

Changes in fish mercury concentrations over 20 years in an acidified lake subject to experimental liming

Martti Rask^{a,*}, Roger I. Jones^b, Marko Järvinen^c, Anna Paloheimo^d,
Maiju Salonen^a, Jari Syväranta^b, Matti Verta^d

^a Finnish Game and Fisheries Research Institute, Evo Fisheries Research Station, FIN-16970 Evo, Finland

^b University of Jyväskylä, Department of Biological and Environmental Science, P.O.Box 35, FIN-40014 Jyväskylä, Finland

^c University of Helsinki, Lammi Biological Station, FIN-16900 Lammi, Finland

^d Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki

Available online 18 March 2007

Abstract

Lake Iso Valkjärvi (southern Finland, Europe) was divided in two with a plastic curtain in 1991. One half was neutralized with CaCO₃, and the other acted as a control. Mercury concentrations of perch (*Perca fluviatilis*) and northern pike (*Esox lucius*) in the limed and control side of the lake were studied both before and after the treatment. Average Hg concentrations of perch and pike were 0.40 and 1.2 μg g⁻¹ (ww) in the early 1980s and 0.25 and 0.72 μg g⁻¹ (ww) a decade later at the time of liming. Ten years after the liming the Hg concentrations of perch in the limed and control sides of the lake were 0.21 and 0.28 μg g⁻¹ (ww) and those of pike were 0.69 and 0.43 μg g⁻¹ (ww), respectively. Nitrogen isotope ratios (δ¹⁵N) for perch in the sampling period 2002–2004 showed wide variation suggesting variable trophic positions for individual fish. Pike formed two groups according to their δ¹⁵N-values, suggesting that zoobenthos dominated the diet of pike around 20 cm in length and fish that of the larger pikes. Because the δ¹⁵N-values of fish were at similar levels in the limed and control sides of L. Iso Valkjärvi, differences in food web structure cannot account for the different fish Hg concentrations. A more likely explanation is water quality induced differences in the dynamics and bioavailability of Hg, leading to decreased formation of methyl Hg.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Numerous lake surveys have documented a negative correlation between lake water pH (acidification) and fish Hg concentrations (see e.g., Lathrop et al., 1991; Lindqvist et al., 1991; Spry and Wiener, 1991; Watras et al., 1998; Greenfield et al., 2001). This has been suggested to result from several pro-

posed biochemical mechanisms that are based on catchment and/or in-lake processes. The relative importance of these mechanisms is still poorly understood and many of them are not independent but may occur simultaneously. Based on a literature review, Winfrey and Rudd (1990) and Ullrich et al. (2001) concluded that the decreased pH would stimulate methyl Hg production in the water column and at the water–sediment interface. Decreased pH may also decrease the loss of volatile Hg from lake water and increase Hg binding to particles –factors

* Corresponding author. Fax: +358 205 751 429.
E-mail address: martti.rask@rktl.fi (M. Rask).

that may enhance the bioavailability of Hg for methylation.

Sulphate-reducing bacteria (SRB) are the main methylators of inorganic Hg to methyl Hg (MeHg) in many environments (e.g., [Compeau and Bartha, 1985](#); [Gilmour and Henry, 1991](#); [King et al., 2001](#)) and, consequently, atmospheric SO₄ addition linked to acidification may enhance methylation by stimulating the activity of SRB in lakes and catchments. In general, de-acidification (or recovery from acidification) coincides with a decrease in atmospheric Hg deposition while the decrease in the biota MeHg concentration may also be a result of Hg deficiency. This may be true if Hg^(II) concentration or availability limits the methylation and further if the low pH increases the bioavailability of Hg ([Winfrey and Rudd, 1990](#); [Fitzgerald et al., 1991](#)).

Previous studies in Scandinavia have shown that experimental liming of lakes can lower the Hg levels in fish ([Andersson et al., 1995](#); [Meili, 1995](#)), thus having an opposite effect from acidification. More recently, the de-acidification of an acidified basin of a seepage lake in Wisconsin (USA) led to a clear (up to 30%) decrease in fish (yellow perch) Hg concentration within 6 a of recovery ([Hrabik and Watras, 2002](#)). At the same time, a more moderate decrease (5%) was observed in the non-acidified reference basin which was also attributed to de-acidification. A simultaneous and additional decrease from 27% to 30% in fish Hg concentration was attributed to lower atmospheric deposition of Hg ([Hrabik and Watras, 2002](#)). These studies support the hypothesis that changes in acid rain and/or experimental de-acidification may substantially affect Hg cycling and bioaccumulation in small seepage lakes over relatively short periods of time.

In this study Hg concentrations of fish were examined in Lake Iso Valkjärvi, a 4 ha seepage lake in Lammi, southern Finland, which had become acidified and was the target of a liming experiment in the early 1990s. Attention was paid to possible trends in fish Hg concentrations over a 20 a time period as well as to the comparisons of Hg concentrations between the limed and control side of the lake during and after the experimental liming.

The pH of Lake Iso Valkjärvi had decreased to 4.9–5.2 due to atmospheric precipitation ([Rask, 1991](#)) and alkalinity was close to 0 or negative by the late 1980s ([Fig. 1](#)). In spring 1991, the lake was divided in two with a plastic curtain. One half was neutralized with CaCO₃, and the other acted as a control ([Järvinen et al., 1995a,b](#)). Water quality

and responses of plankton, macrozoobenthos, fish and waterfowl to the liming were studied intensively during 1991–1993 ([Rask, 1991](#); [Järvinen, 1993](#); [Kuoppamäki, 1993](#); [Järvinen et al., 1995a](#); [Pöysä et al., 1994](#); [Rask et al., 1996](#)). Also the concentrations, amounts and dynamics of Hg were studied before and during the liming experiment ([Metsälä and Rask, 1989](#); [Rask and Metsälä, 1991](#); [Rask and Verta, 1995](#); [Matilainen, 1995](#); [Verta and Matilainen, 1995](#)).

An almost complete kill of the perch population (>95%; from a density of 1800 ind. ha⁻¹ to <50 ind. ha⁻¹) took place in the control side of the lake in autumn 1992 ([Pöysä et al., 1994](#)), whereas no dead pike were found. This collapse of the perch population produced biological responses at different trophic levels in the following years ([Rask et al., 1996](#)). Among these, decreased Hg concentrations of perch were recorded. This was thought to be due to increased growth of the remaining perch, the so called growth dilution ([Göthberg, 1983](#); [Rask et al., 1996](#)). The remaining perch in the control side increased their weight in summer 1993 from an average of 40–50 g to 110–140 g and length from 15–16 cm to 20–22 cm, whereas the mean size of perch in the limed side remained at 40 g and 15 cm ([Rask et al., 1996](#)). Therefore, at that time, 1993–1995, the Hg concentrations of perch were higher in the limed than in the control side of the lake, contrary to original expectations. The specific reason for the fish kill remained unclear, but most probably it was the interactions of acidity, Ca and labile Al, in concentrations detrimental to fish, known as the mixing zone effect ([Rosseland et al., 1992](#)), possibly connected to the polymerization of Al ([Poléo, 1995](#)). Redox conditions and Fe may have also affected the fish kill because it took place during the autumn turnover ([Rask et al., 1996](#)).

The remaining perch in the control side reproduced effectively, resulting in a population density similar to that in the limed side of the lake as soon as 1995 ([Rask et al., 1996](#)). By the last sampling of this study in 2002–2004, the age structure of the perch population in both sides of the lake had also become similar. The aim of the 2002–2004 sampling was to evaluate the possible liming-induced differences in fish Hg concentrations after a period of a decade. Based on Swedish and North-American experiences ([Meili, 1995](#); [Hrabik and Watras, 2002](#)), it was hypothesized that the Hg concentrations of fish should be lower in the limed than in the control side of the lake. In 2002–2004, Hg deter-

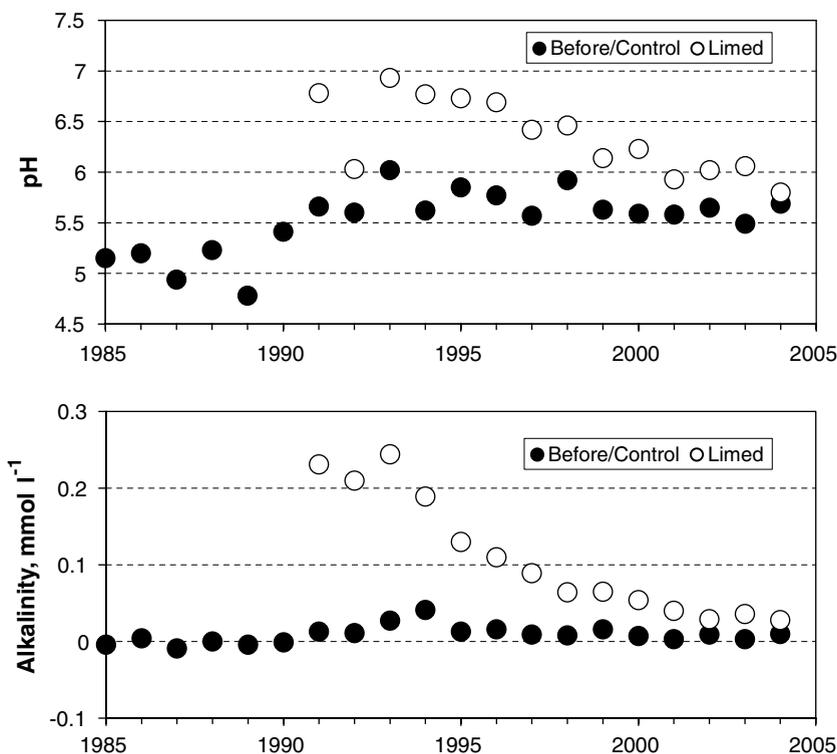


Fig. 1. Surface water pH and alkalinity during autumnal mixing (October–November) in L. Iso Valkjärvi in 1985–2004. Analyses performed in the laboratory of the Lammi Biological Station, University of Helsinki, according to common standards for water quality analyses (SFS-EN).

minations were accompanied by ^{15}N stable isotope analysis (SIA) to test possible differences in the trophic position of the fish between the limed and control sides of the lake.

2. Material and methods

Samples of perch and pike were collected during three sampling periods by wire traps (1 cm square mesh) and pike samples also by angling. The first period was in 1983–1984 (6 perch, 21 pike), the second one during the liming experiment in 1990–1995 (87 and 78 perch, 14 and 23 pike from control and limed side of the lake, respectively) and the third in 2002–2004 (20 and 20 perch, 22 and 20 pike). Total length and weight of the fish were measured and in the last sampling period opercular bones from perch and cleithral bones from pike were removed for aging of the fish. A sample of white muscle tissue was dissected from each fish posterior to the dorsal fin, wrapped in Al foil and stored frozen for later Hg and stable isotope analyses.

Mercury concentrations of fish samples in 2002 were determined in the Department of Biological

and Environmental Sciences, University of Helsinki, using a cold vapour atomic absorption spectrophotometric technique (Armstrong and Uthe, 1971) and a Bacharach Coleman 50b MAS analyzer (detection limit $0.01 \mu\text{g Hg g}^{-1}$). Prior to and after the analyses, the calibration of the instrument was checked with Hg standard solution, and acid-permanganate solutions were used as blank samples during the analyses. The values of fish Hg concentrations are given as $\mu\text{g Hg g}^{-1}$ of fresh muscle tissue (wet weight). For ascertaining the quality of analyses, two common reference materials were used: dogfish muscle (National Research Council Canada, Certified Reference Material DORM-1) and cod muscle (European Commission Community Bureau of Reference-BCR BCR-422, Table 1). The Hg analyses in

Table 1
Measured and reference Hg concentrations (Hg, $\mu\text{g l}^{-1}$, mean \pm SD) from the calibration materials

	Measured value	<i>n</i>	Reference value
Dogfish	0.875 ± 0.060	6	0.794 ± 0.074
Cod	0.519 ± 0.031	4	0.559 ± 0.016

the 1980s and 1990s were performed in the same laboratory with similar cold vapour atomic absorption spectrophotometry techniques and corresponding quality controls as in 2002. In 2003 and 2004, Hg determinations were conducted in the Institute for Environmental Research, University of Jyväskylä, Finland, also using the cold vapour atomic absorption spectrophotometric technique (Armstrong and Uthe, 1971) and a Perkin–Elmer Flow Injection Mercury System with a measurement uncertainty ($2U = 95\%$) of 15% for samples containing $\text{Hg} \geq 0.01 \mu\text{g g}^{-1}$.

Stable isotope analyses (SIA) of ^{15}N isotope were used to compare the trophic positions of perch and pike in both sides of the lake. A small piece of frozen fish muscle tissue was oven-dried for 48 h at 60°C . Dried samples were then ground to a fine powder using a mortar and pestle and stored frozen. These samples were analysed at the Max Planck Institute of Limnology, Plön, Germany, using an

Eurovector elemental analyser coupled to a Micro-mass Isoprime continuous flow isotope ratio mass spectrometer. The SIA analyses of 2004 were done at the Institute for Environmental Research, University of Jyväskylä, Finland, using a Thermo Finnigan FlashEA 1112 elemental analyser coupled to a Thermo Finnigan DELTA^{plus} Advantage isotope ratio mass spectrometer. Nitrogen stable isotope ratios are expressed as parts per thousand (‰) delta values ($\delta^{15}\text{N}$) referred to an international standard (atmospheric N_2 , Peterson and Fry, 1987). Precision of stable isotope analyses was determined from multiple internal standards used in every analysis and was always better than ± 0.3 ‰. A common macrocrustacean, the isopod *Asellus aquaticus*, was used as a baseline indicator for $\delta^{15}\text{N}$ signatures because it is the best available primary consumer-detritivore in Lake Iso Valkjärvi. Pooled samples of *Asellus* were collected using a hand net and subsequently dried and ground to a fine powder, and stored fro-

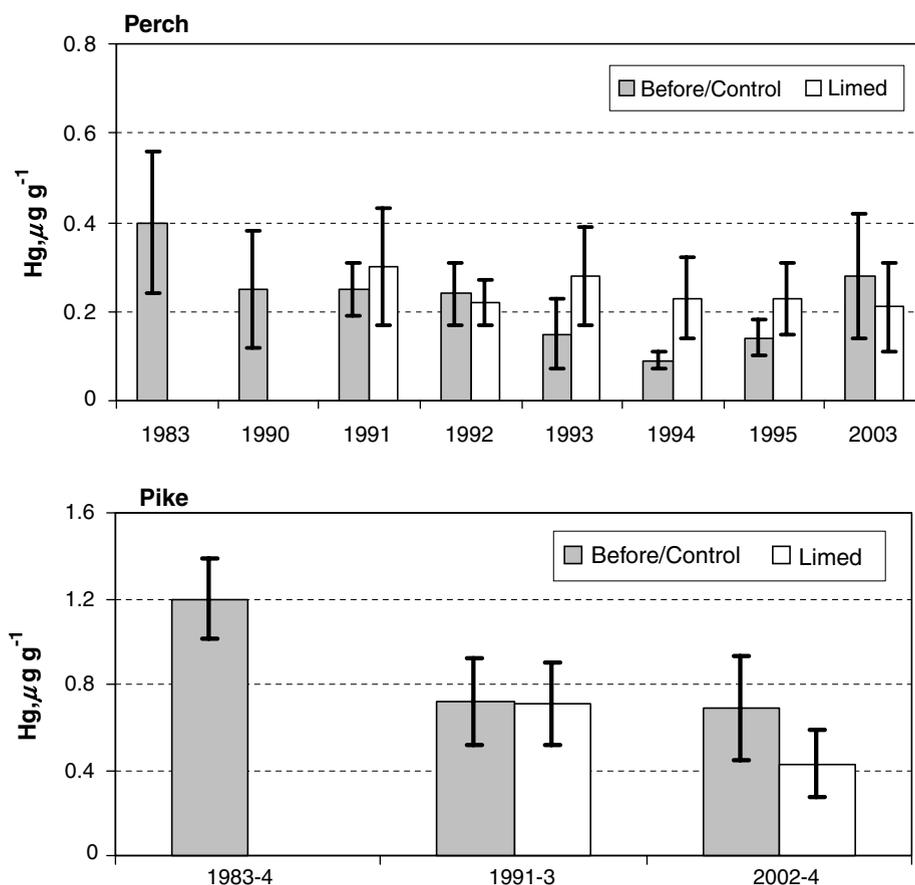


Fig. 2. Mercury concentrations (mean \pm SD) of perch ($n = 211$) and piscivorous pike (>40 cm, $n = 47$) in L. Iso Valkjärvi during the three sampling periods 1983–2004.

zen until SIA. Long-lived primary consumers such as mussels and snails are generally preferred as baseline indicators (Cabana and Rasmussen, 1996), but these are not available from small humic and acidic lakes.

Statistical analyses for observing the differences in fish Hg concentrations between the three sampling periods or between the limed and the control part of the lake were performed using linear regressions between Hg concentration and size-describing parameters of fish and a bivariate dummy-variable (Tremblay et al., 1998). Use of a dummy-variable increases the freedom degrees of the models compared to separate linear models for different sampling periods or limed and control sides and therefore, also the reliability of the model is better. Behind the use of a dummy-factor is the assumption that other factors affecting the fish Hg concentrations are similar and only the effect of sampling time or liming is tested. Weight and age of fish were used as size-describing variables. Linear regressions were formed as follows:

$Hg = a + b \times \text{size} + d \times \text{time}$ (comparisons between sampling periods) or $Hg = a + b \times \text{size} + d \times$

liming (comparisons between limed and control side of the lake)

When Hg concentrations of fish were examined between the three sampling periods during 20 a, three comparison pairs were formed (1980s vs. 1991s, 1980s vs. 2000s and 1990s vs. 2000s) and the dummy variable used for each was 0 to describe the earlier time and 1 the later time. In comparisons of fish Hg concentrations between the two sides of the lake, liming was the bivariate (0 or 1) dummy-variable describing whether sampling was done from the limed (1) or from the control (0) side of the lake. Statistical significances of the models (F-test, significance $p < 0.05$) and of the parameter d (t -test, significance $p < 0.05$) were used in model evaluation. Statistical analyses were performed using SAS 9.1 software (SAS Institute Inc.).

3. Results

The highest Hg concentrations of perch in L. Iso Valkjärvi of $0.40 \pm 0.16 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 6$) were recorded during the first sampling period 1983. During the second sampling period at the time of

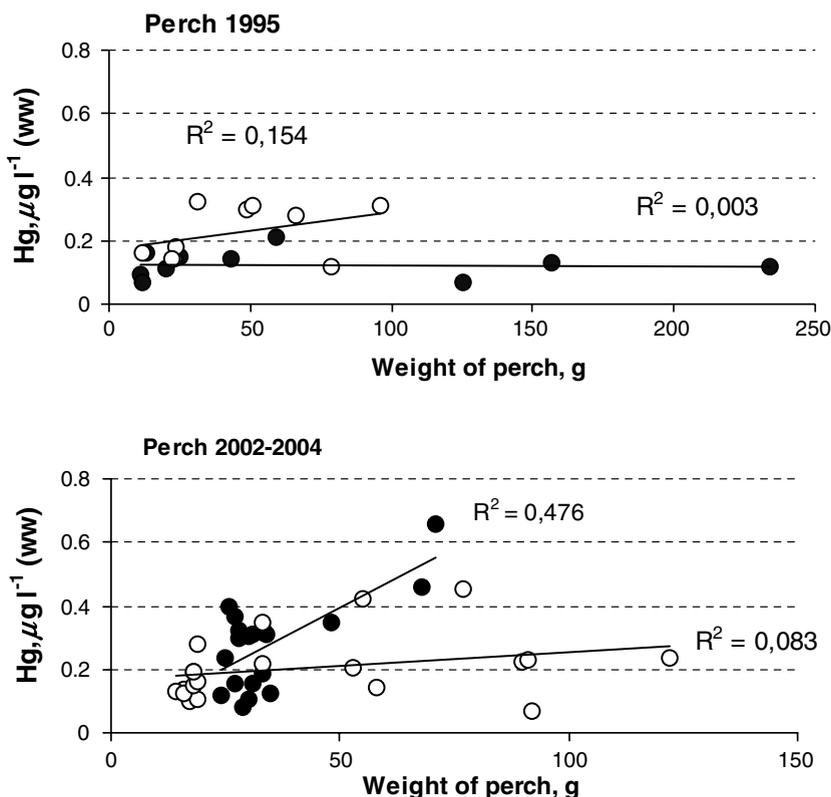


Fig. 3. Mercury concentrations of perch related to fish mass from the limed and the control side of L. Iso Valkjärvi in 1995 (top, $n = 10 + 10$) and 2002–2004 (bottom, $n = 20 + 20$). White circles = limed side, black circles = control side.

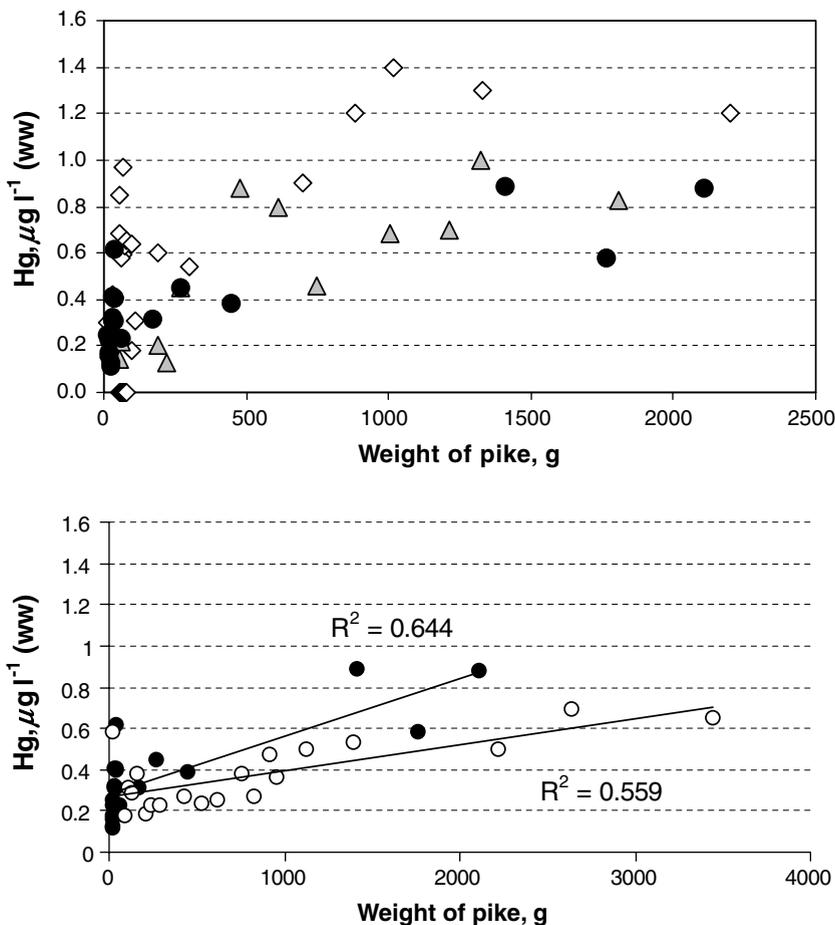


Fig. 4. Mercury concentrations of pike related to fish mass in the control side of L. Iso Valkjärvi during the 3 sampling periods (top, $n = 21 + 14 + 22$) and in both sides of the lakes in 2002–2004 (bottom, $n = 22 + 20$). White circles = limed side, black circles = control side.

liming in 1991, the Hg concentrations of perch were lower than in 1983: $0.25 \pm 0.06 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 19$) in the control and $0.30 \pm 0.13 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 20$) in the limed side of the lake. In the following years the mean Hg concentration of perch in the limed side of the lake remained around $0.22\text{--}0.28 \mu\text{g g}^{-1}$ and was $0.21 \pm 0.10 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 20$) in the third sampling period 2002–2004 (Fig. 2). After the collapse of the perch population in the control side and the subsequent growth increases of the remaining fish, lower mean Hg concentrations ($0.09\text{--}0.015 \mu\text{g g}^{-1}$) of perch were recorded compared to the limed side (Fig. 2). In the years following the fish kill, there was almost no correlation between perch size and Hg concentration (Fig. 3). However, in the third sampling period 2002–2004, the perch Hg concentrations of the control side had increased to $0.28 \pm 0.14 \mu\text{g g}^{-1}$

(mean \pm SD, $n = 20$) (Fig. 2) and were higher than in the limed side of the lake (Fig. 3).

Also for piscivorous pike (>40 cm), the highest Hg concentrations of $1.2 \pm 0.19 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 5$) were recorded during the first sampling period 1983–1984. In the next period (pooled samples of 1991–1993) the Hg concentrations of pike were similar in both sides of the lake: $0.72 \pm 0.21 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 13$) in the control and $0.71 \pm 0.19 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 13$) in the limed side. In the third sampling period 2002–2004, the Hg concentrations of piscivorous pike in the control side remained similar to the previous sampling, $0.69 \pm 0.24 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 4$), whereas in the limed side the concentrations were lower, $0.43 \pm 0.16 \mu\text{g g}^{-1}$ (mean \pm SD, $n = 12$) (Fig. 2). Relating the pike Hg concentration to the mass of individual fish indicates that the differences between

Table 2
Statistical output of equation parameter values for estimating Hg from fish mass

Species	Liming	RMSE	Intercept (a)	Mass, g (b)	Dummy (d)	Freedom degrees	R ²	p (F, model)	p (t, dummy)
Perch	0	0.085	0.282	2.48×10^{-3}	-0.0942	22	0.485	0.0007	0.0484
Perch	1	0.124	0.254	3.08×10^{-3}	-0.0525	23	0.311	0.0138	0.388
Pike	0	0.228	0.561	0.44×10^{-3}	-0.3137	32	0.592	<0.0001	0.0005
Pike	1	0.233	0.624	0.24×10^{-3}	-0.2275	41	0.384	<0.0001	0.0066

Hg = $a + b \times \text{mass} + d \times \text{period}$. Comparison between study periods 1983 and 1991 (liming: 0 = control, 1 = limed; RMSE = root mean-square error).

Table 3
Statistical output of equation parameter values for estimating Hg from fish mass

Species	Liming	RMSE	Intercept (a)	Mass, g (b)	Dummy (d)	Freedom degrees	R ²	p (F, model)	p (t, dummy)
Perch	0	0.118	0.200	4.27×10^{-3}	-0.0685	23	0.438	0.0013	0.2356
Perch	1	0.110	0.333	1.36×10^{-3}	-0.1872	23	0.440	0.0013	0.0013
Pike	0	0.204	0.588	0.36×10^{-3}	-0.3297	40	0.646	<0.0001	<0.0001
Pike	1	0.224	0.632	0.22×10^{-3}	-0.4427	38	0.531	<0.0001	<0.0001

Hg = $a + b \times \text{mass} + d \times \text{period}$. Comparison between study periods 1983 and 2004.

the time periods, as well as between the limed and the control sides of the lake, were mainly due to differences in large (piscivorous) individuals, whereas the variation in smaller fish was always wide (Fig. 4).

According to the regression analyses the decreases in Hg concentrations between the first two sampling periods were statistically significant in all cases but not for the perch of the limed side (Table 2). When comparing the fish Hg concentrations between the first and the last sampling period (Table 3), the decrease in concentrations were signif-

icant in all other cases but not for the perch of the control side. Regression analyses comparing the fish Hg concentrations of the second and third sampling periods indicated significant decreases for both species in the limed side of the lake but for neither perch nor pike in the control side (Table 4).

To assess differences in fish Hg concentrations between the limed and the control sides of the lake, regression models were constructed for both species at the time of liming (second sampling period, 1991 for perch, pooled samples of 1991–1993 for pike), for perch in 1995 to underline the effects of popula-

Table 4
Statistical output of equation parameter values for estimating Hg from fish mass

Species	Liming	RMSE	Intercept (a)	Mass, g (b)	Dummy (d)	Freedom degrees	R ²	p (F, model)	p (t, dummy)
Perch	0	0.092	0.102	6.10×10^{-3}	-0.0341	36	0.330	0.0007	0.3214
Perch	1	0.115	0.255	1.39×10^{-3}	-0.1110	37	0.223	0.0093	0.0051
Pike	0	0.160	0.311	0.33×10^{-3}	-0.0453	33	0.636	<0.0001	0.4257
Pike	1	0.146	0.502	0.14×10^{-3}	-0.2504	40	0.645	<0.0001	<0.0001

Hg = $a + b \times \text{mass} + d \times \text{period}$. Comparison between study periods 1991 and 2002–2004.

Table 5
Statistical output of equation parameter values for estimating Hg from fish mass (g)

Species	Period	RMSE	Intercept (a)	Mass, g (b)	Liming (d)	Freedom degrees	R ²	p (F, model)	p (t, liming)
Perch	1991	0.100	0.176	2.95×10^{-3}	0.030	36	0.180	0.0279	0.3872
Perch	1995	0.069	0.117	0.11×10^{-3}	0.104	17	0.393	0.0144	0.0043
Perch	2002	0.116	0.219	1.74×10^{-3}	-0.090	37	0.204	0.0146	0.0217
Pike	1991	0.197	0.377	0.22×10^{-3}	0.048	34	0.474	<0.0001	0.4983
Pike	2002	0.131	0.313	0.18×10^{-3}	-0.088	39	0.528	<0.0001	0.0471

Hg = $a + b \times \text{mass} + d \times \text{period}$.

Table 6
Statistical output of equation parameter values for estimating Hg from fish age (years)

Species	RMSE	Intercept (a)	Age, yr (b)	Liming (d)	Freedom degrees	R^2	p (F, model)	p (t, liming)
Perch	0.088	0.023	0.0413	-0.0611	37	0.549	<0.0001	0.0340
Pike	0.123	0.162	0.0547	-0.1102	39	0.586	<0.0001	0.0107

$Hg = a + b \times age + d \times period$.

tion collapse on perch Hg concentrations, and for both species in the third sampling period 2002–2004 (Table 5). At the time of and soon after the liming, there were no significant differences in fish Hg concentrations between the lake sides. In 1995, the differences in perch Hg concentrations were significant between the lake sides. For the sampling period 2002–2004, the models indicated significant liming-induced decrease in the Hg concentrations for both perch and pike (Table 5). Fish age data were available only from the sampling in 2002–2004. Especially for perch, age appeared to be a bet-

ter predictor than weight for Hg concentrations in regression models (Table 6).

The age range of examined perch was 4–11 a in both sides of L. Iso Valkjärvi. For northern pike, the individuals were 2–11 a old from the limed side and 1–10 a old from the control side (Fig. 5). The perch of 8 a and older were clearly larger in the limed than in the control side (Mann–Whitney test, $U = 5$, $P = 0.005$), whereas for the 4–5 a-old perch the situation was opposite (Mann–Whitney test, $U = 53$, $P = 0.036$). The length-at-age values of pike were fairly close to each other in the limed and con-

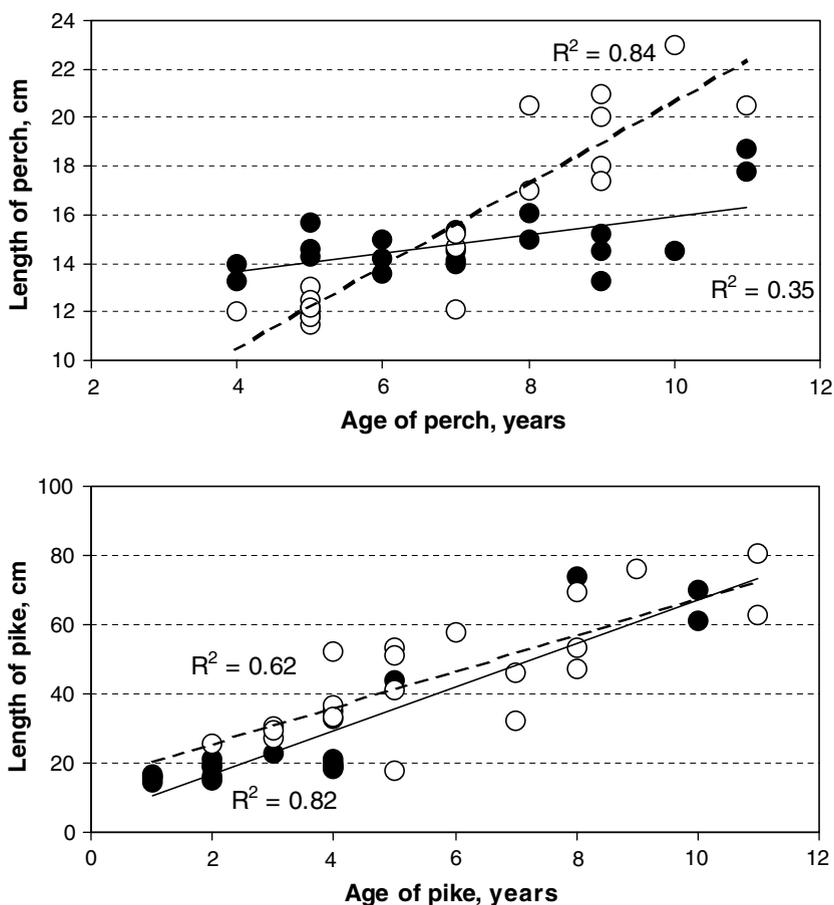


Fig. 5. Length-at-age values of perch ($n = 40$) and pike ($n = 42$) in L. Iso Valkjärvi in 2002–2004. White circles = limed side, black circles = control side.

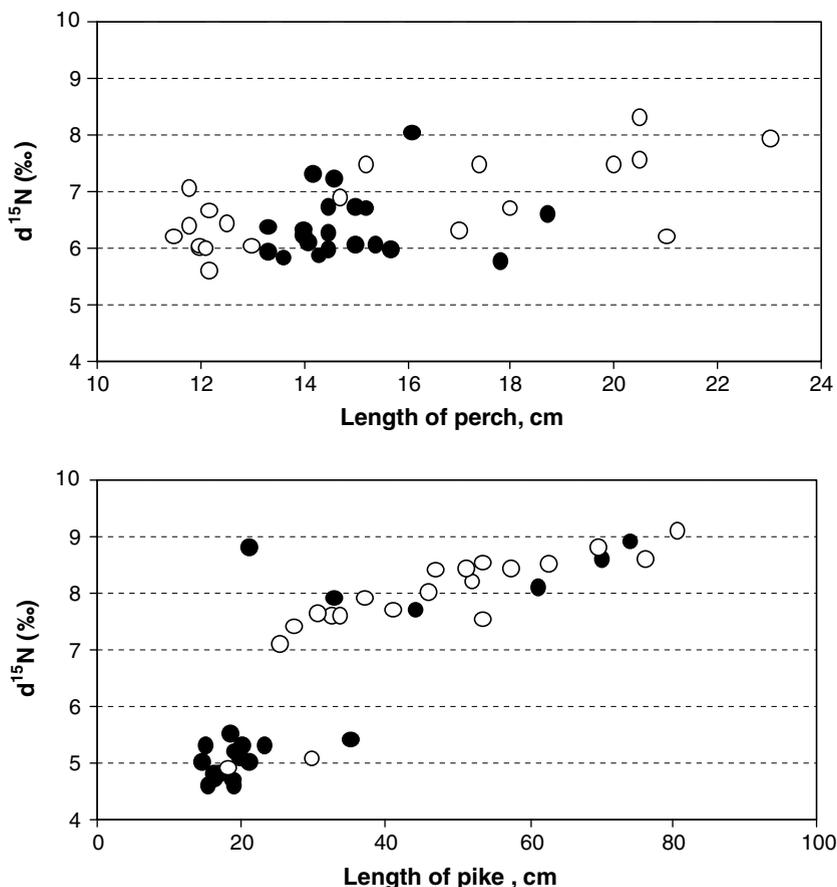


Fig. 6. $\delta^{15}\text{N}$ values from perch and pike in L. Iso Valkjärvi in 2002–2004. The $\delta^{15}\text{N}$ values were adjusted for both sides of the lake by subtracting the corresponding baseline value from all fish samples (1.9‰ for the limed and 1.6‰ for the control side). White circles = limed side, black circles = control side.

control side of the lake (Fig. 5). However, in the age groups 2–5 a, the pike from the limed side were systematically slightly larger than those from the control side (Mann–Whitney test, $U = 5$, $P = 0.005$).

The $\delta^{15}\text{N}$ values of both perch and pike increased with size of fish but there were no systematic difference between the limed and control side of the lake (Fig. 6). For perch, the $\delta^{15}\text{N}$ values increased linearly with length of fish but showed wide variation and no significant difference between the control and limed side of the lake (Mann–Whitney test, $U = 143$, $P = 0.123$). In pike two distinct groups were detected. The fish around 20 cm in length generally had $\delta^{15}\text{N}$ values of 4.5–5.5, whereas pike >40 cm showed values >7.5, increasing slightly with increasing length of fish. In both groups, no significant difference was recorded between the lake sides (Mann–Whitney test, $U = 18$, $P = 0.778$ for small pikes, $U = 72$, $P = 0.230$ for large ones).

4. Discussion

The effects of liming on the pH and alkalinity of L. Iso Valkjärvi lasted longer than predicted from model calculations (Sverdrup, 1985; Järvinen et al., 1995b). The reasons for this may have been the long retention time of the lake and the effective reduction of acidifying emissions and the subsequent decreases in acidic deposition and the rapid chemical recovery of acidified lakes in general in Scandinavia (Skjelkvåle et al., 2001).

The decreasing trend in the fish Hg concentrations in L. Iso Valkjärvi from 1983–1984 to 1991–1993 may have been a response to the decreased atmospheric loads and deposition of Hg from the 1980s to the early 1990s (Munthe et al., 2001; Porvari, 2003), similar to the trend suggested for the Little Rock Lake control (Hrabik and Watras, 2002). The annual bulk deposition in the Lammi

area decreased from $11 \mu\text{g m}^{-2} \text{a}^{-1}$ in 1987–89 to $4.7 \mu\text{g m}^{-2} \text{a}^{-1}$ in 1995 but remained between 4.7 and $8 \mu\text{g m}^{-2} \text{a}^{-1}$ after that (Iverfeldt, 1991; Porvari, 2003). Thus, the decrease in fish Hg concentration from 1993 onwards in the limed basin cannot be explained by decreased deposition of Hg. This conclusion is supported by observations from other lakes in the same area indicating no common decreasing trend in the fish Hg concentrations (Salonen, 2005).

Lower Hg concentrations of fish in the limed side of Lake Iso Valkjärvi in 2002–2004 compared to the control side are consistent with observations that Hg concentrations of fish tend to decrease during the years after liming (Andersson et al., 1995; Meili, 1995) and de-acidification (Hrabik and Watras, 2002). The acidifying deposition decreased substantially during the study period. For instance, the SO_4 deposition in southern Finland decreased some 60% from the late 1980s to 2000 (Vuorenmaa, 2004). Since no change in fish Hg concentration in the control basin of L. Iso Valkjärvi was observed, SO_4 seems not to be the determining factor for Hg methylation in Lake Iso Valkjärvi, in contrast to Little Rock Lake (Hrabik and Watras, 2002).

At the time of liming both sides of L. Iso Valkjärvi received equal amount of Hg from deposition (ca. $4 \mu\text{g m}^{-2} \text{a}^{-1}$, Rask and Verta, 1995) and somewhat more during later years (see earlier). Within the lake, clear MeHg maxima and production were recorded in the O_2 -free hypolimnia of both basins. These were linked to the activity of SO_4 -reducing bacteria and transport from the epilimnion through sedimentation. (Matilainen, 1995; Verta and Matilainen, 1995). Concentrations of total MeHg in the water column of the limed basin were more than twice as high at the start of the experiment compared to the control (0.11 – 0.34 ng l^{-1} and 0.06 – 0.07 ng l^{-1} , respectively, after spring turnover). This was due to the higher proportion of anoxic hypolimnion in the treatment basin during the division. Until the end of summer stratification in 1993, the overall concentrations were somewhat lower in the limed basin than in the control (0.056 – 2.19 ng l^{-1} and 0.129 – 2.65 ng l^{-1} , respectively) (Rask and Verta, 1995). Most of the MeHg was dissolved (79–81%) in the epilimnion of both basins and in the hypolimnion of the limed basin (56%) but in the control basin 77% was found in particles (Verta and Matilainen, 1995). The total burden of MeHg in water of the limed basin decreased from 37–49 mg in August 1991 to 15 mg in August 1992 and

32 mg in 1993. The burden in the control basin remained unchanged (from 17 to 19 mg) (Rask and Verta, 1995).

No MeHg analyses have been performed since then, but based on these early measurements, it is evident that division of the lake and liming decreased the MeHg formation in the limed basin. The annual wet deposition on the lake was estimated to be only 4 mg and the possible maximum flux from the catchment 30–40 mg. The estimated MeHg burden in the fish biomass varied from 47 to 59 mg before the fish kill (Rask and Verta, 1995). Consequently, the total burden in the lake would exceed the annual flux to the lake by a factor of about three and the internal MeHg production would be significant and would probably dominate the seasonal Hg balance of the basins.

The slight increase, but with wide variation, in $\delta^{15}\text{N}$ values for perch suggests variable diets of individual fish, from zooplankton to zoobenthos and even to fish along with increasing size of the perch. Most perch from both sides of the lake had $\delta^{15}\text{N}$ values between 5 and 7‰ and thus, had generally similar trophic position. For smaller pike, $\delta^{15}\text{N}$ values around 5‰ suggest a macroinvertebrate diet (see Jones and Grey, 2004) and values >7 ‰ for larger pike suggest a fish-dominated diet (see also Beaudoin et al., 1999). Pike from both groups were found in both sides of the lake suggesting similar alternative trophic positions. However, different size structure of both species and different length-at-age values of perch between the two sides of the lake may indicate different biological interactions, for example more piscivory in the limed side.

In conclusion, generally similar patterns of $\delta^{15}\text{N}$ values of perch and pike in both sides of L. Iso Valkjärvi suggest that food web structure as such cannot account for the observed differences in fish Hg concentrations. A more likely explanation is liming-induced differences in the dynamics and bio-availability of Hg leading to decreased formation of MeHg.

References

- Andersson, P., Borg, H., Kärrhage, P., 1995. Mercury in fish muscle in acidified and limed lakes. *Water Air Soil Poll.* 80, 889–892.
- Armstrong, F.A.J., Uthe, J.F., 1971. Semiautomated determination of mercury in animal tissue. *At. Absorp. Newsl.* 10, 101–103.
- Beaudoin, C.P., Tonn, W.M., Prepas, E.E., Wassenaar, L.I., 1999. Individual specialization and trophic adaptability of

- northern pike (*Esox lucius*): An isotope and dietary analysis. *Oecologia* 120, 386–396.
- Cabana, G., Rasmussen, J.B., 1996. Comparison of aquatic food chains using nitrogen isotopes. *Proc. Natl. Acad. Sci.* 93, 10844–10847.
- Compeau, G., Bartha, R., 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol.* 50, 498–502.
- Fitzgerald, W.F., Mason, R.P., Vandal, G.M., 1991. Atmospheric cycling and air–water exchange of mercury over mid-continental regions. *Water Air Soil Poll.* 56, 745–768.
- Gilmour, C.C., Henry, E.A., 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Poll.* 71, 131–149.
- Greenfield, B.K., Hrabik, T.R., Harvey, C.J., Carpenter, S.T., 2001. Predicting mercury in yellow perch: Use of water chemistry, trophic ecology, and spatial traits. *Can. J. Fish. Aquat. Sci.* 58, 1419–1429.
- Göthberg, A., 1983. Intensive fishing – a way to reduce the mercury levels in fish. *Ambio* 5, 259–261.
- Hrabik, T.R., Watras, C.J., 2002. Recent declines in mercury concentration in a freshwater fishery: Isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. *Sci. Total Environ.* 297, 229–237.
- Iverfeldt, Å., 1991. Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water Air Soil Poll.* 56, 251–266.
- Järvinen, M., 1993. Responses of pelagial ciliates on liming in an acidified humic lake. *Verh. Internat. Verein. Limnol.* 25, 534–538.
- Järvinen, M., Iivonen, P., Kuoppamäki, K., Rask, M., 1995b. Effect of liming on physical and chemical properties of L. Iso Valkjärvi. Riista- ja kalatalouden tutkimuslaitos. Kalatutkimuksia-Fiskundersökningar 101, 11–24. (In Finnish).
- Järvinen, M., Kuoppamäki, K., Rask, M., 1995a. Responses of phyto- and zooplankton to liming in a small acidified humic lake. *Water Air Soil Poll.* 85, 943–948.
- Jones, R.I., Grey, J., 2004. Stable isotope analysis of chironomid larvae from some Finnish forest lakes indicates dietary contribution from biogenic methane. *Boreal. Environ. Res.* 9, 17–23.
- King, J.K., Kostka, F.M., Fisher, M.E., Saunders, F.M., Jahnke, R.A., 2001. A quantitative relationship that demonstrates mercury methylation rates in marine sediments are based on community composition and activity of sulfate reducing bacteria. *Environ. Sci. Toxicol.* 35, 2491–2496.
- Kuoppamäki, K., 1993. Effects of liming on crustacean zooplankton in an acidified, artificially divided forest lake in southern Finland. *Verh. Internat. Verein. Limnol.* 25, 529–533.
- Lathrop, R.C., Rasmussen, P.W., Knauer, D.R., 1991. Mercury concentrations in walleyes from Wisconsin (USA) lakes. *Water Air Soil Poll.* 56, 295–307.
- Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Håkanson, L., Iverfeldt, Å., Meili, M., Timm, B., 1991. Mercury in the Swedish environment – recent research on causes, consequences and corrective methods. *Water Air Soil Poll.* 55, 193–216.
- Matilainen, T., 1995. Involvement of bacteria in methylmercury formation in anaerobic lake waters. *Water Air Soil Poll.* 80, 757–764.
- Meili, M., 1995. Liming effects on mercury concentrations in fish. In: Henrikson, L., Brodin, Y.W. (Eds.), *Liming of Acidified Surface Waters*. Springer-Verlag, Berlin-Heidelberg, pp. 83–398.
- Metsälä, T., Rask, M., 1989. Mercury concentrations of perch, *Perca fluviatilis* L., in small Finnish headwater lakes with different pH and water colour. *Aqua Fennica* 19, 41–46.
- Munthe, J., Kindbom, K., Kruger, O., Petersen, G., Pacyna, J.T., Iverfeldt, Å., 2001. Examining source–receptor relationships for mercury in Scandinavia. Modelled and empirical evidence. *Water Air Soil Pollut. Focus* 1, 299–310.
- Peterson, B.J., Fry, B., 1987. Stable isotopes in ecosystem studies. *Annu. Rev. Ecol. Syst.* 18, 293–320.
- Poléo, A.B.S., 1995. Aluminium polymerisation – a mechanism of acute toxicity of aqueous aluminium to fish. *Aquat. Toxicol.* 31, 347–356.
- Porvari, P., 2003. Sources and fate of mercury in aquatic ecosystems. Ph.D. Thesis, Department of Limnology and Environmental Protection, University of Helsinki.
- Pöysä, H., Rask, M., Nummi, P., 1994. Acidification and ecological interactions at higher trophic levels in small forest lakes: The perch and the common goldeneye. *Ann. Zool. Fennici* 31, 397–404.
- Rask, M., 1991. Iso Valkjärvi research: An introduction to a multidisciplinary lake liming study. *Finnish Fish. Res.* 12, 25–34.
- Rask, M., Metsälä, T.-R., 1991. Mercury concentrations in northern pike, *Esox lucius* L. in small lakes of Evo Area, southern Finland. *Water Air Soil Poll.* 56, 369–378.
- Rask, M., Verta, M., 1995. Concentrations and amounts of methylmercury in water and fish in the limed and acid basins of a small lake. *Water Air Soil Poll.* 80, 577–580.
- Rask, M., Järvinen, M., Kuoppamäki, K., Pöysä, H., 1996. Limnological responses to the collapse of the perch population in a small lake. *Ann. Zool. Fennici* 33, 517–524.
- Rosseland, B.O., Blakar, I.A., Bulger, A., Krokklund, F., Kvellstad, A., Lydersen, E., Oughton, D.H., Salbu, B., Staurnes, M., Vogt, R., 1992. The mixing zone between limed and acidic river waters: Complex aluminium chemistry and extreme toxicity for salmonids. *Environ. Poll.* 78, 3–8.
- Salonen, M., 2005. Mercury concentrations of pike in small forest lakes of the Evo Area, southern Finland. M.Sc., Department of Biological and Environmental Sciences, University of Helsinki (In Finnish).
- Skjelkvåle, B.L., Mannio, J., Wilander, A., Andersen, T., 2001. Recovery from acidification of lakes in Finland, Norway and Sweden 1990–1999. *Hydrol. Earth Syst. Sci.* 5, 327–337.
- Spry, D.J., Wiener, J.G., 1991. Metal bioavailability and toxicity to fish in low-alkalinity lakes: A critical review. *Environ. Poll.* 71, 243–304.
- Sverdrup, H., 1985. Calcite dissolution kinetics and lake acidification mitigating. Ph.D. Thesis, Lund Institute of Technology.
- Tremblay, G., Legendre, P., Doyon, J.-F., Verdon, R., Schetagne, R., 1998. The use of polynomial regression analysis with indicator variables for interpretation of mercury in fish data. *Biochem. J.* 40, 189–201.
- Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the aquatic environment: A review of factors

- affecting methylation. *Crit. Rev. Environ. Sci. Technol.* 31, 241–293.
- Verta, M., Matilainen, T., 1995. Methylmercury distribution and partitioning in stratified Finnish forest lakes. *Water Air Soil Poll.* 80, 585–588.
- Vuorenmaa, J., 2004. Long-term changes of acidifying deposition in Finland (1973–2000). *Environ. Poll.* 128, 351–362.
- Watras, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., Wentz, S.P., 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219, 183–208.
- Winfrey, M.R., Rudd, J.W.M., 1990. Environmental factors affecting the formation of methylmercury in low pH lakes. *Environ. Toxicol. Chem.* 9, 853–869.