

Concentrations of heavy metals in food web components of small, boreal lakes

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The concentrations of heavy metals in different food web components, such as zooplankton, benthic invertebrates and fish, were examined in small humic lakes from southern Finland. Variation in metal concentrations in zooplankton was observed between different lakes and in benthic invertebrates between different animal groups. We found a significant relationship between lakewater pH and Cd concentration in isopods (*Asellus aquaticus*), while no relationship between the humic content of lakewater and Cd or Hg concentrations was observed. Annual variation in Cd, studied over a six-year period, was correlated with the amount of discharge, which indicated the importance of the annual loading of Cd from the catchment in determining accumulation in isopods. The metal concentrations in perch (*Perca fluviatilis*) were higher in a humic and acid lake than in a slightly humic lake and may partly be explained by the varying dietary regime of perch.

Introduction

In aquatic systems, the natural concentrations of metal ions are principally dependent on the ambient distribution, weathering and leaching of these elements from the soil in the catchment area. Human activities, such as industrial and traffic emissions and various land-use practices may increase heavy metal loading into aquatic ecosystems (Nriagu and Pacyna 1988, Mukherjee 1989, Tarvainen *et al.* 1997). Heavy metals are carried to the lakes through atmospheric deposition and/or discharge. The characteristics of the water, such as acidity or the amount of organic matter, are known to be important factors in determining the fate of heavy-metals in lakes (Verta *et al.* 1990, Mannio *et al.* 1993, Skjelkvåle *et al.* 2001).

Increased loading of heavy metals into lakes may have several ecological consequences. Elevated trace metal concentrations may lead e.g. to toxic effects or biomagnification in aquatic environments. Accumulation of heavy metals in the food web can occur either by bioconcentration from the surrounding medium such as water or sediment, or by bioaccumulation from the food source. Aquatic organisms have been widely used in biological monitoring and assessment of safe environmental levels of heavy metals. However, better understanding of the transfer of metal ions from catchments to lakes and especially of the bioaccumulation and trophic transfer in the various components of the food webs are needed. In Finland, the effects of acidification on heavy-metal concentrations in aquatic plants, benthic

invertebrates and fish have been investigated in lakes that have low total organic carbon (TOC) concentrations (Verta *et al.* 1990, Iivonen *et al.* 1992, Berninger and Pennanen 1995). Among the heavy metals, the accumulation of Hg has been determined in reservoirs (Porvari 2003) and in humic lakes (Metsälä and Rask 1989). Low water pH affects the accumulation of some heavy metals in aquatic biota by increasing the free metal ion concentrations in the water and thus their bioavailability for organisms (Lithner *et al.* 1995, Mason *et al.* 2000, Scoullou and Pavlidou 2003). In contrast, the high concentration of dissolved organic carbon (DOC) may decrease the bioavailability and toxicity of heavy metals and thus reduce accumulation rates (Cambell and Stokes 1985, Iivonen *et al.* 1992), although high DOC concentration may also increase accumulation of some metals (Metsälä and Rask 1989, Kozuch *et al.* 1998, Porvari 2003). Significant positive correlations were observed between the level of heavy-metal loading in lakes and the level of heavy metals accumulated by the aquatic organisms (Farkas *et al.* 2003). Accumulation of heavy metals in aquatic organisms may also be attributed to the variability in size and age of individuals, feeding habits and seasonal changes in living conditions (van Hattum *et al.* 1993, 1996, Köck *et al.* 1996, Farkas *et al.* 2003).

Due to the toxicity of heavy metals, accurate information on their concentrations in aquatic ecosystems is needed, especially from natural, uncontaminated habitats (Janssen *et al.* 2000). This is because environmental risk assess-

ment requires sufficient evaluation of different regional background levels and also seasonal and annual variation of metals in different components of the food web (Petri and Zauke 1993). In the present study, we hypothesize that the high content of organic matter in humic, naturally acid lakes reduces the accumulation of metals in aquatic biota. Our study is focused on small, boreal lakes with varying concentrations of dissolved organic matter and with water pH ranging from acid (5.4) to neutral (7.1). We examined three trophic levels of a food web, i.e. herbivores, detritus feeders and predators by analyzing heavy-metal concentrations in zooplankton, aquatic insects, isopods and fish. The annual variations of Cd and Hg concentrations in isopods and fish were also studied over a six-year period in two of the lakes.

Methods

The lakes studied are situated mainly in the Evo forest area (61°14'N, 25°12'E) of Lammi, southern Finland. The morainic soil of the study area overlies granodiorite and gneiss bedrock. The lakes, most of them pristine headwaters, are humic lakes with high organic matter contents; only one of the lakes is an oligohumic, clear-water lake. The lakes have rather low nutrient concentrations and can be classified either as oligotrophic or mesotrophic lakes. The maximum depths and surface areas of the lakes and some chemical characteristics of the epilimnetic water

Table 1. Area, maximum depth and some chemical characteristics (mean values in surface water in October 1998–2001) for the study lakes situated in southern Finland.

Lake	Area (ha)	Max. depth (m)	pH	Colour (Pt mg l ⁻¹)	P _{tot} (µg l ⁻¹)	N _{tot} (mg l ⁻¹)
Nimetön	0.4	11	5.6	325	37	0.78
Mekkojärvi	0.4	4	6.1	330	23	0.66
Tavilampi	0.8	7	6.0	165	22	0.68
Horkkajärvi	1.1	12	5.9	351	28	0.70
Majajärvi	3.9	11	5.9	287	19	0.64
Iso-Valkjärvi	3.9	8	5.7	35	17	0.47
Valkea Kotinen	4.1	7	5.3	159	12	0.49
Onkimanjärvi	6.3	4	6.3	261	25	0.68
Pitkäniemenjärvi	13.9	10	6.4	192	28	0.53
Kynnäröjärvi*	25.0	3	7.1	274	45	1.81

* from 1997–1998.

are shown in Table 1. Forestry is practically the only human activity in the catchments; however, the catchment of Kynärjärvi also comprises cultivated land. Two of the lakes were monitored more intensively over a six-year period: Horkkajärvi with a mean summer pH value ranging from 5.5 to 5.7 and DOC concentrations from 16 to 25 mg C l⁻¹ and Tavilampi with a pH value from 5.7 to 6.0 and DOC concentration from 10 to 14 mg C l⁻¹ (Tulonen *et al.* 2005).

Water samples were taken with a tube sampler from surface water in October 1998–2001. Water pH was determined with an Orion SA 720 meter and colour at 420 wavelength with a Shimadzu UV-2100 spectrophotometer. Total nitrogen (N_{tot}) and phosphorus (P_{tot}) concentrations were analysed after persulphate digestion with Lachat Instrument/Quickchem 800. Cd concentrations in surface water were analysed in summer 1998 and 2004 from four lakes (Nimetön, Horkkajärvi, Tavilampi and Valkeakotinen). For the estimation of the discharge in the study area, water flow was measured weekly from the inflow of Nimetön.

Zooplankton samples were collected in June–July 1997–1998 from seven lakes by pulling a 50- μ m mesh net in surface water behind a rowing boat. The samples, one from each lake, were rinsed with distilled water, stored in plastic HD-PE bottles and frozen for later analysis of heavy metals (Cd, Cr, Pb, Zn, Cu). The samples were preserved in formaldehyde and later identification and estimation of the predominant species was examined using inverted and light microscopes.

Benthic invertebrates (odonates, trichopterans, ephemeropterans, chironomids, oligochaetes and isopods) were collected from the littoral zones of two lakes, Tavilampi and Horkkajärvi, with a macrofauna net in August 1997–1999 (oligochaetes in 2001). Samples of the isopod *Asellus aquaticus* were taken from the same lakes in August or September 1997–2002 and additionally from six other lakes and from an oligohumic spring (Kellolanlähde) in 2002. The animals were sorted in the laboratory and held for about 12 h in clean water for gut clearance, after which they were stored frozen for later analysis. Heavy metals (Cd, Cr, Pb) were determined in pooled samples consisting of from 3 to

100 animals. The odonate nymph samples consisted of species from the families *Coenagrionidae*, *Libellulidae* and *Aeschnidae*.

Fish were caught in traps (1-cm² mesh) from Tavilampi and Horkkajärvi in August–September 1997–2002. Using the same time period for sampling every year, we could minimize the effects on seasonal variation in metal concentrations observed at least with some fish species (Farkas *et al.* 2003). We selected only individuals of perch *Perca fluviatilis*, which is a common top predator in small forest lakes of the area (Rask 1989). The bodyweights, lengths and sexes of ten perch per lake per year were determined. The ages of perch individuals were determined from the opercular bones according to Tesch (1971). In 1997–1998 stomach contents of the fish caught monthly (May–September) from the lakes were analysed to determine the main food items of benthic invertebrates taken by perch. For the determination of heavy metals (Cd, Cr, Hg), the liver was removed and pieces of muscle were dissected above the lateral line between the dorsal fin and tail; the samples were kept frozen until analysis. The heavy-metal concentrations in muscle were analysed every year, except for the Cr analyses from the year 2000 and the Hg analyses from 2001. The heavy metals in liver were determined in 1998 (Cd, Cr) and 2000–2002 (Cd).

The heavy metals were analysed with an atomic absorption spectrometry analyser (Varian SpektrAA-400 with a GTA-96 graphite tube atomizer; Varian Inc., Palo Alto, CA, USA; Varian 1988). The Hg was analysed using the cold vapour method with a Varian VGA-76 gas-liquid separator. The frozen samples were melted and the wet weight (w.w.) and dry weight (d.w.) determined. The fish muscle tissues were homogenized and digested in concentrated HNO₃; other samples were digested whole. The results represent a mean of two replicates, in sparse samples only one replicate. Standards for AAS by Merck & Co., Inc. (Whitehouse Station, NJ, USA) and Reagecon Diagnostics Ltd: (Shannon, Co. Clare, Ireland) were used. Individual programmes (Cd, Hg, Cr, Cu, Zn, Pb; Varian 1988) were optimized and palladium (Pd) modifier solution was used for Cd. The data was statistically tested with Exel Data Analysis for Windows, using regression analyses.

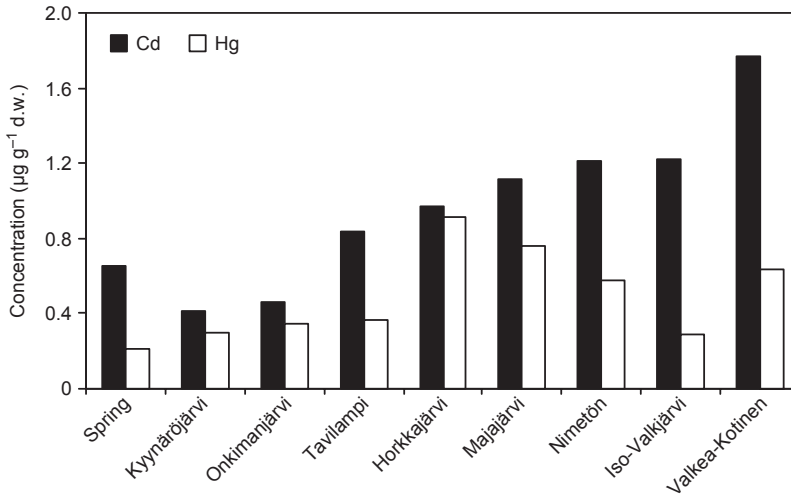


Fig. 1. Cd and Hg concentrations in the isopod *Aselelus aquaticus* in the study lakes and in a spring.

Results

Zooplankton

The mean heavy-metal concentrations in zooplankton, sampled from seven different lakes, were (in $\mu\text{g g}^{-1}$ d.w.): Cd 0.54, Cr 13.6, Pb 7.5, Zn 251 and Cu 184 (Table 2). In general, lower concentrations were determined in samples with rotifers as the predominant zooplankton group and the higher concentrations in samples with *Daphnia* as the predominant species. The heavy-metal concentrations in zooplankton sampled from the clearwater lake, Iso-Valkjärvi, did not

differ from the concentrations in humic lakes, only with higher Cu concentrations. Zooplankton in the small and highly humic Mekkojärvi had high heavy-metal concentrations compared with zooplankton in other lakes. The highest Cd concentrations were found in Pitkäniemenjärvi.

Benthic invertebrates

Wide variation was shown in heavy-metal concentrations between different animal groups in the two lakes studied (Table 3). The Cd concentrations ranged from 0.11 to 3.93 $\mu\text{g g}^{-1}$ d.w. and

Table 2. Heavy-metal concentrations ($\mu\text{g g}^{-1}$ d.w.) in zooplankton sampled from different lakes. Values are based on one sampling/lake. n.d. = not determined.

Lake	Year	Cd	Cr	Pb	Zn	Cu	Dominant species
Nimetön	1997	0.27	17.8	8.7	n.d.	53	<i>Keratella cochlearis</i>
Mekkojärvi	1998	0.70	61.6	18.2	n.d.	n.d.	<i>Daphnia longispina</i>
Tavilampi	1997	0.46	6.7	6.5	432	26	<i>Bosmina longispina</i> , <i>B. longirostis</i>
	1998	0.46	2.2	3.8	258	n.d.	<i>Ceriodaphnia quadrangula</i>
Horkkajärvi	1997	0.55	2.9	2.6	297	11	<i>Ceriodaphnia quadrangula</i> , <i>Bosmina longispina</i>
	1998	0.30	1.5	2.6	145	n.d.	<i>Keratella cochlearis</i> , <i>Asplanchna priodonta</i>
Majajärvi	1997	0.56	4.9	5.2	230	307	<i>Bosmina longispina</i> , <i>Thermocyclops</i> sp.
	1998	0.73	11.2	9	207	n.d.	<i>Bosmina</i> spp., <i>Keratella cochlearis</i> , <i>Polyarthra</i> spp.
Iso-Valkjärvi	1997	0.47	18.2	4.7	n.d.	523	<i>Holopedium gibberum</i> , <i>Heterocope appendiculata</i>
Pitkäniemenjärvi	1998	0.91	8.5	13.8	191	n.d.	<i>Daphnia cristata</i>
Mean		0.54	13.6	7.5	251	184	
S.D.		0.20	17.9	5.1	93	225	

Cr from 3.5 to 16.7 $\mu\text{g g}^{-1}$ d.w. The highest Cd concentration was found in oligochaetes and the highest Cr concentration in chironomids. Trichoptera, odonates and chironomids had lower Cd concentrations than isopods, but the Cr or Pb concentrations did not clearly vary between the invertebrate groups.

The mean Cd concentrations in *Asellus*, collected from a single spring and eight lakes, varied from 0.41 to 1.77 $\mu\text{g g}^{-1}$ d.w. (Fig. 1). We found no statistically significant relationship between water colour in the lakes (mean values of water samples taken in October 1998–2001) and mean Cd concentrations in *Asellus*. The highest concentrations of Cd and the lowest water colour values were observed in two lakes, Iso-Valkjärvi and Valkea Kotinen. However, a highly significant correlation between water pH and Cd concentrations in *Asellus* was observed ($r^2 = 0.82$, $p < 0.001$, $n = 9$, Fig. 2). The Hg concentrations in *Asellus* varied from 0.21 to 0.91 $\mu\text{g g}^{-1}$ d.w. and no statistically significant correlations were found, either between water colour or pH and Hg concentration in the lakes. The Cd concentrations in *Asellus* ranged from 0.6 to 1.3 $\mu\text{g g}^{-1}$ d.w. in the two lakes sampled over six years (Fig. 3). The Cd concentrations in lake water were always $< 0.02 \mu\text{g l}^{-1}$. In most years, the concentrations in *Asellus* were higher in the more humic and acid Horkkajärvi than the slightly humic Tavilampi. The annual changes in concentrations were similar in both lakes.

Fish

The mean Cd, Cr and Hg concentrations in the muscles ($\mu\text{g g}^{-1}$ d.w.) and in the liver ($\mu\text{g g}^{-1}$ w.w.) of perch are shown in Table 4. The Cd and Cr concentrations in muscles were slightly higher in humic and acid Horkkajärvi than in Tavilampi.

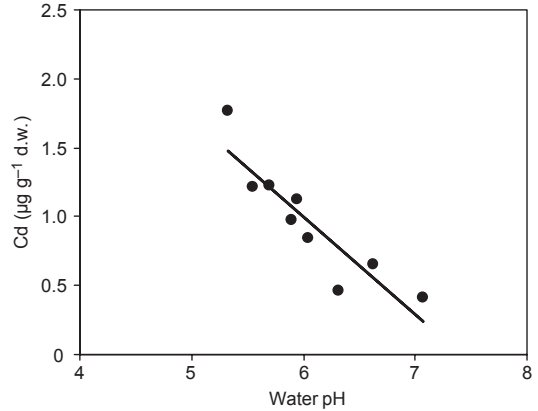


Fig. 2. Relationship between Cd concentration in *Asellus aquaticus* and water pH in the studied lakes (linear regression, $r^2 = 0.82$, $p < 0.001$, $n = 9$).

However, clearly higher mean concentrations of Hg in muscles and Cd and Cr in liver were found in Horkkajärvi. Our data also showed some annual variation in the metal concentrations: in Hg the variation could be threefold and in Cd twofold (Fig. 4). The monthly diet of perch was

Table 3. Cd, Cr and Pb concentrations ($\mu\text{g g}^{-1}$ d.w., mean \pm S.D.) in aquatic insects and isopods collected from two lakes, Tavilampi (T) and Horkkajärvi (H) in 1997–2002. n.d. = not determined.

Species	Lake	Cd	Cr	Pb
Trichoptera	T	0.37 \pm 0.17	8.1 \pm 5.8	4.5 \pm 1.1
	H	0.20 \pm 0.09	6.5 \pm 4.7	3.5 \pm 0.3
Odonata	T	0.13 \pm 0.06	4.3 \pm 2.8	0.6*
	H	0.18 \pm 0.04	6.8 \pm 1.4	3.2*
Ephemeroptera	T	0.95*	3.5*	n.d.
Chironomidae	T	0.32*	13.0*	n.d.
	H	0.11*	16.7*	n.d.
Oligochaeta	T	1.76 \pm 2.02	4.0*	n.d.
	H	3.93 \pm 0.47	7.1*	n.d.
Asellus	T	0.86 \pm 0.27	5.4 \pm 5.2	5.0*
	H	0.99 \pm 0.20	5.5 \pm 3.3	3.4*

*samples collected in one year.

Table 4. Lengths, weights, ages and heavy-metal concentrations (mean \pm S.D.) in muscle and liver of perch, *Perca fluviatilis*, taken from Tavilampi and Horkkajärvi in 1997–2002.

Lake	Length (cm)	Weight (g)	Age (yr)	Muscle (in $\mu\text{g g}^{-1}$ d.w.)			Liver (in $\mu\text{g g}^{-1}$ w.w.)		
				Cd	Cr	Hg	Cd	Cr	Hg
Tavilampi	14.0 \pm 2.1	31.6 \pm 15.9	5.1 \pm 3.1	0.027 \pm 0.018	1.32 \pm 1.20	0.6 \pm 0.4	0.36 \pm 0.22	0.41 \pm 0.30	0.09 \pm 0.02
Horkkajärvi	12.5 \pm 1.8	21.9 \pm 10.9	4.2 \pm 2.1	0.030 \pm 0.017	1.65 \pm 2.37	1.8 \pm 1.0	1.01 \pm 0.66	0.89 \pm 0.89	0.37 \pm 0.14

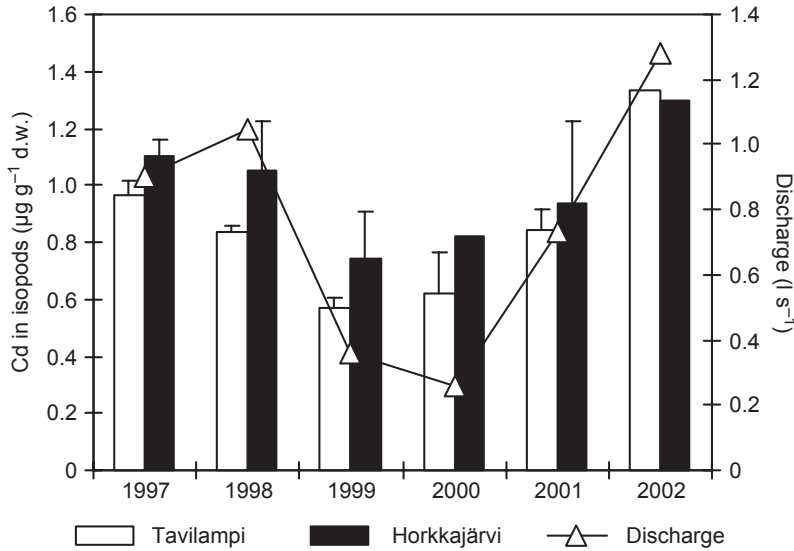


Fig. 3. Annual mean Cd concentrations in *Asellus aquaticus* from Tavilampi and Horkkajärvi and mean discharge in May–August, 1997–2002. Bars indicate standard deviation of the mean.

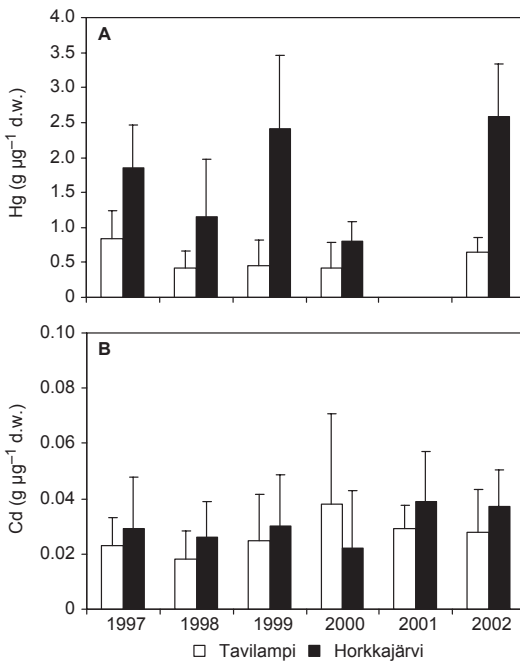


Fig. 4. Annual mean Hg (A) and Cd (B) concentrations in muscle of perch from Tavilampi and Horkkajärvi in 1997–2002. Bars indicate standard deviation of the mean.

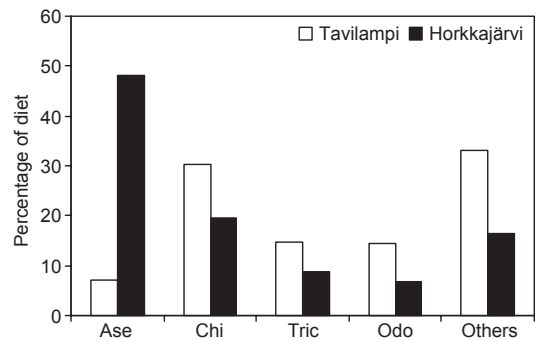


Fig. 5. Dietary composition of perch in Tavilampi and Horkkajärvi in 1997–1998. Ase = *Asellus aquaticus*, Chi = Chironomidae, Tric = Trichoptera, Odo = Odonata.

studied in both lakes in May–September 1997–1998 (Fig. 5). In Tavilampi the proportion of isopods in the diet varied between 0% and 17% (mean 7%) and in Horkkajärvi between 21% and 71% (mean 48%).

Discussion

The concentrations of heavy metals in boreal lakes are primarily controlled by bedrock and overburden of the catchment (Skjelkvåle *et al.* 2001). The heavy metal budget calculated previously for the catchment of Valkea-Kotinen and the low concentrations measured in the lake water indicated low inputs of heavy metals from the forested catchment areas into lakes (Ukonmaanaho *et al.* 1998, 2001). In the present study, in four lakes we measured very low Cd concentrations ($< 0.04 \mu\text{g l}^{-1}$), which were close to the detection limit of Cd analysis. We suggest that the analysis of heavy metals in biological communities may reveal the behavior of trace metals

in natural lake ecosystems more accurately than background concentrations in lake water.

Plankton species are widely used in many toxicity tests, but few data are available on heavy-metal concentrations in natural communities of zooplankton, especially from freshwaters (Balogh 1988, Chen *et al.* 2000). Zooplankton are often the main diet for many predators and may remarkably contribute to the transfer of heavy metals to higher trophic levels. However, it is technically difficult to completely separate the phyto- and zooplankton fractions from water samples. In the present study, some phytoplankton may also have been present in the zooplankton samples. In the lakes studied, the Cd concentrations in zooplankton were clearly lower than in 20 lakes investigated in North America from contaminated to pristine watersheds, where Chen *et al.* (2000) measured mean Cd concentrations of $2.7 \mu\text{g g}^{-1}$ d.w. for small and $1.6 \mu\text{g g}^{-1}$ d.w. for large zooplankton. The Pb concentrations in zooplankton were also lower in lakes from Finland than in those from North America, but the Zn concentrations were similar. Low Cd concentrations similar to those in this study were also observed in calanoid copepods from arctic marine ecosystems, ranging from 0.1 to $0.7 \mu\text{g g}^{-1}$ d.w. (Ritterhoff and Zauke 1997).

The benthic community is a heterogeneous group including detritivorous, herbivorous and carnivorous species. In Finland knowledge of heavy-metal concentrations in different benthic species is sparse. Our results showed that in some detritus feeders (oligochaetes, chironomids) the concentrations were higher than in other invertebrate groups, which may also indicate the presence of species-specific uptake mechanisms for different metal ions. Verta *et al.* (1990) measured similar Cd and Pb concentrations in trichopterans from headwater lakes in Finland. The isopod *Asellus aquaticus* is a cosmopolitan species and a test animal commonly used in ecotoxicological studies (Green *et al.* 1986, Migliore and De Nicola-Guidici 1990) and in environmental studies (Lithner *et al.* 1995, van Hattum *et al.* 1996, Eimers *et al.* 2001). In the present study, the Cd concentrations in *Asellus* varied from 0.41 to $1.77 \mu\text{g g}^{-1}$ d.w. Cd concentrations in *Asellus* were also determined by van Hattum *et al.* (1996) in various freshwaters, from unpol-

luted lakes to polluted rivers in the River Rhine estuary in the Netherlands. In unpolluted lakes the Cd concentrations were clearly lower than in humic lakes from Finland ranging from 0.05 to $0.21 \mu\text{g g}^{-1}$ d.w. However, in waters in the vicinity of industrial, municipal or agricultural discharges the Cd concentrations were clearly higher, ranging between 0.9 and $10.0 \mu\text{g g}^{-1}$ d.w. In the Netherlands, even in unpolluted freshwaters, Pb concentrations in *Asellus* appeared to be higher (from 2.6 to as high as $30 \mu\text{g g}^{-1}$ d.w.) than in lakes from Finland ($3.4\text{--}5.0 \mu\text{g g}^{-1}$ d.w., Table 3).

It is known that the content of dissolved organic matter and humic compounds in lakes reflects water colour rather well (Kortelainen 1993). We found no statistically significant relationships between water colour in the lakes (mean values of water samples taken in October 1998–2001) and the mean Cd concentrations in *Asellus*. The highest Cd concentrations were observed in lakes with the lowest colour values. Previously, Eimers *et al.* (2001) showed that the increased amount of organic matter in sediment could decrease the Cd accumulation in isopods. In contrast, Kozuch *et al.* (1998) found that humic substances stimulated Cd accumulation in mussels. The present results indicate that the effect of low pH on the lability and bioavailability of Cd may increase the accumulation rates of Cd in isopods (Eimers *et al.* 2001, Scoullou and Pavlidou 2003). Thus, water acidity may be a more important factor than the content of organic matter in Cd accumulation (Fig. 2). We also focused on the annual variation in Cd concentration in isopods sampled from two lakes (Fig. 3). The annual changes in concentrations were similar in both lakes, which support the hypothesis that external factors such as weather conditions could affect the leaching of metals from the catchment and further accumulation in the biota. According to Ukonmaanaho *et al.* (1998) metal concentrations in soil water measured in the catchment of Valkea-Kotinen are multiple compared with concentrations in lake water. We found a clear relationship between the mean discharge measured between May and August from the inflow of Nimetön, situated in the vicinity of the studied lakes, and Cd concentrations in *Asellus* ($r^2 = 0.76$, $p < 0.01$, $n = 12$).

Few published results are available on Cd concentrations in fish muscles, measured as d.w., in uncontaminated lakes. The present results (Table 4) agreed well with the findings of Allen-Gil *et al.* (1997) who measured similar low Cd ($< 0.04 \mu\text{g g}^{-1}$ d.w.) and Hg ($< 2.2 \mu\text{g g}^{-1}$ d.w.) concentrations in fish from arctic lakes in Alaska. Porvari (2003) measured mean Hg concentrations of $0.45 \mu\text{g g}^{-1}$ w.w. in northern pike (*Esox lucius*) from lakes in Finland. In the present study, the Hg concentrations in perch calculated for w.w. were similar, about $0.36 \mu\text{g g}^{-1}$ w.w. Hg accumulates mostly in muscles, while the highest Cd levels are often found in gills, liver or kidney (Berninger and Pennanen 1995, Farkas *et al.* 2000, Olsvik *et al.* 2001). Our data showed that the Hg concentrations clearly differed in muscle and liver tissues between the two lakes, but for Cd concentrations this difference was clearly seen only in the liver of perch.

In general, wide uncertainty exists on the predominant source or uptake route (food vs. water) of metals to fish (Chen *et al.* 2000, Bervoets *et al.* 2001). Some studies emphasized the role played by fish diet (Allen-Gil *et al.* 1997, Burgos and Rainbow 2001); e.g. in the present study the differences in Cd concentrations in liver between the studied lakes may be explained by the varying diet of perch in these lakes (Fig. 5). During the summer months in Horkkajärvi, a mean of 48% of the perch diet consisted of *Asellus* with slightly elevated Cd concentrations compared with isopods in Tavilampi. The perch clearly feed less on *Asellus* in Tavilampi (averaging 7% of perch diet) and more on animals with lower contents of Cd (trichopterans, chironomids, odonates, Table 3). In addition to the dietary effects or exposure to aqueous concentrations, water chemistry may also affect the uptake rates of heavy metals. Previous studies (Iivonen *et al.* 1992, Berninger and Pennanen 1995) showed that Cd and Pb concentrations in the liver of perch increased in parallel with the increase in water acidity, which is consistent with the results of our study. Iivonen *et al.* (1992) also suggested that organic matter could reduce metal accumulation, because they found negative correlations between Pb and Cd in perch liver and TOC concentration in headwater lakes from Finland with

low or moderate contents of humic substances. The positive effect of TOC on Hg accumulation has been shown in various studies (Mannio *et al.* 1986, Metsälä and Rask 1989, Porvari 2003). In the present study, the concentrations of some heavy metals (Cd, Cr, Hg) both in muscles and liver were higher in the more humic Horkkajärvi than in Tavilampi. Evidently, further data from humic lakes are needed to estimate the role played by organic substances in the accumulation of heavy metals in fish.

Although the need for information on the annual variation in heavy-metal concentrations in biota is evident (Couture and Rajotte 2003), this has so far hardly been studied or monitored in different environments. Our data showed some annual variation in the concentrations; in Hg, the variation could be threefold on a yearly basis and in Cd a twofold variation was observed (Fig. 4). The low Cd concentrations with high standard deviation (Table 3) made it especially difficult to distinguish between natural variation and the variation due to heavy-metal analysis. Recently, seasonal variation in metal accumulation in fish was observed in many aquatic environments (Köck *et al.* 1996, Farkas *et al.* 2000, Audet and Couture 2003), which may be a consequence of enhanced metabolic rates or higher feeding rates at higher water temperatures. Thus, it is always necessary to carry out examination of heavy-metal concentrations in fish with samples taken at the same time each year. In the present study, we wanted to guarantee as similar conditions as possible by catching fish every year in August–September.

In conclusion, data collected from ten small, boreal lakes situated in southern Finland showed wide variation in heavy-metal concentrations in various food web components. Several factors, such as water chemistry, diet or water discharge, were shown to affect accumulation of heavy metals in aquatic biota. The results confirm the necessity to collect background data across a broad spectrum of lake types. Our hypothesis that high humic content would reduce the accumulation of heavy metals in the aquatic biota was not inclusively supported, which emphasizes the importance to increase our understanding of the role of organic substances in the accumulation of heavy metals.

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