 total phosphorus method (Hach Company, 2014). Samples were run unfiltered and blended for COD and filtered for sCOD using the closed reflux colorimetric method from standard methods 5220 D. Total suspended solids followed the standard methods procedure 2540 D, and volatile suspended solids followed the standard methods procedure 2540 E.

2.6 Un-ionised Ammonia-nitrogen Calculations

Temperature and pH affect the concentration of un-ionised ammonia and ammonium in equilibrium that make up total ammonia-nitrogen (Environment Canada, 1999; Jofre and Karasov, 1999).

(1) $$NH_4^+ \leftrightarrow NH_3 + H^+$$

Equation 1 shows the equilibrium that exists between ammonium and ammonia in aqueous solutions. Using this reaction the pH dependent dissociation constant K_a can be determined using equation 2 (Erickson, 1985).

(2) $$K_a = \frac{[NH_3]\,[H^+]}{[NH_4^+]}$$

The amounts of each product and reactant are also dependent on the temperature which can be seen in equation 3 (Emerson et al, 1975).

(3) $$pK_a = 0.0901821 + 2729.92 / T_K$$

The temperature is reported in Kelvin. Absolute zero in Kelvin is -273.15 ˚C; using equation 4 the temperature can be converted into Kelvin (CEQG-CCME, 2010).

(4) $$T_K = T_{^\circ C} + 273.15$$

Emerson et al (1975) developed equation 5 based on the solution's temperature and pH to determine the fraction of free ammonia.

(5) $$f_{NH3} = 1 / [10^{(pKa - pH)} + 1]$$

Only pH and temperature are necessary for the equation to determine the fraction of un-ionized ammonia. However, the total ammonia-nitrogen determined analytically can be multiplied by the calculated fraction to determine the concentration of free ammonia.

Chapter 3: Results and Discussion

3.1: Environmental Factors

3.1.1 Wind

The nearest weather station to the wastewater stabilization ponds is in Kleefeld, Manitoba. The weather station is approximately 18 km from Niverville and 22 km from Lorette. The approximate wind speed and relative humidity for the Lorette and Niverville lagoon sites are averaged for each full month over the monitoring period (Environment Canada, 2015) and are shown in Table 4 below. Over the 189 day monitoring period there were only 44 days when the wind did not reach speeds of at least 18 km/h (Environment Canada, 2015).

Table 4: Approximate average relative humidity and wind speed at the lagoons in Niverville and Lorette over the period May 5 to November 9, 2015, as measured in Kleefeld, Manitoba (Environment Canada, 2015).

Month	Average Relative Humidity (%)	Average Wind Speed (km/h)
May	60.2 ± 23.5	16.2 ± 9.7
June	67.9 ± 18.2	11.3 ± 6.7
July	73.4 ± 14.9	12.1 ± 7.4
August	70.9 ± 17.7	12.2 ± 7.8
September	68.0 ± 17.7	13.6 ± 6.4
October	71.9 ± 15.9	14.5 ± 8.0

According to Badrot-Nico et al (2010) if the wind speed is greater than 18 km/h well mixed conditions in the lagoon can be assumed. The average wind speed was greater in May and October with the highest monthly average in May. Gu and Stefan (1995) collected data over a couple of years in Harris, MN and concluded the cells are completely mixed 45% of the time. A Figure with the TSS/VSS and COD/sCOD concentrations can be seen in Appendix A

In Lorette and Niverville the average wind speeds are all greater than 11 km/h which is more than half of 18 km/h. The Lorette and Niverville wastewater lagoons are surrounded by agricultural fields with very few trees that could also contribute to greater rates of mixing. Likely the lagoons are completely mixed more than 45% of the time as measured by Gu and Stefan (1995).

Greater mixing from the wind contributes to aeration, and evaporation at the air-water interface (Rockne and Brezonik, 2006). It helps break up stratification when it forms in the ponds (Gu and Stefan, 1995). In the Niverville and Lorette lagoons the facultative pond cells freeze in the winter and aren't mixed when the cells are ice-covered. This indicates when the cells are covered with ice they become stratified and anaerobic until the ice melts, as found by Middlebrooks et al. (1982).

3.1.2 Rainfall

The rainfall, or precipitation, was measured onsite from June onwards. The rainfall data from Oakbank, Manitoba, the nearest weather station with precipitation data, was used before onsite measurements were recorded.

Figure 4 shows the cumulative monthly rainfall for the lagoons. They are similar with the exception of July when Niverville received almost twice as much rainfall as Lorette.

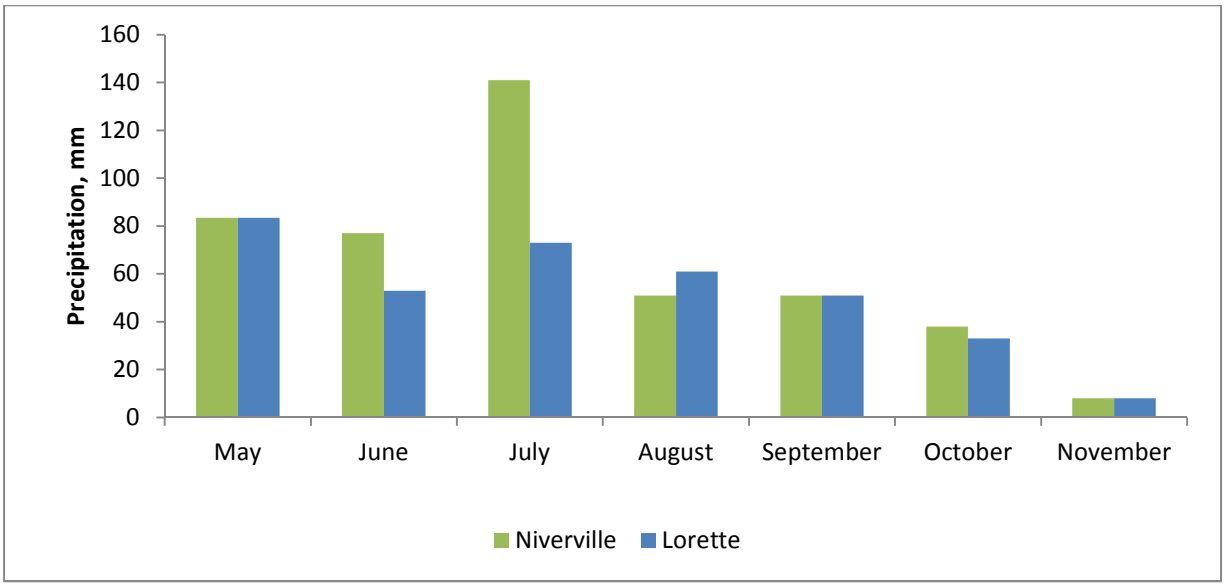


Figure 4: Monthly cumulative precipitation in Niverville and Lorette over the period May 5 to November 9, 2015. Estimated in May and measured onsite from June to November.

The largest rainfall event added approximately 60 mm of precipitation over the entire surface area of the lagoons. When the Niverville primary and secondary lagoons, and Lorette secondary lagoons, are at maximum capacity they have a depth of 1.5 meters. A 60 mm inflow represents a 4% increase in the total volume of liquid in these cells. The Lorette primary cells have a maximum capacity of 3.6 meters and 60 mm represents a 1.7% increase in volume.

The opposite effect of precipitation in these lagoons is evaporation. These are large shallow human-made bodies of water with plenty of surface area for evaporation to take place. The evaporation rate is affected by relative humidity and the air and water temperature. The nearest weather station has hourly temperature and relative humidity data. The temperature of the water's surface is based on sporadic measurements. To get a more accurate idea of the evaporation rate more surface water temperature information is needed; however, they were estimated in Appendix B.

Based on the information in subsequent sections there did not seem to be any resulting drops in analyte concentrations following a rainfall event of greater than 20 mm in a day. The estimated evaporation rate is calculated in Appendix B. The evaporation rate estimate accounts for between 15 and 45 mm/month water loss from the lagoon surface between May and October.

3.1.3 Temperature

Surface temperature results are shown for all four cells in Lorette and Niverville in Figure 5. When the external temperature was warmer, from June to September, primary cell 1 in Niverville had a lower temperature than the succeeding secondary cell, and primary cell 1 in Lorette had a lower temperature than primary cell 2. When the external temperature was colder, on some days in May, October and November the opposite was true. In general all of the lagoon cells followed a similar pattern to the external temperature.

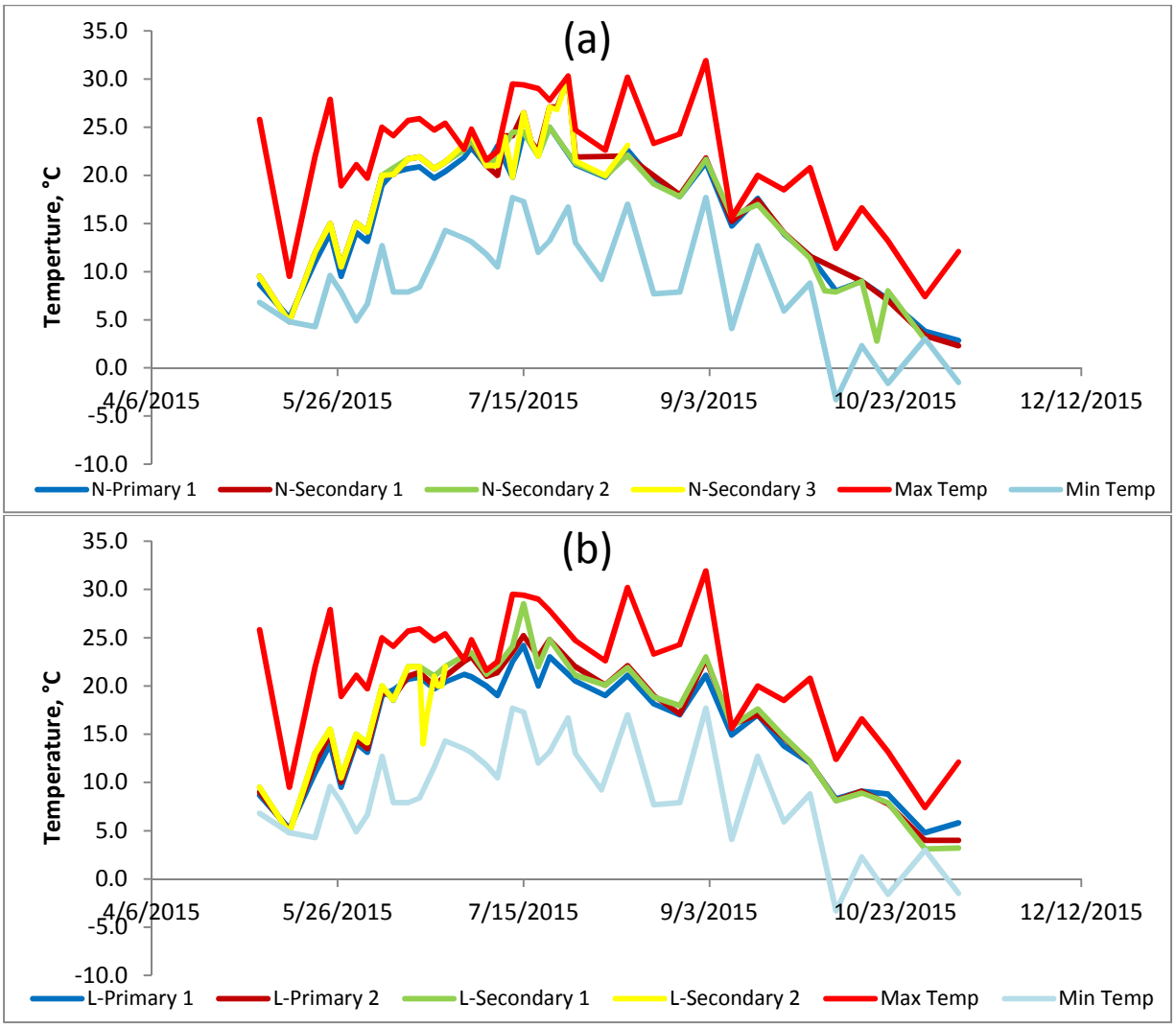


Figure 5: Surface water temperature, maximum and minimum air temperature (Kleefeld, Manitoba) for the same day of all four cells in (a) Niverville and (b) Lorette over the period May 5 to November 9, 2015 (Environment Canada, 2015).

The water temperature of the cell is impacted by the air temperature due to the large surface area. For example when it is hot outside the wastewater in the lagoons warm up and when it is cold outside it cools down. Primary cell 1 in Niverville and primary cell 1 in Lorette follow a similar trend to the other cells, but are generally lower than the other cells – with some exceptions in May, October and November. This is because these cells are impacted by the influent temperature more than the other cells. The communities' lift stations are well below

grade and the majority of the water is from groundwater sources. Groundwater is less affected by air temperature and maintains a fairly consistent year round temperature.

The air temperature and surface water temperatures in Figure 5 follow a similar pattern. This illustrates the relationship between the air temperature and the surface water temperature in the lagoon cells. Surface sampling alone does not capture the water temperature changes with depth when the lagoons are stratified. When the lagoons are well mixed the cells will have currents with cooler water circulating off the bottom of the cells. One day in June a survey was conducted from a canoe in the centre of each cell where samples were collected from the surface and the bottom of the lagoon cells. On the day the samples were collected it appears the cells were well mixed because there was little variation between the sample collected from the surface and the bottom. The results can be seen in Appendix D.

There are other times when the change in air temperature will contribute to the mixing of the cells. According to Middlebrooks et al (1982) the spring turnover has the most pronounced effect on the cells after they have been operating in stratification over the winter under the cover of ice.

Lagoon ponds turnover when there is a large enough change in the diurnal temperature (Gu and Stefan, 1995). When the lagoons warm up during the day, and the wind dies down at night, the ponds stratify with warmer water near the surface. As the air temperature cools it cools the lagoon surface layer. When the lagoon surface layer cools to less than the bottom layer the cell mixes and the layers reverse position. Gu and Stefan (1995) found that in Harris, MN this stratification and subsequent diurnal turnover occurred 28% of the time in the cells they were monitoring.

3.2: pH

Niverville and Lorette pH results from all four cells, over the monitoring period, are shown in Figure 6. Niverville secondary cell 1 does not follow the same pH trend as the other cells in May. The other three cells show a peak in pH near the end of May followed by a drop in pH. The typical lagoon operation schedule for Niverville can be seen in Table 1. Secondary cell 1 had been isolated since fall of 2014 and was not receiving any primary effluent for more than 5 months. As a result it does not follow the same trend as the other secondary cells.

During the last week of May in Figure 6 (b) all four Lorette lagoon cells show a peak pH of nearly 10 before decreasing drastically and stabilizing between about 7.5 and 9 pH units for the remainder of the monitoring period. The pH of the two secondary cells was initially higher before decreasing ahead of the peak the last week of May. Conversely the pH of the two primary cells was lower ahead of the peak the last week of May.

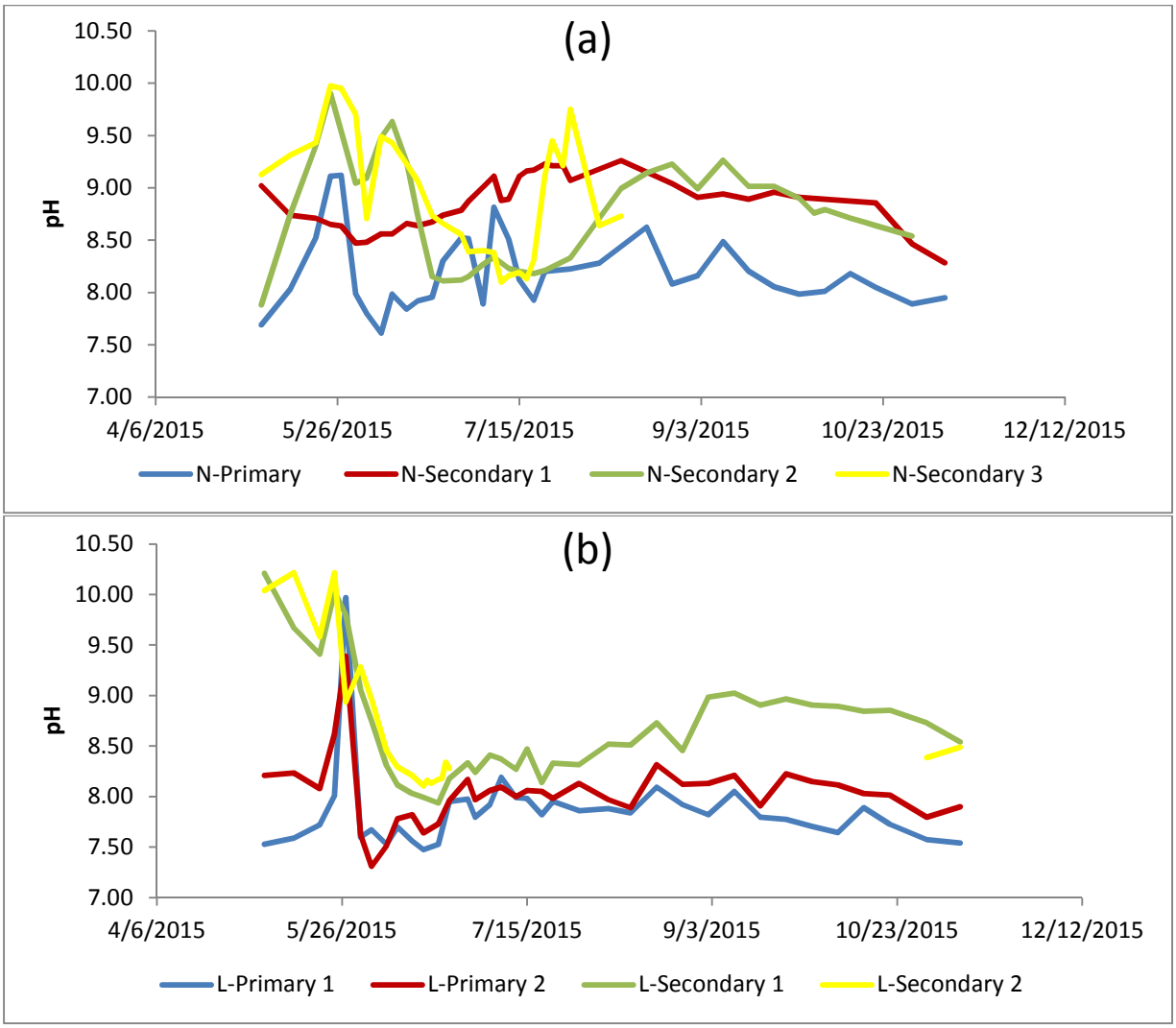


Figure 6: pH of all four cells in (a) Niverville and (b) Lorette over the period May 5 to November 9, 2015.

Table 5 shows the average monthly pH values for both lagoons over the monitoring period. The effect of the peak in late May from Figure 6 can be seen in Table 5 with the highest average pH for each cell for the month except Niverville secondary 1. The colours in the Table below approximate the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue) as shown in Table 1 and Table 2.

Niverville secondary cell 3 was offline after it was discharged and there is no data for September or October. Lorette secondary cell 2 was discharged at the end of June and the level of the lagoon was too low to collect samples until October.

Table 5: pH averaged for each month in all of the cells in Niverville and Lorette from May to October. The colour represents the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue).

Niverville Monthly Average pH								
Month	N-Primary 1		N-Secondary 1		N-Secondary 2		N-Secondary 3	
	pH	Std Dv	pH	Std Dv	pH	Std Dv	pH	Std Dv
May	8.41	0.61	8.70	0.18	9.09	0.71	9.58	0.35
June	7.99	0.29	8.64	0.10	8.82	0.63	8.98	0.37
July	8.28	0.32	9.08	0.13	8.24	0.07	8.63	0.58
August	8.36	0.23	9.15	0.16	9.02	0.23	8.69	0.06
September	8.18	0.19	8.92	0.03	9.04	0.14	No Data	No Data
October	8.03	0.12	8.73	0.23	8.69	0.09	No Data	No Data
Lorette Monthly Average pH								
Month	L-Primary 1		L-Primary 2		L-Secondary 1		L-Secondary 2	
	pH	Std Dv	pH	Std Dv	pH	Std Dv	pH	Std Dv
May	8.07	0.95	8.36	0.60	9.70	0.42	9.71	0.53
June	7.67	0.19	7.74	0.26	8.21	0.26	8.30	0.24
July	7.94	0.12	8.04	0.06	8.32	0.10	No Data	No Data
August	7.93	0.11	8.07	0.19	8.55	0.12	No Data	No Data
September	7.83	0.13	8.13	0.13	8.96	0.05	No Data	No Data
October	7.71	0.14	7.99	0.14	8.83	0.07	8.39	0.07

There is a spike in pH in the two primary cells in Lorette and the primary and secondary cells 2 and 3 in Niverville near the end of May. One reason could be increased algae growth after the ice cover melts. When the cells are ice covered they will be anaerobic and the bacteria will be more active than the algae because there is not as much available light. In the winter the aerated primary cells can be partially ice covered too. The bacteria, and existing sludge, are still active, but at very low reaction and growth rates because of the low temperature. As a result of the bacterial action under the ice there may be a surplus of carbon dioxide. This would cause a lower pH in solution because carbon dioxide takes the form of

carbonic acid. This as well as volatile fatty acids produced over the winter will depress the pH. Then when the ice cover melts and water temperatures rises this excess of available carbon is used in a quick burst of algal growth. It is a short burst of growth quickly exhausted because the bacteria are still operating at slower rates and cannot replenish the carbon dioxide as fast as it is consumed.

Photos were taken of most of the samples collected and very green wastewater is seen in all of the cells that showed the pH spike at the end of May. See Appendix C for some of the photos during and after May 27, 2015 that illustrate this theory. Generally the primary aerated cells in Lorette showed little to no algae growth, but during this pH spike they were more green than usual. The secondary cells in Lorette showed the opposite pattern; when the first sample was collected May 5, 2015 the pH was initially much higher and began decreasing until May 20, 2015 before spiking on May 27, 2015 with the other lagoon cells. One reason could be that there was a pH spike before May 5th in the Lorette secondary cells when monitoring began and only part of the spike was captured in the data.

Niverville secondary cell 1 did not receive any primary effluent after it was completely isolated in fall of 2014. It did not follow the same trend as the other lagoon cells. It is possible the full water column in the cell completely froze. If it froze to the bottom, or nearly to the bottom the microbial action would so slow there would not be excess carbon dioxide. This cell may also be nutrient limited because it had not received any primary effluent for a long time and this could contribute to the different pH pattern in this cell.

The primary aerobic cells seem to have a consistently lower pH than the primary facultative cell as seen in Table 5. This may be because the aeration generally favours bacterial

activity over algal activity. It would be favoured in part because of the increased light shielding from aeration due to solids in suspension.

In Figure 7 and Figure 8 below the pH is shown with the TSS for all the cells in Niverville and Lorette. In Figure 7 (c) and Figure 8 (c) there is a large spike in the TSS that represents an algal bloom in Niverville secondary cell 2 and Lorette secondary cell 1. The large spike in TSS is followed by increased pH. There are photos of the algae bloom in Appendix C.

This seems to confirm what is expected, that increases in algae growth result in increased pH over the monitoring period. It is especially apparent after increases in the TSS concentration resulting from algae blooms shown in the Figures below.

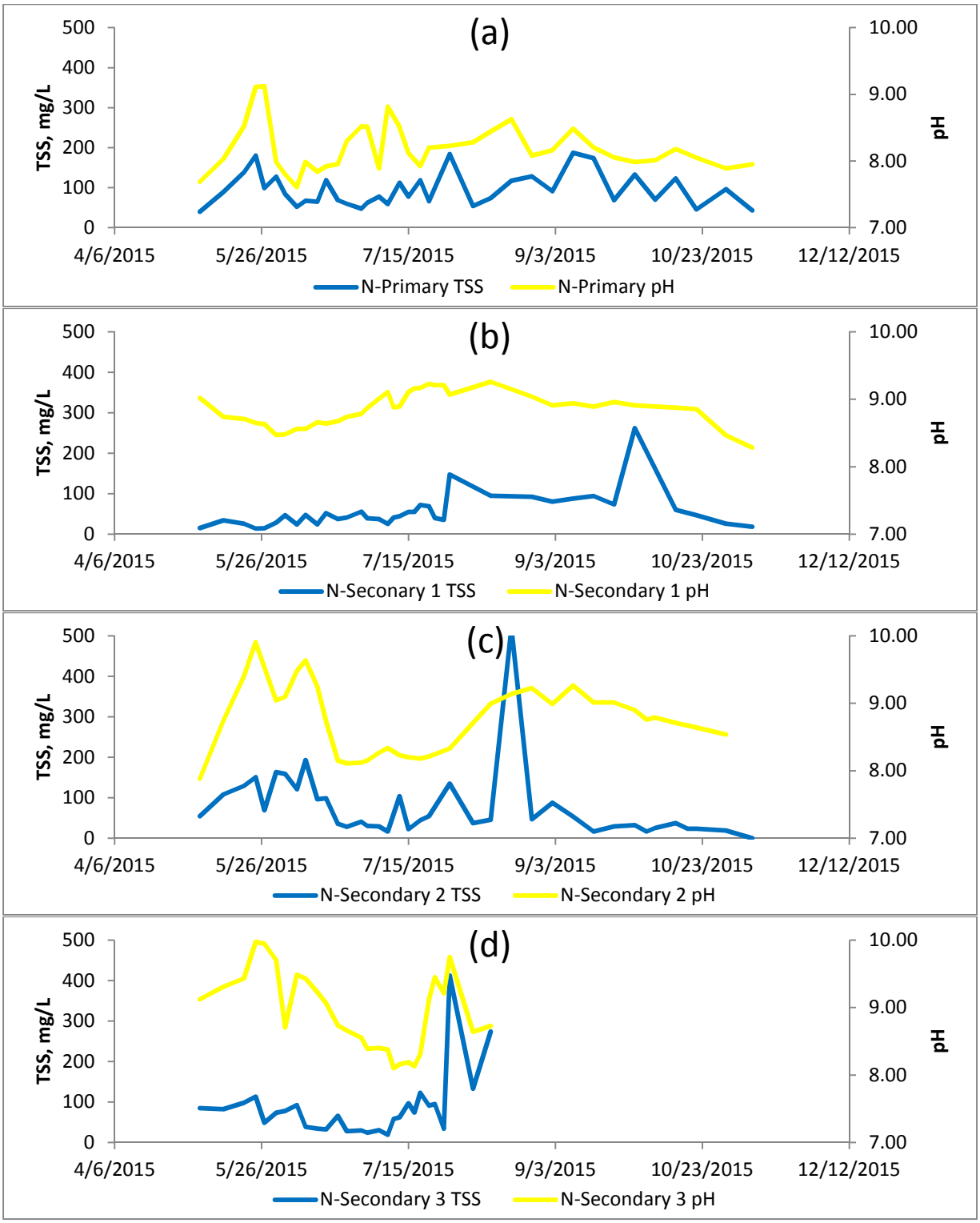


Figure 7: TSS concentration and pH in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

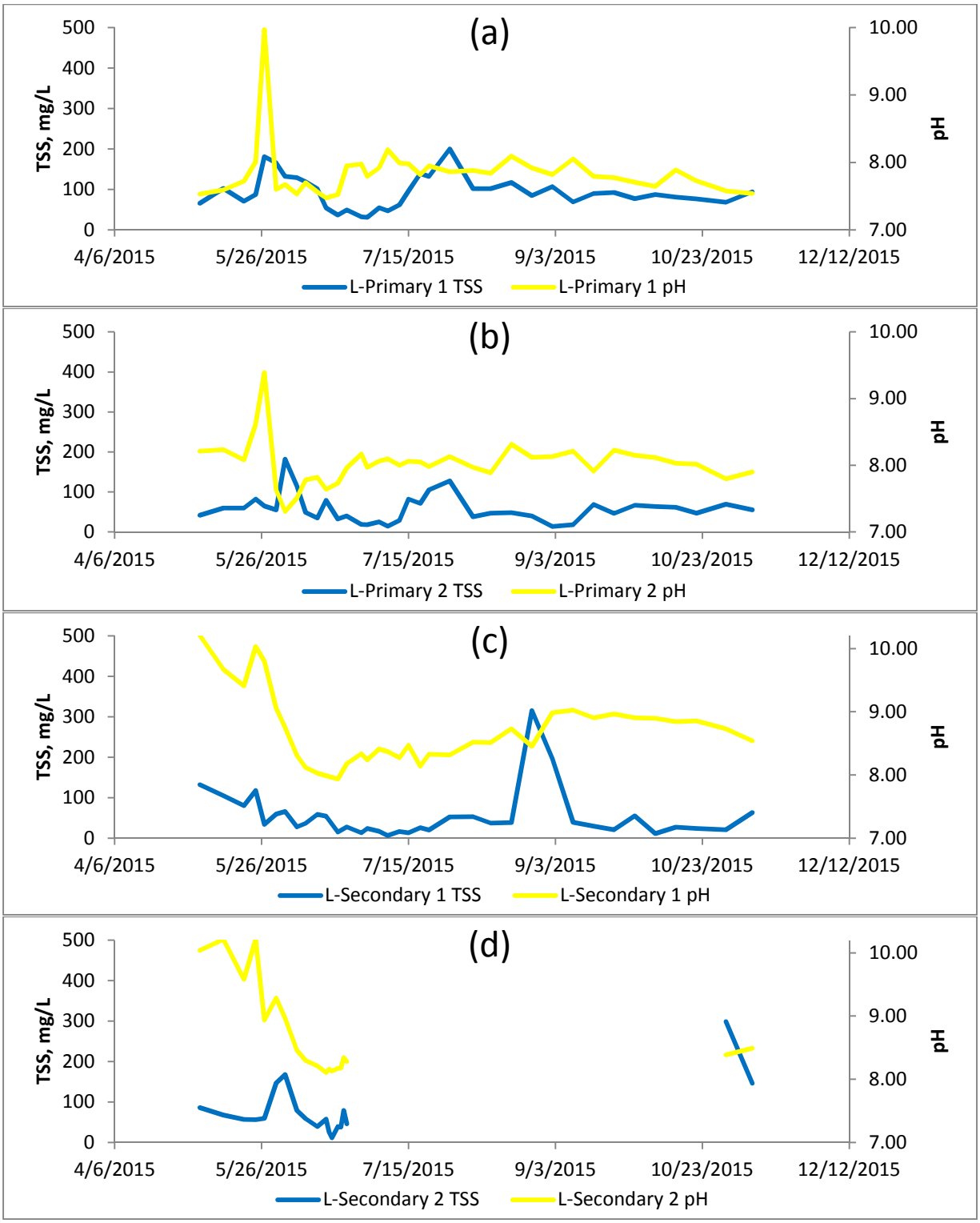


Figure 8: TSS concentration and pH in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

To measure some of the diurnal changes in the pH samples were collected every hour between 8:00 AM and 6:00 PM on September 13, 2015 from Niverville secondary cell 2. The results are shown in

Table **6** below. There is an expected change in the diurnal pH with a peak near 12:00 PM and lower values in the morning and evening when there is less photosynthesis from algae.

Table 6: One day pH monitoring in Niverville, Manitoba – secondary cell 2. The pH was analyzed each hour from all four corners of the cell to make a four corner cell composite.

Date	Time	N-S2-composite	units	pH
13/09/2015	8:00 AM	1-2-3-4	pH units	9.10
13/09/2015	9:00 AM	1-2-3-4	pH units	9.11
13/09/2015	10:00 AM	1-2-3-4	pH units	9.09
13/09/2015	11:00 AM	1-2-3-4	pH units	9.11
13/09/2015	12:00 PM	1-2-3-4	pH units	9.20
13/09/2015	1:00 PM	1-2-3-4	pH units	9.18
13/09/2015	2:00 PM	1-2-3-4	pH units	9.15
13/09/2015	3:00 PM	1-2-3-4	pH units	9.14
13/09/2015	4:00 PM	1-2-3-4	pH units	9.14
13/09/2015	5:00 PM	1-2-3-4	pH units	9.15
13/09/2015	6:00 PM	1-2-3-4	pH units	9.12

In general the pH follows patterns that would be expected in ponds with mixed microbial populations. The pH rose when algae were most active and declined when they were less active both seasonally and diurnally

3.3: Nitrogen

The total ammonia nitrogen results for all four cells in Niverville and Lorette are shown in Figure 9. There is a marked difference in the ammonia-N from the primary cells to the secondary cells. There is a decrease of ammonia-N in May and then an increase of ammonia-N in September for the lagoon cells that is most noticeable in the primary cells for Niverville and Lorette. The ammonia nitrogen is higher in the Lorette primary cells than in the Niverville primary cell.

In the Figure below Niverville secondary cells 2 and 3 and Lorette secondary cells 1 and 2 show an increase in June and eventual decrease near the end of July. There is almost no total ammonia remaining in secondary cell 1 which was isolated for more than five months.

In the Figure below from June until nearly October Lorette primary cell 2 had a higher ammonia concentration than primary cell 1. In May and October the ammonia concentration was lower in primary cell 2 and higher in primary cell 1.

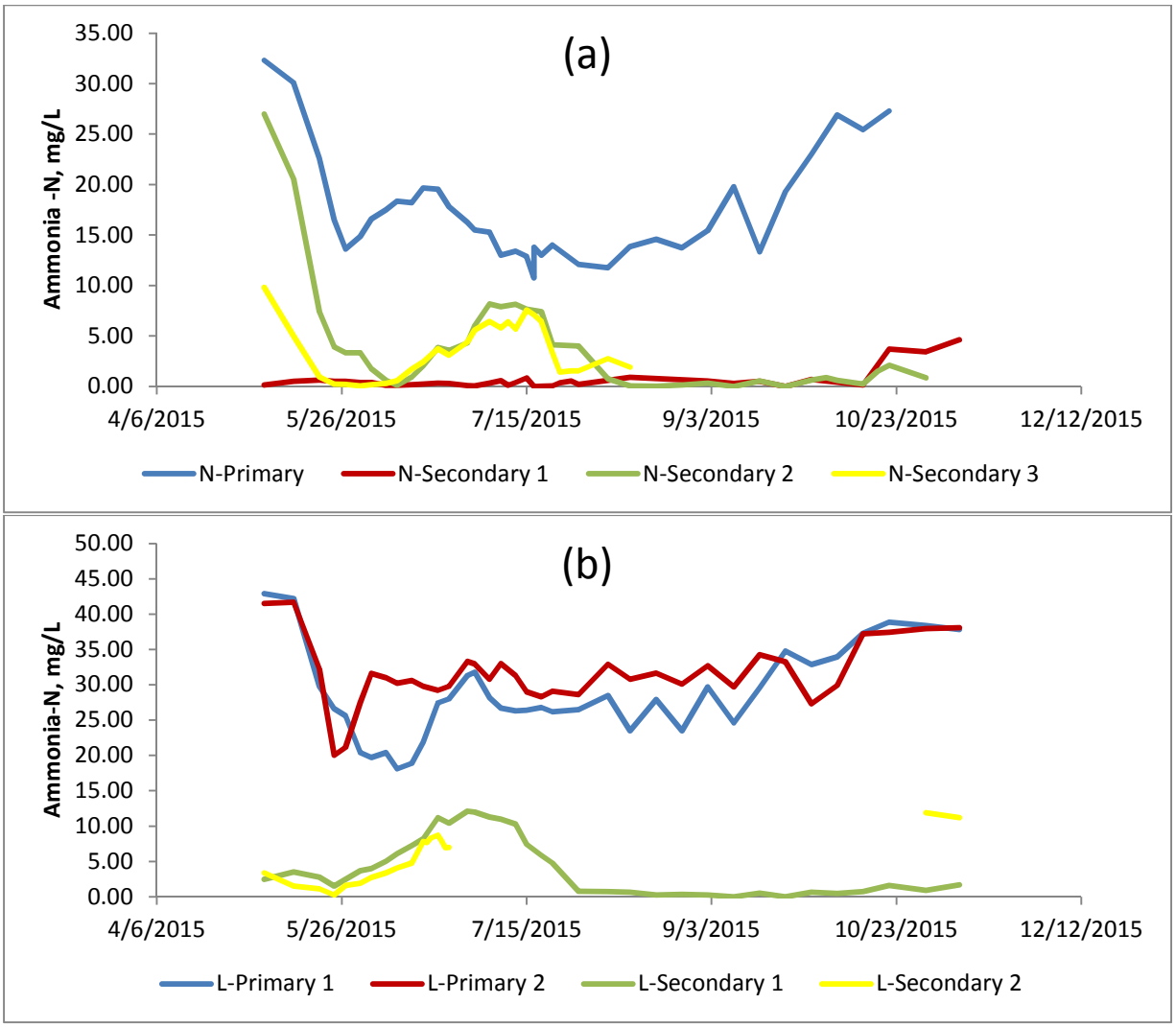


Figure 9: Total ammonia-N of all four cells in (a) Niverville and (b) Lorette over the period May 5 to November 9, 2015.

In Table 7 the average monthly concentrations from the different cells in Niverville and Lorette are shown. As shown in Table 7 and seen in Figure 9 there is a noticeable difference in the ammonia-N from the primary to the secondary cells. There is no data for Niverville secondary cell 3 in September or October because it was empty. There is no data for Lorette secondary cell 2 in July, August or September because the water level was too low to collect samples. Again the colours in the following Table approximate the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue).

Table 7: Total Ammonia-N averaged for the month in all of the cells in Niverville and Lorette from May to October. The Period Ave refers to the average for the whole period. The colour represents the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue).

Niverville Monthly Average Total Ammonia Nitrogen (mg/L)								
Month	N-Primary 1		N-Secondary 1		N-Secondary 2		N-Secondary 3	
	NH_3-N	Std Dv	NH_3-N	Std Dv	NH_3-N	Std Dv	NH_3-N	Std Dv
May	21.66	8.04	0.45	0.17	10.92	10.27	2.71	3.95
June	17.99	1.23	0.22	0.12	2.15	1.59	2.05	1.63
July	13.46	1.49	0.30	0.27	6.69	1.75	4.91	2.29
August	12.93	1.17	0.80	0.18	0.25	0.35	2.34	0.59
September	15.39	2.59	0.41	0.27	0.31	0.30	No Data	No Data
October	23.66	3.32	2.98	1.98	1.03	0.67	No Data	No Data
Period Ave	17.56	5.36	0.64	1.03	3.92	5.58	3.44	2.73
Secondary Cells Average			Average 2.60		Std Dv 3.96			
Lorette Monthly Average Total Ammonia Nitrogen (mg/L)								
Month	L-Primary 1		L-Primary 2		L-Secondary 1		L-Secondary 2	
	NH_3-N	Std Dv	NH_3-N	Std Dv	NH_3-N	Std Dv	NH_3-N	Std Dv
May	31.25	9.26	30.67	9.54	2.74	0.80	1.63	1.03
June	23.22	4.97	30.69	1.30	8.03	2.97	6.30	2.15
July	27.36	1.90	30.38	1.91	7.93	3.94	No Data	No Data
August	25.85	2.72	31.36	1.21	0.49	0.24	No Data	No Data
September	30.30	3.88	31.44	2.87	0.28	0.29	No Data	No Data
October	37.13	2.21	35.63	3.83	0.93	0.49	11.55	0.49
Period Ave	28.70	6.39	31.55	4.49	4.25	4.13	5.38	3.51
Secondary Cells Average					Average 4.64		Std Dv 3.9	

Using the raw wastewater total ammonia data in Table 3 and the averaged secondary cells in Table 7 the overall ammonia-N concentration reduction can be calculated. The Niverville overall ammonia-N concentration reduction equals 30.64 mg/L, and of that 14.89 mg/L is lost between the primary and the secondary cells. In Lorette the overall ammonia-N concentration reduction equals 30.87 mg/L, of which 26.74 mg/L is removed between primary cell 2 and secondary cells. The thought process in using the averaged secondary cells is that it will even out the differences in lagoon cell operation and represent removals for the lagoon as

a whole. Specific dates the secondary lagoons cells were isolated from the primary cell(s) was not available because it is not recorded.

There would be a greater dilution of the raw wastewater as it enters the Niverville primary cell because it is much bigger than the Lorette primary cells. Another effect is longer retention time in Niverville allowing for more ammonia removal by volatilization and biomass assimilation. In Appendix A it can be seen that there is generally higher TSS in the Lorette primary cells, likely a result of mixing from mechanical aeration. Most of the time the higher solids could shield more light and limit algal growth reducing the ammonia removal in the Lorette primary cells.

Overall Niverville and Lorette lagoons achieve very similar ammonia removals. In Niverville it appears about half of the ammonia removal occurs in the primary cell. In Lorette the majority of the ammonia removal occurs in the secondary cells.

Ammonia is affected by changes in pH and temperature as seen in Figure 10, Figure 11, Figure 12, and Figure 13. The temperature and pH changes (i.e. increased temperatures and increased pH) from ice covered operation to open water operation result in better ammonia removals from late May until late October. This is especially apparent in all the primary cells in Figure 10 (a), Figure 11 (a) and (b), Figure 12 (a), and Figure 13 (a) and (b) showing the total ammonia trend with pH and temperature for all of the cells.

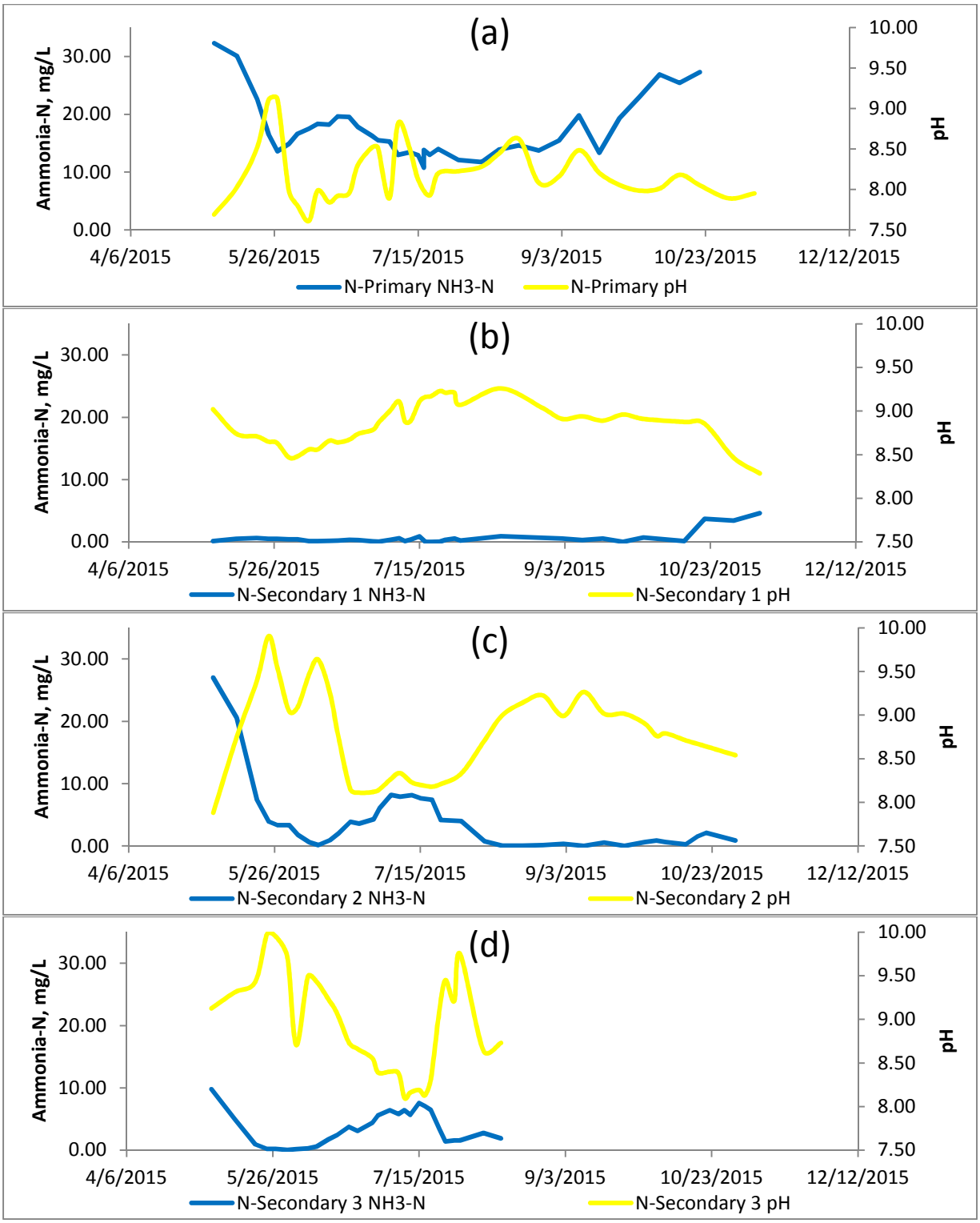


Figure 10: Total Ammonia nitrogen concentration and pH in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

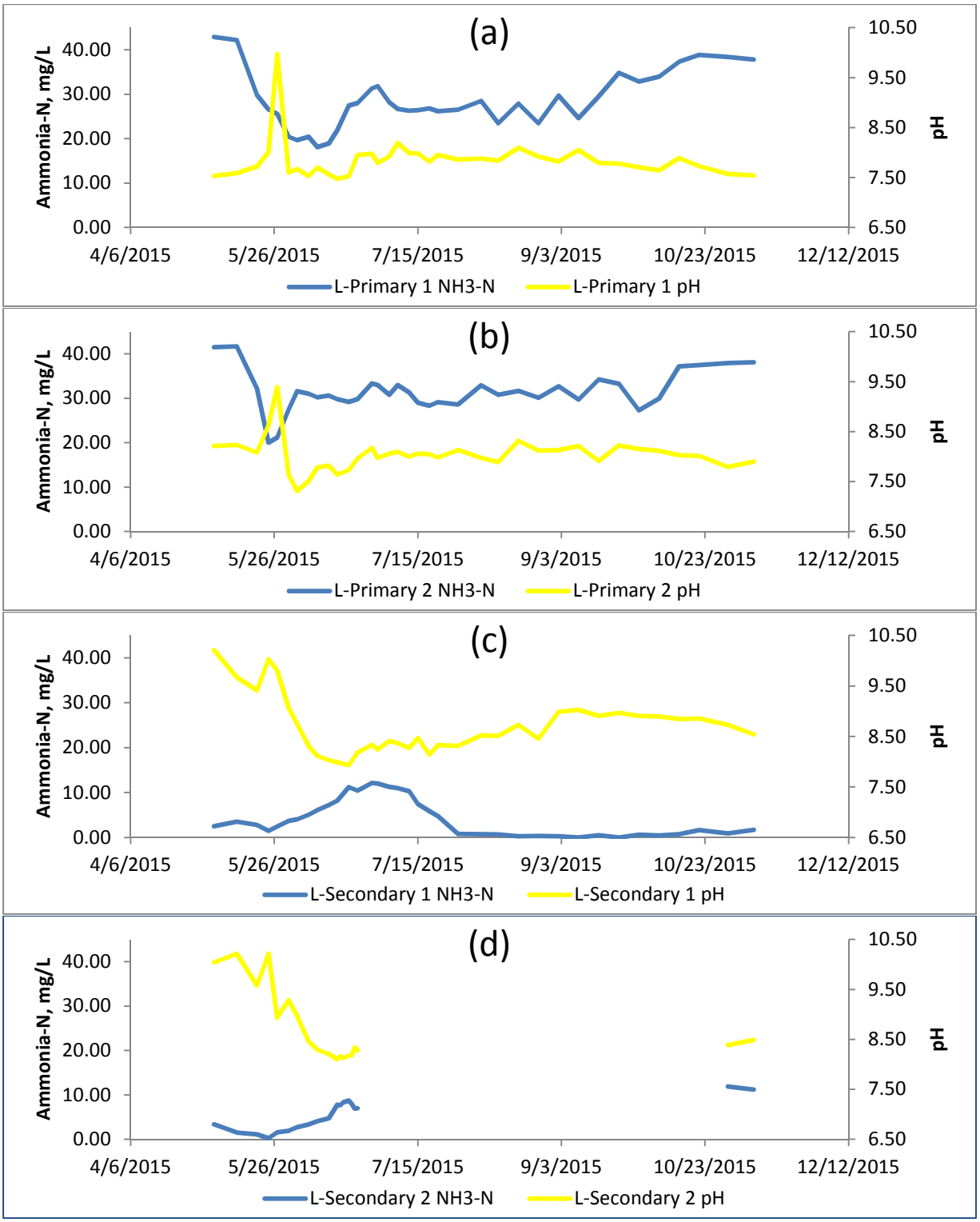


Figure 11: Total ammonia nitrogen concentration and pH in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

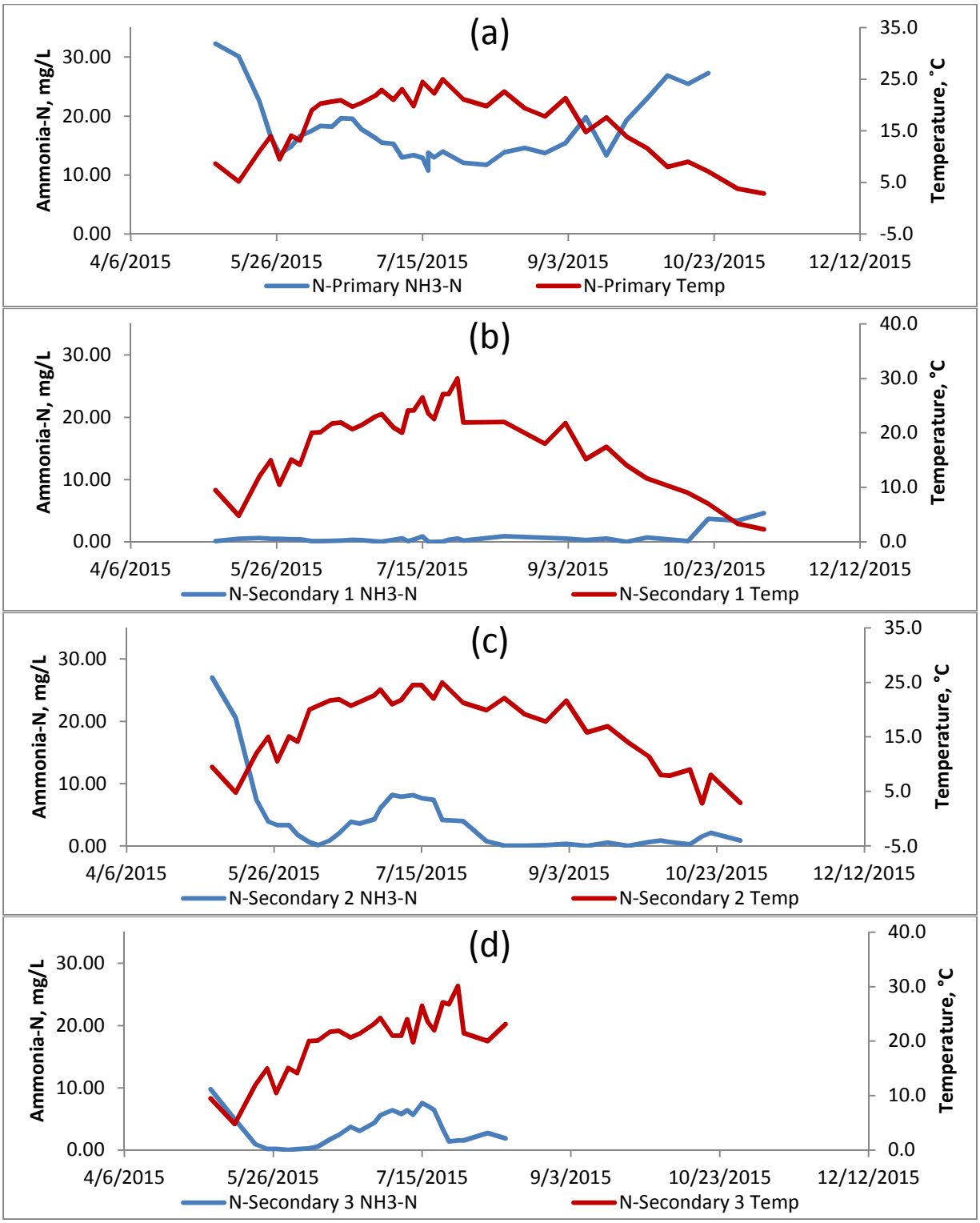


Figure 12: Total Ammonia nitrogen concentration and temperature in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

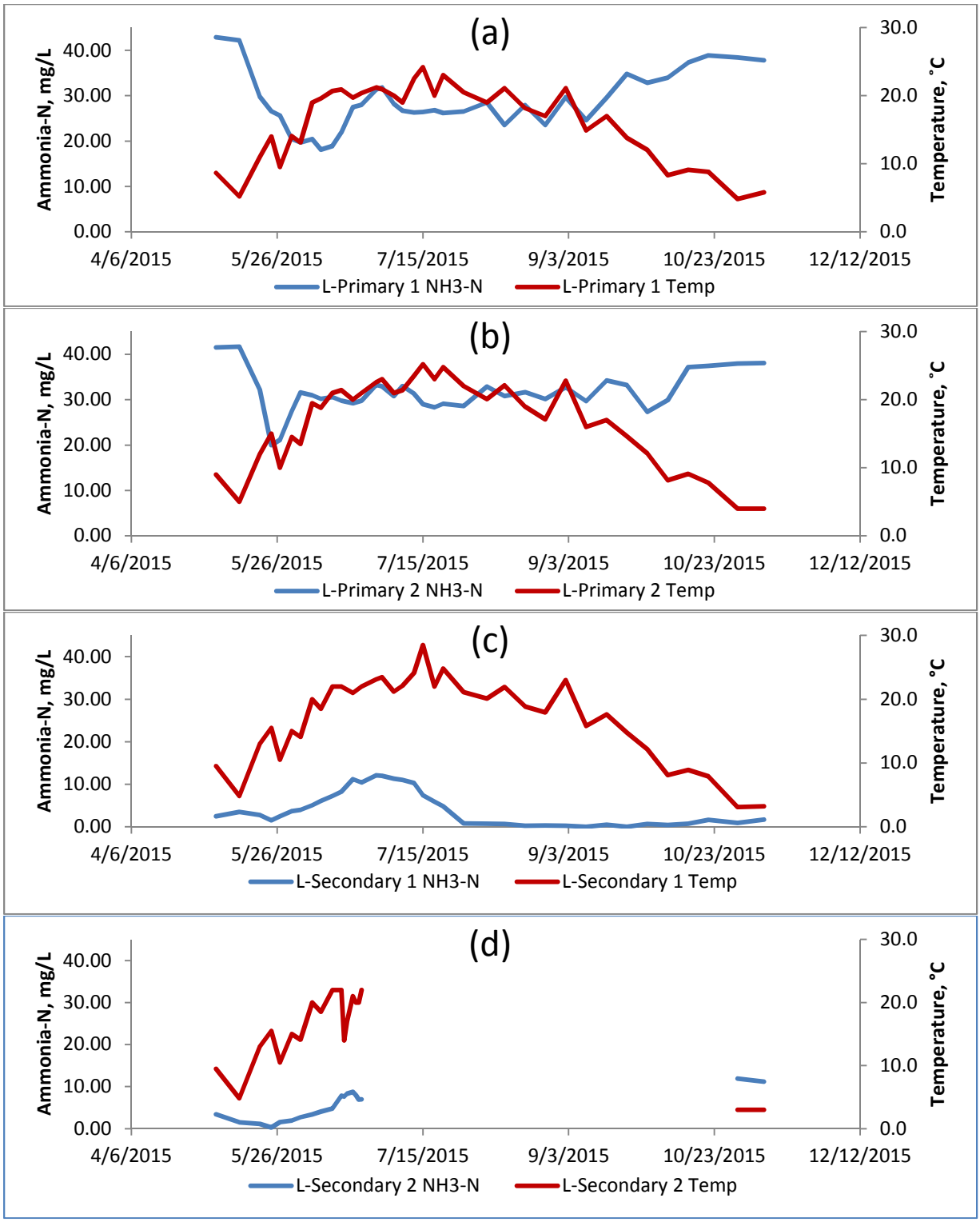


Figure 13: Total ammonia nitrogen concentration and temperature in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

In Figure 14 the un-ionized ammonia concentration can be seen for all the lagoon cells in Niverville and Lorette. It is calculated with equation 5 using the temperature and pH to determine the fraction of un-ionized ammonia in the cells. The measured concentration of total ammonia-N is then multiplied by the fraction to determine the concentration of un-ionized ammonia.

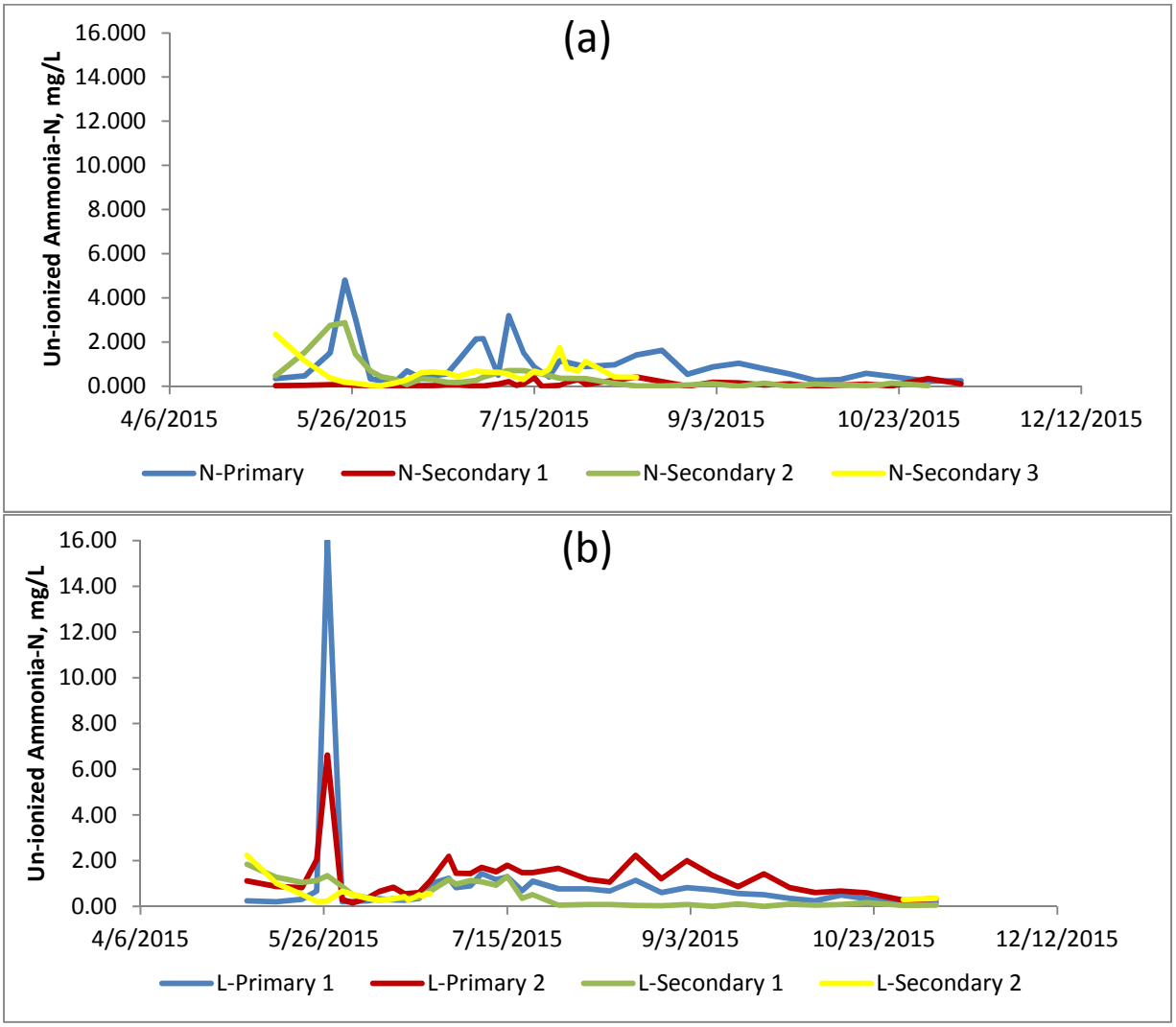


Figure 14: Calculated un-ionized ammonia-N of all four cells in (a) Niverville and (b) Lorette over the period May 5 to November 9, 2015.

There is a main peak, at the end of May, in the Niverville and Lorette un-ionized ammonia Figure, and the peak concentration is much higher in Lorette than in Niverville. The

Lorette un-ionized ammonia peak for primary cell 1 reaches 16 mg/L and almost 7 mg/L in primary 2. The Niverville un-ionized ammonia peak in primary cell 1 is less than 5 mg/L.

The monthly average un-ionized ammonia-N for each cell in Niverville and Lorette is shown in Table 8. The averages from the Table show reductions in un-ionized ammonia from the Niverville primary cell to the secondary cells. Lorette primary cell 2 has a higher average un-ionized ammonia concentration then primary cell 1, except for the month of May. Following primary cell 2 the un-ionized ammonia concentration is reduced in the secondary cells. As with the earlier monthly average Tables the colours in the Table below approximate the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue).

Table 8: Un-ionized ammonia-N averaged for the month in all of the cells in Niverville and Lorette from May to October. The colour represents the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue).

Niverville Monthly Average un-ionized ammonia (mg/L)								
Month	N-Primary 1		N-Secondary 1		N-Secondary 2		N-Secondary 3	
	NH_3	Std Dv	NH_3	Std Dv	NH_3	Std Dv	NH_3	Std Dv
May	1.51	1.53	0.04	0.02	1.51	0.95	0.59	0.72
June	0.81	0.63	0.03	0.02	0.29	0.13	0.49	0.30
July	1.32	0.93	0.12	0.12	0.52	0.15	0.72	0.35
August	1.13	0.48	0.20	0.21	0.05	0.05	0.40	0.00
September	0.70	0.30	0.08	0.06	0.07	0.06	No Data	No Data
October	0.39	0.16	0.16	0.17	0.06	0.04	No Data	No Data
Lorette Monthly Average un-ionized ammonia (mg/L)								
Month	L-Primary 1		L-Primary 2		L-Secondary 1		L-Secondary 2	
	NH_3	Std Dv	NH_3	Std Dv	NH_3	Std Dv	NH_3	Std Dv
May	2.94	6.40	1.96	2.35	1.25	0.33	0.81	0.76
June	0.49	0.39	0.81	0.63	0.51	0.29	0.42	0.11
July	1.02	0.27	1.57	0.14	0.79	0.43	No Data	No Data
August	0.80	0.24	1.42	0.54	0.06	0.03	No Data	No Data
September	0.60	0.18	1.29	0.49	0.06	0.05	No Data	No Data
October	0.31	0.14	0.54	0.18	0.09	0.05	0.30	0.04

At higher pH there is a greater concentration of un-ionized ammonia in the lagoons. This is especially evident in the Niverville and Lorette primary cells in Figure 14. In May there is

a dramatic change in the pH, seen in Figure 10 and Figure 11, and a concurrent change in the concentration of un-ionized ammonia. Ammonia gas loss from the lagoon is effected by pH, temperature and mixing (Middlebrooks et al, 1982). When biological activity is slowed by lower temperatures, but the lagoons are open and well mixed, such as in the spring and fall, these present ideal conditions for ammonia stripping to the environment (Middlebrooks et al, 1982). In May a greater concentration of the ammonia nitrogen is in the more volatile un-ionized form and would be stripped to the atmosphere.

As the temperature increases so too does the microorganism activity; this contributes to ammonia removal during times of microbe growth from June to September (Middlebrooks et al, 1982). After the spike in un-ionized ammonia for both Niverville and Lorette in May the equilibrium shifts to more ammonium and less ammonia. Ammonium is the preferred form of nitrogen for algae growth followed by nitrate (von Sperling, 2007).

In Figure 15 and Figure 16 the TSS is compared to the ammonia nitrogen and in Figure 17 and Figure 18 the TSS is compared to the nitrate for all four cells in Niverville and Lorette. There is a small TSS spike in May, visible in Figure 15 (a) and Figure 16 (a) below, succeeding elevated concentrations of ammonia nitrogen. Visible in Figure 17 (c) and Figure 18 (c) below there is a major TSS concentration spike from an algae bloom (photos in Appendix C) following spikes in the nitrate concentration.

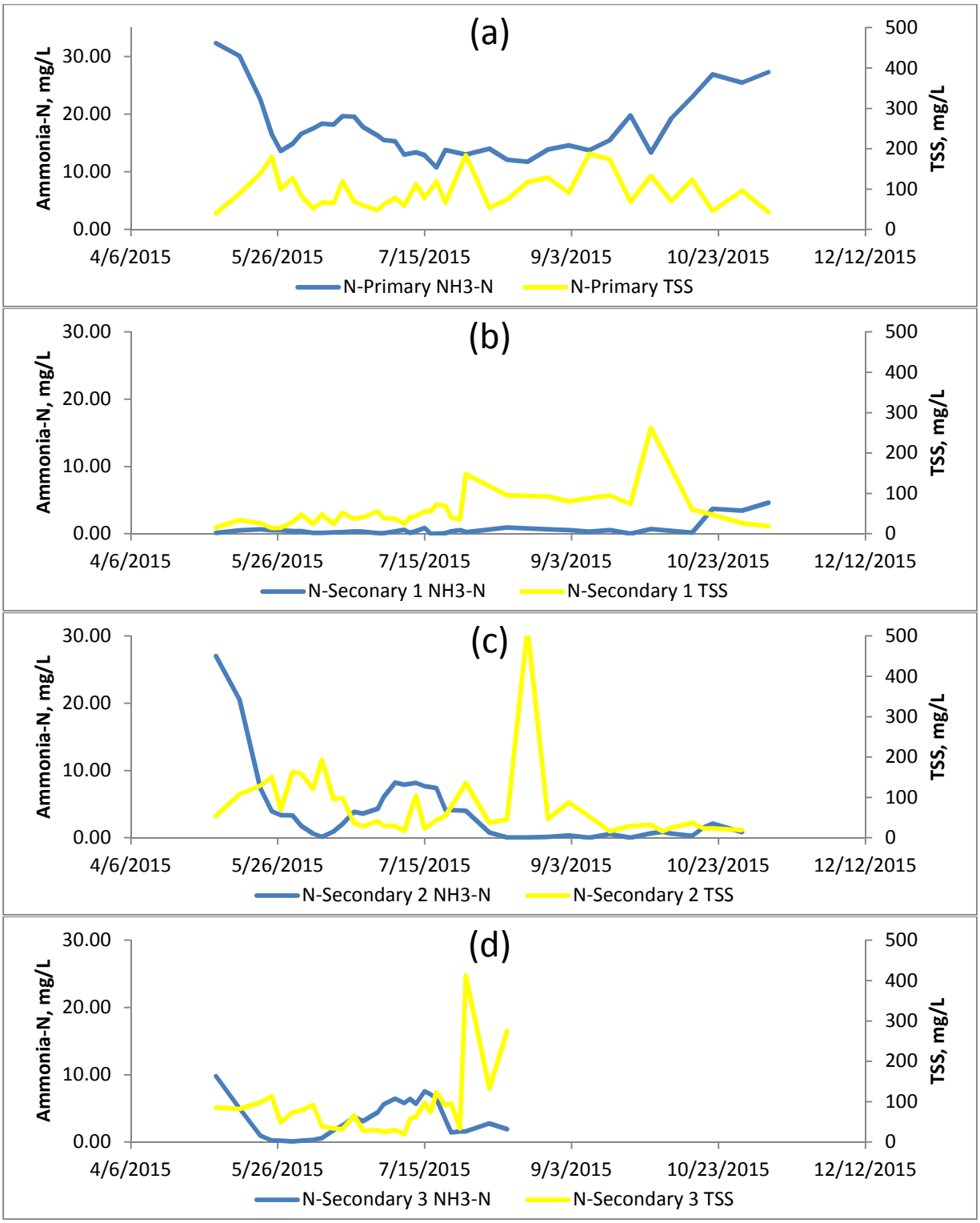


Figure 15: Total ammonia nitrogen and TSS concentration in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

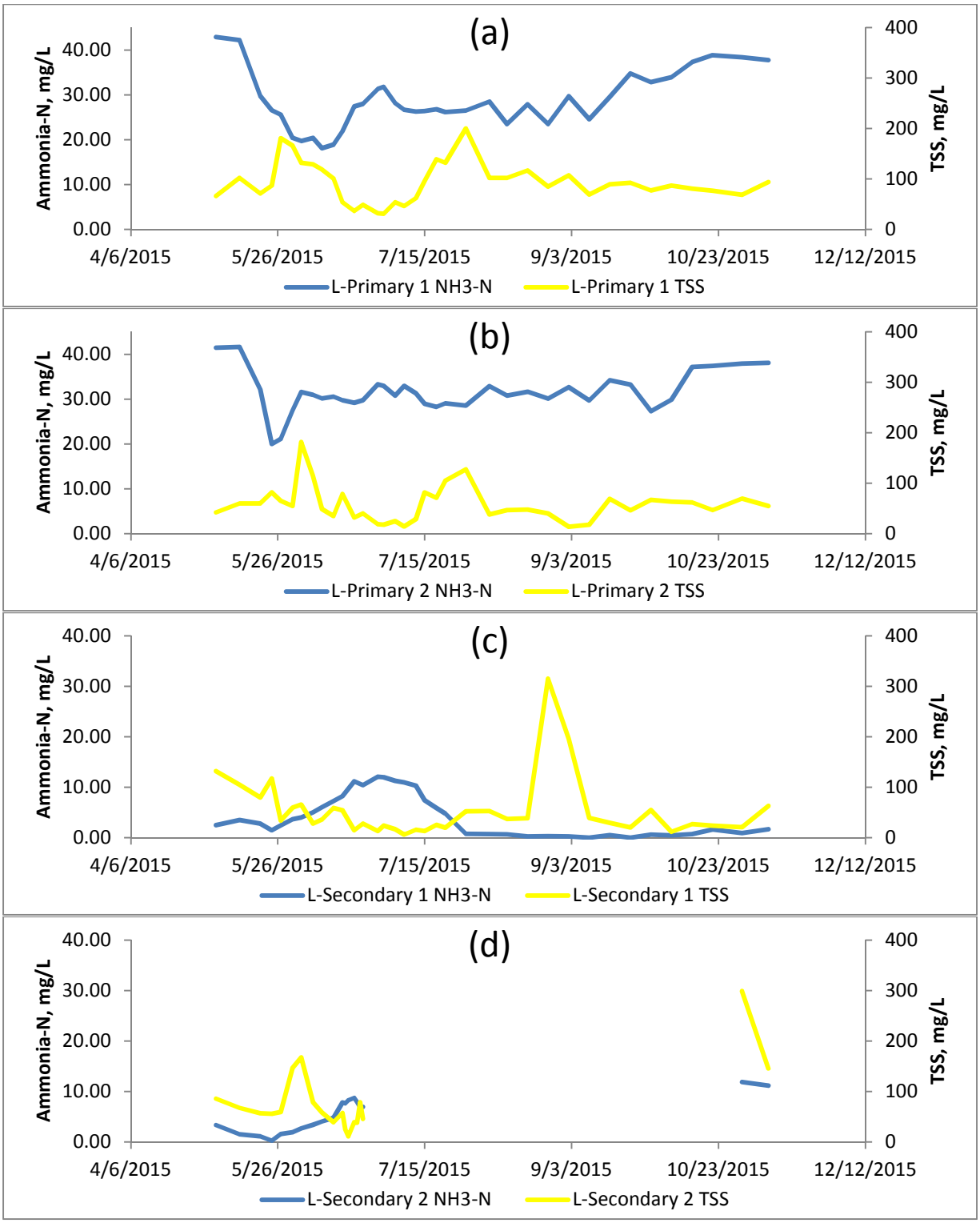


Figure 16: Total ammonia nitrogen and TSS concentration in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

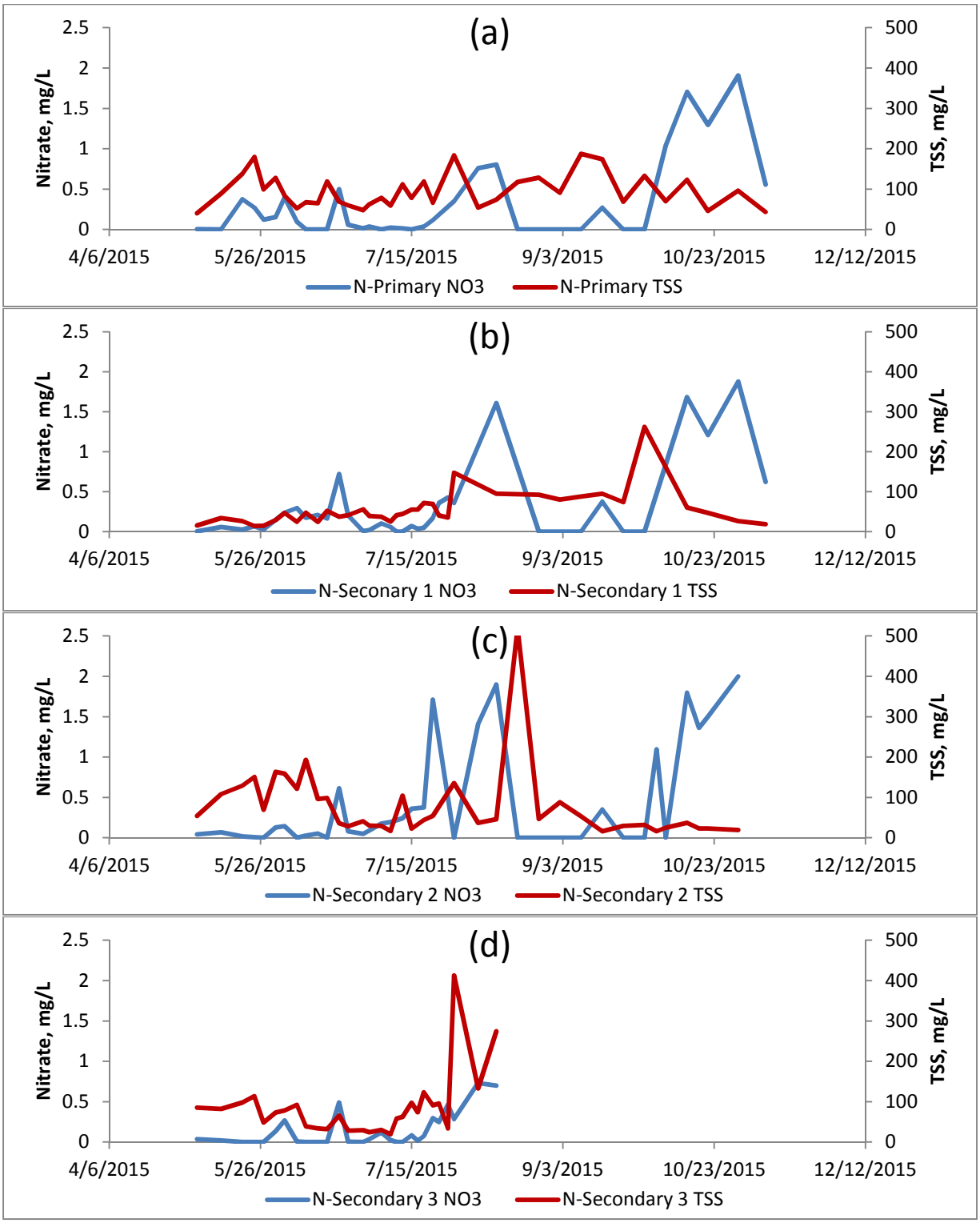


Figure 17: Nitrate and TSS concentration in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

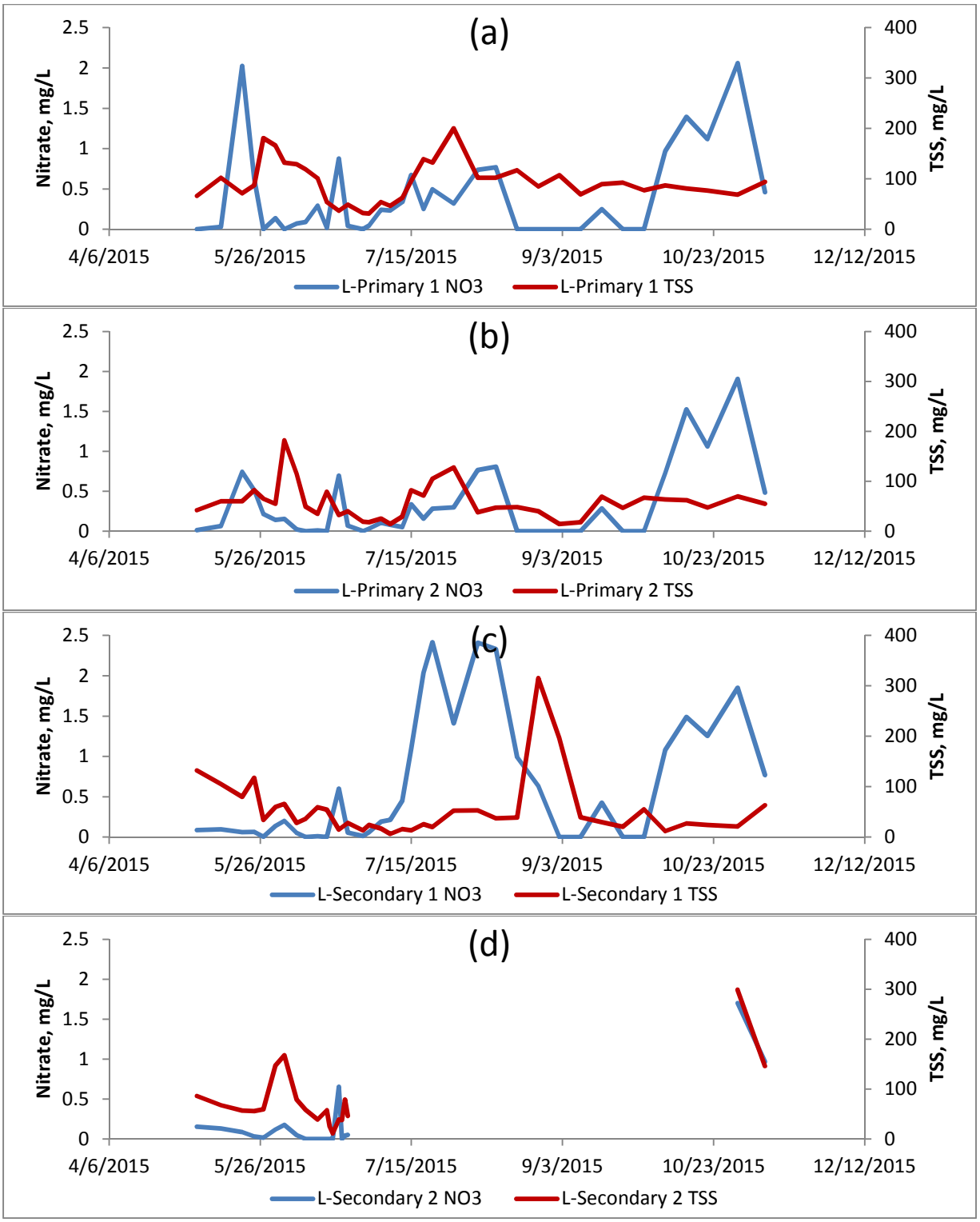


Figure 18: Nitrate and TSS concentration in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

In the previous four Figures the TSS concentration spike in May corresponds to the spike in pH visible in Figure 7 and Figure 8. This may represent both ammonia nitrogen loss to volatilization and assimilation into biomass. The large spike in TSS during the algae bloom in mid-August visible in (c) of the preceding four Figures happens at a time when there is very low ammonia nitrogen in Niverville secondary cell 2 and Lorette secondary cell 1. It occurs after a spike in nitrate concentration indicating biomass may consume nitrate as well. This agrees with von Sperling (2007) that ammonia and nitrate are assimilated into biomass in wastewater stabilization ponds.

There is a nitrate spike in October and November for all active cells in Figure 17 and Figure 18 above. It occurs at a time when algae growth would be slowing, with less light and lower temperatures, and does not correspond to any increases in TSS. The trends in the Figures above appear to confirm Rockne and Brezonik's (2006) findings that as well as ammonia volatilization, biological growth in the cells is also responsible for nitrogen removals.

After the winter ice cover melts, the ponds warm and are mixed; the increased sunlight and temperatures impact the wastewater treatment. There was increased total ammonia in all the secondary cells recently fed with primary effluent from mid-June to mid-July (Niverville secondary cells 2 and 3; Lorette secondary cells 1 and 2). This was likely a result of the settled solids in the primary cells degrading with increased temperature causing the release of additional ammonia. The only secondary cell that did not exhibit this trend in May is secondary cell 1 in Niverville, and it had not received any primary effluent since October/November of 2014. This could indicate that the higher ammonia concentrations are from the settled solids releasing ammonia in the primary cell and carrying over in the effluent.

In Lorette from June to September there was higher total ammonia in primary cell 2 than in primary cell 1. One reason for this trend could be that the settled solids were decomposing as the cell, and solids, temperature increased, and there is carry-over of total ammonia from primary cell 1 into primary cell 2. In May and October the total ammonia is lower in primary cell 2 than primary cell 1, but the cell, and settled solids, temperature is lower and there would not be as much ammonia released from the settled solids resulting in less carry over.

Figure 19 below shows nitrite concentrations for all four cells in Niverville (a) and Lorette (b), and nitrate concentrations for all four cells in Niverville (c) and Lorette (d). It appears there could be a few instances when a little nitrification may be occurring in some lagoon cells. There are times when the nitrite or nitrate concentrations are over 1 mg/L and they seem to follow a similar trend in Niverville and Lorette. In Figure 19 (a) and (b) Niverville secondary cell 2 and Lorette secondary cell 1 show a spike in nitrite concentration in late July. In Figure 19 (c) and (d) Niverville secondary cell 2 and Lorette secondary cell 1 show a similar pattern of two spikes in nitrate in July and August.

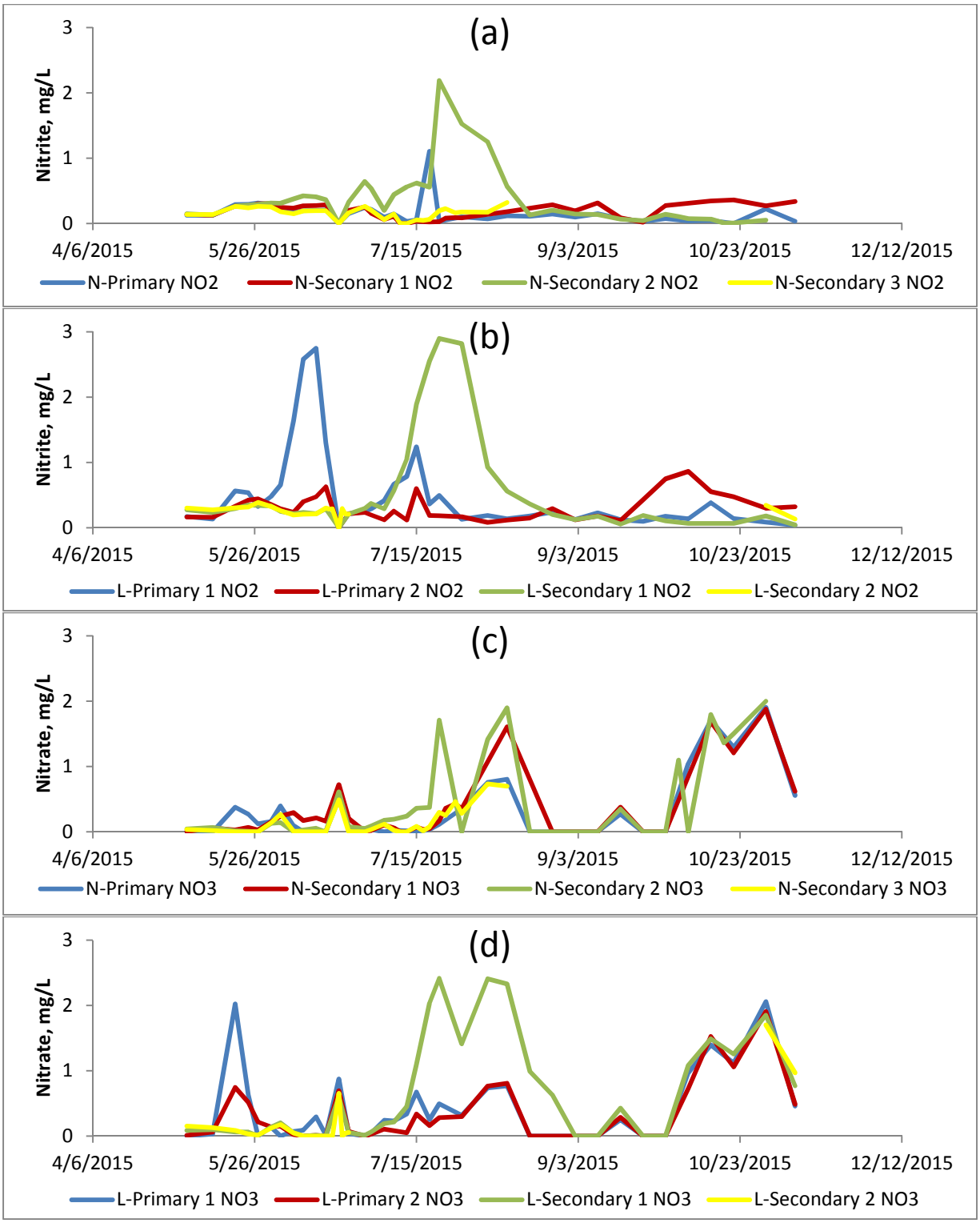


Figure 19: Nitrite concentration of all four cells in (a) Niverville and (b) Lorette and nitrate concentration of all four cells in (c) Niverville and (d) Lorette over the period May 5 to November 9, 2015.

The nitrate spikes in the prior Figure could represent a small amount of nitrification occurring in these cells. The raw wastewater feeding the primary cells (shown in Table 3) has a total ammonia concentration greater than 30 mg/L in both communities. Nitrite and nitrate concentrations are generally below 1 mg/L and the higher concentration spikes are less than 3 mg/L. It appears nitrification does not account for significant changes in the aerated or facultative cells.

Niverville secondary cells 1 and 3 (the cells isolated for discharge) have average total ammonia nitrogen concentrations in June of 0.22 and 2.05 mg/L respectively. They also have average un-ionized ammonia concentrations of 0.03 and 0.49 mg/L respectively. Lorette secondary cells 1 and 2 have average total ammonia nitrogen concentrations in June of 8.0 and 6.3 mg/L, and un-ionized ammonia concentrations of 0.51 and 0.42 mg/L respectively. All of the cells isolated would meet the 1.25 mg/L free ammonia requirements for discharge; however, the Niverville secondary cells are isolated for a longer period of time and show lower total ammonia nitrogen values. This appears to confirm that a longer hydraulic residence time results in greater ammonia reductions (Larsdotter, 2006).

The intermittent discharge licence for both communities allows discharges after June 15 and before November 1. Previously rural municipalities were issued licences that allowed them to discharge after May 15. The delay to discharge until after June 15 gives a safety factor for additional ammonia treatment (CEQG-CCME, 2010). The information collected over the monitoring period shows by waiting a month longer to discharge the lagoons there is less total and un-ionized ammonia remaining, and they would meet the discharge limits.

3.4: Phosphorus

As visible in Figure 20 (a) the Niverville primary cell shows a gradual increase in dissolved phosphorus from late May until the end of the monitoring period. The secondary cells show a decrease in orthophosphate concentration in late May followed by an increase in the orthophosphate concentration of varying duration.

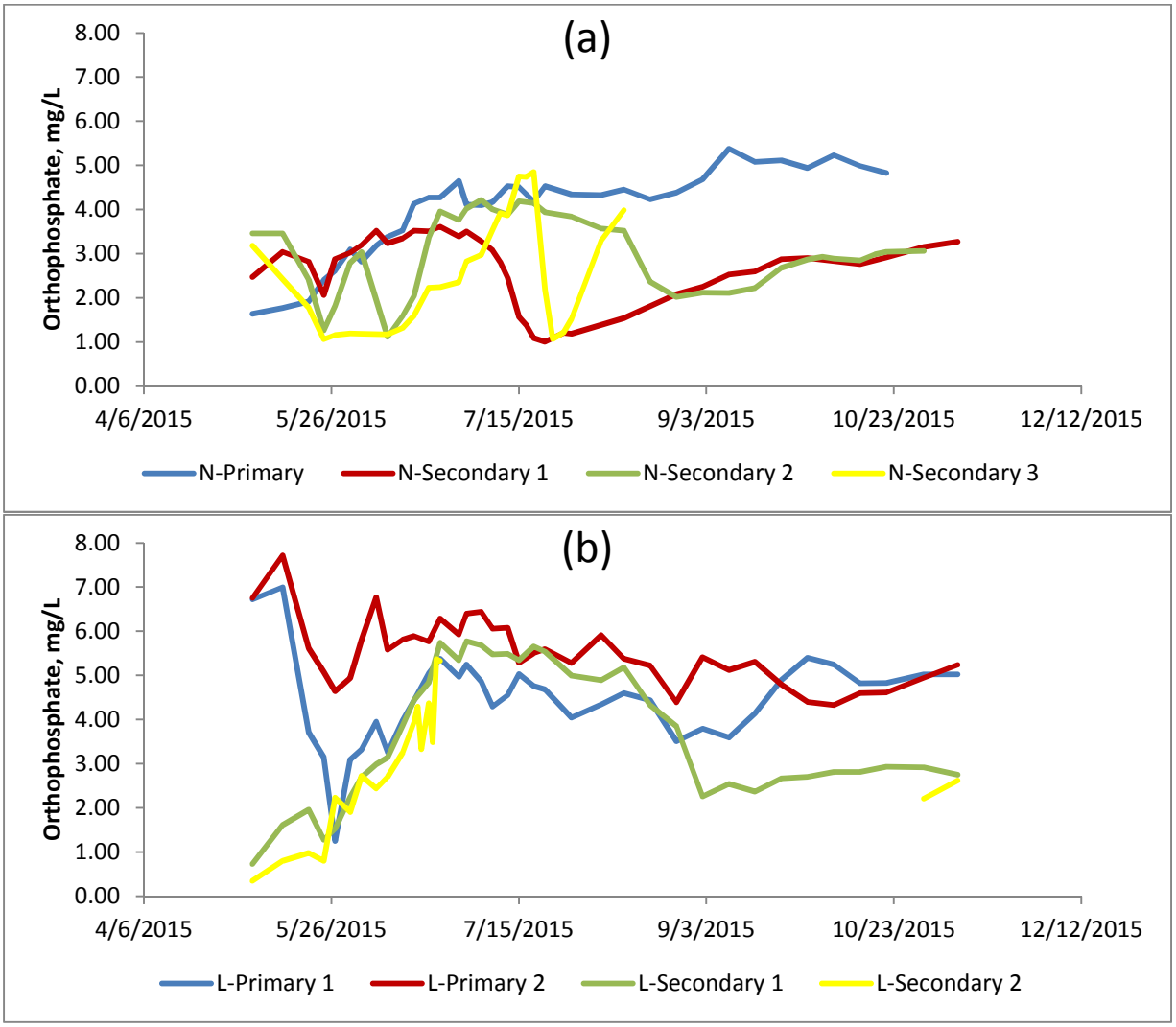


Figure 20: Orthophosphate of all four cells in (a) Niverville and (b) Lorette over the period May 5 to November 9, 2015.

In the above Figure (b) Lorette primary cell 1 and 2 show a relatively consistent orthophosphate concentration over the monitoring period with the exception of the drop in

concentration in May. Secondary cell 1 shows a similar pattern to the secondary cells in Niverville with an increase in concentration followed by an eventual decrease in early September.

Using the raw wastewater data in Table 3 (raw = 2.76 mg/L) and the Niverville secondary cells average in Table 9 (secondary cell average = 2.71 mg/L) the overall orthophosphate reduction is 0.05 mg/L and the reduction from the primary to secondary cells average is 1.30 mg/L. In Lorette the overall orthophosphate reduction is 0.66 mg/L (raw = 4.01 mg/L; and secondary cell average = 3.35 mg/L) and the reduction from primary cell 2 to the secondary cell average is 2.17 mg/L.

Secondary cell 3 in Niverville was offline from mid-August until the last sample was collected November 9, 2015; there is no data. There is no Lorette data for secondary cell 2 from July to September because the liquid level in the cell was too low to collect samples. An approximation of the cell status is shown based on the colours in the following Table: online-active (green); isolated (orange); offline (red); and discharging (blue).

Table 9: Dissolved phosphorus averaged for each month in all of the cells in Niverville from May to October. The Period Ave refers to the average for the whole period. The colour represents the cell status: online-active (green); isolated (orange); offline (red); and discharging (blue).

Niverville Monthly Average Orthophosphate (mg/L)								
Month	N-Primary 1		N-Secondary 1		N-Secondary 2		N-Secondary 3	
	PO_4	Std Dv	PO_4	Std Dv	PO_4	Std Dv	PO_4	Std Dv
May	2.69	1.20	2.72	0.38	2.53	0.88	1.80	0.85
June	3.38	0.58	3.42	0.15	2.70	1.11	1.73	0.53
July	4.32	0.22	1.97	0.97	4.03	0.14	3.12	1.38
August	4.41	0.10	1.81	0.39	2.87	0.79	3.65	0.49
September	4.75	0.48	2.63	0.27	2.40	0.35	No Data	No Data
October	5.02	0.13	3.03	0.20	2.96	0.08	No Data	No Data
Period Ave	4.01	0.98	2.60	0.82	2.99	0.87	2.51	1.25
Secondary Cells Average			Average 2.71		Std Dv 0.98			
Lorette Monthly Average Orthophosphate (mg/L)								
Month	L-Primary 1		L-Primary 2		L-Secondary 1		L-Secondary 2	
	PO_4	Std Dv	PO_4	Std Dv	PO_4	Std Dv	PO_4	Std Dv
May	4.15	2.26	5.79	1.20	1.56	0.53	1.18	0.73
June	4.29	0.80	5.98	0.38	4.13	1.14	3.75	1.01
July	4.68	0.39	5.83	0.47	5.49	0.24	No Data	No Data
August	4.22	0.49	5.23	0.63	4.56	0.59	No Data	No Data
September	4.36	0.76	5.01	0.41	2.51	0.19	No Data	No Data
October	4.99	0.20	4.75	0.25	2.84	0.07	2.42	0.29
Period Ave	4.45	1.03	5.52	0.75	3.65	1.52	2.80	1.47
Secondary Cells Average					Average 3.35		Std Dv 1.54	

Figure 21 shows the pH and orthophosphate for all of the lagoon cells in Niverville over the monitoring period. In the Figure the relationship between orthophosphate and pH can be seen. When there is an increase in pH it seems to be mirrored by a decrease in orthophosphate.

In Figure 22 the pH values and dissolved phosphorus of all four cells are shown for Lorette. During the majority of the monitoring period the orthophosphate concentration is higher in primary cell 2 than in primary cell 1. As with the cells in Niverville there is evidence of a relationship between the concentration of orthophosphate and pH.

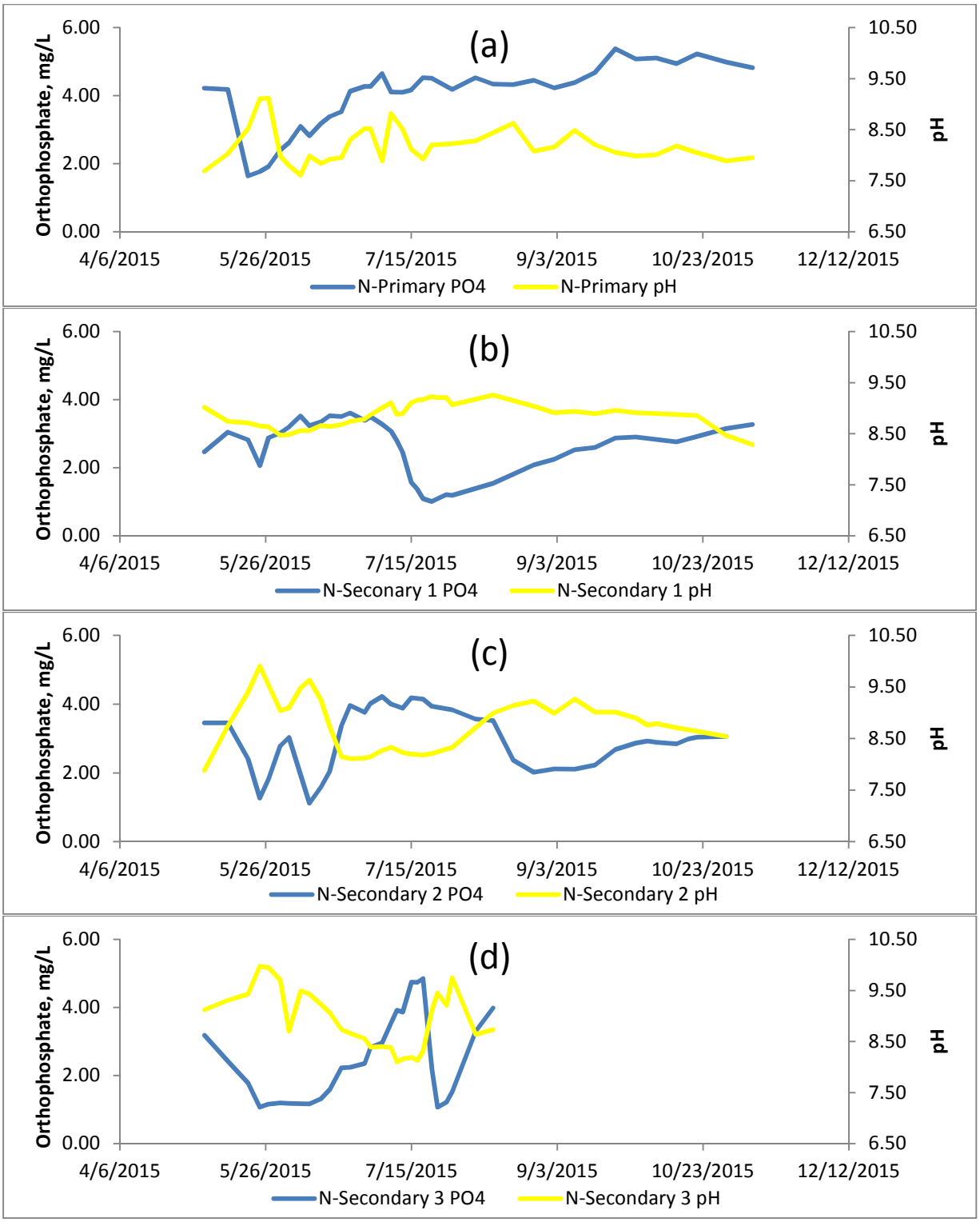


Figure 21: Orthophosphate concentration and pH in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

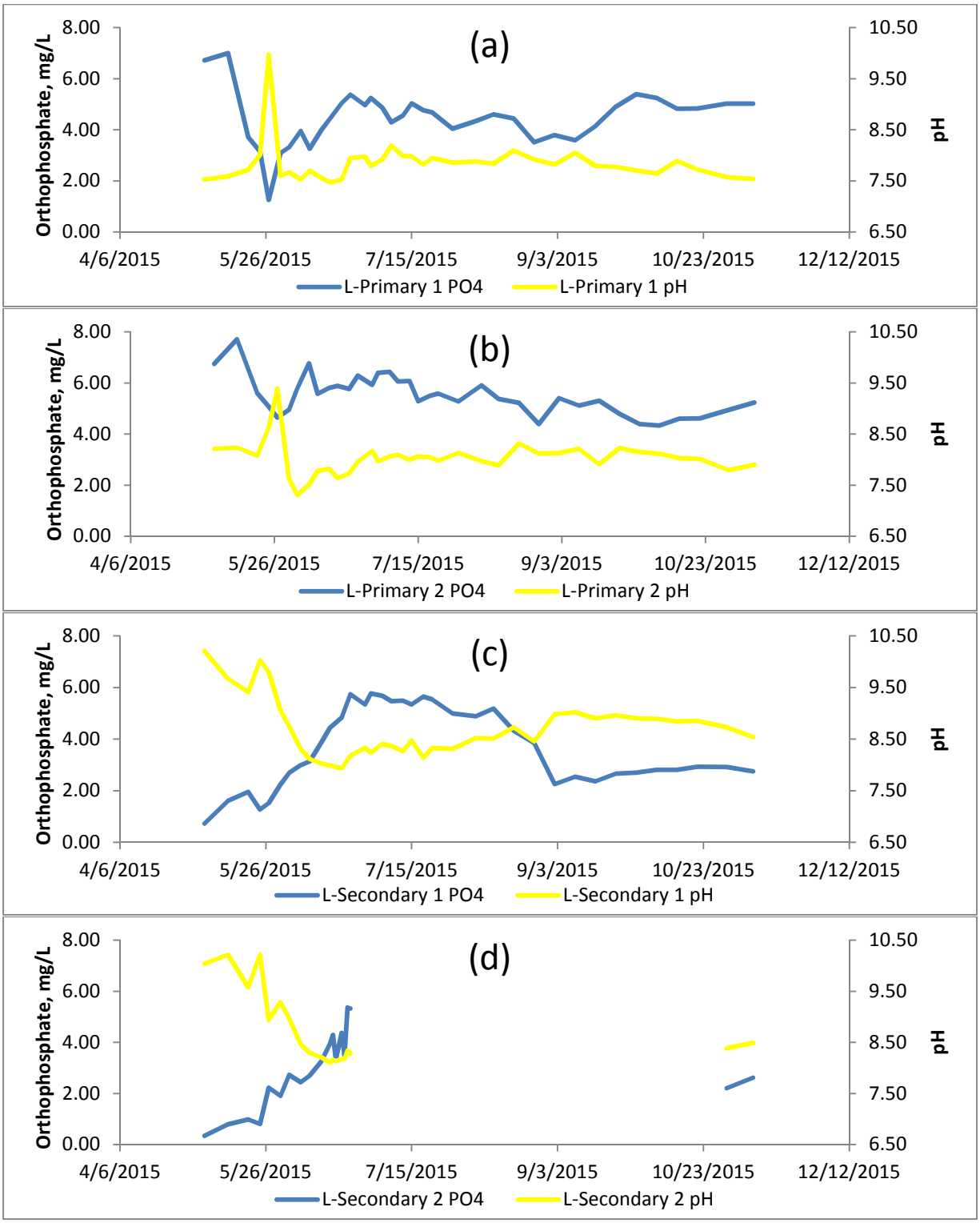


Figure 22: Orthophosphate concentration and pH in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

A correlation analysis was conducted on the orthophosphate and pH data. An inverse relationship with a value approaching negative one has a greater likelihood of correlation. There was a poor correlation between the primary cell orthophosphate and pH; however the secondary cells correlation values between -0.748 and -0.881 indicate evidence of an inverse relationship.

The main mechanisms of phosphorus removal in the lagoon cells are phosphorus assimilation into cellular biomass (Bitton, 1999; Brown and Shilton, 2014; Crites and Tchobanoglous, 1998; Larsdotter et al, 2010; von Sperling, 2007), and phosphorus precipitation (Doran and Boyle, 1979; Mesple et al, 1996; Moutin et al, 1992; Tam and Wong, 2000; von Sperling, 2007). There are some conditions that favour the growth of bacteria and algae that could consume the available phosphorus. These conditions include greater light intensity and quantity, increased temperature, alkaline pH (Larsdotter, 2006; Powell et al, 2006a), and all necessary minerals and nutrients (Tomaselli, 2004). Meeting these conditions will help to ensure the biomass will remove as much phosphorus as possible.

Table 10: The ratio of Nitrogen to Phosphorus (N/P) calculated for the raw wastewater and each of the cells for Niverville and Lorette (based on data from Table 3, Table 7, and Table 9 – sample calculations in Appendix E).

Niverville					
	N-Raw	N-Primary 1	N-Secondary 1	N-Secondary 2	N-Secondary 3
N/P Ratio	12.1	4.45	0.37	1.45	1.43
Lorette					
	L-Raw	L-Primary 1	L-Primary 2	L-Secondary 1	L-Secondary 2
N/P Ratio	8.90	6.54	5.77	1.32	2.00

The information in Table 10 shows that theoretically all the lagoon cells have less than the ideal nitrogen to phosphorus (N/P) ratio of 7.24 for algal cell growth, and except for the

Lorette primary cells they are less than the ideal N/P ratio of 5.43 for bacterial cell growth. The secondary cells are the most nitrogen limited based on their N/P ratios in comparison to the ideal N/P ratio. However, there is plenty of nitrogen available in the raw wastewater for Niverville and Lorette, and based on the ratio it is phosphorus limited.

The N/P ratio shows that bacteria and algae may not consume more phosphorus in the secondary cells because they become nitrogen limited. If nutrients necessary for cellular growth are limited they may need to be supplemented (Beuckels et al, 2015; Boelee et al, 2012; Converti et al, 2009; Solovchenko et al, 2008). A greater quantity of phosphorus can be assimilated into biomass by ensuring sufficient nitrogen is supplied (Beuckels et al, 2015; Griffiths, 2009).

In Table 10 the N/P ratio in the raw wastewater is nitrogen rich. The loss of ammonia to volatilization likely contributes to the apparent nitrogen limited conditions in the secondary cells because it is not available for cellular growth. Instead of using an external source of nitrogen to supplement microorganism growth some other possibilities are to improve primary effluent distribution within the secondary cells, blend some raw wastewater with the primary effluent distributed to the secondary cells, or promote nitrification because it is less volatile than ammonia in the lagoons. Increased algae growth will only exacerbate the ammonia stripping by continuing to increase the pH, which is why converting it to a less volatile form like nitrate could reduce, or eliminate, any needed external nitrogen sources.

Based on the nitrogen data in section 3.3 aeration in the Lorette primary cells do not seem to promote significant nitrification. Alternative nitrification processes could be used to keep the ammonia from being stripped to the atmosphere and becoming unavailable for

cellular growth. Processes such as SAGR® (Submerged Attached Growth Reactor), IFAS (Integrated Fixed-film Activated Sludge), or more simple fixed film processes that don't require addition energy could be used.

Other photosynthetic biomass, such as green algae, often outnumbers cyanobacteria (Cho et al, 2015) which would limit their ability to fill the nitrogen deficiency in these systems. To further complicate the issue some species of cyanobacteria cannot fix nitrogen in the presence of nitrate, ammonia, and oxygen (Chorus and Bartram, 1999). However, another avenue of future research is into creating a symbiotic relationship with nitrogen-fixing cyanobacteria and another organism (ESF, 1999).

Sample Calculation
Algal Solids Produced with Supplemental Nitrogen

*assume no other limitations to algae growth

*assume algae population >> bacteria in lagoon

*assume algae removes bulk of N and P

N – S1 [Ortho-P] = 2.60 mg/L

Limit = 1 mg/L need to remove 1.60 mg/L P

$$\text{Ideal N/P Ratio} = 7.24 = \frac{[N]}{[P]} = \frac{\text{mg N}}{1.6 \text{ mg/L}}$$

$$[N] = (7.24) \times (1.6) = 11.58 \text{ mg/L} - \text{existing } [N] = 11.58 - (0.64 + 0.31) = 10.63 \text{ mg/L N } (NH_3\text{-N} + NO_3)$$

$$\frac{10.63 \text{ mg N}}{1 \text{ L}} \times \frac{1000 \text{ mg algae}}{63.1 \text{ mg N}} = 168.5 \text{ mg/L algae concentration}$$

Figure 23: A sample calculation of the theoretical algae solids produced from supplemental nitrogen. Results for all Niverville and Lorette lagoon cells are shown in Table 11.

Table 11: Theoretical algae solids produced in Niverville and Lorette, and alum solids produced by jar test with Niverville raw wastewater. A sample calculation is shown in Figure 23 above.

Niverville				
	N-Primary 1	N-Secondary 1	N-Secondary 2	N-Secondary 3
mg/L algae	62.3	169	159	117
Lorette				
	L-Primary 1	L-Primary 2	L-Secondary 1	L-Secondary 2
mg/L algae	0.0	13.5	228	118
Alum Jar Test				
Average: 178 mg/L		Max: 300 mg/L		Min: 120 mg/L

If additional nitrogen is available there will be more biomass growth and those solids should be removed from the lagoon cells. The amount of theoretical additional algae growth from an external nitrogen source is calculated in Figure 23 and shown in Table 11. The

theoretical algae solids produced are less than the average alum solids with the exception of secondary cell 1 in Lorette, but they all fall within the alum solids range. If not removed the additional biomass settles to the bottom of the ponds and can be released as the organisms decay. In the summer the lagoons contain large quantities of algae and when settled they do not decompose as rapidly as do bacterial cells. This allows for more time to remove them before phosphorus is re-dissolved in solution (i.e. dead settled algae takes days to release phosphorus and dead settled bacteria release phosphorus in hours) (Brown and Shilton, 2014). If the biomass is not removed, or allowed time to settle, the lagoon effluent may not comply with licence and regulatory requirements (25 mg/L TSS), and it might be necessary to add intermittent sand filters or another solids removal process.

One advantage to natural phosphorus removal processes is that the phosphorus is still available for reclamation and reuse from the solids. If the solids are collected they can be reused for compost or energy production. Chemical precipitation using alum or ferric results in nutrients bound within solids in a form that is energy intensive to capture and reuse (Brown and Shilton, 2014).

One noticeable trend in the lagoon cells in Lorette and Niverville is the apparent relationship between orthophosphate and pH. This may account for natural phosphorus removal. In Figure 21 and Figure 22 it can be seen that at elevated pH there is less dissolved phosphorus in the water. One of the major contributors to increased pH is the algae in the cells. Figure 24 and Figure 25 below show the orthophosphate and TSS concentrations plotted together. As observed in Figure 7 and Figure 8 the TSS is linked to the algal cell concentration and they have an effect on the pH. The relationship with orthophosphate and pH may be an

indirect relationship. It might have more to do with the growth of algae increasing the pH and consuming phosphorus.

There is an algal biomass bloom in Niverville secondary cell 2 and Lorette secondary cell 1 near mid-August visible in the following two Figures. The effects of the algae bloom are visible in Figure 24 (c) and Figure 25 (c). This bloom appears to result in a decrease in dissolved phosphorus concentration. Based on this information it appears assimilation into algae is likely one mechanism for dissolved phosphorus removal in the lagoons.

A longer hydraulic residence time appears to increase orthophosphate removal, confirming Larsdotter's (2006) findings (apparent in Lorette secondary cell 1 – June to October; and Niverville secondary cell 1 – May 2015 to July 2015).

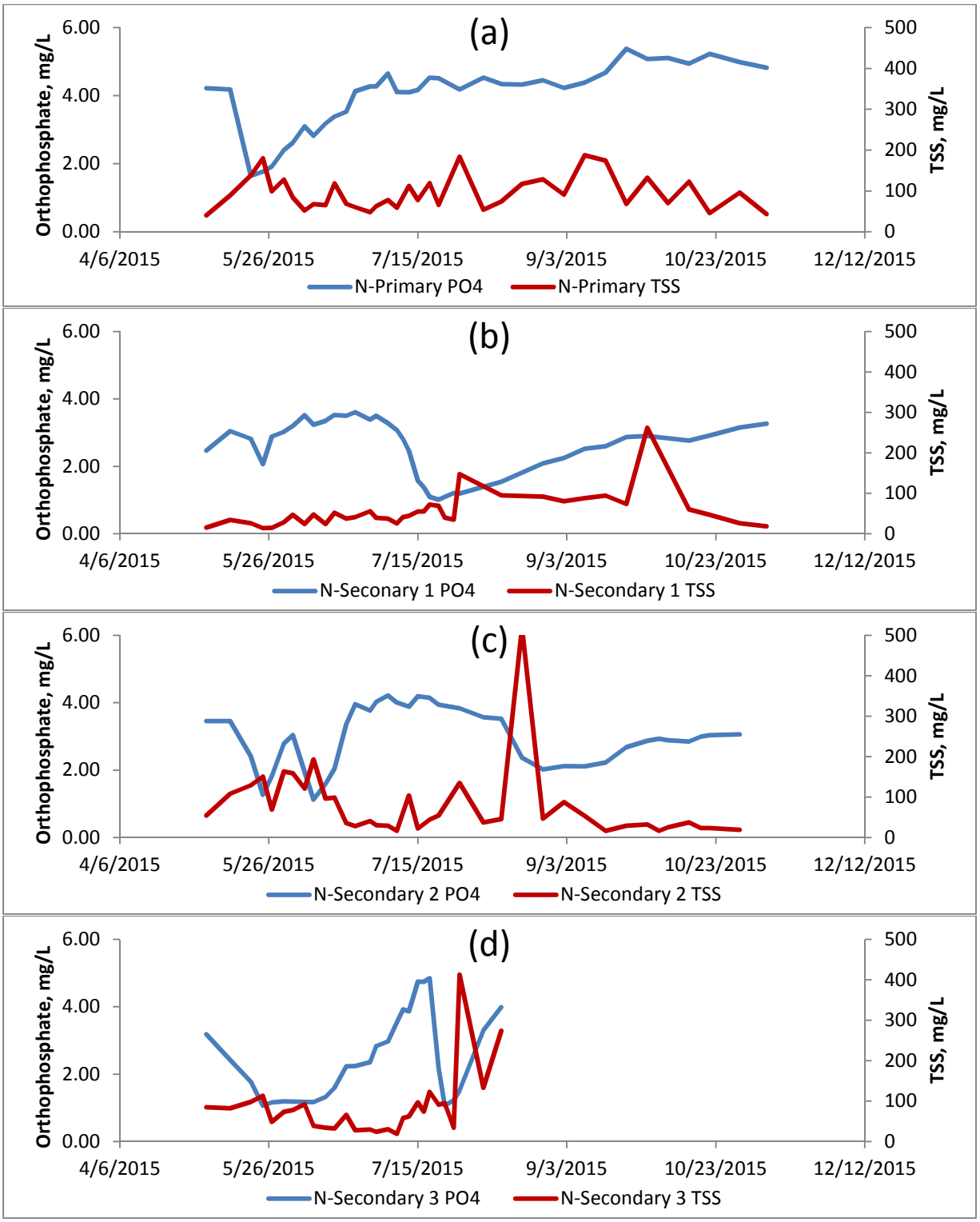


Figure 24: Orthophosphate and TSS concentration in Niverville over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) secondary cell 1; (c) secondary cell 2; (d) secondary cell 3.

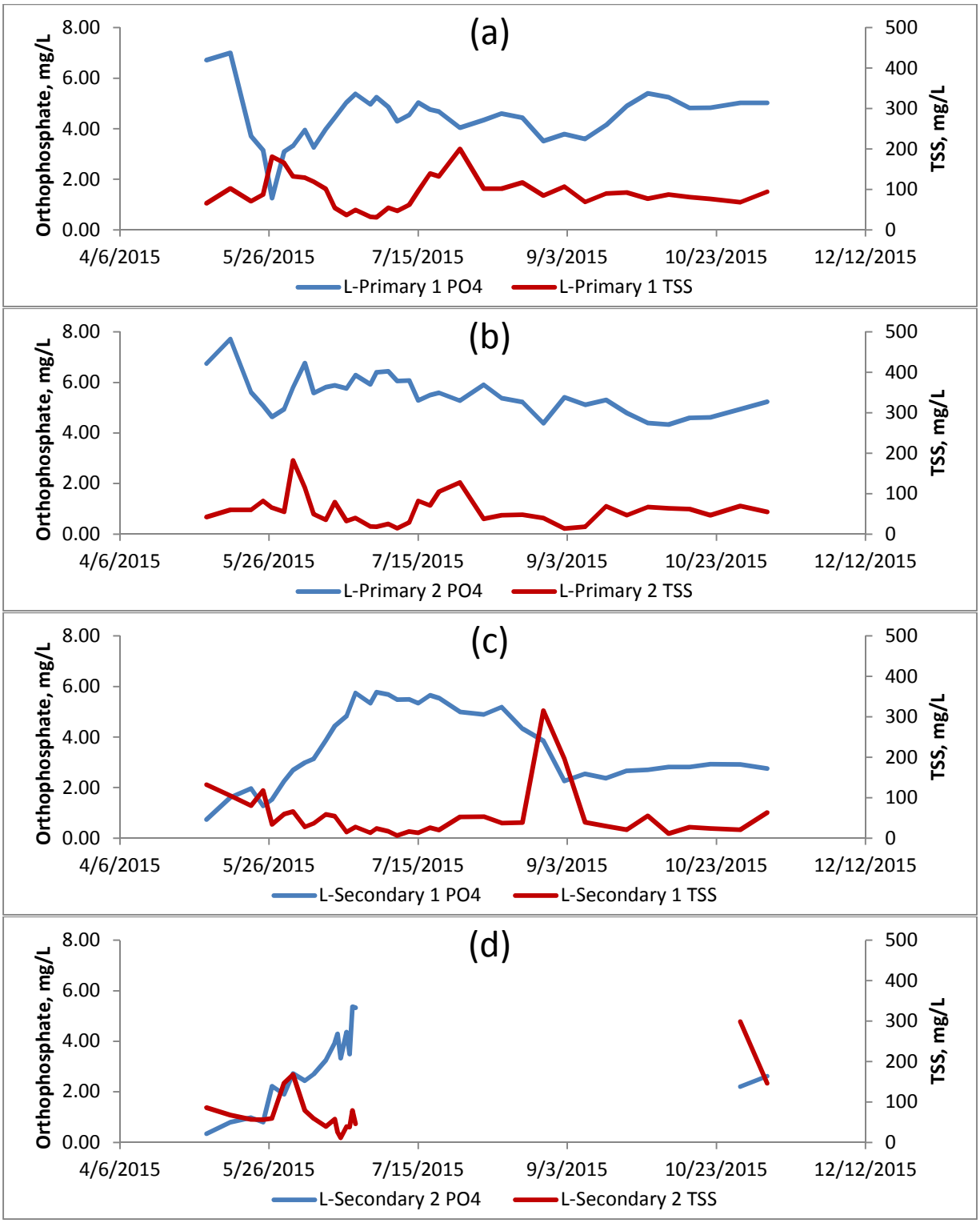


Figure 25: Orthophosphate and TSS concentration in Lorette over the period May 5 to November 9, 2015 for: (a) primary cell 1; (b) primary cell 2; (c) secondary cell 1; (d) secondary cell 2.

The primary cells in Niverville and Lorette have higher orthophosphate concentrations than the raw wastewater, and the primary cell in Niverville shows a gradual increase over the monitoring period. The primary cells likely have the most settled solids. Thus one reason for this increase in orthophosphate could be from the settled solids releasing more phosphates into solution. This may explain why the phosphate concentration in Lorette primary cell 2 was a little higher than in primary cell 1 from late May to August.

Marais (1974) found the release of phosphorus into solution from sludge is related to the temperature of the settled solids. In early May and September/October the cell temperature is lower and the orthophosphate concentration in Lorette primary cell 2 is lower than cell 1. The lower temperatures likely result in less carryover of re-dissolved phosphorus from cell 1. There is a notable increase in the orthophosphate from June to August in Lorette secondary cell 1 and Niverville secondary cell 2 that most likely represents the release of phosphates from settled solids.

It would be beneficial if the phosphorus could be bound in the sediments without being released. If the phosphorus can be bound in the sediments it will make it more stable and less likely to be released from the settled solids. There is a commercial product available called Phoslock® that is meant to bind phosphorus in sediments (Lin et al, 2015). By immobilizing the phosphorus in the sediments it would potentially increase the removal efficiency in the lagoon cells.

Based on the findings above, it appears there may be a phosphorus removal and release cycle (i.e. phosphorus is assimilated into microbes; they settle; they decay; and phosphorus is released to repeat the cycle). In essence some phosphorus may be assimilated into biomass

more than once. This would contribute to poor overall phosphorus removal in the lagoon cells because it can be released again when the settled biomass decay.

Table 12: Cations analysis on samples collected November 9, 2015 and hardness calculated from Ca & Mg concentrations (for full cations analysis and sample calculations see Appendix F).

Niverville				
	Primary 1	Secondary 1	Secondary 2	Secondary 3
Magnesium (mg/L)	68.25	81.24	No Data	No Data
Calcium (mg/L)	64.93	68.82	No Data	No Data
Hardness (mg/L $CaCO_3$)	443.5	506.8	No Data	No Data
Lorette				
	Primary 1	Primary 2	Secondary 1	Secondary 2
Magnesium (mg/L)	75.01	69.99	74.40	84.38
Calcium (mg/L)	70.28	69.62	64.16	75.55
Hardness (mg/L $CaCO_3$)	484.7	462.4	466.9	536.5

Likely the second mechanism of phosphorus removal is through precipitation. Phosphate precipitation would be aided in Niverville and Lorette lagoons by their hard water. The wastewater from these communities has concentrations of calcium and magnesium in excess of 60 mg/L and hardness over 440 mg/L $CaCO_3$, as seen in Table 12. There is no data for secondary cells 2 and 3 in Niverville because they were empty and offline when samples were collected on November 9, 2015.

Calcium phosphate precipitation may be a mechanism of phosphorus removal in the lagoons. In the open water season there is greater algae activity that will increase the pH and cause greater natural precipitation. According to Larsdotter et al. (2007) calcium concentrations in excess of 50 mg/L contribute to phosphorus removal by precipitation as calcium phosphates. The solubility of calcium salts is largely pH dependent and according to von Sperling (2007) pH values over 9 contribute to significant phosphorus precipitation. As

visible in Figure 6 and Table 5 there are periods of time when all the cells have a pH greater than 9. A calcium concentration around 70 mg/L in Niverville and Lorette, and pH values over 9 indicate it is likely that some phosphates precipitate out of solution in the lagoons.

It may be possible to add a mix of calcium and nitrogen to encourage both the growth of phosphorus consuming biomass and calcium phosphate precipitates. Griffiths (2009) found that using sodium nitrate or urea achieved the best external nitrogen supplementation; however, if calcium nitrate is used instead of sodium nitrate it would add both calcium and nitrogen.

Niverville and Lorette lagoons remove very little dissolved phosphorus from the wastewater. The release of phosphorus from the settled solids means more has to be removed in the lagoon cells than enters the cells in the influent. The aerated lagoon in Lorette performs slightly better at reducing orthophosphate than the facultative lagoon in Niverville. It appears the majority of the phosphorus is removed by assimilation into biomass. There is likely some phosphorus removed by precipitation based on conditions conducive to calcium phosphate precipitation, i.e. alkaline pH and calcium concentrations over 50 mg/L. However, Niverville and Lorette will require additional treatment to comply with the 1 mg/L phosphorus limit.

Chapter 4: Conclusions

In this thesis two lagoons were monitored from May 5, 2015 to November 9, 2015. The goals are: to determine what the chemical and biological nutrient removal mechanisms are for an aerated and facultative lagoon; compare the two lagoons; and determine if they will comply with discharge requirements. The following are the conclusions:

- There didn't appear to be any significant effects from rainfall on lagoon treatment and a portion of the additional liquid is lost to evaporation.
- The large surface area of the lagoons is affected by air temperature. Surface sampling alone doesn't capture the changes with depth in the cells, or the effects wind and temperature have on mixing.
- The pH was lower in the aerated primary cells than the facultative primary cell likely due to mixing from aeration keeping solids in suspension and limiting algae growth.
- The pH in the secondary cells shows that the aerated and facultative lagoons follow similar patterns, and increases in pH are related to algal activity.
- There is evidence that the settled solids in the stabilization ponds are releasing ammonia and phosphorus into solution.
- Longer hydraulic residence times increased nitrogen and phosphorus removals.
- The greatest ammonia removal is likely from free ammonia volatilizing to the atmosphere.
- Ammonia and nitrate assimilation into biomass is likely the other mechanism of nitrogen removal over the monitoring period.

- Based on the data collected nitrate and nitrite levels are low in both the aerated and facultative lagoon cells indicating very little nitrification is occurring.
- Phosphorus assimilation into biomass appears to be the greatest contribution to phosphorus reduction in the aerated and facultative lagoon cells.
- The N/P ratios in the lagoons show there is nitrogen limiting conditions in the secondary cells that could reduce phosphorus removal.
- Based on calcium concentrations and pH levels, calcium phosphate precipitation is another likely mechanism of phosphorus removal. The higher pH in the facultative cells favours phosphate precipitation over the aerobic cells.
- There is slightly more phosphorus removed in the aerated lagoons overall and from the primary cell to the secondary cells than in the facultative lagoons.
- Aside from the reduced footprint of the primary aerated cells there is no apparent advantage for nitrogen removal between the aerated and facultative cells.
- The lagoons will comply with the limits for un-ionized ammonia between their allowed discharge periods of June 15 to October 31.
- The lagoons will not comply with the 1 mg/L phosphorus discharge limit. To comply with the discharge limit additional treatment is necessary.

Chapter 5: Engineering Significance

The data gleaned from this thesis indicates that, except for space savings, there didn't seem to be any significant benefit to an aerated lagoon over a facultative lagoon for wastewater treatment. If land is available similar treatment can be reached without aeration and the added cost savings in reduced energy consumption. Longer HRT resulted in lower nutrient concentrations. If the lagoons could be designed even larger it would allow a longer HRT resulting in increased nutrient removals.

In Niverville and Lorette, aerated and facultative lagoons achieve sufficient nitrogen removal to comply with limits for effluent discharges, but need treatment for phosphorus. Based on the results of this thesis there are some natural processes that could be used to minimize the need for alum or ferric chemical addition to precipitate phosphorus.

There is a relationship with reduced phosphate concentration at an alkaline pH due to algae blooms. Another phosphorus removal process is natural precipitation of calcium phosphate salts at pH over 9 and calcium concentrations over 50 mg/L. Niverville and Lorette lagoon wastewater has calcium concentrations around, or above, 70 mg/L, and there are times when the lagoon cells reach pH values over 9.

Based on their N/P ratios there is nitrogen limiting conditions in the secondary lagoon cells. Ammonia stripping to the atmosphere may be responsible for creating nitrogen limiting conditions in the wastewater stabilization ponds. Nitrogen may need to be supplemented, or the treatment process could be modified, to enhance phosphorus removal. The raw wastewater has a large enough N/P ratio to theoretically remove all the phosphorus. The

treatment process could be modified to encourage significant nitrification so ammonia is not lost to volatilization, or some nitrogen rich raw wastewater could be blended with primary effluent and more evenly distributed throughout the secondary cells.

Another method to supplement nitrogen would be adding it from an external source. The addition of calcium nitrate could result in greater precipitation and supplemental nitrogen for algal/bacterial growth to further reduce phosphorus concentrations. It might be possible to retrofit existing alum or ferric chemical dosing systems to add supplemental nitrogen. However, new solid removal systems may be needed, or existing solid removal systems could be re-purposed, to remove the additional biomass.

Appendix E shows some sample calculations for the theoretical increase in algae concentration that would result from adding nitrogen. The average algae concentration, for all five secondary cells, is 158 mg/L with a maximum value of 228 mg/L and a minimum value of 117 mg/L. An alum jar test was carried out on the raw wastewater at the Environmental Engineering Laboratory resulting in an average of 178 mg/L alum solids with a maximum value of 300 mg/L and a minimum value of 120 mg/L. This theoretically demonstrates that adding nitrogen to supplement algae growth will result in about the same solids concentration as achieved by dosing with alum to remove phosphorus.

When settled solids re-dissolve nutrients in solution they increase the necessary nitrogen and phosphorus concentrations for treatment. It would be beneficial to find a way of removing the solids before they settle, or using a product like Phoslock® to keep them from releasing phosphorus into solution when they decompose.

Chapter 6: Future Research – Potential Directions

There are several directions for additional research and process development surrounding wastewater lagoons and their biomass, especially algae. The first is to develop additional processes to aid in further nutrient removal and recycle, or re-capture the nutrients removed in biomass for fertilizer. The second is fuel production from the lagoon biomass. Biodiesel can be produced from some species of algae grown in wastewater, or biomethane can be produced from fermented biomass. The third is electrical energy generation by taking advantage of the redox gradient from aerobic to anaerobic zones in facultative lagoons. The fourth and last discussed is growing algae for the production of nutraceuticals.

There is a product called Phoslock® that is designed to immobilize phosphorus in bottom sediments (Lin et al, 2015). This product, or similar products, binds to the settled solids so they did not release back into solution. This could be helpful to reduce the phosphorus treatment necessary in lagoon cells because there is no release of phosphorus from the settled solids once they are immobilized.

It was postulated that the use of calcium nitrate could increase phosphorus removal, but this would need to be investigated. The thought is that it might work to supplement nitrogen for phosphorus removal in nitrogen limited systems, and supply additional calcium for natural calcium phosphate precipitation. If proven that more phosphorus removal is possible with the addition of calcium nitrate existing chemical dosing systems could be retrofitted to dose it instead of alum or ferric. The biomass will likely need to be harvested more frequently than it is now, but it could be useful for compost. Extracting nutrients from ferric and alum

sludge is energy intensive; usually the least expensive option is taking it to landfill (Brown and Shilton, 2014).

Another potential vein of research into nitrogen limitations for cellular growth is in converting more ammonia to nitrate so it is not lost to volatilization at high pH. It might involve existing technologies like IFAS or SAGR®, perhaps used in ways they weren't originally intended. There is also the potential to exploit the nitrogen-fixing capabilities of cyanobacteria and find a symbiotic way it can be used by other microorganisms.

It is good practise to recapture phosphorus that is not wanted and use it where it is; i.e. for fertilizer (Brown and Shilton, 2014; Griffiths, 2009; Larsdotter, 2006). The available phosphorus for anthropocentric use is finite and may be depleted in less than 100 years (Abelson, 1999). Therefore, it is important to reuse this resource where possible. Phosphorus is needed for fertilizer production, but too much phosphorus in the natural aquatic environment causes eutrophication (Brown and Shilton, 2014). It is beneficial to have the phosphorus where it is needed for things like food production not where it causes adverse effects to receiving waters.

It may be possible to develop a wastewater treatment scheme where mixed facultative pond microbes are grown in a nutrient limited environment before being introduced to a nutrient rich one (Larsdotter, 2006). A community of microbes grown in nutrient limited conditions consume nutrients more readily when they are introduced to them (i.e. excessive eating after a period of starvation) (Cembella et al, 1984; Hernandez et al, 2006; Larsdotter, 2006; Vymazal, 1995). Nutrient starved algae assimilate nitrogen and phosphorus faster than those living in a nutrient rich environment (Cembella et al, 1984; Hernandez et al, 2006;

Larsdotter, 2006; Vymazal, 1995). This knowledge could be used to enhance nutrient removal by adding side stream processes to change typical lagoon design and operation.

Another possible use of the biomass removed from wastewater lagoons is for the production of biodiesel (Kring et al, 2013; Pires et al, 2013), or biomethane (Griffiths, 2009). It has been demonstrated that algal biomass can be turned into biodiesel (Christi, 2007; Hu et al, 2008; Olaizola, 2003; Schenk et al, 2008; Sheehan, 1998). Biomethane could be produced from anaerobically digesting the collected biomass (Griffiths, 2009). For it to be cost effective the quantity necessary would be substantial, and it might be necessary to set up a central facility that would accept stabilization pond sludge from all nearby rural municipalities.

The reduction/oxidation, or redox, gradient that exists in wastewater stabilization ponds can be used to generate power (Ewing et al, 2014). This can be accomplished by a process Ewing et al (2014) have termed a "lagoon microbial fuel cell", or LMFC. The redox potential that exists between the aerobic zone and anaerobic zone in a facultative wastewater lagoon can be used to generate electricity (Ewing et al, 2014).

The last potential avenue for future research discussed is for nutritional supplements, sometimes called nutraceuticals. These nutraceuticals can be produced by algae (Griffiths, 2009; ENP Newswire, 31 July 2014) as well as animal feed (ENP Newswire, 31 July 2014). These are mainly in the forms of proteins and carotenoids that are harvested from algae and incorporated into various products (ENP Newswire, 31 July 2014).

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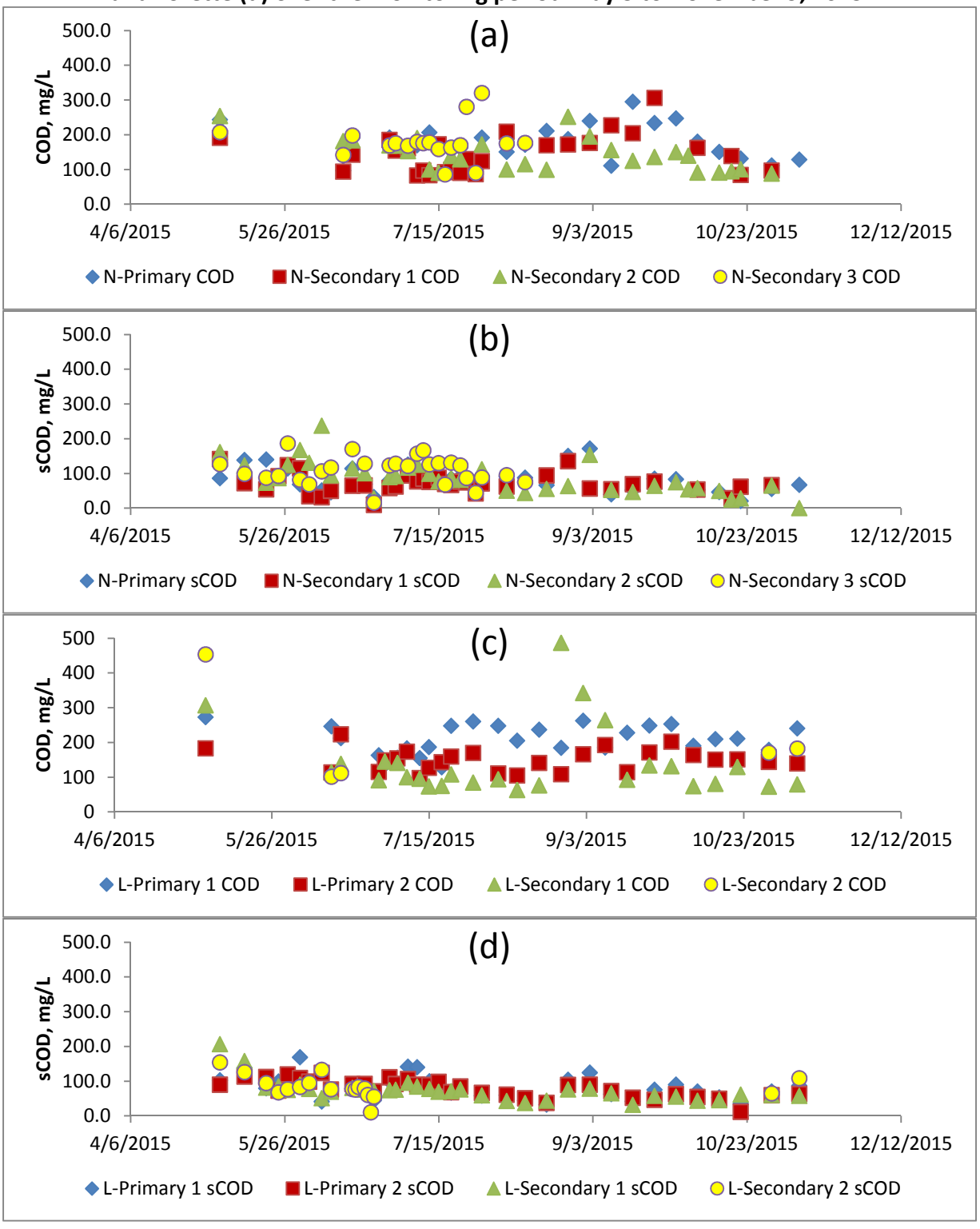
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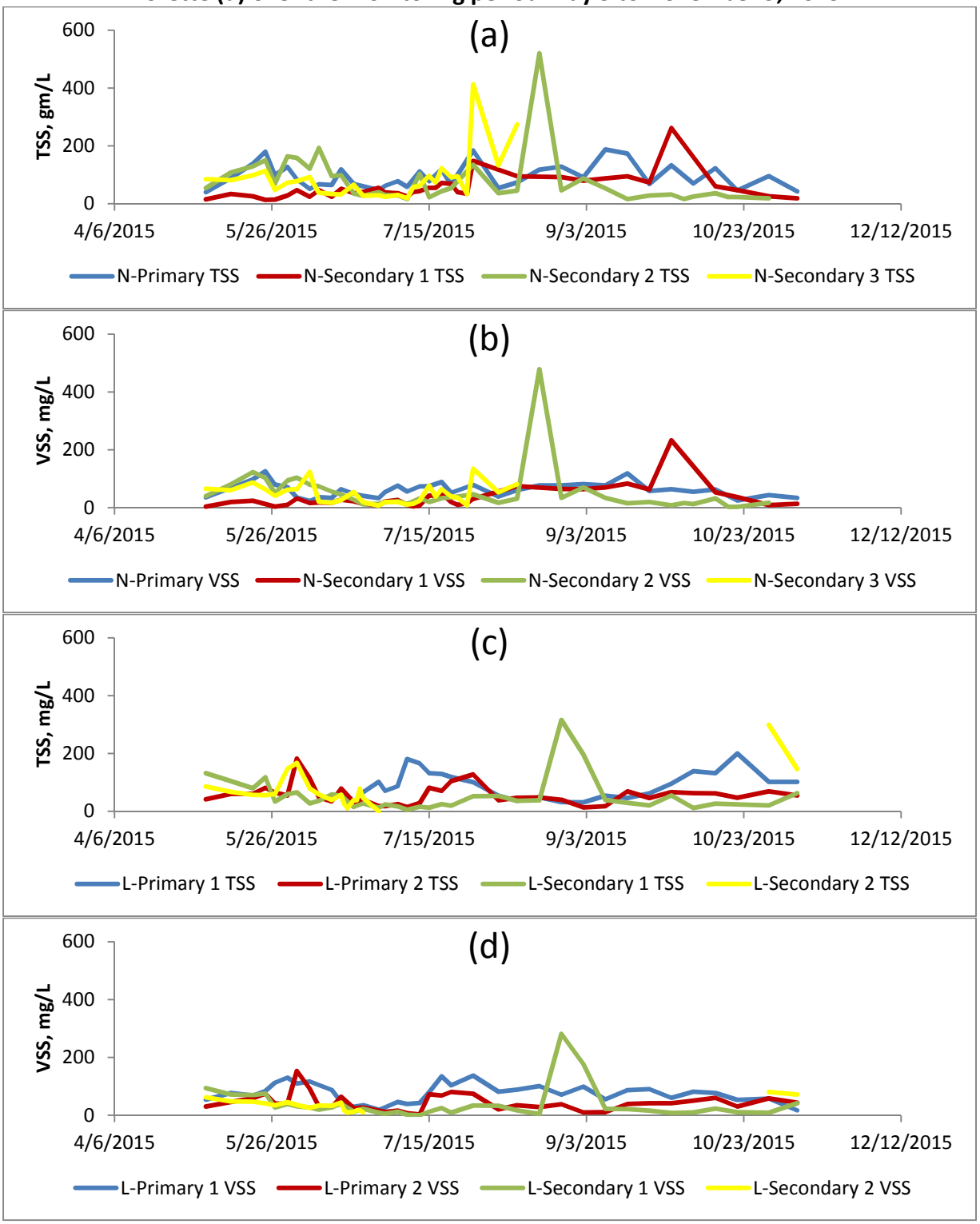
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Appendix A – TSS and COD Data

COD of all four cells in (a) Niverville and (c) Lorette and sCOD of all four cells in Niverville (b) and Lorette (d) over the monitoring period May 5 to November 9, 2015.



TSS of all four cells in (a) Niverville and (c) Lorette and VSS of all four cells in Niverville (b) and Lorette (d) over the monitoring period May 5 to November 9, 2015.



Appendix B – Evaporation Calculation

Mass Transfer Method:

Vapour pressure gradient and wind speed drive evaporation (Bedient et al, 2008). For Meyer's Formula (an empirical equation for calculating the evaporation rate) the saturation vapour pressure just above the water surface is needed (6) (Bedient et al, 2008). The saturation vapour pressure at 8 meters above the water surface is needed (7) and the actual vapour pressure at 8 meters can be calculated (8) (Bedient et al, 2008). This data can be used to calculate the cm/day evaporation rate using the Meyer's formula (9) (Bedient et al, 2008) which when multiplied by 10 and the number of days in a month gives the evaporation rate in mm per month. The average surface water temperature is estimated based on data collected over the monitoring period. The average air temperature, average relative humidity and average wind speed is taken from Kleefeld, Manitoba weather station (Environment Canada, 2015). It is assumed the air temperature will be the same at Kleefeld as both lagoons that the wind speed and relative humidity measured is the same at 8 meters elevation. It is assumed that the air temperature just above the water surface is approximately equal to the water temperature.

(6) $e_s = 2.7489 \times 10^8 \exp[-4278.6/(\text{water surface temp}) + 242.79]$

(7) $e_{s8} = 2.7489 \times 10^8 \exp[-4278.6/(\text{air temperature}) + 242.79]$

(8) $e_{a8} = (\text{Relative Humidity}) \times e_{s8}$

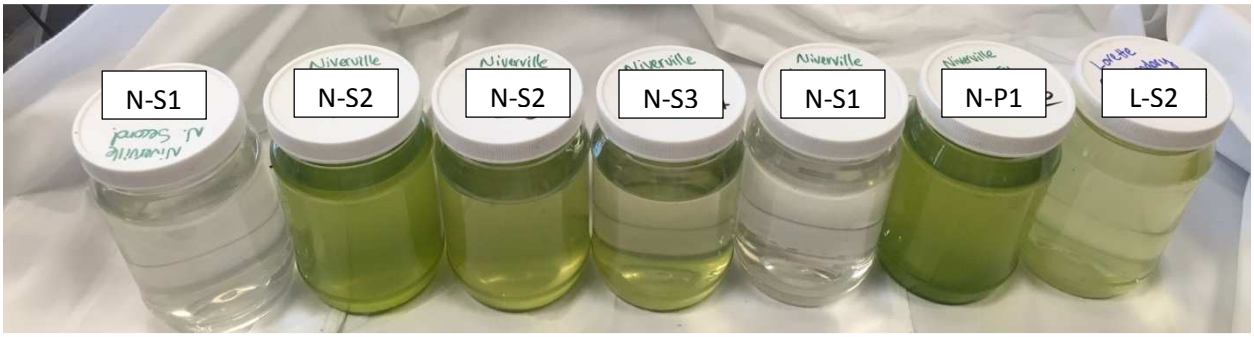
(9) $E = 0.0269 [1 + (\text{wind velocity at 8 m, km/h})/16] (e_s - e_{a8})$

Table of values used to calculate an estimated evaporation rate for the lagoon cells in Niverville and Lorette.

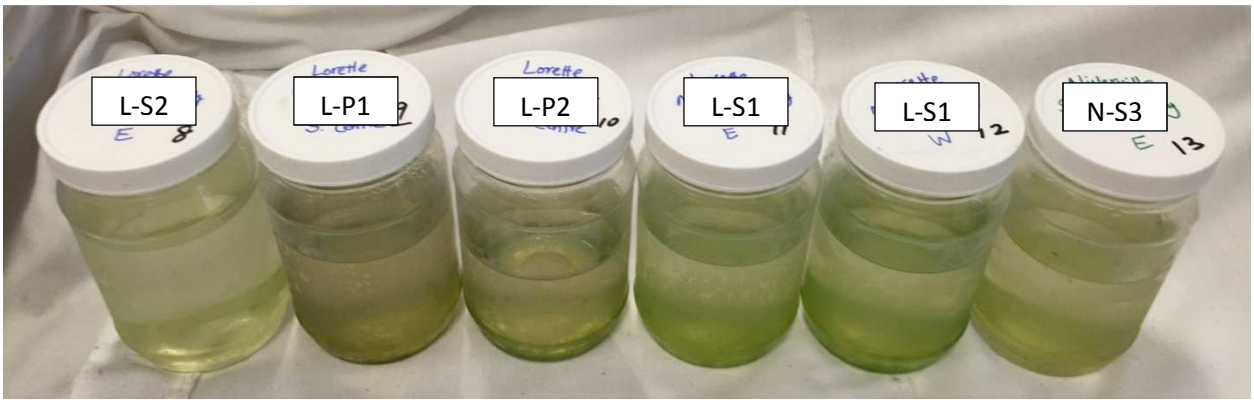
Month	Average Temp (˚C)	Est. Ave. Water Temp (˚C)	Ave Relative Hum (%)	Ave Wind Sp (km/h)	e_s (mbar)	e_a (mbar)	Evaporation, (mm/mo)
May	11.4	7.5	60.2	16.2	10.35	8.10	37.77
June	17.4	14.5	67.9	11.3	16.48	13.45	41.75
July	20.4	18.0	73.4	12.1	20.61	17.56	44.66
August	18.6	15.5	70.9	12.2	17.58	15.22	34.74
September	15.8	11.5	68.0	13.6	13.55	12.17	20.55
October	7.3	4.5	71.9	14.5	8.41	7.35	16.83

Appendix C – Lagoon Cell and Sample Photos

Lagoon Sample Photos – May 24, 2015

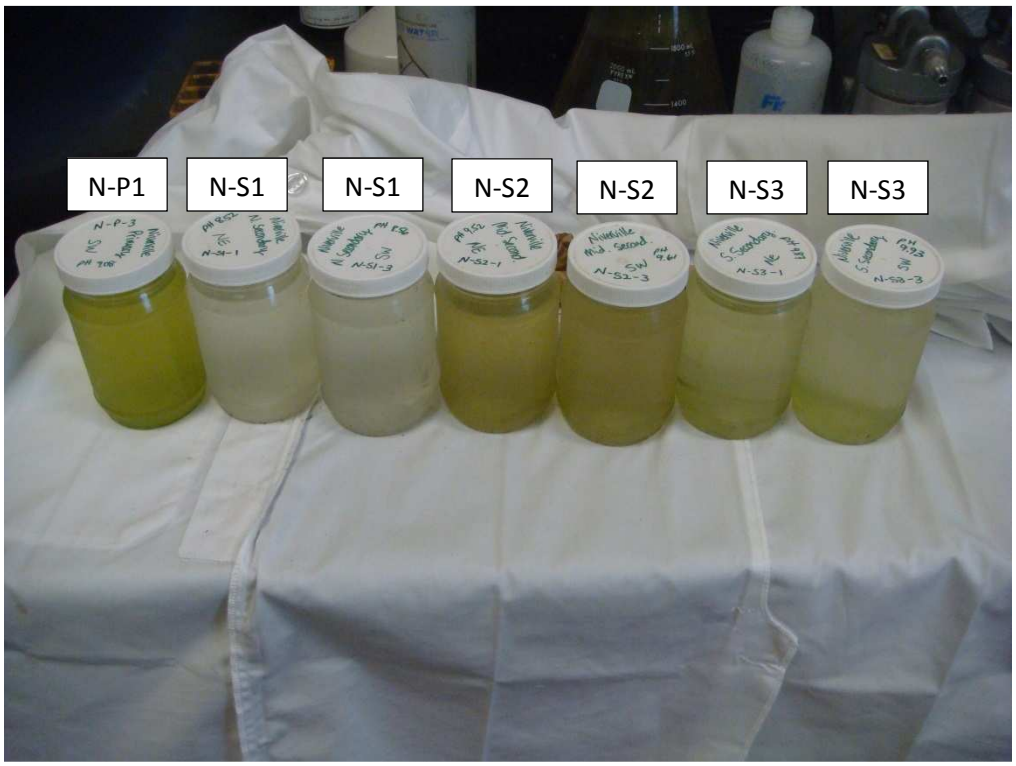


Niverville

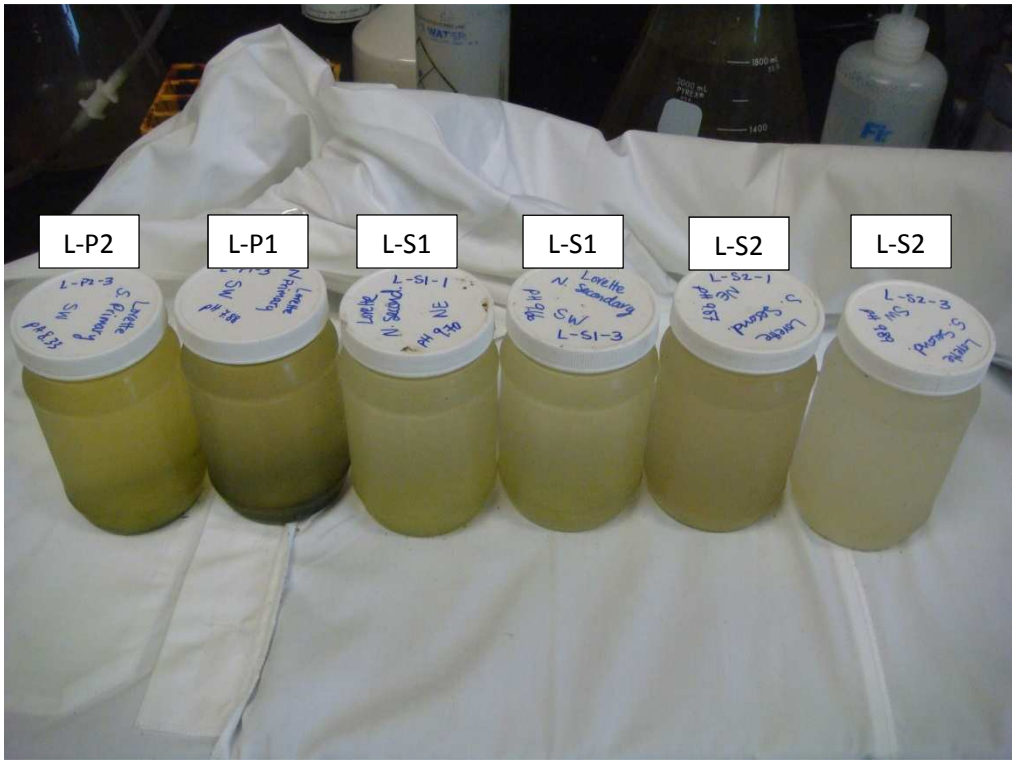


Lorette

Lagoon Sample Photos – May 27, 2015



Niverville

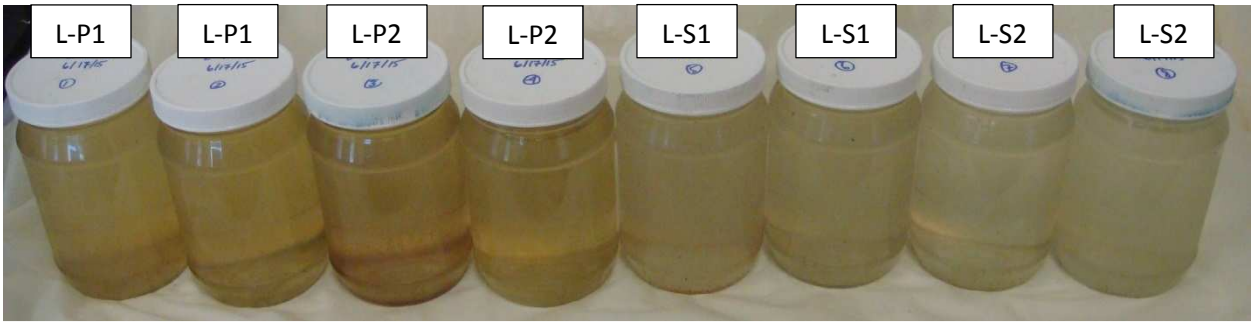


Lorette

Lagoon Sample Photos – June 17, 2015

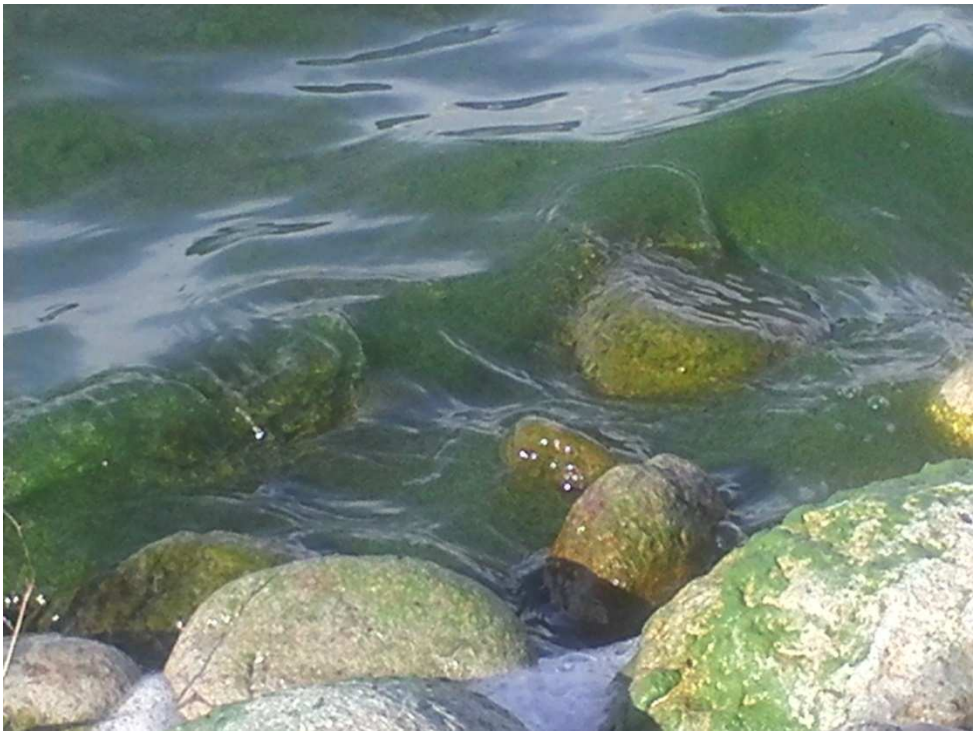


Niverville

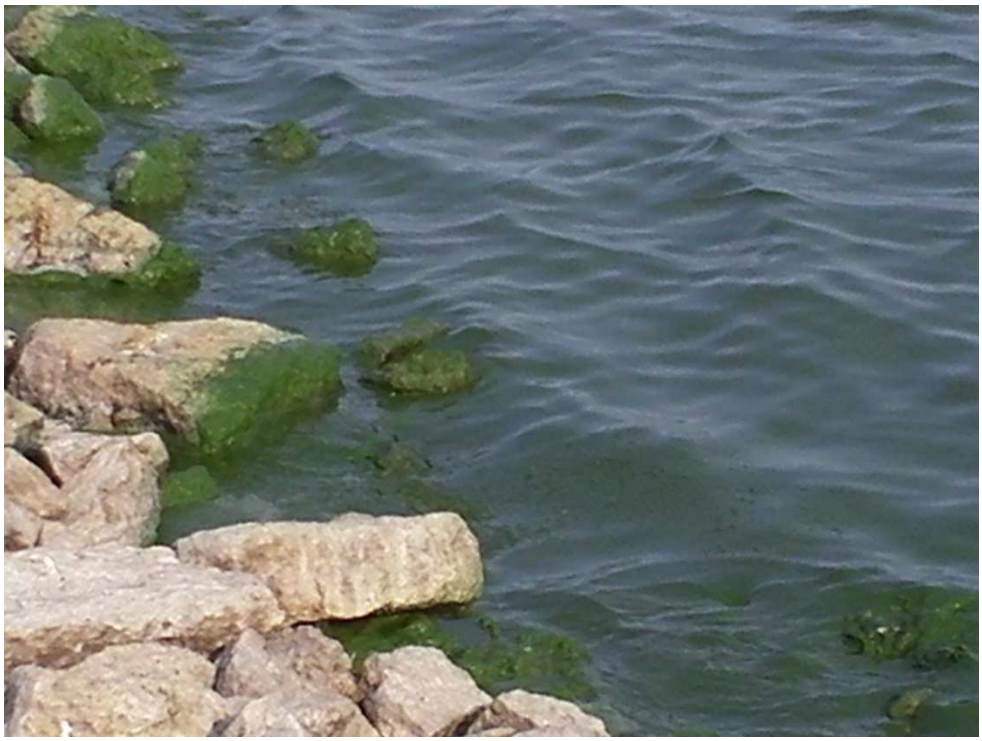


Lorette

Niverville Lagoon Algae Bloom (secondary cell 2) – August 19, 2015



Lorette Lagoon Algae Bloom (secondary cell 1) – August 26, 2015



Appendix D – Lagoon Canoe Survey

Table of results from Canoe Survey in Niverville and Lorette for dissolved oxygen, pH, temperature, and cell depth. Dissolved oxygen, pH, and temperature were measured at the surface and bottom of all the lagoon cells except Lorette primary cells 1 and 2 because of the aeration equipment.

Niverville 10/06/2015	N-Primary		N-Secondary 1		N-Secondary 2		N-Secondary 3	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Dissolved Oxygen (mg/L)	7.81	7.19	8.42	8.47	16.97	16.45	4.08	3.69
pH	7.68	7.64	8.52	8.57	9.60	9.56	9.51	9.51
Temperature (˚C)	20.6	20.0	21.7	21.4	22.4	22.6	21.8	21.6
Cell Depth (m)	1.10		1.10		0.45		0.90	
Lorette 10/06/2015	L-Primary 1		L-Primary 2		L-Secondary 1		L-Secondary 2	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Dissolved Oxygen (mg/L)	6.99	NoData	3.13	NoData	0.98	1.70	2.90	3.79
pH	7.53	NoData	7.56	NoData	7.94	7.96	8.22	8.24
Temperature (˚C)	19.6	NoData	20.4	NoData	20.4	20.0	20.7	20.7
Cell Depth (m)	No Data		No Data		1.15		1.00	

Appendix E – Sample Calculations

Calculation – Theoretical N/P Ratio

Algae: $C_{106}H_{263}O_{110}N_{16}P$
1 mol = 3553 grams

$$\text{N in 1 gram algae} = \frac{1 \text{ mol algae}}{3553 \text{ g algae}} \times \frac{16 \text{ mol N}}{1 \text{ mol algae}} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 63.1 \text{ mg N}$$

$$\text{P in 1 gram algae} = \frac{1 \text{ mol algae}}{3553 \text{ g algae}} \times \frac{1 \text{ mol P}}{1 \text{ mol algae}} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 8.72 \text{ mg P}$$

$$\text{Ideal Algae N/P Ratio} = \frac{\text{mg N}}{\text{mg P}} = \frac{63.1}{8.72} = 7.24$$

Bacteria: $C_{60}H_{87}O_{23}N_{12}P$
1 mol = 1375 grams

$$\text{N in 1 g bacteria} = \frac{1 \text{ mol bacti}}{1375 \text{ g bacti}} \times \frac{12 \text{ mol N}}{1 \text{ mol bacti}} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 122.3 \text{ mg N}$$

$$\text{P in 1 g bacteria} = \frac{1 \text{ mol bacti}}{1375 \text{ g bacti}} \times \frac{1 \text{ mol P}}{1 \text{ mol bacti}} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 22.5 \text{ mg P}$$

$$\text{Ideal Bacteria N/P Ratio} = \frac{\text{mg N}}{\text{mg P}} = \frac{122.3}{22.5} = 5.43$$

Sample Calculation
Algal Solids Produced with Supplemental Nitrogen

*assume no other limitations to algae growth

*assume algae population >> bacteria in lagoon

*assume algae removes bulk of N and P

N – S1 [Ortho-P] = 2.60 mg/L

Limit = 1 mg/L need to remove 1.60 mg/L P

$$\text{Ideal N/P Ratio} = 7.24 = \frac{[N]}{[P]} = \frac{\text{mg N}}{1.6\ \text{mg/L}}$$

[N] = (7.24) x (1.6) = 11.58 mg/L - existing [N] = 11.58 - (0.64 + 0.31) = 10.63 mg/L N (NH_3-N + NO_3)

$$\frac{10.63\ \text{mg N}}{1\ \text{L}} \times \frac{1000\ \text{mg algae}}{63.1\ \text{mg N}} = 168.5\ \text{mg/L algae concentration}$$

Table of theoretical algae solids production

Niverville				
	N-Primary 1	N-Secondary 1	N-Secondary 2	N-Secondary 3
mg/L algae	62.3	169	159	117
Lorette				
	L-Primary 1	L-Primary 2	L-Secondary 1	L-Secondary 2
mg/L algae	0.0	13.5	228	118
Alum Jar Test				
Average: 178 mg/L		Max: 300 mg/L		Min: 120 mg/L

Appendix F – Wastewater Cation Concentration and Hardness

Table of Cation Concentrations in Niverville, Manitoba – September 11, 2015

11/09/2015	Cell Average (mg/L)	Cell Average (mg/L)
Cations	Niverville-Primary 1	Niverville-Secondary 1
Sodium Na	368.76	414.65
Magnesium Mg	68.25	81.24
Potassium K	19.26	17.34
Calcium Ca	64.93	68.82
Boron B	0.161	0.138
Aluminum Al	0.086	0.05
Chromium Cr	0.005	0.005
Iron Fe	0.144	0.069
Manganese Mn	0.258	0.09
Nickel Ni	0.006	0.007
Copper Cu	0.005	0.006
Zinc Zn	0.021	0.018
Arsenic As	0.009	0.02
Zirconium Zr	0.0007	0.0005
Cadmium Cd	0.00004	0.00002
Antimony Sb	0.0002	0.0003
Lead Pb	0.0008	0.0007
Uranium U	0.004	0.005

The samples were analyzed by a Perkin-Elmer ICP-MS in a CALA accredited laboratory.

Total Hardness (mg/L as $CaCO_3$) = 2.50 x $[Ca^{2+}]$ + 4.12 x $[Mg^{2+}]$

N-P1 Hardness = (2.5 x 64.93) + (4.12 x 68.25) = 443.5 mg/L as $CaCO_3$

N-S1 Hardness = 506.8 mg/L as $CaCO_3$

Table of Cation Concentrations in Lorette, Manitoba – September 11, 2015

11/09/2015	Cell Average (mg/L)	Cell Average (mg/L)	Cell Average (mg/L)	Cell Average (mg/L)
Cations	Lorette-Primary 1	Lorette-Primary 2	Lorette-Secondary 1	Lorette-Secondary 2
Sodium Na	292.01	295.37	306.50	318.99
Magnesium Mg	75.01	69.99	74.40	84.38
Potassium K	23.84	23.47	18.73	21.46
Calcium Ca	70.28	69.62	64.16	75.55
Boron B	0.212	0.208	0.195	0.174
Aluminum Al	0.051	0.029	0.191	0.437
Chromium Cr	0.003	0.003	0.003	0.004
Iron Fe	0.21	0.141	0.314	0.897
Manganese Mn	0.079	0.078	0.11	0.187
Nickel Ni	0.004	0.004	0.009	0.012
Copper Cu	0.017	0.011	0.008	0.009
Zinc Zn	0.049	0.036	0.032	0.036
Arsenic As	0.003	0.003	0.017	0.009
Zirconium Zr	0.001	0.001	0.001	0.002
Cadmium Cd	0.00005	0.00002	0.00007	0.0001
Antimony Sb	0.0003	0.0003	0.0004	0.0005
Lead Pb	0.001	0.001	0.001	0.002
Uranium U	0.006	0.007	0.004	0.012

The samples were analyzed by a Perkin-Elmer ICP-MS in a CALA accredited laboratory.

Total Hardness (mg/L as $CaCO_3$) = 2.50 x $[Ca^{2+}]$ + 4.12 x $[Mg^{2+}]$

L-P1 Hardness = (2.5 x 70.28) + (4.12 x 75.01) = 484.7 mg/L as $CaCO_3$

L-P2 Hardness = 462.4 mg/L as $CaCO_3$

L-S1 Hardness = 466.9 mg/L as $CaCO_3$

L-S2 Hardness = 536.5 mg/L as $CaCO_3$