Operational Paper

Monitoring aluminium before and after filtration

Denis Bérubé and Mark Soucy

ABSTRACT

Fractionation analysis was used to examine treated water before and after filtration at 17 drinking water plants performing aluminium coagulation. Before the filtering units, soluble Al (s:Al) was ≤150 µg/l, except for the three plants also using lime softening. Particulate Al (p:Al) was completely acid leachable, except for two plants. Concentrations before and after filtering units indicated changes in s:Al for many plants. These changes ranged from +42 to −88 µg/l, affected the Al filtration balance and implied reactions occurring in the filter media. These reactions could also generate residual p:Al. Without s:Al change, only problems of filtration effectiveness were likely to cause residual p:Al. After the filtering units, s:Al remained >150 µg/l when using lime softening. When using only alum or polyaluminium chloride, s:Al was ≤80 µg/l. Decreases in s:Al across filtering units occurred for both coagulants and produced s:Al <40 µg/l. Factors influencing equilibria and rates of treatment processes (e.g. pH, temperature, plant design) could explain the s:Al results. Increases in s:Al or partially leachable p:Al were associated with performance deteriorations producing high residual p:Al at the end of filter runs. Residual p:Al contributed to give concentrations >100 µg/l at five plants. The different behaviours constituted supplementary information to optimise plant operation.

Key words | coagulation, filtration balance, fractionation analysis, particulate aluminium, soluble aluminium, water treatment

INTRODUCTION

Aluminium compounds are widely used to perform coagulation in drinking water treatment. Their use however is not without potential problems. High concentrations of aluminium in distribution systems can cause high turbidity, pipe wall deposits and disinfection inhibition (Letterman & Driscoll 1988). Health problems such as neurological disorders have also been associated with the presence of aluminium in drinking water (Health Canada & USEPA 1997; Exley 2001). All these concerns dictate that residual aluminium should be kept at a minimum level. The regulations and guideline values established by different national or international organizations vary between 50 and 200 µg/l (Driscoll & Letterman 1995). In Canada, operational guidance values have been established at 100 µg/l for conventional treatment plants, and 200 µg/l for plants using other processes such as alum coagulation accompanied by lime softening (Health Canada 1998).

Past studies based on determinations of various aluminium species have resulted in a better understanding of the main factors influencing the residual concentrations in distributed water (Driscoll & Letterman 1988; Van Benschoten & Edzwald 1990; Driscoll & Letterman 1995). In many instances, residual soluble concentrations have shown good agreement with predictions by solubility equilibria depending on pH and temperature (Hayden & Rubin 1974; Van Benschoten & Edzwald 1990b; Van Benschoten et al. 1994; Pernitsky & Edzwald 2003). These works have contributed to improving the minimization of residual aluminium and to defining procedures based on
the control of pH and filtration (Driscoll et al. 1987; Letterman & Driscoll 1994). It is difficult to add to this general approach because aluminium coagulation depends on numerous other factors including the water composition (Letterman & Vanderbrook 1983; Edzwald 1993; Eikebrokk 1999; Srinivasan et al. 1999) or the time intervals used for the treatment processes (Jekel & Heinzmann 1989). Factors specific to the treatment plants, such as seasonal variations or plant design, can affect the ease with which residual aluminium can be controlled. The municipal treatment plants have in addition to meet other objectives such as removing TOC (Edzwald & Tobiason 1999).

Aluminium fractionation was used in the present study as a monitoring tool. Determinations were performed along the treatment sequence to describe the concentration changes of aluminium species. These methodologies can detect anomalies in the treatment processes and improve the understanding of the origin of residual aluminium. The following describes the results obtained during a monitoring exercise performed before and after filtering units at 17 Canadian treatment plants using aluminium coagulation under various conditions.

**METHODS**

**Materials and instrumentation**

Polypropylene vials (Sarsted, 50 ml), syringes (Millipore, 50 ml) and beakers (Nalgene, 1 l) were soaked in 1% HNO₃ (24 h) and rinsed with water before use in the sampling kits. Ultrapure nitric acid (Seastar) and distilled deionized (DD) water (≥18.2 Mohm) were used. Polystyrene-encapsulated membranes of cellulose esters (Millipore, 0.45 µm, 25 mm) were used for syringe filtration. A Floyd microwave oven (RMS-150) was used for digestion and a Perkin Elmer (Sciex/Elan 5000a) Inductively Coupled Plasma Mass Spectrometer (ICPMS) was used for measurement of Al. The calibration and spiking solutions were from High Purity Standards. Accuracy checks were performed with the Certified Reference Materials #1643d from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) as well as #TM27 and #TMDA51 from NWRI (National Water Research Institute, Burlington, Ontario, Canada).

**Aluminium fractionation**

The method has been previously described (Bérubé & Brulé 1999). The fractionation analysis focussed on measuring three sample types (Scheme 1): (1) soluble Al (s:Al), (2) acid leachable Al (l:Al), (3) recoverable Al (r:Al). In the field, these sample types were generated in triplicate by filling pre-acidified vials (HNO₃ 18%, 0.5 ml). The s:Al samples were generated by syringe filtrations directed into the pre-acidified vials. The syringe filtrations were performed after rinsing of the filter assembly (syringe and membrane filter) with sampling water. In the laboratory, a syringe filtration of the samples acidified in the field (HNO₃ 0.18%) completed the preparation of l:Al samples. An acid digestion (HNO₃ 7%) with microwave heating in a teflon closed vessel completed the preparation of r:Al samples. The concentrations of the three sample types were determined by ICPMS. Control measurements were within the values previously described (digestion and field blanks <2 µg/l, travelling blanks <0.8 µg/l).

In addition to the soluble fraction, two supplementary fractions were calculated by differences between the sample types. In Equation 1, the differences between r:Al and s:Al gave the amounts of particulate Al (p:Al). Similarly, in Equation 2, the differences between l:Al...
and $s:Al$ gave the amounts of leachable particulate Al $(lp:Al)$.

$$p:Al = r:Al - s:Al$$  \hspace{1cm} (1)$$lp:Al = l:Al - s:Al$$  \hspace{1cm} (2)

**Sampling**

The 17 treatment plants listed in Tables 1 and 2 were from different locations across Canada and had flow rates from 10 to 180 Ml/day, serving populations from 25,000 to 400,000. The samplings were performed from January to July 1999, with one exception. For this plant (site #4), the sampling had to be postponed because of repairs to the treatment plant, and was performed in October. In Table 1, sites #1 to #11 used alum as coagulant, sites #12 to #14 used alum with lime softening, and sites #15 to #17 used polyaluminium chloride (PACl). The sampling kits were made at the Health Canada laboratory in Ottawa and included a questionnaire to record on-site parameters as well as a protocol for sampling and shipping. The

**Table 1** | Chemicals used before filtration

<table>
<thead>
<tr>
<th>Site #</th>
<th>Coagulant</th>
<th>Type(^b) of coagulant aids</th>
<th>Sequence (coagulant addition as reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Earlier</td>
<td>With</td>
</tr>
<tr>
<td>1</td>
<td>Alum</td>
<td>i (-)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Alum</td>
<td>i (-)</td>
<td>Cl₂</td>
</tr>
<tr>
<td>3</td>
<td>Alum</td>
<td>i (-)</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Alum</td>
<td>o (-)</td>
<td>KMnO₄, lime</td>
</tr>
<tr>
<td>5</td>
<td>Alum</td>
<td>o (+)</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Alum</td>
<td>i (-)</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Alum</td>
<td>i (-) &amp; o(-)</td>
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<td>Alum</td>
<td>i (-) &amp; o(n)</td>
<td>-</td>
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<tr>
<td>10</td>
<td>Alum</td>
<td>o (n)c</td>
<td>KMnO₄, lime</td>
</tr>
<tr>
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</tr>
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<td>Alum (lime)</td>
<td>-</td>
<td>KMnO₄</td>
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<td>14</td>
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</tr>
<tr>
<td>15</td>
<td>PACl</td>
<td>-</td>
<td>Cl₂</td>
</tr>
<tr>
<td>16</td>
<td>PACl</td>
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<td>-</td>
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<tr>
<td>17</td>
<td>PACl</td>
<td>o (-)</td>
<td>KMnO₄</td>
</tr>
</tbody>
</table>

\(^a\)The abbreviations are defined in the Notation.
\(^b\)The charge is given in parentheses.
\(^c\)Not in use at the time of sampling.
personnel at the different sites were instructed to perform the sampling during a period of normal operation. The sampling points were located before (point BF) and after (point AF) one filtering unit (Scheme 2). This filtration unit had to be selected among several filtering units in use at the plants (Table 2). The sampling points were usually existing taps located in the laboratory or elsewhere in the plant. However, for many samplings before the filtering unit, samples had to be collected at the top of the filtering unit.

The sampling was performed in two series (1 and 2) of sampling sessions. The samplings of series 1 (sampling sessions BF1 and AF1) were performed at times as close as possible after a filter backwash, i.e. after the backwash and the return to service. For series 2 (sampling sessions BF2 and AF2), the samplings were replicated at points BF and

Table 2
<table>
<thead>
<tr>
<th>Site #</th>
<th>Treatment type</th>
<th>Sedimentation type</th>
<th>Filter media</th>
<th>Number of filtering units</th>
<th>Filter run period (h)</th>
<th>Filter rate (m/h)</th>
<th>Time of first sampling (h)</th>
<th>Tb (°C)</th>
<th>pH b</th>
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</thead>
<tbody>
<tr>
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<td>Up</td>
<td>s</td>
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<td>65</td>
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<td>0.5</td>
<td>1</td>
<td>6.1</td>
</tr>
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<td>0.8</td>
<td>6.1</td>
</tr>
<tr>
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<td>Up</td>
<td>s, a</td>
<td>5</td>
<td>197</td>
<td>3.2</td>
<td>0.5</td>
<td>1.4</td>
<td>6.1</td>
</tr>
<tr>
<td>4</td>
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<td>Up</td>
<td>g, s, a</td>
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<td>87</td>
<td>6.2</td>
<td>3.5</td>
<td>12.0</td>
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<td>Up</td>
<td>s</td>
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<td>3.9</td>
<td>4.0</td>
<td>4.1</td>
<td>6.5</td>
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<td>3.9</td>
<td>1.0</td>
<td>1</td>
<td>6.6</td>
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<tr>
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<td>Up</td>
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<td>5</td>
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<td>9.2</td>
<td>0.5</td>
<td>25.5</td>
<td>6.9</td>
</tr>
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<td>Conv</td>
<td>Up</td>
<td>s, a</td>
<td>4</td>
<td>160</td>
<td>5.2</td>
<td>0.5</td>
<td>18</td>
<td>7.0</td>
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<td>13</td>
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<td>—</td>
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<td>55</td>
<td>4.5</td>
<td>1.0</td>
<td>21.8</td>
<td>6.3</td>
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<tr>
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<td>—</td>
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<td>30</td>
<td>5.0</td>
<td>3.0</td>
<td>4</td>
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<tr>
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<td>Ho</td>
<td>s, a</td>
<td>9</td>
<td>30</td>
<td>4.9</td>
<td>1.0</td>
<td>4.0</td>
<td>8.0</td>
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<tr>
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<td>Soft</td>
<td>Up</td>
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<td>48</td>
<td>5.7</td>
<td>0.5</td>
<td>5</td>
<td>8.8</td>
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<td>Soft</td>
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<td>1.0</td>
<td>10.6</td>
<td>9.7</td>
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<td>Ho</td>
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<td>0.5</td>
<td>2.0</td>
<td>7.5</td>
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<tr>
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<td>35</td>
<td>3.9</td>
<td>0.5</td>
<td>10</td>
<td>7.6</td>
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<tr>
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<td>Up</td>
<td>s, a</td>
<td>12</td>
<td>90</td>
<td>5.2</td>
<td>25.0</td>
<td>1</td>
<td>7.8</td>
</tr>
</tbody>
</table>

a The abbreviations are defined in the Notation.
b These values are for sampling session AF2.
c This site used a plates and tubes system; the other sites used sludge blanket systems.
AF, at times as close as possible before the next filter backwash. The first sampling series was generally performed within 4 h after the return to service (median 1.0 h), except at sites #9 and #17 where sampling series 1 was performed 1 day later (Table 2). The samplings generally covered more than 87% of the filter run periods, which lasted between 19 h and 8 days (Table 2). In 4 cases (#1, #5, #9, #17), only 53–74% of the filter run period was covered by the sampling sessions. A fifth sampling session PO2 was also performed on finished water to complete sampling series 2. The sampling point PO was located at the outlet of the plant, after combination of all filter effluents. The time intervals between the sampling sessions of the same series took into account the flow-through time of the water in the treatment system.

**Changes inside filtering units**

The changes occurring in the filtering units were described by taking as a reference the value of soluble Al at sampling point BF, i.e. ‘s:Al(BF)’. The changes in s:Al were determined by the value ‘dS’, defined as the difference between the s:Al concentrations in the effluents (sampling point AF) and the influents (sampling point BF) of the filtering units. The values dSx for the different sampling series ‘x’ (dS1 and dS2) were calculated by using Equation 3. From Equation 3, negative values of dSx were equivalent to decreases in s:Al as the water flowed through the filtering units. An additional value ‘dF’ was used to include the presence of p:Al in the effluents of filtering units. The value dFx was the difference between recoverable Al after the filtering units ‘r:Al(AFx)’ and the same reference soluble Al before the filtering units ‘s:Al(BFx)’ (Equation 4).

\[
dS_x = s:Al(AF_x) - s:Al(BFx)
\]

\[
dF_x = r:Al(AF_x) - s:Al(BFx)
\]

In addition to indicating the presence of residual particulate Al when compared with dSx, the value dFx constituted an aluminium balance of the filtration. Thus, the value dFx was the sum of the positive contribution of residual particulate Al ‘p:Al(AFx)’ and of the negative, null or positive changes in s:Al inside the filtering units (Equation 5). In terms of minimization of aluminium, this value constituted a measure of the overall performance of the filtering units.

\[
dF_x = dS_x + p:Al(AFx)
\]

**RESULTS AND DISCUSSION**

Figure 1a presents measurement results for recoverable Al (r:Al), leachable Al (l:Al) and soluble Al (s:Al) at each of the five sampling sessions performed at site #7. The concentrations of l:Al and r:Al in the filter influents (sampling sessions BF1 and BF2) were high compared to s:Al, because large amounts of suspended particulate Al were present in coagulated water of these filter influents. After subtraction of s:Al (Equations 1 & 2), the similarity of p:Al and l:Al (Figure 1b) also indicated that the particulate Al was completely leachable in the conditions of weak acidity (1.5<pH<2) used to generate the l:Al samples. This is the behaviour normally observed for fresh aluminium flocs (Van Benschoten & Edzwald 1990a).

The filter effluents (sampling sessions AF1 and AF2) showed similar concentrations for the three sample types, indicating that the measured aluminium was completely
soluble (Figure 1a). As may be expected for filtration, the particulate Al (p:Al and lp:Al, Figure 1b) was entirely removed and only the soluble Al passed through the filter media. As shown in Figure 1c, there was no change in soluble Al (dS = 0, Equation 3). Furthermore, there was no deficit or excess in the Al filtration balance (dF = 0, Equation 4) because particulate Al was also absent in the filter effluents (Equation 5). For the plant effluent (sampling session PO2), the soluble Al remained the predominant form and its concentration was similar to the low levels (<40 µg/l) measured in the influents and effluents of the filtering unit.

The results described in Figure 1 were as expected when the coagulation processes are well controlled and the filter performance is normal. Conversely, in Figure 2 (site #1), the results at BF1 and BF2 showed large differences between the measured values l:Al and r:Al (Figure 2a). As shown in Figure 2b, this was due to the fact that p:Al was not completely leachable (lp:Al $\neq$ p:Al). The sampling session AF2 also showed the presence in the filter effluent of a large amount of non-leachable particulate Al. The observation of partly leachable p:Al in both the influent and effluent of the filtering unit denoted poor filtration effectiveness at sampling series 2. In parallel, s:Al remained in a narrow range (dS2 = −1 µg/l, Figure 2c), indicating that the unsatisfactory filtration performance (dF2 = +79 µg/l) was mostly due to the presence of residual particulate Al in the filter effluent. The problems of filtration effectiveness apparently were worse for the additional three filtering units of this treatment plant (Table 2), p:Al increasing from p:Al(AF2) = 80 µg/l immediately after the monitored filtering unit to p:Al(PO2) = 116 µg/l at the plant outlet.

Concentrations before filtering units

In Figure 2 (site #1), the leachable p:Al (lp:Al) represented p:Al fractions (lp:Al/p:Al) of 0.64 (BF1) and 0.55 (BF2). Site #14 also showed partly leachable p:Al before the filtering unit [lp:Al/p:Al = 0.37 (BF1), 0.47 (BF2)]. The presence of non-leachable particulate Al was likely to originate from raw water and to indicate that the coagulation processes were not effective in removing natural
turbidity. The three sites using PACl as coagulant (#15 to #17), nine sites using alum (#2 to #5, #7 to #11) and one site using alum with lime softening (#12) (see Note (1)), all showed particulate Al with $l:p:Al$ between 0.89 and 1.09. These sites can be considered to have demonstrated good coagulation control by removing natural

In Figure 3, the three sites using alum with lime softening presented the highest $s:Al$ concentrations (180–840 µg/l) and the highest pH values (7.9–10.1) before the filtering unit. In all cases, lime had been added after alum to meet the additional objective of water softening. Such practices are known to create difficulties in controlling aluminium because the large increase in pH interferes with aluminium precipitation (Health Canada 1998). Sites #12 and #14 used recarbonation after lime addition and before the filtering unit (Table 1). The pH values measured before as well as after the filtering unit however remained too high ($pH \geq 7.9$) (see Note (2)). The other site (#13) did not perform recarbonation and presented the highest $s:Al$ levels.

The three sites using PACl showed $s:Al$ concentrations between 53 and 148 µg/l (mean = 86 µg/l). The pHs ranged from 7.6 to 7.9, and are within the range of pH values usually observed for PACl coagulation (Simpson et al. 1988; Van Benschoten & Edzwald 1990b). The additional nine sites described in Figure 3 used only alum and exhibited particulate Al with the leachability of fresh flocs. Their $s:Al$ concentrations were between 18 and
104 µg/l (mean = 49 µg/l). For one site (#8), small amounts of lime had been added, after alum and before sampling point BF. This addition was not for the purpose of softening but of pH adjustment. The pH values were 7.5 (BF1) and 7.1 (BF 2), while the s:Al levels remained <40 µg/l. The pH of the other sites ranged from 5.6 to 7.0, in agreement with values generally achieved for alum coagulation (Faust & Aly 1999; Letterman et al. 1999). However, many confounding factors can also overwhelm the effect of temperature. For example, the extent to which the plants implemented winter practices, by changing water flow or pH adjustment, can be important. The trend witnessed for s:Al could just reflect the fact that important seasonal variations create larger changes in optimal conditions and therefore more difficulties in controlling aluminium levels.

As illustrated in Figures 1, 2 and 3, the sessions BF1 and BF2 generally showed similar Al concentrations for samplings performed at intervals of one to several days. The differences between series 1 and 2 averaged 9% (range 2–34%) for r:Al. For s:Al, the differences averaged 12% (range 1–37%) when excluding two sites using carbonation at the time of alum addition (Table 1). These sites presented s:Al in a range of 18–43 µg/l and differences of 63% (#4) and 124% (#10). These two sites were fed with soft water and added lime before alum addition.

Changes inside filtering units

The filtering units were gravity filters generally using dual media made of anthracite and sand (11 sites) or granular activated carbon (GAC) with sand (1 site). As shown in Table 2, the other filtering units used sand alone (three sites) or triple media made of anthracite-sand-garnet (two sites). The sites generally used flow rates <6 m/h (Table 2). One site (#7) used a higher flow rate (9 m/h) and operated with the shortest filter run period. Except for sites #13 and #15, the filtration was generally preceded by the use of coagulation aids (Table 1). More than one coagulation aid was used in many instances. These aids were polymers of organic or inorganic types. The organic polymers could be neutral as well as negatively or positively charged. The inorganic polymers were silicates (sites #2 and #7), aluminates (site #3), or mixtures of both (sites #1, #6 and #9). Site #14 also used small amounts of
PACl at two points to help the alum-based processes. Except for sites #6 and #11, chemicals with oxidation properties such as permanganate or chlorine were used before filtration.

Figure 5 uses the values dF and dS to compare the changes occurring inside the filtering units at sampling series 1 (dF₁, dS₁) and 2 (dF₂, dS₂). Among the 15 sites examined in Figure 5, only one site (#15) presented dF₁ and dF₂ at large positive values of similar magnitude. These reproducible positive filtration balances (dF>0) represented an unsatisfactory filter performance in terms of Al minimization. Since the dF values were in parallel with negligible values of dS₁ and dS₂, this performance was caused by the presence of residual particulate Al after the filtering unit. The amounts of residual particulate Al were in the range of 45–60 µg/l, as shown in Figure 5 (p:Al = dF – dS) and Figure 6 (p:Al = r:Al – s:Al). The operation of this plant differed from the others by the absence of coagulation aids and the use of a different dual media filter (GAC-sand). On the other hand, six sites (#5, #7, #9, #11, #14, #17) can be considered as having reproducibly demonstrated a satisfactory filter performance (dF<0) at both sampling series. The filtration balances of these sites were close to zero (<10 µg/l) or at negative values (dF<0). The negative filtration balances all occurred in parallel with decreases in s:Al (dS<0).

In Figure 5, the decreases in s:Al were notably large for sites #9, #11 and #16 (dS = −30 to −88 µg/l). Unlike the other sites, site #9 added the chemicals chlorine and lime inside the filtering unit rather than before the filtering unit. This unusual practice resulted in the monitoring of a filtering unit in which reactions and pH changes were produced by the addition of these chemicals. The purpose of these additions was to remove, by quick oxidation and precipitation, unacceptable amounts of iron and manganese emerging sporadically in spring and summer. These reactions could also have contributed to give the large negative dS observed at site #9. For the other sites, the use of additives as well as of coagulation aids of various types and charges (Table 1) was apparently not related to the changes in s:Al inside the filtering units.

Sites #16 and #11, contrary to site #9, showed large differences between dF and dS, indicating the presence of residual p:Al in parallel with negative dS. For sampling series 1 at site #16, the negative dS₁ (−30 µg/l) was in parallel with a large positive dF₁ (+132 µg/l). The residual p:Al (162 µg/l, turbidity = 0.52 ntu) was much larger than the s:Al decrease. This showed opposite contributions to filtration balance and demonstrated that independent phenomena were implicated. While the presence of residual p:Al had to be attributed mostly to the failure of physical processes responsible for filtration effectiveness, the decrease in s:Al involved chemical reactions. Model reactions, such as precipitation or adsorption of s:Al in the filter media, could be promoted by mass transport or liquid-solid interactions complementary to

Figure 5 Comparison of Al filtration balance (dF) and change in soluble Al (dS) inside filtration unit for sampling series 1 (dF₁, dS₁) and 2 (dF₂, dS₂). The 15 sites have been placed in decreasing order of filtration balance at sampling series 2.
what had been achieved at previous stages. These reactions could contribute to improving coagulation completeness and to decreasing filtration balance, but could not eliminate problems of filtration effectiveness.

The sampling series 2 at site #16 also showed a large residual pAl (67 µg/l, turbidity = 0.28 ntu). The filtration however resulted in a negative dF₂ (−16 µg/l) due to a negative dS₂ of −83 µg/l. This behaviour, a negative dF accompanied by dS of larger negative magnitude, was observed for sites #16, #11 (both sampling series) and many other sites (Figure 5). As also illustrated in Figure 6 (sites #16 and #17), the decreases in s:Al were larger than the amounts of particulate Al after the filtering unit. These observations raise the possibility that the formation of precipitate from the decreasing soluble Al could entirely explain the presence of residual particulate Al. Precipitates could have been formed late enough in the filter media to reach the outlet of the filtering unit. In such cases, the problem primarily would not be one of effectiveness but of carryover, similar to what is observed for in-line treatment process (Monscvitz et al. 1978). In accordance with the principle that preceding treatment must be completed to ensure successful filtration (Cleasby & Logsdon 1999), this behaviour suggested that an improvement at the coagulation stages was needed to free the filter media of the supplementary role of completing the coagulation processes.

Conversely, sites #3 and #12 revealed increases in s:Al (Figure 5). These positive dS were observed at all sampling series and reached +42 µg/l. These results could be due to reactions such as dissolution or desorption of aluminium. In contrast with negative dS which are equivalent to coagulation processes, these positive dS are likely to occur when unfavourable coagulation conditions arise. Such conditions could also alter floc properties, influencing their filterability or favouring floc detachment. Although various phenomena could be involved, a positive dS suggested causes different than negative dS to explain the presence of residual p:Al. Both sites #3 and #12 showed large amounts of residual p:Al.

In the cases of sites #3 and #12, the filter performances based on filtration balance were particularly unsatisfactory (dF>0), due to contributions from both s:Al increase (dS>0) and residual p:Al (dF≠dS). As previously
described, other unsatisfactory filter performances (dF>0) were caused only by residual p:Al (dS = 0). The filter performance could be qualified as satisfactory (dF ≤ 0) for a large number of cases. However, few cases (e.g. site #7, Figure 1) showed a normal performance (dS = 0, dF = 0).

The anomalous s:Al decreases (dS<0) witnessed at many sites were usually responsible for negative filtration balances (dF<0). Although more than satisfactory in terms of minimization of residual Al, these negative filtration balances were in many instances associated with unsuccessful filtration due to the presence of residual p:Al (dF ≠ dS). As indicated in Table 3, most of the possible behaviours were observed. The missing observation was a positive dS in absence of residual p:Al (dS>0, dF − dS = 0).

Changes in filter performance

In Figure 5, eight sites showed marked differences of filter performance when comparing sampling series 1 and 2. A positive dF₁ was observed at four sites (#4, #8, #10 and #16) while sampling series 2 showed a satisfactory filter performance (dF₂ ≤ 0). The values dF₁ were of the order of + 20 µg/l, except for site #16 (dF₁ > 100 µg/l). These positive dF₁ were in parallel with relatively small dS₁. The small dS₁ could not explain the presence of residual particulate Al, which then was mainly attributable to problems of filtration effectiveness. These results suggested that the samplings of series 1 had been performed when the filter media had not completely ripened. These sites used anthracite-sand (#8 and #10) or triple media (#4 and #16) filtering units (Table 2). The samplings had been performed 1.0 h or less after the return to service, with the exception of site #4 (3.5 h).

The filter performance deteriorated by a factor of >2 at four sites. Increases in residual p:Al were largely responsible for these deteriorations. For site #2, dF remained small (dF₂ = + 15 µg/l). For the additional sites (#1, #3, #12), dF₂ ranged from + 79 to + 142 µg/l. For sites #3 and #12, the presence of residual p:Al (dF≠dS) at sampling series 1 could be due to incomplete ripening. However, the observation of positive dS₁ suggested other causes such as floc detachments. The increase of flocs in the filter media during the filter run could then explain the deteriorations. In the case of site #1, the negative dF₁ indicated a satisfactory filter performance. As explained above (Figure 2), the large positive dF₂ was due to problems of filtration effectiveness (dS₂=0). This deterioration could be related to the nature of the suspended particulate matter, which did not exhibit the complete acid leachability of fresh flocs. Sites #2, #3 and #12 used anthracite-sand as filter media, while site #1 used sand alone.

In Figure 5, it is noticeable that the magnitude of negative dS at sampling series 2 was generally larger than at sampling series 1. This trend was attributable to filter ripening, but also could be due to the accumulation of filtered particles in the filter media. Conversely, when considering the negative dS observed at sampling series 1 for site #1, the absence of negative dS at sampling series 2 could be due to a loss of reactivity or to channelling of the filter media.

Concentrations after filtering units

After the filtering units, soluble Al for both sampling series remained >150 µg/l for the sites using lime softening. For the other sites, s:Al(AF) was < 80 µg/l. Higher concentrations reaching 150 µg/l had been witnessed before filtration. Sites #9 and #11 showed large s:Al decreases from 65–105 µg/l to <30 µg/l. The contributions of residual p:Al at these two sites were absent or small enough to keep r:Al(AF) <50 µg/l. In five cases, residual p:Al contributed to give r:Al(AF) >100 µg/l. As described

<table>
<thead>
<tr>
<th>Observed behaviours</th>
<th>dS</th>
<th>p:Al(AF) [or dF−dS]</th>
<th>dF</th>
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Table 3
in Figure 5, these amounts of residual p:Al were associated with positive (#3), null (#1, #2, #15) or negative dS (#16). Except for site #16, all were low temperature (low-T) sites (T<5°C).

Most of the 12 sites not using lime softening and showing the leachability of fresh flocs achieved s:Al(AF) <40 µg/l (Figure 7). For the concentrations >40 µg/l at pH close to 6, both sites #2 and #3 used alum and were low-T sites. The s:Al changes at site #2 (dS = 0) and site #3 (dS >0) implied different origins for the high concentrations of s:Al(AF). Site #3 exhibited concentrations <40 µg/l before filtration [s:Al(BF1) = 35 µg/l; s:Al(BF2) = 50 µg/l]. The releases of soluble Al from the filtering unit (dS1 = +35 µg/l; dS2 = +19 µg/l) were accompanied by high residual p:Al, and could be induced by an instability of aluminium particles. The positive dS could also originate from a non-optimal pH generating the development of unfavourable solubility equilibria in the filter media. For site #2, the behaviour (dS = 0) suggested that solubility equilibria had already been achieved. This behaviour could also be due to a low reactivity of aluminium species generated at previous stages. The other sites using alum (#4, #5, #7 to #11) demonstrated good coagulation completeness after filtration by achieving s:Al(AF) <40 µg/l in parallel with null or negative dS (Figure 5).

In Figure 8, after elimination of sites involving pH adjustment (#8 and #9) or intermediate temperature (#4) as well as dS >0 (#3), three low-T sites (#2, #5, #11) and two high-T sites (#7 and #10, T>21°C) were considered for comparison with thermodynamic calculations of solubility equilibria (Van Benschoten & Edzwald 1990b, Van Benschoten et al. 1994). The comparisons showed a reasonable agreement with the V-shaped pH-dependent curves. However, the three low-T sites had higher concentrations than the theoretical values while the two high-T sites had lower concentrations. These tendencies counteracted the solubility differences predicted by the theoretical curves at 4 and 25°C. The comparisons also provided some explanations for the temperature trend observed for s:Al(BF) in Figure 4a. The levels at site #2 (dS = 0) seemed mostly related to a too low pH for the winter season. At this low temperature (1°C), the low pHs close to 6 could be considerably far from optimal values for minimum solubility. The levels at the other low-T sites (dS<0) were closer to optimal pH and seemed more related to slow rates. Thus, s:Al(BF) at these two sites was an order of magnitude (9 to 14 times) higher than the theoretical values, and s:Al(AF) in Figure 8 resulted from the removal of 21–24% (#5) and 66–69% (#11) of s:Al(BF). The present results unfortunately give no information whether
different contact times with the filter media would have generated larger s:Al changes.

In Figure 7, the two sites (#15 and #16) showing s:Al levels >40 µg/l at pH ≥7.5 used PACl. In addition to producing coagulation less dependent on temperature and at higher pH (Van Benschoten & Edzwald 1990b; Faust & Aly 1999; Letterman et al. 1999), the chemical characteristics of this polymeric coagulant are variable. Thus, the basicity of PACl ranged from 50% (#15) to 42–45% (#16) and 30% (#17). These characteristics showed some parallel with the s:Al levels. However, a similar parallel was also apparent for the plant designs, horizontal-flow sedimentations being used at sites #15 and #16 (Table 2). These plant designs were likely to be less efficient not only in performing solid removal, but also in producing solid contact and mass transport helpful to achieve coagulation completeness before reaching the filtering unit.

Although the polymeric species generating PACl coagulation differ from those involved in alum coagulation, PACl coagulants with low-to-medium basicity similar to those used at sites #15–#17 have also been shown to exhibit minimum solubility at pH<7 (Pernitsky & Edzwald 2003). The coagulation pH at sites #15–#17 could therefore deviate from optimal pH for minimum solubility, similarly to sites #2 and #3 using alum at pH close to 6. On the other hand, PACl results showed behaviours indicating the possibility that equilibrium state had not been reached even after the filtering unit. Thus, site #16 presented negative dS of magnitude similar to those at sites #9 and #11, but the s:Al levels in the filter influent [s:Al(BF1,BF2) = 108,148 µg/l] required larger dS to achieve similar low levels in the filter effluent (<30 µg/l). Site #17 also showed decreases in s:Al. Site #17 however achieved s:Al(AF) <40 µg/l, similar to most of the alum sites.

In summary, PACl results were comparable to alum results in many aspects. Sites #15 and #2 also showed similar s:Al levels and null dS. These last sites both used horizontal-flow sedimentations. All these results could be dependent on additional parameters at previous stages (e.g. rapid mixing). The monitoring of soluble Al with regard to variations in the operation conditions remains the best way to identify and correct the source of problems.

**CONCLUSIONS**

The description of changes occurring inside filtering units by aluminium balance (dF) and soluble Al difference (dS) allowed an easier comparison of the investigated sites and the definition of distinct filtration behaviours. These behaviours have different implications for the origin of soluble Al as well as of particulate Al. When the soluble Al was constant (dS = 0), the positive aluminium balances (dF>0) were due to residual particulate Al and were likely to originate only from problems of filtration effectiveness. When the soluble Al changed (dS≠0), the decreases or increases were indicators of different reactions occurring in the filter media. Model reactions could be precipitation or adsorption for the decreases, and dissolution or desorption for the increases. The formation of particulate Al by precipitation or precipitate detachment could accompany these changes of soluble Al. The residual particulate Al could then not originate from problems of filtration effectiveness.

The study of these different plants also showed consistent results. Complete leachability of particulate Al was generally observed. Exceptions to this behaviour of fresh flocs were indications of coagulation problems. During the filter runs, similar concentrations were observed before filtration. This indicated that stable operation conditions had been achieved for the coagulation processes. On the other hand, in many instances, the filter performance changed in the course of the filter runs. A large part of these changes were improvements, which could be attributed to the ripening of the filter media. For the deteriorations, it is noteworthy that anomalous behaviours such as increases in soluble Al (dS>0) or the presence of partly leachable particulate Al (lp:Al/p:Al <1) accompanied the increases in residual particulate Al. These observations offer links to the causes of difficulties in controlling residual particulate Al. By adding the decreases in soluble Al (dS<0) which also accompanied residual particulate Al, all these different results emphasize that the present methodologies can differentiate a variety of situations potentially giving rise to residual particulate Al.

Although various treatment processes were involved, the soluble Al concentrations were in agreement with the predominant influence of pH in controlling Al solubility.
Other observations indicated the importance of temperature, which can change optimal conditions by influencing both process rates and solubility equilibria. Except for sites using lime softening, only small deviations from optimal operation conditions could be suspected. On the other hand, divergences from normal behaviours for particulate Al \((lp:Al/p:Al = 1)\), filtration \((dS = 0, dF = 0)\) or filter run (constant \(dF\)) were witnessed. These divergences were rationalized by invoking problems with the effectiveness, equilibria and rates of the treatment processes. The observations however were only for the set of conditions prevailing during one filter run, and could only suggest causal factor(s). The variety of behaviours nevertheless showed that methodologies based on fractionation analysis along treatment sequences can provide supplementary information, able to trigger a course of action to improve the understanding and minimization of the levels of soluble Al or particulate Al, or both.

**ACKNOWLEDGEMENTS**

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**NOTATION**

\(dF_x\)  
\(dF\) for sampling series \(x\)  
\([dF_x = r:Al(AF_x) − s:Al(BF_x)]\)

\(dpH\)  
\(pH\) difference measured before and after filtering units

\(dpH_x\)  
\(dpH\) for sampling series \(x\)  
\([dpH_x = pH(AF_x) − pH(BF_x)]\)

\(dS\)  
\(s:Al\) difference measured before and after filtering units

\(dS_x\)  
\(dS\) for sampling series \(x\)  
\([dS_x = s:Al(AF_x) − s:Al(BF_x)]\)

\(F\)  
fluoride compound

\(g\)  
garnet

\(GAC\)  
granulated activated carbon

\(Ho\)  
horizontal-flow sedimentation

\(i\)  
inorganic polymer

\(l:Al\)  
(total) acid leachable Al

\(lp:Al\)  
leachable particulate Al \((lp:Al = l:Al − s:Al)\)

\(MnO_4\)  
permanganate

\((n)\)  
nonionic polymer

\(NH_3\)  
ammonia

\(o\)  
organic polymer

\(PO\)  
sampling point for finished water at plant outlet

\(PO_2\)  
sampling session at PO during sampling series 2

\(p:Al\)  
particulate Al \((p:Al = r:Al − s:Al)\)

\(PAC\)  
powdered activated carbon

\(PACl\)  
polyaluminium chloride

\(r:Al\)  
(total) recoverable Al

\(r:Al(AF_x)\)  
\(r:Al\) at sampling session \(AF_x\)

\(s\)  
sand

\(s:Al\)  
(total) soluble Al

\(s:Al(BF_x)\)  
\(s:Al\) at sampling session \(BF_x\)

\(Soft\)  
processes of coagulation with lime softening

\(Up\)  
upflow sedimentation

\(x\)  
sampling series number \((x = 1\ or \ 2)\)

**NOTES**

(1) In addition to site #14, the complete leachability of pAl could not be demonstrated for site #13 because the amounts of pAl were insignificant. Also, the s:Al levels of this site were out of proportion (Figure 3) and
did not show significant changes. The results at site #6, which used only alum, also were misleading because it was realized late that the samplings before filtration had been erroneously performed on raw water. Sites #6 and #13 are therefore not considered in subsequent sections.

(2) Among the sites using lime softening, only site #14 showed pH differences before and after the filtering units \( \Delta \text{pH} = \text{pH}(\text{AF}) - \text{pH}(\text{BF}) \) of large magnitude \( \Delta \text{pH} = -0.8; \Delta \text{pH} = -0.3 \). Most of the sites presented filtration \( \Delta \text{pH} \) of small magnitude \( \Delta \text{pH} < 0.1 \) for both sampling series. The exceptions were site #9 \( \Delta \text{pH} = +0.8, \Delta \text{pH} = +0.7 \) and two sites using PACl \( \#15: \Delta \text{pH} = -0.17, \Delta \text{pH} = -0.16; \#17: \Delta \text{pH} = -0.15, \Delta \text{pH} = -0.10 \). Other sites showed large \( \Delta \text{pH} \) only at sampling series 1 \( \Delta \text{pH} = +0.3 \) \( \Delta \text{pH} = +0.11, \Delta \text{pH} = -0.31 \) except for site #9, all sites using alum without lime softening showed small \( \Delta \text{pH} \) at sampling series 2.

REFERENCES


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