Tri-Halo Methanes & their Treatment/Prevention

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Introduction

The occurrence of tri-halomethanes, (THMs) in Canadian drinking water supplies is relatively low in light of the organic laden water from which we make potable water. The health related risks of THMs are well documented yet the basic ingredients of THMs are often over-looked on the door-step of water plants that treat our drinking water.

Body

The sources of many municipal drinking waters are laden with decaying plant and animal materials as well as some industrial waste carrying organic material. These organics are referred to as precursors of disinfection bi-products. Organics are only half of the THM equation. In very simple terms, the formation of tri-halomethanes is the result of disinfection chemicals, such as chlorine, breaking hydrogen bonds on a typical six-sided organic molecule and replacing it with chlorine atoms. The most commonly occurring chlorinated organic in treated water is chloroform, three chlorine atoms on a methane format of organic molecule, CH_4.

Most often, THMs are formed post filtration in the disinfection stages of water treatment. Organic materials pass through coagulation and filtration and are subjected to highly reactive disinfection chemicals. Precursors are usually soluble and dissolved molecules and easily pass through treatment systems. THMs are the specific result of disinfection chemicals and organic materials yet a larger group of target compounds are referred to as *disinfection bi-products* (DBPs).

Humic materials are an ideal example of high molecular weight compounds and are common organic in water sources in Western Canada caused by the decomposition of plant materials[1]. Leaves, branches and barks are all decomposed into humic material. Humic material in soils, is valuable fertilizer. In potable water, humic materials give the water a tea like appearance and imply that the water is unfit for human consumption. Many Prairie towns' and cities' raw water supply is influenced by muskeg water sheds, a highly concentrated source of humic organics. Similar applies to the other organics that make up contaminants in our water supplies. Lignins and fulvic materials are all caused by decomposition of living organisms. To–date there has not been any health risks associated with colour of these materials alone. However, the presence of colour at the tap or in the tub implies that the water is unsafe. The removal of colour is one of the most daunting challenges faced by Western Canadian water operators.

The influences of our Canadian climate will have significant impact on the levels of organics in raw water and potentially of THMs/DBPs in potable water. Cold winter months virtually stop decomposition of organic materials. A federal government sponsored study of THMs showed that, at a handful of Prairie water treatment plants (WTP) THM incidence dropped to near zero from January to March, then made a steady climb throughout the summer peaking in late August[2]. As the sun heats the water supplies, organic materials break down faster and are drawn into our water treatment plants at higher concentrations.

Present water treatment knowledge relies heavily on good coagulation and filtration followed by disinfection. Chlorine has been used in many forms to provide good, cost effective,

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[1] Chemistry For Environmental Eng – Sawyer & McArty, pg 153, McGraw-Hill 1978

[2] One Year Survey of Halo DBPs in Distrib.System of Treatment Plants Using 3 Different Disinfection Processes, LeBel, et el, Health Canada, Ottawa, 1996

stable and measurable disinfection. Exclusion of chlorine to prevent THM formation simply is not practical. In the 1400s, the famous Black Plaque raced through Europe via the waterways and drinking water supplies. Water supplies are ready and willing reservoirs for deadly diseases such as anthrax, typhoid, cholera and plague related bacteria. Since these disease-causing organisms have been understood and identified, chlorination has become commonplace and simply the safest known disinfectant.

Post filtration disinfection with chlorine, for example, changes the typical organic molecule into a chlorinated form of itself, such as chloroform. Many investigations into the health risks of chlorinated organics have determined that chlorine is similar to any medicinal drug: just the right dose will aid us significantly, while long-term exposure to elevated levels has negative health effects.

In recent years, research into health effects of DBPs has shown that THMs are linked to the occurrence of digestive tract cancers, birth defects and reproductive disruption. More recent research has shown that hot showers and baths volatilize THMs, which are inhaled and are linked to the occurrence of respiratory disorders, including lung cancers.

For these reasons, the US EPA has issued a *limit* on the concentrations of THMs in American drinking water supplies not to exceed 100μg/l. The Canadian government has issued a *guideline* on acceptable THM levels in our drinking water, also 100μg/l[3].

It is important to point out that not all organics subjected to disinfection will result in THMs. Specific conditions must be present, as must specific types or organic molecules to form THMs. These factors are influenced by the raw water source and it's varying chemistry. Typically, highest THM incidents is a function of higher molar mass organics[4], which tend to have both hydrophilic and hydrophobic sites on the compound, making it difficult to break-down for coagulation.

Water plant operators are able to reduce the potential of THMs/DBPs by reducing the colour of treated water. Colour being an organic molecule, an operator can use colour measurements as an indicator of organic removal through the water treatment plant. Colour measurements are simple light absorption of platinum cobalt (PtCo) light sources while THM analysis is labor and equipment intense and the results interrupted by experienced chemists and complicated computer programs. The commonly accepted method of THM analysis, at this time, is by 'purge & trap', followed by gas chromatographic separation and detection by mass spectroscopy. The resulting data is referenced to known standards and is extremely accurate and reproducible.

The high molecular weight molecule of organic material in water is the main cause of colour, the absorption of light wavelengths. There is a direct relation between the amount of organic material in water and simple colour readings. Many methods exist to measure colour in water, but the most common is referenced to 455nm wavelength and based on 1 color unit being equal to 1 ppm platinum as chloroplatinate ion in solution.[5] Organic material that may pass through filtration can be measured by this method. A close study of daily colour readings will aid operators reduce DBP formation and will demonstrate valuable trends they may be used to monitor and predict organic excursions and ward against them.

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[3] Guidelines for Canadian Drinking Water Quality, 6th Edition, Ottawa, Health Canada, 1996

[4] Collins, Amy & Steelink, Molecular Weight Distribution, Carboxylic Acidity & Humic Substances Content of Aquatic Organic Matter, Envir. Sci & Tech, 1028, 1986

[5] Hach Water Analysis Hand Book, 3rd Edition, pg 524

The least labor and expense intense method to prevent THM/DBP formation is to remove the organic precursors **before** disinfection in the coagulation stages of water treatment. The correct doses of the appropriate coagulants will de-stabilize and break-up the organic molecules, allowing charge neutralization and the formation of solid, settlable precipitate that is readily separated from water. Coagulation is the application of metals, in a soluble form, to provide many positively charged sites to the water being treated to bind the negatively charged turbidity and organics. All organics and natural colour exists in water primarily as negatively charged colloidal particles.[6] Colloidal organics in water are uniform sizes and possess unipolar charges that cause individual particles to repel each other, thus staying in suspension indefinitely. Appropriate use of positively charged coagulants has two important impacts on organics/colour. First, coagulants deliver a pH change to destabilize the high molecular weight organic compound, and secondly provides highly charged positive metals on which the negative organics can now bond to form a solid.

It is believed that coagulants and the reaction of forming precipitates in water treatment programs first begin destabilization of organics in the soluble phases, then neutralize the charges of turbidity. Meaning that the optimization of a coagulant must consider the organic demand as well as the demand of turbidity. Daily colour and turbidity readings provide operators the tools to assess the efficiency of the coagulation programs they operate.

Most Western Canadian water plants treating surface water have straightforward treatment programs of coagulation, flocculation, agglomeration and sedimentation, followed by filtration. Applying a metal salt such as aluminium to water must be done via a liquid or powder such as alum, poly-aluminium chloride, (PAC) or poly-aluminium silicate sulphate, (PASS). All these products are manufactured by 'dissolving' aluminium in acids. The end products have varying pH values and varying concentrations of aluminium. Determining which products are best suited to the type of water and water treatment process becomes a challenge every operator must face. Water treatment plant characteristics and the chemistry of the raw water will determine which coagulant is best suited to a treatment program. Many Canadian water plants experience extreme raw water changes throughout the seasons that different coagulants may be used at specific times of the year.

Common sand/anthracite media, used in water treatment post coagulation and sedimentation, is incapable of removal of colloidal and dissolved organic carbons, precursors of DBPs. For practical purposes, colloids behave like true solutions[7]. Disinfection is routinely added post filtration and allowed ample contact time before the water is stored. Based on filtration limitations, it is imperative to address organics in the first stages of water treatment, by coagulation.

Unfortunately there isn't a single coagulant that will accomplish all water treatment goals on it's own, or at all sites. Costs also have a significant impact on the coagulants accessible to most operators. Combinations of coagulants and polymers, varying retention times, and sludge removal rates all must be accounted for at a water treatment plant to maximize DBP precursor removal.

Alum has been used for many years for coagulation, but in light of the new focus on DBPs, it has been studied extensively and determined that there are other coagulants that do a more efficient and complete job of precursor removal. Numerous factors impact how well a coagulant works such as temperature, alkalinity and the format of the metal coagulant. Alum is a monomeric form of aluminium while PACs and PASS are polymeric aluminium coagulants. The

[6] Sawyer & McCarty, Chemistry for Environmental Engineering, 1979 pg. 337
[7] Lippmann & Schlesinger, Chemical Contaminants in the Human Environment, 1981, pg 170

advantages of polymeric aluminium have been described as high-charge, moderate-molar-mass species that are immediately available for coagulation, (rather than being formed insitu as happens with alum use), and less temperature and pH dependent compared to alum[8]. Our Canadian climate's effect on water temperature is a significant reason for alum's inefficiency to remove organic precursors for much of the year. According to Exall/Vanloon et al[6] , the increased viscosity of cooler water may hinder coagulant dispersal and sedimentation, combined with the characteristically small floc formed by alum, at low temperatures, result in poor removal of organic precursors of DBPs.

Poly-aluminium chloride, (PAC) has been identified as the most economical and efficient coagulant for the removal of organic materials[8]. PAC commonly is delivered to the customer pre-hydrolzyed, meaning that it is eager to react, quickly forming valuable reactions with soluble Al(OH)x necessary for charge neutralization and later solids contact. During the manufacture of acidic PAC or PASS, a soluble base material partially neutralizes the end product. This simply means that the end product has numerous OHs in it, instead of depending on the water source to give up OHs during the formation of Al(OH)x as is the case with alum.

Kilo-for-kilo, PAC is slightly more costly than alum and alum can be used at excessive doses to achieve stubborn colour removal. Yet the proper use of PAC will balance costs since less is needed to reach the same water quality goals. The highly charged metal ions of alum and PAC are necessary for coagulation and PAC simply makes better use of the positive charges on aluminium. Common aluminium polymer charges in alum are Al^{3+} while in PACs the common aluminium charges are Al^{7-10+}[9]. Issues of aluminium in human physiology also come into play when dosing high alum to achieve good coagulation and colour removal.

CASE STUDY

A small Northern Alberta community was treating water with upwards of 250ppm alum to drive colour and turbidity values down to government regulated guidelines and usually reached the goals. However, handling pH adjustment chemicals and costs of the program forced the operation to change to PAC. PAC replaced alum at 70 ppm and the resulting colour dropped even further. A follow-up study of the before and after PAC transition of organic carbon analysis showed that organic carbon was reduced from 0.11 mg/l ave. to 0.045 mg/l ave. Organic carbon being an indicator of potential precursor of DBPs. A similar reduction in true colour was noted, from average 14 PtCo units to 8 PtCo.

Another town on the prairies used alum to treat water in a pre-settling pond and again in a direct filtration application down stream of the ponds. It was determined from routine water quality analysis that total THM values of alum treated water were reduced from 210 μg/l to 100 μg/l when PAC was used and optimized. Colour measurements were not indicators as both treatment programs reduced colour to below detection.

Our knowledge of and experiences of potential water borne contaminants has lead the modern world to disinfect drinking water supplies with chlorine. There has not been an advance in this technology to date. The down side to chlorine application has been found to be the formation of organic molecules laden with chlorine, condensed into disinfection bi-products such as THMs in our drinking water. Exclusion of the disinfection step is not possible, therefore the prevention of DBPs must be addressed before disinfection chemicals are added to our drinking

[8] ExallVanloon, AWWA Journal 11/00 pg 94 - 102

[9] Vogel's Quantitative Inorganic Chemistry & Analysis, pg 218, 1981

water. The most effective method of removing DBP precursors is the optimization of coagulation methods.

Performance differences of metal-based coagulants have been studied and many point to poly-aluminium chloride being the most effective and economical[10]. A few Western Canadian site specific transitions from alum to PAC have been used to illustrate the impact of enhanced coagulation with PAC.

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[10] G Crozes, et el, Enhanced Coagulation: Effects on NOM Removal & Chem Costs, AWWA Journal, January, 1995