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Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)
Relationships between organic matter, pH, ANC and Al concentration and speciation

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Introduction

While acidification implies a pH reduction, it is the increased concentration of toxic forms of aluminum that is the prime cause for loss of fish populations. Atlantic salmon (Salmo salar) has a low tolerance to aluminum (Al) and even very low concentrations can have an effect on population health (Kroglund et al. 2008). In water Al is present on various forms differing in chemical properties and toxicity. Only Al present on the form operationally defined as positively charged, cationic (inorganic monomeric or labile) contains the Al species that are toxic (Lydersen et al. 1990b; Oughton et al. 1992; Teien et al. 2005). Other forms of Al have no known adverse affect, but are still important, either as a source for cationic Al or representing forms of Al generated during various transformation processes (Teien et al. 2004). Any physico-chemical factor affecting Al concentration and speciation can have a profound effect on salmon population status. Here pH, organic matter, ionic strength and temperature are recognized as the more important factors controlling Al concentration and speciation. This has been the topic of several review articles (Gensemer and Playle 1999; Lydersen et al. 2002; Rosseland and Staurnes 1994; Staurnes et al. 1995). In general, high pH, high organic content and high calcium reduces toxicity. Several studies have shown that water quality and fish status often is better predicted from ANC (the sum of cations minus anions; acid neutralizing capacity) than from the chemical composition of the water (Baldigo and Lawrence 2000; Bridcut et al. 2004; Kroglund et al. 2008; Kroglund et al. 2002; Lien et al. 1996; Lydersen et al. 2004).

Total Al concentrations in water have increased due to acid rain (Driscoll et al. 1980; Exley 2003; Gensemer and Playle 1999). Reduced pH causing increased transportation of Al to freshwater implies that more Al can be on forms that are toxic to fish. Although reference concentrations for total Al are poorly defined for Norwegian freshwaters, the assumption is that the total Al-concentrations were lower prior to acidification. Reduced acid rain should over time result in reduced mobilization of Al from soils and increased pH, both acting to reduce water toxicity (Palmer and Driscoll 2002). Besides acidification, organic matter transports Al to streams, resulting in higher Al levels in organic rich waters than in waters with low organic content (Gjessing et al. 1989; Guibaud and Gauthier 2003; Lydersen 1998).

Over the last decades, acid rain has been reduced. The sulphate concentration in precipitation over Norway is reduced by 62-85% since 1980, where the range depends on the region (SFT, 2008). This reduction in acid deposition should over time increase pH and alkalinity, reduce Al concentration (reduced mobilization from soils) and affect Al-speciation (due to increased pH). However, the transport of organic matter has increased over the same time period (De Wit et al. 2007; Evans et al. 2005; Laudon and Buffam 2008). This transport can affect both mobilization and transport of Al, and Al speciation as pH is reduced with increased concentration of natural organic acids (Bishop et al. 2004). Similar relationships between TOC and pH have not been observed in Norway (Lydersen 1998).

The toxicity of acidified water is currently counteracted by liming in numerous lakes and > 20 rivers in Norway (Sandøy and Langåker 2001; Sandøy and Romundstad 1995). The chemical target is to reduce Al-related toxicity. This target is met by increasing pH, where pH is used as the operational target. When pH is raised, Al is transformed from its toxic forms to forms that have reduced or no toxicity. Transformation rates are fast and cationic Al is reduced to low concentrations when pH values are around 6.4, but slow and less complete when pH is 6.0 or lower. The pH-target thus affects the volume of water downstream a lime doser or downstream the confluence between acid and non-acid waters containing toxic Al (Kroglund et al. 2001a; Kroglund et al. 2001b; Teien et al. 2004).
transformation rates are further modified by temperature, where the rate is low at low temperature (Lydersen et al. 1990c). As there is a large variance in life cycle sensitivity for salmon, the pH target is seasonally stratified. Because salmon smolt are extremely sensitive to cationic Al, the pH-target is set high in spring (pH 6.4). The pH-target is set at 6.0 from summer to late winter (protection of parr and adults), and at 6.2 from late winter to early spring. Present day pH targets are linked to the relationship that exists between transformation rates of Al and pH where critical limits for cationic Al is based on fish responses (Kroglund et al. 2008). pH thus acts as a surrogate for the “true” toxic component being cationic Al. Behind the rationale using pH as a surrogate for water quality lies knowledge regarding pH-Al relationships and transformation rates.

Reduced acidification is improving water quality based on pH and ANC increases (Evans et al. 2001; Monteith and Evans 2005; Skjelkvåle et al. 2007; Skjelkvåle et al. 2005; Wright et al. 2005). However, the base cation concentration is reduced at many sites to levels assumed to be below the natural background. This increases the relative toxicity of Al. Climate changes can affect Al mobilization and speciation and toxicity in numerous manners (Evans et al. 2008; Monteith et al. 2007; Wright et al. 2006; Kroglund et al., 2008). It has long been apparent that climate affects both the acidification and recovery of surface waters. The effects and pressures caused by climate can be episodic and related to seasalt events affecting Al mobilization and speciation (NAO-index) (Hindar et al. 1995; Hindar et al. 2004), by drought affecting soil redox processes (Dillon et al. 1997; Dillon et al. 2003a; Dillon et al. 2003b), seasonal, such as the typical pattern of low concentrations of NO3 in summer and high concentrations in winter (Stoddard et al. 1999), and long-term, such as the increase in dissolved organic carbon concentrations in many surface waters during the 1990s (Dillon and Molot 2005; Evans et al. 2005). As climate changes can affect acidification and recovery processes, climate will have an effect on current liming strategies; by affecting water quality and hydrology. Where all changes in Al mobilization will impact water quality, changes in pH and e.g. calcium will moderate toxicity. Climate change can further affect liming strategies by affecting the seasonal variation in water flow, timing of events (e.g. periods with high or low water discharge) and the timing of, duration and intensity of acidification episodes. Changes in temperature can both affect Al-related toxicity, but also smoltification (preadaptation to seawater life stage). The seasonally stratified pH-targets might have to be changed. Furthermore, the observed increase in total organic carbon (TOC) can affect both Al mobilization and speciation. This increase in organic matter could reduce Al related toxicity, but can also result in increased concentrations of cationic Al as total Al is increased and pH is reduced.

Both reduced acidification and climate related pressures affecting Al mobilization and Al speciation and water quality indicators can affect the rationale underlying present day pH targets.

The current delivery focuses on relationships between pH/TOC/ANC in relation to total Al and various forms of Al. Understanding how these relationships are interrelated and affect Al concentration and speciation can aid in understanding how climate can affect water quality, thereby affecting current liming strategies.

Method & material

The aim of this work was to identify relationships between Al species and other water chemical constituents. Data from the national monitoring program undertaken in 1995 is used to establish these relationships (Henriksen et al. 1996). This dataset contains data from 1500 lakes, where the lakes to be sampled were chosen randomly. All chemical protocols are defined in this article. The Al speciation protocol includes both total Al (measured on an ICP; no prior filtration) and the Al forms defined as pyreocatechol reactive (RAI), organic labile Al (NLAl) and cationic or labile or inorganic monomeric Al (LAI). Cationic Al is calculated as RAI minus NLAl (Røgeberg and Henriksen 1985). As the particular carbon fraction is generally low (<10%), TOC = DOC.

The prime toxic components in acidified waters are H+ and cationic Al. In numerous studies, acid neutralizing capacity (ANC) has proven to give a good prediction of fish status and acts as a surrogate
for water quality. ANC is defined as the equivalent difference in equivalent sum of base cations (Ca, Mg, Na, K) minus the equivalent sum of strong-acid anions (SO4, Cl, NO3) (Reuss and Johnson 1986). HCO3-dominated waters have positive ANC, while acidified waters have negative ANC. An ANC threshold of 20 μeq l-1 marks water quality assumed sufficient for protecting most key indicator organisms. These levels have been criticized as they do not always predict correctly, especially in organic rich waters (McCartney et al. 2003).

Based on prior studies, a stratification of data with respect to pH and organic matter can improve relationships relating to water quality and fish status (Hesthagen et al. 2008; Kroglund 2007). All data is therefore sorted and grouped into distinct TOC and pH classes. All data is furthermore separated into “Southern” Norway (SN) and “Northern” Norway (NN) providing a simple geographical separation between sites receiving acid rain and sites where water quality is less impacted. Northern Norway is composed of the counties Møre and Romsdal, North and South Trønderlag, Nordland, Troms and Finnmark, all located outside the region regarded as affected by acidification. “Southern” Norway receives acid rain but not all water bodies are equally affected, where the effects are minor at some sites due to local/regional variation in geology. Southern Norway is therefore split with respect to ANC, where water having high ANC (>75 ueq/l) are understood as “not being affected” (SNhigh), while water with lower ANC can be impacted (SN). This splitting is a convenient method to reduce variability in the material.

Results

TOC classes, differences between regions

Based on previous published data, one can expect there to be relationships between TOC, pH and ANC. Likewise, TOC and pH shall affect Al concentrations and speciation.

There was no clear relationship between TOC and pH within a region in the 1995-lake survey (Fig.1a). Average pH was higher in NN and SNhigh than in SN, regardless of TOC class. Similar regional differences were observed between TOC and ANC (Fig 1b). However, here there was a clear increase in ANC with increased TOC. This effect was most profound in the non-acid lakes.

Fig. 1. Relationship between TOC and a) pH or b) ANC. The y-axis values are presented as average ±1 SD values stratified on the regions North (Northern Norway), South, ANC >75 μeq/l (Southern Norway, high ANC) and South, ANC<75 μeq/l (Southern Norway, low ANC).

Total Al increased with TOC in all regions (Fig. 2a). The concentrations in SN were on the average around 50 μg higher than average levels measured in regions “not” affected by acid rain. The increase in SN supports the assumption that both acid rain and TOC affects total Al concentrations. RAl increased with increasing TOC in all regions (Fig. 2b). The concentration was higher >75 μg/l higher
in SN than in the other regions. This increase is linked to pH. The increase in RAl in SN was due to increased cationic Al when TOC was low and to increased NLAl when TOC was high. More Al was present as NLAl as TOC was increased and the concentration was highest within the acid affected region (Fig. 2c). There was no clear effect of TOC on average cationic Al concentrations within region (Fig. 2d). The variation around the average was high in SN illustrating a large spread in measured values.

**TOC & pH classes, relationships based on data from Southern Norway**

Within a pH class, ANC increased with increasing TOC in SN (Fig. 3). In the two most acid pH-classes, ANC values were negative when TOC was low and positive when TOC was high. ANC levels were as such strongly related to TOC. Assuming 20 µeq ANC/l represents “safe” water qualities, these levels were met when TOC is >10 mg C/l in acidic water or at TOC>0 when pH was high (Table 1).

**Tab. 1. Relationships between TOC and ANC stratified on pH classes for lakes within Southern Norway having ANC values <75 µeq/l.**

<table>
<thead>
<tr>
<th>pH class - ANC</th>
<th>Equation</th>
<th>R²</th>
<th>ANC&gt;20 µeq/l when TOC&gt;</th>
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<tbody>
<tr>
<td>4.4-5.0</td>
<td>y = 5.54x - 38.60</td>
<td>= 0.98</td>
<td>10</td>
</tr>
<tr>
<td>5.0-5.5</td>
<td>y = 5.29x - 13.10</td>
<td>= 0.89</td>
<td>6</td>
</tr>
<tr>
<td>5.5-6.0</td>
<td>y = 6.15x + 1.38</td>
<td>= 0.96</td>
<td>2.5</td>
</tr>
<tr>
<td>6.0-6.5</td>
<td>y = 7.64x + 39.07</td>
<td>= 0.91</td>
<td>0.4</td>
</tr>
<tr>
<td>6.5-7.0</td>
<td>y = 7.99x + 16.10</td>
<td>= 0.96</td>
<td>0</td>
</tr>
</tbody>
</table>
Total Al was generally highest in lakes having the lowest pH and highest TOC values (Fig. 4a). This trend was less obvious for the most acid lakes. Here, total Al was in the range around 125 µg Al/l when TOC was < than 2 mg C/l or around 175 µg Al/l when TOC was > 2 mg C/l. When pH was > 5.0, total Al was related to TOC (Table 2). Acid lakes with low TOC could have lower total Al concentrations than non-acid lakes with high TOC (Fig.4). This variation in concentration with TOC/pH was more evident for RAl where the concentration of Al defined as RAl seems independent of TOC when pH is low (Fig 4b). Slightly more RAl was present as NLAi in the most acid lakes relative to the non acid lakes (Fig 4c). NLAi was mainly related to TOC, but with some effects of pH on concentration levels. This difference was not significant but can still be important. While cationic Al decreased with TOC in the most acidic waters (pH <5), there is no clear variation in cationic Al with increased TOC at other pH-levels (Fig 4d).

![Fig.3. Relationships between TOC and ANC stratified on pH classes for lakes within Southern Norway having ANC values <75 µeq/l. Average values ±1 SD for each ph class is presented in the graph.](image)

<table>
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<tr>
<th>pH class – total Al</th>
<th>Equation</th>
<th>R²</th>
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<tr>
<td>4.4-5.0</td>
<td>y = 8.1042x + 137.07</td>
<td>R² = 0.616</td>
</tr>
<tr>
<td>5.0-5.5</td>
<td>y = 10.115x + 83.88</td>
<td>R² = 0.6304</td>
</tr>
<tr>
<td>5.5-6.0</td>
<td>y = 11.731x + 50.148</td>
<td>R² = 0.6779</td>
</tr>
<tr>
<td>6.0-6.5</td>
<td>y = 7.896x + 37.481</td>
<td>R² = 0.3955</td>
</tr>
<tr>
<td>6.5-7.0</td>
<td>y = 18.27x + 7.046</td>
<td>R² = 0.5295</td>
</tr>
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</table>
ANC & aluminum relationships: TOC classes

Based on the relationship between TOC and ANC above (data presented from regions) one can expect that TOC will affect the relationship between ANC and pH. The relationship between pH and ANC in SN was clearly affected by TOC, where low TOC implies that a pH target will be met at a lower ANC level than at high TOC levels (Fig. 5a). E.g. a pH target of 6.4 is met at an ANC value of 20 µeq/l in low TOC waters while ANC must be >50 µeq/l to meet the same pH target in high TOC waters. Likewise, the relationship between ANC and total Al, RAl and cationic Al varied with TOC (Fig 5b-d).

As for pH, ANC values associated with low concentrations of cationic Al increases with increased TOC although the relationships were less clear than for pH. Assuming 10 µg cationic Al/l as an indicator of “safe” water, ANC had to be >10 µeq/l when TOC was < 2 mg C/l, >25 µeq/l when TOC was in the range of 2-4 mg C/l, and 50 µeq or higher when TOC was > 4 mg C/l. At the same time, cationic Al concentrations could be lower than 10 µg/l at all ANC concentrations down to around -10 µeq/l. A low ANC can, but does not have to imply impaired water. Regardless of this uncertainty, a critical ANC increases with TOC because pH decreases and cationic Al increases with TOC. Similar effects of TOC on the ANC/pH and RAI relationships were also observed in the other regions but not so for cationic Al (Fig. 6a-f). Cationic Al in these regions were generally very low.
Fig. 5. Relationships between ANC and a) pH, b) total Al, c) PCV reactive Al (RAI) or d) cationic Al (LAI) stratified on TOC classes for lakes within Southern Norway having ANC values <75 µeq/l. Each “dot” represents one lake.

Total Al concentration can be calculated reasonably well ($p=0.0000; R^2>65$) using only TOC and pH within the regions (equations 1-3). Using these equations, total Al is calculated to be higher in SNHight than in SN for a given pH-TOC combination. However, due to differences in acid deposition and geology, lakes in SNHight and most lakes in NN have pH values that are substantially higher than what is normally measured in SN. Due to this, total Al is lower in lakes outside the acidified region. Due to less Al and higher pH, the amount of Al measured as cationic Al will be reduced.

1) SN  
Total Al = 329.208 - 50.7519*pH + 16.1504*TOC  
$R^2=70.7$

2) South high ANC  
Total Al = 445.251 - 64.7375*pH + 11.7697*TOC  
$R^2=81.9$

3) North  
Total Al = 196.065 - 28.4906*pH + 14.7329*TOC  
$R^2=65.9$
Discussion

The toxic effects of Al in acidified waters have been acknowledged since the late 1970’s (Dickson 1978; Schofield 1977). Since the 1990’s, it has in a similar manner been accepted that only cationic forms of Al exhibit toxic properties (Lydersen et al. 1990a; Lydersen et al. 1990b; Oughton et al. 1992; Teien et al. 2005). Toxicity is moderated by H⁺, ionic strength, organic matter and temperature, all affecting Al concentration and speciation, by biological properties e.g. related to species, strain, life history stage variation in sensitivity in addition to various physico-chemical factors acting directly on e.g. membrane integrity and metal accumulation rates. Understanding how historic acidification, present reduced acidification and climate change affects cationic Al is essential for understanding how these anthropogenic pressures can affect water quality in the future. In addition, differencing effects related to acid rain from effects related to naturally occurring organic acids is
essential for the understanding of effects caused by a pressure from water qualities representing reference conditions.

The regional separation used in this study results in distinct water types differences with respect to pH and ANC. While NN and SNhigh had pH values that normally were >pH 6, SN had values that normally were <5.5. The “unaffected” regions had on the average ANC values >100 µeq/l while SN had values <50 µeq/l. The dataset defined as “unaffected” by acid rain contained as such lakes where “elevated” Al concentrations were not related to reduced pH. The clear correlation between total Al and TOC suggests that Al in these regions is transport from the edaphic to the aquatic environment with organic matter.

Relative to the “unaffected” regions, total Al in SN was on the average increased by 50 µg Al/l. This increase can be related to the pH decrease alone and represents an average increase related to acid rain. In the most acidic lakes, total Al could exceed 150 µg/l, while concentrations were <100 µg/l when pH was >5.5 and TOC was <3 mg C/l. The results are as such in agreement with old literature where it is concluded that acidification of soil water systems causes an increased transfer of Al from edaphic to aquatic environments (e.g. Cronan and Schofield 1979, Dickson 1980). In addition to pH, the total Al concentration was related to TOC in all regions.

TOC had no major effect on pH in this dataset. This does not exclude the possibility that effects can be observed when related to time series from individual sites. A pH reduction with increased TOC is however reported in other studies (Hruska et al. 2003; Laudon and Buffam 2008) or when TOC is high (Lydersen and Henriksen 1994). Possible causes for such differences are discussed in Lydersen (1998). Based on lake survey data from 1995, an increase in TOC is not expected to decrease pH by more than 0.2 pH units, but is expected to increase total Al. An increase in total Al will not result in an increase in cationic Al unless pH is reduced. A pH change of ±0.2 units is estimated to affect cationic Al by <10 µg Al/l.

Based on this, the observed increase in TOC observed over the last 2 decades has most likely no or only minor effect on cationic Al but will have an effect on total and PCV reactive Al. This will however imply elevated Al related toxicity in estuaries where colloidal and organic Al is the source for toxic conditions (Bjerknes et al. 2003; Teien et al. 2006). An increase in TOC will however increase critical ANC limits as the relationship between ANC & pH and ANC & cationic Al is affected (Hesthagen et al. 2008; Lydersen et al. 2004; McCartney et al. 2003).

The increase in TOC is not expected to result in any need for any major change in liming strategies in Norway. Changes in seasonal temperature and hydrology can affect the seasonal cost. Current liming strategies are on the whole robust enough to cope with this.

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