

Mortality of Smolt of Atlantic Salmon, *Salmo salar* L., at Low Levels of Aluminium in Acidic Softwater

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The level of aluminium toxic to freshwater fish depends on chemical factors, such as pH, calcium concentration, concentrations of ligands and chelators, and degree of chemical stability; on biological factors, such as species, lifestage and physiological status, as well as on temperature (Baker and Schofield 1980; Driscoll et al. 1980; Rosseland and Skogheim 1984a; Skogheim et al. 1984a; Brown 1983).

Presmolt of Atlantic salmon (*Salmo salar* L.) are more sensitive to acidic waters than yearlings and eggs, and also more sensitive than other species of salmonids (Rosseland and Skogheim 1984a). Even at relatively low concentrations of labile aluminium (30-70 µg Al/L), mortality of salmon smolts occurs when the concentration of calcium is low (<1 mg Ca/L) (Henriksen et al. 1984).

Skogheim et al. (1984b) observed sublethal physiological stress (measured as a depletion of plasma chloride) in smolts of Atlantic salmon reared in the chronically acid (pH = 4.9-5.4) Lake Liervatn, SW Norway, at labile Al concentrations of 25-50 µg Al/L. To establish toxic levels of labile Al in this water, we exposed sublethally stressed salmon smolts from Lake Liervatn to lake water (pH = 5.07, Ca = 1.3 mg/L, labile Al = 38 µg Al/L) enriched with inorganic aluminium to three concentration levels of labile Al: 75, 137 and 177 µg Al/L.

MATERIALS AND METHODS

Experiments were performed in plastic enclosures (volume 3.1 m³, height 4 m) in Lake Liervatn, with no sediment contact. Keepnets (volume 40 L) containing 22 fishes were placed in the middle of each enclosure. Fish were frequently checked for mortality. Four enclosures were used: Enclosure I contained natural

lake water and Enclosures II - IV contained natural water enriched with AlCl_3 . Aluminium was added in solution and was effectively dispersed with a pump for 15 minutes prior to the transfer of fish. Water samples were taken daily and immediately prepared for analyses of aluminium as described by Skogheim and Rosseland (1984). pH was measured with a Radiometer PHM80. All other chemical analyses were performed according to methods outlined by Skogheim and Rosseland (1984) and Skogheim et al. (1984b).

Aluminium speciation was calculated by the computer program MINEQL (Westall et al. 1976). Ion strength was estimated to be $1.14 \cdot 10^{-3} \text{M}$. Further details are given by Rosseland and Skogheim (1984a).

Smolts of Atlantic salmon used in this experiment had been raised from the fingerling stage in net cages in Lake Liervatn. The average weight and length of the fish \pm SD were 38 ± 5 g and 16 ± 1 cm ($n=19$), respectively. Plasma chloride levels in fish at the beginning of the experiment varied between 95 and 115 meq Cl/L. Typical levels for unstressed fish of this age are 120 to 130 meq Cl/L (methods and levels according to Rosseland and Skogheim 1984a). Shortly after completion of this experiment, Lake Liervatn was limed, increasing lake pH to 6.3 - 6.6, and decreasing labile Al to $<20 \mu\text{g Al/L}$. One month after liming, levels of plasma chloride had increased to 125 ± 3 meq Cl/L in five fish from the same population. Prior to liming, several hundred individuals from this stock were transferred to a nearby lake with circum neutral pH. One month after the transfer levels of plasma chloride were 122 ± 6 meq Cl/L ($n = 5$). These measurements indicate that the testfish used in this experiment were sublethally stressed due to osmoregulatory disturbance as a result of adverse water quality conditions.

Water in the enclosures was from Lake Liervatn. pH in the lake varied between 4.9 and 5.4 during the year. The mean concentration of calcium was 1.3 mg/L. Conductivity was relatively high; 60 $\mu\text{S/cm}$, due to high concentration of sea salts (especially Na and Cl). The concentration of total Al averaged 175 $\mu\text{g Al/L}$, with only 110 $\mu\text{g Al/L}$ included in the acid-reactive fraction. Concentrations of labile Al, consisting principally of inorganic monomeric forms of aluminium, were approximately 40 $\mu\text{g Al/L}$. Organically-chelated Al is included in the non-labile fraction; lake water concentrations averaged about 70 $\mu\text{g Al/L}$. Concentrations of dissolved organics in the lake were relatively low. Measured against a Pt-standard, water colour ranged from 5 to 10 mg Pt/L. The concentration

of dissolved organic matter estimated by UV-absorbance was ca. 0.120 cm^{-1} at wavelength 254 nm; the corresponding KMnO_4 -consumption was 3.1 mg O/L. Further information on the lake water quality is given in Rosseland and Skogheim (1984b) and Skogheim et al. (1984b).

RESULTS AND DISCUSSION

Water quality was relatively stable in all enclosures during the experiment; data for Enclosure II are summarized in Table 1. The only significant trends through time were decreases in acid-reactive Al and labile Al in Enclosure II (time v.s. concentration; $r > 0.9$, $p < 0.01$), and a corresponding increase in non-labile Al ($r = 0.55$, $p < 0.05$).

Table 1. Mean (M), standard deviation (SD) and number of observations (n) for pH, conductivity (COND_{25}), calcium (Ca), organic matter measured as UV-absorbance (ORG), and aluminium measured daily in enclosure II.

	pH	COND_{25} $\mu\text{S}/\text{cm}$	Ca mg Ca/L	ORG cm^{-1}	--Aluminium- $\mu\text{g Al/L}$ --		
					Acid- reactive	Non- labile	Labile
M	5.06	56.0	1.29	0.121	163	88	75
SD	0.06	0.7	0.03	0.001	7	6	11
n	18	18	18	18	17	17	17

Differences in water quality among the four enclosures were principally acidity and the level and composition of the various fractions of aluminium (Table 2).

No mortality occurred during the 20-days exposure in Enclosure I containing unaltered lake water. In enclosures enriched with labile Al, higher aluminium concentrations resulted in less time to 50 % mortality (Figure 1). In Enclosure II with pH = 5.06 and 75 $\mu\text{g Al/L}$ of labile Al, 50%-mortality (LT_{50}) was reached at 108 hours. In Enclosure III with pH = 4.92 and 137 $\mu\text{g Al/L}$ of labile Al, 50% mortality was reached after 38 hours. In Enclosure IV with pH = 4.9 and 177 $\mu\text{g Al/L}$ of labile Al, 50% mortality was reached after 32 hours (Figure 2).

Addition of inorganic Al to acidic lake water induced chemical reactions leading to increased acidity and changes in aluminium speciation. Levels of labile

Table 2. Mean values of pH, measured fractions of aluminium and calculated species of aluminium in the four enclosures. Calculation of aluminium species is based on solubility constant $K_{SO}=10^{9.4}$ for: $Al(OH)_3+3H^+ = Al^{3+} + 3H_2O$. All concentrations of aluminium are given as μg Al/L; n= number of observations.

ENCLOSURE	I	II	III	IV
Addition of Al ($\mu g/L$)		55	120	168
pH	5.07	5.06	4.92	4.90
Analyzed fractions of aluminium:				
Acid reactive Al	108	163	233	277
Non-labile Al	70	88	96	95
Labile Al	38	75	137	177
n	12	17	5	3
Computed distribution of labile Al:				
Al^{3+}	6	18	50	107
$Al(OH)_2^+$	7	18	36	30
$Al(OH)_2^{2+}$	6	15	22	12
AlF_2^+	16	22	26	26
AlF_2^+	3	2	1	1
$AlSO_4^+$			1	
Equilibrium concentration of inorganic monomeric Al	176	184	346	382

aluminium were, however, still unsaturated relative to theoretical concentrations of inorganic monomeric Al that could be present in equilibrium with a solid phase with solubility corresponding to synthetic gibbsite. Earlier studies suggest that concentrations of Al in acidic waters in Norway approximate levels expected for solutions in equilibrium with gibbsite, with a solubility constant (K_{SO}) of $10^{9.4}$ at $4^\circ C$ (Seip et al. 1984; Skogheim et al. 1984a). Slight increase in the acid-reactive Al fraction were also observed, a small fraction of the added aluminium apparently having been chelated by dissolved organic matter in the lake water (Table 2). The concentration of non-labile Al was similar in Enclosure III and IV, indicating that the

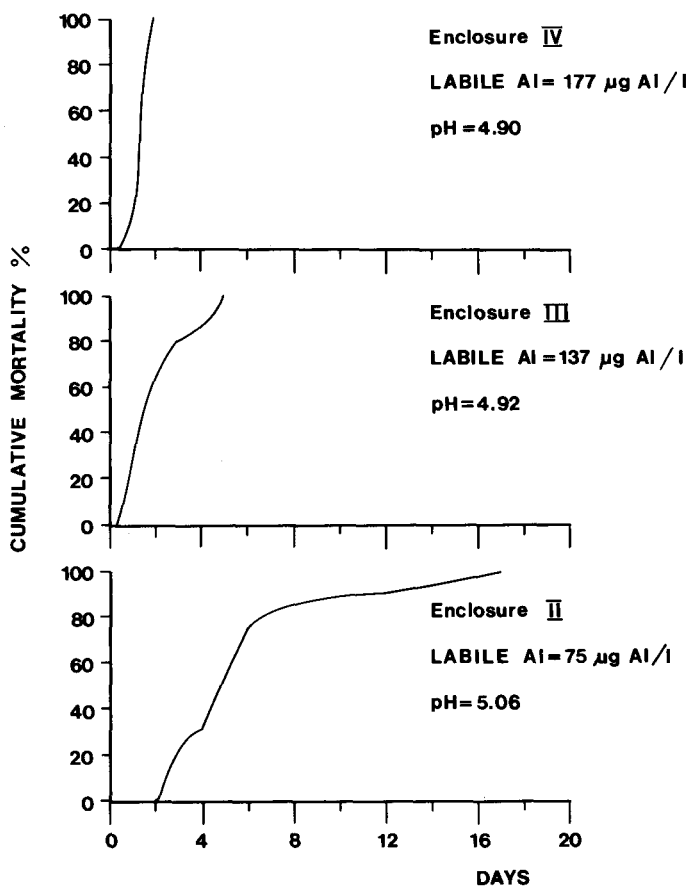


Figure 1. Cumulative mortality in Enclosures II, III, and IV containing lake water enriched with labile Al (Table 2). In Enclosure I containing natural lake water, no mortality occurred during the 20-days exposure.

chelating capacity of organic matter in water from Lake Liervatn amounts to about 95 µg Al/L (Table 2).

In all enclosures almost all fluoride (21 µg F/L) is complexed with aluminium. Aluminium additions resulted in increases principally in concentrations of Al-hydroxides and free aquo Al^{3+} . Concentrations of Al-fluoride were fairly constant among treatments. At the actual concentration of sulphate (5.2 mg/L) the concentration of Al-sulphate was very low (Table 2). The distribution of Al-species in the Al enriched enclosures changed slightly during the experiment. Trends through time were, however, only important in Enclosure II as a result of the long duration of this

exposure (17 days). The concentration of labile Al decreased by $2 \mu\text{g Al/L}$ per day from $96 \mu\text{g Al/L}$ at the start of the experiment. The concentration of non-labile Al increased by $0.7 \mu\text{g Al/L}$ per day. Levels of acid-reactive Al decreased with time, but pH levels were fairly constant. The loss of labile (inorganic) Al in Enclosure II over time may reflect either a transfer from inorganic to organically-chelated Al, or precipitation of aluminium trihydroxide. Precipitation of $\text{Al}(\text{OH})_3$ is unlikely, however, since no Al oversaturation was observed. The disappearance of inorganic Al not accounted for by the increase in the non-labile fraction, may simply be due to adsorption of Al to the plastic walls of the enclosure.

Additions of Al resulted in increased acidity in Enclosures III and IV. Thus, decreases in pH (from pH = 5.07 to pH = 4.90) may play some role in the higher mortalities in Enclosures III and IV. Several types of evidence, however, suggest that mortalities in Enclosures III and IV resulted principally from Al toxicity. For example, Enclosures I and II had similar pH levels, but salmon died only in Enclosure II with Al additions. Enclosures III and IV had similar pH, but fish died faster in Enclosure IV with higher Al levels.

Experiments in softwaters (pH = 6.13, COND = $6 \mu\text{S/cm}$, Ca = $.62 \text{ mg/L}$) acidified with H_2SO_4 in the absence of labile Al, induced no mortality and depletion of plasma chloride in brown trout at pH levels down to 4.5 (Leivestad et al. 1980).

Calcium ameliorates the toxic role of aluminium (Leivestad et al. 1980; Brown 1983), but no experiments with salmon smolts exposed to labile Al at various levels of Ca have been reported.

At a calcium concentration of 1.3 mg/L and pH = 5.07 salmon smolts were sublethally stressed at a labile Al concentration of $38 \mu\text{g Al/L}$. Increasing labile Al concentration to $75 \mu\text{g Al/L}$ induced 50% mortality within 108 hours (Figure 2). Episodic changes in pH and aluminium concentration in this range have been observed in connection with fish kills in a Norwegian river (Henriksen et al. 1984). Thus the sensitivity of Atlantic salmon to aluminium during smoltification may be critical to survival of salmon populations.

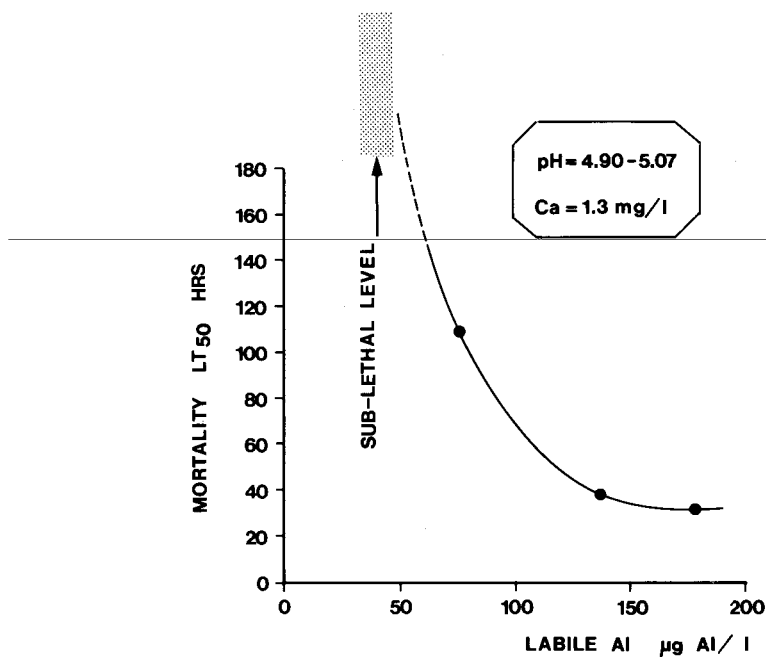


Figure 2. Mortality measured as time to 50% mortality (LT₅₀), as a function of concentration of labile Al. Mean calcium level = 1.3 mg/L; pH range 4.90-5.07.

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