

Investigation into Chlorine Levels and Water Treatment Facility at CFB Wainwright for 3<sup>rd</sup> Canadian Division

For:

Engineering Services - 3 Canadian Division Support Group

Prepared by:

RMC Green Team

January 2015

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#### **EXECUTIVE SUMMARY**

A recent series of investigations associated with fish kill events at CFB Wainwright yielded positive results for elevated chlorine levels at CFB Wainwright in the vicinity of the Water Treatment Plant near Betty Lake. These chlorine 'hits' were recorded by sampling and colorimetric chlorine analysis techniques that were employed by CFB Wainwright staff, DST and Hatfield consultants.

The objective of the project undertaken by the RMC Green Team was to determine potential analysis interferences, alternative sampling methodologies and potential sources of chlorine, with a view to determining a baseline that should be used as a benchmark for chlorine analysis and to provide recommendations to Engr Svcs 3 CDSG / Base Environmental staff in this regard. Further, recommendations as to the potential source, conditions or causes of the fish kills were also investigated within the overall framework and context of the investigation.

The major findings of the investigation were:

- 1. Chlorine Levels. Due to possible Monochloramine and Manganese interferences in Chlorine testing in water samples from Betty Lake and Battle River, Chlorine levels need to be accurately determined and re-assessed. As discussed in Sections 4.5.1.1. and **4.5.1.2.** of this report, the Battle River water, which feeds Betty Lake, has been historically characterised by elevated manganese (Mn) concentrations. Also, ammonia and chlorine have been identified in measurable concentrations in water samples from the river. Manganese interference has been reportedly a problem in the determination of free both inorganic monochloramine chlorine concentrations. Chloramines, and dichloramine, and the organochloramines can also break through in free chlorine determinations causing an over-estimation of the disinfectant residual present. As the potential of a false-positive of free chlorine values can have a significant impact on water treatment processes and water quality, the Hach Method 10241 is recommended for chlorine detection (Annex E).
- 2. <u>Fish Kills</u>. According to the INRS report (2011), ammonium concentrations exceeding the CCME guideline for aquatic life have been found in the Battle River upstream and downstream of the CFB Wainwright in the first three to four months of the year. In 2005, most high NH<sub>4</sub> concentrations were related to high total dissolved solids (TDS).

Further, naturally high ammonia concentrations have been found downstream of the Forestburg Reservoir, which remains ice-free and well-oxygenated in winter, contributing nitrate to the river. The biological oxidation of ammonia or ammonium to nitrite followed by the oxidation of the nitrite to nitrate is called nitrification. Nitrate leaches into groundwater producing acute toxicity in multiple species of wildlife and contributing to the eutrophication of standing water. Soil consisting of polyanionic clays and silicates generally has a net anionic charge. Consequently, ammonium ( $NH_4^+$ ) binds tightly to the soil but nitrate ions ( $NO_3^-$ ) do not. As nitrate is more mobile, it leaches into groundwater fish, and

insects are sensitive to nitrate levels and have been known to cause death and developmental anomalies in affected species. In addition, because they easily leach into groundwater, nitrates contribute to eutrophication, a process in which large algal blooms reduce oxygen levels in bodies of water and lead to death of oxygen-consuming creatures due to anoxia (Health Canada, 2013).

Municipal discharges and agricultural non-point sources may also contribute much nitrogen to the Battle River and its tributaries. Ammonia occurs naturally in many groundwater systems, especially in central Alberta, east of Red Deer (Groundwater Chlorination - Alberta, 2013). Due to its limited dilution capacity, ammonia and other nitrogen substances can be identified downstream of the points of introduction. Relevant literature on ammonia concentrations in Wainwright area has indicated total ammonia exceedances of the CCME guidelines (INRS, 2011).

In a secondary role, potassium permanganate may be useful in controlling the formation of trihalomethanes (THMs) and other disinfection by-products (DBPs) by oxidizing precursors and reducing the demand for other disinfectants (Hazen and Sawyer, 1992). The source water from Betty Lake (Battle River) has been characterised historically as prone to the creation of THMs (WTPOP, 2000). The mechanism of reduced DBPs may include moving the point of chlorine application further downstream in the treatment train by using potassium permanganate to control taste and odours, colour, algae, etc. instead of chlorine. Although potassium permanganate has many potential uses as an oxidant and it is routinely used in the CFB Wainwright Water Treatment Plant (WTP), it is a poor disinfectant. Further, permanganates have been reported to kill fish in 8 to 18 hours at concentrations of 2.2 to 4.1 mg/L (EPA, 1999). On March 23 2013, the daily dosage for potassium permanganate in the CFB Wainwright WTP was 4.20 mg/L. The following days until the fish kill was reported, the KMnO<sub>4</sub> ranged from 2.44 mg/L to 2.07 mg/L. Several such spikes in KMnO<sub>4</sub> dosages have been observed by the RMC Green Team in the historical water treatment operation data regarding chemical usage. There is no indication as to why these spikes occurred.

Each of these main points above are explained in detail within the body of the report. The following are the recommendations that are consistent with the findings and/or suggested follow-up activities of this study:

1. Determination of the specific properties of the source water. There is a need to assess and characterize the source water. It is recommended that a determination and quantification of the chemical constituents be conducted as well as a mass-balance of these constituents in an effort to map these components within the water source system. The figure below summarizes the 'cycling' of these elements and by-products within a holistic framework. A holistic assessment and quantification of each known chemical constituent that has been identified in this report needs to be conducted in order to understand the potential by-products and their environmental impact. i.e. determining the effects and quantities of these items (and processes) with respect to Betty Lake, Battle River and the Water Treatment Plant. In this way, efforts can be made to optimize the water cycle (volumes of water from Battle River for instance) and effluent from the WTP. For example, the source water needs to be evaluated in terms of ammonia levels in order to regulate the dosages of ammonia added by the Water Treatment Plant. As well, the potential influences from the Battle River Power Generating Plant upstream should be investigated. It is recommended that BCE contact Alberta Environment in order to determine if there are any potential environmental issues related to Battle River due to the generating plant's activities (chlorination of and/or temparature effects on Battle River water quality).

2. <u>Re-assessing the current sampling plan</u>. The current sampling plan must be re-examined in order to account for the interferences discussed in this report and to incorporate the recommended sampling method for chlorine (i.e. Hach Method 10241). Sampling locations as well as constituents (i.e. ammonia, copper, manganese, alum etc.) should be re-assessed and a new sampling plan be put into effect whose aim is the characterization of the source water (and relevant environmental influences/impact) as per recommendation 1 above.

#### 3. Determination of dosages of chemicals added within WTP.

- a. <u>Breakpoint Chlorination Curve</u>: As mentioned in **Section 4.5**, ammonia has been detected in the effluent of the CFB Wainwright treatment plant. This may be attributed either to:
  - i. interferences in the ammonia testing (Nessler) method due to the presence of chloramines in the effluent, or
  - ii. to insufficient chlorination during the drinking water treatment processes. The description of the Battle River basin and its river water characteristics reveals that ammonia, potentially nitrites and nitrates as well as organic matter are present in the source water of the water reservoir (Betty Lake) of the CFB Wainwright Water Treatment Plant. According to literature, source waters containing natural ammonia should be monitored to determine if the ammonia concentration is constant and to ensure that the ammonia is compensated for in maintaining the optimum chlorine to nitrogen ratio for a drinking water treatment system. This process is described in detail Section 4.5. It appears in the data from the WTP that ammonia is added during the WTP processes. According to the breakpoint chlorination curve, chloramination takes place. While CFB Wainwright WTP staff routinely tests for free chlorine residual to ensure that free chlorine is available in the distribution system as a biocide, monochloramine may have been actually measured due to interference. Monochloramine, however, is a weal disinfectant (even though it is long lasting). Further, the presence of excess ammonia in the effluent may substantially impact the environment around the WTP and potentially cause adverse effects on the fish population.

b. The dosage of dechlorination tablets to be added at the South Lagoon effluent point needs to be optimized based on the amount of chlorine that is present. As well, the chlorine dosages within the WTP need to be assessed in order to determine if they are operating within the required effective zone of the Breakpoint Curve (Section 4.5 of this report).



Figure. Executive Summary

4. <u>Quality Assurance (QA)</u>. It is recommended that a 3<sup>rd</sup> party conduct QA on behalf of the Base Construction Engineering Cell in order to evaluate and ensure quality in the WTP processes by which effluent (not necessarily the drinking water component) is developed. This will serve to inform the chain of command as to the potential liability and environmental issues associated with the effluent. i.e. impact on the environment in the vicinity of the WTP. All indications are that the effluent from the WTP may be a key factor in impacting its surrounding environment and the source water.

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# **1.0 INTRODUCTION**

## **1.1 Background**

The RMC Green Team was approached by Engr Svcs 3 CDSG staff (CO 3 CDSG Engr Svcs / 3 Div Engr and the Base Environmental Officer) in order to assess elevated chlorine levels at CFB Wainwright. Recent events that have highlighted the need to investigate the potential source of elevated chlorine levels at CFB Wainwright include multiple chlorine release events into Betty Lake, fish kills that have been witnessed in the recent past, disturbances to the water pipeline due to recent waterline renovations, and elevated levels of chlorine that have been recorded due to the sampling and colorimetric chlorine analysis techniques employed.

CFB Wainright staff have been quite proactive in addressing and documenting each of the incidences and following-up with investigations (internal and external) in order to assess and determine the cause (or effect) of each noted incident. In addition to the findings and recommendations of recent consultant reports, the sampling and handling technique associated with the colorimetric chlorine analysis needs to be evaluated in order to determine any influences on laboratory results. As well, a baseline of chlorine in all of its forms in the environment also needs to be established in order to determine the natural chlorine levels within the environment. Without such a baseline, one cannot quantify the chlorine contributions based on the effluent produced by the water treatment plant (WTP).

Such an investigation into proactive measures to protect the environment aligns itself well with the Government of Canada's Federal Code of Environmental Stewardship (Environment Canada, 2007) whereby DND must adhere to the strictest of environmental guidelines, laws and codes at the Federal, Provincial, Municipal or site-specific level. In doing so, DND follows a good neighbour policy with respect to environmental issues including environmental stewardship and protection.

# 1.2 Objective / Scope

The objective of this project was to determine potential analysis interferences, alternative sampling methodologies and potential sources of chlorine, to try and determine the baseline that should be used as a benchmark for chlorine analysis and to provide recommendations to Engr Svcs 3 CDSG / Base Environmental staff.

# 2.0 METHODOLOGY

This project took on a multi-phased approach. The project focused on the following activities with a view of fulfilling the aim of the project:

- a. A study into the geology (geochemical) make-up of the region and CFB Wainwright was also investigated in order to establish a baseline concerning the environment and in particular of the source water and to add value to the site assessment in this regard;
- b. An investigation into the current state of water sampling and testing methods at the WTP and adjacent properties (i.e. Battle River) was conducted;
- c. A comprehensive literature review of geo-environmental factors as well as existing water sampling/testing techniques and technologies that are relevant to the current study was conducted; this included results and lessons learned from relevant projects and processes within Canada and abroad;
- d. An evaluation of the water treatment plant process was also initiated in order to determine its potential effect on the environment (optimization and process control of the WTP was outside the scope of this study);
- e. A fish kill review was also conducted in order to determine the potential factors that may have led to such fish kills in and around the WTP; and,
- f. A site visit was conducted on 02 Oct 2014 (**Annex A**) in order to meet with the Base Environmental Staff, determine the site-specific factors, assess first-hand the water sampling and testing techniques and examine the current state of the WTP infrastructure.

In an attempt to determine the strategy to be employed in this study, the conceptual framework model shown in **Figure 1** was created. This captures all of the relevant parts of the methodology that has been cited above. Even though the project was defined during the proposal stage, many multi-disciplinary elements and complex co-relations were investigated in order to determine potential reasons for the fish kills, the presence of Chlorine in the environment and the potential impact of the water treatment plant (WTP) operations on the environment within the context of this investigation.

The factors and the major topics that were investigated within this report are depicted in **Figure 2**. In order to characterize the site, the geology and the natural environment were investigated to determine the influences, processes and chemical constituents that are abundant in the area of interest. Anthropogenic causes were then studied which included the water treatment plant operations in order to determine their effect on the environment and, primarily the source water. Once these items were defined (i.e. a baseline for the source water was attempted to be established), then sampling techniques as well as what (and where), specifically, to sample for was examined. The report is organized in this manner.



Figure 1. Methodology – Conceptual Framework



Figure 2. Methodology – Major factors and topics of Investigation

# **3.0 SITE ASSESSMENT – CFB WAINWRIGHT**

# 3.1 Location

As seen in **Figure 3**, CFB Wainwright is located in South Eastern Alberta, Canada. The base is located approximately 210 kilometers East of Edmonton and approximately 110 kilometers South West of Lloydminster. The base is one of the busiest training Army bases in Canada. The region of interest for this particular study is in and around Betty Lake; detail of this region can be seen in **Annex A** of this report.

# **3.2 Geology of the Region**

Literature indicates that the Wainwright area is located within the east-central Alberta Plains. It is characterised by a relatively flat, glaciated area underlain by gentle dipping detrital strata of Late Cretaceous age. Bedrock is overlain primarily by till. Till, in turn, is overlain in many places by glaciofluvial and lacustrine deposits, aeolian sands, and thin patches of recent alluvial and lacustrine sediments. The glacial deposits and landforms suggest that they originated from large-scale downwasting and stagnation of the Keewatin ice-sheet, which advanced over the area during Pleistocene time. The glacial deposits are considered to be of Wisconsin age (AGS, 2014). Geologically relevant features of the region can be seen in **Figures 4 to 6**.



Figure 3. Site Map of CFB Wainwright and Area of Interest (modified after Google Map, 2014)



Figure 4. East-West Schematic of Geological Sections (AGS, 2013)



Figure 5. Geological Features as seen at the Surface for the Battle River Basin. (INRS, 2011)



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#### GEOLOGICAL LEGEND

Tertiary Tp Porcupine Hills/Paskapoo Tertiary and Upper Cretaceous TK Cyronas Hills/Bayenscrap/Franchman/Battle/Whitemud/Eastend	ıtion
Tp Porcupine Hills/Paskapoo (generalized geology) Tertiary and Upper Cretaceous TK Cyronas Hills/Bayenscrap/Franchman/Battle/Whitemud/Eastend	ıtion
Tertiary and Upper Cretaceous Tertiary and uppermost Cretaceous	ution
N VYUBSA FILIS/ DAVEDAG AU/ FISICALINA / DAVID BULUCE / SABID	tion
Cretaceous Dunvegan Formation	tion
Cretaceous Colorado Group	tion
Kbp Bearpaw Kwt Wapiti V Cretaceous Pelican (Viking) Forma	
Kpa Pakowki Cretaceous Mannville Group	
Kmr Milk River Ks Smoky Group Klp Lea Park Krm Riding Mountain - Jurassic Kd Durwegan	
Lower Cretaceous Devonian Wabamun Group	
Ksh Shaftesbury Kfsj Fort St. John I Devonian Woodbend-Winterburn'	
- Devonian Beaverhill Lake Group	
Devenian Elk Point Group	
Dwb Wabamun Ordovician-Silurian	
Di Ireton ( Dhr Hay River Dar Sourts River ) Precambrian Shield margin	
Dep Elk Point Canadian Rocky Mountains	
- (highly generalized geology)	
Mesozoic undifferentiated	
O Ordovician Paleozoic undifferentiated	
PC Precambrian Upper and Middle Proterozoic	
Mountains and foothills 'Includes Waterways Fm (Beaverhill Lake Go) and equivalents a	it the b
T Tertiary - scale 1:5 000	000
uK Upper Cretaceous 0 100 200	
K Cretaceous	
Mz Lower Oreaceous, Jurassic and Trassic 0 100	
Ha Unper Profementation (Hardonnian) and Lower Cambrian	
He Middle Proterozoic (Helikian) - Figure 6. Geological Ma	po
B Basement gnelss (Alberta Geological Soci	etv

## **GEOLOGICAL MAP OF WESTERN CANADA**

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	Devonian Woodbend-W	interburn'	12	
	Devonian Beaverhill Lak	e Group	11	
	Devonian Elk Point Grou	qu	10	
	Ordovician-Silurian		9	
	Precambrian Shield mar	gin	5 and 4	
Cana (highly	dian Rocky Mountain generalized geology)	ns		
	Mesozoic undifferentiate	ed		
	Paleozoic undifferentiate	ed	2 and 3	
	Upper and Middle Prote	rozoic	6	
1 Include	es Waterways Fm (Beaverhill Lake	Gp) and equivalents at the base		
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	0 100	200     100	300 kilometres	
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n Canada. (Alberta Geological Society, 2014).

# **3.3** Natural Environment – Characterisitics of Battle River Basin

#### 3.3.1 General

CFB Wainwright water treatment plant receives source water from Betty Lake, which is connected to Battle River. The Battle River flows eastward into North Saskatchewan River. The Battle River basin, a key watershed in east-central Alberta, covers approximately 30,000 sq km and is extremely rich and diverse in plant and animal life. The basin's water supply is derived entirely from rain, snow melt and groundwater, without benefit of the mountain/foothill snowpacks or glacial melt typical of other river basins in Alberta.

The main attributes that characterise the Battle River are the poor quality of its water and the very low flows which prevail most of the year. The Battle River has typically received a Water Quality Index rating of fair. The very low flows result in limited dilution capacity. As a consequence of this and fairly intensive agricultural activity in the Battle River basin, the system tends to experience water quality guideline exceedances for nutrients, pesticides and bacteria. In addition, the topography of most of the land in the drainage basin is rather flat and runoff from much of the land is trapped in small lakes and sloughs. Consequently, flows in the Battle River are usually very low except for a short time in April and May and sometimes in summer. In general, peak flows for the Battle River occur during the months of April and May, corresponding with annual snow melts and spring rains. The lowest flows are observed in the fall and winter. Annual flow volumes of the Battle River may vary greatly from year to year (Anderson, 1999; INRS, 2011).



**Figure 7.** Photos of Battle River near intake for WTP. (a) facing South and (b) facing North. More Photos and site map in **Annex A**.

The Battle River meanders through Samson and Driedmeat lakes, the Forestburg Reservoir, as well as beaver dams and other smaller obstructions. At low flows, weirs on the outlets of Driedmeat Lake and Forestburg Reservoir allow the passage of a constant amount of water. These surface water bodies and several other smaller structures tend to dampen changes in the river flow downstream. As a result, the Battle River water quality is influenced.

The primary factors that influence the composition, quality and processes of and within the source water include: Temperature, Concentrations of Dissolved Oxygen, and the Major Ions Distributions within the source water. These are expanded upon in the following sub-sections (Anderson, 1990; Battle River Watershed Alliance, 2011).

#### **3.3.2** Water Temperature

The Battle River average monthly water temperature ranges from 0 degrees Celcius in winter to 24 degrees Celcius in July. Cooling water effluent from the Battle River Coal-Fired Power Generating Plant is discharged in the upper part of the Forestburg Researvoir. The water cools as it moves through the reservoir. At peak flows in spring, literature indicates that water moves quickly through the reservoir and warms the river downstream. At that time, Alberta Ambient Surface Water Quality Interim Guidelines has been exceeded for as much as 200km downstream because the water temperature rose by 3 degrees Celcius or more. However, in winter, the warmer water from the power plant kept the reservoir ice free which facilitated oxygen exchange and had a positive effect on the water quality of the Battle River downstream (Anderson, 1999; Alberta Environment, 2007; Global Energy Observatory, 2014).

#### 3.3.3 Dissolved Oxygen

Literature indicates that dissolved oxygen increases in surface waters as a result of turbulence and aeration and as a result of plant photosynthesis. Oxygen concentrations decrease when plants and animals respire and as organic material is decomposed by bacteria. The temperature of the water also influences how much oxygen will dissolve. Under otherwise similar conditions more oxygen will dissolve in cold water than in warm water (Anderson, 1999; CCME, 2010; BRWA, 2011; Kentucky Water Watch, 2014).

Over the course of a year, dissolved oxygen concentrations in the Battle River may fluctuate from 0 to 16 mg/L, with 5mg/L being the lowest concentration recommended by the Alberta Ambient Surface Water Quality Interim Guidelines or Canadian Water Quality Guidelines for the protection of aquatic life. During the winter, ice prevents aeration of the water and dissolved oxygen gradually becomes depleted because more dissolved oxygen is being consumed by respiration and decomposition than is produced by photosynthesis. As such, during the winter, dissolved oxygen concentrations in the Battle River drop well below 5mg/L. There are areas within the Battle River where the decline in dissolved oxygen concentration is very severe due to the decomposition of large amounts of organic matter. Once ice melts, oxygen from the atmosphere dissolves in the water and growing plants also produce more oxygen. In the summer, in areas where plant growth is significant, dissolved oxygen concentrations may also drop below 5mg/L. In the Battle River, dissolved oxygen can also fluctuate widely over the course of a day. Lower concentrations usually occur in the early morning and higher concentrations in the early evening (Anderson, 1999; BRWA, 2011).

As well, low dissolved oxygen concentrations are a limiting factor for fish in summer and winter. The presence of dissolved oxygen in water also influences the concentrations of some dissolved substances such as phosphorus, nitrogen and some metals. These substances may also affect fish populations in the Battle River. The Battle River's fish are suffering due to various human activities and land use practices that affect water quality and the overall health of our aquatic ecosystems (Anderson, 1990; INRS, 2011; Battle River Watershed Alliance, 2011).

## **3.3.4 Major Ions Distribution**

The dominant ions in the Battle River upstream of Samson Lake are bicarboante and calcium. Further downstream, sodium and bicarbonate are the dominant ions. The concentration of all ions, but especially sulphate and chloride, increases in a downstream direction. These changes are related to changes in the quality of groundwater which flows to the river, and to changes in the geology of the drainage basin. Municipal wastewater discharges also contribute substantial amounts of ions to the river, especially of sodium, chloride, sulphate and fluoride (Anderson; 1999; INRS; 2011).

# 3.4 Anthropogenic Impact on the Battle River Water Quality

The Battle River differs from other large provincial rivers because it does not receive glacial melt, and its flows depend solely on surface and ground water inputs. Climatic factors strongly influence river discharge, which is typically low, although peaks occur occasionally. Water allocations to municipal, industrial operations (coal mining and power plant operations) and agricultural sectors place further pressure on river levels, a situation that is likely to intensify with further development. The Battle River is subjected to municipal point sources (treated municipal wastewater discharge, urban storm sewers overflows, combined sewers overflows, industrial wastewater discharges from power plants or petrochemical plants) and non-point



**Figure 8.** Map Depicting Potential influence from Battle River Power Generating Plant and the Source Water of Battle River (modified after Google Map, 2014)

industrial (coal mining) as well as agricultural (field crops, irrigation) sources combined with low river flows and limited dilution capacity. As a result of this, the Battle River water is characterised by elevated concentrations of particulate phosphorus and nitrogen and low winter dissolved oxygen levels. In particular, phosphorus and nitrogen exceed guidelines frequently and DO are often below guidelines. Concentrations of suspended solids and dissolved solids increase substantially with distance downstream, possibly because of municipal inputs, ground water inputs and natural runoff from soils relatively high in salts.

The largest user of the Battle River water is the ATCO Battle River Coal-fired Power Generating Plant. ATCO Power's Battle River Generating Station has three units totalling 730 MWs. All units have cold-side electrostatic precipitators and burn subbituminous coal from the close-by Paintearth Mine at a rate of about 400 tonnes coal per hour at full load on all three units. Chlorine is, on average, a highly coalphile element. In subbitumenous coal, chlorine concentrations range between  $120 \pm 20$ ppm. There is no NOx or SO<sub>2</sub> control on any of the units. Fly ash is handled dry and land-filled or sold. Bottom ash is handled wet and land-filled. No data are available with respect to the use of protective membranes in the bottom ash landfill to avoid leaching of metals or other toxic substances in the groundwater (Bowen & Irwin, 2008; Health Canada, 2013).

The power plant draws water from the Forestburg Researvoir. Most of the water that is used by the power plant for cooling is returned to the Reservoir. As mentioned above, the Battle River meanders through Samson and Driedmeat lakes, the Forestburg Reservoir, as well as beaver dams and other smaller obstructions. At low flows, weirs on the outlets of Driedmeat Lake and Forestburg Reservoir allow the passage of a constant amount of water. These surface water bodies and several other smaller structures tend to dampen changes in the river flow downstream. As a result, the Battle River water quality is influenced.

No municipality uses water directly from the Battle River or its tributaries, although several municipalities discharge their wastewaters to the streams. Livestock watering, irrigation and oil injection are other uses for water in the Battle River. Active surface coal mines are located between Forestburg Researvoir and Paintearth Creek. Settling ponds collect on-site runoff and eventually discharge water to Paintearth Creek. Recently mined areas are reclaimed, but spoils from mines which were active in the 1950's are still evident northwest of the Forestburg Reservoir. The power plant on the Forestburg Reservoir uses locally mined coal to generate power and it uses water from the reservoir for cooling. The main influences of this process on the source water is described in the following sub-sections (CCME, 2008; Alberta Environment; 2014).

#### **3.4.1** Chlorine in the Battle River Water

Interferences in free chlorine testing analysis can be skewing the results obtained by CFB Wainwright staff regarding the Battle River water chemistry; this topic will be discussed later in this report. Industrial activities, however, may also be the cause of the free chlorine measurements in the background samples (Battle River) that were tested by DST Consultants in September 2013 (DST, 2013).

The ATCO Battle River Power Generating plant is located upstream of CFB Wanwright (Figure 8). Coal-fired power-generating plants are known for chlorinating the water used in

their processes to eliminate the formation of algae in their systems (Health Canada, 2013). These chemicals are also discharged back into the environment. Chlorine is routinely mentioned in the Battle River Generating Station maintenance reports; however, no specific data were available on the company's site or relevant bibliography on chlorine concentrations used in the plant's operations or any de-chlorination processes prior to release to the Forestburg Reservoir. Chlorine (and other halogens) is used in mercury control technologies within coal-fired power plant to reduce mercury emissions (Alberta Environment, 1999).

Chlorine is also present in subbitumenous coal, the source for the operation of the Battle River Power Plant. Leachate from coal mining activities can contribute water contaminated with chlorine, ammonia and deleterious substances (elevated concentrations of metals such as arsenic, iron and lead) to the river. Dust from coal mining areas can also contribute to the contamination of adjacent surface water bodies with amounts of chlorine and metals (Health Canada, 2013; Alberta Coal Mining Wastewater Guidelines, 1998).

Industrial wastewater from the power plant as well as surface run-off from coal mining tailings that contain chlorine may routinely end up in the Battle River. With limited dilution capacity and low flows, the river water chemistry may be impacted downstream (Alberta Environment; 1999; Health Canada; 2013).

## 3.4.2 Nutrients in the Battle River Water

Point and non-point sources contribute nutrient amounts in the Battle River basin. Sources and seasonal patterns of nitrogen and phosphorous have been identified as similar to those of phosphorous in relevant literature.

## 3.4.2.1 Ammonia in the Battle River Water

Nitrogen occurs in many forms in surface waters. Organic nitrogen includes proteins, amino acids and urea in dissolved form or live cells or dead organic particles. Inorganic nitrogen includes nitrate, nitrite and ammonia. Organic nitrogen is the most abundant form of nitrogen in the Battle River (Anderson, 1999). Higher concentrations were recorded during spring runoff. Inorganic forms of nitrogen were also most abundant at spring runoff. Naturally high ammonia concentrations have been found downstream of the Forestburg Reservoir, which remains ice-free and well-oxygenated in winter, contributing nitrate to the river. As dissolved oxygen levels declined under ice in the river downstream, some of this nitrate was reduced to nitrite and even ammonia (Anderson, 1999; Battle River Watershed Alliance (BRWA), 2011; Alberta Environment and Sustainable Resource Department, 2014).

Nitrification is the biological oxidation of ammonia or ammonium to nitrite followed by the oxidation of the nitrite to nitrate:

- 1.  $2 \text{ NH}_4^+ + 3 \text{ O}_2 \rightarrow 2 \text{ NO}_2^- + 2 \text{ H}_2\text{O} + 4 \text{ H}^+$  (Nitrosomonas)
- 2.  $2 \text{ NO}_2^- + \text{O}_2 \rightarrow 2 \text{ NO}_3^-$  (Nitrobacteria, Nitrospina)
- 3.  $NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$
- 4.  $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$

Nitrate leaches into groundwater, producing acute toxicity in multiple species of wildlife and contributing to the eutrophication of standing water. Soil, consisting of polyanionic clays and silicates, generally has a net anionic charge. Consequently, ammonium  $(NH_4^+)$  binds tightly to the soil but nitrate ions  $(NO_3^-)$  do not. Because nitrate is more mobile, it leaches into groundwater supplies through agricultural runoff. Wildlife such as amphibians, freshwater fish, and insects are sensitive to nitrate levels, and have been known to cause death and developmental anomalies in affected species. In addition, because they easily leach into groundwater, nitrates contribute to eutrophication, a process in which large algal blooms reduce oxygen levels in bodies of water and lead to death of oxygen-consuming creatures due to anoxia (Health Canada, 2013).

Municipal discharges and agricultural non-point sources may also contribute much nitrogen to the Battle River and its tributaries. Ammonia occurs naturally in many groundwater systems, especially in central Alberta, east of Red Deer (Groundwater Chlorination - Alberta, 2013). Due to its limited dilution capacity, ammonia and other nitrogen substances can be identified downstream of the points of introduction. Relevant literature on ammonia concentrations in Wainwright area has indicated total ammonia exceedances of the CCME guidelines (INRS, 2011). According to the INRS report (2011), Ammonium concentrations exceeding the CCME guideline for aquatic life are occurring also in the Battle River upstream and downstream of the military base in first three to four months of the year. In 2005, most high NH<sub>4</sub> concentrations were related to high TDS.

## **3.4.2.2** Phosphorous in the Battle River Water

Elevated Phosphorous concentrations may lead to an increase in algae and weeds production which can subsequently lead to depleted dissolved oxygen conditions and fish kills. Total phosphorous, which is the measure of all phosphorous present in living cells, organic matter, and is related to suspended sediment or dissolved in water, has historically been found elevated in Battle River. Total phosphorous concentrations are typically highest during spring runoff in the entire river. Municipal wastewater discharges also contribute substantially in the river phosphorous levels. Lakes on the Battle River are very rich in nutrients and they may supply phosphorous to the river downstream (Anderson, 1999; Alberta Environment, 2014).

## 3.4.3 Organic Matter

Natural organic compounds are derived from soils, the breakdown of plant and animal cells and the weathering of bedrock. Lakes on the Battle River are rich in algae and organic matter, in general. Dissolved oxygen measured in the Battle River has been frequently below 5 mg/L, indicating that a lot of dissolved oxygen is needed to decompose organic matter in the river basin. As mentioned above, a large variety of man-made organic compounds may also be released in the environment and contaminate surface waters in the Battle River (Anderson, 1999; Battle River Watershed Alliance (BRWA), 2011).

## 3.4.4 Metals (Manganese and Copper)

Metals occur naturally in the Earth's crust and enter surface water systems through weathering and erosion of rocks and soils. There are also various human activities that allow for the release of metals in rivers. Certain metals are of concern because they can be toxic even at low concentrations.

In the Battle River basin, there is no major heavy metal industry. However, there are smaller potential inputs including wind-blown dust, natural weathering of rocks, burning of coal, oil and gasoline as well as coal mining activities. Further, wastewater discharges, phosphate fertilizers and animal feed supplements contain a variety of trace metals such as copper and chromium (Alberta, 1999; Anderson, 1999).

Manganese and copper have historically been found to exceed acceptable limits in Battle River water samples downstream of Forestburg Reservoir and in Wainwright area (INRS, 2011; BRWA, 2011). The fluctuations of dissolved oxygen also influence the concentration of some metals, such as manganese. For instance, in oxygenated waters, manganese forms insoluble salts which precipitate to the bottom. However, under reducing conditions (no oxygen), soluble ions are formed which go into the water. Manganese values frequently exceed Alberta Ambient Surface Water Quality Interim Guidelines during low oxygen conditions in winter (Anderson, 1999). In the Battle River, reducing conditions which lead to high concentrations of manganese are common under ice in the winter, but they can also occur in the summertime, when aquatic vegetation consumes large amounts of oxygen for growth and decomposition purposes. Literature indicates that manganese, although it is considered a naturally occurring element, it can be toxic at high concentrations to aquatic life (Pinisino, 2012). Copper has also been found to exceed Alberta Ambient Surface Water Quality Interim Guidelines and CCME guidelines. Copper concentrations were particularly higher in sediments from the Forestburg Reservoir, potentially affecting the river water chemistry downstream. According to the INRS report (2011), water testing in Betty Lake and Battle River has revealed higher Cu concentration (4 and 7 ppb) than the guideline (2 and 3 ppb) for a total hardness of 16 and 125 mg/L.

## 3.5 Summary

The above mentioned items highlight the fact that chlorine, nutrients (ammonia and phosphorous), metals, organic matter characterize the source water and are present in the raw water that is entering the Water Treatment Plant (WTP).

# 4.0 CFB WAINWRIGHT WATER TREATMENT

# 4.1 General

The Betty Lake WTP (**Figure 9**) is located approximately 10 km West of CFB Wainwright. The plant was originally constructed in 1952 with a nominal design flow of 15.4 Million Liters per day (MLD) (3.4 Million of Gallons per day (MIGD)). It provides treated water to the CFB Wainwright and the Town of Wainwright. The total population serviced is estimated to be 650 - 1500 for the base and 6000 for the town (WTPOP, 2000). The plant has supplied water to the town since 1988. **Figures 10 and 11** are schematics of the Betty Lake WTP distribution system and treatment processes respectively.



Figure 9. Photo of WTP facing north. More Photos and site map in Annex A.

# 4.2 Source Water

From May to October, water from the Battle River is pumped to Betty Lake via 2.2 km of 600 mm (24") diameter pipe (**Figure 10**). Flow from the Battle River is diverted to the pump station by means of a concrete dam constructed in 1988. The pump house is equipped with 4 vertical turbine pumps—two 200 HP pumps with an 11 MLD (2,000 US gpm) capacity and two 60 HP pumps with a 2.7 MLD (500 US gpm) capacity. The river water is not pre-chlorinated by WTP processes. It is estimated that 1.4 million m<sup>3</sup> (300 MIG) are transferred annually from the river to Betty Lake (WTPOP, 2000).

Betty Lake has a surface area of approximately 53 hectares (130 acres) with a maximum depth of about 3 m (10 ft). Turbidities in Betty Lake are low, generally below 10 NTU. The WTP draws water from Betty Lake by means of a 300 m (1000 ft) long 300 mm (12 in) diameter pipe. Approximately 50 m (150') separate the point of discharge of river water to Betty Lake from the WTP intake. The WTP has the capability of treating river water directly. Other factors to consider in terms of the WTP in relation to the environment are:

- a. Distribution System Monitoring and Control. One must ensure that the distribution system is sound and that no leaks are present that could affect the environment. At the time of the site visit, new distribution pipes were being installed;
- b. The average source water turbidity is high. High turbidity from April to June can be attributed to turbid water being pumped from Battle River to Betty Lake. The water is

discharged in close proximity to the plant intake structure. The current practice of sampling directly from Betty Lake instead of the plant intake may not reflect the true water quality to the plant. As such, a holistic assessment should be made;

c. Betty Lake also contributes to high levels of total organic carbon (TOC) due to the decomposition of leaves, algae, etc. in the reservoir. High levels of TOCs in the finished water combined with chlorine produce trihalomethanes (THMs), which are known carcinogens.

# 4.3 Water Treatment

The water treatment plant at CFB Wainwright treats water through a conventional treatment train including coagulation, flocculation, sedimentation and filtration to meet the Canadian Drinking Water Standards. Chemicals added during the treatent process include alum, potassium permanganate, polymers, carbon dioxide, and ammonia. In the past, activated carbon, lime and flouride were also used. Chlorine is added in the form of chlorine gas to eliminate pathogenic organisms, or those organisms harmful to human health. As an additional barrier in the water treatment plant process to protect against the pathogens, an immersed membrane system is utilised that uses ultrafiltration (UF) membranes. Ammonia is added to the drinking water upon leaving the treatment plant which forms a bond with free chlorine to produce chloramines, a weak but long lasting disinfectant. For the production of chloramines, first chlorine gas or hypochlorite is added to the water to produce hypochlorous acid. Then ammonia is added to the water to react with the hypochlorous acid and produce a chloramine (EA WTP, 2011).

Three types of chloramines can be formed in water - monochloramine, dichloramine, and trichloramine. Monochloramine is formed from the reaction of hypochlorous acid with ammonia:

 $\begin{array}{l} Ammonia + Hypochlorous \ Acid \rightarrow Monochloramine + Water \\ NH_3 + HOCl \rightarrow NH_2Cl + H_2O \end{array}$ 

Monochloramine may then react with more hypochlorous acid to form a dichloramine:

Monochloramine + Hypochlorous Acid  $\rightarrow$  Dichloramine + Water

 $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ 

Finally, the dichloramine may react with hypochlorous acid to form a trichloramine:

 $\begin{array}{l} \text{Dichloramine} + \text{Hypochlorous Acid} \rightarrow \text{Trichloramine} + \text{Water} \\ \text{NHCl}_2 + \text{HOCl} \rightarrow \text{NCl}_3 + \text{H}_2\text{O} \end{array}$ 

The number of these reactions which will take place in any given situation depends on the pH of the water. In most cases, both monochloramines and dichloramines are formed. Monochloramines and dichloramines can both be used as a disinfecting agent, called a **combined chlorine residual** because the chlorine is combined with nitrogen. This is in contrast to the free chlorine residual of hypochlorous acid which is used in other types of chlorination.

Chloramines are weaker than chlorine, but are more stable, so they are often used as the disinfectant in the distribution lines of water treatment systems. Despite their stability, chloramines can be broken down by bacteria, heat, and light. Chloramines are effective at killing bacteria and will also kill some protozoans, but they are very ineffective at killing viruses.

De-chlorination of the filter backwash is done with sodium thiosulphate and sodium sulphite "pucks" (**Figure 10**) to ensure that the chlorine levels are below the CCME Guidelines for the Protection of Aquatic Life.



Figure 10. Dechlorinaltion Process at South Lagoon (photos taken in October 2014 by RMC Green Team). (a) Dechlorination 'pucks' or tablets, (b) container of Sodium Sulphite Tablets, (c) Manhole at the effluent culvert from the South Lagoons depicting the perforated container that is filled with dechlorination tablets and placed at the culvert opening and, (d) exiting side of the effluent culvert that discharges to Betty Lake towards the East (in the background)



Figure 11. Schematic of the overall distribution system.



Figure 12. Schematic of the Betty Lake water treatment plant process.

# **4.4 Effluent Characterization**

According to previous reports and relevant bibliography, the effluent of the water treatment plant contains elevated copper, manganese, phosphorous and total ammonia. Nitrate concentrations were also detected in April 2013 by Hatfield consultants and were found below acceptable limits (Hatfield, 2013). Free chlorine was measured by DPD colorimetric method and was determined to be above acceptable limits. However, due to the presence of ammonia and potentially chloramines in the Battle River water that feeds into Betty Lake, the free chlorine testing may have been affected by chloramines interference. In the following sections, monochloramine interference is discussed along with alternative testing methods for free chlorine in the presence of manganese and chloramines. Further, the fluctuations in the dissolved oxygen concentrations of the water treatment plant effluent, as depicted in pertinent literature about the CFB Wainwright water treatment plant, may be attributed to plant growth and/or decomposition, ice cover during winter as well as the use of sodium sulphite "pucks" for dechlorination purposes (this dechlorination agent is known for oxygen scavenging) in the south lagoon.

# 4.5 Observations and Considerations for WTP Process Control

As mentioned previously, ammonia has been detected in the effluent of the CFB Wainwright treatment plant. This may be attributed either to interferences in the Nessler method due to the presence of chloramines in the effluent or to insufficient chlorination during the water treatment processes. Ammonia exists as either  $NH_4$ + or  $NH_3$  depending on the pH and temperature of the water. At a neutral pH and ambient temperature, almost all of the free ammonia exists as  $NH_{4+}$ . As the pH and temperature increase, the amount of  $NH_3$  increases and the amount of  $NH_{4+}$  decreases (LaMotte-Geotech, 2014).  $NH_3$  form of ammonia is toxic to fish (Francis-Floyd, Watson, Petty and Pouder; 2012; Health Canada, 2013). This section discusses water treatment plant operation processes that may affect the effluent water chemistry and, as a result, the environment in the lagoons and Betty Lake.

The description of the Battle River basin and its river water characteristics reveals that ammonia, potentially nitrites and nitrates as well as organic matter are present in the source water of the water reservoir (Betty Lake) of the CFB Wainwright water treatment plant. According to literature, source waters containing natural ammonia should be monitored to determine if the ammonia concentration is constant and to ensure that the ammonia is compensated for in maintaining the optimum chlorine to nitrogen ratio for a treatment system. The ammonia naturally present in the source water becomes part of the total ammonia concentration used to calculate the chlorine to ammonia ratio (AWWA, 2008).

Breakpoint chlorination is the application of sufficient chlorine to maintain a free available chlorine residual. The principle purpose of breakpoint chlorination is to ensure effective disinfection by satisfying the chlorine demand of the water (AWWA, 2008). In waters that contain ammonia such as the source water from Betty Lake (Battle River), breakpoint chlorination is a means of eliminating ammonia to achieve a true free chlorine residual. **Figure 13** shows the theoretical breakpoint chlorination curve. Adding chlorine to water that contains ammonia or nitrogen-containing organic matter produces an increased combined chlorine residual. When chlorine gas is added to water, hypochlorous acid (HOCl) and hydrochloric acid (HCl) is created. If ammonia exists in the water entering the water treatment

plant, the reaction between hypochlorous acid and ammonia is a very important reaction that must be taken into account. Hypochlorous acid and ammonia combine to form inorganic chloramines: monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>) and trichloramines or nitrigen trichloride (NCl<sub>3</sub>). The relative amounts of the chloramines formed are a function of chlorine fed, the chlorine/ammonia ratio, temperature, and pH. In general, monochloramine is formed above pH 7 and dominates at pH 8.3 (Janzen and Beier, 2009).

Interestingly, as shown in **Figure 13**, at any one total chlorine residual, there may have three different chlorine dosages. To move the disinfection process from the monochloramines to breakpoint disinfection or free chlorine, the addition of more chlorine is required. This is best illustrated in the classic chlorine breakpoint curve presented in **Figure 13**. As the chlorine dosage is increased, as shown on the x-axis, you will notice that the total chlorine residual first increases to the top of the peak, and then as more chlorine is added the residual actually drops. At this point the disinfection process is moving out of the monochloramine range and into the diand tri-chloramine stage. This area of the curve generally produces the most chlorine taste and odors associated with the water. As well, in this zone you can see that the ammonia is being decreased to zero. At the breakpoint stage, the total residual starts to increase again. As additional chlorine is added, all ammonia is now destroyed and a free residual exists. At this point, the free chlorine residual should be about 80% of the total chlorine residual (AWWA, 2008).

Monochloramine is a much weaker biocide than hypochlorous acid. The killing power of free residual chlorine (i.e., hypochlorous acid and hypochlorite ion) is as much as 25 times higher than the killing power of combined available chloramines (i.e., monochloramines). Mono-, di-, and trichloramines are commonly referred to as Combined Chlorine. After trichloramines have been created, the further addition of chlorine (HOCl) results in a free chlorine residual (Janzen and Beier, 2009; Hach, 2014).

If organics are present in the water, the hypochlorous acid will react similarly to how it reacts with ammonia and create Organic Amines. Organic Amines are complex chlorine compounds that are the result of the chlorine reaction with organic nitrogen. They have very little ability to disinfect, because reaction rates are slower with organic compounds, but they do show up in the total chlorine test. Though they are slow, these reactions can last for days as organic nitrogen compounds, such as amino acids and proteins, react with the chlorine. In short, if the chlorine is reacting with organic compounds, there may be a prolonged chlorine demand. Organic Amines are the least effective in killing viruses, followed by monochloramines, dichloramines, and trichloramines. With combined amines, the chlorine is bound with nitrogen and hydrogen in the ammonia and is not as available for oxidation and disinfection reactions. Free chlorine (or Hypochlorous Acid) is the most effective (Hach, 2014).



Figure 13. Theoretical Breakpoint Chlorination Curve (AWWA, 2008).

Many factors affect breakpoint chlorination including the initial ammonia nitrogen concentration, pH, temperature, and chlorine demand exerted by other inorganic and organic species. **Table 1** below includes the chlorine demand substances and the corresponding chlorine demand multipliers. Testing of source water to determine the concentrations of chlorine demand substances is essential in maintaining the optimum chlorine to nitrogen ratio for a treatment system.

<b>Chlorine Demand Substances</b>				
Substance Chlorine Demand Multiplie				
Ammonia-N	10 mg/L			
Iron	0.6 mg/L			
Manganese	1.3 mg/L			
H2S	2.1 mg/L			
Nitrite-N	5.0 mg/L			
Organic-N	1.0 mg/L			
TOC	0.1 mg/L			

**Table 1**. Chlorine Demand Substances (Janzen and Beier, 2009).

A weight ratio of **8:1 or greater** of chlorine applied to initial ammonia nitrogen is required for breakpoint chlorination to be reached. If the weight ratio is less, there is insufficient chlorine present to oxidize the chlorinated nitrogen compounds initially formed. For instantaneous chlorine residual, the weight ratio required may be 20:1 or more. Reaction rates are fastest at high temperatures and pH 7-8. Generally, about 10 mg/L of chlorine are required to destroy

1.0 mg/L of ammonia. Both free and total chlorine residuals should then be tested to ensure that the residual does not fall back into the chloramine stages of the curve. If the free chlorine value is not at 88-85 % of the total chlorine residual or higher, then it could be an indication that the breakpoint has not been fully achieved or there is a substantial amount of organics present in the raw water.

In the following Table (**Table 2**), examples of water treatment operation data during the most recent fish kill event of March 2013 are included.

Dates	Total Chlorine Distribution	Free Chlorine Distribution	Combined Chlorine Distribution	Total Chlorine Effluent	Free Chlorine Effluent	Combined Chlorine Effluent
26 March						
2013	1.6	0.11	1.49	2.7	0.33	2.37
27 March						
2013	1.2	0.12	1.08	2.5	0.31	2.19

Table 2. Water Treatment Plant data durin	g the most recent fish kill event of March 2013
-------------------------------------------	-------------------------------------------------

According to the Chlorination Breakpoint Curve, free residual chlorine values should be approximately 80% of the total residual chlorine value in order to ensure that authentic free residual chlorine is available for disinfection while all of the ammonia has been destroyed Hazen & Sawyer, 1992; Janzen and Beier, 2009). The values in **Table 2**, however, indicate that the chlorination process may still be at the chloramine stages. For example, on March 26 2013, the free chlorine concentration is 0.11 mg/L while the total chlorine concentration is at 1.6 mg/L.

## 4.5.1 Determination of Chlorine and Ammonia Concentrations in WTP

While testing for free chlorine residual is conducted to ensure that free chlorine is available in the distribution system as a biocide, monochloramine may have been actually measured due to interference. The following section discusses Monochloramine Interference in DPD colorimetric testing.

## 4.5.1.1 Monochloramine Interference in DPD Method

As mentioned previously, intereferences in free chlorine testing analysis can be skewing the results obtained during previous investigations regarding the Battle River water chemistry. Monochloramine interfers with the DPD free chlorine test. The interference in the DPD free chlorine test can be rather high considering many control ranges are in the 0.25 to 0.5 parts per million (ppm) free chlorine range. The free chlorine test results may be showing a free chlorine residual of 0.4 ppm for example, but if there is ammonia in the source water, this reading may be affected by monochloramine interference (Hazen & Sawyer, 1992; Hach, 2014; AWWA, 2008).

Monochloramine interference in the free chlorine DPD test is open to interpretation. Selected studies have indicated the percent interference in the free chlorine results can vary from 2.6 to 6.0%, depending on the monochloramine concentration and sample temperature. The amount of monochloramine must be substantial in comparison to the free chlorine concentration to indicate an interference in the DPD colorimetric free chlorine determination. As such, monochloramine testing should be performed in conjunction with applying the DPD colorimetric method to

determine free chlorine concentrations; this would allow comparisons between monochloramine levels and the results for free chlorine in order to effectively determine free chlorine in water samples containing monochloramine. The Recommendations section of this report includes a series of steps for the determination of actual free chlorine concentrations in water samples, in the presence of monochloramine (AWWA, 2008).

#### 4.5.1.2 Measuring Free Chlorine in Presence of Manganese and Chloramines

The Battle River water, which feeds Betty Lake, has been historically characterised by elevated manganese (Mn) concentrations. Also, ammonia and chlorine have been identified in measurable concentrations in water samples of the river. Manganese interference has been reportedly a problem in the determination of free chlorine concentrations. Chloramines, both inorganic monochloramine and dichloramine, and the organochloramines can also break through in free chlorine determinations causing an over-estimation of the disinfectant residual present. As the potential of a false-positive of free chlorine values can have a significant impact on water treatment processes and water quality, the Hach Method 10241 is recommended (**Annex E**). This method is based on the indophenol reaction and offers a new tool for determining free chlorine levels directly in samples having manganese or chloramine interference. This eliminates the need to know if manganese or chloramines are present in the sample and prevents the overestimation of the actual free chlorine concentration. This method is also applicable to applications where free chlorine concentrations have been difficult to accurately determine (Pinsino, Matranga & Roccheri, 2012; Hach, 2014).

#### 4.5.1.3 Measuring Ammonia in Presence of Chloramines

Depending on the chlorine concentration of the source water, the ammonia in the source water prior to the addition of chlorine is best determined either by:

- a. the salicylate colorimetric method (**Annex D**) which is has higher accuracy than the Nessler's method and does not require disposal of a hazardous waste –if chlorine is not detected in source water, or
- b. the Hach Method 10200 for laboratory or field testing (Annex E), if chlorine is detected in source water, or
- c. the APA 6000 Ammonia and Monochloramine Analyzer for continuous monitoring if ammonia values are not stable in source water (Annex F).

#### 4.5.2 Potassium Permanganate (KMnO<sub>4</sub>) Dosage

Potassium permanganate (KMnO<sub>4</sub>) is used primarily to control taste and odors, remove color, control biological growth in treatment plants, and remove iron and manganese. In a secondary role, potassium permanganate may be useful in controlling the formation of trihalomethanes (THMs) and other disinfection by-products (DBPs) by oxidizing precursors and reducing the demand for other disinfectants (Hazen and Sawyer, 1992). The source water from Betty Lake (Battle River) has been characterised historically as prone to the creation of THMs (WTPOP, 2000). The mechanism of reduced DBPs may include moving the point of chlorine application further downstream in the treatment train by using potassium permanganate to control taste and odors, color, algae, etc. instead of chlorine. Although potassium permanganate has many

potential uses as an oxidant, it is a poor disinfectant. Further, permanganates have been reported to kill fish in 8 to 18 hours at concentrations of 2.2 to 4.1 mg/L (EPA, 1999). On March 23 2013, the daily dosage for potassium permanganate was 4.20 mg/L. The following days until the fish kill was reported, the KMnO<sub>4</sub> ranged from 2.44 mg/L to 2.07 mg/L. Several such spikes in KMnO<sub>4</sub> dosages have been observed in the historical water treatment operation data regarding chemical usage. There is no indication as to why these spikes occurred.

## 4.5.3 Sodium Thiosulphate Dosage in presence of Copper

Using sodium thiosulphate raises concerns about this chemical's slow reaction with chlorine; it requires more time for dechlorination compared to other dechlorination reagents, such as sodium sulphide. Further, excessive de-chlorination with sodium thiosulphate may encourage thiobacillus and some other bacterial growth in receiving streams, particularly during low flow conditions, similar to Battle River and Betty Lake environment. A drop in pH, caused by the production of sulfuric acid by microorganisms has been reported in literature. This decrease in pH may elevate the toxicity of copper to fish; the toxicity of copper to fish increases as the total alkalinity decreases. As mentioned earlier, elevated concentrations of copper have been measured in the effluent of the CFB Wainwright ater treatment plant as well as in Battle River water samples downstream of the Forestburg Reservoir. Further, sodium thiosulphate can complex cationic metals, such as copper, with unspecified toxicity patterns or levels. It is noted, also, that, in the presence of elevated Zn (II), dechlorination with sodium thiosulfate increased zinc toxicity to aquatic organisms (Oh & Kim, 2008).

## 4.5.4 Dissolved Oxygen (DO) Levels

Two types of dechlorination agents have been used by WTP staff: Calcium/sodium thiosulphate and sodium sulphite. The latter is easily stored (availabe in "pucks") but it is known for scavenging more oxygen in the dechlorination process compared to calcium or sodium thiosulphate. Sodium sulphite was used by WTP staff up in March 2013, at the time of the fish kill event according to CFB staff. Low DO and presence of high ammonia could lead to fish kill events.

In communication with CFB Wainwright staff, information was provided about the use of 1-2 aerators during the time of the fish kill in March 2013. As such, the center of the lake was ice-free. However, if ammonia concentrations were measurable, then with abundant oxygen, it could turn to nitrite and/or nitrate which can be toxic to fish.

# 5.0 WATER SAMPLING

#### **5.1 Previous Sampling**

In response to the observed fish kills, staff from the WTP collected grab samples on April 12, 2013 to analyze for a full suite of water quality variables. Samples were taken from the south lagoon, B699 discharge, north lagoon, north slough, and Betty Lake. Concentrations of five dissolved metals exceeded guidelines at various sampling locations. Chlorine concentrations exceeded acceptable limits in various locations and fluctuations in dissolved oxygen were observed.

Analytical sampling was also conducted by Hatfield staff on April 15, 2013, at two locations, B699 discharge and the south lagoon, as well as in situ water quality was sampled in the south lagoon and channel. In situ water quality results showed low dissolved oxygen and relatively neutral pH (in both the south lagoon and channel). Analysis of water from the B699 discharge and the south lagoon was also undertaken as these were locations where dead fish were observed. The results show that in both samples, chlorine concentrations were less than 0.1 mg/L (Table 6). Guideline exceedances in total aluminum, total copper, total lead, and total manganese were observed in the south lagoon. Guideline exceedances in total copper and total manganese were seen in the B699 discharge. Acute toxicity results for test species, rainbow trout (*Oncorhynchus*) and *Daphnia magna*, indicated 100% survival of all organisms. (Hatfield, 2013).

DST Consultants (DST, 2014) conducted further analytical testing around the water treatment plant at CFB Wainwright in February 2014. Their six (6) sampling locations included MH 699, the Battle River Discharge point into Betty Lake, the north lagoon influent, the north lagoon channel, the north slough and Battle River. An overview of the analytical and in-field testing results of total and free chlorine indicated significant concentrations of chlorine (total and free) in Battle River. Sampling at the manhole in Building 699 indicated the presence of increased total and free chlorine levels. Based on the results of the laboratory analytical program, DST Consultants found that concentrations of total and free chlorine exceeded the applicable CCME guidelines for the protection of aquatic life at all six (6) sampling locations. Additionally, exceedances in concentrations of total and free chlorine above the Government of Canada Wastewater Systems Effluent Regulations were reported in all samples, with the exception of the sample collected from the North Slough. The sampling program by DST Consultants also revealed exceedances in seven metals in various sampling locations.

While ammonia and several metals were found in exceedance or in elevated concentrations, previous investigations did not provide explanations for the analytical results. Also, the significant concentrations of chlorine in background samples from Battle River (as measured by DST Consultants) were not discussed either. As presented in this current report, the source water chemistry which reflects the Battle River water quality (described in previous sections), combined with observations in the water treatment operations and interferences in the testing/sampling methods may play a role in explaining the analytical results of previous investigations conducted after the March 2013 fish kill event.

#### 5.2 Chlorine Sampling Guidelines and Considerations

Testing for chlorine in water can be challenging with respect to obtaining a representative sample. Because free chlorine is a strong oxidizing agent, its stability in natural waters is relatively low. Chlorine readily reacts with various inorganic compounds while it will slowly oxidize organic compounds. Various factors, including reactant concentrations, pH, temperature, salinity and sunlight, influence the decomposition of free chlorine in water. Ideally, analyzing samples for chlorine should be conducted on site (Enkon, 1997).

- a. Sample containers should be pretreated to remove any chlorine demand. A pre-treated glass BOD bottle, with ground glass stopper, makes an ideal sample container for chlorine analysis. Avoid plastic sample containers because they might exert an appreciable chlorine demand.
- b. Pre-treat clean glass sample containers by soaking in a dilute bleach solution (1 ml commercial bleach solution to 1 liter of water) for at least one hour. After soaking, rinse them thoroughly with deionized or distilled water or the sample. Another such treatment is required only occasionally if sample containers are always rinsed with deionized or distilled water after each use.
- c. Ideally, separate and dedicated sample containers should be used for free and total chlorine determinations.
- d. Avoid excess agitation and exposure to sunlight and high temperatures when sampling. Allow several volumes of the container to overflow and cap the sample container to eliminate head space above the sample.
- e. Sample for Chlorine at the monitoring sites (Enkon, 1997; Hach, 2014).

As mentioned above, source water chemistry needs to be tested for and characterised in order for the chlorine and ammonia dosages to be determined correctly in the water treatment operations. This may help with improving the effluent chemistry and minimise environmental impact of the water treatment plant. According to AWWA (2008), if ammonia-N is present in your water supply and you form combined chloramine residual after chlorination, the use of only the DPD colorimetric method to determine free chlorine values is not sufficient.
## 6.0 SUMMARY AND RECOMMENDATIONS

A summary of the concepts, outcomes and findings that were discussed within the report are seen in Table 3 in the form of recommendations. A summary also exists in the Executive Summary.

Item	Findings / Recommendation
Ammonia	Use New Testing Method ( <b>Annex D-F</b> ) a. Salicylate Colorimetric Method b. Hach Method 10200 c. APA 6000 Ammonia and Monochloramine Analyzer
	Criterion for selection of new method: Presence or not of chlorine or chloramines in water sample. If free ammonia is found in effluent and/or Betty Lake water, keep records for all tests, and increase the frequency of testing until the problem is corrected.
	Test raw (source) and treated water samples for ammonia. Factor in the raw water ammonia in the calculations for chlorine and ammonia dosages
Monochloramine	Monochloramine Testing in Battle River water samples (background), Betty Lake and in north/south lagoon; subsequently, subtraction of monochloramine value from free chlorine value.
	If using the DPD Free Chlorine Test, consider the following steps in order to ensure that the test result is an authentic free chlorine residual and not a "pink phantom" (chloramine, if present, converts the iodide reagent to iodine, which reacts with DPD to form a <i>pink</i> colour (known as "pink phantom"):
	a. Perform the DPD Free Chlorine Test, record the immediate reading and <u>observe</u> <u>the sample colour for several minutes.</u> If the sample changes to dark pink and higher

Table 3. Major Findings and Recommendations

Item	Findings / Recommendation
Monochloramine (continued)	readings, monochloramine is present in the sample and free residual chlorine readings are false;
	b. To determine the cause of the problem, analyse raw and treated water for ammonia and analyse treated water for monochloramine;
	c. Calculate the following: free ammonia mg/L = ammonia-N mg/L - monochloramine – N mg/L; and,
	d. To identify the location of your chlorine residual on the chlorination breakpoint curve, calculate your chlorine dosage and demand; then project the approximate value on the breakpoint curve ( <b>Figure 13</b> ).
Chlorine	New method for chlorine ( <b>Annex F</b> ), in order to avoid manganese and chloramine interference.
	Test for total chlorine residual and free chlorine residual to ensure that the residual does not fall back into the chloramines stages of the chlorination breakpoint curve ( <b>Figure 13</b> ).
	Use of Breakpoint Chlorination Curve to determine chlorine dosages ( <b>Figure 13</b> ).
Potassium Permanganate (KMnO <sub>4</sub> )	Avoid excessive, unnecessary use of $KMnO_4$ as it can affect the fish population.
Sodium / Calcium Thiosulphate	Avoid excessive, unnecessary use of Sodium/Calcium Thiosulphate as it can affect the fish population.
Source Water Protection and Quality	a. The base requires an active source water protection program;
	b. An active program is required to control the beavers near the Battle River and in Betty Lake, the geese in Betty Lake, and the amount of vegetation entering the lake; and,

Item	Findings / Recommendation
Source Water Protection and Quality (continued)	c. In addition, investigations should be conducted to determine alternatives for reducing short-circuiting from the Battle River discharge to the Betty Lake intake.
WTP Process Control	a. Data trending and interpretation should be used to support process control adjustments and decisions.
	<ul> <li>b. Public health protection requires tenacious attention by operators to maintain the integrity of each treatment barrier. Current operational practices can be enhanced by: <ol> <li>i. increasing monitoring of the intake and adjusting chemical dosages to respond to changes in raw water quality;</li> <li>ii. calculating chemical dosages;</li> <li>iii. monitoring backwash turbidities; and,</li> <li>iv. sampling from the clarifier in a location which establishes the effectiveness of this treatment barrier,</li> </ol> </li> </ul>
Key WTP Activities	<ul> <li>a. Training / Workshop on source water protection;</li> <li>b. Employ strategies for source water protection;</li> <li>c. Enhanced source water monitoring;</li> <li>d. Data review and interpretation; and,</li> <li>e. Strategic Information gathering.</li> </ul>
Key WTP Issues	<ul> <li>a. Poor source water quality (i.e. TOCs)</li> <li>b. Technologies and Chemicals to treat are expensive</li> <li>c. Operational strategies may be complex</li> <li>d. Ensure adequate, qualified staff</li> </ul>

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## **Site Visit Photos**

The following figures are associated with the photos that were taken as part of the site visit that was conducted with The RMC Green Team and members of the base at CFB Wainwright on 02 October 2014. The following are the members that were present:

- a. Mr. Kelly Sturgess (Base Environmental Officer)
- b. Ms. Julie Hauser (Assistant Base Environnemental Officer)
- c. Mr. Ron Schumacher (Base Environmental Technologist)
- d. Ms. Heather Tesselaar (DCC, Project Management Technical Specialist)
- e. Dr. Nicholas Vlachopoulos (Director, RMC Green Team)

The aim of the meeting was to determine the specific scope of work and to have an opportunity to see first-hand the area of interest as well as the water treatment plant in Wainwright. Shown in Figure 1 is an aerial photo of the area in and around Betty Lake and the water treatment plant (WTP) at CFB Wainwright. The figure also relates the subsequent site visit photos to the locations whereby those photos were taken (white numbers).



Figure 1. Site Map fo Betty Lake and Water Treatment Plant Infrastructure. Also included are the locations that relate to the photos that are shown in the figures of this Annex.



Figure 2: Sampling Pt (1) – Betty Lake Looking North-West



Figure 3: Sampling Pt 1 - ROWPU Site

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Figure 4: Sampling Pt (1) – Betty Lake Looking North-West at WTP



Figure 5: Lime Sludge Spreading near Sampling Point 1



Figure 6: Foam in North Slough – Causeway – Point 2



Figure 7: Foam in North Slough as well as Make-shift raft – Point 2



Figure 8: North Slough – Facing North East – Point 2



 $Figure \ 9: Cause way \ North \ Side - Facing \ North \ East - Point \ 2$ 



Facing 10: Marker – Sampling Pt – Causeway South Betty Lake – Point 3



Figure 11: Sampling Pt - Causeway South – Point 3





A-9



Figure 13: Aquatech – Contracted Plant Operators – between Pts 2 and 3



Figure 14: Causeway Facing Plant (NE) - between Pts 2 and 3



Figure 15: Pump Station – Houses Manhole – Fish Kill Location – Point 4



Figure 16: Pump Station Pipe – Effluent – Fish Kill Location – Point 4



Figure 17: Pump Station Pipe – Effluent – Fish Kill Location – Point 4



Figure 18: WTP - Storage and New Extension - Point 4 facing North



Figure 19: WTP - Point 4 facing North

## RMC #GREEN TEAM



Figure 20: Potassium Permanganate Container - WTP



Figure 21: Potassium Pump - WTP



Figure 22: Ammonia Drums – WTP



Figure 23: Aluminum Sulphate – WTP



Figure 24: Leakage – WTP



Figure25: Turbidimeter – WTP



Figure 26: Chlorine Monitor – WTP



Figure 27: Chlorine Monitor – WTP



Figure 28: Weekly Tests and Info Board - WTP



Figure 29: Colorimeter Used at WTP



Figure 30: Settlement Tanks – WTP



Figure 31: New Filters – WTP



Figure 32: Captor - Dechlorinator-WTP



Figure 33: Captor – Dechlorinator - WTP



Figure 34: Manhole Pump Station – Betty Lake – Point 4



Figure 35: New Effluent Lagoon Monitoring Well – Point 5



Figure 36: New South (Effluent) Lagoons – Facing South West - Point 5



Figure 37: New South Effluent Lagoons – Geomembrane Liners – Point 5



Figure 38: New South Effluent Lagoons - Effluent Pipe to Betty Lake - Facing East - Point 6



Figure 39: New South Effluent Lagoons – Effluent Pipe to Betty Lake with Barrier – Point 6



Figure 40: New Effluent Lagoon – Dechlorination Tablets – Point 6



Figure 41: New South Effluent Lagoon – Dechlorination Tablets – Point 6



Figure 42: New South Effluent Lagoon - Effluent Pipe Manhole to Betty Lake - Point 6



Figure 49: New South Effluent Lagoon - Effluent Pipe to Betty Lake - Point 6



Figure 50: Battle River Intake – Point 7



Figure 51: Battle River Intake – Facing North - Point 7



Figure 52: Battle River Intake – Facing South - Point 7



Figure 53: Battle River Intake – Facing North - Point 7



Figure 54: Battle River Intake – Pump House and Intake Channel - Point 7



Figure 55: Battle River Intake Channel - Point 7



Figure 56: Battle River Intake - Pump House and Intake Channel - Point 7
#### **B.1 Fish Kill Events**

RMC Green Team conducted an extensive literature review of previous information amassed by the CFB Wainwright staff on the matter of chlorine concentrations in the WTP effluent as well as the fish kill events (March 2007 and March 2013). The background information and the associated findings are presented below:

#### **B.2 Background**

The Betty Lake Waste Water Treatment Plant (WTP) is located in CFB/ASU Wainwright Base, located approximately 225 kilometres southeast of Edmonton, Alberta, adjacent to the Saskatchewan border (DST, 2014). The WTP provides drinking water to the Town of Wainwright and CFB/ASU Wainwright. The plant was constructed in 1952, and has been operating since 1957 (EA WTP 2007). The raw water source in Betty Lake is provided by Battle River.

The WTP operates using processes that meet Canadian Water Drinking Standards. Chloramination is used to disinfect the water. In the final stage of water processing, chlorine is added as a disinfectant. Prior to leaving the plant, the water undergoes a filtration process. Chlorinated backwash is dechlorinated using calcium thiosulfate (captor)/sodium thiosulfate, and is discharged into Betty Lake via the south lagoon ditch channels. In addition to the discharge point in the south lagoons, Building 699 contains a manhole that collects water from site draining located around the WTP. Water is discharged into Betty Lake via an above ground pipe to the shoreline of Betty Lake. Due to the presence of chlorine from a pipe leak in December 2007 (Release Report, 2008), the water is also treated with calcium thiosulphate prior to being discharged (Hatfield, 2013).

On March 23, 2007, the first fish kill was reported around the WTP in Betty Lake. Range Biologists were visiting the WTP to investigate a call that fish were using the drainage from the WTP lagoon to Betty Lake as a spawning ground. After investigating the drainage between the lagoons and Betty Lake it was noted that numerous fish (White Suckers) were found in pools in the drainage and at the mouth of the lake. An investigation was conducted and identified chlorine levels in Betty Lake that were above CCME criteria for aquatic life, however, the amounts released would not cause the widespread fish kill that was observed but rather localized fish kill only. Based on the number of fish found (approx. 500), the most likely cause of the die-off was determined to be low dissolved oxygen levels. This conclusion is based on the following facts:

- a. Of four aerators on the lake, only one or two were operational during the winter of 2007;
- b. Early ice cover with significant snow pack reduced light levels leading to death of aquatic vegetation; and,
- c. Decomposing organic material (dead plants) caused H2S odours at the WTP, an indication of low oxygen.

Fish	рН	Ammonia	Chlorine
Species			
Brook Stickleback (Culea inconstans)	The brook stickleback is tolerant of a wide range of alkaline and acid conditions. It occurs in water with a pH from 4.6 to at least 9.5. (1) Minimum range should be 5.0 to avoid kills (8)	Water quality guidelines for un-ionized ammonia for the protection of aquatic life. Aquatic life Guideline value (mg·L) for freshwater fish 0.019 (3)	At a water chloride concentration of 10 mg/L the 24 h LC50 for Nitrite-N is < 5 mg/L. The 96 h LC50 is < 3 mg/L, which increases to < 9 mg/L if the chloride concentration is raised to 20 ug/L. (1) Freshwater fish: Reactive chlorine species
			0.5 (2) ug/l
Lake Chub (Couesius plumbeus)	A pH range of 6.0 to 9.0 is probably optimum for survival and growth of creek chub populations (4)	Water quality guidelines for un-ionized ammonia for the protection of aquatic life. Aquatic life Guideline value (mg·L) for freshwater fish 0.019 (3)	Freshwater Reactive chlorine species 0.5 ug/l (2)
White Sucker (Catostomus commersoni)	White suckers have been collected from areas with a pH as low as 4.3. There have been reported sharp declines in white sucker populations in Canadian lakes when the pH was lowered to 4.5 to 5.0 as a result of acid precipitation. Laboratory studies on the effects of pH on white sucker growth and survival indicated that feeding stops at a pH of 4.5 and death occurs at a pH of 3.0 to 3.8. Maximum successful reproduction occurs at a pH above 5.8. The pH range which is generally considered not harmful to fish is 5.0 to 9.0; the further the pH varies from this range, the lower the water quality. Laboratory data indicate that a pH between 9 and 10 may be harmful to some fish species, and that a pH above 10 usually is lethal to all species (5)	Water quality guidelines for un-ionized ammonia for the protection of aquatic life. Aquatic life Guideline value (mg·L) for freshwater fish 0.019 (3)	Freshwater Reactive chlorine species 0.5 ug/l (2)
Grass Carp ( <i>Ctenopharyn</i> godon idella)	The maximum pH for culture of grass carp was reported as 9.24. Egg hatching was delayed below pH 6.5 and increased mortality and deformation of larvae occurred below pH 6.0 (6) Experiment showed pH 6-9 there was no	Water quality guidelines for un-ionized ammonia for the protection of aquatic life. Aquatic life Guideline value (mg·L) for freshwater fish 0.019 (3)	Freshwater Reactive chlorine species 0.5 ug/l (2)
	Mortality. Optimal growth was pH 7-8. (7) At pH of 4.3 Carp die within 5 days (8)	Median lethal concentration of ammonia was determined to be 1.05 mg/L (6)	

**Table B.1.** Selected Fish Species as related to environmental factors associated with pH,

 Ammonia and Chlorine

Base Environment notified DFO and AB SRD(F&W) on 29 March 2008 of the die-off. Neither organization conducted a site visit. On 30 March, 2008, Base Environment collected some water samples to be analysed for chlorine and aluminium levels.

On March 26, 2013, another fish kill occurred at the WTP. It was observed in 3 locations: beside the discharge pipe of Building 699, in the south lagoon, and in the south lagoon channel. In April of 2013, DCC contracted Hatfield Consultants to investigate the potential causes of the fish kills. Hatfield identified two small-bodied fish species, brook stickleback (*Culea inconstans*) and lake chub (Couesius plumbeus), and two large-bodied fish species, white sucker (Catostomus commersoni) and grass carp (Ctenopharyngodon idella). Hatfield conducted a water quality survey at the locations where the fish kill was observed. Water quality measurements from the south lagoon and channel as well as two (2) analytical water samples were taken from the south lagoon and from the manhole located in building 699. Samples were not collected from Betty Lake due to unsafe conditions. Additionally, WTP staff provided Hatfield weekly field water quality measurements from the south lagoon, north lagoon and Building 699. These measurements indicated low dissolved oxygen levels (1.76 mg/L to 3.19 mg/L) in the south lagoon and south lagoon channel. Analytical water quality samples were collected on April 12, 2013 from the south lagoon, north lagoon, north slough, building 699 and Betty Lake. These samples reported random increases in chlorines levels at all locations, with the highest levels being detected at 0.52mg/L at building 699. Exceedences in total aluminum, total copper, total lead and total manganese were reported in the south lagoon, while exceedences in total copper and total manganese were report in the building 699 discharge. Based on this investigation, Hatfield consultants arrived at the following conclusions:

- a. Due to unsafe ice conditions, dissolved oxygen content was not tested at Betty Lake, although low DO levels were found in the south lagoon and south lagoon channels. Low DO is one factor related to Fish kills. Betty Lake does have an aerator, however, the levels of DO around the time of the fish kills could not be confirmed;
- b. It remains unclear why fish kills occurred in a few isolated areas, which suggests that the cause may have been a result of something in the wastewater. As well, the fish species identified are typically considered tolerant, meaning that low DO should not have resulted in a fish die off; and
- c. Due to evidence of sporadic chlorine levels, a potential cause may have been residual chlorine in the process water. CCME guideline for residual chlorine is .50ug/l, and USEPA guideline is 20ug/L, indicating that the samples provided by WTP staff often exceeded these guidelines.

As this investigation could not provide any conclusive results, Hatfield recommended to undertake further investigation into evaluating and monitoring both chlorine levels in Betty Lake and around the WTP. Based on this recommendation, DCC contracted DST Consultants to conduct a detailed site investigation of Chlorine Contamination at the Betty Lake WTP. The investigation consisted of a surface water sampling event that took place in the fall of 2013, as well as a review of the WTP processes and sampling methodology. Samples were collected at 6 locations: Battle River, discharge point of Battle River into Betty Lake, north lagoon influent, north lagoon channel, north slough, and the manhole in building 699. WTP staff also completed in-field testing of chlorine at all six (6) locations. Based on the results, DST noted

concentrations of total free chlorine exceeded CCME guidelines at all locations, with the exception of the north slough sample. Samples from the north lagoon influent, north lagoon channel and north slough indicated effective de-chlorination. The results also indicated that there were significant concentrations of chlorine in Battle River, indicating that chlorine levels are a results of an unknown source since Battle River is unaffected by WTP processes and was used as a background sample. The samples taken from building 699 indicated the presence of total and free chlorine, however since de-chlorination compounds are being added in the manhole, chlorine levels measure are not representative of the levels being discharged as they do not account for the mixing and time required for the de-chlorination reactions to fully take place. Based on these observations, DST recommended the following:

- a. Ensure sufficient dechlorination agent is provided for treatment of drained water in the manhole in building 699.
- b. Continuous monitoring of total and free chlorine levels in discharge pipes,
- c. Install flow meters in sough lagoon to appropriately manage the correct and accurate volume of water used for filter backwash;
- d. Review staff sampling methodology at WTP to ensure accuracy of results (refer to DST report for details).

#### **B.3** Potential Causes of Fish Kills

According to the website My Wildlife Alberta, summer and winter kills are normal occurrences in Alberta lakes. The amount of oxygen a water body can hold is directly related to the temperature of the water. Generally, the colder the temperature of the water, the more oxygen it can hold. Lowered oxygen levels are caused by different factors, which vary between the summer and winter (My Wildlife Alberta , 2014). Typically northern climates experience fish kills at end of winter and summer as a result of low DO.

#### **B.4** Examples of Similar Fish Kills

Table 2 below also cites and summarizes fish kills of similar fish species or similar environmental conditions within Canada

Fish Species	Location	Cause
Brook Stickleback Salmon Trout	PEI – April 2013	Surface Runoff from neighboring Potato farm (Chemical) (http://www.cbc.ca/news/canada/prince-edward- island/warren-ellis-fined-70-000-after-prince-county-fish- kill-1.2818976)
Salmonoids	Saskatchewan - 2008	Low DO – aerator installed to reduce number of fish kills in 4 lakes as part of watershed stewardship. (http://www.gov.mb.ca/waterstewardship/iwmp/little_sask_r iver/documentation/state_of_the_watershed_little_sk.pdf)

Table B.2. Fish kills of similar fish species within Canada

Fish Species	Location	Cause
Walley	Manitoba – April 2013	Unusually cold spring – fish trapped under ice, low DO http://www.cbc.ca/news/canada/manitoba/fish-found-dead- along-lake-of-the-prairies-1.1332099
large-mouth bass, pumpkin seed sun fish and rock bass	Ontario	Unusually cold weather <u>http://globalnews.ca/news/1290017/winterkill-how-ontarios-dead-fish-are-feeding-lake-ecosystems/</u>

## **Chlorine**, Free

#### Indophenol Method

#### 0.04 to 4.50 mg/L Cl<sub>2</sub>

#### Method 10241

#### **Powder Pillows**

**Scope and application:** For the determination of residual free chlorine levels in the presence of manganese, chloramines and other oxidants that interfere with DPD colorimetric, DPD titrimetric and amperometric methods for free chlorine. For use in potable water, chlorinated drinking water, swimming pool water and treated wastewater effluent. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

#### L Test preparation

#### Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows requirements that can change between instruments, such as adapter and sample cell requirements.

To use the table, select an instrument, then read across to find the applicable information for this test.

Instrument	Adapter	Sample cell orientation	Sample cell
DR 6000	_	The orientation key is toward the user.	4864302
DR 5000	A23618	The orientation key is toward the user.	
DR 3900	LZV846 (A)	The orientation key is away from the user.	
DR 1900	9609900 or 9609800 (C)	The orientation key is toward the arrow on the adapter.	
DR 900	—	The orientation key is toward the user.	
DR 3800 DR 2800 DR 2700	LZV585 (B)	The 1-cm path is aligned with the arrow on the adapter.	5940506

#### Table 1 Instrument-specific information

#### Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.

In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.

This method uses the same program number as the indophenol monochloramine method.

The sample and reagent from one analysis can contaminate other analyses and interfere with the test results. Make sure to rinse the cells and caps several times with deionized water or with the sample water before each test.

Do not switch the caps of the sample cells between the blank and sample during the analysis.

Tap the sample cells lightly on a hard surface or slowly invert the cells to remove air bubbles from the cell walls.

Make sure to keep the cap on the sample cells when not in use to prevent contamination from ammonia.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

#### Items to collect

Description	Quantity
Freechlor F Reagent Solution	5 drops
Monochlor F reagent pillows	2
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 7 for order information.

#### Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

#### **Test procedure**



1. Start program 66, Monochloramine LR. For information about sample cells, adapters or light shields, refer to Instrumentspecific information

on page 1.

**Note:** Although the program name can be different between instruments, the program number does not change.



**2.** Fill two sample cells with 10 mL of sample. Label one cell as the sample. Label the other cell as the blank.



**3.** Add 5 drops of the Freechlor F Reagent to the sample.



**4.** Put the stopper on the sample cell. Invert to mix.



5. Add the contents of one Monochlor F Reagent Powder Pillow to each sample cell.



6. Close the sample cells. Shake the sample cells for approximately 20 seconds to dissolve the reagent. A green color shows if free chlorine is in the sample.



**7.** Start the instrument timer. A 5-minute reaction time starts. Adjust the reaction time for the sample temperature. Refer to Color development time on page 4.



**8.** When the timer expires, invert the blank to mix.



**9.** Clean the blank sample cell.



**10.** Insert the blank into the cell holder.

Zero

**11.** Push **ZERO**. The display shows 0.00 mg/L  $Cl_2$ .



**12.** Invert the prepared sample to mix.





Read

**13.** Clean the prepared sample cell.

**14.** Insert the prepared sample into the cell holder.

**15.** Push **READ**. Results show in  $mg/L Cl_2$ .

#### **Color development time**

Test results are strongly influenced by the sample temperature. The reaction times in the procedure are for samples at 18–20 °C (64–68 °F). Adjust the reaction times for the sample temperature as shown in Table 2. The color is stable for a maximum of 15 minutes after the specified development time.

Sample temperature (°C)	Sample temperature (°F)	Development time (minutes)
5	41	10
7	45	9
9	47	8
10	50	8
12	54	7
14	57	7
16	61	6
18	64	5
20	68	5
23	73	2.5
25	77	2
> 25	> 77	2

Table 2 Color development time

#### Interferences

Table 3 shows the substances that were tested for interference and do not interfere at or below the levels that are shown. Table 4 shows a list of interfering substances and interference levels.

Substance	Interference level
Alanine	1 mg/L N
Aluminum	10 mg/L Al
Bromide	100 mg/L Br-
Bromine	15 mg/L Br <sub>2</sub>
Calcium	1000 mg/L as CaCO <sub>3</sub>
Chloride	18,000 mg/L CI⁻
Chlorine Dioxide	5 mg/L CIO <sub>2</sub>

C-4

#### Table 3 Non-interfering substances

Substance	Interference level
Chromium (III)	5 mg/L Cr <sup>3+</sup>
Copper	10 mg/L Cu
Cyanide	10 mg/L CN <sup>-</sup>
Dichloramine	10 mg/L as Cl <sub>2</sub>
Fluoride	5 mg/L F <sup>−</sup>
Glycine	1 mg/L N
lodine	4 mg/L l <sub>2</sub>
Iron (II)	10 mg/L Fe <sup>2+</sup>
Iron (III)	10 mg/L Fe <sup>3+</sup>
Lead	10 mg/L Pb
Manganese (+7)	3 mg/L MnO <sub>4</sub> <sup>-</sup>
Nitrate	100 mg/L N
Nitrite	50 mg/L N
Oxone <sup>®1</sup> (potassium peroxomonopersulfate)	30 mg/L
Phosphate	100 mg/L PO <sub>4</sub> <sup>3–</sup>
Silica	100 mg/L SiO <sub>2</sub>
Sulfate	2600 mg/L SO <sub>4</sub> <sup>2–</sup>
Tyrosine	1 mg/L N
Urea	10 mg/L N
Zinc	5 mg/L Zn

#### Table 3 Non-interfering substances (continued)

<sup>1</sup> Oxone is a registered trademark of E.I. du Pont de Nemours & Co., Inc.

#### Table 4 Interfering substances

Interfering substance	Interference level	
Ozone <sup>1</sup>	> 1 mg/L O <sub>3</sub>	
Sulfide <sup>1</sup>	> 0.5 mg/L S <sup>2-</sup>	

<sup>1</sup> This compound does not normally exist with free chlorine.

#### **Test applications**

#### Finished chlorinated drinking waters and distributions systems

Finished waters contain free chlorine and various levels of organic chloramines and inorganic contaminants. The reaction of free chlorine with easily oxidizable species is thought to be complete and the remaining free chlorine is in a steady-state equilibrium. Replicate analyses for free chlorine on this type of water should give equivalent results. It is especially important when testing water where free chlorine residual levels are low to obey all precautions that refer to sample cell cleanliness, water temperature and sampling techniques.

#### At breakpoint

These waters can contain a mixture of free chlorine, chloramines and nuisance residuals depending on water temperature, mixing efficiencies, sampling location and distance beyond the theoretical breakpoint. The water can be in a state of "dynamic equilibrium" and the chemical speciation can change quickly, especially if at or near the breakpoint. The chemical speciation can change dynamically in both the blank cell and the sample

cell. Start the analysis immediately on these types of samples. Test results can be difficult to reproduce on duplicate samples because of the dynamics of the water. Test results are best used to identify free chlorine trends and to monitor changes because of different mixing efficiencies, sampling locations, temperature changes, increased chlorine feed rates, and so forth.

#### In chloramination kinetic studies

These waters will contain a mixture of free chlorine and chloramines depending on water temperature, mixing efficiencies, sampling locations, feed rates for chlorine and ammonia and contact time. The water is in a state of "dynamic equilibrium" and the chemical speciation can change quickly depending on water conditions. The chemical speciation can change dynamically in both the blank cell and the sample cell. Start the analysis immediately on these types of samples. Test results can be difficult to reproduce on duplicate samples because of the dynamics of the water. Test results are best used to identify free chlorine trends and to monitor changes based on changes in mixing efficiencies, sampling locations, water temperature changes, increased chlorine feed rates, and so forth.

#### With other oxidants

Other oxidants can include Oxone, permanganate, chlorine dioxide, bromine and iodine. It is assumed that the free chlorine residual has stabilized in the presence of the other oxidants. Replicate analyses for free chlorine on this type of water is expected to give equivalent results. The levels of alternate oxidants that can be present without interference have been tested only in laboratory bench studies (refer to Table 3 on page 4). Field data for free chlorine in the presence of these oxidants is not available.

#### Accuracy check

#### Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample. Items to collect:

- Chlorine Standard Solution, 2-mL PourRite<sup>®</sup> Ampule, 25–30 mg/L (use concentration on label)
- Ampule Breaker, PourRite Ampules
- Pipet, TenSette<sup>®</sup>, 0.1–1.0 mL and tips
- 1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
- 2. Go to the Standard Additions option in the instrument menu.
- **3.** Select the values for standard concentration, sample volume and spike volumes.
- 4. Open the standard solution.
- Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.
- 6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
- 7. Select Graph to compare the expected results to the actual results.

**Note:** If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.

#### Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
66	3.51 mg/L Cl <sub>2</sub>	3.47–3.55 mg/L Cl <sub>2</sub>	0.04 mg/L Cl <sub>2</sub>

#### Summary of method

An ammonia solution at a pH of 8.3 is added to a sample that contains free chlorine. The free chlorine is immediately converted into monochloramine (NH<sub>2</sub>Cl). In the presence of a cyanoferrate catalyst, the monochloramine reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green indophenol compound, which is proportional to the amount of free chlorine in the sample. A sample blank that contains Monochlor F Reagent corrects for background color from the reagent and sample. The measurement wavelength is 655 nm for spectrophotometers or 610 nm for colorimeters.

#### **Consumables and replacement items**

#### **Required reagents**

Description	Quantity/Test	Unit	ltem no.
Freechlor F Reagent Solution	5 drops	50-mL SCDB	2964926
Monochlor F Reagent Pillows	2	100/pkg	2802299

#### **Recommended standards**

Description	Unit	ltem no.
Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette <sup>®</sup> Ampule, 50–75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampule, 25-30 mg/L	20/pkg	2630020

#### **Optional reagents and apparatus**

Description	Unit	ltem no.
PourRite <sup>®</sup> Ampule Breaker, 2-mL	each	2484600
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	50/pkg	2185696



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## **AMMONIA-NITROGEN - LOW RANGE**

#### SALICYLATE METHOD • CODE 3659-01-SC

QUANTITY	CONTENTS	CODE
60 mL	*Salicylate Ammonia #1	*3978-H
10 g	*Salicylate #2	*7457-D
2 x 5 g	*Salicylate #3	*7458-C
1	Spoon, 0.1 g, plastic	0699
1	Spoon, 0.15 g, plastic	0727
1	Pipet, 1.0 mL, plastic	0354

\*WARNING: Reagents marked with an \* are considered hazardous substances. To view or print a Material Safety Data Sheet (MSDS) for these reagents see MSDS CD or our web site. To obtain a printed copy, contact us by e-mail, phone or fax.

Ammonia nitrogen is present in various concentrations in many surface and ground water supplies. Any sudden change in the concentration of ammonia nitrogen in a water supply is cause for suspicion. A product of microbiological activity, ammonia nitrogen is sometimes accepted as chemical evidence of pollution when encountered in natural waters.

Ammonia is rapidly oxidized in natural water systems by special bacterial groups that produce nitrite and nitrate. This oxidation requires that dissolved oxygen be available in the water. Ammonia is an additional source of nitrogen as a nutrient which may contribute to the expanded growth of undesirable algae and other forms of plant growth that overload the natural system and cause pollution.

APPLICATION:	Low concentrations of ammonia in fresh, brackish and salt water: fresh and salt water aquariums.
RANGE:	0.00 - 1.00 ppm Ammonia-Nitrogen
METHOD:	Salicylate and ammonia react at high pH in the presence of a chlorine donor and an iron catalyst to form a blue indophenol dye, the concentration of which is proportional to the ammonia concentration in the sample.
Sample Handle & Preservation:	Ammonia solutions tend to be unstable and should be analyzed immediately. Samples may be stored for 24 hours at 4°C or 28 days at –20°C.
INTERFERENCES:	There are few interferences in most natural waters. High concentrations of reducing agents, such as hydrazine, react with the chlorine donor and can result in negative interferences. Color and turbidity can also interfere

#### **PROCEDURE - FRESH WATER**

- 1. Press and hold **ON** button until colorimeter turns on.
- 2. Press **ENTER** to start.
- 3. Press ENTER to select TESTING MENU.
- Select ALL TESTS (or another sequence containing 3 Ammonia-NLF) from TESTING MENU.
- 5. Scroll to and select 3 Ammonia-NLF from menu.
- **6.** Rinse a clean tube (0290) with sample water. Fill to the 10 mL line with sample.
- 7. Insert tube into chamber, close lid and select SCAN BLANK. (See Note.)
- 8. Remove tube from colorimeter. Use the 1.0 mL plastic pipet (0354) to add 2.0 mL of \*Salicylate Ammonia #1 (3978). Cap and mix.
- **9**. Use the 0.15 g spoon (0727) to add two measures of \*Salicylate #2 Reagent (7457). Cap and mix until dissolved. Wait 1 minute.
- **10.** At end of 1 minute waiting period use 0.1 g spoon (0699) to add two measures of \*Salicylate #3 Reagent Powder (7458). Cap and shake vigorously for at least 30 seconds and all solid has dissolved. Wait 12 minutes for maximum color development.
- 11. At the end of the 12 minute waiting period, immediately mix and insert tube into chamber, close lid and select SCAN SAMPLE. Record result.
- 12. Press **OFF** button to turn colorimeter off or press **EXIT** button to exit to a previous menu or make another menu selection.

#### CALCULATIONS:

To express results as Unionized Ammonia (NH<sub>3</sub>):

#### ppm Unionized Ammonia (NH<sub>3</sub>) = ppm Ammonia-Nitrogen (NH<sub>3</sub>–N) x 1.2

To express results as Ionized Ammonia (NH<sub>4</sub>):

#### ppm Ionized Ammonia (NH<sub>4</sub>+) = ppm Ammonia-Nitrogen (NH<sub>3</sub>-N) x 1.3

To determine the percentages of Unionized and Ionized Ammonia-Nitrogen, consult the Appendix.

#### NOTE:

For the best possible results, a reagent blank should be determined to account for any contribution to the test result by the reagent system. To determine the reagent blank, follow the above test procedure to scan a distilled or deionized water blank. Then follow the above procedure to perform the test on a distilled or deionized water sample. This test result is the reagent blank. Subtract the reagent blank from all subsequent test results of unknown samples. It is necessary to determine the reagent blank only when a new lot number of reagents are obtained.

#### **PROCEDURE - SALT WATER**

- 1. Press and hold **ON** button until colorimeter turns on.
- 2. Press **ENTER** to start.
- **3**. Press **ENTER** to select TESTING MENU.
- Select ALL TESTS (or another sequence containing 4 Ammonia-NLS) from TESTING MENU.
- 5. Scroll to and select 4 Ammonia-NLS from menu.
- **6.** Rinse a clean tube (0290) with sample water. Fill to the 10 mL line with sample.
- 7. Insert tube into chamber, close lid and select SCAN BLANK. (See Note.)
- 8. Remove tube from colorimeter. Use the 1.0 mL plastic pipet (0354) to add 2.0 mL of \*Salicylate Ammonia #1 (3978). Cap and mix.
- **9**. Use the 0.15 g spoon (0727) to add two measures of \*Salicylate #2 Reagent (7457). Cap and mix until dissolved. Wait 1 minute.
- **10.** At end of 1 minute waiting period use 0.1 g spoon (0699) to add two measures of \*Salicylate #3 Reagent Powder (7458). Cap and shake vigorously for at least 30 seconds and all solid has dissolved. Wait 20 minutes for maximum color development.
- 11. At the end of the 20 minute waiting period, immediately mix and insert tube into chamber, close lid and select SCAN SAMPLE. Record result.
- 12. Press **OFF** button to turn colorimeter off or press **EXIT** button to exit to a previous menu or make another menu selection.

#### CALCULATIONS:

To express results as Unionized Ammonia (NH<sub>3</sub>):

#### ppm Unionized Ammonia (NH<sub>3</sub>) = ppm Ammonia-Nitrogen (NH<sub>3</sub>–N) x 1.2

To express results as Ionized Ammonia (NH<sub>4</sub>):

#### ppm Ionized Ammonia (NH<sub>4</sub>+) = ppm Ammonia-Nitrogen (NH<sub>3</sub>-N) x 1.3

To determine the percentages of Unionized and Ionized Ammonia-Nitrogen, consult the Appendix.

#### NOTE:

For the best possible results, a reagent blank should be determined to account for any contribution to the test result by the reagent system. To determine the reagent blank, follow the above test procedure to scan a distilled or deionized water blank. Then follow the above procedure to perform the test on a distilled or deionized water sample. This test result is the reagent blank. Subtract the reagent blank from all subsequent test results of unknown samples. It is necessary to determine the reagent blank only when a new lot number of reagents are obtained.

## Chloramine (Mono) and Nitrogen, Free Ammonia

#### Indophenol Method<sup>1</sup>

#### 0.04 to 4.50 mg/L Cl<sub>2</sub>

#### 0.01 to 0.50 mg/L NH<sub>3</sub>-N

**Scope and application:** For the determination of free ammonia and monochloramine simultaneously in finished chloraminated water. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

<sup>1</sup> U.S. Patent 6,315,950

#### L I Test preparation

#### Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows requirements that can change between instruments, such as adapter and sample cell requirements.

To use the table, select an instrument, then read across to find the applicable information for this test.

Instrument	Adapter	Sample cell orientation	Sample cell
DR 6000	—	The orientation key is toward the user.	4864302
DR 5000	A23618	The orientation key is toward the user.	
DR 3900	LZV846 (A)	The orientation key is away from the user.	
DR 1900	9609900 or 9609800 (C)	The orientation key is toward the arrow on the adapter.	
DR 900	—	The orientation key is toward the user.	
DR 3800 DR 2800 DR 2700	LZV585 (B)	The 1-cm path is aligned with the arrow on the adapter.	5940506

#### Table 1 Instrument-specific information

#### Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.

In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.

For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Method 10200 Powder Pillows

#### Items to collect

Description	Quantity
Free Ammonia Reagent Solution	1 drop
Monochlor F Reagent Pillows	2
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument- specific information on page 1.)	2

Refer to Consumables and replacement items 01015 for order information.

#### Sample collection and storage

- Analyze samples immediately after collection.
- Collect samples in clean glass bottles.
- Open the sample valve or spigot and let the water flow for a minimum of 5 minutes.
- Rinse the sample bottle several times with the sample and let the sample overflow each time, then cap the container so that there is no head space (air) above the sample.

#### Powder pillow procedure



1. Start program 66, Monochloramine LR. For information about sample cells, adapters or light shields, refer to Instrumentspecific information on page 1.

**Note:** Although the program name can be different between instruments, the program number does not change. 10 mL





2. Fill two sample cells to the 10-mL line with sample. Write Free Ammonia on one sample cell. Write Monochloramine on the second sample cell. 3. Clean the monochloramine sample cell.

4. Insert the **monochloramine** sample cell into the cell holder.



**5.** Push **ZERO**. The display shows 0.00 mg/L Cl<sub>2</sub>.



**6.** Remove the sample cell from the cell holder.



7. Add the contents of one Monochlor F Reagent Powder Pillow to the sample for monochloramine measurement.



8. Put the stopper on the sample cell. Shake the sample cell for about **20 seconds** to dissolve the reagent. A green color will show if monochloramine is present.



**9.** Add **one** drop of Free Ammonia Reagent Solution to the sample cell for **free ammonia** measurement. Close the reagent bottle to keep the reagent stable.



**10.** Close the **free ammonia** sample cell. Invert the sample cell to mix the reagent. If the sample gets cloudy by the end of the reaction

period, pre-treat the sample and do the test again. Refer to Interferences on page 5.



**11.** Start the instrument timer. A 5-minute reaction time starts.

For samples colder than 18 °C, refer to Table 2 on page 4.



**12.** When the timer expires, clean the **monochloramine** sample cell.



**13.** Insert the **monochloramine** sample cell into the cell holder.



 Exit program 66. Start program 388 N, Ammonia Free.



**16.** Leave the **monochloramine** sample cell in the cell holder. Push **ZERO**. The display will show 0.00 mg/L NH<sub>3</sub>–N f.

14. Push READ. Results

show in mg/L Cl<sub>2</sub>.



**17.** Remove the monochloramine sample cell from the cell holder.



**18.** When the reaction time in step 11 is complete, add the contents of one Monochlor F Powder Pillow to the Free Ammonia sample cell.



 Put the stopper on the sample cell. Shake the sample cell for about
 seconds to dissolve the reagent. A green color will show if monochloramine is present.



**20.** Start the instrument timer. A 5-minute reaction time starts.

For samples colder than 18 °C, refer to Table 2 on page 4.





Read

**21.** When the timer expires, clean the **free ammonia** sample cell.

**22.** Insert the **free ammonia** sample cell into the cell holder.

**23.** Push **READ**. The results are in mg/L  $NH_3$ –N f.

#### Color development time

Test results are strongly influenced by the sample temperature. The reaction times in the procedure are for samples at 18–20 °C (64–68 °F). Adjust the reaction times for the sample temperature as shown in Table 2. The color is stable for a maximum of 15 minutes after the specified development time.

Sample temperature (°C)	Sample temperature (°F)	Development time (minutes)
5	41	10
7	45	9
9	47	8
10	50	8
12	54	7
14	57	7
16	61	6
18	64	5
20	68	5
23	73	2.5
25	77	2
> 25	> 77	2

Table 2	Color	develo	pment	time
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#### Interferences

This method is intended for finished, chloraminated drinking water samples that have a measurable combined (total) chlorine disinfectant residual. Samples that do not have a disinfectant residual and samples that have a chlorine demand can cause low ammonia test results. Blanks and ammonia standards that are analyzed without a disinfectant residual must be prepared with high quality, reagent grade water.

The substances that are shown in Table 3 do not interfere in the free ammonia determination at or below the given concentration.

Substance	Maximum level tested
Al	0.2 mg/L
CI⁻	1200 mg/L
Cu	1 mg/L
Fe	0.3 mg/L
Mn	0.05 mg/L
NO <sub>3</sub> <sup>-</sup> -N	10 mg/L
NO <sub>2</sub> N	1 mg/L
PO <sub>4</sub> <sup>3-</sup>	2 mg/L
SiO <sub>2</sub>	100 mg/L
SO4 <sup>2-</sup>	1600 mg/L
Zn	5 mg/L

#### Table 3 Non-interfering substances

Samples that contain high levels of both total hardness and alkalinity may become cloudy after the addition of the Free Ammonia Reagent Solution. If this occurs by the end of the first reaction period, the sample for Free Ammonia measurement must be pretreated as follows:

- 1. Measure 10 mL of sample into the sample cell for Free Ammonia.
- 2. Add the contents of one Hardness Treatment Reagent Powder Pillow to the sample.
- 3. Tighten the cap on the sample cell and invert until the reagent is dissolved.
- 4. Remove the cap.
- 5. Use the pretreated sample in the test procedure for the Free Ammonia sample.

Note: The sample for Monochloramine measurement does not need pretreatment.

#### Accuracy check

#### Standard solution method

Items to collect:

- Buffer Powder Pillow, pH 8.3
- Nitrogen, Ammonia Standard Solution, 100-mg/L as NH<sub>3</sub>–N
- Chlorine Solution Ampules, 50–70 mg/L
- 100-mL Class A volumetric flask
- 50-mL graduated cylinder
- Pipet, TenSette<sup>®</sup>, 0.1–1.0 mL and tips
- Pipets, Volumetric, 2-mL Class A and Mohr, 5-mL
- Pipet bulb
- Organic-free water

- 1. Prepare a 4.5-mg/L (as Cl<sub>2</sub>) monochloramine standard immediately before use as follows.
  - **a.** Add the contents of one Buffer Powder Pillow, pH 8.3 to approximately 50 mL of organic-free water in a clean 100-mL Class A volumetric flask. Swirl to dissolve the powder.
  - **b.** Use a Class A volumetric pipet to add 2.00 mL of Nitrogen, Ammonia Standard Solution, 100-mg/L as NH<sub>3</sub>–N into the flask.
  - **c.** Dilute to the mark with organic-free water. Mix well. This is a 2.00-mg/L buffered ammonia standard.
  - **d.** Use a graduated cylinder to add 50.00 mL of the buffered ammonia standard into a clean 100-mL beaker. Add a stir bar.
  - **e.** Find the exact concentration of the Chlorine Solution Ampules, 50–70 mg/L from the label on the package.
  - **f.** Calculate the volume of the Chlorine Solution to add to the ammonia standard: mL chlorine solution required = 455/(free chlorine concentration).
  - **g.** Open an ampule and use a glass Mohr pipet to add the calculated amount of Chlorine Solution slowly to the ammonia standard in the beaker. Keep the beaker on a stir-plate at medium speed during the chlorine addition.
  - **h.** Stir the monochloramine solution for 1 minute after the Chlorine Solution addition is complete.
  - i. Quantitatively transfer the monochloramine solution to a clean 100-mL Class A volumetric flask. Dilute to the mark with organic-free water and mix well. This is a nominal 4.5-mg/L (as Cl<sub>2</sub>) monochloramine standard.
- **2.** Use this standard within 1 hour of preparation. Use the test procedure to measure the concentration of the monochloramine standard solution.
- 3. Compare the expected result to the actual result.

**Note:** The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

#### Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample. Items to collect:

- Ammonium Nitrogen Standard Solution, 10 mg/L NH<sub>3</sub>–N
- 50-mL mixing cylinders
- Pipet, TenSette<sup>®</sup>, 0.1–1.0 mL and tips
- 1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
- 2. Go to the Standard Additions option in the instrument menu.
- **3.** Select the values for standard concentration, sample volume and spike volumes.
- 4. Open the standard solution.
- Prepare three spiked samples: use the TenSette pipet to add 0.3 mL, 0.6 mL and 1.0 mL of the standard solution, respectively, to three 50-mL portions of fresh sample. Mix well.
- **6.** Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
- 7. Select Graph to compare the expected results to the actual results.

**Note:** If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.

#### Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Ammonium Nitrogen Standard Solution, 10 mg/L NH<sub>3</sub>–N
- 100-mL plastic volumetric flask with stopper, Class A
- 2-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water—must be free of ammonia, chlorine and chlorine demand, for example 18 MΩ-cm water from a deionizer system.
- 1. Prepare a 0.20 mg/L ammonia nitrogen standard solution as follows:
  - **a.** Use a pipet to add 2.00 mL of 10 mg/L ammonia nitrogen standard solution into the volumetric flask. (*Alternate preparation: add 0.4 mL of a 50 mg/L ammonia nitrogen standard solution to the volumetric flask.*)
  - b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
- **2.** Use the test procedure to measure the concentration of the prepared standard solution.
- 3. Compare the expected result to the actual result.

**Note:** The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

#### Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
66	2.60 mg/L Cl <sub>2</sub>	2.58–2.62 mg/L Cl <sub>2</sub>	0.04 mg/L Cl <sub>2</sub>
388	0.20 mg/L NH <sub>3</sub> –N	0.19–0.21 mg/L NH <sub>3</sub> –N	0.01 mg/L NH <sub>3</sub> –N

#### Summary of method

Monochloramine (NH<sub>2</sub>Cl) and free ammonia (NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>) can exist in the same water sample. Added hypochlorite combines with free ammonia to form more monochloramine. In the presence of a cyanoferrate catalyst, monochloramine in the sample reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green-colored indophenol, which is proportional to the amount of monochloramine present in the sample. Free ammonia is determined by comparing the color intensities, with and without added hypochlorite. The measurement wavelength is 655 nm for spectrophotometers or 610 nm for colorimeters.

#### **Consumables and replacement items**

#### **Required reagents**

Description	Quantity/test	Unit	ltem no.
Free Ammonia Reagent Set, includes:	—	50/pkg	2879700
Free Ammonia Reagent Solution	1 drop	4 mL SCDB	2877336
Monochlor F Reagent Pillows	2	100/pkg	2802299

#### Recommended standards and apparatus

Description	Unit	ltem no.
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Chlorine Standard Solution, 10-mL Voluette <sup>®</sup> Ampule, 50-75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampule, 50-75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampules, 25–30 mg/L	20/pkg	2630020
Hardness Treatment Reagent Pillows	50/pkg	2882346
Nitrogen Ammonia Standard Solution, 10-mg/L NH <sub>3</sub> -N	500 mL	15349
Nitrogen Ammonia Standard Solution, 10-mL Voluette <sup>®</sup> Ampule, 50-mg/L NH $_3$ –N	16/pkg	1479110
Nitrogen Ammonia Standard Solution, 100-mg/L as NH <sub>3</sub> -N	500 mL	2406549
PourRite <sup>®</sup> Ampule Breaker, 2-mL	each	2484600
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
Water, organic-free	500 mL	2641549

#### **Optional reagents and apparatus**

Description	Unit	ltem no.
Beaker, 100-mL, polypropylene	each	108042
Beaker, glass, 100-mL	each	50042H
Mixing cylinder, graduated, 50-mL	each	2088641
Flask, volumetric, Class A, 100-mL glass	each	1457442
Free Ammonia Reagent Set	250/pkg	2879701
Monochloramine/Free Ammonia SpecCheck™ Kit	each	2507500
Pipet filler, safety bulb	each	1465100
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	1000/pkg	2185628
Pipet, Mohr, glass, 10-mL	each	2093438
Pipet, volumetric, Class A, 2-mL	each	1451536
Pipet, volumetric, Class A, 50-mL	each	1451541
Scissors	each	2883100
Stir bar, octagonal	each	2095352
Stirrer, magnetic	each	2881200
Thermometer, -10 to 110 °C	each	187701
Wipes, disposable	280/pkg	2097000



## (HACH)<sup>®</sup> Application Note 123

### Monitoring Chloramination using the APA6000<sup>™</sup> Ammonia/Monochloramine Analyzer

#### Introduction

Chloramination, a process often used for disinfection of drinking water and wastewater, involves mixing chlorine and ammonia to form chloramines. The relative concentrations of both chlorine and ammonia are essential for optimum disinfection. Some reactions between ammonia and chlorine are still being investigated, but in general, if chlorine is added to ammonia at a relatively neutral pH (similar to most municipal applications) a predictable series of reactions will occur.

First, the chlorine will react with free ammonia to form monochloramine. As more chlorine is added, additional monochloramine is made until all the free ammonia is consumed. When all the free ammonia is gone, the chlorine will begin to react with the monochloramine to form dichloramine. This reaction will continue until all the monochloramine is gone. If more chlorine is added, the chlorine will react with the dichloramine to form trichloramine (also called nitrogen trichloride) until all dichloramine has been reacted. This is called breakpoint and no more reactions are possible between the ammonia and chlorine. If more chlorine is added, it will remain as free chlorine in solution.

Each chloramine has a different effect on disinfection and the key to chloramination is to produce the correct chloramine species. Monochloramine is an effective disinfectant, is relatively stable in solution, and is often the preferred disinfectant in drinking water. Dichloramine is also a strong disinfectant but often gives an off taste and odor in drinking water. Trichloramine is unstable in solution and decomposes quickly.

The current analysis techniques available to monitor chloramination typically rely on the measurement of total chlorine along with the measurement of free ammonia. These two analyses are typically performed independently using two different process analyzers. The measure of total chlorine provides a good indication of chlorine level, but provides no detail as to which species of chlorine is being produced. In some cases, a second chlorine analyzer is added to measure free chlorine (which occurs at breakpoint). Doing so provides an indication of extreme chlorine overfeed condition but does not prevent or predict the incorrect ratios of ammonia and chlorine that result in the production of dichloramines and trichloramines.

An extreme chlorine overfeed condition results in poor disinfection despite a positive chlorine residual. In addition, many total chlorine tests are affected by interferences, resulting in a false high reading. The addition of a free ammonia analyzer lets the operator know that ammonia is being overfed but does not always give reliable results near the ammonia lower limit of detection. When the chloramination process is in control, a low ammonia concentration is the goal and the analyzer must monitor near the limit of detection. In many ion selective electrode-based ammonia analyzers, these low readings are difficult to reliably achieve because of interferences in the sample stream.

In summary, adequately monitoring chloramination with current technology requires three separate analyzers and the end result is still better suited to identify out-of-control conditions than to fine tune and optimize chloramination.

The APA6000<sup>™</sup> Ammonia/Monochloramine Analyzer was developed based on input from customers performing chloramination. The analyzer addresses the process analyzer weaknesses described above to provide an accurate indication of both the monochloramine concentration and the ammonia concentration. The focus is on an analyzer capable of

optimizing chloramination by specifically monitoring monochloramine. It does not detect dichloramine, trichloramine, or free chlorine so instead of only catching upset conditions, it also can focus on controlling and optimizing typical operating conditions.

In addition, the analyzer monitors ammonia levels by determining a 'total ammonia' value. Total ammonia is defined as the concentration of monochloramine plus free ammonia. By monitoring monochloramine and total ammonia, the analyzer is capable of calculating the free ammonia as well as the chlorine to nitrogen ratio. This allows control and optimization of chloramination using a single analyzer.

Figure 1 shows the response for total chlorine, monochloramine, total ammonia, and free ammonia when ammonia feed is constant and the chlorine feed is changing. All results are reported in mg/L as N. This figure is separated into three regions.

Region #1 is the operating region for most chloramination systems. In this region, as chlorine feed increases, the chlorine reacts with ammonia to form monochloramine. This results in an increase in monochloramine and a decrease in free ammonia. The desired set point is often the point at which free ammonia reaches zero. This is also the maximum point for monochloramine.

Feeding more chlorine results in operating in region #2. In this region, dichloramine and trichloramine (nitrogen trichloride) are formed. Monochloramine decreases with increased chlorine feed and no free ammonia is present. Operating in region #2 is not desired in most chloramination systems since it requires more chlorine, provides less disinfection, and often results in taste and odor problems.

Finally, in region #3, chloramination is no longer being performed. All nitrogen species have been consumed by chlorine, leaving free chlorine as the disinfectant.

The current approach to monitoring chloramination using a total chlorine analyzer and a free ammonia analyzer provides information, but has some practical difficulty. The total chlorine value can be used to control chlorine feed. However, the same chlorine value can be obtained in region #1, #2, and #3. So this analyzer alone does not provide enough information for control. If ammonia feed changes suddenly, the chlorine feed could be adjusted to maintain a given total chlorine value in region #2, or #3. The practical limitation of a total chlorine measure is that it responds equally to all chloramines and free chlorine, yet these different species do not provide the same disinfection properties. Speciation is important.

The goal in chloramination is to maximize the reaction of ammonia and chlorine to form monochloramine. When monochloramine production is maximized, free ammonia is minimized, potentially at or very close to zero. The addition of a free ammonia analyzer adds more control to the chloramination process by monitoring and controlling ammonia feed. Unfortunately, using a free ammonia value as the basis of control is flawed because this analysis requires the presence of a measurable concentration of ammonia. Because of this, the chloramination process is limited by the detection limits of an analyzer. If a measurable concentration of ammonia is present, monochloramine production is not maximized.

Operating at or near the detection limits of any analyzer offers challenges. It is difficult to obtain reliable readings near the detection limit because of factors such as interferences, drift, and changes in ambient temperature. Operating at higher levels of free ammonia does not allow process optimization.

The APA6000 Ammonia/Monochloramine Analyzer uses a single instrument to address the shortcomings of independent chlorine and ammonia analyzers. Monochloramine is

measured instead of total chlorine, allowing the chlorine feed to be controlled using a monochloramine set point.

Because monochloramine is also produced in region #2, monitoring only monochloramine could result in the process operating in region #2. The APA6000 warns the operator of this condition by outputting dashed lines for the ammonia values. So, chlorine feed can be optimized to operate in region #1 based on monochloramine. The ammonia feed can also be optimized based on the total ammonia value. Total ammonia is a good indication of ammonia feed as opposed to the remaining free ammonia. Figure 1 assumes a constant ammonia feed and the total ammonia value indeed remains constant throughout all of region #1. Total ammonia can be used to control ammonia feed. If the conditions change and the process extends into region #2, the total ammonia will begin to decrease as dichloramines are formed. However, this condition, as mentioned above, is indicated by dashed lines for the ammonia species. So, in a single analyzer, both chlorine and ammonia feeds can be controlled and the process optimized. The analyzer indicates when the process goes out of control, yet it is designed to fine tune proper operation.

## Figure 1 Monitoring Chloramination using an APA6000 Ammonia/Monochloramine Analyzer—Chlorine feed Changing/Ammonia Feed Constant



Figure 2 shows the response for total chlorine, monochloramine, total ammonia, and free ammonia when the chlorine feed is constant and the ammonia feed is changing. The results are all reported in units of mg/L as N. This figure is separated into two regions. Region #1 indicates low ammonia feed which would result in the formation of dichloramines and trichloramines. Region #2 is the operating region for most chloramination systems. The setpoint for control would likely be at the transition from region #1 to region #2. At this point the monochloramine reaches a maximum while the free ammonia is still zero. Region #2 indicates adequate ammonia feed and monochloramine values do not change in this region. Total chlorine values are also constant. This figure clearly shows the direct relationship of the ammonia feed to the total ammonia value. Current methods monitor for free ammonia is not present until after the optimum setpoint, when ammonia is being underfed, monitoring for free ammonia provides no information. Monitoring instead for total ammonia will provide a value to base ammonia feed.

Figure 2 Monitoring Chloramination using an APA6000 Ammonia/Monochloramine Analyzer—Ammonia feed Changing/Chlorine Feed Constant



Performing a straight free ammonia measurement on ISE analyzers often fails to provide accurate readings at low levels (such as those seen in the control region) because the values are very close to the lower limit of detection for the analyzer. Ideally, the free ammonia values of an ISE analyzer and those calculated by the APA6000 will be identical. In reality, free ammonia measurements made by an ISE near the limit of detection can exhibit a slow response, be affected by other interferences, or show electrode drift.

The APA6000 ammonia/monochloramine analyzer offers the ability to control and optimize chloramination. The ammonia feed can be controlled based on the total ammonia value and the chlorine feed can be controlled based on the monochloramine value. By setting the total ammonia control point slightly higher than the monochloramine control point, chloramination can be optimized using a single analyzer.

#### Operation of the APA6000<sup>™</sup> Ammonia/Monochloramine Analyzer

The APA6000<sup>™</sup> analyzer uses a colorimetric chemistry to measure total ammonia and monochloramine. The chemistry is a modified Phenate approach optimized for stability, dynamic range, and fast reaction time. The same chemistry is used to monitor both total ammonia and monochloramine.

In the measure of monochloramine, a buffer and indicator are added step-wise to the sample. The buffer and indicator form a green color when monochloramine is present. The color increases in intensity with increasing monochloramine. A short reaction time is allowed and the mixture of sample and reagents flow through an LED-based single wavelength colorimeter. The concentration is determined based on the absorbance at 650 nm.

Total ammonia is determined in much the same way. However, prior to adding the buffer and indicator, an excess of hypochlorite is added at a high pH to convert any free ammonia present in the sample to monochloramine. The remainder of the analysis is identical to the monochloramine method. The total ammonia result indicates the combination of any monochloramine initially present in the sample plus any monochloramine formed from free ammonia. Maintaining the proper pH prevents the formation of dichloramine even when excess chlorine is present.

The monochloramine analysis and the total ammonia analysis cycle alternately. Following each cycle, the free ammonia and the chlorine to nitrogen ratio is calculated and reported.

Free ammonia and the chlorine to nitrogen ratio are calculated from the total ammonia and monochloramine values. If the total ammonia and monochloramine values are equal (indicating no free ammonia is present) the analyzer defaults to dashed lines for both the total ammonia and free ammonia values, indicating a potential overfeed of chlorine. (Ask your Hach sales or service personnel to disable this default condition if desired.) As noted in Figure 1, once the monochloramine feed. Therefore, if a monochloramine value is present, but dashed lines are indicated for total and free ammonia, it can be assumed the total ammonia value is equal to the monochloramine value and the free ammonia content is zero.

The method used in the APA6000 is a patented technique called Carrierless Sequential Injection Analysis (CSIA). This technique mixes sample and reagents in small volumes in a very reproducible way for faster analysis. The method relies on a multi-port valve to select either samples, reagents, or standards and to direct the fluid to the mixing chamber or detector. The fluid is moved by a high precision burette. A small mixing chamber and a single wavelength LED-based colorimeter complete the modules found in an APA6000. Temperature control is used to ensure accurate results and the detector line is maintained under a slight back pressure to minimize outgassing.

The analyzer auto-calibrates using ammonia standards. It treats these known concentration standards the same as a sample. Each of the two standards provided with the analyzer is measured for total ammonia. Thus all the ammonia in the standard is converted to monochloramine. The absorbance is related to the concentration through these known standards which accounts for any slight changes in the reagents over time. To assure the reagents are still operational, a third standard is made by the analyzer. This third standard is an equal mixture of the two provided standards. The analyzer determines if the absorbance of the third standard is within the proper range. If not, it warns of the potential degradation of a reagent. The reagent most susceptible to degradation is Reagent 3 (the hypochlorite reagent) because it is highly light sensitive. Typical shelf life for Reagent 3 is six months. Failure to protect it from light may lead to faster degradation.

#### Please forward feedback to:

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For more information, visit our AquaTrend<sup>®</sup> Technical Information site at: http://www.aquatrend.com



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## CFB Wainwright - Base Environmental Office 08 Dec 2014

## Investigation into Chlorine Levels and Water Treatment Facility at CFB Wainwright for 3<sup>rd</sup> Canadian Division

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# **Presentation Outline**

- Background
- Methodology
- Results
- Discussion
- Follow-up







# Aim

- To determine potential chlorine analysis interferences, alternative sampling methodologies and potential sources of chlorine;
- To try and determine the baseline that should be used as a benchmark for chlorine analysis;
- Took a multidimensional form...after we reviewed all of the relevant communication and available literature.



Plant

## Location



# Background

#### **Background**

• Fish Kills 2007, 2013

• Investigation yielded Chlorine 'hits' found in samples near WTP, Betty Lake and Battle River

> Determine potential interferences of sampling techniques and interpret results i.e. why Chlorine 'hits'?


# Methodology



- What chemicals being used? At what concentrations?
- How have the operations altered?
- Dechlorination?
- Why fish kills in the vicinity of the WTP, specifically?

# Characterization of Source Water

- Ammonia
- Nitrate/Nitrite
- Chlorine/Chlorides
- Chloramines
- Organic Matter
- Manganese
- Copper
- Effluent Interaction





## Geology and Natural Environment



## **Potential Influences**



# WTP

Chemicals added during the treatment process include:

- Alum,
- Potassium permanganate,
- Polymers,
- Carbon Dioxide, and
- Ammonia

### In the past:

- Lime
- Fluoride
- Activated Carbon



## Dechlorination



# Theoretical Breakpoint Chlorination Curve. (AWWA, 2008)

#### **Breakpoint Chlorination Curve Interpretation\***

Comparing total and free chlorine, total ammonia-N, and free ammonia will help you determine your location on the breakpoint curve.



## Chlorine Demand Substances in Source Water

Chlorine Demand Substance	es
Substance	Chlorine Demand Multiplier
Ammonia-N	10 mg/L
Iron	0.6 mg/L
Manganese	1.3 mg/L
H2S	2.1 mg/L
Nitrite-N	5.0 mg/L
Organic-N	1.0 mg/L
TOC	0.1 mg/L

## WTP Data

Dates	Total Chlorine Distribution	Free Chlorine Distribution	Combined Chlorine Distribution	Total Chlorine Effluent	Free Chlorine Effluent	Combined Chlorine Effluent
26 March						
2013	1.6	0.11	1.49	2.7	0.33	2.37
27 March						
2013	1.2	0.12	1.08	2.5	0.31	2.19

Further, permanganates have been reported to kill fish in 8 to 18 hours at concentrations of 2.2 to 4.1 mg/L (EPA, 1999).

On March 23 2013, the daily dosage for potassium permanganate was 4.20 mg/L. The following days until the fish kill was reported, the KMnO<sub>4</sub> ranged from 2.44 mg/L to 2.07 mg/L.



- Ammonia
- pH, Temperature

## **Summary and Recommendations**

- Refer to Section in Report and we will discuss
  - Source Water Testing
  - Monochloramine Testing
  - Analytical Methods (without already identified interferences)
  - Chemical Dosages in WTP
    - Dechlorination Practices etc.



# Thank You

### DND = One Team



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