

## Practical Paper

### Monitoring aluminium after filtration

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#### ABSTRACT

Aluminium speciation was characterized to examine the changes after filtration, in drinking water systems with low ( $\leq 56 \mu\text{g l}^{-1}$ ) and high ( $> 100 \mu\text{g l}^{-1}$ ) aluminium concentrations at plant outlet. The treatment chemicals were also examined, and only lime showed significant aluminium contamination. This contamination varied from 0.4 to  $2.5 \mu\text{g mg}^{-1}$  and was largely water soluble (mean: 85%). The amounts of aluminium in lime added after filtration were equivalent to water concentrations ranging from 8.6 to  $34 \mu\text{g l}^{-1}$  (mean:  $17.5 \mu\text{g l}^{-1}$ ). By using the less contaminated lime supply, the aluminium concentration contributions could have been four times lower (mean:  $4.1 \mu\text{g l}^{-1}$ ). When determining the concentration differences between the effluents of one filtering unit and plant outlet, the aluminium changes at the nine low-aluminium plants were associated with lime addition, and were mostly detected in soluble form. The changes at the eight high-aluminium plants paralleled problems occurring at previous stages and were mostly attributed to variations occurring at additional filtering units. These situations prevented detection of other changes (e.g. post-precipitation). The monitoring of leachable particulate aluminium and of various parameters (pH, turbidity, Al–turbidity relationship) was also useful in differentiating particulate matter and demonstrating the effects of undesirable lime properties (dissolution delays, particulate residues).

**Key words** | additive contamination, drinking water treatment, lime, particulate aluminium, soluble aluminium, turbidity

#### INTRODUCTION

Concentration limits varying between 50 and  $200 \mu\text{g l}^{-1}$  have been recommended by different governmental or international organizations to control aluminium in drinking water (Driscoll *et al.* 1987; WHO 2004). In Canada, practical considerations resulted in recommended concentrations of  $100 \mu\text{g l}^{-1}$  for conventional systems and  $200 \mu\text{g l}^{-1}$  for other systems such as treatments using lime softening (Health Canada 1998). These operational goals recognize the need to minimize residual aluminium when large amounts of aluminium compounds are added to treat water. The main concerns behind these recommendations are problems caused by particulate aluminium in the distribution systems (Driscoll & Letterman 1995; Bérubé 2004) and possible

adverse health effects from chronic exposure to aluminium. These health effects depend on the solubility of the aluminium and its transport to biological tissues; this can explain why there are more demonstrations of health effects from drinking water than from other sources with greater oral intakes, such as solid foods or antacids (Gardner and Gunn 1995; Neibor *et al.* 1995; Yokel and Golub 1997). The demonstrations of adverse effects are, however, too weak to define health-based concentration limits, but current knowledge of aluminium neurotoxicity invites prudence (Yokel 2000). This is particularly so when considering that aluminium intake from drinking water has been linked to its presence in the brain as well as to effects in the brain (Walton *et al.* 1995; Flaten 2001; Campbell *et al.* 2004).

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Keeping in mind that other goals are also involved (e.g. control of pathogens or disinfection by-products; Health Canada 1998; Edzwald & Tobiason 1999), the operation of treatment plants with respect to the recommended values for aluminium requires good control of the coagulation process and of the subsequent filtration to remove the suspended particulate Al (Letterman & Driscoll 1994; Gregory *et al.* 2003; Becker *et al.* 2004). In addition, contaminants in chemicals used after filtration can contribute to residual Al. During a survey of Al in treatment plants (Lettermann & Driscoll 1988), some deliveries of lime were reported to have high Al content and to significantly increase Al concentration in treated water. Subsequently, it was recommended that the effect of lime addition be taken into account when optimizing residual Al (Lettermann & Driscoll 1994).

In a preceding paper, a fractionation method was used to characterize aluminium at sampling points located before and after filtration (Bérubé & Soucy 2004). This paper described the changes in soluble and particulate Al occurring in filtering units, and demonstrated ways to improve the understanding of problems in minimizing residual Al. The present paper describes the changes observed after filtration at the same Canadian surface water plants. The contamination of treatment additives is also investigated to define their contribution to Al species. These results put into perspective the Al concentrations obtained for finished water at the plant outlet.

## EXPERIMENTAL

The instrumentation, materials and methods have been previously described (Bérubé & Brûlé 1999; Bérubé & Soucy 2004). The sampling points were located after one of the filtering units (point AF), at the treatment plant outlet (point PO) and in the distribution system (points Di). The samplings were performed at the end of a filter run and at time intervals taking into account the flow-through time of the water in the systems. Parameters including temperature, pH and turbidity were recorded. The preserved samples (HNO<sub>3</sub> 0.18%) were generated by transfer in polypropylene vials pre-acidified at the laboratory. These samples were of three types:

(1) recoverable Al (r:Al), (2) acid leachable Al (l:Al), and (3) soluble Al (s:Al). For the s:Al samples, the transfer was preceded by an on-site syringe filtration (cellulose esters 0.45 µm, 25 mm, Millipore), after rinsing with sampling water. Before determinations by inductively coupled plasma mass spectrometer (ICPMS), supplementary preparations were performed in the laboratory. These were closed-vessel acid digestion for r:Al and, for l:Al, filtration of on-site acidified water after a minimum of one day. Subtractions between the sample types gave the amounts of particulate Al (p:Al = r:Al - s:Al) and leachable particulate Al (lp:Al = l:Al - s:Al).

The changes occurring between sampling points AF and PO were described by the values  $dr_{PO-AF}$  for recoverable Al (Equation 1) and  $ds_{PO-AF}$  for soluble Al (Equation 2).

$$dr_{PO-AF} = r:Al_{PO} - r:Al_{AF} \quad (1)$$

$$ds_{PO-AF} = s:Al_{PO} - s:Al_{AF} \quad (2)$$

As shown when rearranging Equation (3), the difference between the values  $dr_{PO-AF}$  and  $ds_{PO-AF}$  was equivalent to the difference between p:Al<sub>PO</sub> and p:Al<sub>AF</sub> (Equation 4).

$$\begin{aligned} dr_{PO-AF} - ds_{PO-AF} &= r:Al_{PO} - r:Al_{AF} - s:Al_{PO} + s:Al_{AF} \quad (3) \\ &= (r:Al_{PO} - s:Al_{PO}) - (r:Al_{AF} - s:Al_{AF}) \end{aligned}$$

$$dr_{PO-AF} - ds_{PO-AF} = p:Al_{PO} - p:Al_{AF} \quad (4)$$

For all equations, negative values were equivalent to decreases in Al concentration. For example, precipitation or adsorption of soluble Al to the pipe walls resulted in a negative value of  $ds_{PO-AF}$  in parallel with a negative value of  $dr_{PO-AF}$  of the same magnitude. The zero difference between these values implied no change in suspended particulate Al (Equation 4) and indicated a complete loss of this aluminium for the aqueous media. On the other hand, the occurrence of post-precipitation producing only suspended particulate Al resulted in a negative value of  $ds_{PO-AF}$  in parallel with a zero value of  $dr_{PO-AF}$ . The positive difference between these values implied the generation of suspended particulate Al (Equation 4), but did not represent a gain (or a loss) of aluminium for the aqueous media ( $dr_{PO-AF} = 0$ ).

Samples of the lime chemicals used by the treatment plants were also collected during this 1999 campaign. For the determination of the total Al content, 10–15 mg of the sample was digested with 3.5 ml of concentrated nitric acid. The closed vessel digestions were driven by a microwave power ramp of 20 min followed by a plateau of 10 min ( $P \sim 700$  kPa). Digestions were also performed after adding 0.4 ml of hydrofluoric acid to the nitric acid media. After cooling and dilution to 100 ml, the digestion solutions were determined by ICPMS. For comparison purposes, lime products were also shaken in  $\text{HNO}_3$  3.5% for 24 h. The resulting solutions were then filtered before ICPMS determinations. Similar methods were used for the other chemical products.

For the solubility experiments, lime was mixed with 1 l of distilled and deionized (DD) water in polypropylene bottles. Amounts from 5 to 50 mg were used to give concentrations similar to the lime dosage. After horizontal shaking at room temperature for 1 h (100 rpm, Precision Scientific, model 50), a first aliquot (25 ml) was filtered and acidified ( $\text{HNO}_3$  0.18%) before ICPMS determination. A second aliquot was similarly processed after 24 h. A third aliquot was taken at this same time, and was directly acidified prior to filtration one day later. The potential contribution to soluble Al ( $s:\text{Al}_{\text{lime}}$ ) was obtained by using the result of the second aliquot (after 24 h). The potential contribution to recoverable Al ( $r:\text{Al}_{\text{lime}}$ ) was obtained from the total Al content.

## RESULTS AND DISCUSSION

Table 1 lists the chemicals used to produce the finished water of the 17 treatment plants. These chemicals were generally added after filtration and are listed according to their use (e.g. disinfection, pH adjustment, fluoridation). No significant aluminium contamination was found in the hydrofluorosilicic acids ( $\text{H}_2\text{SiF}_6$ ), various sodium salts ( $\text{Na}_2\text{SiF}_6$ ,  $\text{NaOH}$ ,  $\text{NaF}$ ) or phosphate-based corrosion inhibitors.

### Aluminium in lime

As shown in Table 2, the examined lime products had Al contents in a range from 0.4 to  $2.5 \mu\text{g mg}^{-1}$  (mean =  $1.55 \mu\text{g mg}^{-1}$ ). Similar Al contents (range = 0.5 to  $3 \mu\text{g mg}^{-1}$ )

were reported for lime products examined over two decades ago (Boynton 1980). The present determinations were performed after microwave digestion in concentrated nitric acid, with or without the addition of supplementary hydrofluoric acid. The results in both experimental conditions were indistinguishable from each other, indicating the absence of particularly inert Al (e.g. aluminosilicate forms).

Water solubility experiments (Table 2) showed that a large fraction of the aluminium content was soluble after 24 h (mean = 85%; range = 71–107%). A large part of this soluble Al was in solution after 1 h (mean = 73%; range = 54–90%). These experiments resulted in solutions with basic pH ( $\sim 10$ ) and were considered to represent maximum Al solubility. The use of a weakly acid media ( $\text{HNO}_3$  0.18%) for one supplementary day generally did not succeed in completely dissolving the aluminium content (mean = 89%; range = 75–104%). Parallel trials in more concentrated nitric acid (3.5%, 24 h) gave quantitative dissolutions for most of the lime samples (mean = 96%; range = 85–108%). This last medium could dissolve aluminium associated with more resistant solid residues (e.g. iron oxide). These results indicate that a large part of the aluminium in the examined lime products could contribute to the soluble Al in finished water. The non-dissolved aluminium from lime could contribute to the leachable Al and the recoverable Al.

All lime products used at the sites, including those used at pre-treatment and coagulation stages, were examined and reported in Table 2. The lowest contamination levels were  $0.38 \mu\text{g mg}^{-1}$  in hydrated (H) lime ( $\text{Ca}(\text{OH})_2$ ) and  $0.47 \mu\text{g mg}^{-1}$  in quick (Q) lime ( $\text{CaO}$ ). Both chemical products were from the same supplier (Table 2) and were used before filtration: for pH adjustment at site #8 (Table 1) and for coagulation at site #12 (Table 2). If only these less contaminated supplies had been used at the seven sites adding lime after filtration (Table 3), the potential contributions to water concentrations would have been  $7.1 \mu\text{g l}^{-1}$  or lower (mean( $r:\text{Al}_{\text{lime}}$ ) =  $4.1 \mu\text{g l}^{-1}$ ). The potential contributions by the lime products actually used (Table 3) were, however, four times higher, varying from 8.6 to  $34 \mu\text{g l}^{-1}$  for recoverable Al (mean( $r:\text{Al}_{\text{lime}}$ ) =  $17.5 \mu\text{g l}^{-1}$ ) and 7.9 to  $26 \mu\text{g l}^{-1}$  for soluble Al (mean( $s:\text{Al}_{\text{lime}}$ ) =  $15.1 \mu\text{g l}^{-1}$ ). These potential contributions can represent large fractions

**Table 1** | Chemicals used to produce finished water and parameters at plant outlet

Site#	Disinfection	pH adjustment	Fluoridation	Others	T (°C)	pH
1	Cl <sub>2</sub>	Lime	–	–	1	7.3
2	NH <sub>3</sub> /Cl <sub>2</sub>	Lime	H <sub>2</sub> SiF <sub>6</sub>	–	0.8	7.7
3	ClO <sub>2</sub>	Lime	H <sub>2</sub> SiF <sub>6</sub>	PO <sub>4</sub>	1.4	7.7
4	Cl <sub>2</sub>	NaOH	H <sub>2</sub> SiF <sub>6</sub>	PO <sub>4</sub> (lime)**	12.0	7.5
5	Cl <sub>2</sub>	Lime	–	O <sub>3</sub>	6.1	7.5
6	ClO <sub>2</sub>	Lime	Na <sub>2</sub> SiF <sub>6</sub>	O <sub>3</sub>	1	7.9
7	NH <sub>3</sub> /Cl <sub>2</sub> *	–	Na <sub>2</sub> SiF <sub>6</sub>	–	25.6	6.8
8	Cl <sub>2</sub>	Lime*	NaF	–	18	7.1
9	Cl <sub>2</sub>	Lime*, Lime	–	–	10	7.5
10	Cl <sub>2</sub>	Lime	H <sub>2</sub> SiF <sub>6</sub>	(Lime)**	22.0	8.4
11	Cl <sub>2</sub>	–	–	–	4	7.0
12	NH <sub>3</sub> /Cl <sub>2</sub> *	CO <sub>2</sub> *	H <sub>2</sub> SiF <sub>6</sub> *	(Lime)**	4.0	8.1
13	Cl <sub>2</sub> *, NH <sub>3</sub>	–	Na <sub>2</sub> SiF <sub>6</sub> *	(Lime)**	6	8.9
14	Cl <sub>2</sub>	CO <sub>2</sub> *	Na <sub>2</sub> SiF <sub>6</sub>	(Lime)**	10.0	7.9
15	Cl <sub>2</sub>	–	H <sub>2</sub> SiF <sub>6</sub>	–	3.5	7.3
16	NH <sub>3</sub> /Cl <sub>2</sub> *	–	H <sub>2</sub> SiF <sub>6</sub>	–	12	7.5
17	NH <sub>3</sub> /Cl <sub>2</sub>	–	H <sub>2</sub> SiF <sub>6</sub>	–	1	7.8

\*Added immediately before filtration

\*\* Additional lime, used at pre-treatment or coagulation stages

of residual Al at point PO, especially when coagulation and filtration were successful in keeping Al at low levels. These fractions are shown in the first columns of Table 4 for the four low-Al ( $r:Al_{PO} \leq 56 \mu\text{g l}^{-1}$ ) and the three high-Al ( $r:Al_{PO} > 100 \mu\text{g l}^{-1}$ ) sites.

### Changes after filtration

Figure 1 displays the concentration differences observed between points AF and PO for recoverable Al ( $dr_{PO-AF}$ ) and soluble Al ( $ds_{PO-AF}$ ) at the nine low-Al sites ( $r:Al_{PO} \leq 56 \mu\text{g l}^{-1}$ ). For the five sites not using lime after filtration

(#4, #7, #8, #11 and #17),  $dr_{PO-AF}$  ranged from  $-4.9$  to  $+6.4 \mu\text{g l}^{-1}$  (mean =  $+0.32 \mu\text{g l}^{-1}$ ) and  $ds_{PO-AF}$  ranged from  $-3.3$  to  $+2.2 \mu\text{g l}^{-1}$  (mean =  $-0.18 \mu\text{g l}^{-1}$ ). Considering that point PO represented a combination of parallel filter effluents while point AF represented only one of these filter effluents, these positive and negative differences with mean values close to zero could be due to concentration variations in the parallel filter effluents.

The sites #5, #6, #9 and #10 added lime after filtration, and showed  $dr_{PO-AF}$  ranging from  $+7.9$  to  $+26 \mu\text{g l}^{-1}$  (mean =  $+14.3 \mu\text{g l}^{-1}$ ) and  $ds_{PO-AF}$  ranging from  $+4.3$  to  $+23 \mu\text{g l}^{-1}$  (mean =  $+10.1 \mu\text{g l}^{-1}$ ). These positive

**Table 2** | Al content and solubility of aluminium in lime products

Site#	Lime type*	Supplier#	Addition stage	Al content ( $\mu\text{g}/\text{mg}$ )	Soluble fraction (%)	
					After 1 h	After 24 h
1	H	1	After filtration	$1.64 \pm 0.05$	79	88
2	Q	1	After filtration	$1.42 \pm 0.47$	70	86
3	H	1	After filtration	$1.65 \pm 0.14$	90	107
4	H	3	Pre-treatment	$1.39 \pm 0.20$	66	75
5	H	1	After filtration	$1.74 \pm 0.15$	76	90
6	Q	1	After filtration	$2.24 \pm 0.44$	54	76
8	H	2	Before filtration	$0.38 \pm 0.11$	76	82
9	H	1	Before & after filtration	$1.71 \pm 0.15$	83	92
10	H	3	Pre-treatment & after filtration	$1.48 \pm 0.23$	67	80
12	Q	2	Coagulation	$0.47 \pm 0.15$	66	71
13	Q	2	Coagulation	$1.98 \pm 0.38$	76	87
14	Q	2	Coagulation	$2.51 \pm 0.57$	72	81

\*Q: Quicklime; H: Hydrated lime

differences were concordant with a lime effect. These gains were predominantly in the soluble form at sites #5, #9 and #10 ( $dr = ds$ ), whereas an increase in particulate Al was also observed at site #6 ( $dr > ds$ ). The Al forms were not defined for the lime effects reported in the literature (Driscoll *et al.* 1987; Lettermann & Driscoll 1988). However, in a private report obtained recently, one example of lime addition after filtration had been shown to result in an Al increase predominantly in the soluble form (Dixon *et al.* 1988).

The differences observed at the eight high-Al sites ( $r:\text{Al}_{\text{PO}} > 100 \mu\text{g}/\text{l}^{-1}$ ) are described in Figure 2. The potential contributions from lime addition at sites #1, #2 and #3 were in the range of  $14\text{--}16 \mu\text{g}/\text{l}^{-1}$  (Table 3) and, in comparison with the low-Al sites, represented smaller fractions of the residual Al at point PO (Table 4). The lime effects could also be more difficult to detect because of larger variations of the filter effluents. Thus, when lime was not added after filtration, differences were as high as

$150 \mu\text{g}/\text{l}^{-1}$  (site #12). When adding lime, the observed differences at site #3 (Figure 2) were 300 to 400% larger than the potential contributions (Table 4), while the small differences at site #2 were positive or negative. At site #1,

**Table 3** | Potential contribution of aluminium from lime added after filtration ( $\mu\text{g}/\text{l}^{-1}$ )

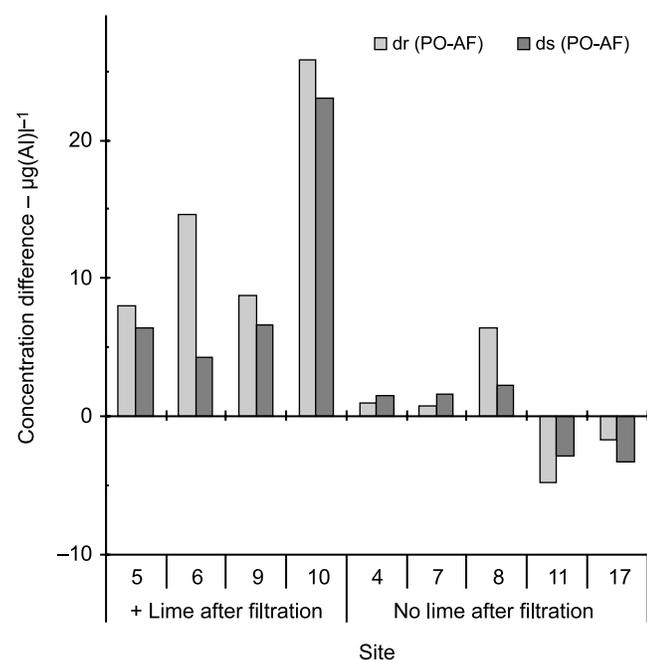
Site#	Using site supply		Using best supply	
	Recoverable	Soluble	Recoverable	Soluble
1	16.4	14.4	3.8	3.1
2	14.2	12.2	4.7	3.3
3	14.9	15.9	3.4	2.8
5	19.8	17.9	4.3	3.6
6	33.6	25.5	7.1	5.0
9	8.6	7.9	1.9	1.6
10	14.8	11.8	3.8	3.1

**Table 4** | Fractions (%) of the concentrations at point PO for the potential contributions and observed differences when adding lime after filtration

Site	Al levels	Potential contribution		Observed difference		Ratio Observed/Potential	
		r:Al <sub>lime</sub> /r:Al <sub>PO</sub>	s:Al <sub>lime</sub> /s:Al <sub>PO</sub>	dr <sub>PO-AF</sub> /r:Al <sub>PO</sub>	ds <sub>PO-AF</sub> /s:Al <sub>PO</sub>	dr <sub>PO-AF</sub> /r:Al <sub>lime</sub>	ds <sub>PO-AF</sub> /s:Al <sub>lime</sub>
5	Low <sup>a</sup>	43	47	17	17	40	36
6		94	123	41	21	43	17
9		26	33	27	28	102	84
10		27	26	46	50	174	195
1	High <sup>b</sup>	6	26	55	27	921	104
2		13	16	9	-9	64	-53
3		7	14	20	58	286	422

a: r:Al<sub>PO</sub> ≤ 56b: r:Al<sub>PO</sub> > 100 µg l<sup>-1</sup>

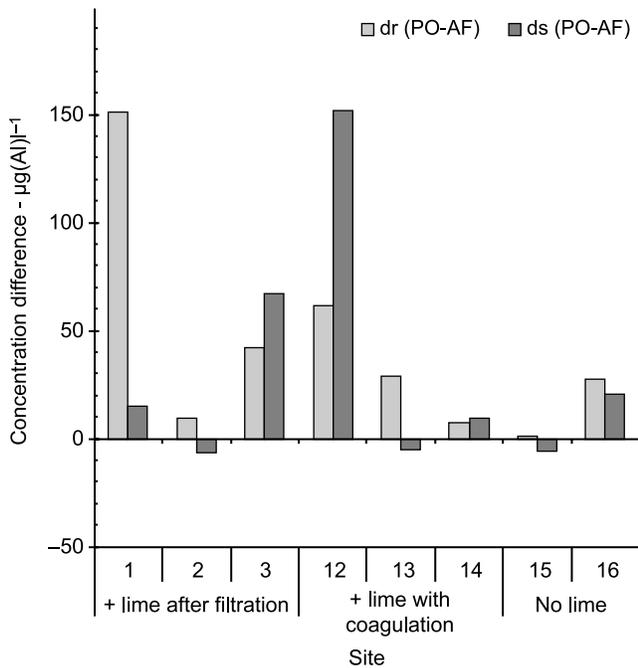
the increase in r:Al was also very large (dr<sub>PO-AF</sub> = +151 µg l<sup>-1</sup>; dr<sub>PO-AF</sub>/r:Al<sub>lime</sub> = 921%). However, the smaller increase in soluble Al (ds<sub>PO-AF</sub> = +15 µg l<sup>-1</sup>) could mostly be caused by lime (ds<sub>PO-AF</sub>/s:Al<sub>lime</sub> = 104%).

**Figure 1** | Concentration differences of recoverable Al (dr<sub>PO-AF</sub>) and soluble Al (ds<sub>PO-AF</sub>) for the nine low-Al sites (r:Al ≤ 56 µg l<sup>-1</sup>). The four sites adding lime after filtration are displayed first.

### Concentrations at plant outlet

When considering the concentrations in finished water at the plant outlet (Figure 3), most of the sites showed equivalent concentrations of recoverable Al and leachable Al (r:Al = l:Al). Only site #1 clearly showed the presence of non-leachable particulate aluminium (r:Al ≠ l:Al). The nine low-Al sites had low levels of both soluble Al (s:Al<sub>PO</sub> = 21–46 µg l<sup>-1</sup>) and particulate Al. The p:Al values (p:Al<sub>PO</sub> = r:Al<sub>PO</sub> - s:Al<sub>PO</sub>) were generally < 10 µg l<sup>-1</sup>, but were 15–18 µg l<sup>-1</sup> at sites #6 and #11. For site #11, the particulate Al was already present at point AF (dr = ds, Figure 1). For site #6, the change in particulate Al after point AF (dr > ds) could be due to non-dissolved aluminium from the quicklime used at this site. Another site (#2) used quicklime during the winter season and showed a similar behaviour (dr > ds, Figure 2). The quicklime used at site #2, however, showed higher Al solubility (70% after 1 h, Table 2) than the quicklime of site #6 (54% after 1 h). In addition to lime contamination, other possible explanations for the changes in particulate Al (dr > ds) were effluent variations, post-precipitation as well as Al adsorption on suspended particulate residues.

The next five sites in Figure 3 (#1, #2, #3, #15, #16) showed large amounts of both soluble Al (s:Al<sub>PO</sub> = 56–116 µg l<sup>-1</sup>) and particulate Al (p:Al<sub>PO</sub> = 32–216 µg l<sup>-1</sup>).



**Figure 2** | Concentration differences of recoverable Al ( $dr_{PO-AF}$ ) and soluble Al ( $ds_{PO-AF}$ ) for the eight high-Al sites ( $r:Al > 100 \mu g l^{-1}$ ). The three sites adding lime after filtration are displayed first.

For all these sites, particulate Al was already present at point AF. Thus, at site #1, the large change in p:Al ( $dr_{PO-AF} - ds_{PO-AF} = +136 \mu g l^{-1}$ , Figure 2) explained the PO value only in part ( $r:Al_{PO} - s:Al_{PO} = 216 \mu g l^{-1}$ , Figure 3). As described in the preceding paper (Bérubé & Soucy 2004), a deterioration of filtration effectiveness had occurred during the filter run. Such deteriorations were likely to largely vary between the different filtering units and to produce p:Al values even larger than those found in the effluent of the monitored filtering unit ( $p:Al_{AF} = 80 \mu g l^{-1}$ ). On the other hand, s:Al had remained at similar low levels during the filter run as well as before and after filtration, supporting the explanation that the observed value of  $ds_{PO-AF}$  at site #1 was not due to effluent variations but to lime addition.

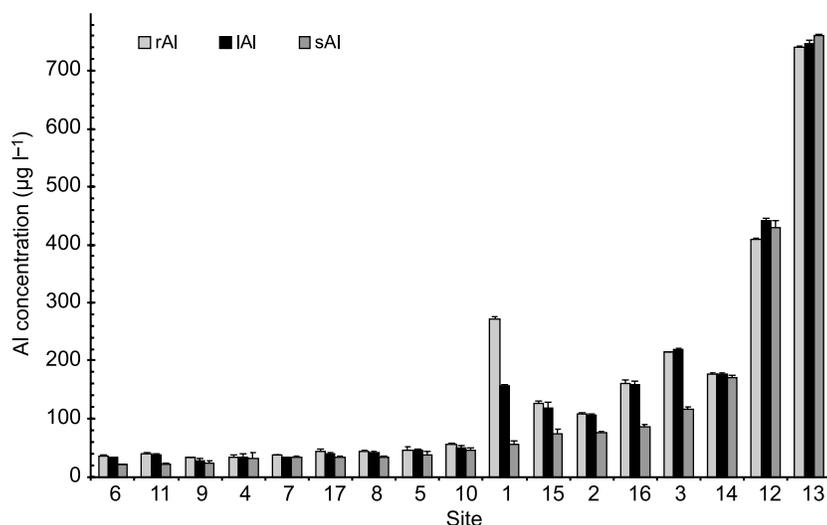
Other sites presented parallel findings. The large differences for both  $dr_{PO-AF}$  and  $ds_{PO-AF}$  at sites #3 and #12 also coincided with problems at filtration stages (floc detachment, Al dissolution) producing large deteriorations during the filter run. The smaller differences for sites #2 and #15 also coincided with filtration problems but, in contrast to sites #1, #3 and #12, these problems had not resulted in

large deteriorations during the filter run and were therefore less likely to produce large variations between the filter effluents. The differences at site #16 involved mainly soluble Al ( $dr = ds$ ) and paralleled large decreases in soluble Al occurring in the filtering unit (Bérubé & Soucy 2004). The largest differences described in Figure 2 therefore originated more from variations produced at filtration stages than from changes occurring between points AF and PO.

All comparisons of points AF and PO suffered from their dependence on the stability of the treatment systems. The monitoring of only one filtering unit created difficulties in defining the Al changes as well as species interchanges such as post-precipitation. Such situations could also explain why, even when a good control was achieved at the low-Al sites, the ratios of the observed differences to the potential contributions were in a wide range, from 17% (#6) to 195% (#10) (Table 4). In the case of site #10, large variations in soluble Al measured before filtration had already been noted during the filter run in the previous paper (Bérubé & Soucy 2004). It had also been noted that these large variations were observed when lime was used at the pre-treatment stage (sites #4 and #10).

### Lime properties

Lime properties also could affect the fractions in solution or in suspension at point PO. Dissolution delays and the occurrence of particulate residues were demonstrated by the solubility experiments (Table 2). A supplementary sampling series had also been performed at site #2 in the summer ( $T_{PO} = 21^\circ C$ ), and included sampling points located in the distribution system. In Figure 4a, the same treatment resulted in r:Al levels between 53 and 66  $\mu g l^{-1}$  at distribution points with flow-through time of 8 hours (D1, D2), 2 days (D3, D4), and 8 days (D5). The speciation at these points remained similar, most of the aluminium being present as soluble Al (mean( $r:Al$ ) = 59.8  $\mu g l^{-1}$ ; mean( $s:Al$ ) = 55.0  $\mu g l^{-1}$ ). Immediately after filtration (point AF), the Al concentrations were lower (35–38  $\mu g l^{-1}$ ). When comparing with point PO,  $dr_{PO-AF}$  and  $ds_{PO-AF}$  had positive values of 13–15  $\mu g l^{-1}$  and implied mostly changes in soluble Al. Lime addition can explain these differences as well as the increases in turbidity

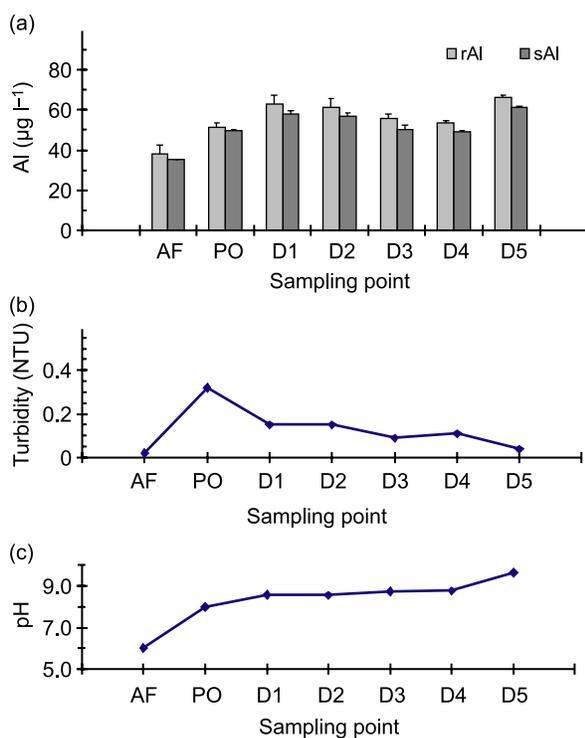


**Figure 3** | Concentrations of recoverable Al (r:Al), leachable Al (l:Al) and soluble Al (s:Al) measured at sampling point PO. The sites are placed in order of increasing s:Al concentrations.

(Figure 4b) and pH (Figure 4c). Delayed effects of lime were also apparent in the distribution system, where the Al concentrations and pH continued to increase at the first sampling points while the turbidity decreased but remained higher than at point AF.

In Figure 5, the correlation between turbidity and particulate Al (p:Al) was better after removal of the data involving lime at plant outlet. The resulting relationship was attributable to floc residues since the particulate Al of the remaining data showed the leachability behaviour of aluminium flocs ( $l:p:Al = p:Al$  or  $l:Al = r:Al$  in Figure 3) (Van Benschoten & Edzwald 1990; Koether *et al.* 1997; Bérubé 2004). In most of the cases, lime had generated a turbidity larger than expected by this relationship, because the Al content of its residual particulate matter was low. For site #1, lime and an additional type of suspended particulate matter were involved. The presence of this additional type of particle was detected by large amounts of non-leachable particulate Al ( $l:Al \neq r:Al$  in Figure 3). Particulate matter presenting poor aluminium leachability can have a high Al content (Driscoll & Letterman 1995; Bérubé 2004). This could explain the result of site #1: that is, a turbidity lower than expected by the relationship attributed to floc residues. For sites #1 and #3 in Figure 5, lime effect on turbidity apparently was not predominant.

In addition to factors intrinsic to the lime products (e.g. origin, particle size, hydration), the operational conditions can influence the lime effects described in Figures 4 and 5. The handling (e.g. pre-mixing of lime) and stirring



**Figure 4** | Results for aluminium fractionation (a) performed in triplicate as well as turbidity (b) and pH (c) readings along a drinking water system adding lime after filtration (site #2).

(e.g. pumping parameters) could be important factors but their impacts were not examined in this survey. The uncertainties associated with lime properties, the monitoring of only one filtration unit and the limited number of observations preclude drawing conclusions about the effects of parameters such as temperature or pH of finished water.

The turbidity problems caused by lime can be minimized by improving sedimentation or adding lime as a saturated solution (AWWA 1995). The addition of lime just before filtration is a supplementary option. This was performed at site #8 and, in part, at site #9. However, the changes caused by lime contamination were not determined. Similarly, there was no determination of the changes caused by lime softening performed at the coagulation stages of sites #12, #13 and #14. For these three sites, the resulting large concentrations of soluble Al ( $s:Al_{PO} = 171\text{--}760\ \mu\text{g l}^{-1}$ , Figure 3) with low amounts of particulate Al ( $r:Al = s:Al$ ) were explained by the high pH caused by lime addition (Bérubé & Soucy 2004). This soluble Al could originate from both Al compounds and lime and, once in solution after the coagulation stages, was not prevented from crossing the filtration media and reaching point PO as well as the distribution system. Similarly, when mixing lime with water for pH adjustment before or after filtration, the generation of high pH conditions should favour the

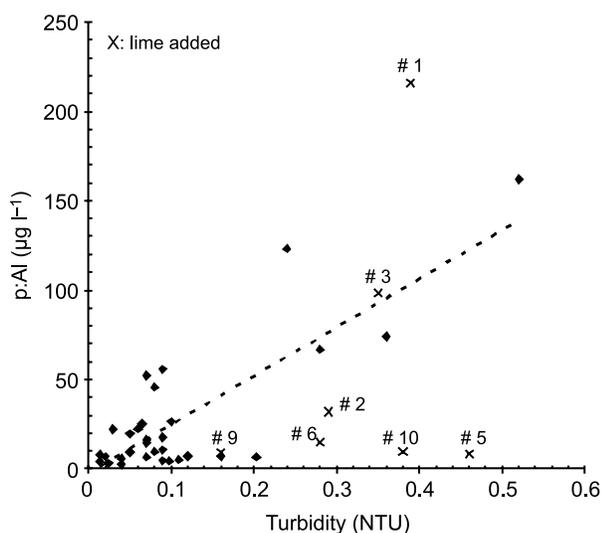
production of soluble Al and the likelihood of reaching the distribution system.

## CONCLUSIONS

Solubility experiments on lime products showed large fractions of potentially soluble Al. Digestion experiments showed the absence of inert aluminium in these lime products. The results also indicated that the Al content of lime was high and could vary over nearly an order of magnitude. A considerable reduction of the potential contributions to residual aluminium was possible by choosing the best sources of lime. An appropriate choice of lime products or alternative chemicals could ease the attainment of low residual aluminium concentrations.

When the main processes of coagulation and filtration were well controlled and resulted in low levels of residual aluminium, it was possible to detect the effects of lime contamination by using the differences  $dr$  and  $ds$ . These effects were mostly in the form of soluble Al ( $dr = ds$ ). The parallel between  $dr$  and  $ds$  also allowed detection of changes in particulate Al species ( $dr \neq ds$ ). These results complemented a previously reported survey focusing on the changes occurring inside one filtering unit per treatment plant. The absence of data on the additional filter effluents created uncertainties for the determination of the changes after filtration. Further study of Al changes after filtration should involve all filter effluents. More attention should also be given to the influence of the conditions of lime use because lime properties, such as dissolution delays and particulate residuals, can be sources of variability.

Aluminium fractionation was used to characterize aluminium speciation by determining soluble Al ( $s:Al$ ), particulate Al ( $r:Al$ - $s:Al$ ) and the leachability of particulate Al ( $r:Al$  vs.  $l:Al$ ). In situations involving only floc residues ( $r:Al = l:Al$ ), the fractionation results allowed a determination of a relationship between the concentration of suspended flocs and turbidity. Discrepancies from this relationship could help to demonstrate the presence of lime residues or other particulate residues presenting Al content differing from aluminium flocs. It is also noteworthy that the levels of  $r:Al$  and  $l:Al$  were equal for most of the sites. After ensuring that  $r:Al$  and  $l:Al$  are equal, monitoring using



**Figure 5** | Particulate aluminium (p:Al) concentration versus turbidity measured at sampling points AF and PO. The correlation ( $r^2 = 0.36$ ;  $y = +161x + 4.2$ ) was better after elimination of data points  $\times$  at plant outlet involving lime addition ( $r^2 = 0.66$ ;  $y = +273x - 2.7$ ).

the simpler l:Al determination should result in the same information.

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## NOTATION

AF	sampling point after filtration
Di	sampling point i (i = 1, 2, 3, etc) in the distribution system
Cl <sub>2</sub>	chlorine
ClO <sub>2</sub>	chlorine dioxide
CO <sub>2</sub>	carbon dioxide
dr	difference in recoverable Al
dr <sub>PO-AF</sub>	dr between sampling points PO and AF, $dr_{PO-AF} = r:Al_{PO} - r:Al_{AF}$
ds	difference in soluble Al
ds <sub>PO-AF</sub>	ds between sampling points PO and AF, $ds_{PO-AF} = s:Al_{PO} - s:Al_{AF}$
H	hydrated lime (Ca(OH) <sub>2</sub> )
H <sub>2</sub> SiF <sub>6</sub>	hydrofluorosilicic acid
l:Al	(total) acid leachable Al
Na <sub>2</sub> SiF <sub>6</sub>	sodium fluorosilicate
NaOH	caustic soda
NaF	sodium fluoride
NH <sub>3</sub>	ammonia
PO	sampling point for treated (finished) water at the plant outlet
O <sub>3</sub>	ozone
p:Al	particulate Al (p:Al = r:Al - s:Al)
PO <sub>4</sub>	phosphate based corrosion inhibitor
Q	quicklime (CaO)
r:Al	(total) recoverable Al
r:Al <sub>x</sub>	(total) recoverable Al at sampling point x (AF, PO or Di)
r:Al <sub>lime</sub>	potential contribution from lime contamination
s:Al	(total) soluble Al
s:Al <sub>x</sub>	(total) soluble Al at point AF, PO or Di
s:Al <sub>lime</sub>	potential contribution in soluble Al from lime contamination

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