Synthesis

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The objective of this chapter is to present a comprehensive review of the mercury (Hg) issue in natural aquatic ecosystems and hydroelectric reservoirs in northern Québec. This synthesis is based on the findings of over ten years of studies reported by research teams from three universities, one governmental agency and Hydro-Québec.

15.1
Mercury in Natural Ecosystems of Northern Québec

15.1.1
Sources of Mercury

Although there are no direct industrial or municipal sources, the presence of Hg in natural lakes and terrestrial systems is ubiquitous throughout northern Québec, at sites located hundreds to more than a thousand kilometers away from the closest industrial centers. Airborne Hg of natural origin has progressively been accumulating in the organic layers of terrestrial soils since the beginning of soil formation after the last glaciation, some 5 to 8 thousand years ago. In addition to this natural Hg, anthropogenic Hg has also started to accumulate in remote soils of northern Québec during the last century. In the humic horizon of unaltered soils, Hg, essentially in its inorganic form, the methylated form representing usually less than 1%, appears to remain very stable, being strongly attached to humified organic matter. However, a fraction of the newly deposited Hg is entrained to the lacustrine systems by surficial runoff, with organic material, without fully penetrating the humic horizons.

In lacustrine ecosystems, sediments constitute the main reservoir of Hg. The quantity of Hg brought to a lake appears directly proportional to the amount of carbon leached from the surrounding soils in the drainage basin. Like in humic horizons of soils, Hg is quite stable in lacustrine sediments, being strongly bound to organic matter mostly of terrigenous origin, and little diagenic remobilization is observed once it is sedimented. This latter characteristic makes it possible to give

historic interpretations of the deposition of this heavy metal in remote regions. Since the onset of the industrial era at the end of the last century, northern Québec has witnessed 2- to 3-fold increases in atmospheric Hg deposition rates as revealed by lake sediments samples taken between latitudes 45ºN and 56ºN.

A series of independent indices with fairly constant values measured between latitudes 45ºN and 54ºN in Québec, such as the carbon normalized anthropogenic enrichment factor in lake sediments, the Hg concentrations in various inferior and superior plants, the carbon normalized Hg content in the humic horizon of soils and the Hg/Al and Hg/Si ratios in lichens, suggest that the entire region is submitted to the deposition of airborne Hg of a uniform intensity and common source, most probably originating from the industrial area of the Great Lakes. North of latitude 54ºN, atmospheric Hg appears to originate from an additional source, as indicated by contrasted Hg/Al and Hg/Si ratios. This remote region may be under the influence of Hg either volatilized from the nearby Hudson Bay or transported from Eurasia. Similarly, measurements of Hg concentrations in a number of fish species and a variety of birds have failed to reveal any latitudinal gradient of Hg concentrations between latitudes 45ºN and 56ºN.

15.1.2
Sediments and the Water Column

In northern Québec, lake sediments usually bear Hg concentrations ranging from 50 to 300 ng g^{-1} dw, which is 4 to 5 orders of magnitude higher than Hg concentrations (dissolved plus particulate) in the water column, which are usually well below 10 ng L^{-1}. Even though the concentrations in lake sediments are of the same magnitude as those in soils, aquatic organisms will bioaccumulate much more Hg than their equivalent counterparts (in terms of trophic position in the food chain) in the terrestrial ecosystems. This is due to the much higher bioavailability of that heavy metal in aquatic environments, principally because the inorganic forms of Hg are methylated via microbial activity at various levels of the aquatic system. In lake sediments, methylmercury (MeHg) usually represents less than 2% of the total Hg content. Although only a small fraction of the total Hg burden in a lake is transformed into MeHg, the form accumulated by organisms, it is sufficient to account for an increase factor in the order of 150 from low trophic level plankton (25 ng g^{-1} dw) to large piscivorous fish (0.6 mg kg^{-1} ww). MeHg is readily accumulated in organisms as a result of both its strong affinity for proteins and low elimination rates, especially in fish.

15.1.3
Invertebrates

Total Hg concentrations in invertebrates of over 20 natural lakes of northern Québec cover a wide range of values, from 25 to 575 ng g^{-1} dw in plankton and from

31 to 790 ng g^{-1} dw in insect larvae. In northern Québec, differences in deposition rates among lakes do not appear to be a factor as they seem to be relatively uniform over the whole region. The fraction of Hg under the methyl form increases along the invertebrate food chain and biomagnification factors of about 3 are observed from one trophic level to another.

Statistical analyses indicate that variations in concentrations of total and MeHg in invertebrates could be explained by feeding behavior (trophic level) and, to a lesser extent, by water quality parameters such as color and dissolved organic carbon, and water temperature.

15.1.4 Fish

In over 180 sampling stations located in natural lakes and rivers of northern Québec, total Hg concentrations in fish were found to be relatively high compared to other regions of North America. Concentrations measured for non-piscivorous species, such as longnose sucker (*Catostomus catostomus*) and lake whitefish (*Coregonus clupeaformis)*, are always well below the Canadian marketing standard of 0.5 mg·kg^{-1}, while those obtained for piscivorous species often exceeded this standard. Inter-lake variability within a same region is important for all fish species, as estimated mean concentrations often vary by factors of 3 to 4 for neighboring bodies of water. Mean concentrations for 400-mm non-piscivorous fish ranged from 0.05 to 0.30 mg kg^{-1} ww, while those of piscivorous species (walleye *(Stizostedion vitreum)* or pike *(Esox lucius)* of 400 and 700 mm of total length respectively) ranged from 0.30 to 1.41 mg kg^{-1} ww, from one lake to another. Highest concentrations in fish (of all species surveyed) were usually found in bodies of water with high organic content, as described by color and concentrations of tannins, as well as total and dissolved organic carbon, where bioavailability at the base of the food chain would be greater.

An average biomagnification ratio of about 5 was found between mean concentrations in standardized-length lake whitefish (400 mm), a benthic feeder, and pike (700 mm) or walleye (400 mm), which are piscivorous fishes. Our data show that the biomagnification factor between these fish species is quite variable from one lake to the next. This variability may be explained by differences in fish community structure, resulting in differences in diet for the top predators, and consequently, in differences in Hg concentrations.

Wide distributions of Hg concentrations are observed in individual fish of the same size from a given lake. For example, lake trout (*Salvelinus namaycush*) of about 575 mm captured the same year in Hazeur lake show Hg concentrations ranging from 0.67 to 1.28 mg kg^{-1}. Individual physiology, growth rate or feeding habit, may explain such high individual variability. Stomach content analyses

show that pike from the western part of the La Grande region prey on a wide variety of fish of different trophic levels, which further highlights the importance of diet in the process of bioaccumulation of Hg.

15.1.5 Aquatic Birds

The importance of diet, and consequently of trophic level, is also demonstrated by the concentrations obtained for aquatic birds of northern Québec which clearly show a general progression of total Hg, in muscle, liver and feathers, from herbivorous species to piscivorous ones. Concentrations in muscle are typically below or about 0.05 mg kg^{-1} for herbivorous species, while they range from 0.16 to 0.21 mg kg^{-1} (ww) for benthivorous species and from 0.8 to 1.6 mg kg^{-1} for partly or strictly piscivorous species, showing the influence of the aquatic system on wildlife, via the methylation and increased bioavailability of Hg through the aquatic food chain. In fact, for species having similar feeding habits, concentrations in fish or aquatic birds of northern Québec are quite equivalent.

15.1.6 Mammals

Hg concentrations measured in terrestrial mammals of northern Québec further demonstrate the link between the aquatic and terrestrial ecosystems, with fish acting as the transfer vehicle, as levels again vary with diet, with piscivorous species showing maximum concentrations. Indeed, muscle concentrations in strictly herbivorous species, such as hare (*Lepus americanus*) or caribou (*Rangifer caribou*), exhibit levels around or below 0.05 mg kg^{-1}. Corresponding concentrations in carnivores, such as ermine (*Mustela erminea*), marten (*Martes americana*) and red fox (*Vulpes fulva*) range from 0.15 to 0.30 mg kg^{-1}, while concentrations in partly piscivorous species such as mink (*Mustela vison*) vary around 2.5 mg kg^{-1}.

The importance of diet is also demonstrated in marine mammals collected off the coast of Hudson Bay, for which muscle concentrations in benthivorous or partly piscivorous species, such as the ringed seal (*Phoca hispida*) and the bearded seal (*Erignathus barbatus*), showed Hg levels usually well below the Canadian marketing standard of 0.5 mg kg^{-1} (ww), ranging between 0.1 and 0.7 mg kg^{-1}, while those in the mostly piscivorous beluga (*Delphinapterus leucas*) ranged from 0.9 to 6.2 mg kg^{-1}. Mean liver concentrations ranged from 2 to 5 mg kg^{-1} in seals and reached 20 mg kg^{-1} in beluga.

All these measures show that health risks associated with the consumption of Hg-rich resources from northern Québec are essentially limited to piscivorous species, be they fish, aquatic birds, or terrestrial and marine wildlife.

Although the links between inorganic airborne Hg, deposited either directly on lakes or via runoff from the surrounding terrestrial environment, its methylation in aquatic systems and the MeHg biomagnification from invertebrates to fish and fish eating wildlife, are well understood, the effect of recent 2- to 3-fold increases in atmospheric Hg deposition rates on fish Hg levels, and consequently wildlife Hg levels, still remains unknown. Although no temporal trend in fish Hg levels was observed for all species monitored in 5 natural lakes for periods of up to twelve years, this time span is too short, considering the great variability of fish Hg levels, to confirm or refute any direct relationship.

Considering the reduction observed in Hg levels in fish and other aquatic organisms from industrially contaminated sites once the inputs of Hg was reduced (as in the cases of the English Wabigoon and Saguenay rivers), one may suppose that there is a relationship between airborne Hg deposition and concentrations in fish and wildlife. This relationship would imply first, that Hg concentrations in fish and other wildlife of northern Québec have not always been so elevated, and second, that levels would decrease if anthropogenic releases of Hg in the atmosphere would be reduced. As a matter of fact, the recent closure of the industries of former East Germany has led to a dramatic decrease in the Hg atmospheric deposition rates onto the lakes of Sweden, as evidenced by the sharp decrease in the Hg concentrations in the most recent sediments of the lakes of the region. In that particular case, the expected decrease in the Hg concentrations in fishes would clearly demonstrate that the Hg burden in aquatic organisms is dependant upon the local atmospheric deposition rates of the heavy metal.

15.2 The Mercury Issue at the La Grande Hydroelectric Development Complex

Monitoring of fish Hg levels at the La Grande complex was initiated in the late 1970s, before the impoundment of the first reservoir. Like in other reservoirs in Canada and abroad, Hg levels in fish of La Grande complex reservoirs increased strikingly and rapidly in the early 1980s immediately following impoundment. Because this increase could not have resulted from a sudden and drastic increase of Hg from atmospheric fallout, as Hg levels in adjacent unaltered natural lakes remained stable, and because the link between flooded organic materials and fish Hg levels had been evidenced in other reservoirs, research programs were initiated in the early 1990s.

15.2.1
Methylation and Passive Transfer from the Flooded Soils and Vegetation to the Water Column

Both *in vitro* and *in vivo* studies demonstrated the impact of flooding vegetation and organic soils on the methylation and release of Hg to the water column and subsequent transfer through the aquatic food chain.

In vitro experiments revealed significant releases of both total and MeHg to overlying waters and allowed the evaluation of the magnitude, relative importance and duration of Hg releases to the water column from different soil and vegetation types under different conditions of dissolved oxygen, pH and temperature of the overlying water. Diffusion rates obtained at 20ºC show that virtually all the releasable Hg would be released within a year, and most within the first few months. Regardless of the environmental conditions applied, total amounts of Hg released after approximately 6 months of flooding, range from 4 to 40 ng g^{-1} for different vegetation types, and from 4 to 45 ng m^{-2} for soil humus samples. Corresponding amounts of MeHg range from 1 to 5 ng g^{-1} for vegetation and from 0.3 to 1 ng m^{-2} for soil humus. For the green part of vegetation, a significant proportion of the initial total Hg content is released to the water phase in about 6 months, from 20% to up to 50-100%, depending on vegetation type. For flooded soils, which represent a far greater biomass of organic matter, only a small fraction of the initial Hg pool is released to the water after one year of flooding. In fact, due to the great variability of the Hg burden in samples, the actual percentage of the initial Hg pool which is released can not be determined.

In situ measurements in flooded soils confirm that only a small fraction of the Hg pool of flooded soils is released to the water column. Indeed, after a decade or more, most flooded soils, except those eroded in the drawdown zone at the rim of the reservoirs, show no significant loss of their Hg burden. This observation seems related to the fact that little structural changes occur within the flooded organic matter aside from the partial biodegradation of the green organic matter flooded. As a matter of fact, even if the bacterial activity in the reservoirs is intense enough to provoke a strong oxygen demand in the flooded soils and in the bottom waters for a few years following impoundment, losses in carbon burdens in these flooded soils is not measurable, being smaller than the inherent variability of these burdens encountered in nearby soils.

The progressive methylation of Hg through time associated with the bacterial activity in the flooded soils is the major observable change in the soils after their flooding. Whereas less than 1% of the total Hg in natural soils was under the organic form, this amount reached maximum values of approximately 10 and 30% after 13 years for peatlands and podzolic soils respectively. For peatlands and podzolic soils, initial methylation rates are similar after the first year but are pro-

longed in the podzolic soils. An explanation proposed for that observation is that the organic matter of podzolic soils appears more sensitive to degradation after flooding than that of peatlands which is already water saturated under pre-flood conditions with the exception of the living ground cover.

The methylation rates appear similar in shallow areas and in deep areas (10 to 20 meters of depth) lying below the photic zone but still above the seasonal thermocline. Once Hg is methylated in the flooded soils, no net demethylation can clearly be observed during winter months or through time, up to 15 years. Thus, it seems that once formed, most of the MeHg accumulates in the flooded soils, probably due to its strong affinity for terrigenous organic matter.

Passive release of total or MeHg from the flooded soils, confirming *in vitro* observations have only been measured *in situ* over non-eroded soils located in shallow areas at the periphery of the reservoirs, with relatively long water residence times. Elsewhere in reservoirs, the anticipated Hg releases of the order of a few ng m^{-2} (MeHg) to a few tens of ng m^{-2} (total Hg) over a six month period, according to the *in vitro* experiments, are not detectable by current analytical methods as increases in total Hg or MeHg concentrations in the water column. Indeed, the dilution rates are much to great in these very large bodies of water. Moreover, a fraction of the Hg released in the water column may also be adsorbed on suspended particulate matter and as such transferred up the food chain, which further reduces the possibility of detection of the passive release of dissolved Hg in the water column. In shallow areas with reduced dilution rates, such as the LA-40 impoundment, an average increase factor of about 5 has been measured for dissolved MeHg concentrations compared to natural lakes, with mean values reaching 0.3 ng L^{-1}, confirming that a certain fraction of that heavy metal initially bound to the terrestrial system is leached to the water column during the first few months of impoundment. It should be noted that calculations for the Robert-Bourassa reservoir, derived from *in vitro* flooding experiments, generate comparable water column values as the net increase for the first 5 years would have been on the order of 0.2 ng L^{-1} for MeHg. Furthermore, *in situ* measurements show that the proportion of total dissolved Hg which is in the methylated form is, on average, 4 times greater in reservoirs than in natural lakes (12% vs 3%).

Despite the release to the water column of a significant fraction of available Hg originally contained in the green part of the flooded vegetation, the overall burden of Hg in the flooded environment remains almost intact through time. The fact that a total loss in the initial Hg burden of probably less than 5% is sufficient to greatly increase the Hg contamination of the entire food chain of the reservoirs demonstrates how Hg, mostly under its methylated form, is highly efficiently transferred and bioaccumulated through the food chain.

15.2.2 Mercury Increases in Organisms at the Base of the Aquatic Food Chain

Increases in MeHg concentrations, from natural lakes to reservoirs, are relatively constant, usually varying from factors of 3 to 5, for the dissolved fraction (< 0.45 µm), the fine particulate matter (0.45 to 63 µm), the zooplankton (> 150 or > 210 µm), as well as for non-piscivorous and piscivorous fish of standardized length. For example, concentrations measured in invertebrates of 5 different reservoirs of the La Grande complex range from 45 to 680 ng g^{-1} in insect larvae and from 350 to 550 ng g^{-1} in zooplankton (> 150 µm), representing an average increase factor of 3 compared to natural lakes.

Furthermore, comparable biomagnification factors exist from one trophic level to another in invertebrates, zooplankton and insects, as well as in fish, in both La Grande complex reservoirs and neighboring natural lakes. Thus, results show that an increase in the bioavailability of Hg at the base of the food chain in reservoirs is reflected throughout the food chain up to non-piscivorous and piscivorous fish. Moreover, differences in stable isotopes analyses between natural lakes and reservoirs for fine particulate matter and zooplankton suggest that Hg-rich organic detritus of terrigenous origin in suspension in the water column is being ingested by zooplankton, and then transferred to fish which feed on zooplankton.

The importance of the role played by both the dissolved inorganic Hg and the dissolved MeHg, directly released to the water column of the reservoirs, on the contamination of the aquatic food chain remains uncertain. Because of the absence of an adequate series of data concerning Hg concentrations in pure phytoplankton samples, the role played by these organisms (although expected to be the most influenced by the dissolved phase) in the transfer of Hg through the food chain remains unknown. However, the absence of significant increases in MeHg in the 63 to 210 µm fraction (which mostly contains phytoplankton and some microzooplanktonic organisms) in the LA-40 impoundment compared to natural lakes, suggests that phytoplankton may not represent a key step in the transfer of Hg from the water to higher organisms in the food chain. This assumption would be corroborated by the calculation of fluxes of biomass and of Hg in the Robert-Bourassa reservoir, using data obtained from the environmental effects monitoring program (RSE). Indeed, the results of this exercise show that the pelagic food chain alone, from dissolved Hg to phytoplankton, zooplankton and fish, was insufficient to explain both the biomass and Hg concentrations found in non-piscivorous fish of this reservoir. Calculations suggested that the greatest vector of Hg transfer to fish must have been through the littoral invertebrates, i.e., both aquatic insects and zooplankton. Fish diet studies, as well as *in situ* biomass and Hg concentration measurements carried out in the Robert-Bourassa and Laforge 1 reservoirs, as well as in the LA-40 impoundment, corroborate this finding.

On the other hand, it is probable that dissolved Hg readily released from the flooded soils to the supernatant water column rapidly re-binds to fine particulate matter in suspension, thus rendering this Hg more bioavailable to filter feeding organisms at the base of the food chain. Although probably not dominant, the role of pelagic zooplankton, enhanced by the filtering of Hg-rich detritus of terrigenous origin, may not be negligible. Indeed, complementary studies to the RSE monitoring program using pelagic nets, as opposed to the standard littoral nets used for fish monitoring, have revealed an abundance of small cisco *(Coregonus artedii)* in the Robert-Bourassa reservoir, which are strictly plankton feeders.

15.2.3 Additional Active Transfer from the Flooded Soils to the Aquatic Food Chain

In addition to the passive release from the flooded vegetation and soils to the water column and through the planktonic food chain, Hg may also be transferred to the aquatic food web by active mechanisms implicating biotic and abiotic processes. First, as MeHg is accumulated in the flooded soils, insect larvae burrowing in the first centimeters, feeding on partially degraded Hg-rich organic matter, rapidly bioaccumulate significant concentrations of the heavy metal and transfer it to higher aquatic organisms as they emerge into the water column. Estimates derived from *in situ* measurements in La Grande complex reservoirs suggest that, for shallow areas, the Hg burden may be up to 6 times greater in aquatic insects than in zooplankton. For pelagic areas however, the Hg burden in zooplankton is probably greater, as the density of benthic organisms is reduced, the periphyton layer is absent and as the lower temperatures are less favorable to methylation.

Second, during the first few years of impoundment of reservoirs in northern Québec, most of the shallow and exposed flooded soils of the drawdown zone are progressively eroded. In particular, the organic horizon of podzolic soils is susceptible to erosion by wave and ice action. A rapid sorting of the eroded soil particles then occurs, maintaining for some time the Hg-rich fine organic particles in suspension in the water column. Filter feeding organisms ingesting these particles may constitute a prime way for Hg to enter the aquatic food chain of reservoirs. These particles may eventually settle back on the surface of other flooded soils, where they may become in turn MeHg-rich food available for benthic feeders.

Third, the release of nutrients resulting from the bacterial degradation of flooded terrigenous organic matter stimulates autochthonous production. Degradation of the resulting fairly labile organic matter, as opposed to the lignocellulosic compounds of flooded soils, promotes additional methylation. This process may be of particular importance in shallow areas, with relatively long water residence times, where the combined effect of light penetration and mineralization of nutrients leads to the development a layer of periphyton, benthic algae

growing in symbiosis with the bacterial colonies, which promotes the methylation of Hg and constitutes a prime source of MeHg-rich food for zooplankton and insect larvae. Zooplankton collected in these areas continue to show high concentrations after 13 or 15 years of flooding, contrary to pelagic zooplankton which showed pre-impoundment Hg concentrations after about 8 years of flooding.

15.2.4
Mercury Increases in Fish

15.2.4.1
Reservoirs

In La Grande reservoirs, concentrations in all fish species increased rapidly after impoundment to levels 3 to 7 times those measured in surrounding natural lakes. Maximum concentrations in lake whitefish and longnose sucker, non-piscivorous species, were reached 5 to 9 years after impoundment. Maximum concentrations in 400-mm lake whitefish ranged from 0.4 to 0.5 mg kg^{-1} (total Hg, ww), from one reservoir to another, slightly surpassing the Canadian marketing standard of 0.5 mg kg^{-1} only in the Robert-Bourassa reservoir.

For piscivorous species such as northern pike and walleye, concentrations for standardized-length fish (400 mm for walleye and 700 mm for pike) increased for a longer period of time, peaking 10 to 13 years after impoundment. Maximum concentrations obtained for northern pike, varying from 1.7 to 4.2 mg kg^{-1} depending on the reservoir, are 3 to 8 times greater than the Canadian marketing standard of 0.5 mg kg^{-1}.

Fish stomach content studies showed that non-piscivorous fish from both natural lakes and reservoirs have a similar diet and that the total Hg increases observed in reservoir fish are more related to changes in the concentrations of MeHg in the organisms of the food web than in changes in feeding habits, again stressing the importance of increased methylation at the base of the food chain. Lake whitefish of both environments shift from a zooplankton dominated diet to one dominated by benthos with increasing fish size. Cisco and longnose sucker feed mainly on zooplankton and benthos respectively, regardless of size. In the western part of the La Grande complex, small cisco is the most common prey found in piscivorous fish stomachs. Pike of this region also feed on a variety of species, from strictly non-piscivorous species to strictly piscivorous species. As they grow in size, pike feed less on coregonids and more on piscivorous fishes, such as walleye, pike and burbot. These latter species may represent up to 60% of the ingested biomass for large pike (> 400 mm). Such a feeding behavior exposes them to large concentrations of MeHg. In the eastern part of the territory, the piscivorous species diet is highly dominated by lake whitefish, a behavior contributing to lower Hg concentrations.

15.2.4.2
Downstream from Reservoirs

Monitoring of fish Hg levels at the La Grande complex has also shown that Hg is exported downstream from reservoirs. Studies at the La Grande complex indicate that Hg is mostly exported by Hg-rich organic debris as well as by plankton, aquatic insects or small fish and suggest that the magnitude of increase in downstream fish Hg levels, as well as the distance over which it occurs, depends on: (1) the importance of downstream tributaries diluting the Hg-rich debris or organisms (food source for fish) originating from the reservoir and, (2) the presence or absence of large bodies of water downstream (lakes or other reservoirs) permitting the sedimentation of organic material or the biological uptake of the Hg-rich organisms. The importance of large bodies of water downstream is further corroborated by the absence of a cumulative effect in fish Hg levels passing from the Caniapiscau reservoir to the La Grande 4 reservoir, via the Fontanges and Vincelotte reservoirs. The results obtained from this series of reservoirs strongly suggest that in the case of a chain of large deep reservoirs, the downstream effect of one reservoir, on fish Hg levels, is limited to the first reservoir located immediately below. Furthermore, spatial distributions of fish Hg levels within a given receiving reservoir show that this effect, in the case of large reservoirs, is limited to the area located near the input from the upstream reservoir.

15.2.5
Duration of Increased Mercury Levels in Fish

After peaking 5 to 9 years after impoundment, concentrations in standardized-length lake whitefish then significantly and gradually declined in all reservoirs, actually reaching background levels measured in neighboring lakes after 10, 11 and 17 years in the case of the La Grande 4, Caniapiscau and Robert-Bourassa reservoirs respectively. These data, in addition to the similar evolution measured in longnose sucker, strongly suggest that concentrations return to levels normally found in natural lakes of the region after 10 to 25 years for all non-piscivorous species.

Concentrations in piscivorous species, such as walleye and pike, started to decline significantly in all La Grande complex reservoirs after 15 years. In other reservoirs of northern Québec and Labrador, concentrations in pike have returned within the range of concentrations measured in natural lakes in all reservoirs older than 20 to 30 years. A similar duration has also been observed in Finland and Northern Manitoba (Verta et al. 1986b; Strange and Bodaly 1997). Although the age of the La Grande complex reservoirs varied only from 10 to 17 years at the time of the latest monitoring campaign, the general evolution of Hg levels in piscivorous species appears to follow the same time trend.

A number of key processes in the increase of Hg levels in fish in reservoirs either have a temporary effect or are greatly reduced after a few years of impoundment. These processes include (1) the passive release of Hg to the water column from the flooded vegetation and soils via degradation of terrigenous organic matter; (2) the release of nutrients stimulating autochthonous production with its labile organic matter promoting methylation; (3) the erosion of organic material in the drawdown zone releasing Hg-rich organic particles for filter feeding organisms; (4) the active transfer from burrowing aquatic insects; (5) the development of a periphytonic layer at the water-flooded soil interface promoting methylation and active transfer of Hg by aquatic insects and grazing zooplankton.

15.2.5.1
Degradation of Terrigenous Organic Matter and Release of Nutrients

Water quality monitoring at the La Grande complex has shown that intensive decomposition of flooded organic matter is short lived due to the rapid depletion of readily decomposable organic matter. Water quality modifications due to this decomposition, such as dissolved oxygen depletion and increases of CO_2 and phosphorus concentrations (release of nutrients) are virtually over after 8 to 14 years after impoundment depending on the reservoir's hydraulic and morphological characteristics. *In vitro* flooding experiments confirmed that, at temperatures characteristic of the waters of the La Grande complex, virtually all the releasable Hg would be liberated within a few years, a good portion of which would be released within the first year. These experiments further suggest that only a fraction of the green part of the flooded vegetation biomass (including the ground cover) decomposes, releasing significant amounts of their initial Hg burden, the remainder being composed of substances resistant to biochemical degradation. Ligneous components of flooded vegetation remained virtually unaffected after many decades, as spruce tree trunks had lost less than 1% of their biomass after 55 years of flooding in the Gouin reservoir located in Québec.

15.2.5.2
Erosion

Field observations at the La Grande complex reservoirs have shown that the erosion of organic material in the drawdown zone was highest during the first few years and was virtually over within a 5 to 10 year period. Thus, the increased availability of Hg-rich fine organic particles in suspension for filter feeding organisms is also short lived.

15.2.5.3
Active Transfer from Burrowing Insects and Periphyton

Furthermore, the area of active biological transfer of MeHg, from flooded organic soils to water column, by benthic organisms is also greatly reduced after a few years, as organic material is removed in areas of the drawdown zone exposed to ice and wave action. At the La Grande complex, where surficial materials are mostly derived from glacial till, large proportions of the rim of the reservoirs are thus rapidly brought to sand, gravel and rocks, greatly reducing both the passive and active transfer of Hg from the flooded soils to the water column. As a result, zooplankton and benthic organisms collected from stomach contents of white suckers of the Desaulniers reservoir, located close to the Robert-Bourassa reservoir, had MeHg concentrations equivalent to those of natural lakes, 17 years after impoundment. Hg concentrations in zooplankton collected in the pelagic zone of a number of La Grande complex reservoir also had MeHg levels equivalent to those of zooplankton of surrounding natural lakes 8 to 10 years after impoundment.

Thus, after a rapid upsurge of Hg through the reservoir food chain, through both diffusion and active biological transfer from flooded soils (by zooplankton filtering fine particulate organic debris or grazing on periphyton growing on the flooded soils, as well as by invertebrates burrowing in or feeding on these soils), the intensity of these processes diminishes in time. After a certain period of time the rate of transfer of Hg from the flooded vegetation and soils to the aquatic food chain of reservoirs becomes equivalent to the rate of transfer from sediments to the aquatic food chain of lakes, with the result that Hg concentrations in fish gradually return to levels typical of surrounding natural lakes.

15.2.6
Morphological and Hydrologic Factors Influencing the Evolution of Mercury Levels in Fish in Reservoirs

Monitoring at the La Grande complex indicates that all reservoirs show a similar trend in fish Hg levels, although they exhibit differences in the magnitude of the post-impoundment increases, as well as in the rates of increase and subsequent decrease. Our results suggest that these differences among reservoirs may be explained, at least in part, by a limited number of physical and hydrologic characteristics, related to the principal factors identified as responsible for the increase of fish Hg levels, such as: the extent of land area flooded, the annual volume of water flowing through, the filling time and the proportion of flooded area in the drawdown zone. These characteristics may be used to obtain a preliminary evaluation of the order of magnitude of the increase of Hg levels in fish of proposed reservoirs.

15.2.6.1
Land Area Flooded to Annual Volume of Water Ratio

The ratio between the land area flooded (in km^2) and the annual volume of water (in km^3) flowing through the reservoir (LAF/AVW ratio) should be a good indicator of the magnitude of the post-impoundment increase of Hg levels in fish. The land area flooded indicates the amount of organic matter stimulating bacterial methylation and also the passive and active release of Hg. The annual volume of water flowing through a reservoir is also considered a key factor because: (1) it is an indicator of the diluting capacity of the Hg released into the water column, (2) it plays a role in the extent of oxygen depletion (as anoxic conditions are believed to promote methylation), (3) it determines the extent of export of Hg out of a reservoir, and (4) it plays a role in the extent of export of nutrients out of a reservoir, which reduces the autochthonous bioproduction, thus reducing the additional methylation and release of Hg brought about by the degradation of the particularly labile phytoplankton and periphyton.

15.2.6.2
Flooded Land Area in Drawdown Zone

The proportion of the total land area flooded located in the drawdown zone would be a good indicator of the magnitude and duration of the active biological transfer of MeHg from the flooded soils to fish. On the one hand, it would be a good indicator of the erosion of organic material in the drawdown zone increasing availability of Hg-rich fine organic particles in suspension for filter feeding organisms. On the other hand, it would be an indicator of the duration of the transfer of Hg from burrowing aquatic insects, as well as from zooplankton grazing on the periphyton layer. This biological transfer could play a significant role during a prolonged period (at least 15 years based on *in situ* measurements) in shallow areas, protected from wave action, where organic matter has not been eroded. At the La Grande complex reservoirs, the flooded soils are generally very thin and are rapidly eroded and subsequently deposited in deeper colder areas, less favorable to bacterial methylation. This erosion reduces the surface of flooded soils where biological transfer of Hg by invertebrates still takes place. Thus, for reservoirs such as those found at the La Grande complex, where the organic layer of flooded soils is quickly removed by wave action, the greater the proportion of the flooded land area located in the drawdown zone, the quicker the return to background fish Hg levels because of the reduction of the Hg transfer from the flooded soils to fish through the benthic organisms.

15.2.6.3
Filling Time

The time it takes to fill a reservoir is also considered an important factor in determining post-impoundment peak Hg levels in fish, as *in vitro* studies have shown that the release of Hg from flooded organic material to the water column is very rapid, with most of the Hg being released in the first few months. In the case of a reservoir filled over a number of years, Hg is continuously liberated over a longer period of time, but at a slower rate. Water quality modifications, indicative of bacterial decomposition, peaked after 2 to 3 years in reservoirs filled within a year (Robert-Bourassa and Opinaca), but peaked after 6 to 10 years in the Caniapiscau reservoir, filled in 3 years. Thus, considering all other factors equal, the longer the filling time, the lower would be the peak Hg levels in fish, but the longer would be the period necessary to return to concentrations typical of neighboring lakes. The filling time, as it relates to the rate of flooding or increasing water levels, is also a good indicator of the rate of erosion of the flooded organic soils during filling. In a large reservoir filled slowly, such as the Caniapiscau, the water level in the drawdown zone rising only a few centimeters per day may permit the complete erosion, during the filling period, of thin podzolic soils in areas subjected to important wave action. For the Caniapiscau reservoir, this is thought to have contributed to shortening the period of elevated concentrations in lake whitefish.

15.2.7
Risk to Wildlife

Two terrestrial animals, mink (*Mustela vison*) and Osprey (*Pandion haliaetus*), feeding occasionally or exclusively on fish, have served as models for the study of potential effects of increasing Hg levels in reservoir fish on terrestrial animals.

15.2.7.1
Mink Experiment

Mink, a partly piscivorous mammal, is a species widely distributed in northern Québec. Wild specimens obtained from Cree trappers and domesticated specimens were used to carry out *in vivo* and *in vitro* exposure studies respectively.

An *in vitro* exposure experiment was conducted, in which female domesticated mink were exposed to daily diets containing 0.1, 0.5 and 1.0 µg g^{-1} of total Hg. These diets were prepared with reservoir fish, so that the Hg was essentially assimilated under the MeHg form. Mink exposed to daily diets of 0.1 and 0.5 µg g^{-1} of total Hg showed no effects, while those exposed to a daily diet of 1.0 µg g^{-1} showed reductions in fertility, as well as mortality (2/3 of the animals) with neurotoxic signs after 3 months or more.

Mean concentrations in all tissues of wild mink caught in natural habitats of northern Québec are all below those measured in the group exposed to daily diets of 0.1 µg g^{-1}. The ecotoxicologic risk from MeHg to mink populations inhabiting natural habitats of northern Québec is thus very low, despite the increase of the Hg burden in the environment over the last 60 years, since no clinical or other signs of Hg intoxication were observed at daily diets of 0.1 and 0.5 µg g^{-1}.

Along most reservoir shorelines, the risks also appear weak, despite important increases in fish Hg levels, since adult territorial mink have little possibility of finding suitable permanent habitat. However, shorelines of the Boyd-Sakami diversion, which shows little water level fluctuations, may offer mink more suitable habitat. Fish along this diversion have shown average Hg levels 5 times higher than those living in natural lakes and rivers. Since mean Hg levels in the tissues of wild mink from northern Québec are well below the mean levels obtained for the laboratory mink fed a diet of 0.1 µg g^{-1} of Hg, the average Hg concentration in the diet of wild mink must be well below 0.1 µg g^{-1}. Assuming that Hg levels in the diet of mink of the Boyd-Sakami area would increase proportionally to the increase in fish (factor of 5), which was not observed for mink along the comparable Churchill-Nelson diversion route in northern Manitoba, then the average Hg concentration in the diet of wild mink inhabiting the Boyd-Sakami area should be below 0.5 µg g^{-1}. This level remaining below the diet of 0.5 µg g^{-1}, at which no clinical or other signs of Hg intoxication were observed in domesticated mink, the risks for the mink population inhabiting the Boyd-Sakami shorelines would also be low. Furthermore, this assumed level in the diet of wild mink of this area is well below the dose of 1.0 µg g^{-1} in the diet at which the first effects were observed. This evaluation appears conservative since environmental factors, such as the 6 month long ice covered period of northern Québec lakes and ponds rendering fish inaccessible to mink, whose cumulative effect would tend to reduce rather than increase Hg exposure to mink.

Reservoir fish attempting to spawn in streams accessible from reservoir can be an additional source of MeHg exposure to mink along their shorelines. In such situations, fish ascending from a nearby reservoir would be diluted with endemic populations of the stream. Furthermore, incoming fish spawning in spring or fall depending of the species would stay only for the duration of reproduction, moving back to reservoir thereafter. Such movements are usually limited to the first rapids of a stream. Therefore, the added exposure would be less than that encountered by mink inhabiting the shorelines of the Boyd-Sakami diversion.

15.2.7.2 Breeding Success of Osprey

The breeding success of Osprey nesting near La Grande complex reservoirs was also studied, as they are top predators relying on highly efficient sight and neuro-

motor co-ordination to feed their young, functions particularly sensitive to Hg intoxication. Results for Osprey nesting in the region of the La Grande complex show that, with the exception of eggs, which are usually laid when reservoirs are still ice covered, total Hg levels were significantly higher in tissues of adult Osprey and nestling living close to reservoirs than in those inhabiting natural environments. Adult and nestling feathers collected near reservoirs contained 3.5 and 5 times more total Hg, respectively, than those from natural habitats. On average, feathers contained 16.5 mg kg^{-1} dw of total Hg in adult Osprey in natural habitats as compared to 58.1 mg kg^{-1} in adults near reservoirs. A similar pattern was observed in feathers of 35-45 day-old chicks, but concentrations tended to be lower than those found in adults (7.0 mg kg^{-1} dw in natural habitats compared to 37.4 mg kg^{-1} near reservoirs). Despite a much higher total Hg exposure for Osprey fishing in reservoirs, the number of young fledged was not statistically different between nests located near reservoirs and those located near natural lakes and rivers.

Our results suggest that growing feathers, either in molting adults or in nestlings, provides a good excretion route for total Hg. For example, feathers from chicks 5 to 7 weeks old contain approximately 86% of the total Hg burden, excluding other tissues containing keratin for which total Hg was not measured. Nevertheless, the good breeding performance of Osprey nesting near reservoirs cannot be explained solely by the partial molt that adults undergo in summer. Several studies have reported that demethylation is a significant detoxification route for MeHg in birds of prey, so that, in spite of their high exposure due to their position as the final link in the food chain, they tolerate MeHg better than had previously been believed.