

Characterisation and concentration profile of aluminium during drinking-water treatment

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Abstract

An aluminium(Al) characterisation study was conducted at a surface water treatment plant (Buffalo Pound Water Treatment Plant (BPWTP) in Moose Jaw, Saskatchewan, Canada) to understand better the effect of alum coagulant on various Al fractions. The raw water source for BPWTP is Buffalo Pound Lake water. The Al sources at BPWTP are:

- present naturally Al in the raw water and
- Al derived due to use of alum as a coagulant.

Seasonal evaluations of Al at BPWTP showed that raw lake water total concentrations were highly variable. Suspended (filterable) Al was the predominant species of raw water total Al. Organic-bound or organo-Al complex Al appeared to be the predominant species of dissolved Al in both raw and treated water during the September to November 1997 Al characterisation study. However, during October to December 1998, inorganic Al dominated dissolved Al content. Characterisation of Al at BPWTP showed that the use of (liquid) Al sulphate (alum) did not increase the concentration of total Al levels.

This was because:

- alum coagulation was practised at pH 7, at which the Al is least soluble
- clarifier and filtration units effectively removed particulate Al and
- granular activated carbon (GAC) was capable of removing part of the organic dissolved Al.

The study showed that BPWTP would be able to comply with the requirement of Health Canada Guideline value (for conventional treatment plants) for Al of less than 100 µg/ℓ as total Al. Turbidity and dissolved organic carbon of the raw water influenced the applied alum dose at BPWTP.

Introduction

The presence of Al in treated water for distribution has been a subject of concern for many years. Links have been established between Al in drinking water and human neurological disorders such as dialysis encephalopathy (Parkinson et al., 1979). A recent study by Berend and Trouwborst (1999) showed that excess Al in dialysate fluid was harmful to dialysis patients. Additionally, links in the case of Alzheimer's disease have been proposed (McLachlan et al., 1991). Although much more work is needed before the full implication of the toxic effects of Al is known, it is generally agreed that the knowledge of the form or type of Al species in the water system is of importance since both bio-availability and toxicity are critically dependent on the chemical form of the individual species of a metal. Speciation or characterisation may be defined as the determination of the individual concentrations of the various chemical forms of an element which together make up the total concentration of that element in a sample. The words "characterisation" and "speciation" are used interchangeably in this paper.

Aluminium which is present in alum and naturally present Al in raw water are transformed into various forms during water treatment. The literature indicates that the use of a coagulant containing Al may either increase or decrease Al concentration in the finished water, depending on its speciation in the source water as well as species (change or distribution) of Al during water treatment and conditions of water treatment. It is reported that when

alum (i.e. $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$) is used as a coagulant for water treatment there is a 50% chance that it can lead to increased concentrations of Al in the treated water compared to the raw water itself (Miller et al., 1984; Driscoll and Letterman, 1987; Driscoll and Letterman, 1988; Driscoll and Letterman, 1995). A high concentration of Al (3.6 to 6 mg/ℓ) in the treated water contributes to turbidity, reduced disinfection efficiency, and precipitation of Al hydroxide within the distribution system. Most water treatment plants measure effluent levels of total or dissolved Al. However, profiles of various forms of Al levels through a water treatment plant are rarely performed. Added to this, few countries set standards (based on aesthetic considerations only) for Al. In addition, Al is not a routine monitoring parameter in finished water in many water treatment plants. Furthermore, relatively little attention has been paid to the speciation of Al in raw, treated and distributed waters (AWWA Committee Report, 1993). It is generally accepted that free (hydrated) metal ion is the form which is most toxic to aquatic life. Strongly complexed metal or metal associated with colloidal particles is much less toxic (Florence and Batley, 1980). Hence, determination of the total concentration of a metal in a water sample provides very little information about the toxicity of that water.

Aluminium characterisation was conducted at the Buffalo Pound Water Treatment Plant (BPWTP) which is located approximately 85 km west of Regina. The plant supplies drinking water to the cities of Regina and Moose Jaw. The raw water source is Buffalo Pound Lake (29 km long, and 1 km wide, with an average depth of 3 m), a shallow reservoir in the Qu' Appelle Valley. Raw water from Buffalo Pound Lake passes through a series of unit operations including prechlorination, cascade degassification, coagulation and flocculation, clarification, filtration, and carbon adsorption (during summer months). The plant uses liquid Al

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sulphate (alum) as coagulant. No polymer is added during coagulation.

The objectives of the present research work were to:

- conduct seasonal Al characterisation (speciation) studies at BPWTP (September to November 1997 and October to December 1998);
- examine the profile of Al from raw to the treated water and identify the factors influencing profile changes;
- evaluate the Al removal efficiency of major unit operations such as clarifiers/filters at the plant; and
- identify the factors influencing residual Al in treated water.

Materials and methods

Materials

Nalgene 500-mL high-density polyethylene (HDPE) bottles were used for water sample collection and storage. Nucleopore polycarbonate 0.45 µm membrane filters (Corning Separations Division, Acton, MA 01720) were used for the separation of total and dissolved Al. Filtration of samples was carried out using a vacuum pump and 1 L polypropylene filtering flasks were used to collect the filtrate. No glass containers were used in order to avoid the problem of Al leaching. A strongly acidic cation exchange resin, Amberlite IR-120 plus (sodium form, -16-50 mesh US standard screens, -Rohm and Hass Company, PA 18105), was used for speciation of dissolved Al. A variable-speed peristaltic pump (E-07553-70 L/S, Cole-Parmer Instrument Company, Ill) was used to pump filtered water into cation column of 1 cm internal diameter × 30 cm height (C 6169, Sigma Aldrich Canada Ltd).

A Perkin Elmer graphite furnace atomic absorption spectrophotometer (GFAAS) (2380 Spectrophotometer, -HGA 400 furnace with D₂ arc background corrector and AS 40 auto sampler) was used for measurement of Al present in water samples during both phases of Al characterisation study at BPWTP. Standard Al solutions (10, 30, 50, 80 and 100 µg/L) were prepared by diluting Anachemia AAS grade Al reference (stock) solution of 997 µg/L for calibration of GFAAS. Magnesium nitrate (0.1%) was used as a matrix modifier for the measurement of Al by GFAAS. All chemicals used were of ACS reagent grade. Distilled-deionised water was used for dilution of stock solutions as well as for any reagent preparation. All containers used in this study were cleaned using distilled-deionised water, as follows:

- cleaned with 1+1 HCl and then stored in 1+1 HCl for 12 h;
- rinsed with distilled-deionised water and then stored in distilled deionised water for 12h; and
- rinsed with distilled-deionised water.

It is reported that membrane filters were used freshly and the first 50 mL of sample was avoided to prevent any contamination due to filters.

Method selection for speciation of drinking water Al

The speciation method developed by Driscoll and Letterman (1995) was adopted in the present study with some changes. Water samples during this speciation experiment were given the same pretreatment (acid digestion, 0.45 µm membrane filter separation and cation exchange resin treatment) as proposed in Letterman and Driscoll (1994), but oxine-methyl isobutyl ketone (MIBK) extraction was not used, as indicated in Driscoll and Letterman (1995) -

instead pretreated samples were analysed for Al by GFAAS. Digestion procedure (for total/dissolved plus colloidal Al) involved lowering sample pH to 1 using trace metal grade nitric acid (A 509B-500 Fisher) and keeping the sample at pH = 1 for 2 h before measurement. A detailed method development related to measurement of drinking water Al using GFAAS along with interlaboratory quality control and method validation that were part of the Al speciation study can be found elsewhere (Srinivasan et al., 2000).

Assumptions involved in the present Al speciation protocol

- Filtration of samples through 0.45 µm membrane filters removes filterable (suspended) Al and does not remove colloidal particles or dissolved Al.
- Acid digestion step solubilises all the colloidal Al present in the sample.
- After the samples were pretreated, the samples were measured for Al using a GFAAS (instead of the conventional oxine extraction used in Al speciation study) since the authors' extensive preliminary work demonstrated that the time of extraction, sample pH, extraction pH, and the order of adding reagents during oxine extraction influence the oxine extraction results very much. A recent work by Allan (1997) involving Al speciation study in Whetstone Brook in western Massachusetts; and an Al speciation protocol developed by Berube and Brule (1994) of Health Canada for the speciation of Al present in shallow wells of Atlantic Provinces of Region of Canada using inductively coupled plasma-mass spectrometry (ICP-MS) did not use the oxine extraction step.
- The capability of the graphite furnace to detect colloidal-bound Al lies in the fact that the acid solubilisation improves the furnace performance in atomising the samples effectively, leading to a difference in value between acidified and non-acidified sample values. Bloom and Erich (1989) suggested that even at high temperatures, minerals-bound colloidal Al is not decomposed during atomisation, whereas acid solubilisation ameliorates the sample decomposition.
- The sum of filterable (suspended) and colloidal Al concentrations provides particulate Al concentration according to this Al speciation protocol. Colloidal Al can be associated with colloidal particles/clay of various size ranges (which is essentially a part of filterable (suspended) form of Al); but a 0.45 µm membrane filter can let colloidal Al pass through it. However, subsequent acid solubilisation releases this Al to the sample environment. Hence, Al retained by a 0.45 µm membrane filter (filterable or suspended Al) and Al passed through a 0.45 µm membrane filter (colloidal Al) are added to get particulate Al.

Protocol for characterisation of Al

Al was fractionated into eight different forms. Filters have "self adsorption/absorption" capacity for Al and, hence, initial filtrates would not have the same Al content as samples. After discarding the initial filtrate volume of 30 to 40 mL, samples (30 mL volume) were collected for Al analysis. The different forms were as follows:

- Total Al (Al_T) (acidification of samples at room temperature at pH 1 for 2h).
- Colloidal and dissolved Al (Al_(C+D)) (sample filtered through 0.45 µm polycarbonate membrane filter, and acidified to pH 1 for 2 h).

- Dissolved (inorganic and organic) Al $Al_{(I+O)}$ (sample filtered through 0.45 μ m polycarbonate membrane filter but not acidified).
- Organic Al (Al_o) (organo Al complexed with NOM) - a strongly acidic cation exchange resin of Amberlite IR 120 Plus, was used to fractionate dissolved Al into two fractions, namely, inorganic and organically-bound Al; Al complexed by the inorganic ligands such as hydroxide, fluoride, sulphate and silicate (known as inorganic Al) was removed (i.e., exchanged for sodium or hydrogen ion present in the resin) and organic Al was not removed; filtered water sample is passed through cation exchange resin and effluent was analysed without any acidification for organically-bound Al.
- Filterable (suspended) Al (Al_{ss}) was estimated as the difference between $(Al_p) - (Al_{(C+D)})$.
- Colloidal Al Al_c was estimated as the difference between $(Al_{(C+D)}) - (Al_{(I+O)})$ dissolved fraction.
- Total particulate Al (Al_{Tp}) was estimated as the sum of (Al_{ss}) and (Al_c) .
- Inorganically-bound Al (Al_i) was estimated as the difference between dissolved Al $Al_{(I+O)}$ and organically bound Al (Al_o). Table 1 shows the various Al fractions obtained during the present study.

Analytical methods used in this study for the measurement of other water quality parameters such as pH, sulphate, fluoride, and dissolved organic carbon (DOC) are shown in Table 2. A schematic diagram of BPWTP and locations at which samples were collected for speciation of Al are shown in Fig. 1.

Cation column studies

The cation exchange column used in this study was a chromatography column of 1cm internal diameter by 30 cm height filled with a 10 mL of sodium form of Amberlite IR 120 Plus, a strongly acidic cation-exchange resin. Letterman and Driscoll (1994) reported that the pH change when samples are processed through the cation-exchange column has to be minimal. If the pH change is significant, equilibrium between organic and inorganic Al species will be disturbed and will eventually lead to competition between hydrogen ion and Al for dissolved organic matter present in water. This may lead to incorrect measurement of either the organic or inorganic fraction of dissolved Al. The pH of the samples before and after the column during this study indicated that insignificant pH changes occurred. Results of cation exchange columns are also influenced by flow rate through the column. Optimum flow rate (20 mL/min) as recommended by Letterman and

TABLE 1
Aluminium fractions obtained during the present study

| Description | Pretreatment | | | Fraction groups determined by difference |
|------------------------------|---------------|---------------------------|---|--|
| | Acidification | Filtration (0.45 μ m) | Cation exchange | |
| 1. Total Al | Yes | | | |
| 2. Colloidal + Dissolved Al | Yes | Yes | | |
| 3. Dissolved Al | | Yes | | |
| 4. Organic Al | | | 3 through cation resin (removes inorganic Al) | |
| 5. Filterable (suspended) Al | | | | 1 - 2 |
| 6. Colloidal Al | | | | 2 - 3 |
| 7. Particulate Al | | | | 5 + 6 or 1 - 3 |
| 8. Inorganic Al | | | | 3 - 4 |

TABLE 2
Analytical methods/instruments used in this study

| Test | Method/instrument | Reference |
|--------------------------|---|---|
| pH | Orion SA 720 pH meter | Operation manual |
| Alkalinity | HCl titration | <i>Standard Methods</i> , 1995 |
| Dissolved organic carbon | Astro 2001 System II Carbon Analyzer | Operations Manual, <i>Standard Methods</i> , 1995 |
| Particle count | HIAC model PC - 320 automatic particle size analyzer | Operation manual |
| Silica | Spectrophotometer | <i>Standard Methods</i> , 1995 |
| Fluoride | Orion fluoride electrode- orion Model 701 A, digital ion-analyzer | <i>Standard Methods</i> , 1995 |
| Conductivity | Horiba Model DS- 12 conductivity meter | Operation manual |
| Hardness | EDTA titration | <i>Standard Methods</i> , 1995 |
| Chloride and sulphate | Ion chromatography (Dionex 2000 i/ SP) | <i>Standard Methods</i> , 1995 |
| Turbidity | HACH 2001 | <i>Standard Methods</i> , 1995 |

Driscoll (1994) was used throughout the experiments. Dissolved organic carbon of the influent to the cation-exchange column should be equal to dissolved organic carbon of the cation resin treated water, i.e. cation exchange column from a chemistry point of view should not remove any dissolved organic carbon. However, organic carbon may leach from the resin itself. This was verified by running a UV scan (pattern) from 220 nm to 360 nm (*Standard Methods*, 1995). According to *Standard Methods* (1995), typical

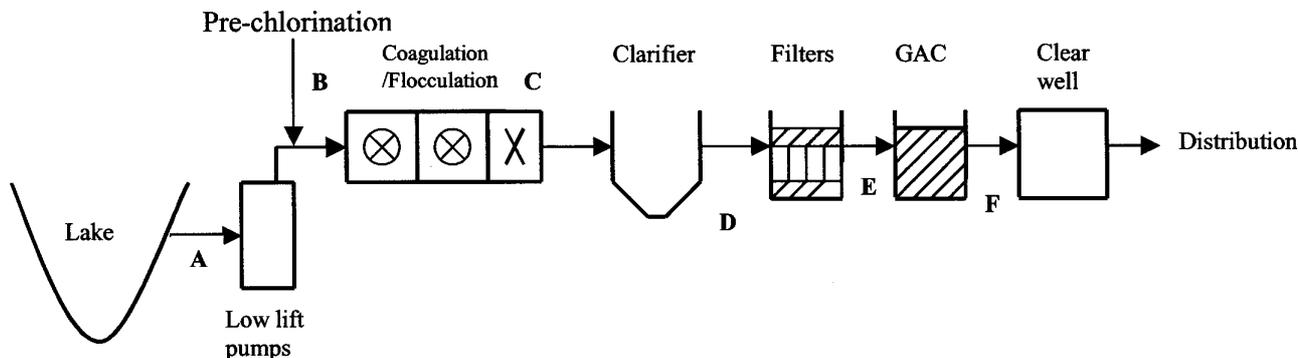


Figure 1
Schematic diagram of the BPWTP and sampling locations for Al speciation

TABLE 3
Average raw and treated water (Clear Well - Regina)
characteristics of BPWTP during the speciation study

| Parameter | Unit | Raw water | Treated water |
|---------------------------|---------------------------|-----------|---------------|
| pH | pH units | 8.3 | 7.3 |
| Alkalinity | mg/l as CaCO ₃ | 153 | 120 |
| Hardness | mg/l as CaCO ₃ | 181 | 181 |
| Dissolved organic carbon* | mg/l | | |
| Fluoride | mg/l | 0.18 | 0.11 |
| Sulphate | mg/l | 119 | 146 |
| Silica** | mg/l | | |
| Chloride | mg/l | 16 | 19 |
| Particles | per ml | 31150 | 24 |
| Conductivity | µS/cm | 583 | 602 |
| Temperature | °C | 4 | 4 |
| Turbidity | NTU | 6.5 | 0.1 |

*(Sept. to Nov. 1997, Raw = 8.8, Treated = 3.6) (Oct. to Dec. 1998, Raw = 8.4, Treated = 5.3)
 **(Sept. to Nov. 1997, Raw = 6.2, Treated = 5.7) (Oct. to Dec. 1998, Raw = 0.72, Treated = 0.8)

absorbance scans of natural organic matter are featureless curves of increasing absorbance with decreasing wavelength. Sharp peaks or irregularities in the absorbance scan may be indicative of inorganic interferences or unexpected organic contaminants (e.g. leaching of organic carbon). In the present study, the authors analysed UV absorbance patterns for raw (before column) and cation - exchange treated water between 220 nm to 360 nm. This was a featureless curve (no sharp peaks) and absorbance increased with decreasing wavelength. This indicated that no organic carbon leached from the resin.

Results and discussion

Average raw and treated water (clear well - Regina) characteristics of BPWTP during the Al characterisation study period are shown in Table 3. Table 4 shows the mean Al fractions (in µg/l) obtained through the plant during September to November 1997 and October to December 1998 at the BPWTP. Table 5 shows the associated standard deviations for various Al fractions reported in Table 4. Figure 2 shows the total, particulate, and filterable (suspended) Al profiles obtained (on logarithmic scale) at BPWTP from raw water to the treated water. Figure 3 shows the profiles of colloidal + dissolved, dissolved, inorganic, organic and colloidal Al obtained at BPWTP from raw water to the treated water. Tables 6 and 7 respectively present the Al data pertaining to mean total, organic, inorganic and colloidal Al values for September to November 1997 and October to December 1998 periods individually in order to explain some of the trends observed in these Al values.

Particulate Al removal/dissolved Al formation and its characteristics

It was observed during the entire Al characterisation period that consistently good removal of particulate Al (an average of 92% particulate Al

TABLE 4
Mean Al fractions obtained through the plant during Al characterisation
study (No of sample (n) = 9 for all except for filtered
water for which n = 7)

| Al fraction | Raw water | Pre-chlorinated water | Flocculated water | Clarified water | Filtered water | Water after GAC (clear well) |
|--------------|-----------|-----------------------|-------------------|-----------------|----------------|------------------------------|
| Particulate | 558 | 471 | 5 064 | 323 | 53 | 17 |
| • Filterable | 547 | 463 | 5 054 | 318 | 49 | 14 |
| • Colloidal | 12 | 8 | 10 | 5 | 4 | 2.7 |
| Dissolved | 22 | 24 | 48 | 46 | 40 | 33 |
| • Inorganic | 10 | 9 | 24 | 23 | 17 | 21 |
| • Organic | 11 | 19 | 24 | 24 | 22 | 12 |
| Total | 580 | 494 | 5112 | 370 | 92 | 50 |

Note: All values are in µg/l

| Al Fraction | Raw water | Pre-chlorinated water | Flocculated water | Clarified water | Filtered water | Water after GAC (clear well) | Ovellall SD |
|--------------|-----------|-----------------------|-------------------|-----------------|----------------|------------------------------|-------------|
| Particulate | 400 | 315 | 858 | 85 | 16 | 18 | 282 |
| • Filterable | 402 | 397 | 860 | 85 | 16 | 14 | 296 |
| • Colloidal | 18 | 13 | 13 | 2 | 4 | 4 | 9 |
| Dissolved | 10 | 11 | 13 | 13 | 7 | 10 | 10.6 |
| • Inorganic | 7 | 9 | 25 | 13 | 16 | 15 | 14 |
| • Organic | 10 | 12 | 17 | 13 | 15 | 11 | 13 |
| Total | 397 | 314 | 859 | 85 | 15 | 24 | 282 |

Note: All values are in $\mu\text{g}/\ell$

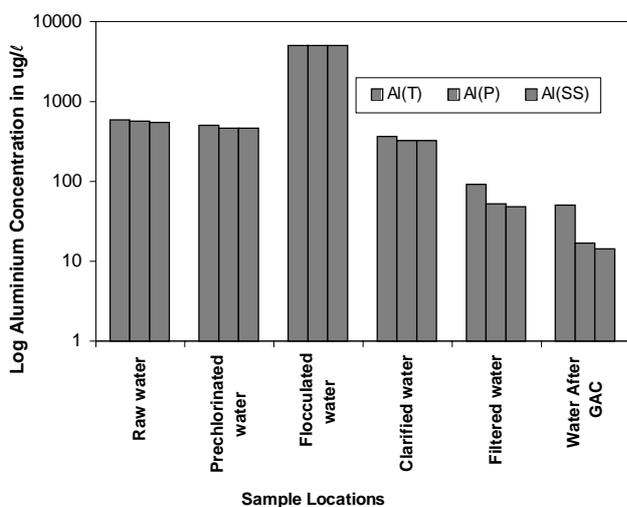


Figure 2

Profiles of total, particulate, and filterable Al obtained during the Al characterisation study period (on logarithmic scale) at BPWTP

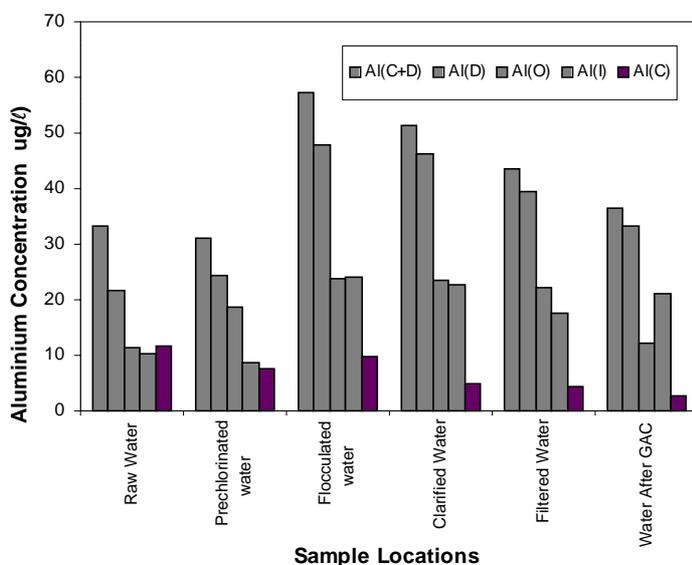


Figure 3

Profiles of colloidal + dissolved, dissolved, organic, inorganic and colloidal Al obtained during the Al characterisation study period at BPWTP

was precipitated as $\text{Al}(\text{OH})_3$ and removed as sludge) was observed at the clarifier (Channel I) and an average of 85% of particulate Al was further removed by sand filtration (Table 4).

Dissolved Al levels rose prior to filtration and alum was responsible for such an increase in dissolved Al by virtue of its hydrolysis products (Fig. 3). Dissolved Al increased from $22 \mu\text{g}/\ell$ to $48 \mu\text{g}/\ell$ due to alum addition (Fig. 3). However, sedimentation, filtration and GAC following alum addition decreased dissolved Al to 32 to $33 \mu\text{g}/\ell$ in treated water (Table 4 and Fig. 3).

Comparison of the mean dissolved inorganic Al value before and after alum addition indicated that alum addition increased nearly three times (9 to $24 \mu\text{g}/\ell$) the dissolved inorganic Al (Fig. 3). There was a $5 \mu\text{g}/\ell$ increase in organic Al due to alum addition and its levels remained relatively constant at channel ($24 \mu\text{g}/\ell$) and sand filters ($22 \mu\text{g}/\ell$). However, in finished water, the organic Al value was reduced to 12 to $15 \mu\text{g}/\ell$, implying the capability of GAC to remove part of dissolved Al in organic form (Table 4).

Characterisation and variations in total Al at the BPWTP raw water

Al characterisation studies showed that raw lake water total Al concentrations were highly variable (262 to $1189 \mu\text{g}/\ell$) during the September to November 1997 period (Table 6). This variability could be due to the fact that high wind and rain occurred during some of the days of sampling, altering water quality characteristics of influent to the treatment plant. It can be seen from Fig. 2 that almost all raw water particulate Al (predominant species of total Al) was present in filterable (suspended) form. An Al speciation study by Letterman and Driscoll (1994) at three water treatment plants and an Al speciation study by Van Benschoten and Edzwald (1990) at two water treatment plants showed that particulate Al was the dominant species in raw water total Al. Benes et al. (1976) who analysed metal contents present in a freshwater lake also reported that much of the Al was present in particulate form. Particulate form of Al continued to be the dominant form in total Al until the raw water passed through the channel (clarifier) of the plant (Fig. 2). The mean raw water total Al concentration increased nearly seven times due to alum addition during the September to November 1997 Al characterisation study period (Table 6).

| TABLE 6 Mean total, organic, inorganic and colloidal Al values of Al characterisation study period Sept. to Nov. 1997 | | | | | | |
|--|---------------------|------------------------------|--------------------------|------------------------|-----------------------|-------------------------------------|
| Al fraction | Raw water | Pre-chlorinated water | Flocculated water | Clarified water | Filtered water | Water after GAC (clear well) |
| Total | 830 *(262-1 189) | 670 | 5 758 | 301 | 85 | 32 |
| Organic | 9 | 24 | 40 | 29 | 30 | 19 |
| Inorganic | 7 | 2 | 6 | 13 | 6 | 5 |
| Colloidal | 17 | 1.2 | 3.5 | 20 | 5.9 | 0.8 |
| Note: *Value in bracket is range All values are in $\mu\text{g}/\ell$ | | | | | | |

| TABLE 7 Mean total, organic, inorganic and colloidal Al values of Al characterisation study period October to December 1998 | | | | | | |
|--|-------------------|------------------------------|--------------------------|------------------------|-----------------------|-------------------------------------|
| Al fraction | Raw water | Pre-chlorinated water | Flocculated water | Clarified water | Filtered water | Water after GAC (clear well) |
| Total | 380 *(180-600) | 354 | 4 576 | 427 | 102 | 65 |
| Organic | 14 | 15 | 11 | 19 | 12 | 7 |
| Inorganic | 13 | 14 | 39 | 31 | 32 | 33 |
| Colloidal | 7.2 | 12.7 | 14.3 | 5.0 | 2.2 | 3.6 |
| Note: *Value in bracket is range All values are in $\mu\text{g}/\ell$ | | | | | | |

During October to December 1998 the raw water had a mean total Al of $380 \mu\text{g}/\ell$ compared to a mean value of $830 \mu\text{g}/\ell$ for September to November 1997 (Tables 6 and 7). This indicated that the total Al was highly variable between the two study periods. It was interesting to note that a comparison of raw and treated water characteristics indicates that during October to December 1998 raw water silica content (Table 3) was much less ($0.72 \text{ mg}/\ell$) than during September to November 1997 ($6.2 \text{ mg}/\ell$) implying that soil-bound Al silicate may be less available to contribute to raw water Al, and, therefore, lower raw water total Al values were observed during 1998. These variations in total Al are not surprising because Al concentration can be a very dynamic parameter in treated drinking water and can change quite rapidly with changes in raw water quality or with plant upsets or operational changes (Health Canada, 1996). Raw water total Al after alum addition increased 12 times (approximately) during October to December 1998. The difference (between raw water and after alum addition) in total Al was $1 182 \mu\text{g}/\ell$ less during October – December 1998 study period than September – November 1997 (Tables 6 and 7). A reduction in the applied alum dose during October to December 1998 ($55 \text{ mg}/\ell$) compared to September to November 1997 ($70 \text{ mg}/\ell$) was responsible for the decrease in total Al. During October to December 1998 alum addition nearly increased three times the inorganically bound Al (from the raw water level of $14 \mu\text{g}/\ell$ to $39 \mu\text{g}/\ell$ at the point

of alum addition) and such an increase remained relatively constant through the rest of the treatment plant (Table 7).

Al speciation – A comparison

Inorganically- and organically-bound Al levels at BPWTP (Tables 6 and 7) indicated that:

- alum addition increased inorganically-bound dissolved Al during October to December 1998 but not in September to November 1997;
- inorganically-bound Al thus formed was removed by sand filtration (approximately 10%), implying that fine Al hydroxide flocs that leave from clarifier are captured by the sand filtration leading to the removal of inorganically-bound Al;
- organic Al was the dominant form present in the dissolved Al during September to November 1997 whereas there was a shift in this condition, i.e. during October to December 1998, inorganic Al dominated in dissolved Al; and
- colloidal bound Al at clarifier was $15 \mu\text{g}/\ell$ higher during September to November 1997 compared to October to December 1998 (Tables 6 and 7).

However, such colloidal Al (over all) formed was removed largely during the subsequent unit processes, namely through filters which reduced their concentration in treated water to less than $5 \mu\text{g}/\ell$ (Table 4).

Al speciation study at the BPWTP (overall) indicated that:

- raw water total Al varied considerably;
- as expected, alum addition increased total Al levels;
- total, filterable (suspended) and particulate Al formed due to the use of alum was subsequently removed by clarifier and filtration (more than 90%); and
- particulate Al was the dominant species of total Al.

Role of GAC in dissolved Al removal at BPWTP

Figure 4 shows the percentage removals of particulate and dissolved Al at clarifier, sand filters and GAC units during September to November 1997 Al characterisation study period. As shown in Fig. 4, there was not much dissolved Al removal (less than 10%) by clarifiers and sand filters, respectively. Comparison of mean dissolved and organic Al values between sand - filtered effluent and GAC-filtered effluent showed that GAC was capable of removing 33% dissolved Al (Table 6 and Fig. 4). From data given in Table 6, it was calculated that 37% of the organic form of Al was removed by GAC unit.

Figure 5 shows the percentage removal of particulate and dissolved Al levels at clarifier, sand filters and GAC units during October to December 1998. As shown in Fig. 5, there was not much dissolved Al removal (less than 10%) at all stages, namely at clarifier, sand filters and GAC filtration. During both study periods, it was observed that GAC was capable of removing the organic fraction of dissolved Al. However, total dissolved Al removal during September to November 1997 (33%) was higher than October to December 1998 (9%) (Figs. 4 and 5). The difference in dissolved Al removal capability of GAC was due mainly to the composition of dissolved Al, i.e. during September to November 1997 dissolved Al was dominated by organic Al, whereas during October-December 1998 inorganically-bound Al was the dominant fraction of dissolved Al (Tables 6 and 7). This implies that GAC is capable of removing efficiently organic Al, but not inorganically bound Al.

Residual aluminium at BPWTP

Residual Al consists of particulate and dissolved forms of Al present in treated waters and enters into the water distribution system. Reduction in residual Al, as far as possible, would eliminate post-precipitation of Al in the form of $\text{Al}(\text{OH})_3$ during the distribution of the treated water, and reduction of residual Al would also enhance the quality of the treated water.

Aluminium speciation results (overall) of treated water supplied to Regina (clear well, Regina, Table 4) indicated that the residual Al consisted of 33% particulate Al. Speciation of dissolved Al into organic/inorganic Al differed considerably between the two Al characterisation periods. During September to November 1997, dissolved Al present in the clear well water of Regina was 76% in organic form. It was observed that the organic form of Al was the dominant form in dissolved Al during September to November 1997 (Table 6). During October to December 1998, dissolved Al speciation of clear well of Regina showed that organically-bound

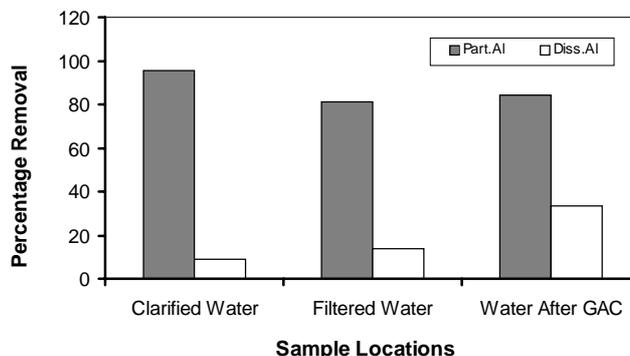


Figure 4

Particulate and dissolved Al removals at BPWTP during September to November 1997

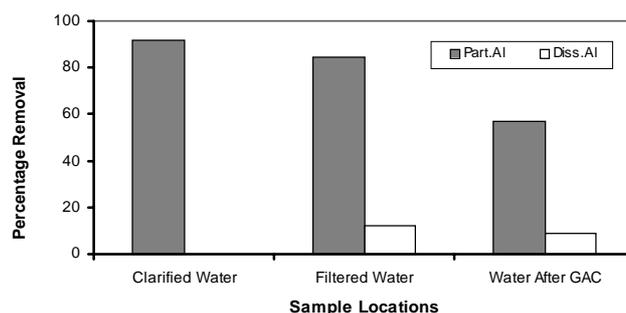


Figure 5

Particulate and dissolved Al removals at BPWTP during October to December 1998

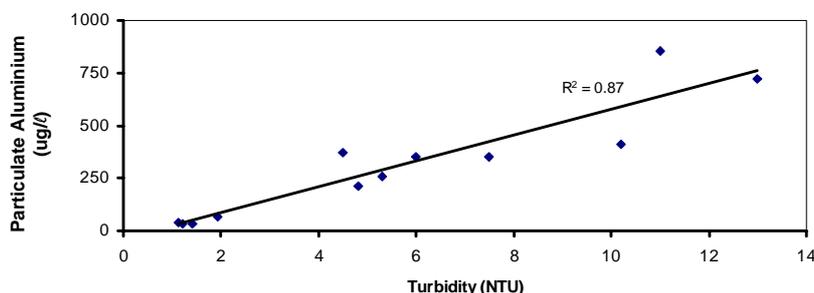


Figure 6

Mean monthly average particulate Al vs. turbidity (raw water) for 1996 to 1998

Al was only 17.5%, whereas inorganically-bound Al was 82.5%, indicating a shift in the distribution of organic/inorganic Al in dissolved Al speciation, compared to the distribution of organic/inorganic Al observed during September to November 1997 (Table 7). Aluminium characterisation studies demonstrated that particulate Al was a major species present in residual Al in treated waters at BPWTP and it is likely that both organic and inorganic dissolved species of Al could equally dominate in residual Al.

Particulate Al is derived mostly from turbidity-causing substances, and organic Al is the result of complexation of dissolved Al with dissolved organic matter. Data relating to mean monthly average values of raw water turbidity (NTU) and raw water particulate Al (for the year 1996, 1997 and 1998) were analysed by linear regression as shown in Fig. 6. Particulate Al correlated well

($R^2 = 0.87$) with turbidity. Raw water dissolved organic carbon of 8.4 mg/l was reduced to 3.9 mg/l in treated water after treatment during September to November 1997, resulting in 53% of dissolved organic carbon removal. The remaining 47% of the dissolved organic carbon available would combine with Al to give dissolved Al complexes in the form of organic Al. Even though a very similar DOC removal was observed (8.4 mg/l to 5.3 mg/l; 37% removal) (Table 3) during October to December 1998, organic Al was not the dominant form of dissolved Al, rather inorganic Al was the dominant form. Tables 6 and 7 show that raw water organic Al values in 1997 and 1998 were fairly similar. The big difference in 1997 occurred in the prechlorination and alum (addition) processes for reasons unknown. pH variations could be the likely cause of the differences observed. In spite of the fact that dissolved Al levels were less than 50 µg/l, efficient removal of dissolved organic carbon and proper usage of alum dose could further reduce the dissolved Al in the treated water. Recently 100 µg/l has been recommended as an operational - guideline value (for conventional water treatment plants) for Al in drinking water (Health Canada, 1999). Al speciation studies at the BPWTP indicated that the Al levels were less than the guideline value of 100 µg/l.

Conclusions

Characterisation of Al at BPWTP showed that raw lake water total Al concentrations were highly variable and that the filterable (suspended) form of Al was the predominant species of raw water total Al. Organically, Al appeared to be the predominant species of dissolved Al through (raw to treated) the BPWTP during September to November 1997. However, there was a shift in this condition during October to December 1998, i.e., inorganic Al dominated in dissolved Al. Alum addition (55 to 70 mg/l) efficiently coagulated filterable Al. The clarifier removed those in the form of $Al(OH)_3$ precipitate. Alum floc was effectively removed during clarification.

The present study showed that total Al after (liquid) alum treatment did not increase in treated water at BPWTP mostly because:

- alum coagulation was practised at pH 7, at which the Al is least soluble;
- clarifier and filtration units removed particulate Al efficiently (the major species of total Al); and
- GAC was also capable of removing part of the organic dissolved Al;
- total dissolved Al itself was less than 50 µg/l all through the plant; and
- turbidity and dissolved organic carbon of the raw water influenced the applied alum dose.

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