MERCURY BIOACCUMULATION IN RAINBOW TROUT (*ONCORHYNCHUS MYKISS*) AND THE TROUT FOOD WEB IN LAKES OKAREKA, OKARO, TARAWERA, ROTOMAHANA AND ROTORUA, NEW ZEALAND

JONATHAN P. KIM[1*] and SHANE BURGGRAAF[2]
[1] *Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand;* [2] *Inter Ag, Ltd., Hamilton, New Zealand*
([*] author for correspondence, e-mail: jkim@alkali.otago.ac.nz)

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Abstract. Methyl mercury (Hg) was determined in rainbow trout (*Oncorhynchus mykiss*) and organisms in the lower tropic levels: smelts (*Retropinna retropinna*), bullies (*Gobiomorphus cotidianus*), koura (*Paranephrops planifrons*); and zooplankton (*Daphnia carinata* and *Calamoecia lucasi*) in Lakes Okareka, Okaro, Tarawera, Rotorua and Rotomahana, New Zealand. Water concentrations of total Hg (Hg_T) and methyl Hg were also measured. Mean methyl Hg concentrations in the trout, the prey species (smelts, bullies and koura) and zooplankton increased linearly with mean Hg_T and methyl Hg chloride (CH_3HgCl) concentrations in water. Most of the bio-magnification of methyl Hg occurred in the lower trophic levels of the trout food web ($10^{4.72}$) between the zooplankton and water. The bioaccumulation factors between the forage fish and zooplankton were $10^{0.73}$ for bullies and $10^{1.06}$ for smelt. Methyl Hg was $10^{0.41}$ to $10^{0.95}$ times greater in the trout then their prey.

Keywords: bioaccumulation, mercury, methyl mercury, tropic levels, trout

1. Introduction

Methyl mercury (Hg) is extremely toxic to living organisms. For humans, the uptake of methyl Hg can occur through the consumption of fish. The most tragic example of methyl Hg poisoning by this vector was during the late 1950s at Minamate bay (Takizawa, 1979). More recently, in North America and Europe, there is concern for the potential risk to human health from fish containing high levels of methyl Hg living in lacustrine environments far from known anthropogenic Hg sources (Bjorklund *et al*., 1984; Hakanson *et al*., 1990; Sorensen *et al*., 1990; Wiener *et al*., 1990a, b; Spry and Wiener, 1991; Wiener and Spry, 1996).

There is little known concerning methyl Hg in fish and methyl Hg bioaccumulation in the aquatic food web effected by Hg from geothermal emanations. Within New Zealand, two early studies reported high total Hg concentrations in trout resident in lakes impacted by geothermal waters (Weissberg and Zobel, 1973; Brooks *et al*., 1976). More recently, results concerning methyl Hg concentrations in trout in New Zealand lakes with varying degrees of geothermal input were reported (Kim, 1995). Methyl Hg in the trout was influenced by trout length and age for a

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TABLE I

Lake volume, % geothermal of total water input, pH, mean methyl and total Hg ($\pm$1 standard deviation) in water for Lakes Okareka, Okaro, Tarawera, Rotorua and Rotamahana, New Zealand

Lake	Lake volume ($\times 10^7$ m^3)	Geothermal input (%)	pH	Methyl Hg (ng L^{-1})	Total Hg (ng L^{-1})
Okareka	6.9	6	6.9	0.09 ± 0.06	0.92 ± 0.62
Okaro	0.3	6	6.8	0.51 ± 0.13	1.90 ± 1.05
Tarawera	205.1	37	7.5	0.21 ± 0.07	0.57 ± 0.23
Rotorua	76.8	43	7.0	0.23 ± 0.15	1.47 ± 0.57
Rotomahana	47.7	53	6.7	0.36 ± 0.42	4.58 ± 0.82

particular lake. Between lakes, the input of geothermal water could account for differences of methyl Hg levels in fish. To study the bioaccumualtion of methyl Hg in the trout food web, a parallel investigation was conducted focusing on methyl Hg concentrations in the organisms at the lower tropic levels.

Here we report these results on the concentrations of Hg_T and methyl Hg in water, and the methyl Hg concentrations in organisms of the trout food web in Lakes Okareka, Okaro, Tarawera, Rotorua, and Rotomahana, New Zealand. The trophic levels investigated in these lakes were as follow: zooplankton; smelts, bullies and koura (a fresh water crayfish) representing the trouts' prey and the trout themselves. The main aim of this work was to examine the bioaccumulation of methyl Hg in the trout food web in order to further elucidate the mechanism(s) responsible for methyl Hg in fish at the top of the food chain.

2. Methods

2.1. Study area

Five lakes were selected for this investigation (Figure 1). These lakes lie within the Taupo Volcanic Zone (TVZ), which encompasses both geothermal regions and active volcanos (eg. Mt. Ruapehu and White Island). The geothermal waters in the TVZ are high in Hg compared to other natural waters in New Zealand (Weissberg, 1975; Weissberg and Rohde, 1978; Timperley, 1988; Kim, 1995). Lakes Okarekea and Okaro have few geothermal sources (6% of the total water input, Table I). Lakes Tawarera, Rotorua, and Rotomahana have greater inputs from hot springs, estimated at 37, 43 and 53%, respectively. Other lake characteristics are also presented in Table I, such as water pH and lake volumes (data from Livingston *et al.*, 1986; Timperley and Vigor-Brown, 1986).

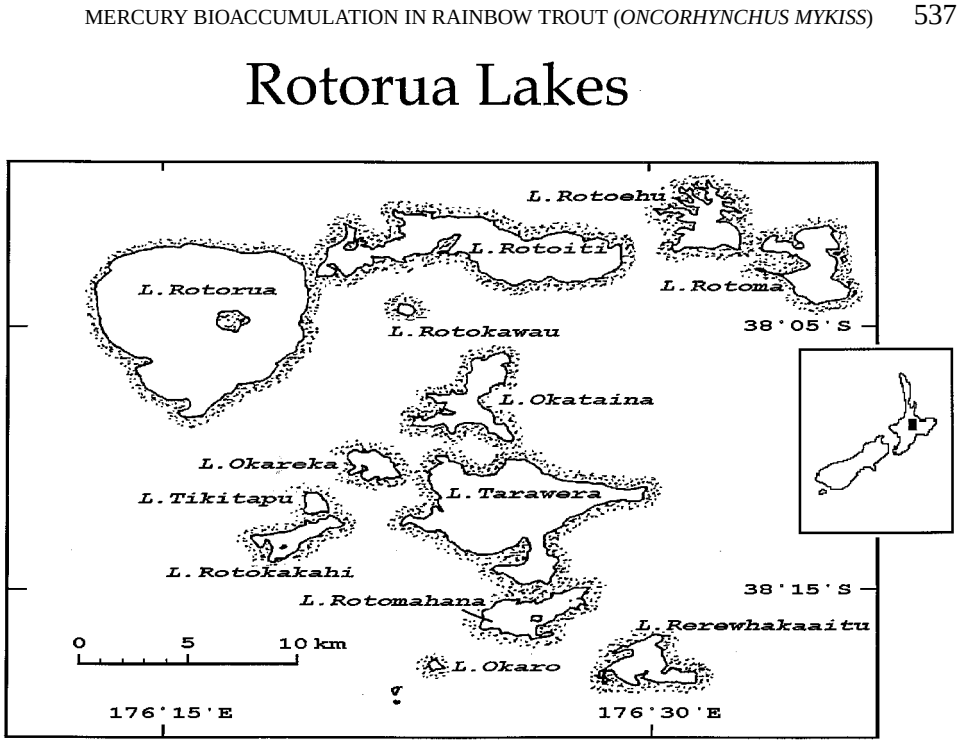

Figure 1. Locations of Lakes Okarekea, Okaro, Tarawera, Rotorua and Rotomahana on the central North Island plateau, New Zealand.

The lakes were sampled during the Austral summer and autumn of 1993 and 1994. Four sampling trips were conducted. The first occurred on February 25, 1993, when samples for zooplankton, smelts and bullies were collected. Not all of the biota were collected for a given lake, due to their absence in some of the lakes. Trout were caught from Lakes Okaro and Rotomahana during the second sampling (March 22–23, 1993). During this time, water samples were also obtained. Water samples for the other lakes were collected a week later (March 29, 1993). Additional trout specimens were obtained from Lakes Okareka (January 27–29, 1993) Tarawera (April and May, 1993) and Rotorua (April 11–May 16, 1993). Finally, during the following years (March 3–4, 1994), water and biota in the lower tropic levels were collected from all five lakes.

2.2. SAMPLE COLLECTION

2.2.1. *Water*

Surface water for Hg was collected in acid-cleaned Teflon® bottles by hand-dipping, under trace metal 'clean' conditions (eg. Bruland *et al*., 1979; Gill and Fitzgerald, 1985) and preserved in the field with 5 mL of Hg-free concentrated hydrochloric (HCl) acid. Additional surface water samples were collected by snorkelling into

'clean' water and filling a Teflon® bottle. A few water samples at depth were also obtained by SCUBA diving.

2.2.2. *Zooplankton*

Zooplankton were collected with an acid-cleaned nylon phytoplankton net attached to plastic rope. After several vertical hauls, the zooplankton were concentrated under trace metal clean conditions and stored frozen in acid-cleaned glass vials. A zooplankton sub-sample was also preserved with Lugol's solution (Parsons *et al*., 1984) for species identification and quantification.

2.3. SMELTS, BULLIES, KOURA AND TROUT

Smelts (*Retropinna retropinna*) and bullies (*Gobiomorphus cotidianus*) were caught with a beach seine. Koura, a freshwater crayfish (*Paranephrops planifrons*), was obtained by SCUBA diving. These biological specimens were stored in plastic ziplocked bags and stored frozen until analysis. Rainbow trout (*Oncorhynchus mykiss*) from Lakes Okareka, Okaro, and Rotomahana were caught with (10 m long, 3 m deep) panel gill nets (Mesh sizes: 110, 80, 60, 40 mm) set overnight. Trout from Lake Rotorua were procured by anglers and specimens from Lake Tarawera were captured from a fish trap operated by the Eastern Fish and Game Council, New Zealand, on a tributary stream feeding the lake. The trout specimens were stored in a freezer.

2.4. SAMPLE PROCESSING AND ANALYTICAL METHODS

Methyl Hg in water was measured by solvent extraction of methyl Hg chloride (CH_3HgCl) into dichloromethane, transfer of methyl Hg to nanopure water by evaporation and subsequent ethylation with sodium tetraethylborate (Bloom, 1989; Liang *et al*., 1994). Yield recoveries for methyl Hg were >90%. Hg_T in water was determined by oxidation with mono bromine chlorine (Bloom and Crecelius, 1983), followed by stannous chloride reduction and two stage gold amalgamation and detection by atomic fluorescence spectrometry (AFS, Gill and Bruland, 1990). Participation in an international-aqueous mercury speciation intercomparison exercise for water from a Wisconsin lake yielded excellent results for both Hg_T and methyl Hg (Bloom *et al*., 1995).

Methyl Hg in biological tissues were determined by digestion in alcoholic KOH solution (Bloom, 1989), followed by the ethylation procedure. For zooplankton, an amount of tissue (wet weight, ww) was analysed. Methyl Hg in koura was determined in the muscle tissue extracted from each crafish tail. The smelt and bully samples consisted of homogenised tissue from 3–5 individuals. Lastly, for trout, a portion of muscle tissue was carefully dissected from each fish (Bloom, 1992). Yield recoveries of methyl Hg for a DORM-1 fish standard were good ($102.7 \pm 17.8\%$).

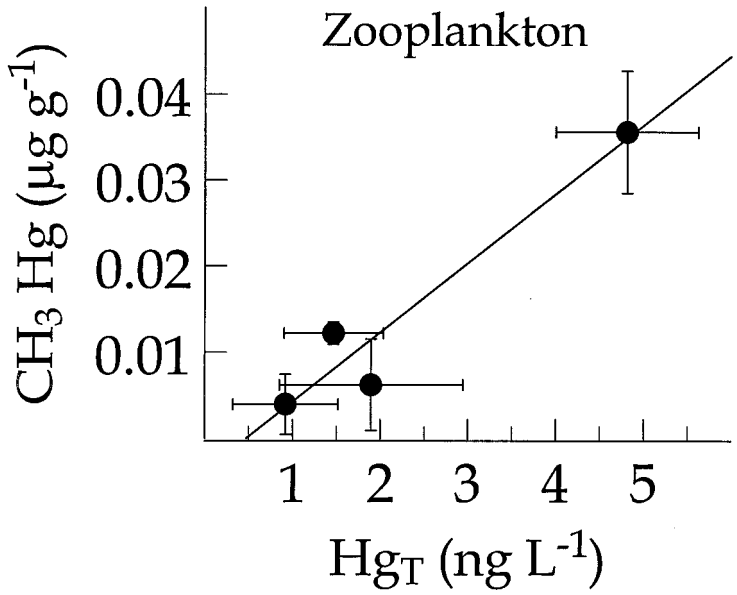

Figure 2. Mean methyl Hg levels and 1 standard deviation in zooplankton versus Hg_T concentrations in Lakes Okarekea, Okaro, Rotorua and Rotomahana. The linear regression line is also depicted in the figure.

3. Results and Discussion

Mean concentrations of Hg_T and methyl Hg in water for the Rotorua lakes are presented in Table I. The Hg_T means ranged from 0.57 to 4.58 ng Hg L^{-1}, while methyl Hg means varied between 0.09 and 0.51 ng L^{-1}. Methyl Hg comprised between 8–37% of the Hg_T in water. These Hg levels are similar to that observed in other lacustrine systems in North America (Wiener *et al*., 1990; Gill and Bruland, 1990; Bloom *et al*., 1991; Cossa *et al*., 1994; Watras and Black, 1995; Watras *et al*. 1995a, b), but are lower than that found in Lake Onondaga, a polluted lake in New York (Bloom and Effler, 1990).

It is interesting that the increase in geothermal input as a percentage of the total water flow to these lakes does not result in relatively high Hg_T levels due to elevated levels of Hg often found in geothermal waters (Table I). This in part, may be due to dilution of Hg sources of geothermal origin because of the large lake volumes of Lakes Tarawera, Rotorua and Rotomahana. There was no linear relationship observed between methyl Hg and Hg_T in these lakes, in contrast to that for lakes in Wisconsin and in Montana (Watras *et al*., 1995a, b). In addition, there was no apparent relationship between mean methyl Hg concentrations and either pH, because of the narrow range of pH of these lakes, or dissolved organic carbon, due to a lack of data for the latter constituent.

A linear relationship between mean methyl Hg in zooplankton and Hg_T in water, that was statistically significant (n = 4, r = 0.9631, p = 0.05), was observed for 4 of the lakes (Figure 2). There were no zooplankton caught in Lake Tarawera. However, no relationship was observed with methyl Hg in water. The samples consisted primarily of one zooplankton species for a given sample. *Calamoecia lucasi* was the major species in Lakes Okaro, Rotorua and Rotomahana, while *Daphnia carinata* was dominant in lake Okareka. Methyl Hg in zooplankton varied between 0.004–0.036 μg g^{-1} (ww). These values are in the lower range of those observed for zooplankton in Wisconsin lakes (Watras and Bloom, 1992; Watras and Back, 1995).

Mean methyl Hg in the trouts' prey (koura, bullies and smelt) in the lakes are plotted against Hg_T in water (Figures 3a, c). There is a paucity of data for koura (Figure 3a) because crayfish were only obtained in 3 lakes. Methyl Hg (0.024–0.156 μg g^{-1}) appears to increase with Hg_T in water. However, due to the limited data, no significant linear trend was found by regression analysis. Methyl Hg in bullies (Figure 3b) showed a linear increase with Hg_T in water (n = 5, r = 0.9044, p = 0.05), ranging up to about 0.2 μg methyl Hg g^{-1} in Lake Rotomahana. Methyl Hg in smelts (Figure 3c) also exhibited a linear correlation with Hg_T in water (n = 5, r = 0.9884, p = 0.01), and attained roughly twice as much methyl Hg than bullies in Lake Rotomahana. No trends were observed between methyl Hg in the prey species and methyl Hg in water.

Lastly, the relationship between the mean methyl Hg concentrations in trout and Hg_T in water is depicted in Figure 4. As with the other lower trophic levels, no relationship with methyl Hg in water was evident. The mean methyl Hg levels in trout ranged from 0.22–1.84 μg g^{-1} and also linearly covaried with Hg_T in water (n = 5, r = 0.9982, p = 0.01). This result is different from that found for lakes in California (Gill and Bruland, 1990), where Hg_T in fish was correlated with dissolved organic Hg in water. These results indicate that Hg_T in water of the Rotorua lakes is an important factor in determining the methyl Hg concentrations in the upper 3 tropic levels of the food web and support the 'substrate' hypothesis (Mason and Fitzgerald, 1991). Higher Hg_T water concentrations could result in more Hg, assumed to be in labile inorganic form, available for microbial methylation and subsequent bioaccumulation of elevated methyl Hg levels in aquatic biota.

The chemical speciation was calculated for the uncharged methyl Hg species (CH_3HgOH and CH_3HgCl) in the water of these lakes. This was accomplished using the mean methyl Hg concentrations ($[CH_3Hg^+]_{total}$), pH and major ions for these lakes (Timperley and Vigor-Brown, 1986) and the equilibria for CH_3HgOH and CH_3HgCl (Stumm and Morgan, 1981). Chemical activities were calculated using the Davies equation. For all lakes except Lake Rotomahana, CH_3HgOH was the major species.

Linear regression analysis between the mean methyl Hg concentrations in the organisms at the different trophic levels and either $[CH_3Hg^+]_{total}$ or CH_3HgOH in water yielded no apparent relationships. In contrast, a similar analysis with

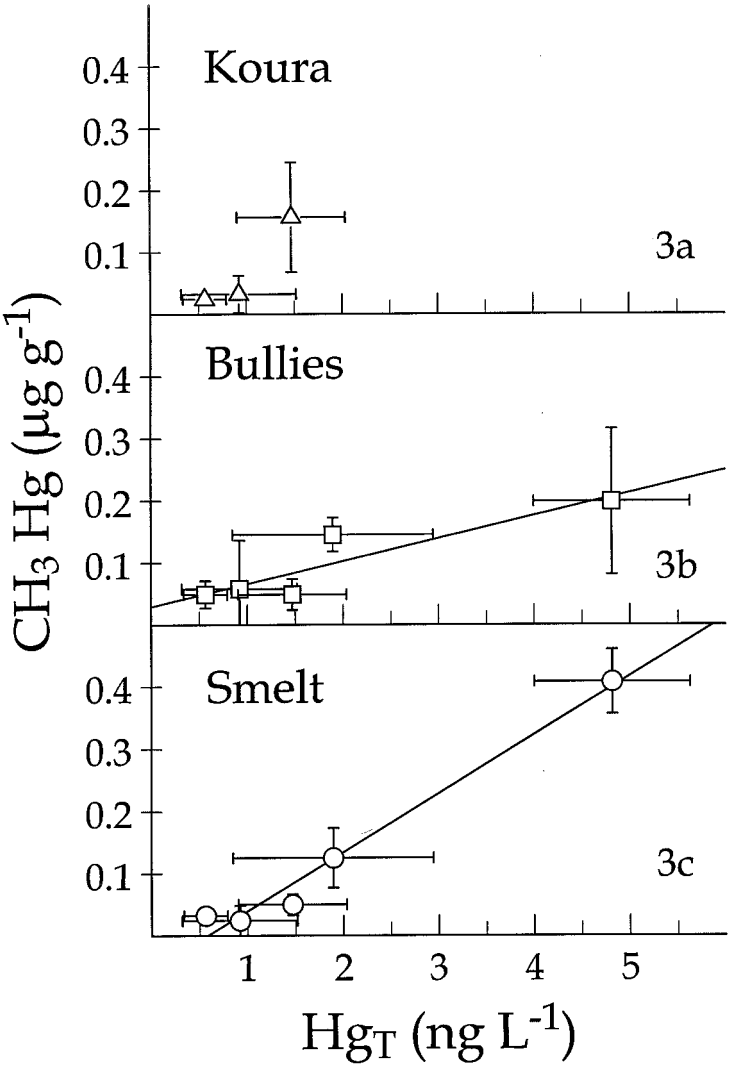

Figure 3. Mean methyl Hg concentrations and 1 standard deviation in the prey species of trout (koura, bullies and smelt) in relation to Hg_T in water. Best fit linear regression lines are depicted for bullies and smelt.

CH_3HgCl (Figures 5a, c) was significant for trout (n = 5, r = 0.9655, p = 0.05), smelts (n = 5, r = 0.9641, p = 0.05) and zooplankton (n = 4, r = 0.9928, p = 0.01), but not for bullies or koura. These results suggest that the bioaccumulation of methyl Hg may be controlled by diffusion of CH_3HgCl in water across the biological membranes of these organisms. The diffusion of uncharged methyl Hg species from water to biota has been observed in the laboratory for a coastal diatom *Thalassiosira weissflogii*, and has been proposed to occur for biota in lacustrine systems (Mason *et al.*, 1996). This is most likely the case for the zooplankton,

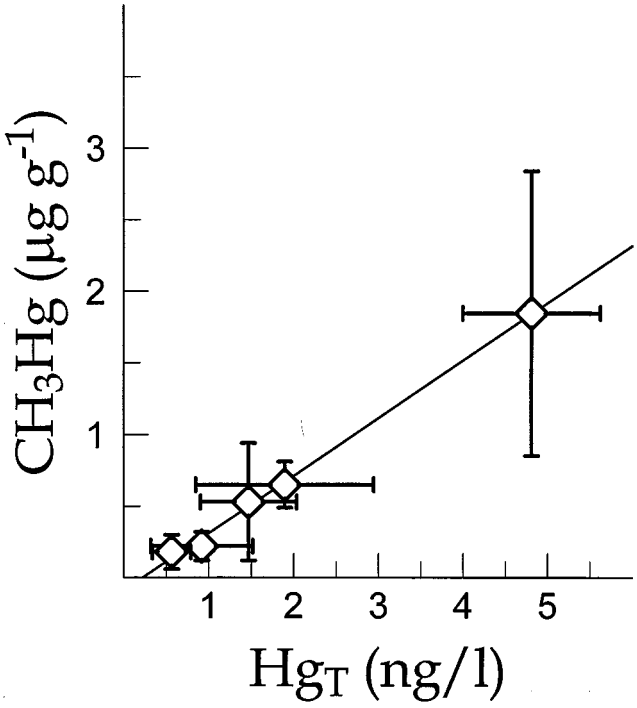

Figure 4. Mean methyl Hg levels and 1 standard deviation in trout from the five lakes versus Hg_T in water. Linear regression lines are shown for the trout.

which have a large surface area due to their small size. However, because these CH_3HgCl concentrations were low (0.008–0.32 ng L^{-1}), other processes, such as ingestion of methyl Hg by diet, are probably more important for the much larger organisms in the upper tropic levels (trout, smelts and bullies).

A bioaccumulation model of methyl Hg for these lakes is presented in Figure 6. Regression analysis between the methyl Hg in trout and smelt indicated that methyl Hg is bioaccumulated about 4.1 times ($10^{0.61}$ between these trophic levels (n = 5, r = 0.9886, p = 0.01). Similar calculations yielded significant linear regressions between trout and koura (n = 3, r = 0.9987, p = 0.01) and bullies (n = 5, r = 0.8933, p = 0.05). Likewise, the bioaccumulation factors for the smelts and and bullies relative to zooplankton were calculated in a similar manner. The bioaccumulation of methyl Hg between zooplankton and water ($10^{4.72}$) was estimated as a ratio of the means for methyl Hg in zooplankton and water from Lakes Okareka, Okaro, Rotorua and Rotomahana.

It is most apparent that the greatest bioaccumulation of methyl Hg occurs at the lower tropic levels, for example, between zooplankton and water. This result has been observed in other lakes in Wisconsin (Watras and Bloom, 1992). The bioaccumulation of methyl Hg to the next tropic level containing the trouts' prey, is less, with the smelt ($10^{1.06}$) accumulating roughly twice as much as the bullies

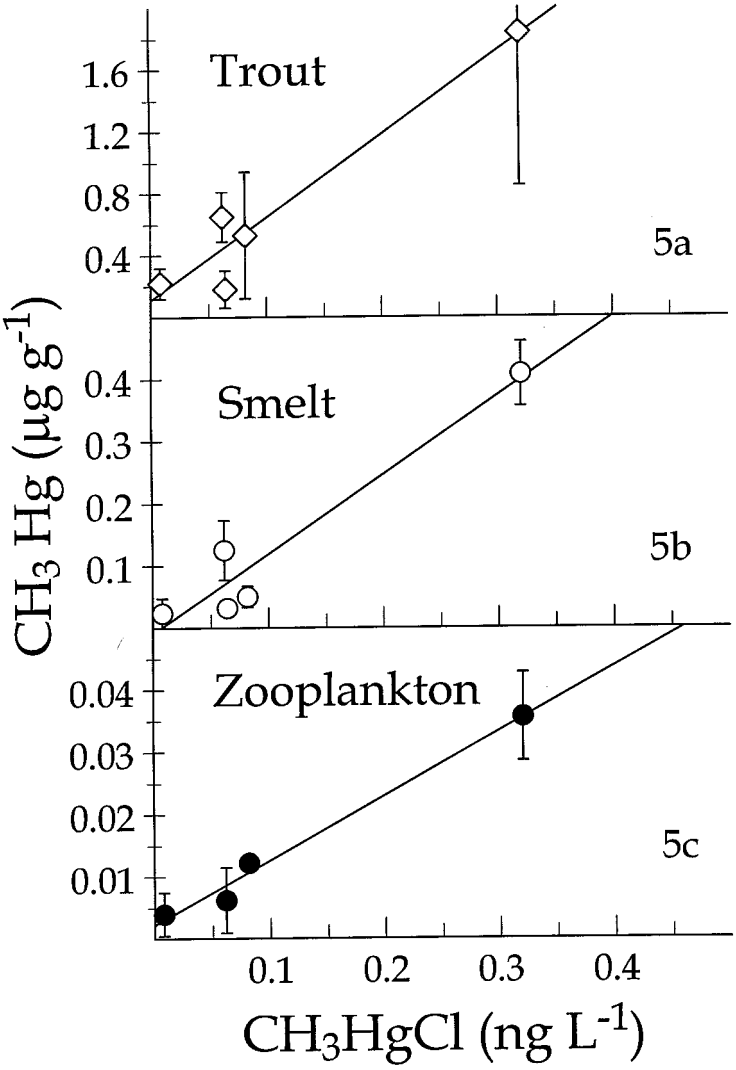

Figure 5. Mean methyl Hg concentrations and 1 standard deviation in trout from the five lakes versus methyl Hg chloride levels in water. Linear regression lines are also depicted in the Figure.

($10^{0.73}$). The uptake of methyl Hg for koura from the lower tropic levels is not known as they probably feed on macrophytes and detritus rather than zooplankton. However, they have a large bioaccumulation factor with respect to methyl Hg in water ($10^{5.99}$). The bioaccumulation of methyl Hg in trout from its prey varies among the individual prey species. Trout consumption of bullies had the greatest bioaccumulation factor ($10^{0.95}$), followed by smelt ($10^{0.61}$) and koura ($10^{0.41}$).

The bioaccumulation model indicates that koura (caught in only 3 lakes) would have the highest methyl Hg concentrations, followed by smelt and then bullies.

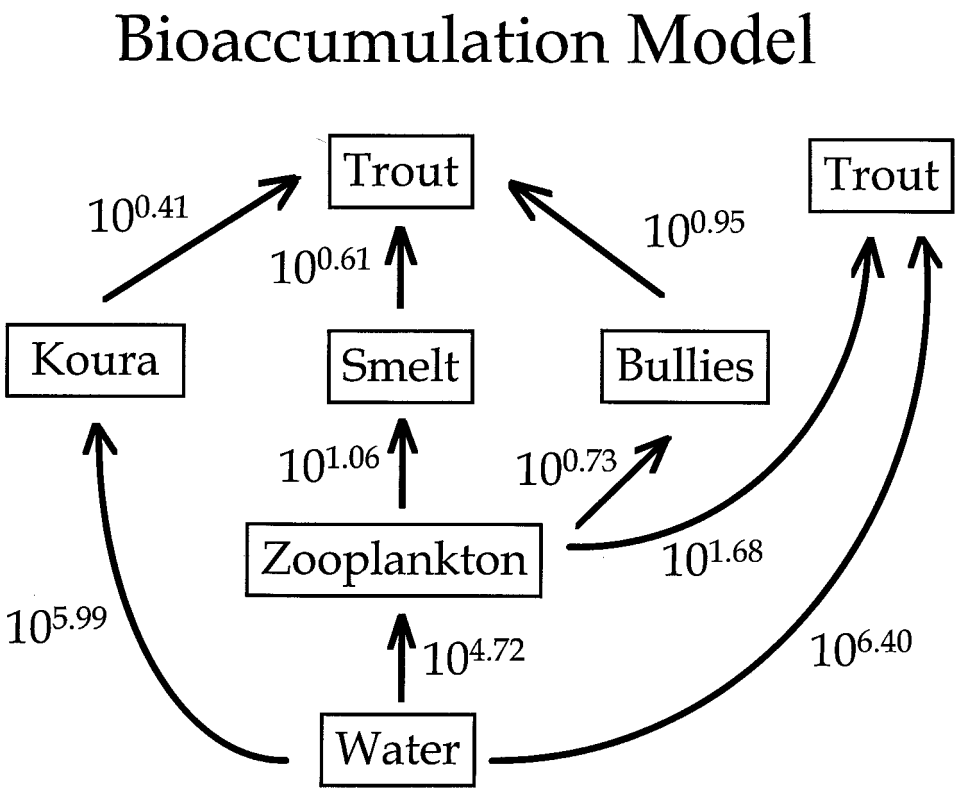

Figure 6. Bioaccumulation model for the trout food web. Bioaccumulation factors for methyl Hg between each tropic level and water are also shown in the figure.

Recently, it was suggested (Kim, 1995) that elevated methyl Hg concentrations in larger trout in these lakes could be due to a change in diet from smelt, a shoaling, pelagic fish, to larger prey such as bullies or koura, which live on the benthos. These organisms could bioaccumulate more methyl Hg, and attain higher methyl Hg levels due to their proximity to the sediments, where microbial methylation could occur. If this conjecture is valid, than the larger trout with high methyl Hg concentrations are probably feeding on koura rather then bullies.

4. Conclusions

In summary, methyl Hg concentrations in zooplankton, smelts, bullies and trout exhibited linear increases with Hg_T in water but not with methyl Hg. This may be due to rapid cycling of methyl Hg within these lake. Both Hg_T and CH_3HgCl appears to be an important factor in determining the methyl Hg concentrations of these organisms.

Most of the bioaccumulation of methyl Hg occurred in the lower tropic levels of the trout food web, where the methyl Hg bioaccumulation factor was $10^{4.72}$ in the zooplankton compared to water. These concentration factors from the zooplankton to the prey trophic level were $10^{0.73}$ and $10^{1.01}$ for bullies and smelt, respectively. The bioaccumulation factor between trout and their prey ranged between $10^{0.41}$ to $10^{0.95}$ depending on the particular species.

Finally, as most of the biomagnification of methyl Hg occurs in lower tropic levels, more research is necessary in this part of the food web. The chemical speciation calculations for uncharged methyl Hg species, coupled with the linear regression analysis of CH_3HgCl with methyl Hg in the zooplankton suggest that CH_3HgCl may be bioaccumulated in zooplankton by diffusion from the water. More detailed studies on the bioaccumulation of methyl Hg by phytoplankton (logistically very difficult) and zooplankton in relation to methyl Hg and its chemical speciation in the water are needed.

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