Mercury Bioaccumulation by Aquatic Biota in Hydroelectric Reservoirs: Review and Consideration of the Mechanisms

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Abstract

The mercury bioaccumulation process in man-made reservoirs is a phenomenon recently (1969) recognized in several countries such as USA, Canada, Sweden, Finland, Brazil. In many cases, no specific pollution source is identified and many occurrences of elevated Hg levels in tissues of fish have been detected in regions considered to be remote from sources of Hg. In impoundments the increase of mercury bioavailability are usually related with quality and amount of flooded vegetation, bacterial activity in sediments and high level of humosity of the surface waters. Dissolved organic acids, abundant in darkwater aquatic systems, increase the reactivity of all forms of mercury both present in flooded sediments and deposited from atmosphere. The recent discovery of water-soluble species of mercury in the atmosphere, usually produced by coal-wood combustion, named reactive gaseous mercury (RGM), has heightened concerns that this form of mercury can react quickly in large surface reservoirs increasing the bioavailability of the pollutant. It has also been demonstrated the capability of some organisms of methylating mercury organic complexes in their intestines. In this case, there is a strong possibility that the high residence time of mercury in the water column contributes to increase the bioavailability of mercury-organic complexes and their consequent internal methylation in organisms. This paper shows preliminary experiments with invertebrates to corroborate this point and reviews the main natural variables related to promoting and enhancing mercury bioavailability in hydroelectric reservoirs. Examples of contaminated biota from Canadian and Venezuelan reservoirs are reported as well as the mitigation procedures attempted and/or implemented in these countries. The importance of health and environmental risk management is stressed. The physico-chemical characteristics of the aquatic system are stressed as significant parameters to indirectly predict the ability of organisms to bioaccumulate mercury. The importance of the trophic level distribution on mercury bioaccumulation in aquatic biota is also discussed.

OUTLINE

1. Background on Methylmercury in Reservoirs
   - When it was recognized
   - Case One: James Bay, Canada
   - Case Two: Tucuruí, Brazil
   - Case Three: Experimental Flooding Project, Canada
   - MeHg in Recently Formed Reservoirs

2. Sources of Mercury

3. Role of Organic Matter

4. Case Study - Guri Reservoir

5. Health Advisories

6. Conclusion

1. METHYLMERCURY IN RESERVOIRS

   The Hg bioaccumulation process in man-made reservoirs is a phenomenon recently (1969) recognized in several countries such as USA, Canada, Sweden, Finland, Brazil.

   High levels of Hg in fish from flooded areas are a concern for commercial markets and local consumption.

   In 1969, Dept. of Fisheries embargoed commercial fishing catches from reservoirs located in Manitoba and Saskatchewan, Canada. This represented a hazardous situation for Ojibway Indians who were strongly reliant on fish in their diet.

      - Several Hg sources were identified: waste waters from a pulp and paper factory and from a chlor-alkali plant.

   In many cases, no specific source of Hg pollution is identifiable.

   Since 1969, the Oregon Health Division, USA has been monitoring fish from Cottage Grove Reservoir and its drainages.

      - This region is highly affected by run-off waters that leach mercury-rich minerals and contaminates the downstream watercourses. The average levels of Hg in 1997 in bass and squawfish exceeded 0.63 ppm.
Case One: James Bay, Canada

- Northwestern Quebec (covers an area ~32,000 km²)
- About 10,000 Aboriginal People in 9 Cree communities.
- Before impoundment:
  - sources of Hg: pulp & paper, mining, smelting
  - in 1975 intense hair monitoring
  - half of adults > 6 mg/kg (ppm) Hg in hair
  - intensive counseling has brought to < 2.5 mg/kg Hg in hair
- After impoundment of 13,670 km² - La Grande Hydroelectric Complex (8 reservoirs).
  - level of Hg in fish increased 3 - 6 fold
  - non-carnivorous fish accumulate Hg faster than carnivorous species
  - typical concentration for pike (carnivorous): 1 to 2.5 mg/kg
  - whitefish and suckers typically 0.2 to 0.5 mg/kg

Typical curve of Hg bioaccumulation in Canadian reservoirs
Elevated Hg levels detected in fish in James Bay resulted in-depth studies into the causes for the mercury pollution in reservoirs.

- Monitoring program from 1978 to 1988 concluded that the evolution of mercury accumulation in fish depends on:
  - type of reservoir
  - flooding rate
  - type of fish (and population)
- Cn$ 18 million (1986-1996) spent by Hydro-Québec on reservoir studies
  - environmental studies
  - socio-cultural issues and health assessments
- Hg in fish downstream from the La Grande reservoir increased over time with Hg levels matching those found in fish sampled in the reservoir
- Methylmercury (CH$_3$Hg$^+$) exported downstream from La Grande reservoir was estimated to be the following:

<table>
<thead>
<tr>
<th>% Me-Hg exported</th>
<th>phase</th>
<th>Me-Hg (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.3</td>
<td>particles &lt; 0.45 µm</td>
<td>0.00005*</td>
</tr>
<tr>
<td>33.2</td>
<td>particles 0.45 to 50 µm</td>
<td>0.00003</td>
</tr>
<tr>
<td>1.54</td>
<td>Zooplankton</td>
<td>86</td>
</tr>
<tr>
<td>0.85</td>
<td>Phytoplankton</td>
<td>27</td>
</tr>
<tr>
<td>0.11</td>
<td>fish and invertebrates</td>
<td>126 - 487</td>
</tr>
</tbody>
</table>

* same as dissolved Me-Hg in natural lakes of the area

- On average: 87 µg Me-Hg/1000 m$^3$ of water or 5.2 g Hg/day or almost 2kg/a is exported.
- Upon examination of fish stomachs, it was determined that zooplankton is an important source of MeHg
- Methylmercury also transported from flooded soils by insects: 0.2 g MeHg/km$^2$/a

**Case Two: Tucuruí Hydroelectric Reservoir, Brazil**

Located in the Brazilian Amazon, the Tucuruí Hydroelectric Reservoir covers an area of 2430 km$^2$. The total area flooded is 1180 km$^2$ (in 1984) and the catchment area covers 758,000 km$^2$. Sampling programs in 1994, which involved the collection of 230 fish yielded the following results (after Povari, 1995):

- Average of 2.6 mg/kg Hg in 15 samples of tucunaré (*Cichla temensis*)
- Average of 1.2 mg/kg Hg in 700g tucunaré (N=33)
- 92% of carnivorous fish > 0.5 mg/kg Hg
- Some authors attribute Hg to Serra Pelada (250 km upstream the reservoir)
- Prevailing wind direction blows from Tucuruí to Serra Pelada (indicating low influence of Hg atmospheric)
• Erosion of the soils in the catchment areas is also increasing Hg load into the reservoir.
• Significant correlations identified between organic matter and Hg content in sediments
• Load of suspended solids into the reservoir is 550 kg/a and output is 315 kg/a
• Around 86,000 living around the reservoir.
• Average of most commonly eaten fish: 0.99 to 1.3 mg/kg Hg
• Average of 65 ppm Hg in hair of fish-eating people
• People eat 200 to 300 g of fish daily

Case Three: The ELARP - Experimental Lake Areas Reservoir Project

In response to Hg issues in many Canadian hydroelectric reservoirs, the Experimental Lake Areas Reservoir project (ELARP) was developed to study the behavior of Hg in these conditions.

• In 1993, an experimental field study was conducted in Northwestern Ontario wherein a 14.4 ha wetland area was flooded to a depth of 1.3 m to investigate the mobilization of Me-Hg in a reservoir.
• Two years after flooding:
  ➢ little change in the total Hg concentration has been observed;
  ➢ methylmercury levels in water have increased 10 times (0.9 ng/L).

Methylmercury that represented 4% of the total Hg before impoundment became as high as 73% (average of 32%) of the total Hg in solution.
Main findings of the project:

- Me-Hg production in flooded sediments increased (this was more important than release of pre-existing Me-Hg)
- Time lag of 2 weeks before increase Me-Hg in water
- Me-Hg photodegradation decreased because water became darker after flooding
- Increased CH$_4$ concentration after flooding
- After 2 years Me-Hg increased 3 times in forage-fish (0.1 to 0.32 mg/kg). Fish uptake was small compared to the uptake by vegetation and peat.
- More time for fish to come to equilibrium with the ecosystem
- MetaAlicus Project (2000 to 2004): Simulate atmospheric Hg deposition
  - $^{202}$Hg isotope added to 500 m$^2$ of wetland
  - 35 g/annum of HgCl$_2$ to be added for 3 years to a 60 ha lake. This represents 58 µg/m$^2$/a of atmospheric deposition

**Me-Hg in Recently Formed Reservoirs**

The following additional observations were derived from additional Canadian studies:

- Bacterial activity increases in flooded areas and as does the methylation rate of Hg(II)
- Nutrients are introduced into the water column and in interstitial waters when soils are flooded
- The amount and quality of organic matter in flooded sediments affects microbial activity. Material resistant to decomposition may inhibit rate of methylation.
- Aerobic conditions enhance the availability of Hg (II) but depress methylating capacity. Anaerobic conditions have the reverse effect.
- The Methylation/Demethylation ratio increases after flooding
- Shoreline erosion influences the amount of organic matter
- Composition of upper soil horizons and vegetation in the flooded area influences the organic matter content

### 2. SOURCES OF Hg IN RESERVOIRS

**Local Sources:**
- chlor-alkali plants
- pulp and paper
- Hg pesticides
- smelting
- gold mining

**Disperse Sources:**
- evaporation from soils, water and vegetation
- run-off water and erosion of the catchment
- forest fires
- fossil fuel combustion
- Hg-rich minerals
Global emission of Hg to atmosphere from all sources is 5000 - 6000 tonnes/a
Mercury deposition rate in the Northern hemisphere: 11 to 14 µg/m²/a
Mercury deposition rate from all sources in Amazon: 10 and 16 µg/m²/a

**Atmospheric Deposition**

- RGM - Reactive Gaseous Mercury: recent discovery of water-soluble species of mercury in the atmosphere,
- RGM is formed in combustion processes.
- The nature of RGM is believed to consist of one or more simple Hg (II) compounds, such as HgCl₂.
- In Tennessee, the RGM form of mercury represents 3 to 5 % of the total gaseous mercury in the atmosphere.
- In Florida, this species of mercury represents the dominant form of total Hg in the atmosphere associated with dry deposition.
- Seasonal trends might exist in RGM concentrations; this variability was primarily associated with temperature, solar radiation, O₃, SO₂, and TGM.
- Rainfall events are significant to RGM's removal from the atmosphere.

### 3. THE ROLE OF ORGANIC MATTER

- Darkwater streams: fish have more Hg
- It is well known that dissolved organic matter forms more stable Hg complexes than any of the inorganic species.
- Metallic Hg reacts quickly with natural organic acids in aerobic environments to form soluble complexes.

Equilibrium boundaries of Hg⁰(aq) and Hg-organic complexes.

Results from mining-impacted rivers in the Amazon Basin, Brazil.
In the Amazon, higher methylation rates (10^2%/g/h) were found in organic rich sediments in dark water forest streams than in rivers with cloudy or clear waters.

Then...why do fish from darkwaters have higher levels of Hg?

Is may be possible that Hg complexed to organics is directly bioavailable to organisms – experiments involving earthworms have indicated that Hg-organic complexes may undergo methylation within the intestinal tract and the same has also been suggested for fish. It is apparent that the mechanisms influencing Hg-organic complex bioavailability are not fully understood. More insight can be derived from evaluating mercury behavior in various darkwater systems and subsequent impacts to biota. Results from a study conducted at Guri Reservoir in Venezuela are presented below.

4. GURI RESERVOIR, VENEZUELA

In 1995, an official resolution suggested that fish from the Guri Reservoir should be exploited commercially. This necessitated a study of fish quality, which subsequently identified high levels of Hg in fish. Results are summarized as follows:
Caroni is a blackwater river with the following parameters.

- Low suspended solids (1.6 to 10 mg/l)
- pH ranges from slightly acidic (5.3 in rainy season) to neutral (6.8 to 7 in dry season)
- Low biomass productivity
- Conductivity is low (7.5 to 11 µS/cm)
- Dissolved oxygen level in Guri ranges from 5 to 8.2 mg/l

In 1995, a monitoring program conducted by a Committee consisting of CVG, Min. Environment, Min. Agriculture, National Guard, Universities, Non-Governmental Organizations, etc., obtained the following information:
• About 219 fish samples were captured in 7 different areas of Guri during the dry season (April, 1995).
• About 52% of samples were carnivorous fish.

**Mercury Levels in Fish from Guri reservoir (Guri Committee, 1995)**

(Hg- mg/kg w.w. or ppm in muscles of fish)

<table>
<thead>
<tr>
<th>Fish Name</th>
<th>Fish (scientific name)</th>
<th>Hg (ppm)</th>
<th>Hg range</th>
<th>N</th>
<th>Remarks Hg level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aimara (c)</td>
<td>Hoplias malabaricus</td>
<td>1.32</td>
<td>0.5 - 4.55</td>
<td>5</td>
<td>high</td>
</tr>
<tr>
<td>Caribe (c)</td>
<td>Serrasalmus sp.</td>
<td>0.51</td>
<td>-</td>
<td>1</td>
<td>high</td>
</tr>
<tr>
<td>Coporo (d)</td>
<td>Prochilodus nigricans</td>
<td>0.17</td>
<td>0.04 - 0.84(?)</td>
<td>61</td>
<td>low</td>
</tr>
<tr>
<td>Curvinata (c)</td>
<td>Plagioscion squamosissimus</td>
<td>0.80</td>
<td>0.16 - 2.96</td>
<td>39</td>
<td>high</td>
</tr>
<tr>
<td>Guitarrilla (c)</td>
<td>Oxydoras niger</td>
<td>0.28</td>
<td>0.09 - 0.46</td>
<td>14</td>
<td>medium</td>
</tr>
<tr>
<td>Pavon (c)</td>
<td>Cichla ocellaris</td>
<td>0.32</td>
<td>0.14 - 0.54</td>
<td>6</td>
<td>medium</td>
</tr>
<tr>
<td>Payara (c)</td>
<td>Raphiodon vulpinus</td>
<td>2.70</td>
<td>0.17 - 8.25</td>
<td>31</td>
<td>very high</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
<td>157</td>
<td></td>
</tr>
</tbody>
</table>

N = number of samples

• From 157 samples, 40% Hg levels >0.5 ppm Hg (guideline recommended by WHO for human consumption)
• No pre-impoundment data available

Potential Sources of Hg in Guri

• Mining activities in the area (1934 and in the 80’s)
• Mercurial pesticides were likely used in the 70s (?)
• Suspended sediments entering Guri
• Atmospheric deposition from industrial sources and forest fires (if we considered deposition rate of 13 µg/m²/a Hg, then in 4,000 km², 52 kg of Hg is deposited/annum)
• If the part of the pre-existing Hg in soils was mobilized after flooding in 1986:

![Diagram showing 0.1 m³ = 100 kg of soil/m²]

- If soil has 0.1 ppm Hg and 1% is methylated = 1 ppb (mg/t)
- 1 mg/t Me-Hg x 100 kg soil/m² = 0.1 mg Me-Hg/m²
- Guri dam flooded 4000 km² = 400 kg of Me-Hg
- If fish biomass = 400,000 tonnes

\[
\text{Me-Hg in fish} = \frac{400,000 \text{ g Me-Hg}}{400,000 \text{ tonnes fish}} = 1 \text{ ppm Me-Hg}
\]
This model is extremely simplistic, in part as a portion of the MeHg is adsorbed in the soil and vegetation and is therefore not readily bioavailable. However, it does illustrate how relatively low concentrations of Hg can impact a large volume of biota. Further study of Hg partitioning in these systems is obviously needed. In conclusion:

- The effect of impoundment in bioaccumulating mercury in Guri seems to be evident
- Hg complexation with soluble organics is possible
- The reduction of light penetration and thus photoreduction process (Hg\(^0\) volatilization) seems to be an extremely significant mechanisms in darkwaters.

Ultimately, conditions at Guri Reservoir seem to be extremely favorable for long term impacts to biota from Hg.
Guri Reservoir, Venezuela

Cross section of the Caroni River

- Orinoco River
- Macagua dam
- Bajo Caroni mining activities
- Guri dam
- Medium Caroni
- High Caroni mining activities

70 km

119 fish sampled
5.8% > 0.5 ppm Hg

600 km

219 fish sampled
42.4% > 0.5 ppm Hg
5. HEALTH ADVISORIES

Once pollution of biota has been identified at a given location, human health risks should be identified. Simplified guidelines (e.g. 0.5 ppm in fish) are established, often only for legal purposes. However, it is the daily ingestion of MeHg that should be determined to more accurately determine risks. The World Health Organization has adopted an ADI (Allowable Daily Intake) of 30 µg Me-Hg for a 70-kg adult. In 1988, Health Canada adopted the following guidelines:

<table>
<thead>
<tr>
<th>Individual affected</th>
<th>µg Me-Hg/kg of body weight</th>
<th>Approximate weight (kg)</th>
<th>ADI µg Me-Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>women of child-bearing age</td>
<td>0.2</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>child under 10</td>
<td>0.2</td>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>adults</td>
<td>0.47</td>
<td>70</td>
<td>33</td>
</tr>
</tbody>
</table>

It has been determined that hair from the scalp is a good indicator of Me-Hg exposure:

<table>
<thead>
<tr>
<th>ppm Hg in Hair</th>
<th>Situation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 6</td>
<td>unexposed</td>
</tr>
<tr>
<td>&lt; 6</td>
<td>normal for fish-eating people</td>
</tr>
<tr>
<td>6 - 10</td>
<td>slight risk for pregnant</td>
</tr>
<tr>
<td>10 - 30</td>
<td>elevated risk for pregnant</td>
</tr>
<tr>
<td>30 - 60</td>
<td>first signs of intoxication</td>
</tr>
<tr>
<td>&gt; 60</td>
<td>toxic symptoms</td>
</tr>
</tbody>
</table>

- Clarkson (1973) showed that, for a 70-kg individual:
  \[
  \text{Hg in blood (ppb)} = 0.95 \times \text{Hg (mg) daily intake from fish}^{33}.
  
- Hg in hair ~ 300 Hg in blood (this depends on which part of the hair is sampled)

- Then... \[ H = W \times F \times 0.285 \]
  \[
  H = \text{Hg in hair (ppm)}
  \]
  \[
  W = \text{Mass of fish consumed daily (g)}
  \]
  \[
  F = \text{Hg in fish (ppm)}
  \]

- A Japanese study derived a different relationship: \[ H = W \times F \times 0.167 \]

- In this case, one person eating 200 g of fish with 0.3 ppm Hg/day would expect to have between 17 and 10 ppm Hg in hair, which is already a risk for pregnant woman.

Typical responses to hazardous situations involving consumption of Hg-laden fish include the following recommendations:

- reduce carnivorous fish ingestion
- change diet
- dilute fish with vegetables
- put up signs around the reservoir or other impacted water body

- Fact Sheets or information pamphlets outlining the problem can also be distributed. The following recipe was included in a pamphlet given to the public in James Bay:

**Express Fish Casserole (4 serving):**

- 1 lb fish fillets,
- 4 medium potatoes, peeled and sliced
- 1 can (12 ounces) kernel corn
- 1 can (10 ounces) green peas
- salt and pepper

- Example of hypothetical signs in Guri

<table>
<thead>
<tr>
<th>Don't Eat</th>
<th>Payara</th>
<th>Did you try Coporo?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>Payara</td>
<td>it's Healthy and with Iuca is Delicious !!</td>
</tr>
<tr>
<td>Carnivorous Fish</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Most Effective Measures:
  - public education
  - public involvement in decisions
  - destruction of myths and taboos

- Consumption advisories and other public information campaigns are essential when human health risks exist. However, the cultural, economic and health implications should also be considered. In a community in Northern Canada, consumption advisories and the resulting reduction in the culturally and economically important fishery resulted in increased alcoholism and suicide rates, and – due to dietary modifications – the frequency of diabetes escalated. How information is communicated, consideration of potential impacts, and appropriate measures to address these impacts are vital to the success of any campaign.
Veiga, M.M. and Hinton, J.J.

Advisory prepared by Inst. de Salud Public del Estado Bolivar with Fundacion La Salle, 1997

<table>
<thead>
<tr>
<th></th>
<th>EMBARAZADAS</th>
<th>NIÑOS</th>
<th>ADULTOS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CUANTIDAD POR SEMANA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Una Ración es una presa o una rueda de pescado de 200 grs</td>
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</tr>
<tr>
<td><strong>PAYARA</strong></td>
<td></td>
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<tr>
<td><strong>AIMARA</strong></td>
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<tr>
<td><strong>CURVINATA</strong></td>
<td></td>
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<tr>
<td><strong>PAVON</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>GUITARRILLA</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>COPORO</strong></td>
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</tbody>
</table>
6. CONCLUSIONS

- The Hg bioaccumulation process in man-made reservoirs is a phenomenon related to increase of bacterial activity after flooding areas and subsequently increase of methylation rate of pre-existing Hg(II) in soils and vegetation.

- Specific point sources of Hg are not needed to increase Hg bioaccumulation in fish.

- The characteristics (type, abundance etc) of the flooded organic matter are important factors.

- Methylmercury formed in reservoirs can be exported to downstream watercourses.

- Residence time of Hg in darkwater can be higher than in clearwaters.

- Darkwater systems form Hg-complexes that may be bioavailable.

- It is debatable whether bioaccumulation is a temporary phenomenon.

- Phenomena observed in reservoirs are not completely understood and highly site specific: more study is needed.

- Public Health Advisories are ABSOLUTELY NECESSARY, but should be sensitive to cultural and socio-economic implications.
References


