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FACULTY OF ENGINEERING, SCIENCE & MATHEMATICS

School of Civil Engineering and the Environment

Industrial mercury pollution with particular emphasis on its impact in the aquatic environment

by

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ABSTRACT

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INDUSTRIAL MERCURY POLLUTION WITH PARTICULAR EMPHASIS ON ITS IMPACT IN THE AQUATIC ENVIRONMENT

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Mercury (Hg) is one of the most hazardous contaminants that may be present in the aquatic environment. Inorganic Hg discharged to lakes and watercourses by industrial enterprises may be converted to organic methylmercury (MeHg), a highly toxic compound that is readily accumulated by aquatic biota. Despite a vast body of literature on the subject, many of the Hg transformation and distribution processes operating in the natural aquatic environment are still poorly understood. The current work includes a detailed investigation of the mutually interacting factors that influence the conversion of inorganic Hg to MeHg, and identifies areas where further research is needed.

Two case studies of industrial Hg pollution were carried out to investigate the impacts of these industries on the surrounding environment, and in particular on aquatic ecosystems. The first study at a derelict chlor-alkali plant in northern Kazakhstan found that a nearby lake was severely impacted by Hg from past wastewater inputs, resulting in a serious build-up of Hg in the aquatic food chain. Potential risks to the local population were evaluated and remediation options for the lake were considered in the light of experiences made at other sites.

The second case study investigated the transport, fate and bioavailability of Hg in the Nura, an industrially contaminated river in central Kazakhstan. In this study, a significant inverse relationship was found between total Hg concentrations and the percentage of MeHg formed in sediments. This appears to indicate that at high Hg levels in severely contaminated sediments, the accumulation of MeHg may be limited by increasingly efficient demethylation processes, which may be the underlying reason why MeHg levels in surface water are often found to be higher at less contaminated downstream sites compared to upstream sites. It could also be one reason why Hg concentrations in fish on this river did not decrease significantly for a considerable distance downstream from the source of the pollution.

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Preface

The present work was achieved within the framework of several collaborative research projects between the School of Civil Engineering & the Environment at Southampton University and the BG Chair of Environmental Technology in Kazakhstan. The majority of the work was formally co-ordinated by the School, and I therefore acted as the scientific advisor for the team in Kazakhstan and was responsible for the planning and supervision of the field work, design of sampling protocols, procurement of equipment for Hg analysis, advising on analytical methods and quality control, and the overall scientific direction of the work. I was solely responsible for all data interpretation and for the writing of the scientific articles, which are hereinafter presented in the form of four separate chapters of the thesis.

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Units and Abbreviations

BAF	Bioaccumulation factor
BTF	Biotransfer factor
CLAP	Chlor-alkali plant
CV-AAS	Cold-Vapour Atomic Absorption Spectrometry
CV-AFS	Cold-Vapour Atomic Fluorescence Spectrometry
DiMeHg	Dimethylmercury
DL	Detection limit
DOC	Dissolved organic carbon
d.w.	Dry weight
FD	Field duplicate
Hg	Mercury
HPLC	High Pressure Liquid Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
mg/kg	Milligrams per kilogram
mg/L	Milligrams per litre
m^3/s	Cubic metres per second
MDL	Method detection limit
MeHg	Methylmercury
ND	Not detected at or above the MDL
OM	Organic matter
PET	Polyethylene terephthalate
QA/QC	Quality assurance/Quality control
RPD	Relative percent difference
SRB	Sulfate-reducing bacteria
THg	Total mercury
w.w.	Wet weight
µg/kg	Micrograms per kilogram
µg/L	Micrograms per litre

Introduction

Mercury (Hg) is a persistent, globally cycling pollutant that readily accumulates in the food chain. Because of its toxic and bioaccumulative nature and its capacity to affect even remote areas that are far from industrial point sources, Hg and its compounds have been identified as priority hazardous substances under the EU Water Framework Directive (European Commission, 2001). Small amounts of Hg are naturally present in the aquatic environment, however.

The work presented in this thesis is the result of several studies conducted at mercury-contaminated industrial sites in Kazakhstan, Central Asia. Particular emphasis was placed on the impact of Hg emissions from industrial point sources on the aquatic environment. A detailed literature review on Hg methylation in aquatic systems was also carried out.

It is well known that inorganic Hg in aquatic systems may be converted to a highly toxic organic form, methylmercury (MeHg), which is the main species that is accumulated by aquatic biota. However, although there is a vast body of literature on the subject of MeHg formation, many of the processes controlling Hg transformation reactions in the natural environment are still poorly understood. While a large number of studies have examined the influence of individual factors such as pH, redox conditions, organic matter complexation, or sulphate/sulphide concentrations on MeHg formation, there are relatively few studies that have considered two or more factors simultaneously. I carried out a detailed review of the factors that influence the conversion of inorganic Hg to MeHg in aquatic systems, and identified areas where further research is needed (Chapter 1 – published in 2001). I found that past research has often been hampered by the fact that many of the factors that influence Hg methylation are mutually interacting and cannot therefore be viewed in isolation. Furthermore, physical processes such as the distribution of Hg between the sediment and water phases and the evasion of volatile Hg species are also influenced by environmental factors, which may to a certain extent confound the primary effects of these variables on methylation/demethylation rates. For example, studies investigating the effect of pH or redox conditions on Hg methylation should consider that increased MeHg concentrations in the water phase at low pH or under anoxic conditions are likely to be at least partly attributable to increased desorption of MeHg from sediments and suspended particulates and do not necessarily reflect increased Hg methylation.

Two case studies of industrial Hg pollution were carried out with the aim of investigating the impacts of these industries on the surrounding environment, and in

particular on aquatic ecosystems. The first study at a derelict chlor-alkali plant in northern Kazakhstan found that a nearby lake was so strongly polluted by Hg from past wastewater inputs that it could be the most severely impacted lake ecosystem known to date. The results of a survey of sediment and water contamination are presented in Chapter 2 (in press), and potential remediation options for the lake are discussed in the light of experiences made at other Hg-contaminated sites. The extent of Hg bioaccumulation in the aquatic food chain and potential human health risks were also assessed (Chapter 3 – in press). Comparisons between different fish species suggested that Hg is accumulated in the order dace > carp > tench, and that the trophic level of fish is not always a good indicator of the degree of Hg accumulation.

Another case study served to investigate the transport, fate and bioavailability of Hg in an industrially contaminated river-reservoir system in central Kazakhstan. Mercury concentrations in the river Nura were found to be highly dependent on seasonal hydrological conditions, with Hg transport being largely dominated by the remobilisation of contaminated sediments and river bank erosion during the spring flood. Although total Hg and MeHg concentrations are not normally thought to be related, I found that there was a significant inverse relationship between total Hg concentrations and the percentage of MeHg formed in the sediments, which was irrespective of the sampling depth. This would seem to be analogous to the inverse relationship reported by Schaefer et al. (2004) for surface waters and appears to indicate that at high Hg levels in severely contaminated sediments, the accumulation of MeHg may be limited by increasingly efficient demethylation processes. As it is generally accepted that MeHg is formed mainly in sediments rather than in the water phase, the observed relationship may be the underlying reason why MeHg levels in surface water are often found to be higher at less contaminated downstream sites compared to upstream sites. It could also be one reason why Hg concentrations in fish on the Nura did not decrease significantly for a considerable distance downstream from the source. The results of the Nura case study are presented in Chapter 4 (paper in review).

Chapter 1

Mercury in the Aquatic Environment: A Review of Factors affecting Methylation

ABSTRACT: Mercury is one of the most hazardous contaminants that may be present in the aquatic environment, but its ecological and toxicological effects are strongly dependent on the chemical species present. Species distribution and transformation processes in natural aquatic systems are controlled by various physical, chemical and biological factors. Depending on the prevailing environmental conditions, inorganic mercury species may be converted to many times more toxic methylated forms such as methylmercury, a potent neurotoxin which is readily accumulated by aquatic biota. In spite of a considerable amount of literature on the subject, the behavior of mercury and many of the transformation and distribution mechanisms operating in the natural aquatic environment are still poorly understood. This review examines the current state of knowledge on the physicochemical behavior of mercury in the aquatic environment, and in particular the environmental factors influencing its transformation into highly toxic methylated forms.

1. Introduction

Mercury (Hg), a toxic element, is widely distributed in the environment and is naturally present in aquatic systems in very low concentrations. The extensive past industrial use of the metal and its compounds together with widespread agricultural application of organomercurials has frequently resulted in serious contamination of surface waters and sediments (e.g. Hosokawa[147], Wilken and Wallschläger[334], Heaven et al.[140]). Long-range atmospheric transport of Hg from fossil fuel combustion and other sources has led to increased concentrations in freshwater systems and biota even in remote areas that are free from direct anthropogenic influences (Rada et al.[265], Lindqvist[200]).

The chemistry of Hg is complex, making it difficult to predict the behavior of mercuric pollutants in the natural environment. Sediments act both as sinks and potential sources of Hg (Covelli et al.[81]) and once contaminated may pose a risk to aquatic life for many years (Kudo[187]). Depending on the prevailing physical, chemical and biological conditions, Hg compounds in aquatic systems can be interconverted and can be released from sediments to the water phase, taken up by aquatic biota, be lost to the atmosphere, or be transported with sediment particulate matter to new, previously uncontaminated locations.

The ecological and toxicological effects of Hg are strongly dependent on the chemical form (species) present (Clarkson[63]). Inorganic Hg forms may be transformed to organic, methylated species that are many times more toxic to aquatic organisms (WHO[332,333], Boening[46]). The formation of methylmercury (MeHg), a potent neurotoxin, is of particular importance. Owing to its lipophilic and protein-binding properties, MeHg is readily accumulated by aquatic biota

and may thus also pose a threat to humans and other fish eating animals. Notorious incidents of mercury poisoning occurred in the 1950s and 60s at Minamata Bay and on the Agano River in Japan (Takizawa[310]).

Many of the chemical and biological processes that control Hg methylation and bioaccumulation are still insufficiently understood, but if Hg pollution is to be effectively managed, we need to have a better understanding of the behavior of mercuric contaminants in the natural environment. This review discusses the behavior of Hg in aquatic systems and the factors that are thought to play a role in environmental MeHg formation. It also identifies areas in need of further research.

2. Mercury in the aquatic environment

2.1 Mercury species in aquatic systems

Mercury occurs in three valence states (0, +1 and +2) and may be present in various physical and chemical forms in the natural aquatic environment. The nature and reactions of these species determine the solubility, mobility and toxicity of Hg in aquatic ecosystems, as well as the potential for methylation. The main dissolved Hg species are elemental mercury (Hg^0), complexes of Hg(II) with various inorganic and organic ligands, and organic Hg forms, mainly methylmercury (MeHg) and dimethylmercury (DiMeHg). Between 10-30% of the dissolved Hg in the ocean is present as Hg^0 (Kim and Fitzgerald[176], Mason and Fitzgerald[212]), and similar concentrations have been found for freshwaters (Vandal et al.[313], Xiao et al.[341]). Hg^0 in surface waters occurs mainly from the reduction of Hg(II) compounds by aquatic microorganisms (Furukawa et al.[111], Nelson et al.[250], Mason et al.[216]) as well as from abiotic reduction by humic substances (Alberts et al.[3], Miller[237], Allard and Arsenie[4]), decomposition of organic Hg forms (Mason and Fitzgerald[212], Mason and Sullivan[223]) and from anthropogenic discharges, a typical source being the chloralkali industry. Recent studies have shown that photoreduction of divalent Hg is another important mechanism of Hg^0 production in a wide range of aquatic systems (Xiao et al.[341,342], Schroeder et al.[288], Amyot et al.[5-9], Krabbenhoft et al.[181]) and that this process is mediated by humic material (Costa and Liss[79,80]). Hg^0 is relatively unreactive and is stable under mildly-oxidizing or reducing conditions, but can be oxidized to Hg(II), particularly in the presence of chloride ions (Demagalhaes and Tubino[89], Yamamoto[347]). Amyot et al.[5,6] have demonstrated the oxidation of Hg^0 in lake water and coastal seawater.

Most surface waters are supersaturated in Hg^0 relative to the atmosphere, especially in summer (Vandal et al.[313], Fitzgerald et al.[104]). Due to its relatively high volatility, elemental Hg is readily lost from the aquatic environment at normal temperatures. The evasion of Hg^0 from water surfaces plays an important part in the global Hg cycle (Mason et al.[214], Fitzgerald and Mason[105]). It has also been suggested that Hg^0 production is an important mechanism in aquatic

systems for reducing the Hg(II) substrate used in the microbiological synthesis of MeHg (Fitzgerald et al.[103,104], Mason et al.[215]).

Hg(I) is only stable as a dimer (Hg_2^{2+}) in aqueous solution, and readily disproportionates into Hg^0 and Hg^{2+}, the most stable form in water. Until very recently, it was generally considered that the Hg^{2+} ion is the main species that is methylated, in a bacterially-mediated process (cf. section 3). Recent research, however, has shown that uncharged Hg complexes are much more likely to be taken up by bacteria (cf. section 3.2.1). Hg speciation is therefore a primary factor governing the methylation potential of a system.

The chemical form of Hg in aquatic systems is strongly influenced by redox (E_h) and pH conditions as well as by the concentrations of inorganic and organic complexing agents. Both the Hg^{2+} ion and the methylmercuric (CH_3Hg^+) cation have a high tendency to form complexes, in particular with soft ligands such as sulfur. Lindqvist[200] gives a list of potentially important inorganic and methylmercury complexes for fresh and sea water, and predominance diagrams showing the relative regions of stability of various soluble Hg species can be found in the literature (Hem[90], Gavis and Fergusson[118], Lockwood and Chen[201], Beneš and Havlík[24], Hudson et al.[148], Stumm and Morgan[304]). In the absence of sulfide, the speciation of inorganic Hg in freshwaters is dominated by three uncharged complexes, $Hg(OH)_2$, HgOHCl, and $HgCl_2$ (cf. Fig. 1). In the presence of increasing chloride ion concentrations, Hg^{2+} forms $HgCl^+$, $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ complexes, and in full strength seawater (3.5% salinity), containing an average concentration of 0.56 M of Cl^-, it exists primarily as $HgCl_4^{2-}$ and $HgCl_3^-$ (Lockwood and

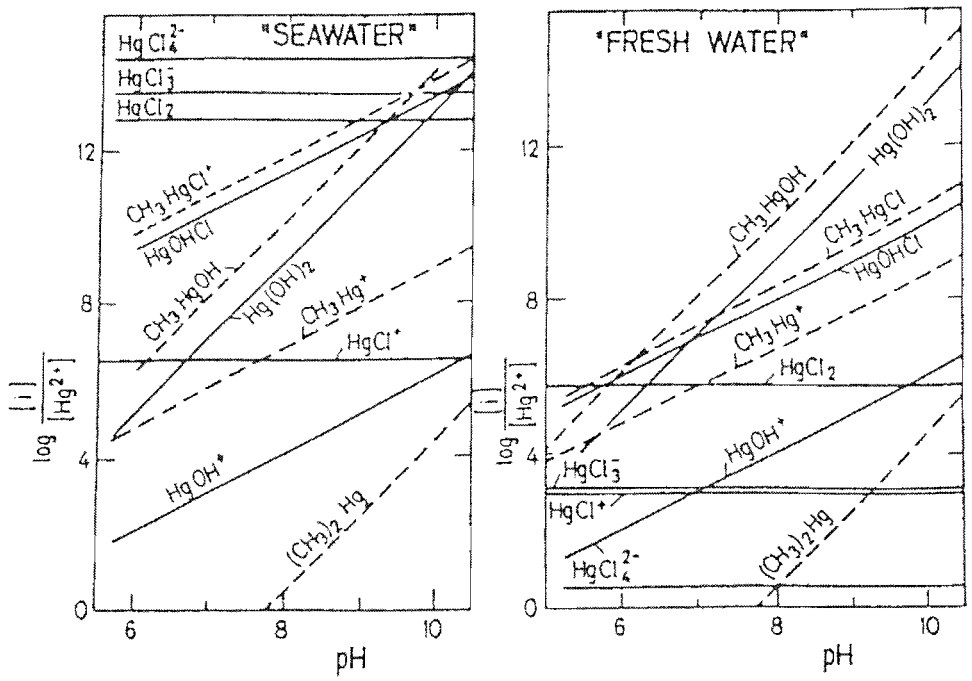

FIGURE 1. Concentration ratio diagrams illustrating the relative thermodynamic stability of mercury species in fresh water and sea water. Conditions: sea water $[Cl^-] = 0.6$ *M*, $[CH_{4(aq)}] = 10^{-4}$ *M*: fresh water $[Cl^-] = 2 \times 10^{-4}$ *M* $[CH_{4(aq)}] = 10^{-4}$ *M*. (Source: Stumm and Morgan.[304] Reprinted by permission of John Wiley & Sons, Inc.)

Chen[201], Hahne and Kroontje[134], Stotzky and Babich[303]). Methylmercuric hydroxide, CH_3HgOH, is the most stable methylmercury species in the freshwater environment, whereas in seawater, MeHg is present mainly as the chloride, CH_3HgCl (Craig[82], Stumm and Morgan[304]). Equilibrium constants for MeHg and some of its complexes have been published e.g. by Stumm and Morgan[304].

Predominance diagrams do not usually consider organic complexation due to a paucity of thermodynamic data on Hg and especially MeHg binding with polyfunctional natural ligands such as humic and fulvic acids. Hg speciation in natural waters is largely dominated by organic rather than chloride or hydroxide complexes, however (Lövgren and Sjöberg[202], Coquery et al.[71]). Particularly strong associations are formed with humic matter, where the Hg atom is most likely bound to thiol (-RSH) groups (Gavis and Fergusson[118], Reimers et al.[275], Beneš and Havlík[24], Lindqvist[200]). Organic colloids comprise a substantial proportion of the traditionally defined dissolved Hg fraction (<0.45 μm) in freshwater, estuarine and marine environments (Mason et al.[213], Watras et al.[326], Leermakers et al.[195], Stordal et al.[302], Guentzel et al.[129]). In freshwaters more than 90% of Hg is complexed by organic matter (Mantoura et al.[208], Meili[233]). Most MeHg (>70%) is probably also associated with dissolved organic carbon (DOC) in lake water (Lindqvist[200], Hudson et al.[148]). Hudson et al.[148] have modeled the cycling of Hg in Wisconsin lakes and have calculated that 94-99+% of Hg(II) and 72-97% of MeHg in lakewaters is complexed by dissolved humic matter. In seawater, however, the proportion of Hg^{2+} bound to humics is decreased due to chloride ion competition (Lindberg and Harriss[198], Mantoura et al.[208], Leermakers et al.[195]). Hg complexation with humic matter also varies greatly depending on redox and pH conditions (cf. section 2.3), and the presence of sulfide ligands. Hudson et al.[148] calculated that in oxic waters, sulfide may outcompete humic acid for Hg(II) and MeHg at a concentration of 10 μM.

While organic complexation is likely to dominate in oxic fresh water, under anoxic conditions the chemistry of Hg is mainly controlled by sulfide. In sediments Hg is mainly bound to sulfur as well as organic matter and inorganic particles (Morel et al.[242], Lindberg and Harriss[198], Dyrssen and Wedborg[95], Fabbri et al.[97], Mason and Lawrence[225]). Mercuric sulfide (HgS) is the main insoluble ($L_{HgS}=10^{-53}$ mol^2 l^{-2}) inorganic Hg compound in aquatic systems. Mercuric oxide (HgO) which is sparingly soluble (10^{-4} mol l^{-1}) is also commonly encountered in contaminated environments (Sakamoto et al.[283]). Hg compounds in the mud of Minamata Bay for example were mainly sulfides and oxides (Fujiki and Tajima[110]). HgS formation is generally favoured at low pH and low sulfide concentrations. Under low E_h and high pH conditions, or if an excess of sulfide ions is present, HgS can be converted to soluble Hg-S complexes such as HgS_2^{2-}. Organic matter also enhances the solubility of HgS and may lead to a significant release of Hg into solution (Ravichandran et al.[270]), but other complexing agents do not appear to

enhance HgS dissolution (Frimmel[109], Ravichandran et al.[270]). Early work suggested that mercury in the HgS form is not available for bacterial methylation under anaerobic conditions, which was believed to be the reason for the generally lower MeHg concentrations encountered in sulfidic sediments, but recent research suggests that dissolved HgS^0 can in fact be methylated (Benoit et al.[26]), and that the mechanism of sulfide inhibition of Hg methylation is more complex (cf. section 3.2.6).

At high sulfide concentrations, e.g. in sulfidic marine waters and interstitial waters of bottom sediments, Hg forms soluble bi- and polysulfide complexes such as $HgSH^+$, $Hg(SH)_2$, $Hg(SH)S^-$, HgS_2^{2-}, $Hg(S_x)_2^{2-}$, or $Hg(S_x)OH^-$, depending on pH and E_h conditions and S^0/S^{2-} concentrations (Gardner[117], Dyrssen and Wedborg[95], Paquette and Helz[257], Jay et al.[163]). Methylmercury also forms highly stable complexes with sulfur ligands (Zepp et al.[348]), but in contrast to Hg^{2+}, the chloride complex dominates at low concentrations (0.1 nM) of H_2S and thiols (Dyrssen and Wedborg[95]). The most important sulfide complex of methylmercury is CH_3HgS^-.

Organomercurials may be present in surface waters due to natural processes such as biomethylation of inorganic Hg or human activities. Many of these compounds have in the past been widely used e.g. as fungicides, slimicides, or industrial catalysts, but with most of these uses now banned in many parts of the world, transformation of inorganic Hg is the predominant source of methylated Hg compounds in aquatic systems (Craig[82]). Atmospheric deposition is the main source of inorganic Hg to oceanic waters (Mason et al.[215], Mason and Fitzgerald[220]) and many lakes (Watras et al.[328]), but is not a significant source of MeHg (Mason and Fitzgerald[210,211]). Precipitation and surface run-off can be important sources of MeHg to freshwaters besides internal methylation (Rudd[280]).

Only methyl and dimethylmercury are thought to occur naturally in waters, where they can be formed from divalent inorganic Hg by various mechanisms (cf. section 3). MeHg is the most ubiquitous organomercury compound in freshwater and estuarine systems, while DiMeHg is not normally detected. MeHg is kinetically inert toward decomposition, which accounts for its remarkable stability in natural waters (Stumm and Morgan[304]). It is efficiently degraded by microbial action, however, and can also be decomposed photochemically (cf. section 3.1.4). Organomercury compounds other than MeHg decompose rapidly in the environment (Jensen and Jernelöv[166], Craig[82]), with typical breakdown products being organic compounds such as ethane and inorganic Hg (Hg^0 and Hg^{2+}). Compounds such as dimethyl and diphenyl Hg are volatile, nonpolar and very poorly soluble in water. Unlike MeHg, DiMeHg is readily lost from aquatic systems by evaporation (Talmi and Mesmer[311]) and is not considered to be available for accumulation by aquatic organisms (Morel et al.[243]).

In contrast to freshwater systems, DiMeHg is the dominant methylated species in deep ocean waters (Mason and Fitzgerald[210,211], Cossa et al.[75], Mason et al.[218]), where it appears to be

produced from labile inorganic Hg complexes predominantly, although not exclusively, in the low-oxygen region (Mason and Fitzgerald[210,211,220], Cossa et al.[77], Mason et al.[221]). Little or no methylated Hg species are found in oceanic surface waters (Mason and Fitzgerald[210,211], Cossa et al.[75], Mason et al.[218,221], Mason and Sullivan[223]), with enhanced demethylation, evaporation, and/or photodegradation of DiMeHg, and particulate scavenging of MeHg from surface waters being suggested as potential loss mechanisms (Mason and Fitzgerald[212], Mason et al.[218,221]).

2.2 Mercury concentrations in the aquatic environment

2.2.1 Water

Mercury is naturally present in waters at very low levels. It should be noted that accepted background levels have fallen steadily in recent years following significant improvements in both sampling and analytical techniques (Horvat[146]), while previously reported high results are now believed to have resulted from sample contamination. Recently established Hg levels in aquatic systems in Antarctica have been suggested as global baseline values. Total Hg in surface waters of antarctic lakes and glacial streams ranged from 2.2-9.5 pM, dissolved Hg from 0.5-2.2 pM and MeHg from <0.4 to 2.1 pM (Vandal et al.[314], Lyons et al.[206]). Uncontaminated freshwaters generally contain <5 ng l^{-1} (≅ 25 pM) total Hg (Bloom[37], Craig[82]), although up to 10 or 20 ng l^{-1} can be found in humic lakes or rivers rich in particulate Hg (Meili[233]). Total Hg concentrations in the marine environment are much lower and were found to range between 0.5 and 4 pM in the Mediterranean and North Atlantic (Cossa et al.[77], Mason et al.[221]). Mercury concentrations in contaminated waters can be in the μg l^{-1} range. Dissolved Hg concentrations in the River Nura in Central Kazakhstan were typically between 0.2 and 0.5 μg l^{-1}, for example, depending on season and suspended solids content (Heaven et al.[140]). Considerably less data is available on organic Hg compounds in natural waters. Recommended water quality criteria in the Netherlands give target values of 0.05 μg l^{-1} for total dissolved Hg and 0.005 μg l^{-1} for organic Hg (Stumm and Morgan[304] after Behra *et al.* 1993).

The proportion of MeHg to total Hg is usually higher in the water column than in sediments, and is higher in freshwater than in estuarine environments. In estuarine and marine waters, MeHg is typically less than 5% of total Hg content (Coquery et al.[71], Mason and Sullivan[223]), whereas up to about 30% of total Hg can be found as MeHg in freshwater lakes and rivers (Kudo et al.[186], Meili[233], Leermakers et al.[196]). Elevated concentrations of both total Hg and MeHg are frequently found in anoxic waters. Bloom[37] reported MeHg concentrations in natural surface waters are typically in the range of 0.02-0.1 ng l^{-1} (0.1-0.5 pM), but found up to 4 ng l^{-1} (37% of total Hg) in the anoxic bottom waters of a stratified pristine lake. DiMeHg has not been detected in temperate freshwater lakes (e.g. Vandal et al.[313], Cossa et al.[74]) but is the

most common methylated species in the marine environment. Up to 280 fM MeHg and 670 fM DiMeHg were found below the thermocline in the equatorial Pacific (Mason and Fitzgerald[210]) and up to 0.29 pM DiMeHg were detected in the Western Mediterranean (Cossa et al.[75]); average DiMeHg concentrations in the North Atlantic were 0.08 pM (Mason et al.[221]).

2.2.2 Sediments

Sediments constitute the main reservoir of Hg in freshwater systems. Background levels of Hg in uncontaminated sediments are comparable to levels in unpolluted surface soils, with average concentrations in ocean sediments in the order of 0.02 to 0.1 μg g^{-1} (Lindqvist et al.[199]). Craig[82] reported concentration ranges of 0.2-0.4 μg g^{-1} total Hg for uncontaminated sediments, whereas sediments in urban, industrial, or mineralized areas can contain up to 100 μg g^{-1} total Hg and up to 100 ng g^{-1} MeHg. Methylmercury concentrations in sediments are typically only about 1-1.5% of total Hg content and tend to be lower (typically <0.5%) in estuarine and marine environments (Olson and Cooper[251], Bartlett and Craig[21], Craig and Moreton[85], Craig[82], Bubb et al.[53], Gobeil and Cossa[126], Gagnon et al.[114], Benoit et al.[25]). Total Hg concentrations in sediment porewaters are usually much higher than in the overlying watercolumn, however (e.g. Gobeil and Cossa[126], Cossa and Gobeil[78]), and the proportion of MeHg can reach between 30 and 85% (Gagnon et al.[114], Covelli et al.[81], Hines et al.[141]).

Contaminated sediments may exhibit extremely high total Hg concentrations. Mud from Minamata Bay contained up to 908 μg g^{-1} (d.w.) Hg (Fujiki and Tajima[110]). MeHg was mostly less than 0.005 μg g^{-1} (d.w.) with a maximum of 0.03 μg g^{-1} (Hosokawa[147]), however, possibly due to the high sulfide content of the sediment, or inhibition of microbial activity at high Hg levels (Chen et al.[59]). The River Nura has average sediment concentrations between 150 and 240 μg g^{-1} (d.w.) total Hg in the most polluted section (Heaven et al.[140]), and River Elbe sediments were found to contain 12 μg g^{-1} (d.w.) total Hg and 35 ng g^{-1} (d.w.) MeHg (Hintelmann and Wilken[142]). DiMeHg has rarely been detected to date, but Quevauviller et al.[263] reported 211-233 ng g^{-1} DiMeHg (d.w.) in subsurface mangrove sediments.

Sediment quality criteria for Hg have been set in some countries, but due to the uncertainties regarding the bioavailability of Hg, it has been suggested that these should be applied with caution and in concert with other site-specific data (Chapman et al.[58]). It is also important to note that there has been considerable controversy in recent years regarding the 'true' methylmercury content of environmental samples, in particular sediments, after it was found that MeHg may be artificially formed during the sample preparation process. Although methods have since been devised to overcome this problem (e.g. Hintelmann et al.[144]), MeHg values cited in the literature should be interpreted with caution, and it is now generally accepted that values in excess of ca. 1% of total Hg content are probably unrealistic.

2.2.3 Biota

Freshwater biota can accumulate detectable quantities of Hg even from natural sources, and most fish nowadays have analysable levels in their tissues. Maximum background levels for Hg in uncontaminated freshwater fish are about 0.2 μg g^{-1}, although considerably more can be found in large predators and in fish from waters near geological sources. Craig[82] reported concentration ranges of 0.01-1.5 μg Hg g^{-1} and 0.14-0.75 μg Hg g^{-1} for unpolluted marine fish and shellfish, respectively, and 0.2-1 μg g^{-1} for uncontaminated freshwater fish. For comparison, fish and shellfish from the highly polluted Minamata Bay contained up to 15 μg Hg g^{-1} (w.w.) and 178 μg Hg g^{-1} (d.w.), respectively (Fujiki and Tajima[110]). Human exposure to mercury occurs mainly from the ingestion of contaminated fish and seafood (Myers et al.[245]), and quality criteria have been set by various regulatory bodies. EEC quality objectives state a limit value of 0.3 μg Hg g^{-1} (w.w.) in fish (Craig[82]), whereas WHO[332] and the U.S. Food and Drug Administration (FDA[101]) have suggested maximum permissible concentrations of 0.5 and 1 μg Hg g^{-1}, respectively.

2.3 Mercury transport and distribution in surface waters

Mercury has a high tendency to be sorbed on surfaces. In natural waters it is therefore mostly bound to sediments, and a large proportion of Hg in the water phase is attached to suspended particles (Andren and Harriss[11], Craig[82], Mason et al.[213], Cossa et al.[76]). MeHg is also strongly sorbed (Craig[82], Baeyens et al.[14], Rytuba[282]), although usually to a lesser extent than inorganic Hg (e.g Suchanek et al.[305]) Suspended matter thus plays an important role in the transport of Hg and MeHg in aquatic systems (Kudo et al.[183,185], Baeyens and Leermakers[13], Coquery et al.[71], Mason and Sullivan[222,223], Maurice-Bourgoin et al.[230], Lawson et al.[191]). Particulate transport is more important in particle-rich fresh and coastal waters than in the open sea (Coquery and Cossa[69], Coquery et al.[71], Fitzgerald and Mason[106]). Particulate Hg consists of Hg bound to inorganic particles and particulate organic matter, as well as biogenic particles such as bacteria, algae and phytoplankton. Inorganic Hg tends to bind more strongly to mineral particles and detrital organic matter whereas MeHg is more strongly associated with biogenic particles (Hurley et al.[150], Meili[233]). In freshwater lakes, the distribution of Hg and MeHg is largely controlled by particulate scavenging in surface waters and particulate dissolution at the redox boundary (Hurley et al.[149]). Settling of particulate matter is considered a major Hg delivery mechanism to the sediment/water interface, the main site for methylation, whereas (redox-driven) upward diffusion from sediment porewater is probably less important (Hurley et al.[149,151], Watras et al.[323]). Similarly, vertical transport of particulate matter in the ocean is the

main supplier of Hg to low-oxygen waters and is thus a major factor controlling Hg methylation (Mason and Fitzgerald[212,220], Mason and Sullivan[223]).

Oxyhydoxides and organic matter are the main vectors controlling the mobility and transport of Hg in aquatic systems. Due to the high stability of Hg-humic complexes, a high percentage of Hg in natural waters is present in organically complexed form (cf. section 2.1), and Hg concentrations in lake water or in the interstitial waters of sediments are often significantly correlated with dissolved organic matter (Lindberg and Harriss[198], Meili et al.[232], Watras et al.[325,326]). Hg concentrations in sediments or suspended particles are also often closely related to organic content (Lindberg and Harriss[198], Coquery et al.[70], Benoit et al.[25], Mason and Lawrence[225], Harland et al.[139], Lawson et al.[191]). Hg appears to be more strongly sorbed by humic substances than MeHg (Hudson et al.[148], Sjöblom et al.[291]), which may be the reason why it is less easily mobilized from sediments than MeHg (Bloom et al.[42], Gill et al.[119]). In watersheds, MeHg is also considered more mobile than inorganic Hg (Bishop and Lee[33], Mason and Sullivan[222], Hurley et al.[152], Lawson et al.[191]). The strong association of Hg with humic matter has important implications for the watershed transport of Hg (Bishop and Lee[33]). Transport of terrestrial organic matter with surface runoff can be a major source of Hg and MeHg to lakes and rivers (Mierle and Ingram[236], Verta et al.[317], Hurley et al.[152], Lee et al.[194]) and may even constitute the main source of MeHg in drainage lakes receiving high amounts of runoff (Lee and Hultberg[193]). In seepage lakes, on the other hand, the relative importance of atmospheric MeHg deposition and in-lake MeHg production is increased (Verta et al.[317]). Watershed characteristics such as catchment type, land use, and soil organic content play an important role in Hg and MeHg fate and transport (Bringmark[52]). Wetlands and peatlands are sites of active MeHg production and have been recognized as important sources of MeHg for freshwaters (St. Louis et al.[301], Hurley et al.[152], Branfireun et al.[49-51], Waldron et al.[330]). Soil erosion and increased mobilization of Hg by runoff is an important source of Hg to tropical aquatic ecosystems, especially during the rainy season (Roulet et al.[278], Maurice-Bourgoin et al.[230]), and in arid regions, storm-driven runoff following forest fires may lead to elevated sediment Hg levels whilst simultaneously providing a carbon source for microbial methylation processes (Caldwell et al.[54]).

Iron and manganese oxides play a particularly important role in the cycling and transport of Hg in aquatic systems. This is due to their large surface areas and high capacity to adsorb and co-precipitate Hg, and to re-release it upon their dissolution (Fagerström and Jernelöv[99]). Many workers have found the distribution and concentration of dissolved and particulate Hg species to be influenced, among other factors, by the redox cycling of Fe, and less frequently Mn (e.g. Mason et al.[213], Hurley et al.[151], Bonzongo et al.[47], Gagnon et al.[115], Regnell et al.[274], Quemerais et al.[262], Gobeil et al.[127], Bloom et al.[41]). Bloom et al.[41] reported, for example, that the mobility of MeHg in estuarine surface sediments was linked to the Fe redox cycle, while the mobility of

Hg(II) was controlled by the formation of soluble polysulfide or organic complexes. The formation and dissolution of Fe and Mn oxides is strongly controlled by the redox state and oxygen content of waters and sediments. In anoxic conditions, oxyhydroxides dissolve and release any associated Hg (Gobeil and Cossa[126], Gagnon et al.[115], Cossa and Gobeil[78]), which is thought to be one reason for the frequently observed Hg and MeHg enrichment in (seasonally) anoxic waters (Hurley et al.[149], Cossa et al.[74], Watras et al.[327]). Seasonal and diurnal trends in MeHg concentrations in sediment porewaters (Covelli et al.[81], Gill et al.[119]) may also be linked with redox effects. Meili[233] noted that oxyhydroxides form labile complexes with organic matter and clay minerals, which may further increase their metal scavenging capacity. The formation and dissolution of oxyhydroxides and organic complexes may influence methylation by controlling the availability of inorganic Hg.

Sediments can act both as sinks and as secondary sources of Hg. Covelli et al.[81] estimated that in the Gulf of Trieste, up to 25% of Hg may annually be released from sediments and recycled at the sediment/water interface, and Stein et al.[300] have reviewed the chemical and physical processes governing the distribution of Hg between environmental media. Partition coefficients describe the equilibrium partitioning of Hg between the solid and dissolved phases. Sediment-water partition coefficients (K_d = mg sorbed Hg per kg sediment / mg dissolved Hg per liter) vary widely both within and between systems but are broadly in the order of 10^4-10^6 for Hg and 10^3-10^5 for MeHg (Hurley et al.[150], Watras et al.[326], Stordal et al.[302], Coquery et al.[71], Lyon et al.[205], Mason and Sullivan[222], Bloom et al.[41], Lawson et al.[191]). Sorption/desorption phenomena and precipitation reactions are also likely to affect Hg bioavailability (King et al.[177]) and need to be taken into account when estimating rates of MeHg production in the natural environment (Bisogni[35]).

2.4 Influence of environmental factors on Hg partitioning

The cycling and distribution of Hg between the sediment and water phases may be physically, chemically or biologically mediated, and may hence be affected by parameters such as pH, temperature, redox changes, availability of nutrients and complexing agents. This should be considered when evaluating the effect of environmental factors on Hg methylation. The degree of binding of MeHg by sediments for instance depends on sediment properties as well as pH and dissolved oxygen concentrations (Reimers et al.[275], Kudo et al.[182], Gambrell et al.[116]). Although the proportion of Hg in dissolved form may sometimes decrease under anoxic conditions due to the formation of reduced species such as HgS (Baeyens and Leermakers[13]), oxic conditions generally favor sediment uptake of Hg and MeHg, whereas anoxic conditions favor Hg release (Wang et al.[320], Regnell and Tunlid[272], Regnell et al.[273]). The observed effects are most likely linked to the precipitation and dissolution of Fe and Mn oxides and oxyhydroxides. The

solubility of Hg and MeHg under anoxic conditions may also be increased due to the formation of soluble sulfide complexes (Regnell et al.[273], Benoit et al.[25]). Apart from redox effects, seasonal variations in the partitioning of Hg and MeHg may also be related to changes in biotic particulate matter (Hurley et al.[149], Watras et al.[323], Coquery et al.[70]).

Methylmercury release from sediments also increases with increasing temperature and nutrient addition (Wright and Hamilton[339]) and decreasing pH. Miller and Akagi[238] reported that a change in pH from 7.0 to 5.0 doubles the release of MeHg from sediments, and Hintelmann et al.[143] found that the binding of MeHg to humic and fulvic acids decreases with decreasing pH. The observed pH-dependent changes in the partitioning of MeHg between the sediment and water phases may be partly responsible for the often noted increased Hg concentrations in fish from low-pH lakes (e.g. Lindqvist et al.[199]).

The presence of organic or inorganic complexing agents also affects the partitioning of Hg. Formation of soluble humic complexes may significantly increase the solubility and mobility of Hg in aquatic systems (Miller[237], Reimers et al.[275], Miskimmin[239], Melamed et al.[234,235], Ravichandran et al.[270,271]), especially above pH 5, while $HgCl_2$ is effectively sorbed at lower pH values (Stein et al.[300] after Bodek et al. 1988). The situation in sediments may be comparable to that in soils, where adsorption of Hg to humus predominates in acidic conditions, and Hg is preferentially sorbed to mineral particles (Fe oxides and clay minerals) in the neutral to alkaline pH range, due to formation of the more particle reactive $HgOH^+$ species (Bringmark[52]). High chloride concentrations appear to reduce the amount of Hg associated with suspended particulate matter and organic colloids, most likely due to competition of Cl^- for binding sites. Increased mobilization of Hg with increasing salinity was observed both in model experiments (Reimers et al.[275]) and in estuarine and marine environments (Cossa and Noel[72], Cossa and Martin[73], Leermakers et al.[195], Guentzel et al.[129]).

2.5 Accumulation in aquatic biota

Mercury, and in particular methylmercury, is effectively taken up by aquatic biota, and bioconcentration factors in the order of 10^4-10^7 have been reported (WHO[332], Stein et al.[300]). Accumulation in the aquatic food chain can therefore be high even at the generally very low environmental MeHg concentrations. While MeHg typically constitutes between 10 and 30% of total Hg in the water phase, more than 85-90% of Hg in fish is present in the MeHg form (Grieb et al.[128], Bloom[39], Southworth et al.[292]). Other organomercurials are also sometimes detected. Fish caught downstream of a source of phenylmercury effluent contained both methyl and ethylmercury (Ashby and Craig[12] after Frieberg 1971), and methylmercury methanethiol (CH_3HgSCH_3) has been found in shellfish (Ashby and Craig[12] after Kitamura 1963 and Lofroth 1969). The Hg content of aquatic organisms and the percentage present as MeHg usually

increases with increasing size and increasing level in the food chain (Boudou and Ribeyre[48], Meili[233], Watras et al.[329], Mason et al.[226]). Hg concentrations in fish often remain high for many years after Hg inputs have ceased or contaminated sediments have been dredged (Rada and Findley[264], Kudo[187], Francesconi et al.[108], Southworth et al.[293]).

The precise factors controlling the accumulation of Hg in aquatic biota are poorly understood. The high tendency of MeHg for bioaccumulation is usually explained by its high stability and lipid solubility, and by its high tendency to bind to -SH groups associated with proteins. However, this alone cannot account for the predominance of MeHg in fish muscle tissue (Mason et al.[217], Boudou and Ribeyre[48]). MeHg is taken up by fish mainly through their diet, while direct uptake from the water is of minor importance (Bodaly et al.[45], Boudou and Ribeyre[48], Meili[233]). Hg concentrations in fish are thus primarily determined by the accumulation of MeHg at the base of the food chain, i.e. in phyto- and bacterioplankton (Mason et al.[217,219], Watras et al.[329]). The predominance of MeHg in fish appears to be the result of its greater trophic transfer efficiency compared to inorganic Hg (Watras and Bloom[322], Mason et al.[219]). Uptake into biota is influenced by the physicochemical form in which Hg exists in the water. Uncharged lipophilic chloride complexes ($HgCl_2$ and CH_3HgCl) appear to be most bioavailable (Mason et al.[217], Mason et al.[219], Laporte et al.[190]), whereas DiMeHg and Hg^0 are not bioaccumulated (Morel et al.[243]). A number of other factors such as temperature, DOC, alkalinity, and in particular pH may also influence Hg bioaccumulation as well as methylation (Watras and Bloom[322], Boudou and Ribeyre[48], Meili[233], Watras et al.[329]). The accumulation of Hg in the aquatic food chain has recently been reviewed (Bodaly et al.[45], Boudou and Ribeyre[48]).

3. Methylation of mercury in the aquatic environment

3.1 General aspects

The methylation of inorganic Hg in waters and sediments constitutes a key step in the cycling of Hg in aquatic systems (Fitzgerald and Mason[106]) and takes place in both remote and impacted environments (Cossa et al.[74]). It is important to note that since both methylation and demethylation processes occur, environmental MeHg concentrations reflect *net* methylation rather than actual rates of MeHg synthesis. It appears that the combined effect of MeHg production and degradation leads to a state of equilibrium with a near constant level of MeHg in sediments (Beijer and Jernelöv[23], Pak and Bartha[256]) that rarely exceeds 1-1.5% of total Hg concentration (cf. section 2.2.2), whereas the proportion of MeHg in fish and other aquatic biota may be much higher (cf. section 2.5). On the basis of mass balance studies, estimated rates for MeHg production in temperate freshwater lakes currently range from 0.5-5 g MeHg per km^2 per year (Watras et al.[328]).

Methylation occurs predominantly in sediments and to a lesser extent in the water column (Olson and Cooper[251], Robinson and Tuovinen[277], Callister and Winfrey[55], Korthals and Winfrey[180], Xun et al.[343]), but it should be borne in mind that water column methylation is potentially more important, since the volume of water is typically much larger than the volume of surficial sediments. Maximum methylation rates usually occur at the redox boundary, which may vary seasonally and frequently coincides with the sediment-water interface, and decrease with increasing sediment depth (Rudd et al.[279], Korthals and Winfrey[180], Matilainen[227]). In tropical systems, the root zones of floating aquatic macrophytes are further important sites of methylation (Mauro et al.[231], Guimarães et al.[130]).

The effects of environmental factors on MeHg formation and decomposition were studied in the past mainly by relating MeHg concentrations in sediments, water and aquatic biota to changes in environmental conditions. In recent years the use of radiotracers and stable isotopes has made it possible to distinguish between the two opposing processes of MeHg formation and decomposition, but it must be borne in mind that rates measured after Hg additions may differ considerably from *in situ* rates. Gilmour and Henry[122] give an overview of the techniques that are typically employed for measuring MeHg concentrations and methylation/demethylation rates in aquatic systems, and their limitations.

The methylation of Hg requires the presence of a suitable methyl donor molecule. In the natural aquatic environment, a large variety of potential donor molecules are present, most of which are biologically synthesized. While it had first been assumed that Hg methylation requires the presence of bacteria, both microbially mediated and abiotic methylation mechanisms are now known, although the latter is thought to be of only minor importance.

3.1.1 Biomethylation

Biological methylation of inorganic Hg was first observed in sediments from aquaria and lakes and in coastal waters in Sweden (Jernelöv[167], Jensen and Jernelöv[165]) and has since been studied by many other workers. Hg methylation by organisms may be enzymatic or non-enzymatic. Enzymatic methylation requires the presence of actively metabolizing organisms, while non-enzymatic methylation requires only the methylated products of active metabolism. Detailed mechanisms for Hg methylation were first proposed by Wood et al.[336] and Landner[188]. Wood et al.[336] suspected that methylcobalamin, a vitamin B_{12} derivative (methylcorrinoid) produced by many organisms, is involved in microbial Hg methylation, and suggested that the process involves non-enzymatic transfer of the methyl group of methylcobalamin to the mercuric ion. DeSimone et al.[91] have shown that methyl transfer to Hg^{2+} is a carbanion (CH_3^-) process. While there are many potential methyl donor molecules in the aquatic environment, methylcobalamin is thought to be the only natural methylating agent capable of transferring methyl groups as

carbanions (Ridley et al.[276]). This together with its prevalence in anaerobic ecosystems and living organisms makes it the most likely methyl source for environmental Hg methylation.

Metabolically produced methylcobalamin can spontaneously methylate Hg^{2+} in aqueous solution (Bertilsson and Neujahr[31], Imura et al.[154]), but little is known about the biochemistry of MeHg formation in the natural environment. Organisms capable of Hg methylation have been found among anaerobes, facultative anaerobes and aerobes, but the potential for microbial methylation is generally thought to be higher under anaerobic conditions, and sulfate-reducing bacteria have been identified as the principal methylators of inorganic Hg in anaerobic sediments (Compeau and Bartha[66]). Methylation of Hg is generally thought to occur inside bacteria by transfer of a methyl group from a methylcorrinoid donor molecule, although Parkman et al.[258] suggested that methylation is an extracellular process that is enhanced by the activity of bacterial exoenzymes that also catalyze the microbial decompositon of organic matter. Choi and Bartha[60] demonstrated that methylcobalamin is the methyl group donor when divalent Hg is methylated by the LS strain of *Desulfovibrio desulfuricans*. Within the cell, Hg methylation appears to be an enzyme-catalyzed process rather than a spontaneous chemical reaction, with the rate of methylation at pH 7 being 600-fold higher than transmethylation by free methylcobalamin (Choi et al.[62]). The process is oxygen sensitive, with optimal methylation conditions at 35°C and pH 6.5. The enzyme responsible for transferring methyl groups from methylcorrinoid protein to Hg^{2+} has yet to be identified. Since biological Hg methylation takes place within microorganisms, cellular uptake of Hg plays a key role in the methylation process. This will be discussed in detail in section 3.2.1.

3.1.2 Abiotic methylation

Purely chemical methylation of Hg is also possible if suitable methyl donors are present. DeSimone[90] showed that water-soluble methylsilicon compounds react with Hg^{2+} to form MeHg. Organosiloxanes and other silicone-related substances have also been considered as possible methylating agents (Nagase et al.[248,249], Watanabe et al.[321]). Akagi et al.[1] demonstrated the photochemically induced alkylation of mercuric chloride with methanol, ethanol, acetic acid and propionic acid. Sewage effluent and industrial wastewater have also been reported as methyl sources in the photochemical methylation of Hg. Hamasaki et al.[136] have summarized some of the available data on photochemical methylation.

Wood[337] suggested Hg methylation can also occur as a result of transmethylation reactions between Hg and lead and tin alkyls used as gasoline additives. Jewett et al.[171] demonstrated that both trimethyllead chloride and trimethyltin chloride are able to transfer methyl groups to Hg^{2+}. Trimethyl lead was found to be a particularly effective methylator for Hg, and high MeHg concentrations in sediments of the St. Clair River were attributed to transmethylation reactions caused by alkyllead emissions (Beijer and Jernelöv[23] after Jernelöv *et al.* 1972). More recent

investigations of Hg methylation by organolead, organotin and organoarsenic compounds have been carried out e.g. by Ebinghaus et al.[96].

Humic matter may be another significant environmental methylating agent (Weber[331]). Abiological formation of MeHg by humic compounds has been demonstrated e.g. by Nagase et al.[246,247]. The capacity for MeHg formation generally increased with increasing temperature and Hg concentration, but was low at naturally occurring temperatures and pH values. Falter and Wilken[100] have shown that small amounts of MeHg can be formed abiotically at environmentally relevant temperatures and pH values, however. More than 400 pg MeHg, corresponding to ca. 0.05% of the added $^{200}Hg^{2+}$ spike, were produced in the acetone extract of a river sediment within 2 h at 40°C between pH 3 and 7. At 35°C, up to 160 pg could still be formed. In the river sediment itself, however, methylation was only detected at 40°C, with between 50 and 100 pg MeHg (0.005-0.01% of added $^{200}Hg^{2+}$) being formed.

Mercury methylation may thus be biotic or abiotic, or may involve a mixture of biotic and abiotic processes, such as the bacterial methylation of tin(IV) species followed by abiotic methyl transfer to Hg. The relative importance of abiotic vs biotic methylation mechanisms in the natural aquatic environment has not yet been established, but it is generally believed that Hg methylation is predominantly a microbially mediated process, and Berman and Bartha[30] demonstrated that in anoxic sediments MeHg levels resulting from chemical methylation were approximately one order of magnitude lower than those formed by biochemical Hg methylation. Ebinghaus et al.[96] reported that organo Pb, Sn and As compounds are more effective methylators than biogenic methyl donors such as methylcobalamin, but this is probably not material in the natural environment, since in vivo Hg methylation is enzymatically catalyzed and is much faster than transmethylation by free methylcobalamin (Choi et al.[62]).

3.1.3 Methylation products

MeHg may be formed from ionic Hg and many divalent Hg compounds (Yamada and Tonomura[344]), as well as from organic Hg compounds and metallic Hg (Jernelöv[168], Jacobs and Keeney[162]), possibly via formation of Hg^{2+}. DiMeHg can be synthesized from both methyl- and ionic Hg (Craig and Moreton[85,86], Baldi et al.[18], Filipelli and Baldi[102]). There is still considerable uncertainty however regarding the pathways of MeHg and DiMeHg formation. Filipelli and Baldi[102] have demonstrated that the initial product of the reaction between methylcobalamin and Hg^{2+} is MeHg, which is then further transformed into DiMeHg. The reaction is pH and temperature dependent and MeHg and DiMeHg formation rates are of similar magnitude at 20°C. Low pH values appear to favor the production of MeHg, while DiMeHg formation is favored under neutral and basic (pH>7) conditions (Jensen and Jernelöv[165], Beijer and Jernelöv[23], Fagerström and Jernelöv[99]). Below pH 5, DiMeHg is thermodynamically unstable and decomposes to form MeHg (Fagerström and Jernelöv[99], Fitzgerald and Mason[106]),

which may be one reason why DiMeHg has not been detected in freshwaters, where the pH is typically lower compared to estuarine and marine systems. Mason et al.[218] suggested that DiMeHg forms directly from Hg(II), but is rapidly decomposed to MeHg in freshwaters and hence does not accumulate to detectable levels. In deep ocean waters, on the other hand, the stability of DiMeHg might be enhanced by low-light, low-temperature and high pH conditions (Fitzgerald and Mason[106], Mason et al.[221]). Pongratz and Heumann[259,260] have also suggested that DiMeHg may be the primary biogenic methylation product in the ocean, and it appears that MeHg in the deep ocean is formed by decomposition of DiMeHg (Mason and Fitzgerald[210,212], Fitzgerald and Mason[105,106], Mason et al.[221], Mason and Sullivan[223]). DiMeHg decomposition is thought to be primarily abiotic (Fitzgerald and Mason[106]), whereas MeHg decomposition is predominantly biologically mediated (see below). Since DiMeHg formation in the ocean also occurs in oxygenated environments (Mason et al.[218,221], Cossa et al.[75]), it has been suggested that it may be formed by a different mechanism than in freshwaters (Mason et al.[220,221], Fitzgerald and Mason[106]).

3.1.4 Demethylation

The biological and abiological decomposition of methylated Hg species is an important process regulating the organic Hg content of sediments and waters. MeHg degradation is thought to be predominantly microbially mediated (Robinson and Tuovinen[277]). Numerous bacterial strains capable of demethylating MeHg are known (Spangler et al.[294,295], Billen et al.[32], Robinson and Tuovinen[277], Oremland et al.[254], Matilainen and Verta[228]), including both aerobic and anaerobic species, but demethylation appears to be predominantly accomplished by aerobic organisms (cf. section 3.2.5). Bacterial demethylation has been demonstrated both in sediments (e.g. Billen et al.[32], Oremland et al.[254]) and in the water column of freshwater lakes (Xun et al.[343], Winfrey and Rudd[335], Matilainen[227]). Degradation of methyl and phenyl mercury by fresh water algae has also been described (Beneš and Havlík[24] after Havlík *et al.* 1979a,b).

Mercury demethylation by bacteria appears to be a predominantly reductive process (Furukawa et al.[111], Spangler et al.[294,295], Nelson et al.[250]). The commonly-accepted mechanism of microbial MeHg decomposition involves cleavage of the carbon-mercury bond by the organomercurial lyase enzyme, yielding methane and Hg^{2+}, followed by the reduction of Hg^{2+} to Hg^0 by the mercuric reductase enzyme (Robinson and Tuovinen[277], Summers[309], Walsh et al.[319]). Synthesis of these enzymes is encoded by the *merB* and *merA* genes in bacteria possessing broad-spectrum Hg resistance. More recent work indicates that *mer* detoxification is not the only microbial degradation pathway, however. Oremland et al.[254] found that while methane was the sole product of MeHg degradation in aerobic estuarine sediments, aerobic demethylation in freshwater sediments and anaerobic demethylation in both freshwater and estuarine sediments produced primarily carbon dioxide, indicating the presence of an oxidative pathway. Oremland

et al.[255] and Hines et al.[141] have since shown that oxidative demethylation is significant in both contaminated and uncontaminated river sediments and is most pronounced at sediment surfaces. Inhibitor studies suggest that both sulfate reducers and methanogens, and possibly other anaerobes, are involved in oxidative demethylation (Oremland et al.[254,255], Marvin-Dipasquale and Oremland[209]). Marvin-Dipasquale and Oremland[209] have recently proposed specific mechanisms for the oxidative demethylation of Hg by sulfate-reducing bacteria and methanogens, and have suggested that methanogens dominate MeHg degradation at in-situ concentrations. Either process produces Hg^{2+}, but it is unclear whether the Hg^{2+} produced in oxidative demethylation is subsequently reduced to Hg^0 as has been demonstrated for the *mer*-mediated pathway (Robinson and Tuovinen[277]). Alternatively, it may be remethylated, bound by sulfur species, or volatilized as DiMeHg (Baldi et al.[16]). At present it is also not known which of the abovementioned degradation pathways (i.e. organomercurial-lyase, or oxidative demethylation by sulfate reducers and/or methanogens) dominate under specific environmental conditions. The relative importance of these pathways has major implications for the fate of Hg in natural systems, however, and may thus ultimately determine its residence time in sediments.

Photolytic decomposition appears to be the only significant *abiotic* decomposition mechanism. DiMeHg in the atmosphere is photolytically decomposed to Hg^0 and hydrocarbons (Craig[82]). Phenylmercury and sulfur-bonded MeHg species (e.g. CH_3HgS^-) can undergo quite rapid photolytic decay, but photodegradation was thought to be insignificant for methylmercuric ion and methylmercuric hydroxide, due to their low sunlight absorption rates (Baughman et al.[22]). Suda et al.[307] have shown that methyl- and ethylmercury are photodegraded by singlet oxgen in seawater, however, and recent work by Sellers et al.[289] demonstrates that MeHg is photolytically decomposed in surface waters, and that this process is potentially an important step in the aquatic Hg cycle. Mass-balance calculations show that microbial demethylation may not be the dominant removal mechanism for MeHg in epilimnetic fresh waters. Model simulations by Branfireun et al.[50] have since confirmed the findings of Sellers et al.[289]. The overall impact of photodegradation on the aquatic Hg cycle is still unclear, however, since the end products of MeHg photodegradation in natural waters have not yet been identified. Furthermore, while photolytic decay contributes to Hg demethylation in the water phase, it is unlikely to be significant in deeper sediments, where bacterial demethylation is more important (Xun et al.[343], Ramlal et al.[268]).

The ability of microorganisms to degrade Hg can be employed in the treatment of sewage (Hansen et al.[138]) and Hg contaminated liquid wastes (Baldi et al.[16,17]). Hansen et al.[138] reported that >98% of Hg present at a concentration of 70 mg l^{-1} can be removed from municipal sewage water by bacterial treatment. However, it should be noted that sewage treatment plants themselves can be sources of MeHg (Gilmour and Bloom[124], Carpi et al.[57]). In the bioremediation field, efforts have been made to devise methods for reducing the amount of

MeHg in contaminated aquatic ecosystems by stimulating the bacterial conversion of MeHg and Hg^{2+} to less harmful elemental Hg (Saouter et al.[284]). Very recently, transgenic plants have been specifically engineered to express bacterial *mer* genes (Rugh et al.[281], Bizily et al.[36]). Such plants show high resistance to inorganic Hg and organomercurials and may in future be used to degrade MeHg at polluted sites and to accumulate Hg for later safe disposal.

3.2 Factors affecting methylation

The synthesis of MeHg in aquatic systems is influenced by a wide variety of environmental factors. The efficiency of microbial Hg methylation generally depends on factors such as microbial activity and the concentration of bioavailable Hg (rather than the total Hg pool), which in turn are influenced by parameters such as temperature, pH, redox potential, and the presence of inorganic and organic complexing agents. Total Hg concentrations are generally not useful in predicting MeHg concentrations (Kelly et al.[174]). While there is no simple relationship, it appears that enhanced rates of MeHg production are linked in particular with low pH, low salinity, and the presence of decomposable organic matter in reducing environments. The main factors known to affect methylation are discussed below; it should be borne in mind, however, that they cannot be viewed independently from each other, as they often interact, forming a complex system of synergistic and antagonistic effects.

3.2.1 Microbiology

Microorganisms play a pivotal role in aquatic Hg cycling and catalyze many of the inter-conversions between different forms of Hg, such as the conversion of Hg^{2+} to methyl and dimethyl Hg and the reduction of Hg^{2+} to Hg^0 (Summers and Silver[308], Robinson and Tuovinen[277], Silver[290]). Mercury compounds are acutely toxic to freshwater microorganisms, but many bacteria are known to have developed resistance mechanims (Baldi[19], Hobman and Brown[145]), and positive correlations are often found in sediments between the distribution of Hg compounds and Hg-resistant microorganisms (Timoney et al.[312], Bubb et al.[53]). Bacterial Hg resistance is inducible and is regulated by the *mer* operon (Baldi[19]). Hg volatilization is regarded as a detoxification mechanism, whereas Hg methylation appears to be an accidental process and not a detoxification mechanism as previously suggested.

A large number of organisms, including strict and facultative anaerobes as well as aerobes, have been shown to methylate Hg *in vitro* (Wood et al.[336], Kitamura et al.[179], Yamada and Tonamura[344-346], Vonk and Sijpesteijn[318], Robinson and Tuovinen[277]), but it is not certain whether these bacteria are responsible for Hg methylation in the natural aquatic environment. Several more recent studies have indicated that anaerobic sulfate-reducing bacteria (SRB) are the principal methylators of inorganic Hg in both freshwater and estuarine sediments (Compeau

and Bartha[66,67], Berman and Bartha[29], Gilmour and Henry[122], Gilmour et al.[123]). Contrary to earlier assumptions (e.g. Wood et al.[336]), methanogenic bacteria seem to play only a minor role in MeHg production. Interestingly, the same bacteria that are primarily responsible for MeHg production also appear to mediate MeHg degradation (Robinson and Tuovinen[277]). Both sulfate reducers and methanogens are important demethylators in estuarine and freshwater sediments (e.g. Oremland et al.[254,255], cf. section 3.1.4). In pure culture, the formation of DiMeHg from MeHg is also mediated by SRB (Baldi et al.[16,18]). DiMeHg formation in the ocean is thought to be microbial (Pongratz and Heumann[259,260], Mason and Sullivan[223]), but is is not known whether SRB or other organisms are the primary methylators (Mason et al.[220,221], Fitzgerald and Mason[106]).

Hg methylation activity in sediments is often significantly correlated with sulfate-reduction rates (Choi and Bartha[61], King et al.[177,178]) or with the distribution of SRB populations (Devereux et al.[92], Macalady et al.[207]), but not all SRB are capable of Hg methylation. Many studies have focussed on *Desulfovibrio* populations (e.g. Baldi et al.[16], Choi and Bartha[60], Choi et al.[62]) but King et al.[178] have recently noted that SRB capable of acetate utilization (ie. members of the family *Desulfobacteriaceae*) appear to methylate Hg more effectively than members of the *Desulfovibrio* group. Macalady et al.[207] also found that *Desulfobacter* populations are important methylators in lake sediments and that they were more abundant than *Desulfovibrio*.

The efficiency of microbial MeHg production appears to depend chiefly on the activity and structure of the bacterial community (Macalady et al.[207]), Hg availability, the availability of nutrients, and the abundance of electron acceptors such as sulfate (Choi and Bartha[61]). At low concentrations, sulfate stimulates both sulfate reduction and methylation (Compeau and Bartha[66], Gilmour et al.[123]). In situ addition of small amounts of sulfate may thus lead to increased MeHg production in freshwater environments when sulfate is limiting (Gilmour et al.[123], Branfireun et al.[51]). Although a sulfate concentration of <10 mg l^{-1} (0.1 mM) generally starts to become limiting for the activities of SRB (Ingvorsen et al.[155], Lovley and Klug[203]), they can remain active even at the very low sulfate concentrations (ca. 3 mg l^{-1}, 0.03 mM) typically encountered in freshwater systems, by successfully competing with methanogens for common substrates, i.e. hydrogen and acetate (Lovley and Klug[203], Matilainen[227]). Compeau and Bartha[66] reported that the methylating potential of SRB is highest when sulfate is limiting and other organic substrates are available that can be utilized in place of sulfate, which may be due to the inhibitory effect of sulfide on Hg methylation. At high sulfate concentrations, the accumulation of sulfide generated by sulfate respiration interferes with Hg methylation, thereby limiting MeHg production (e.g. Baker et al.[15], Compeau and Bartha[66,67], Winfrey and Rudd[335]). Sulfide inhibition was previously ascribed to HgS precipitation, but is now thought to be linked with charged Hg-S complexes (cf. section 3.2.6). Gilmour and Henry[122] proposed an optimal

sulfate concentration range of 0.2-0.5 mM SO_4^{2-} for Hg methylation by SRB in sediments, above which methylation is inhibited, and below which sulfate becomes limiting for methylation and sulfate-reduction processes. For comparison, seawater has ca. 28 mM or 2.7 g l^{-1} SO_4^{2-} (Ingvorsen et al.[155]), which may explain the typically low MeHg levels encountered in estuarine and marine environments (cf. section 3.2.7). Methylation is only partly inhibited by sulfur chemistry, however. For example, King et al.[177] have observed active MeHg formation in the presence of 30 mM sulfate and millimolar concentrations of dissolved sulfide. The addition of amorphous Fe(III) oxyhydroxide to sediments may inhibit both sulfate reduction and methanogenesis (Lovley and Phillips[204]), probably due to iron-reducing bacteria suppressing hydrogen and acetate concentrations. Whether this might lead to lower Hg methylation rates in Fe(III) rich sediments still needs to be determined, however.

Many researchers have noted that net MeHg production in methylation experiments is highest in the first few days or weeks of equilibration (depending on study), after which accumulation apparently stops, and in some cases MeHg concentrations decline, and some studies have noted a cyclical production pattern for MeHg (Jacobs and Keeney[162], Spangler et al.[295], Hamdy and Noyes[137], Olson[253], Furutani and Rudd[112], Ikingura and Akagi[153]). It has been suggested that cyclical variations in the supply of bacterial substrates may be the cause (Starý et al.[297]), but changes in the bacterial population may be a more likely explanation. Bacterial life stages can also affect the speciation and fate of Hg, but the available data appear contradictory. Ramamoorthy et al.[266] found growing bacterial cells promote Hg^0 formation, whereas living but non-growing cells cause demethylation, and dead cells lead to the formation of MeHg. This would appear to agree with Parkman et al.[258] who suggested Hg methylation is an accidental process that does not require the presence of living bacterial cells. In contrast, Ebinghaus et al.[96] observed active methylation during the phase of exponential growth of sediment bacteria, whereas demethylation became dominant when the bacterial population began to die off, and Pongratz and Heumann[260] reported methylated Hg species were preferably formed in the stationary period of bacterial growth.

Compeau and Bartha[65] reported MeHg concentrations approached a steady state after 8 to 12 days of incubation, but renewed addition of Hg^{2+} resulted in MeHg synthesis at the previous rate. The percentage of total Hg converted to MeHg declined significantly with increasing spiking levels, however, a phenomenon which has also been noted by other authors (Berdichevsky et al.[28], Jeffries[164], Lexmond et al.[197], Robinson and Tuovinen[277]). Chen et al.[59] observed an increase in methylation rates when the $HgCl_2$ spike was less than or equal to 15.3 μg g^{-1} d.w., whereas microbial methylation activity appeared to be inhibited at concentrations exceeding this value. Sediments containing high levels of Hg have also shown higher rates of demethylation compared to less contaminated sediments (Gilmour and Henry[122], Oremland et al.[255]). The results suggest that high concentrations of inorganic Hg may depress MeHg

production or may favor demethylation. In water samples on the other hand an increase in specific methylation rates that was proportionally greater than the increase in added Hg^{2+} was observed, possibly due to increased availability of Hg following the saturation of binding sites (Xun et al.[343]). The above results may explain why the ratio of methyl : total Hg in sediments or waters is frequently found to increase with increasing distance from the pollution source (e.g. Suchanek et al.[305], Hines et al.[141]). The apparent cyclical nature of the methylation process together with a possible inverse relationship of net MeHg production with total Hg concentrations may be one reason why MeHg levels in sediments rarely exceed a threshold value of 1%.

The availability of nutrients is an important factor controlling microbial Hg methylation in aquatic systems (Jernelöv[169], Langley[189], Wright and Hamilton[339]). Methylation rates and sulfate reduction rates are therefore generally highest in the upper layers of sediments, where microbial activity and nutrient supply are greatest, and on suspended organic material (Jernelöv[169], Callister and Winfrey[55], Korthals and Winfrey[180], Jorgensen and Bak[172], Bubb et al.[53], Choi and Bartha[61], Gilmour et al.[125], Bloom et al.[41], Hines et al.[141]). Microbial DiMeHg formation in the ocean is also driven by the supply of labile organic matter (Mason and Sullivan[223]). Many studies have found a positive correlation between sediment organic matter content and MeHg production (Callister and Winfrey[55], Jackson[158], Choi and Bartha[61], Hadjispyrou et al.[133], Pak and Bartha[256]). Macalady et al.[207] observed a correlation between microbial community structure and organic carbon content and suggested that organic-rich sediments support microbial communities with higher Hg methylation activity per unit of microbial biomass. Because of the generally stimulating effect of organic matter on microbial activity, bacterial demethylation rates may also be increased (Ramlal et al.[268], Pak and Bartha[256]). Ramlal et al.[268] found net MeHg production in organic-rich soils from a recently flooded reservoir was always higher compared to clay sites, but the organic sites also had rapid demethylation rates.

The creation of new hydroelectric reservoirs and enlargement of lakes significantly increases MeHg production, leading to elevated Hg concentrations in fish that can remain high for several decades (Morrison and Therien[244], Jackson[161], Bodaly et al.[45], Schetagne et al.[286]). Kelly et al.[175] found that MeHg production increased by almost 40 times following the experimental flooding of a boreal forest wetland. Recent data by Montgomery et al.[241] indicate that dissolved MeHg concentrations in flooded environments are on average about 4 times greater than in natural lakes. It is thought that the flooding of vegetation and soils releases associated inorganic Hg as well as large amounts of organic matter and nutrients, thereby stimulating microbial methylation activity (Porvari and Verta[261], Bodaly et al.[45]). The effect is further enhanced by the prevailing anaerobic conditions, but may be mitigated by the provision of additional Hg-binding sites when an excess of organic substrates is supplied (Jackson[161]).

Surprisingly, reservoir creation does not appear to increase microbial demethylation rates (Bodaly et al.[45]).

The availability of Hg to methylating bacteria is frequently believed to be determined by the concentration of free Hg^{2+} ions. However, microbial uptake of Hg involves diffusive transport of Hg across bacterial membranes, which are known to have higher permeability for uncharged molecules than for ionic species (e.g. Gutknecht[131,132]). Whereas uncharged $HgCl_2$ may diffuse rapidly through lipid bilayers, charged chloride complexes HgOHCl and $Hg(OH)_2$ do not cross membranes at a significant rate under physiological conditions, for example (Gutknecht[131]). Recent studies (Mason et al.[219], Barkay et al.[20], Benoit et al.[26], Wright and Mason[340]) have therefore suggested that Hg bioavailability is controlled by the concentration of neutral dissolved Hg complexes. $HgCl_2$ may be the key chemical species determining cellular uptake of inorganic Hg in oxic waters (Morel et al.[243]), while uncharged HgS^0, bisulfide $Hg(SH)_2^0$ or polysulfide HgS_n^0 complexes may be important for bacterial uptake in anoxic waters (Hudson et al.[148], Benoit et al.[26], Jay et al.[163]). Wright and Mason[340] speculated that there may be other mechanisms of uptake besides passive diffusion, since bioavailability is reduced, but not inhibited by organic complexation (Barkay et al.[20]).

Other factors that may affect microbial Hg methylation and/or demethylation will be discussed in the following. In many cases these parameters appear to affect methylation by controlling the bioavailability of inorganic Hg. Net MeHg production rates in natural aquatic systems appear to depend to a large extent on the environmental conditions that determine whether bacterial methylation or demethylation will dominate.

3.2.2 Temperature

It has frequently been observed that Hg methylation rates in aquatic systems peak during the summer months (Jackson et al.[157], Callister and Winfrey[55], Korthals and Winfrey[180], Bubb et al.[53], Hintelmann and Wilken[142], Watras et al.[326]). Most studies have shown maximum methylation activity occurs during mid or late summer, although Bloom et al.[41] found a sharp peak in sediment MeHg production in early spring, followed by a slow decrease throughout the remainder of the year. Seasonal variations in MeHg production and decomposition have generally been attributed to temperature effects, but are probably also linked with seasonal changes in productivity/nutrient supply and redox conditions (cf. section 3.2.5).

Temperature most likely affects methylation as a result of its effect on the overall microbial activity (Bisogni and Lawrence[34]). Wright and Hamilton[339] noted that MeHg release from sediments at 4°C was only 50-70% of that observed at 20°C, suggesting that net MeHg production may be significantly decreased in winter due to lower rates of growth and metabolic activity, and Callister and Winfrey[55] reported microbial Hg methylation in surficial river sediments had a temperature optimum of 35°C. Korthals and Winfrey[180] found that while both

temperature and anoxic conditions were important factors influencing net methylation, temperature alone accounted for about 30% of the variation. The data suggested that increased net MeHg production was partly due to decreased demethylation rather than an increase in the actual methylation rate, however. Several other workers have also found that demethylation is favored by low temperatures, whereas higher temperatures favor methylation, leading to a large increase in net MeHg production in the summer (Bodaly et al.[44], Ramlal et al.[269]). Abiotic methylation by humic substances has also been shown to gain in importance with increasing temperature (cf. section 3.1.2), but is probably of little/minor significance compared to biotic methylation. In contrast to the findings of Ramlal et al.[269] and Bodaly et al.[44], Matilainen et al.[229] found that the highest rates of *both* methylation and demethylation in surficial lake sediments coincided with maximum temperatures. Similarly, Matilainen and Verta[228] found microbial demethylation rates in aerobic surface waters of small forest lakes (up to 13.2% d^{-1}) were decreased by low temperatures.

Temperature is clearly an important factor controlling both methylation and demethylation. It appears that moderately high temperatures have a stimulating effect on Hg methylation, which is most likely due to increased microbial activity. Together with seasonal changes in oxygen levels and organic content/primary production, this seems to account for the increased MeHg production rates usually observed in the summer. The results for Hg demethylation are somewhat contradictory, but most workers found demethylation is favored by lower temperatures. It may be that the rate of methylation increases faster than the rate of demethylation with increasing temperature.

3.2.3 pH

The effect of pH on the methylation of Hg has received considerable attention over the past two decades, in particular with regard to lakewater acidification caused by atmospheric deposition. Many workers have noted elevated Hg levels in fish from acidified lakes (e.g. Scheider et al.[285], Akielaszek and Haines[2], Wren and McCrimmon[338], Lindqvist et al.[199], Håkanson et al.[135], Spry and Wiener[296]), and there has been concern that low pH values may lead to an increase in the production and/or bioaccumulation of MeHg. Modeling results suggest that observed inverse correlations between lakewater pH and fish Hg content are due to a combination of generally higher MeHg concentrations at low pH and lower bioconcentration factors at high pH (Hudson et al.[148]). There are however many ways in which pH changes may influence MeHg concentrations in aquatic systems, and the effect of pH is not necessarily a direct effect on methylation rates. The solubility and mobility of Hg and MeHg is pH dependent, for example, and acid rain/snow may increase Hg inputs from watersheds (Lee and Hultberg[193]). Furthermore, the added sulfate may stimulate MeHg production (Gilmour et al.[123], Branfireun et

al.[51]). Acid mine drainage which is typically high in sulfate has also been linked to elevated MeHg concentrations in lake water (Suchanek et al.[306]).

Low pH conditions generally facilitate the release of heavy metals from sediments and particulate matter, but data on the partitioning and mobility of Hg are somewhat contradictory. Some workers have noted that the mobility of Hg is higher in the acidic pH range (Beijer and Jernelöv[23], Duarte et al.[94]), but Jackson et al.[156] found that Hg was not leached from sediments by HCl, and Schindler et al.[287] reported that lakewater acidification caused a higher proportion of Hg to bind to particulates, thereby decreasing the solubility of Hg in the water column. The amount of dissolved Hg in sediment porewater was also found to decrease with decreasing pH (Ramlal et al.[267]). The available data on the pH-dependent partitioning of MeHg between the sediment and water phases and the transport of MeHg in watersheds (cf. sections 2.3 and 2.4) strongly suggest that the solubility of MeHg is increased at low pH values. Lakewater acidification thus probably does not result in the release of Hg^{2+} from organic sediments, but affects the partitioning of MeHg.

Several studies have indicated that the volatilization of Hg^0 may be positively correlated with lakewater pH (Winfrey and Rudd[335] after Rada *et al.* 1987, Hudson et al.[148], Watras et al.[326]), which may decrease Hg(II) substrate concentrations for methylation in high pH waters (Fitzgerald et al.[103]). Modeling calculations by Hudson et al.[148] predict an increase in the ratio of Hg^0/Hg(II) and Hg^0 evasion rates with increasing pH, whereas low pH values favor methylation over Hg(II) reduction. In agreement with this, Watras et al.[326] observed an increase in Hg^0 and a corresponding decrease in MeHg with increasing pH values. High pH values also favor the formation of volatile DiMeHg (cf. section 3.1.3). Neutral and slightly alkaline conditions may thus reduce MeHg concentrations, whereas low pH waters may contain a relatively higher share of MeHg. This would appear to agree with Swedish field studies that have shown that the treatment of lakes with lime to raise lakewater pH can help reduce the Hg content of fish (e.g. Andersson and Håkanson[10]).

The effect of pH on Hg methylation has been studied both in waters and sediments. MeHg concentrations in lake water have generally been found to increase with decreasing pH (e.g. Xun et al.[343], Bloom et al.[40], Miskimmin et al.[240]). Xun et al.[343] reported that net MeHg production in lake water was about 7 times faster at low pH (ca. 4.5) than at high pH (ca. 8.5), although in samples that were artificially acidified, the observed effect may have been partly due to sulfate stimulation. A pH decrease at the aerobic sediment-water interface resulted in a two- to threefold increase in MeHg production. Miskimmin et al.[240] also reported that a reduction in lakewater pH from 7.0 to 5.0 led to significant increases in net methylation rates. In anaerobic sediments, on the other hand, net MeHg production was generally found to be decreased at low pH values (Steffan and Winfrey[298], Furutani et al.[113], Ramlal et al.[267], Steffan et al.[299]). The acidification of surficial lake sediments always resulted in a significant decrease in ^{203}Hg

methylation rates. Ramlal et al.[267] reported that the decrease in ^{203}Hg methylation with decreasing pH appeared to be linked to a reduction of available inorganic Hg in the sediment porewater which may have been due to increased sorption to particles at low pH. Aerobic methylation in surface sediments was also found to decrease with decreasing water pH (Matilainen et al.[229]).

Demethylation rates are also pH sensitive. Matilainen et al.[229] observed a decrease in anaerobic demethylation in surface sediments with decreasing water pH and speculated that high MeHg concentrations found in the anoxic bottom waters of stratified, low pH lakes may be partly the result of a decrease in demethylation rather than an increase in methylation. Other workers have also found a decrease in demethylation activity at low pH values, but in general, demethylation rates in both sediments and lake water were found to be much less affected by pH than methylation rates (Ramlal et al.[267], Xun et al.[343], Steffan et al.[299]), indicating that the changes observed in net MeHg production are largely due to an effect of pH on methylation rather than demethylation. However, the results of Ramlal et al.[267] and Steffan et al.[299] show that in sediments demethylation may gain in importance at low pH values. Steffan et al.[299] found little change in demethylation over the pH range 8.0 to 4.5, but methylation decreased sharply with decreasing pH, leading to a substantial increase in the relative importance of demethylation vs methylation under acidic conditions. This may also explain why Ramlal et al.[267] did not observe methylation below pH 5.0.

One of the ways in which pH might affect methylation may be by decreasing microbial activity under acidic conditions, causing a corresponding decrease in bacterial methylation rates. The published literature indicates that microbial activity in lakes is not reduced upon acidification, however. Furutani et al.[113] and Kelly and Rudd[173] reported that acidification did not affect general microbial activity ($CO_2 + CH_4$ production) in sediments, and Miskimmin et al.[240] found that microbial respiration rates had only a very small effect on net MeHg production in lake water and were insensitive to pH changes between pH 5 and 7. However, there are indications that the activity of sulfate-reducing bacteria may be significantly decreased in the acidic pH range (Connell and Patrick[68]), and Furutani et al.[113] observed a decrease in sulfate reduction at low pH which was independent of general microbial activity. It may also be that pH affects the population distribution of methylating vs demethylating bacteria in sediments such that demethylation processes dominate at low pH values. This would agree with the results obtained by Ramlal et al.[267] and Steffan et al.[299] and might merit further investigation. It is also possible that pH affects cellular uptake of Hg, but Gutknecht[132] found that the diffusion of Hg^{2+} through lipid bilayer membranes was only dependent on Cl^- concentrations and not on pH.

In summary, it appears that acidic conditions generally favor Hg methylation in lake water and at the sediment/water interface, whereas methylation in anoxic sediments is decreased, possibly due to increased demethylation activity at low pH values. Lakewater acidification may

thus lead to increased methylation in the water phase, but is unlikely to substantially affect methylation in deeper sediments. The observed differences in the effect of pH on Hg methylation in waters and sediments may be related to differences in redox conditions: whereas sediments were generally studied under anoxic conditions, the water samples appear to have been oxygenated to some degree.

It is not clear whether the stimulation of methylation in lake water is a direct effect of low pH on the methylation process, or whether it is related to other factors that are influenced by pH, such as the loss of volatile Hg species from water surfaces, or changes in Hg solubility and partitioning. Winfrey and Rudd[335] hypothesized that the likely decrease in DOC binding sites at low pH values resulting from the protonation of functional groups may stimulate methylation by promoting Hg binding directly onto microbial cells. Increased MeHg concentrations in the water phase at low pH are also likely to be partly attributable to increased desorption of MeHg from surficial sediments (Miller and Akagi[238], Hintelmann et al.[143]) and thus do not necessarily reflect increased methylation.

It should be briefly mentioned that the abiotic methylation of Hg by organic substances is also pH dependent, but the data is somewhat contradictory (Nagase et al.[246,247], Varshal et al.[315], Falter and Wilken[100]). Nagase et al.[246] reported that MeHg formation in fulvic acid solution was strongly enhanced at pH 4 and declined at higher pH values, whereas Varshal et al.[315] found MeHg production increased with increasing pH, for example. While the relative importance of abiotic mechanisms in the methylation of Hg under natural environmental conditions is still unclear, it is generally thought to be low.

3.2.4 Organic material

The role of organic matter in the methylation of Hg is not well understood. Conversion rates of inorganic Hg to MeHg are generally much higher when sediments contain organic substances, and can be very high in or near sewage treatment plants (Jernelöv[168], Jackson[158]). Observed increases in MeHg concentrations in water, sediments or fish tissue with increasing levels of organic carbon (Olson and Cooper[252], Furutani and Rudd[112], Wright and Hamilton[339], Lee and Hultberg[193], Fjeld and Rognerud[107]) have generally been attributed to a stimulating effect of organic nutrients on microbial methylation activity (cf. section 3.2.1), but in some cases transport of (methyl)mercury-DOC complexes to surface waters with runoff (section 2.3) is likely to be an additional factor. Direct abiotic methylation by humic and fulvic acids is generally considered to be of minor importance (cf. section 3.1.2), although it is possible that its influence is increased in organic rich lakes. However, the data of Porvari and Verta[261] indicate that although humic substances are chiefly responsible for the transport of MeHg, they are not themselves active methylating agents. To date it is not clear to what extent abiotic methylation contributes to MeHg production in organic-rich sediments and lake waters.

Many workers have reported decreased methylation at high concentrations of organic matter, and several studies have suggested that dissolved organic carbon (DOC) may have a mitigating effect on the production and/or bioaccumulation of MeHg in natural waters (Grieb et al.[128], Jackson[161], Miskimmin et al.[240], Driscoll et al.[93], Watras et al.[326], Barkay et al.[20]). Miskimmin[239] reported that natural levels of DOC had no effect on the production of MeHg in sediments, although they enhanced the water solubility of MeHg. However, Miskimmin et al.[240] demonstrated that MeHg production in lake water is reduced at high DOC concentrations, presumably as a result of complexation of inorganic Hg with organic matter. A reduction in pH from 7.0 to 5.0 significantly increased methylation rates at both low and high DOC concentrations (500-2600 μM), possibly due to competition of H^+ with Hg^{2+} for negatively charged binding sites and increased bioavailability of Hg. Using a bioindicator that responds exclusively to bioavailable Hg^{2+}, Barkay et al.[20] demonstrated that DOC affects the rate of MeHg synthesis by reducing the availability of the Hg^{2+} substrate to methylating bacteria. The exact nature of the Hg-DOC interaction remains unknown, however. The reduction in bioavailable Hg was more pronounced under neutral (pH 7) than under acidic (pH 5) conditions, which is in good agreement with the study by Miskimmin et al.[240].

The availability of Hg for methylation reactions may also be decreased by complexation with sulfur ligands (cf. section 3.2.6). The degradation of organic matter in aquatic environments leads to the production of low-molecular weight S compounds (Cutter and Krahforst[88]) that can potentially form complexes with Hg^{2+}. On the other hand, increased oxygen consumption during the degradation of organic matter causes progressively more anoxic conditions at the sediment/water interface, which may lead to the mobilization and potential methylation of inorganic Hg (Gagnon et al.[115], Cossa and Gobeil[78]). DOC also significantly enhances the solubility of HgS (Ravichandran et al.[270]) and may inhibit the precipitation and aggregation of HgS even at low concentrations (Ravichandran et al.[271]).

Humic substances are capable of reducing Hg^{2+} to Hg^0 in aqueous systems (e.g. Miller[237]), which may lead not only to reduced availability of Hg^{2+} for methylation, but potentially also to a reduction in the overall Hg content. Allard and Arsenie[4] suggested Hg^0 production is highest in anaerobic systems in the absence of chloride at a pH of about 4.5, but is considerably reduced by the presence of competing ions. In contrast to the findings of Miskimmin et al.[240], Watras et al.[326] observed an increase in the MeHg fraction in Wisconsin lakewaters with increasing levels of DOC, in particular at DOC concentrations >5 mg l^{-1}, whereas the Hg^0 fraction decreased. This is in agreement with modeling calculations by Hudson et al.[148], which predict that as DOC increases, the fraction of Hg(II) that is reduced declines, while the fraction that is methylated increases. The relative importance of Hg^0 evasion is increased in humic rich lakes, however, despite the observed decrease in the Hg^0 fraction. Watras et al.[328] hypothesized that high DOC

conditions in lakes favor either methylation (at low pH) or evasion(at high pH), whereas low pH low DOC conditions favor sedimentation processes.

The role of humic matter in the methylation of Hg remains unclear. It seems that, on the one hand, organic carbon can enhance methylation by stimulating the activity of heterotrophic microorganisms, or through direct abiotic methylation of Hg by humic or fulvic substances. On the other hand, Hg methylation may be inhibited at high DOC concentrations due to increased complexation of Hg with organic ligands, reducing Hg bioavailability to bacteria, particularly in the neutral pH range. The observed differences may partly reflect different methylation mechanisms. Anaerobic methylation was found to be enhanced by high concentrations of organic matter, presumably due to stimulated microbial growth, whereas aerobic methylation has frequently been observed to be suppressed by high organic matter or particulate concentrations, and does not appear to be microbially mediated (cf. section 3.2.5).

3.2.5 Redox conditions

Mercury methylation occurs in both aerobic and anaerobic environments. Early work based on pure culture studies showed that methylation was faster under aerobic conditions (Bisogni and Lawrence[34], Hamdy and Noyes[137], Ramamoorthy et al.[266]), but in the natural environment, methylation rates are highest in anoxic sediments and waters, and it is now generally accepted that Hg methylation takes place mainly in anaerobic conditions (Olson and Cooper[252], Compeau and Bartha[65], Callister and Winfrey[55], Craig and Moreton[87], Jackson[159], Rudd et al.[279], Matilainen et al.[229]). Both methylation rates and the stability of MeHg in sediments appear to be enhanced under anaerobic conditions (e.g. Olson and Cooper[252], Compeau and Bartha[65]), whereas methylation rates are low under aerobic conditions, probably because of the reduced activity of anaerobic sulfate-reducing bacteria. Compeau and Bartha[65] found that Hg methylation in estuarine sediments was strongly favored at low (-220 mV) E_h, for example, and Callister and Winfrey[55] reported that the oxygenation of sediments inhibited microbial methylation activity. Regnell and Tunlid[272] used radiolabelled $HgCl_2$ in model aquatic systems to demonstrate that Hg methylation in freshwater sediments and water is significantly higher under anaerobic than under aerobic conditions. MeHg concentrations in anaerobically incubated water and sediment samples from a Hg contaminated lake were also at least an order of magnitude higher than in aerobic incubation (Regnell et al.[273]); both the production and water solubility of MeHg appeared to be increased under anaerobic conditions.

The degradation of MeHg on the other hand appears to be generally favored by aerobic conditions. Although some workers have found demethylation rates in freshwater sediments were similar under aerobic and anaerobic conditions (Billen et al.[32], Matilainen et al.[229]), most studies have shown that MeHg degradation is faster under aerobic / high E_h conditions (Olson and Cooper[252], Compeau and Bartha[65], Ramlal et al.[268], Oremland et al.[254], Ebinghaus et al.[96]).

Oremland et al.[254] found that demethylation in estuarine sediments was more rapid and extensive under aerobic conditions, but anaerobic sulfate reducers were also important demethylators, suggesting that there are multiple degradation pathways (cf. section 3.1.4).

It may be that different mechanisms are responsible for Hg methylation under aerobic and anaerobic conditions. Anaerobic methylation was found to be enhanced by high concentrations of organic matter, presumably due to stimulated microbial growth (Olson and Cooper[252], Compeau and Bartha[65]). Aerobic methylation on the other hand is frequently observed to be suppressed by high organic matter or particulate concentrations, and does not appear to be microbially mediated (Matilainen et al.[229], Matilainen[227], Matilainen and Verta[228]). Matilainen[227] found, for example, that aerobic methylation was abiotic and was suppressed by humic compounds and particulate matter, whereas methylation in the anaerobic hypolimnion was microbial. Matilainen et al.[229] reported that aerobic methylation in organic-rich surficial lake sediments was abiotic and was slow compared with anaerobic methylation, but increased in importance with increasing sediment mineral content. Aerobic methylation and the methylation/demethylation ratio correlated positively with the Fe and Mn content of the sediment. The authors suggested that sediments with high metal content may have more bioavailable Hg, owing to the interaction of these metals with sulfur, which would appear to agree with more recent results by Gagnon et al.[114] who found that high dissolved Fe concentrations in sediment porewaters seem to limit the amount of dissolved H_2S that may potentially interfere with the methylation process. A possible catalytic effect of Fe on Hg methylation can also not be ruled out. Lee et al.[192] reported that Hg methylation in lake waters in the presence of fulvic acid was increased by the addition of metal ions, and in particular Fe.

In most aquatic sediments, only the upper few millimetres are aerobic, while the rest of the sediment is in an anaerobic state. MeHg concentrations are usually highest in the moderately anaerobic surface sediments and rapidly decline with increasing sediment depth (Korthals and Winfrey[180], Bubb et al.[53], Hintelmann and Wilken[142], Bloom et al.[41], Hines et al.[141]). In sediment porewaters, MeHg concentrations were very low in the oxic zone, but were high in anoxic layers (Gagnon et al.[114]). Bubb et al.[53] suggested that subsurface maxima of methylation activity just below the sediment/water interface are caused by increased MeHg production under moderately anaerobic conditions, whereas bacterial degradation of MeHg dominates in the oxygenated surface zone, and in deeper sediment layers where conditions are strongly reducing, sulfide limits the availability of Hg for methylation (cf. section 3.2.6). MeHg concentrations in sediments are also influenced by the redox cycling of Fe and Mn oxides which partly control dissolved Hg concentrations in sediment porewaters (Gobeil and Cossa[126], Gagnon et al.[115]), thereby influencing Hg bioavailability. In the oxidized surface layers of marine sediments, Hg was found to be primarily associated with fresh particulate organic matter and Fe and/or Mn oxyhydroxides, which was limiting dissolved Hg concentrations (Gagnon et al.[115]). High

dissolved Hg concentrations were observed at the redox boundary, however, due to the accumulation and subsequent dissolution of oxyhydroxides (Gagnon et al.[115]). Similarly, Gobeil and Cossa[126] found that dissolved Hg and Fe concentrations increased below 2 cm from the sediment/water interface.

In the water column, MeHg (and DiMeHg) production is also related to zones of low oxygen concentration (e.g. Bloom et al.[40], Hurley et al.[149], Verta and Matilainen[316], Mason and Fitzgerald[211,212], Mason et al.[214]), whereas levels are typically low in the oxic zone, both in freshwater lakes (Bloom et al.[40], Cossa et al.[74], Watras and Bloom[323]) and ocean waters (e.g. Mason and Fitzgerald[210,211]). In stratified lakes and estuaries, MeHg concentrations are usually highest in the oxic/anoxic boundary layer and in anoxic water layers (Bloom et al.[40], Mason et al.[213], Cossa et al.[74], Parkman et al.[258], Verta et al.[317], Watras and Bloom[323], Watras et al.[324], Matilainen[227]). High MeHg concentrations at the oxic/anoxic boundary do not necessarily reflect in situ MeHg production, but could result from the accumulation of settling particulate matter. For instance, Matilainen[227] found MeHg concentrations were elevated in the particle rich oxic/anoxic boundary layer despite low methylation rates (<0.1% d^{-1}), apparently as a result of the settling of particle bound MeHg from the epilimnion. The low net methylation rates were attributed to the binding of Hg to particles and demethylation by heterotrophic bacteria. Cossa et al.[74] also observed a peak in particulate MeHg in the upper region of the redoxcline. The results suggest that methylation occurs mainly in the low oxygen region, but the concentration and distribution of MeHg are strongly influenced by the redox cycling of Fe and Mn at the oxic/anoxic boundary.

Seasonal variations in MeHg concentrations are also strongly linked to changes in redox state. MeHg levels in hypolimnetic waters of seasonally stratified lakes and reservoirs generally increase during summer stratification, and decrease again following fall turnover (Bloom and Effler[38], Bloom et al.[40], Watras and Bloom[323], Watras et al.[324], Driscoll et al.[93], Regnell et al.[274], Canavan et al.[56]). Similar trends are observed in surface sediments (Korthals and Winfrey[180]). The increased decomposition of organic matter and primary production during the summer months renders sediments and hypolimnetic waters progressively more anoxic, which together with the generally higher temperatures is thought to have a stimulating effect on bacterial methylation activity. Hypolimnetic enrichment of MeHg and Hg in (seasonally) anoxic lake waters may also be due to redox-controlled release of Hg from bottom sediments or sedimenting particles (Hurley et al.[149,151], Mason et al.[224]). Meili[233] suggested that the build-up of MeHg in anoxic waters may be due to suppressed demethylation rather than enhanced methylation, however. Passive uptake of neutral $Hg(SH)_2^0$ and HgS^0 complexes by methylating bacteria may be another reason for increased Hg methylation in anoxic waters (Hudson et al.[148], Benoit et al.[26]). Demethylation processes are expected to dominate when hypolimnetic waters are reaerated during lake turnover.

In summary, it is clear that microbially mediated methylation is generally favored by anaerobic conditions while demethylation is favored by aerobic conditions. Abiotic methylation on the other hand appears to be largely aerobic. Sediment redox state also affects the partitioning of Hg species between the sediment and water phases. Other environmental factors can interact significantly with redox effects, in particular organic matter and pH.

3.2.6 Sulfide

Hydrogen sulfide plays an important role in the chemistry of anaerobic sediments where it is produced as a result of bacterial sulfate reduction. Conditions of high sulfide typically develop in anoxic, organic-rich sediments that are high in sulfate, but can also occur in surface waters as a result of industrial or domestic wastewater discharges. Early studies noted that high sulfide concentrations appear to inhibit MeHg formation in soils, sediments and bacterial cultures (Fagerström and Jernelöv[98], Bisogni and Lawrence[34], Yamada and Tonomura[346], Jacobs and Keeney[162], Talmi and Mesmer[311]), and significant reductions of MeHg in fish were achieved in aquarium experiments by adding sulfides as S^{2-}, FeS or FeS_2 (Jernelöv and Åséll[170]). An inverse relationship between (dissolved) sulfide concentration and MeHg production or concentration in sediments or sediment porewaters has also been noted in many more recent studies (e.g. Craig and Moreton[85], Compeau and Bartha[64,67], Winfrey and Rudd[335], Gilmour et al.[125], Benoit et al.[25,26]). Craig and Moreton[85] found MeHg levels in sediments were initially in direct proportion to sulfide concentrations, but declined sharply beyond a sulfide concentration of about 1.8 mg g^{-1}, and Berman and Bartha[29] observed that Hg added to sediments containing 7.06 mg g^{-1} (d.w.) acid labile and 1.98 mg g^{-1} (d.w.) free sulfide became rapidly unavailable for methylation, whereas increasing amounts of MeHg were formed when the sediment was diluted with a low-sulfide control sediment, or when it was partially depleted of sulfide.

The presence of sulfide clearly decreases the availability of Hg^{2+} for methylation. However, while MeHg production is generally greatly reduced at high sulfide concentrations, it is not usually completely inhibited. Furutani and Rudd[112] found that $^{203}Hg^{2+}$ was actively methylated in anaerobic sediments even in the presence of about 30 μg g^{-1} of bound sulfide (d.w., as amorphous FeS), for example. Furthermore, MeHg levels in sediments are sometimes found to increase with increasing sulfide concentrations (Hintelmann and Wilken[142]), and in stratified lakes and estuaries, high MeHg concentrations are frequently found in the sulfidic boundary layer (Bloom et al.[40], Mason et al.[213], Parkman et al.[258], Verta et al.[317], Watras et al.[324], Matilainen[227]).

In the presence of sulfide, Hg forms insoluble HgS (cf. section 2.1). Several early reports indicated that mercury in the HgS form is not readily available for methylation under anaerobic conditions (Fagerström and Jernelöv[98], Gillespie[121], Yamada and Tonomura[344-346]). In aerobic conditions, the sulfide may be oxidized to sulfate, leading to increased solubility and greater

availability of Hg^{2+} (Fagerström and Jernelöv[98], Jensen and Jernelöv[166]), but aerobic methylation rates are several orders of magnitude lower compared to anaerobic conditions (Fagerström and Jernelöv[98], Gillespie and Scott[120], Jacobs and Keeney[162]). Nevertheless, exposure of contaminated sediments to aerobic conditions may lead to the remobilization and subsequent methylation of Hg (Berman and Bartha[29]).

It is commonly speculated that the inhibitory effect of sulfide on Hg methylation is the result of decreased solubility and bioavailability of Hg^{2+} due to HgS precipitation (e.g. Craig and Bartlett[84], Gavis and Fergusson[118], Blum and Bartha[43], Compeau and Bartha[64,67], Winfrey and Rudd[335], Gilmour and Henry[122]). However, high dissolved Hg(II) concentrations in the porewater of sulfidic sediments (Gagnon et al.[115], Benoit et al.[25], Bloom et al.[41]) indicate that the solubility of Hg is actually increased in the presence of excess sulfide, most likely due to the formation of soluble sulfide complexes. Furthermore, the lack of a relationship between dissolved Hg(II) concentrations in porewater and MeHg production suggests that Hg^{2+} may not be the main species that is methylated (Benoit et al.[25]). The work of Benoit et al.[25-27] shows that sulfide affects the bioavailability of Hg by controlling Hg speciation. Benoit et al.[26] suggest that the bioavailability of Hg in sediments is determined by the concentration of neutral dissolved Hg complexes such as HgS^0 which may readily diffuse across bacterial cell membranes. Under sulfidic conditions, on the other hand, Hg methylation is inhibited due to the formation of charged disulfide complexes which are likely to be less bioavailable (Benoit et al.[27]). The formation of polysulfides (Paquette and Helz[257], Jay et al.[163]) and complexes with dissolved organic matter (Ravichandran et al.[270,271]) may contribute to the solubility of Hg in sulfidic environments. Barkay et al.[20] have shown that DOC complexation reduces the availability of Hg to bacteria, but the effect of polysulfide formation on Hg methylation is not clear. Jay et al.[163] speculate that while the formation of charged polysulfide species may decrease the concentration of bioavailable HgS^0, bioavailability could potentially be increased due to the formation of small concentrations of other lipid-soluble uncharged species such as HgS_5.

A number of studies have suggested that in the presence of high sulfide concentrations, MeHg may be converted to volatile DiMeHg (Craig and Bartlett[84], Craig and Moreton[86], Baldi et al.[16,18]). Craig and Bartlett[84] proposed that the reaction proceeds via the formation of an instable organomercury sulfide intermediate, $(CH_3Hg)_2S$, which decomposes into DiMeHg and HgS. The volatile hydrophobic DiMeHg produced may diffuse through the water column and be lost to the atmosphere, potentially leading to a significant reduction in the organic Hg content of sediments (Craig[83], Craig and Moreton[85]). Craig and Moreton[86] demonstrated the evolution of DiMeHg from a sediment containing a natural unamended level of MeHg on exposure to sulfide. Baldi et al.[18] have shown that MeHg added to polluted sediments can also be converted to DiMeHg, but the study was performed under high sulfide and high MeHg conditions that would thermodynamically favor DiMeHg production. The formation of DiMeHg is considered

a potentially important loss mechanism of MeHg from anaerobic sediments high in sulfide (Craig[83], Baldi et al.[18]), but it is not clear to what extent it occurs in the natural environment.

3.2.7 Salinity

The methylating activity of marine and estuarine sediments is usually lower than that of freshwater sediments (eg. Olson and Cooper[251], Blum and Bartha[43], Compeau and Bartha[67]), which has generally been attributed to salinity effects. Blum and Bartha[43] and Compeau and Bartha[67] observed a strong inverse relationship between the salinity of anaerobic sediments and their ability for Hg^{2+} methylation. High-salinity sediments methylated Hg at only 40% of the level observed in low-salinity sediments (Compeau and Bartha[67]). The inhibitory effect of salinity on Hg methylation is particularly pronounced under reducing conditions, and high salinity conditions appear to promote demethylation processes (Compeau and Bartha[65]). Low salinity coastal waters have also been found to contain a relatively higher proportion of MeHg (Coquery et al.[71]).

The negative effect of salinity on Hg methylation appears to be mainly linked with the microbial production of sulfide from sea salt sulfate. However, while MeHg production in sediments is often strongly reduced in the presence of sulfate (Baker et al.[15], Compeau and Bartha[67], Winfrey and Rudd[335]), methylation does not necessarily stop at high sulfate concentrations. Compeau and Bartha[67] reported that methylation still occurred at 2.4% salinity, corresponding to 19.5 mM sulfate per litre and 7.1 mg sulfide per gram of dry sediment, whereas the same level of sulfide had been found to almost completely inhibit methylation in a freshwater sediment (Berman and Bartha[29]). While it was previously believed that sulfide originating from sulfate-reduction processes limits the bioavailability of Hg in anaerobic sediments due to HgS formation (Blum and Bartha[43], Compeau and Bartha[64,67], Winfrey and Rudd[335]), recent evidence suggests that methylation is inhibited at high sulfide concentrations due to changes in Hg speciation (cf. section 3.2.6).

Not only sulfate, but other sea salt anions may also affect Hg speciation and/or methylation in estuarine and marine environments. Compeau and Bartha[64] demonstrated that bicarbonate has a negative influence on Hg methylation under both aerobic and anaerobic conditions, possibly due to the formation of $HgCO_3$. The authors speculated that the availability of Hg for methylation may hence be higher in 'soft' than in 'hard' (i.e. bicarbonate rich) freshwater systems. Compeau and Bartha[64,67] found no noticeable effect of chloride on Hg methylation, but it has been suggested that the negative charge of mercuric chloride species may reduce their availability to methylating bacteria. Using a mercury-specific bioindicator, Barkay et al.[20] demonstrated that uncharged $HgCl_2$ is indeed more bioavailable than anionic forms. On the basis of the data available to date, it would appear that the formation of charged sulfide and

chloride complexes offers the best explanation for the apparently reduced methylation activity in estuarine and marine environments.

4. Summary and conclusions

Mercury methylation is mainly a microbially mediated process with methylcobalamin being the most likely environmental methyl donor. Abiotic methylation appears to be of minor importance, although its influence may be increased in organic rich lakes. The precise mechanism of MeHg and DiMeHg formation is still unclear. While it is generally believed that DiMeHg is the final product of Hg methylation, MeHg in the ocean appears to be produced mainly by decomposition of DiMeHg, indicating that there may be more than one methylation mechanism. More research is also needed into the factors controlling bacterially mediated and abiotic demethylation processes.

Mercury methylation and demethylation rates in aquatic systems are clearly influenced by both the speciation and biochemical availability of Hg and by a large number of environmental variables, many of which are interrelated. Biological activity, nutrient availability, pH, temperature, redox potential, and the presence of inorganic and organic complexing agents all have significant effects, with the net rate of MeHg production being determined by their complex interaction. Which factors dominate is likely to differ from ecosystem to ecosystem. Furthermore, the distribution of Hg between the sediment and water phases as well as the gaseous evasion of volatile Hg species is also influenced by environmental factors. The inter-relatedness of these processes has often hampered research into the factors controlling Hg methylation. Nevertheless certain general trends are apparent. MeHg formation is generally favored under anaerobic conditions, whereas aerobic conditions promote demethylation processes. In stratified lakes and estuaries, MeHg formation occurs primarily at the oxic/anoxic interface, whether this occurs in bottom waters or surface sediments. Methylation in the ocean is not confined to low-oxygen zones, however, which is another indicator that there may be more than one mechanism for MeHg/DiMeHg formation. Seasonal variations in MeHg production appear to be mainly related to temperature and redox effects, as well as seasonal changes in productivity and hence nutrient availability. Moderately high temperatures have a stimulating effect on methylation, whereas demethylation processes are favored by lower temperatures. Lakewater acidification may lead to increased methylation in the water column, but in sediments methylation is generally found to be decreased, which may be due to a reduction in the activity of sulfate-reducing bacteria, or increased demethylation. It may also be that different mechanisms are responsible for Hg methylation in waters and in sediments, and there are indications that methylation in the water column may be abiotic and linked to particles. Studies investigating the effect of pH on Hg methylation should consider that increased MeHg

concentrations in the water phase are likely to be partly attributable to increased desorption of MeHg from sediments at low pH.

Sulfur chemistry is a particularly important factor controlling methylation. Sulfate-reducing bacteria are important methylators of Hg in anaerobic sediments, and sulfate stimulates microbial Hg methylation at the typically low sulfate concentrations prevailing in freshwater systems. However, at high levels in reducing conditions methylation is inhibited due to sulfide formation, which may be one reason why MeHg levels in sediments rarely exceed 1% of the total Hg concentration. Recent studies have shown that the inhibitory effect of sulfide on Hg methylation is not due to HgS precipitation, but that sulfide lowers the availability of Hg for bacterial methylation by formation of less bioavailable charged Hg-S complexes.

The role of organic matter in the methylation of Hg is not well understood. Humic matter is an important factor controlling the solubility and mobility of Hg in natural waters. Organic nutrients generally stimulate microbial activity and hence Hg methylation, although they may also have an effect on bacterial demethylation activity. Direct abiotic methylation of Hg by humic and fulvic acids has also been reported. High levels of dissolved organic carbon on the other hand appear to have a mitigating effect on both the production and bioaccumulation of MeHg due to Hg complexation, particularly in the neutral pH range. The formation and dissolution of Hg-OM complexes is pH sensitive, with complexation being reduced at low pH.

Unfortunately, despite a vast body of literature on the subject we are still unable to predict Hg methylation rates and the likely effects of environmental perturbations on methylation and demethylation processes in aquatic systems. Owing to the complexity of processes in the natural environment, it is difficult to directly compare the results of the studies that have been published to date. Future laboratory based studies of methylation/demethylation rates which address not only the direct effects of environmental variables but which place particular emphasis on understanding how these factors interact would be desirable. These studies should aim to quantify Hg transformation rates at environmentally relevant concentrations, thereby providing a more realistic assessment of in situ rates than the traditionally large Hg additions. The effect of pH under oxic compared to anoxic conditions should receive particular attention. Further research is also needed on the binding and partitioning of both inorganic and MeHg which is also influenced by the abovementioned factors and which may to a certain extent confound the primary effects of these variables on methylation/demethylation rates. This work is particularly important if we are to find more effective ways of minimizing the ecological risk of mercury in the aquatic environment.

5. References

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Chapter 2

Mercury contamination in the vicinity of a derelict chlor-alkali plant. I. Sediment and water contamination of Lake Balkyldak and the River Irtysh

ABSTRACT: A mercury-cell chlor-alkali plant operated in Pavlodar, Northern Kazakhstan, for 18 years and caused widespread contamination of the surrounding environment. Untreated wastewater from the plant was discharged to Lake Balkyldak, a shallow impounded lake without an outlet. The nearby River Irtysh was also suspected to be impacted by mercury (Hg) via the transport of contaminated groundwater. We took sediment and water samples from both aquatic systems, and also sampled soils along the shoreline of the lake and in the Irtysh flood plain. Sediments from Lake Balkyldak were found to be very heavily contaminated, with Hg concentrations in the surface layer reaching up to ~1500 mg kg^{-1} near the wastewater outfall pipe. The contaminated lake sediments are prone to wind-driven resuspension and are acting as a strong source of Hg to the water column. Unfiltered lake water samples taken in shallow areas within 10-15 m from the shoreline contained from 0.11 μg Hg L^{-1} in the less contaminated northern part of the lake to 1.39 μg L^{-1} near the pollutant outfall in the south (up to 7.3 μg L^{-1} on windy days). Sediments from the River Irtysh were only slightly impacted, with maximum Hg concentrations of 0.046 mg kg^{-1} in the old river channel and 0.36 mg kg^{-1} in floodplain oxbow lakes. In water samples from the River Irtysh, Hg was generally not detected, although trace concentrations (3 to 9 ng L^{-1}) were found in some samples taken from oxbow lakes. We conclude that the river is not significantly impacted by Hg, but the highly contaminated Lake Balkyldak poses a threat and is in need of remediation. Potential remediation options for the lake are reviewed and are discussed in the context of experiences made at other Hg-contaminated sites.

1. Introduction

Pavlodar is a major industrial center in north-east Kazakhstan with heavy engineering machinery, aluminium and chemical plants, an oil refinery and several power stations. The city has a population of approx. 300,000 and is one of the main ports on the 4248 km long river Irtysh connecting China, Kazakhstan and Siberian Russia (Fig. 1). The Pavlodar area is rich in coal and salt deposits, and water from the Irtysh is used for domestic and industrial purposes as well as for irrigated agriculture.

The northern industrial zone of Pavlodar is home to a large chemical plant (Pavlodar Chemical Plant – PCP, formerly known as Khimprom). Between 1975 and 1993, a chlor-alkali workshop operated at the plant, producing chlorine and caustic soda by the mercury (Hg) cell process where liquid elemental mercury (Hg^0) is utilized as a cathode in the electrolysis of a saturated brine solution. Mercury-cell chlor-alkali plants have been identified as major sources of Hg releases to the environment and are now gradually being phased out in Europe and the

U.S. and replaced by cleaner technologies (UNEP, 2002; OSPAR Commission, 2005). However, emissions from existing Hg-cell plants remain significant in less developed countries where stringent environmental controls are lacking (UNEP, 2002; Bhushan and Mukherjee, 2004), and decommissioned plants typically leave behind widespread contamination.

Fig. 1. Map showing the location of the study area in Kazakhstan.

According to initial mass balance calculations, overall Hg losses at the Pavlodar Chemical Plant (PCP) were estimated to be on the order of 1000 t (Lushin et al., 1990). Even though some Hg was later recycled and recovered, more than 700 t of Hg are still unaccounted for. Large amounts of Hg are known to have seeped through the soil below the plant and have entered the groundwater. In addition, soils at the plant and in its surroundings have been contaminated by atmospheric Hg emissions, and a considerable amount of Hg has entered the nearby Lake Balkyldak. Detailed investigations of soil and groundwater contamination at the plant are reported in a separate publication (Ullrich et al., *in preparation*).

Industrial and domestic wastewater from PCP is discharged to Balkyldak settler, an artificial storage lake formed from a natural depression without an outlet. The main workshop of the chlor-alkali plant contained an integrated wastewater treatment plant where effluents were treated by sulphide precipitation. The treated wastewater was pumped via a 5000 m^3 accumulator tank to Lake Balkyldak. However, as the treatment plant was not working effectively, until 1979 the majority of the Hg in the wastewater is thought to have entered the lake (L. Postolov, *pers. commun.*). Typical wastewater volumes at the time were 20-25 m^3 h^{-1}, and Hg concentrations were generally between 15-40 mg L^{-1}. From 1979 onwards the wastewater was cleaned by an ion exchange unit and was pumped to evaporation ponds which had been specifically constructed for this purpose by the lake. Overall, these sludge lagoons are thought to have received between 2.0-2.5 t of Hg with wastewater, and up to 150 t of Hg with

sludges from brine purification and other solid Hg-containing wastes. Direct Hg inputs to the lake with wastewater up to 1990 are thought to be on the order of 10 to 15 t (Lushin et al., 1990; L. Postolov, *pers. commun*).

The primary objective of this study was to investigate the impact of Hg emissions from the chlor-alkali plant on the surrounding environment, and in particular the lake (sediments, water and biota). A smaller-scale survey was carried out on a side channel of the nearby River Irtysh, which was suspected to be potentially impacted by contaminated groundwater from PCP as well as by atmospheric emissions and contaminated run-off from the floodplain. This paper reports on sediment and water contamination and discusses possible remediation options for the lake. Mercury concentrations in aquatic biota are discussed in part II of this paper together with food chain contamination and potential risks posed to the local population.

2. Materials and methods

2.1 Site description

Climate

The climate of Northern Kazakhstan is sharply continental and is characterized by dry, hot summers, cold winters and strong, sometimes severe winds. The average temperature in Pavlodar is -17.8°C in January, and +21.4°C in July. Average annual precipitation is about 250 mm. In winter there is a stable snow cover for about 140 days. The Pavlodar region has many shallow lakes which feed on precipitation and groundwater. The water level of these lakes decreases in summer due to intense evaporation, giving rise to increased mineralization, and small lakes can completely dry up.

Lake Balkyldak

Lake Balkyldak is located ~2 km north of the chlor-alkali workshop of PCP (Fig. 2a). The lake spans about 3.9 km from north to south and 6.4 km from east to west and has an estimated surface area of approx. 15 square km. The shoreline of the lake is not well defined and is overgrown with reeds. The lake has no natural drainage and loss of water is therefore entirely due to permeation and evaporation. Lake water is alkaline and highly saline. The lake is shallow, with a maximum water depth of 8-10 m (mean 4-5 m, 1-2 m near the shore). The water level depends on the amount of effluent received and typically varies by ~1 m between individual years, and from 0.15 to 0.4 m between seasons. Balkyldak received industrial wastewater from various enterprises (mainly from PCP, but also from an oil-refinery, a tractor plant and power station ash dumps) from about 1970, and Hg-containing wastewater from 1975 when the chlor-alkali shop started production. Apart from Hg, wastewaters contained other metals (e.g. Zn, Cr, Fe), sulphate, chloride and organic pollutants. According to unofficial estimates, Balkyldak currently contains 55 million m^3 of settled waste, out of a total capacity of

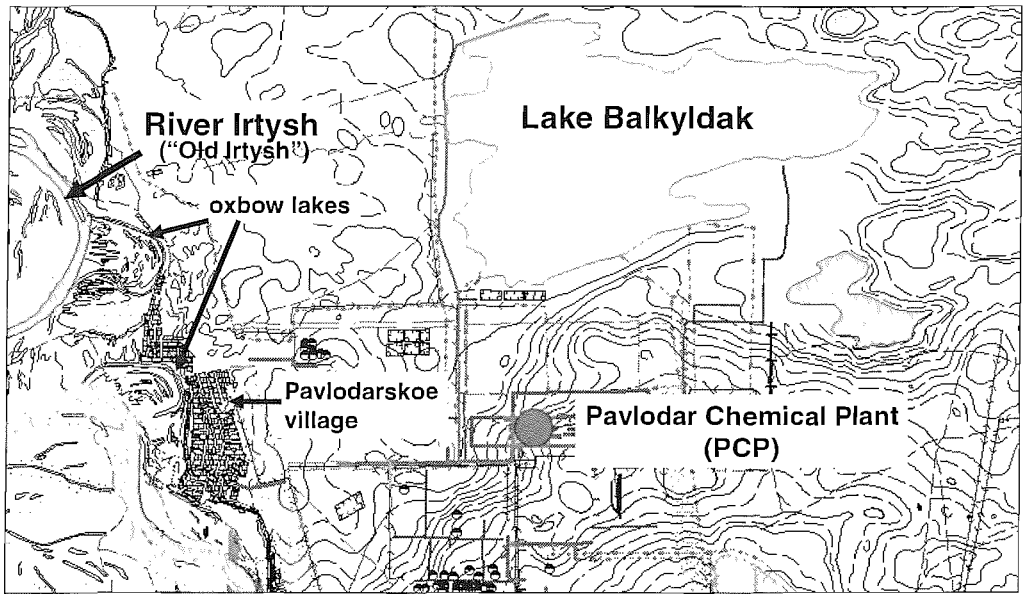


Fig. 2a. Map of the Pavlodar Northern Industrial Zone with key study areas indicated.

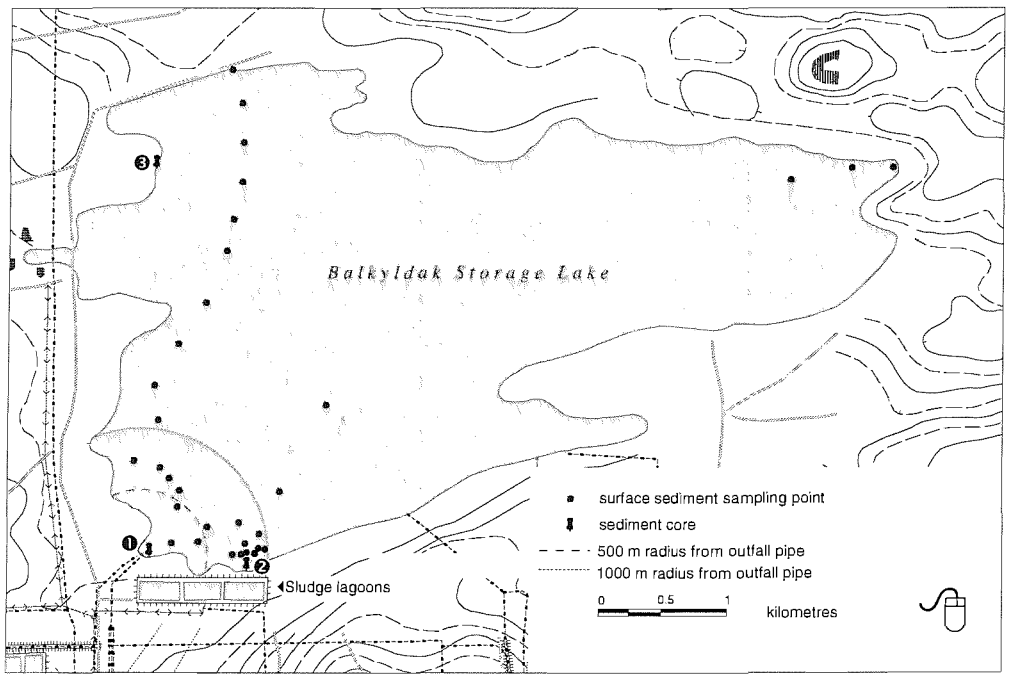


Fig. 2b. Sampling locations for surface sediment samples and sediment cores in Lake Balkyldak. The outfall pipe from the factory is indicated by a dashed and dotted line and effluents enter the lake close to point 1.

74 million m^3 (FASEP-Kazakhstan, 2000). In the second half of 1999 alone it is thought to have received more than 790 000 m^3 of wastewater from various industries, containing ~100 t of chloride, ~60 t of sulphate, and 3.4 kg of Hg (FASEP-Kazakhstan, 2000). At present wastewater discharges from PCP are thought to be minor, since due to the economic climate most of the industrial processes are now out of operation.

River Irtysh

The River Irtysh lies approximately 5-6 km to the west of the chlor-alkali workshop and the lake. The average annual flow of the Irtysh at Pavlodar is 870 $m^3 s^{-1}$. River water temperature varies from 3-4°C in winter to 20-24°C in summer. The river bed is highly braided and divides into a network of several smaller channels. Our sampling programme focused on the "Old Irtysh", a natural side channel of the Irtysh which is of similar size to the main channel, but is not used for commercial navigation. The village of Pavlodarskoye is situated directly by the Old Irtysh and is the nearest residential area to the plant. The Irtysh is the main water supply for Pavlodar city. Water intake points are located 12 km and 5 km upstream of the city. Residents of Pavlodarskoye village mostly have private drinking water wells.

2.2 Sampling

Sediments

The sampling locations for surface sediment samples and sediment cores taken from Lake Balkyldak are shown in Fig. 2b. In August 2001, 55 surface sediment samples were taken from 32 locations in the lake, using stainless steel augers. The sampling depths were 0-2.5 cm, 2.5-5 cm, and 0-5 cm. The majority of samples were taken in the southern part of the lake, within 1 km from the outfall pipe. Additional samples were taken on an approximate north-south transect, and in the eastern part of the lake. It was originally intended to take samples on a regular grid across the whole lake, but this plan had to be abandoned as navigation on the lake was made difficult by strong winds. Surface sediment samples from the lake were stored frozen in acid-cleaned HDPE bottles until analysis.

In order to investigate contamination in deeper lying sediment layers, 20 to 30 cm sediment cores were also taken in three locations: 50 m east of the outfall pipe from the factory (core 1), 750 m east of the outfall (core 2), and 3 km north of the outfall (core 3). To get an estimate of the heterogeneity of sediment Hg concentrations, duplicate cores were taken at distances of 2-3 m from the original cores. Sediment cores were collected from near-shore areas (5-8 m) by pushing an acid-cleaned plastic tube (ø 5 cm) into the sediment until the hard stratum was reached. The tubes were carefully lifted up and closed at both ends with acid-cleaned rubber bungs. The cores were placed in a cool-box (4°C), frozen on the same day and shipped to the

laboratory. Sediment cores were sectioned while still partly frozen, using a stainless steel knife. Samples were analysed at 0-2 cm, 2-5 cm, and thereafter in 5 cm intervals.

Sediments from the River Irtysh were sampled in a separate survey in August 2002. Sixteen locations were sampled in the old braided area of the river, and 9 locations in oxbow lakes. Samples were taken from the 0-10 cm and 10-20 cm sediment layers. Sediment samples from the Irtysh were air-dried at room temperature and analysed in the on-site laboratory.

Water

Surface water samples were taken from Lake Balkyldak in July/August 2001, September 2002 and August 2004. Samples were taken within 8-10 m from the shoreline, at a depth of ca. 0.5 m from the water surface. 500 ml PET bottles were used for sampling and were rinsed three times with lake water before the final sample was collected. The suitability of PET bottles for sampling waters containing Hg in the low ng L^{-1} range has been demonstrated by Fadini and Jardim (2000) who found no significant difference compared to Teflon. All water samples were taken in duplicate. Clean protocols were adopted to avoid contamination during sample collection, handling and storage, and daily field blanks were included in every sampling campaign to check for potential contamination. The total number of water samples taken from the lake was 38. In addition, spot samples were taken from water-filled depressions in the area between the lake and the plant (results are reported in part II of this publication). Surface water samples from the River Irtysh were taken in August 2002 in the same locations as the sediment samples, before the sediments were disturbed. 32 samples were taken from the Old Irtysh, and 18 samples from oxbow lakes of the river near the village. All water samples were acidified with 0.5% v/v conc. HCl, placed in a cool-box and delivered to the laboratory within two hours of collection.

Soils

Littoral soils were sampled in six locations along the northern, eastern and western shoreline of Lake Balkyldak, to investigate the effect of periodic flooding on Hg concentrations in topsoils and subsoils. Samples were taken at 0-10 cm, 10-20 cm, and 20-50 cm depth. Two soil cores up to a depth of 1.5 m were taken in the Irtysh flood plain close to the oxbow lakes. Depth-integrated samples were analyzed from the 0-10 cm, 10-20 cm, 20-50 cm, 50-100 cm, and 100-150 cm layers.

2.3 Analytical methods and quality assurance

Soils and sediments

Soil and sediment samples were dried in the dark at 20-25°C. The dry samples were sieved through a 2 mm nylon screen (mesh size 10) and sub-samples of ~1.0 g were taken for analysis.

Determination of total mercury in soils and sediments was performed using established analytical techniques. Soil and lake sediment samples were digested by hot refluxing in a mixture of HNO_3 and H_2SO_4 (Hatch and Ott, 1968; Adeloju et al., 1994). Total mercury was determined by CV-AAS on a Perkin-Elmer AAnalyst 100 with mercury hydride system MHS-10, after $NaBH_4$ reduction. River sediment samples were digested in hot conc. HNO_3 (Hintelmann et al., 1995). Total mercury in river sediments was determined after $SnCl_2$ reduction and Au pre-concentration on an AGP-01 cold-vapour atomic absorption spectrophotometer. The detection limits for the two methods were 1.5 and 0.05 ng g^{-1}, respectively. Quality assurance included blind determination of certified reference materials, analysis of reagent blanks and duplicate samples. Accuracy was assessed using the certified reference materials CRM023 and CRM024 (R.T. Corporation, Wyoming, USA), with an average percent recovery (%R) of >95% (Table 1). Duplicate samples were analysed for 12% of the lake sediments, 24% of the river sediments, and 12% of the soils. The relative percent difference (RPD) between duplicate samples averaged 5.6% for lake sediments and 5.4% for soils. For river sediments, where Hg concentrations were three to four orders of magnitude lower, the RPD was 18.5%.

Table 1. Quality assurance data for analysis of total mercury in certified reference materials

Reference material	Certified value (mg kg^{-1})	Analytical results* (mg kg^{-1})	Average % recovery* (%R)	No. of samples (n)
CRM023	77.78±6.25	70.27±1.98	90.4±2.6	5
CRM024	0.71±0.05	0.71±0.01	99.4±2.0	5
ORMS-2	30.6±2.3**	30.2±0.2**	98.8±0.65	4

* values represent means ± standard errors

** ng L^{-1}

Water

The chloride content of surface water samples was determined titrimetrically using $AgNO_3$ as a precipitant. The pH and redox potential were determined with portable field equipment (Hanna Instruments). Water samples for total mercury determination were analysed in clean laboratory facilities specifically set up for this purpose on site. Samples were oxidized with BrCl immediately after delivery to the laboratory and were left standing overnight for complete digestion. Excess bromine was destroyed with hydroxylamine hydrochloride and total Hg was determined by CV-AFS after $SnCl_2$ reduction (Jones et al., 1995; PSA, 2001) on a PSA 10.025 Millenium Merlin System (PS Analytical, Kent), using high purity argon (99.99%) as the carrier gas. Quality assurance for water analysis included daily instrument calibration, analysis of blank samples, spike additions and analysis of reference water samples (ORMS-2, National Research

Council, Canada). Calibration standards were prepared fresh every day from two working solutions (50 and 100 μg L^{-1}) prepared by dilution of a mercury standard solution (1000 mg L^{-1}, Merck SpectrosoL). Ultra-pure water (Fistreem Multipure, Fisher Scientific) was used for all dilution purposes. Two field blanks were prepared daily and were treated and analysed in the same way as ordinary water samples, to check for potential contamination. The method detection limit was 2 ng L^{-1}. Measured Hg content of reference water samples is reported in Table 1. All water samples were analysed in duplicate; the quoted results therefore represent the means of duplicate analyses. Analytical precision of replicate lake water samples was 4.1% in 2001 and 2.0% in 2002. The relative percent difference (RPD) between sampling duplicates averaged 17.3% in 2001 (when most of the samples were taken), and 35.4% and 10.1% in 2002 and 2004, respectively. The sometimes large variation between field duplicates is attributable to the variable suspended solids content of the samples which were unfiltered. Mercury in river water samples was generally below the detection limit of 2 ng L^{-1}, but traces of Hg (up to 8 ng L^{-1}) were detected in some of the samples taken from the oxbow lakes in the flood plain. Analytical precision for these samples which were close to the detection limit averaged 9.3%, and the RPD of field duplicates averaged 22.1%.

3. Results and discussion

3.1 Sediments

3.1.1 Lake Balkyldak

A limited study conducted in 1997 in which only eight spot samples were taken along the shoreline of the lake found Hg concentrations in sediments ranged from 0.007-1.91 mg kg^{-1} in the northern and north-eastern part of the lake, and from 0.33 to a maximum of 10.5 mg kg^{-1} in the south (Kamberov et al., 1999). Our results show that Hg concentrations in the sediments of Lake Balkyldak are much higher than previously assumed and establish that the lake is severely contaminated. Mercury concentrations in the 55 surface sediment samples taken from 32 locations in the lake ranged from 0.11-617 mg kg^{-1}. The results are summarized in Table 2. About 50% of the samples were taken in the south of the lake, within 1 km from the outfall pipe (cf. Fig. 2b). In the 23 locations where separate samples were taken from the 0-2.5 cm and 2.5-5 cm sediment layers, Hg concentrations were generally significantly higher in the top layer. Nine of the 23 locations had Hg concentrations in excess of 200 mg kg^{-1} in the top 2.5 cm sediment layer. As expected, the highest concentrations were measured close to the wastewater outfall pipe (approx. distance 250 m). Within 1000 m from the outfall, mean Hg concentrations in the upper 5 cm sediment layer were 167 mg kg^{-1} (med 83.6 mg kg^{-1}, range 0.11-1248 mg kg^{-1},

n=21), while the sediment thickness varied from 0.3 to 1.2 m. However, although Hg concentrations in the upper 5 cm sediment layer declined with increasing distance from the outfall and were generally in the order of 1 to 2 mg kg^{-1} at a distance of more than 2 km, sporadic high concentrations in the order of 40-60 mg kg^{-1} were still found at more remote locations. This is probably associated with sediment transport from the southern part of the lake, but could also be due to additional sources of contamination, such as the disposal of Hg waste. For example, Hg concentrations of ~40 mg kg^{-1} were found in surface sediments in the north-eastern part of the lake where a visual inspection of the shoreline indicated that materials from the derelict plant had been discarded.

Table 2. Total mercury concentrations in surface sediments of Lake Balkyldak, the River Irtysh and oxbow lakes near Pavlodarskoye village

	Hg concentrations in sediments (mg kg^{-1})				
	mean	med	SD	range	n
Lake Balkyldak					
0 - 2.5 cm	151.5	116.6	153.7	0.36 - 617	23
2.5 - 5 cm	48.9	6.34	117.1	0.41 - 439	23
0 - 5 cm	14.1	3.70	26.7	0.11 - 83.6	9
0 - 5 cm*	76.0	31.3	113.3	0.11 - 528	32
River Irtysh bed sediments					
0 - 10 cm	0.012	0.007	0.013	0.001-0.046	16
10 - 20 cm	0.009	0.004	0.011	0.001-0.040	16
oxbow lakes					
0 - 10 cm	0.148	0.170	0.085	0.020-0.280	9
10 - 20 cm	0.157	0.140	0.135	0.010-0.360	9

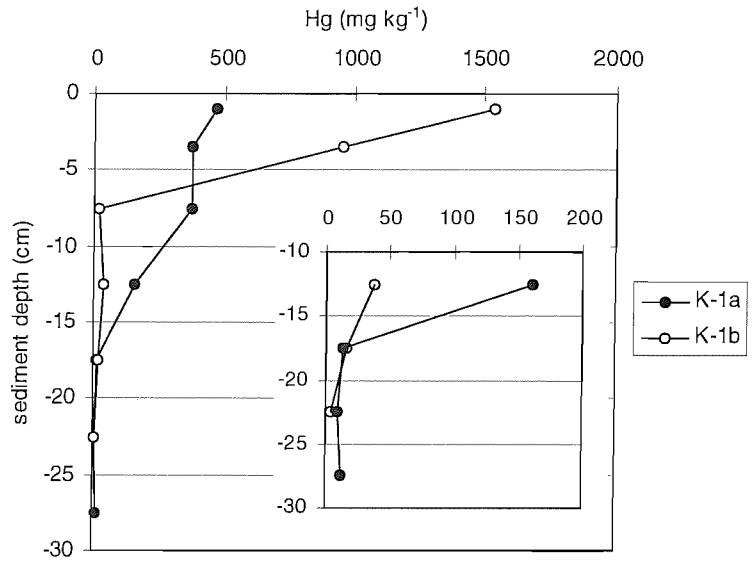
* averaged results for all 32 sampling locations

An important source of Hg to the lake in the south are the three waste lagoons where highly contaminated sludges from the chlor-alkali workshop were deposited. Sludge samples taken by us from the lagoons contained up to 0.01% Hg. The lagoons which were uncovered at the time of our investigation in 2001/2002 are located very close to the southern shoreline of the lake (cf. Fig. 2b) and are leaking Hg to shallow groundwater and the lake, as well as contributing further Hg to the lake via wind erosion.

Information on Hg concentrations in deeper lying sediment layers was obtained from the sediment cores. Fig. 3a shows the variation of Hg concentrations with depth at approximately 50 m from the outfall pipe. Mercury concentrations were highest in the upper 5 to 10 cm of the two cores, ranging between 373 and 1541 mg kg^{-1}. The variability was very high in the upper 10-15 cm sediment layer, however, even though the distance between the two duplicate cores was no more than 2-3 meters. Mercury concentrations in cores 1a and b decreased rapidly with increasing depth, but concentrations were still greater than 10 mg kg^{-1} at a depth of 15-20 cm,

and about 5-10 mg kg^{-1} below 20 cm. The overall thickness of sediments exceeded 1 m near the outfall, but was typically less than 30 cm in other areas of the lake. The data from cores 1a and 1b indicates continued Hg inputs from the factory outfall pipe until very recent times, which was further confirmed by wastewater analysis: In 2002, we determined 1.55 μg Hg L^{-1} in samples taken from a working wastewater drain from the factory, at a distance of ~160 m from the outfall. The outfall itself could not be sampled, as it is under water.

(a)



(b)

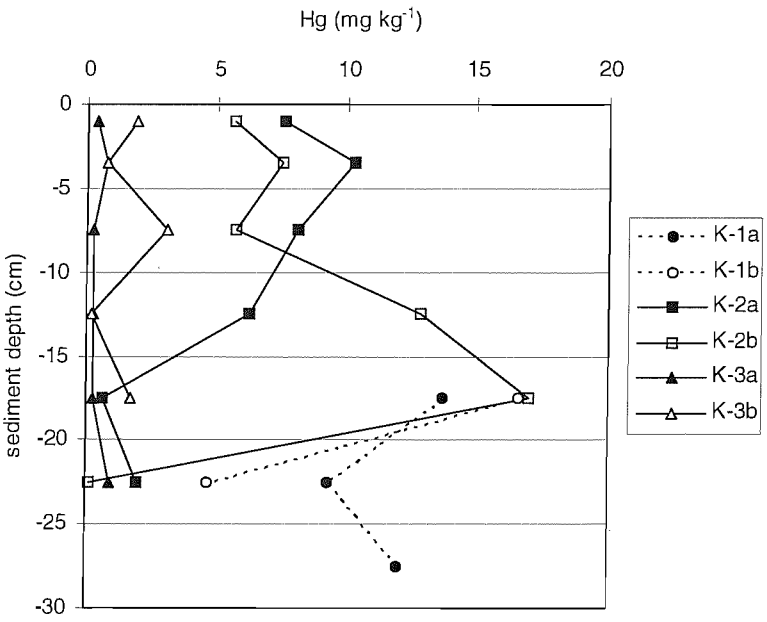


Fig. 3 a and b. Total mercury concentrations in duplicate sediment cores taken at approx. 50 m (K-1a,b), 750 m (K-2a,b) and 3 km (K-3a,b) from the wastewater outfall pipe. Inset in Fig. a shows Hg concentrations below 10 cm depth in cores 1a and 1b at a greater resolution. Concentrations below 15 cm in cores 1a and 1b are also indicated as dotted lines in Fig.b for comparison.

Mercury levels in the top 10 cm of the other two cores were much lower compared to cores 1a and b and ranged from 5.7 to 10.3 mg kg^{-1} in cores 2a and 2b which were taken 750 m east of the outfall, and from 0.17 to 3.1mg kg^{-1} in cores 3a and 3b, taken 3 km north of the outfall (Fig. 3b). Core 2b shows significantly higher Hg levels in the 15-20 cm sediment layer compared to the surface layer, probably reflecting historic deposition and subsequent coverage by cleaner sediments. The enrichment found at 15-20 cm depth in core 2b is not evident in the duplicate core 2a, but the detected Hg concentrations are in good agreement with levels found in cores 1a and 1b at this depth. Below 15 cm depth in core 2a, Hg concentrations appear to approach the lower levels observed in cores 3a and b.

Mercury concentrations in sediments of Lake Balkyldak are of a similar magnitude as those reported by Shaw et al. (1988) and Panda et al. (1990) for the Rushikulya River estuary in India which also received high Hg discharges from a chlor-alkali plant (CLAP). However, other estuarine and marine ecosystems contaminated by CLAP effluents typically have much lower sediment Hg concentrations that rarely exceed 5 or 10 mg kg^{-1}, for example Bellingham Bay in Washington (Bothner et al., 1980), Lavaca Bay in Texas (Bloom et al., 1999 and 2004), and the Tyrrhenian Sea off the western coast of Italy (Baldi and Bargagli, 1984; Baldi and D'Amato, 1986). This seems to be mainly attributable to coastal currents dispersing the pollution and relatively low sedimentation rates. On the other hand, in lake ecosystems with a comparatively low capacity for sediment transport and much lower flushing rates, contaminants are likely to build up to a larger extent. A similar case to Lake Balkyldak that is well documented in the literature is Onondaga Lake in New York State, USA (Table 3). Onondaga Lake is a hypereutrophic, urban drainage lake that received high inputs of Hg from two CLAPs, as well as inputs from a sewage treatment plant (Bloom and Effler, 1990; Wang and Driscoll, 1995). The lake has a similar surface area but greater water depth than Lake Balkyldak. However, although total Hg inputs into Onondaga Lake were considerably higher, sediment contamination is less severe than in Lake Balkyldak, presumably due to rapid flushing. The Wabigoon River system in Ontario (Canada) has also been seriously contaminated by discharges of inorganic Hg from a CLAP (Armstrong and Hamilton, 1973; Parks et al., 1989). About 2 t of Hg were transferred to Clay Lake ~80 km downstream, but this lake is much larger than Balkyldak and is rapidly drained, and sediment Hg concentrations do not exceed 10 mg kg^{-1}. A comparison with the published literature on aquatic systems affected by Hg from CLAP effluents indicates that Lake Balkyldak could be the most severely impacted lake ecosystem known to date (Table 3).

Table 3. Comparison of Lake Balkyldak with other aquatic systems contaminated by chlor-alkali effluents

	Lake Balkyldak[1]	**Onondaga Lake[2]**	**Clay Lake[3]**	**Lavaca Bay[4]**
location	Kazakhstan, Central Asia	New York State, U.S.	Ontario, Canada	Texas, U.S.
water body type	artificial lake, no outlet	drainage lake, 2 main tributaries	drainage lake on Wabigoon River	estuarine bay
point sources	adjoining CLAP & wastebeds	adjoining CLAPs & wastebeds	CLAP discharge to river system ~80 km upstream	adjacent CLAP
hydraulic retention time	water loss by evaporation and seepage, no flushing	rapid flushing, ~4 times y^{-1}	estimated flushing time ~7 times y^{-1}	rapid tidal flushing
surface area	~15 km^2	~12 km^2	~30 km^2	~142 km^2
volume	0.6 x 10^8 m^3	1.4 x 10^8 m^3	2.4 x 10^8 m^3	1.9 x 10^8 m^3
mean water depth	mean 4 – 5 m	12 m	8 m	1.5 m
max. water depth	8 – 10 m	20 m	24 m	
period of main Hg discharges	1975 – 1979 (closed 1993)	1946 – 1970 (closed 1977 and 1988)	1962 – 1970 (closed 1975)	1966 – 1970 (closed 1979)
total Hg inputs	10 – 15 t	~75 t	~10 t (of which ~2 t in lake sediments)	~75 t
other pollutants	Cl^-, SO_4^{2-}, metals, org. pollutants	Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, P, municipal effluents		
THg in sediments	minimum 0.11 mg kg^{-1}, up to >1500 mg kg^{-1} near the outfall	up to 85 mg kg^{-1}	0.1 – 7.8 mg kg^{-1} in upper 6 cm	0.42 mg kg^{-1} in upper 3 cm, 30–80 mg kg^{-1} at depth
contaminant depth	mainly upper 30 cm	upper 50 cm	mainly upper 4 – 6 cm	5 – 60 cm
THg in water	0.11 – 1.39 µg L^{-1}, med 0.23 µg L^{-1} (unfiltered)	2 – 19 ng L^{-1} in surface water, up to 35 ng L^{-1} in hypolimnion (unfiltered)	5 – 80 ng L^{-1} (unfiltered)	mean 47 – 49 ng L^{-1} (unfiltered)
pH	8.4 – 9.0	7.5 – 8.5		
chloride	1365 – 3075 mg L^{-1}	~470 mg L^{-1} (70% drop since closure)		

[1]Lake Balkyldak: Data from this study.
[2]Onondaga Lake: Data from Bloom and Effler (1990), Jacobs et al. (1995), Klein and Jacobs (1995), Wang and Driscoll (1995)
[3]Clay Lake: Data from Parks et al. (1989), Armstrong and Hamilton (1973)
[4]Lavaca Bay: Data from Bloom et al. (1999 and 2004), Santschi et al. (1999)

3.1.2 River Irtysh

In response to concerns that the Irtysh and nearby communities may be impacted by Hg carried in groundwater from the contaminated industrial site (Ullrich et al., *in preparation*), river sediments were investigated at 16 locations on the Irtysh side channel and at 9 locations in the oxbow lakes close to Pavlodarskoye village. Overall, Hg concentrations were found to range between 0.001-0.046 mg kg^{-1} in river bed sediments, and between 0.010-0.360 mg kg^{-1} in oxbow lakes of the river (Table 2). These results are in good agreement with an earlier investigation which reported up to 0.029 mg Hg kg^{-1} in the river bed and up to 0.35 mg kg^{-1} in oxbow lakes (Kamberov et al., 1999). According to the study by Kamberov et al. (1999) which covered a 25 km section of the river starting 4 km south of Pavlodarskoye, regional background concentrations of Hg in bed sediments of the River Irtysh are in the order of 0.001-0.003 mg kg^{-1}. Average Hg concentrations measured by us in the river bed sediments near Pavlodarskoye would therefore indicate a slight enrichment of 3-4 times above regional background. At two thirds of the sampling locations, Hg concentrations were higher in the surface layer (0-10 cm) than in the subsurface layer (10-20 cm). Sediment Hg concentrations at 0-10 cm depth and 10-20 cm depth were correlated ($r=0.692$ for river sediments and $r=0.860$ for oxbow sediments), but the difference was not statistically significant. There was a significant difference, however, between sediment Hg concentrations in oxbow lakes and in river sediments ($p \leq 0.001$ at 0-10 cm, and $p \leq 0.011$ at 10-20 cm depth). Mean and median Hg concentrations in oxbow lake silts were more than an order of magnitude higher than in the predominantly sandy sediments from the river channel, indicating significant enrichment of about 50 times the regional background. This is likely to be due to contaminated surface runoff entering the oxbow lakes from the floodplain soils which are impacted by aerial deposition of Hg emitted from the plant (Kamberov et al., 1999), and possibly also by the application of Hg-containing pesticides on agricultural land (cf. section 3.3.2).

3.2 Water

3.2.1 Lake Balkyldak

Mercury concentrations in unpolluted freshwaters in Kazakhstan are generally less than 2 ng L^{-1}, and no Hg was detected in Lake Muyaldy, a small saline lake located 9 km east of PCP and Lake Balkyldak. Contaminated sediments can act as an important source of Hg to the water column. Initial spot tests carried out in 1997/98 found Hg concentrations in eight surface water samples from Lake Balkyldak ranged between 0.45-2.25 µg L^{-1}, with a mean of 1.02 µg L^{-1} (Kamberov et al., 1999). During our more extensive monitoring campaign in July/August 2001, Hg concentrations in unfiltered fully duplicated lake water samples ranged from 0.11 to 1.39 µg L^{-1} (mean 0.38 µg L^{-1}, med 0.23 µg L^{-1}, n=26). The highest concentrations were measured in the

southern part of the lake where the sediments are most polluted. Water samples taken from northern and north-eastern parts of the lake contained ~0.14 μg L^{-1} Hg. Twelve further samples were taken in the south of the lake in September 2002 and August 2004, at approx. 200 m, 500 m, 750 m and 900 m from the outfall. Fig. 4 illustrates the variation of Hg concentrations in lake water with increasing distance from the outfall pipe during the three sampling campaigns. The much higher Hg concentrations determined in 2002 and 2004 are most likely due to higher amounts of suspended solids in the samples, rather than indicating increased dissolved Hg concentrations. In particular during the August 2004 sampling campaign it was noted that the samples were turbid due to strong winds and waves, which had led to the resuspension of highly contaminated bed sediments in the shallow waters. The Hg concentrations measured in 2001 are therefore thought to be more representative of the general contaminant status of the lake. Nevertheless, Hg concentrations in Lake Balkyldak appear to be 1-2 orders of magnitude higher than those reported for Onondaga Lake (Table 3).

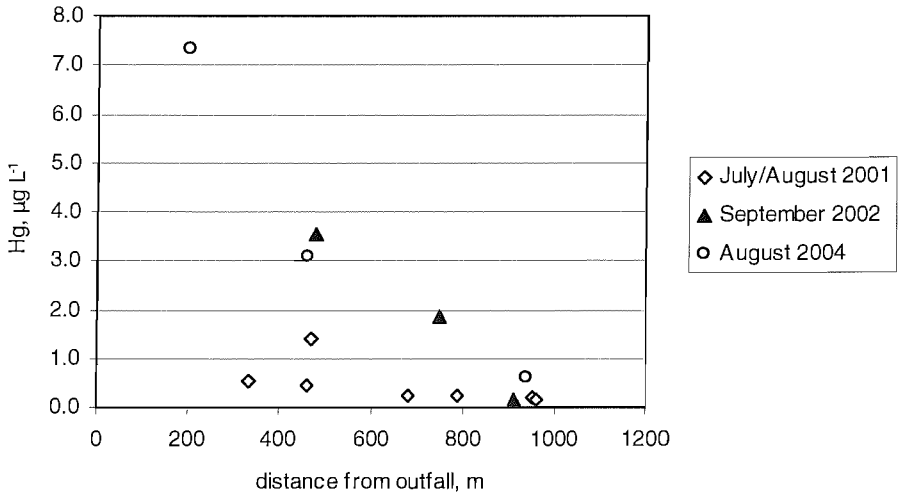


Fig. 4. Mercury concentrations in unfiltered surface water samples taken along the southern shoreline of Lake Balkyldak during three different sampling campaigns.

The water analysis results show that although the lake sediments are a net sink for Hg, they are also acting as a strong source of Hg to the water column, particularly in the south of the lake. Mercury can be released from sediments e.g. via wind-driven resuspension of contaminated particles and bioturbation. The leaking waste lagoons and continuing inputs from the outfall pipe are further sources of Hg to the lake in the south. The form in which the Hg originally entered the lake with the wastewater is not known, but Maserti and Ferrara (1991) reported that 90% of Hg in CLAP wastewater was associated with particulate suspended matter, and only 10% was in dissolved form. In Onondaga Lake, a large fraction (60%) of THg was associated

with particulate matter (Wang and Driscoll, 1995). Inorganic Hg in sediments can be transformed into the highly toxic and bioaccumulative methyl mercury (MeHg) form. Gill et al. (1999) found that MeHg was the predominant form of Hg fluxing out of the sediments into the water column at Lavaca Bay.

Panda et al. (1990) reported that pH was an important factor regulating the availability of Hg from sediments in the Rushikulya estuary (the lower the pH, the higher the availability). The water of Lake Balkyldak is alkaline and highly saline. The pH of lake water samples taken in 2001 ranged between 8.4 – 9.0 (mean 8.9), whereas chloride concentrations ranged from 1365 – 3075 mg L^{-1} (mean 2805 mg L^{-1} or 79 mM). This is two orders of magnitude higher than typical freshwater chloride concentrations which are generally in the range of 5 – 25 mg L^{-1}, and only seven times less than the average seawater chloride concentration of 0.56 M (~20 000 mg L^{-1}). Whereas the alkalinity by itself could offer some degree of protection against Hg desorption from the sediments, the high chloride concentrations would be expected to have the opposite effect and lead to increased mobilization of Hg (Reimers et al., 1975; Bodek et al., 1988; Stein et al., 1996). High levels of chloride were also reported for Onondaga Lake where Cl^- concentrations remained elevated after plant closure, due to continuing inputs from the adjoining waste beds (Bloom and Effler, 1990).

Environmental parameters such as pH and salinity not only affect sediment-water partitioning, but also influence the availability of Hg to methylating bacteria (Ullrich et al., 2001). Predominance diagrams indicate that at the pH and chloride conditions prevailing in Lake Balkyldak, Hg(II) should mainly be present as $HgCl_2$(aq) and $HgCl_3^-$ complexes (Hahne and Kroontje, 1973; Stumm and Morgan, 1996; Morel et al., 1998). Small uncharged complexes such as $HgCl_2$ are thought to be readily available for bacterial methylation, whereas the larger charged chlorocomplexes may not be bioavailable, and the potential for methylation is generally decreased at high pH values (Ullrich et al., 2001). The determination of MeHg in the lake water or sediments was beyond the scope of the present study, but high THg concentrations were found in fish from Lake Balkyldak, which seems to indicate that methylation processes are actively occurring in the lake (cf. part II of this paper). In Onondaga Lake and Clay Lake, elevated concentrations of MeHg were observed in the water column, and biota remained seriously contaminated for many years after major releases of inorganic Hg had ceased (Parks et al., 1989; Wang and Driscoll, 1995).

Accumulation of Hg in fish is potentially not the only problem posed by the contaminated lake water: we hypothesize that the lake may also act as a source of gaseous Hg emissions in the summer when average temperatures of 25-30°C are likely causing increased evaporation of Hg from the water surface. It is well known that dissolved Hg(II) in surface waters can be bacterially or photochemically reduced to gaseous elemental Hg which can subsequently be lost by volatilization (Barkay et al., 1989; Amyot et al., 2004). Hg evasion typically increases with

increasing water pH and temperature, solar radiation, and wind speed (Fitzgerald et al., 1991; Vandal et al., 1991; Watras et al., 1995; Ferrara et al., 2001; Feng et al., 2004). In a marine area polluted by a CLAP in Italy, Hg emission fluxes were 14 ng m^{-2} h^{-1} and were 3-4 times higher during the summer months, for example (Ferrara et al., 2001). The Baihua reservoir in China which is of a similar size as Lake Balkyldak (14.5 km^2) but slightly deeper, with a water pH close to 8 and an average salinity of 0.2‰, is a strong local atmospheric Hg emission source, despite having aqueous THg concentrations that are an order of magnitude lower compared to Lake Balkyldak (Feng et al., 2004). Average evasion flux rates between 4.0-9.7 ng m^{-2} h^{-1} and annual estimated Hg emissions in the order of 750 g, corresponding to 3% of the total Hg in the water body, have been reported for this reservoir (Feng et al., 2004). Mercury emission rates from Lake Balkyldak might thus warrant investigation, as significant volatilization losses of Hg^0 could potentially occur during the summer months owing to the lake's alkalinity, the high average summer temperatures and the frequent strong winds in the region.

3.2.2 River Irtysh

At all 16 sampling locations on the river, Hg concentrations in surface water samples were below the detection limit of 2 ng L^{-1} (n=32). However, traces of Hg were detected in some of the samples taken from the oxbow lakes where Hg concentrations at nine sampling locations ranged from <2 ng L^{-1} to 8.5 ng L^{-1} (n=18). Mercury was only detectable in the immediate vicinity of Pavlodarskoye village; in the three sampling points to the north of the village Hg was below the detection limit. There was no correlation between sediment and water Hg concentrations, and Hg traces in oxbow lakes are likely due to contaminated sediments and surface runoff from the surrounding floodplain. The possibility of transport of contaminated groundwater from Lake Balkyldak or PCP cannot be ruled out with certainty as a source of the contamination (cf. section 3.3.2). However, at the time of our investigation Hg was not detected in any of the groundwater samples taken from Pavlodarskoye village (Ullrich et al., *in preparation*), therefore transport of contaminated groundwater from the factory to Pavlodarskoye seems unlikely and the Hg traces detected in the oxbow lakes more likely result from contaminated surface runoff from the floodplain and agricultural land.

3.3 Soils

3.3.1 Soils around Lake Balkyldak

The water level of the lake fluctuates widely depending on the volume of wastewater received as well as on the climatic conditions. Periodically flooded littoral soils sampled in six locations along the northern, eastern and western shoreline of the lake were found to be impacted by pollution from the lake. Mercury concentrations appeared to be diminishing with depth but were

very variable, hence the difference between Hg concentrations in topsoils and subsoils was not statistically significant. Average Hg concentrations were 2.65 mg kg^{-1} (0.22-5.72 mg kg^{-1}) in the 0-10 cm soil layer, 1.81 mg kg^{-1} (0.28-4.46 mg kg^{-1}) in the 10-20 cm soil layer, and 1.14 mg kg^{-1} (0.23-2.21 mg kg^{-1}) at 20-50 cm depth. Both inorganic and organic Hg species are strongly sorbed onto soils and sediments, but the presence of Cl^- appears to decrease sorption, leading to increased mobility (Bodek et al., 1988; Schuster, 1991). It is therefore not surprising that these littoral soils which are periodically flooded with highly saline lake water were found to be impacted by Hg up to a depth of at least 50 cm.

3.3.2 River Irtysh floodplain cores

Mercury concentrations in the upper 20 cm of the two soil cores taken in the flood plain of the River Irtysh were higher than in nearby oxbow lake sediments, indicating that the source of the sediment contamination is likely to be the flood plain. In core 1, located about 7 km from PCP, Hg concentrations ranged from 0.106-0.321 mg kg^{-1} and were highest in the top 10 cm. Compared to the nearest sediment sampling point at a distance of 14 m from the core, Hg levels in the top 10 cm of the soil core were 20 times higher than in the corresponding sediment layer, and Hg levels at 10-20 cm depth were 2 times higher. Core 2, located in a swampy area 1.5 km further north than core 1 (at 8 km distance from PCP) had slightly lower but broadly similar concentration in the top 10 cm (0.127 mg kg^{-1}), but showed significantly enriched Hg concentrations in the 10-20 cm and 100-150 cm layers (4.30 and 2.34 mg Hg kg^{-1}, respectively – Fig. 5). Compared to the nearest sediment sampling point located just 2.5 m from the core, the soil Hg concentration at 0-10 cm was 3 times higher and the Hg concentration at 10-20 cm was 330 times higher than in the corresponding sediment layer.

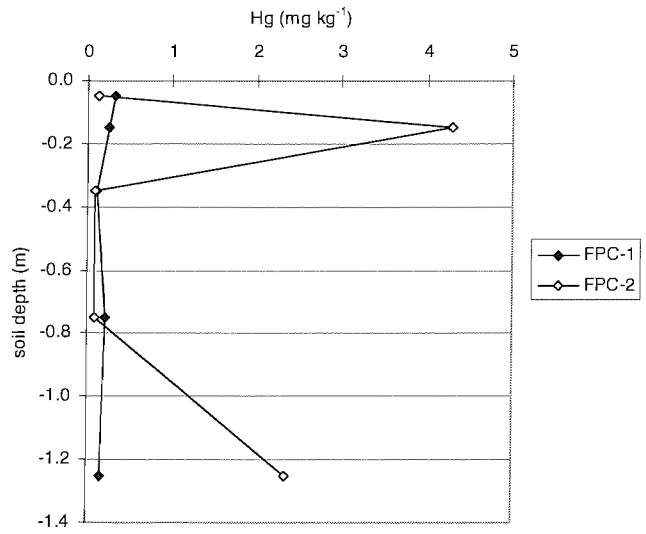


Fig. 5. Mercury concentrations in two soil cores taken from the Irtysh floodplain

The accumulation of Hg in the upper 20 cm of the floodplain cores is likely attributable to past atmospheric deposition of Hg emitted from the plant (Kamberov et al., 1999). Another potential source of Hg in the soils is the use of organic Hg compounds in agricultural pesticides which was widespread during Soviet times. For example, the now prohibited fungicide Granosan (ethylmercury chloride) was among the most frequently used agricultural chemicals in Kazakhstan (UNDP, 1995), and stockpiles of the substance have been found in the Asian part of the Russian Federation (UNEP, 2002). According to information obtained from the Pavlodar Regional Committee for Environmental Protection, it is likely that Granosan has also been stored in Pavlodarskoye, but the storage sites are unknown.

It is not clear what is causing the contamination at depth. In most soils, Hg is strongly retained by organic matter (OM) and its mobility is generally considered to be low (Lodenius, 1994; Biester et al., 2002). While Hg bound to soluble OM complexes can migrate to deeper lying soil layers, clayey soil components inhibit Hg mobility by adsorption of soluble Hg-OM complexes (Biester et al., 2002). In the Irtysh floodplain cores, greyish clays were observed below 20 cm depth, therefore downward migration of Hg would be expected to be fairly limited. During a previous investigation, Kamberov et al. (1999) also noted elevated Hg concentrations in deeper lying floodplain soils and suggested that the contamination at depth could potentially result from Hg transported with shallow groundwater from Lake Balkyldak, located 5 km to the east of the Irtysh. Since the results of the present survey concur with the findings of Kamberov et al. (1999), contaminant migration from the lake appears to be a possibility, but further studies would be required to confirm this hypothesis.

3.4 Remediation options for Hg-contaminated sediments

The sediments of Lake Balkyldak are highly contaminated with Hg and are acting as a strong source of Hg to the water column. The lake therefore presents a significant risk to the aquatic food chain (cf. part II of this publication), and could also be a source of atmospheric Hg emissions. The southern portion of the lake is most polluted because of the proximity to the outfall, and the leaking lagoons are a further source of Hg to the lake. Following our field work, we recommended that the lagoons be surrounded by a cut-off wall and covered with an engineered cap, to stop Hg from leaking into the ground water and the lake, and to contain Hg emissions to air and prevent the infiltration of rain water. A cut-off wall was subsequently built around the lagoons and a temporary clay cover has been put in place. This work has eliminated a major ongoing source of Hg to the lake. However, data from the sediment cores taken close to the outfall as well as wastewater analysis results indicate that the lake is continuing to receive Hg inputs via the old outfall pipe. It is therefore important that this source is stopped before any other remediation efforts are started or can become effective.

Dredging and disposal or *ex-situ* treatment are the most commonly applied remediation methods for contaminated sediments and tend to be most cost-effective. Ultrasound and thermal treatment of sediments contaminated with Hg have been investigated at the laboratory scale, but to our knowledge have not yet been applied in practice. Ultrasound treatment can be used to enhance the release of Hg from contaminated sediments by creating vibrations that loosen the Hg from the sediment matrix. He et al. (2005) found that ultrasound enhanced Hg(II) release from aluminum oxide particles at short treatment times, but with longer exposure times previously desorbed Hg(II) was re-adsorbed back onto the particles. In a follow-up study, ultrasound was applied to release Hg from Al_2O_3, HgS, and marine sediment particles, and a genetically modified green alga (*Chlamydomonas Reinhardii*) with a high Hg binding capacity was used to sequester the metal from the aqueous phase (He et al., 2006). The combination of ultrasound and transgenic algae may thus be a promising means to recover inorganic Hg from contaminated sediments. Preliminary tests carried out on a sediment sample taken from the south of Lake Balkyldak indicated that most Hg was present as elemental Hg, and >95% of the Hg could be removed by ultrasound (unpublished data).

Thermal desorption for Hg removal from sediments has also been investigated at the laboratory scale (Benotti et al., 2004; Manni et al., 2004). For a contaminated sediment containing ~21 mg Hg kg^{-1}, desorption times of 20-30 min at temperatures ranging from 325-350°C yielded residues with a Hg content of <5 mg kg^{-1}. As most Hg in sediments is typically associated with the fine sediment fraction, particle screening can be used to reduce the amount of sediment requiring treatment (Benotti et al., 2004; Manni et al., 2004). Manni et al. (2004) have shown that thermal desorption of Hg may be a viable remediation option for sediments polluted by the chlor-alkali industry. Thermal desorption tests were applied to the finest size sediment fraction containing ~350 mg Hg kg^{-1}. After 3 minutes at 400°C, the treated sediment residue had a Hg content below the Italian regulatory limit of 5 mg kg^{-1} for industrial uses. It should be noted, however, that sediment Hg concentrations of 5 mg kg^{-1} are still likely to lead to unacceptably high Hg concentrations in the water phase, and that stricter limit values are in force in most other countries (ANZECC/ARMCANZ, 2000).

In a recent review paper, Wang et al. (2004) suggested capping and dredging as suitable remedial approaches for aquatic systems contaminated by Hg. However, they cautioned that while *in situ* capping would be a relatively low-cost remedial option, it leaves the contamination in place, thereby posing concerns regarding long-term environmental effects, such as the remobilization of buried Hg, or the possible transformation of inorganic to organic Hg, and migration through the capping layer into the water column. For heavily polluted systems, dredging may therefore be the only effective solution. This has been successfully applied e.g. in Minamata Bay, Japan, where sediments contained up to 600 mg kg^{-1} of Hg (Fujiki and Tajima, 1992; Hosokawa, 1993). Approximately 1.5 million m^3 of sediment containing >25 mg Hg kg^{-1}

were removed from an area of ~2 km^2 and were contained in a reclaimed area of the bay. The reclaimed area was capped with clean soil after stabilization with volcanic ash. Remediation of the remainder of the tidally flushed bay was assisted by natural attenuation.

Disadvantages of dredging are the comparatively high cost, and possible adverse environmental effects in the short term from sediment resuspension. Silt screens should therefore be used to prevent the spread of sediments resuspended during dredging activities. Due to the high costs of treating dredged sediments, safe confinement is the more common alternative. Possible leakage into groundwater from disposal sites is a potential concern that needs to be addressed. Another major concern is that dredging activities could lead to increased methyl mercury (MeHg) production. Bloom and Lasorsa (1999) suggested that the mixing of contaminated sediments with biologically active surface sediments during the dredging process could result in the desorption of metals, e.g. due to changes in redox conditions or nutrient status. High total Hg and MeHg concentrations were observed by these workers in water draining from an upland dredge spoils settling pond, indicating that the settling pond could be source of Hg methylation (Bloom and Lasorsa, 1999). However, these field observations could not be reproduced in laboratory mesocosm studies.

Sediment dredging has been selected as the preferred remedial option at several chlor-alkali contaminated sites. The Santa Gilla lagoon on the southern coast of Sardinia (Italy) was contaminated by 26 tons of inorganic Hg from an on-shore CLAP in the 1960s and 1970s. The lagoon covers an area of 15 km^2 of shallow waters with an average depth of just 1 m. Mercury was found to be confined mainly in the upper 10 cm sediment layer in front of the on-shore industrial area, which had mean sediment Hg concentrations in the order of 20 mg kg^{-1} and peak concentrations of some hundreds of mg kg^{-1}, whereas Hg levels in the remaining lagoon were ~1 mg kg^{-1} (Degetto et al., 1997). Restoration work started in the mid-1980s. The most polluted area near the CLAP (~2.5 km^2) was dyked and was used to receive polluted sediments dredged from other parts of the lagoon. The dyked area was then covered by sediments dredged from cleaner areas and left to dry. By 1997, 6 million m^3 of sediments had been dredged from the central part of the lagoon (Degetto et al., 1997). However, as the results of a subsequent monitoring programme have not been reported, it is difficult to evaluate the overall success of the remediation work at this site.

Mercury contamination at the Lavaca Bay Superfund site is currently being addressed by dredging and capping (USEPA, 2004 and 2006). To date, more than 600000 m^3 of Hg-contaminated dredge spoils and ~70000 m^3 of Hg-contaminated soils have been placed into a fortified disposal facility located on Dredge Island. A final cover for the disposal areas will consist of dredge material taken from an area of the bay with Hg concentrations below human health and ecological risk-based values (USEPA, 2006). Sediments that are not actively remediated are expected to recover to acceptable levels through natural sedimentation within a 5

to 10 year timeframe. Areas north of Dredge Island will receive a thin cap to accelerate the natural recovery process. Marsh areas were identified as active methylation sites and will be remediated by either dredging or filling. The remedial goals are to eliminate exposure to sediments with >0.25 mg kg^{-1} of Hg in marsh habitats, and to sediments with >0.50 mg kg^{-1} of Hg in open water habitats (Baumgarten, 2001). Natural recovery processes due to the influx of low-Hg sediments have already led to a decrease in Hg concentrations in sediments and fish tissue (Wedell et al., 2006), but the fish closure imposed on the bay cannot yet be lifted, and long term monitoring of both sediments and fish will be required to confirm recovery to acceptable levels.

The suggested remedial solution for Onondaga Lake which has a similar size and contamination history to Lake Balkyldak (cf. Table 3) also involves a mixture of dredging and capping, as well as a pilot study on the effectiveness of oxygenation for reducing MeHg concentrations in the water column in the deeper portion of the lake. An estimated 2 million m^3 of contaminated sediments and chlor-alkali waste are to be dredged from the lake, followed by the placement of an isolation cap over an estimated 1.7 km^2 of the shallower portion of the lake with a water depth of less than 9 m. In addition, a thin-layer cap will be placed over an estimated 0.6 km^2 of the deeper portion of the lake where the water depth exceeds 9 m (NYSDEC, 2005).

A two-stage approach of dredging and capping was applied to Lake Turingen in Sweden (Projekt Turingen, 2004). The 197 acre (0.8 km^2) lake was contaminated with ~350 kg of Hg from upstream paper mill effluents. The lake has a maximum depth of 10 m and contained an estimated 225000 m^3 of contaminated sediments with Hg concentrations up to 35 mg kg^{-1}. Stage 1 of the remedial work involved conventional dredging, disposal of dredge spoils and capping of a 0.04 km^2 area near the mouth of the river that feeds the lake with a multi-layer cap consisting of a geotextile, a sealing layer of clean, fine-grained sand and a top layer of crushed rock to protect against erosion and other forms of damage. In stage 2, the remaining lake sediments in the deeper parts of the lake (~0.8 km^2) were capped with an approximately 4 cm thick layer of artificial sediment, formed by chemical precipitation of aluminium hydroxide and reinforced with added sand and cellulose fibers. Resuspension of contaminated sediments was in most places successfully inhibited by the artificial cap, and Hg concentrations in water have decreased significantly, although Hg levels in biota will take considerably longer to decrease to acceptable levels (Projekt Turingen, 2004). The new gel capping method appears to be a promising low-cost technology for moderately contaminated sediments that could potentially find application in Eastern European and developing countries (Swedish EPA, 2004). However, the long-term effectiveness of this very recent technology is still unclear.

Given the wide-ranging existing expertise in dredging and capping Hg-contaminated sediments, as illustrated by the abovementioned case studies, the most straightforward remedial

solution for Lake Balkyldak would be the removal of the heavily polluted lake sediments near the outfall pipe in the south, followed by the disposal of the dredge spoils in a dyked area, stabilization and capping. Encapsulation techniques that can be used to immobilize Hg-contaminated wastes and sediments have recently been reviewed by Randall and Chattopadhyay (2004). Our limited sediment core data would suggest that the removal of the upper 30 cm sediment layer within 800-1000 m from the outfall would reduce sediment Hg concentrations to below 10 mg kg^{-1} in this area of the lake. This would involve the dredging and disposal of between 200,000-300,000 m^3 of contaminated sediments. A decision would then have to be made on how to address the residual contamination in the lake. There are at present no environmental quality standards for sediments in Kazakhstan, although the quality standard for soils (2.1 mg kg^{-1}) is sometimes applied due to the lack of other guidance. Sediment guideline levels, screening levels and trigger levels developed in Canada, the U.S., and Australia/New-Zealand range between 0.2 mg kg^{-1} and 2 mg kg^{-1} (ANZECC/ARMCANZ, 2000). A higher maximum permissible concentration of 10 mg Hg kg^{-1} is in effect in the Netherlands, but this is unlikely to achieve a reduction of Hg concentrations in biota to safe levels. Therefore, after dredging the top 30 cm sediment layer, the remaining sediments in the vicinity of the outfall would have to be capped to prevent further release of Hg into the water column. Gel capping as recently demonstrated in Lake Turingen would be a comparatively economical solution and could potentially be applied to cover these sediments. However, treatment of the whole lake may not be cost-effective due to its large size. Another, not yet proven method would be to cover the most contaminated lake sediments with a thick layer of power station fly ash, followed by stabilization and surface capping. Fly ash is a promising, low-cost adsorbent that is likely to find wider application in the future for the removal of both inorganic and organic pollutants from waste waters (Wang and Wu, 2006). In the case of Lake Balkyldak, a fly ash cap could be a particularly economical solution as there are several power stations nearby that are producing waste fly ash. Research is currently under way to investigate Hg sorption and desorption behavior on fly ash, with a view to its potential use as an adsorptive capping material (W. Kitchainukul, unpublished data).

Lake aeration could potentially be used as an alternative to capping to reduce MeHg concentrations and biouptake in the remainder of the lake, but would probably require considerable investment. Aeration systems are frequently installed in reservoirs to prevent the development of hypolimnetic anoxia during the summer by inducing mixing at the sediment-water interface, thereby promoting the formation of aerobic conditions in surface sediments (Beutel, 2003). Under aerobic conditions, Hg methylation is known to be reduced, whereas anaerobic conditions favor Hg release from sediments and MeHg production (Ullrich et al., 2001). For example, DeLaune et al. (2004) found that MeHg production was lower in oxygenated lakes, and Bloom et al. (2004) reported that aeration appears to be keeping MeHg

levels low in the Venice Lagoon. An oxygenation pilot study is planned to be carried out in the deeper portion of Onondaga Lake to reduce dissolved Hg concentrations and Hg methylation (NYSDEC, 2005). However, in the case of Lake Balkyldak an aeration approach may not be cost-effective, as the lake is comparatively shallow (Table 3) and may not suffer from pronounced hypolimnetic anoxia.

Experience at Lavaca Bay has shown that marsh areas can be active sites for Hg methylation (USEPA, 2004 and 2006; Wedell et al., 2006). Swampy areas with reeds along the shoreline of Lake Balkyldak may therefore have to be excavated and removed, or otherwise dewatered and separated from the lake. Mercury concentrations in the lake water would be expected to gradually decrease following the elimination of ongoing sources and dredging and/or capping the sediments near the outfall. The decrease could potentially be accelerated by using genetically modified algae to sequester Hg from the aqueous phase (He et al., 2006), and subsequent harvesting. Mercury concentrations in fish generally take longer than aqueous concentrations to decrease to acceptable levels (e.g. Parks et al., 1989; Projekt Turingen, 2004; USEPA, 2006; Wedell et al., 2006). Due to the high Hg concentrations found in fish from Lake Balkyldak (cf. part II of this publication), a ban on fishing should be imposed with immediate effect. Whichever remediation option will be chosen for the lake, a long-term monitoring program will have to be put in place that should preferably include both inorganic Hg and MeHg.

4. Conclusions

Sediments from Lake Balkyldak were found to be very heavily contaminated, with Hg concentrations in the surface layer reaching up to ~1500 mg kg^{-1} near the wastewater outfall pipe. The contaminated shallow lake sediments are prone to wind-driven resuspension and are acting as a strong source of Hg to the water column. The lake also appears to be receiving continued Hg inputs via the old outfall pipe.

Sediments from the River Irtysh were only slightly impacted, and Hg concentrations in the water phase were generally below the limit of detection (<2 ng L^{-1}). Mercury concentrations in sediments were higher in the oxbow lakes compared to the river channel, which is likely due to contaminated surface run-off from the surrounding flood plain.

A comparison with other aquatic systems contaminated by Hg from chlor-alkali plant effluents indicates that Lake Balkyldak could be the most severely impacted lake ecosystem known to date. The highly contaminated lake presents a significant risk to human health and the environment and is in urgent need of remediation. Potential remediation options for the lake including both traditional and innovative approaches were discussed, but further studies will be necessary to find an appropriate and cost-effective long-term solution.

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Chapter 3

Mercury contamination in the vicinity of a derelict chlor-alkali plant. II. Contamination of the aquatic and terrestrial food chain and potential risks to the local population

ABSTRACT: This study investigated the environmental impact and level of risk associated with mercury (Hg) contamination near a derelict chlor-alkali plant in Pavlodar, Northern Kazakhstan. Several species of fish were sampled from the highly polluted Lake Balkyldak and the nearby river Irtysh, to assess the extent of Hg bioaccumulation in the aquatic food chain and potential human health risks. A small number of bovine tissue samples, water samples, soil and plant samples from a nearby village were also investigated in order to make a preliminary assessment of potential impacts on the terrestrial food chain. Mercury levels in fish caught from Lake Balkyldak ranged from 0.16 to 2.2 mg kg^{-1} and the majority of fish exceeded current human health criteria for Hg. Interspecies comparisons indicated that Hg is accumulated in the order dace > carp > tench. Site-specific bioaccumulation factors (BAF) were calculated for THg, and were estimated for MeHg. Fish from the river Irtysh and floodplain oxbow lakes contained between 0.075 and 0.159 mg kg^{-1} of Hg and can be regarded as uncontaminated. Soils were found to be impacted by past atmospheric emissions of Hg. Cattle grazing in the surroundings of the factory are exposed to Hg from contaminated soils, plants and surface water, but the consumption of contaminated fish from the lake appears to be the main route of exposure for humans.

1. Introduction

A former chlor-alkali plant near Pavlodar in Northern Kazakhstan has seriously contaminated the surrounding environment with mercury (Hg). Industrial and domestic wastewater from the Pavlodar Chemical Plant (PCP) was discharged directly to Balkyldak settler, an artificial storage lake formed from a natural depression without an outlet. As a result, the sediments and water column of Lake Balkyldak have become highly contaminated with Hg and possibly other substances (cf. part I of this publication). However, although Balkyldak is not a natural lake but a wastewater storage reservoir, it is used regularly by fishermen who catch fish both for their own consumption and for selling it on the local market. This raises potentially serious health concerns, as inorganic Hg can be microbially methylated and transformed into organic methyl mercury. Methyl mercury (MeHg) is a potent neurotoxin which is readily accumulated by aquatic biota and is strongly biomagnified along the food chain (Clarkson, 1998; WHO 1989; U.S. EPA, 2001a). Bioconcentration factors in the order of 10^4-10^7 have been reported (Stein et al. 1996), and more than 90% of Hg in fish is generally present in the MeHg form (Grieb et al.,1990; Bloom 1992; Becker and Bigham, 1995; Mason et al., 2000). Elimination of MeHg from fish is slow and long-term reductions of Hg concentrations in fish are often due mainly to growth of the fish (US EPA, 1997). The consumption of contaminated fish is generally regarded

as the main route of exposure for humans to MeHg (Clarkson et al., 2003), and maximum intake values have been suggested to protect human health (U.S. EPA 2001a,b; JEFCA, 2003).

The primary objective of this study was to investigate the impact of Hg emissions from the chlor-alkali plant on the surrounding environment, and in particular the lake (sediments, water and biota). A smaller-scale survey was carried out on a side channel of the nearby river Irtysh, which was suspected to be impacted by contaminated groundwater from PCP as well as by atmospheric emissions and contaminated run-off from the floodplain. In addition, soil and groundwater samples were taken in the nearby village of Pavlodarskoye. The land surrounding the plant is used on a daily basis for grazing cattle herds from the village and the soils in the vicinity of the plant are likely to be contaminated by atmospheric Hg emissions. The survey was therefore extended by taking a limited number of spot samples of the predominant vegetation, surface water samples from water-filled depressions where cows were seen to be drinking, and milk and tissue samples from dairy cows, with the aim of gaining at least a preliminary insight into the potential for contamination of the terrestrial food chain and the associated level of risk.

2. Materials and methods

2.1 Site description

A detailed site description has already been given in part I of this paper. The Pavlodar region has many shallow lakes that partially dry up in the summer due to intense evaporation. In the area surrounding PCP there are numerous depressions filled with saline surface water. The soils surrounding the plant are saline and the predominant vegetation is *Salicornia* spp. (salt-wort, also known as pickleweed). Cattle are regularly grazing the land and are feeding on pickleweed and on surface water that has accumulated in low-lying areas and ditches.

Lake Balkyldak is located ~2 km north of the chlor-alkali workshop and has an estimated surface area of approx. 15 square km. The lake received industrial wastewater from about 1970, and Hg-containing wastewater from 1975 when the chlor-alkali shop started production. Apart from Hg, wastewaters also contained other heavy metals, sulphate, chloride and organic pollutants.

The River Irtysh lies approximately 5-6 km to the west of the chlor-alkali workshop and the lake (cf. Fig. 2a in part I of this paper). Our investigation focused on the "Old Irtysh", a natural side channel of the Irtysh which is of similar size to the main channel, but is not used for commercial navigation. The village of Pavlodarskoye (population approx. 5,000) is situated directly by the Old Irtysh and is the nearest residential area to the plant (approx. distance 4-5 km). There is no municipal water supply in Pavlodarskoye; all houses therefore have their own boreholes.

2.2 Sampling

Fish

Fish were caught by local professional fishermen using nets. 55 specimens were collected from Lake Balkyldak in August 2001, and 30 from the Old Irtysh and its oxbow lakes in August 2002. The fish were double-wrapped in clean PE bags, frozen and shipped to the laboratory where the weight and length of the fish was recorded. Fish age was generally estimated from scale samples, but in case of ambiguity, vertebral growth bands were also investigated.

Bovine milk and tissue

Milk samples were obtained from 15 cows from Pavlodarskoye village, aged between 2 and 10 years, in September 2002. All samples were analysed in duplicate as soon as possible after milking. Internal organs (liver and kidney) were obtained from a 2 year old cow (70 kg) from the village, frozen and shipped to the laboratory. Tissue samples from uncontaminated animals from a different region in Kazakhstan (Almaty) served as controls.

Soils and plants

Twenty-four soil samples were taken from 12 private gardens in Pavlodarskoye village, the nearest residential area, in August 2001. Samples were taken from the 0-10 cm and 10-20 cm soil layers, air dried and stored in clean PE bags until analysis.

The low-lying land between the factory and the lake is densely populated with pickleweed (*Salicornia* spp.). The aerial parts of the plant were sampled from an area of ca. 10 x 10 cm at 1.0 and 1.5 km distance from the chlor-alkali workshop, respectively. Plant samples were washed, air dried and stored in clean PE bags until analysis. The underlying soils (0-5 cm layer) were also sampled.

Water

Thirty private drinking water wells in Pavlodarskoye village were tested for Hg contamination in August 2001. Duplicate surface water samples were taken from water-filled depressions in the area between the lake and the plant where cows were grazing. All water samples were acidified with 0.5% v/v conc. HCl, placed in a cool-box and delivered to the laboratory within two hours of collection.

2.3 Analytical methods and quality assurance

Fish

Samples of fish muscle tissue were taken with a stainless steel knife from the posterior part of the fish on the left hand side of the body. Tissue samples were digested in a mixture of HNO_3 and H_2SO_4 (Adeloju et al., 1994). This method was found to give better recoveries than either nitric peroxide or aqua regia digestion. Rates of recovery were evaluated using the certified reference material DORM-2 (dogfish muscle tissue; National Research Council Canada). About 1.0 g of tissue was digested with 7 ml conc. HNO_3 and 3 ml conc. H_2SO_4 on a water bath for 1-2 h until the tissue was completely dissolved. The solution was chilled and diluted with ultra-pure water to 100 ml. The mixture was quantitatively transferred to a 0.5 l vessel containing 150-200 ml of ultra-pure water. 25 ml conc. HCl, 10 ml 0.2 *M* KBr and 10 ml 0.2 *M* $KBrO_3$ solution were added and the volume was made up to 0.5 l. Samples were set aside overnight for complete digestion. The solution was then analysed in the same way as described for water samples. The accuracy of the method was assessed by analysis of DORM-2 (certified value 4.64±0.26 mg kg^{-1}), which gave an average recovery of 101.5±1.3% (n=14). All fish samples were analysed in duplicate. The relative percent difference (RPD) between analytical duplicates averaged 4.95% for fish from the lake, and 5.3% for fish from the river. All tissue concentrations are reported as wet weight concentrations.

Plants, milk, liver, kidney

Plant samples, underlying soils, bovine tissue samples and milk samples were digested and analysed by the same method as described for fish samples. The suitability of the HNO_3/H_2SO_4 digestion method for soils as well as for fish and kidney tissue has been demonstrated by Adeloju et al. (1994). Sub-samples of approximately 1.0 g of tissue were taken for analysis. Quality control included sampling and analytical duplicates, analysis of blank samples and spike additions. All samples were analysed in duplicate to assess precision. The method detection limit was 5 μg kg^{-1} for bovine tissue samples and 2 μg L^{-1} for milk samples. All tissue concentrations are reported as wet weight concentrations.

Soils

Soil samples were dried in the dark at 20-25°C. The dry samples were sieved through a 2 mm nylon screen (mesh size 10) and sub-samples of ~1.0 g were taken for analysis. Soil samples were digested by hot refluxing in a mixture of HNO_3 and H_2SO_4 (Hatch and Ott, 1968; Adeloju et al., 1994). Total mercury was determined by CV-AAS on a Perkin-Elmer AAnalyst 100 with mercury hydride system MHS-10, after $NaBH_4$ reduction. The detection limit was 1.5 ng g^{-1}. Quality assurance included blind determination of certified reference materials, analysis of

reagent blanks and analysis of duplicate samples. QA data for soils analysis is reported in part I of this publication.

Water

Mercury in ground water and surface water samples was determined by CV-AFS after BrCl oxidation and $SnCl_2$ reduction, according to established procedures. All water samples were analysed in duplicate. The method detection limit was 5 ng L^{-1} and the analysis of certified reference water samples (ORMS-2, National Research Council, Canada) gave an average recovery of 98.8±0.65 per cent. A more detailed description of the analytical procedure and quality assurance data is given in part I of this publication.

2.4 Data analysis

Data was analyzed using standard statistical procedures such as linear correlation and regression. Parametric tests were preferred, and differences between two sample means were generally assessed using *t*-Tests. For the fish data, where typical assumptions for one-way analysis of variance (ANOVA) were not satisfied, a non-parametric alternative, the Kruskal-Wallis test, was applied for comparing Hg concentrations in more than two fish species simultaneously. Where fish Hg content was significantly correlated with length and weight, the results were analysed by one-way analysis of covariance (ANCOVA).

3. Results and discussion

3.1 Fish

3.1.1 Lake Balkyldak

The fish species encountered in Lake Balkyldak, their feedings habits and approximate trophic position in the aquatic food web are given in Table 1. The majority of fish in the lake belong to the carp family (*Cyprinidae*). Data on fish age, weight, length and Hg content is summarized in Table 2. There was a strong relationship between fish length and weight across all species ($r=0.960$ for the total length and $r=0.902$ for the length measured without the caudal fin, at $p<0.001$). However, there was no significant relationship between the total Hg content in fish muscle tissue and either fish age, weight or length for any of the individual fish species. For carp, there appeared to be a slight decreasing trend of tissue Hg concentrations with increasing age (Fig. 1a), but the sample size was too small to establish statistical significance (n=2, 24, and 4 for carp at age 3, 4, and 5 years, respectively).

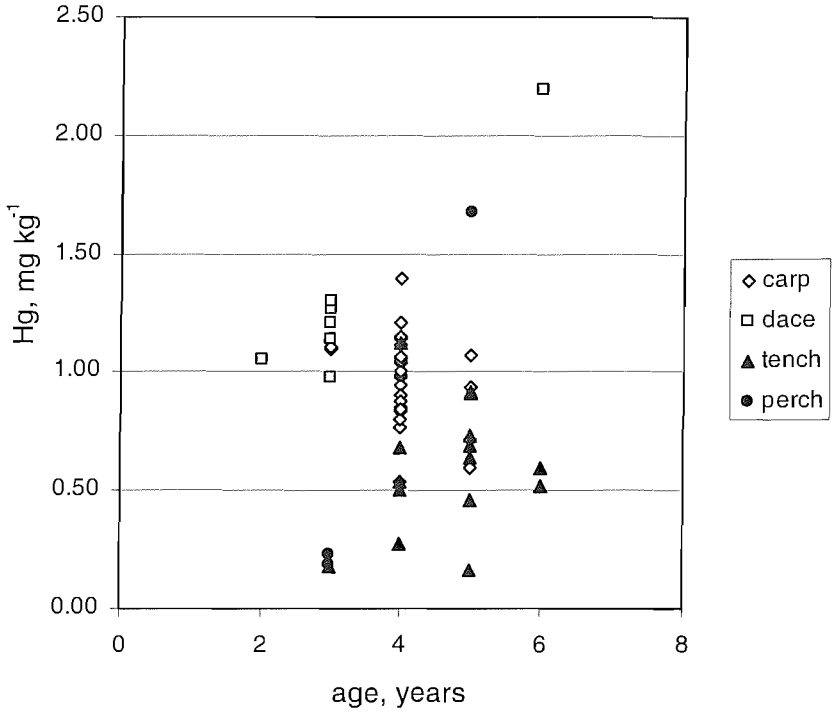
Table 1. Fish species encountered in the investigated water bodies, their feeding habits and approximate trophic position in the aquatic food web

Common name	Scientific name & Family		Feeding strategy[†]	TL[†]	Occurrence
Prussian carp	*Carassius gibelio*	*C*	Herbivore/omnivore. Feeds on aquatic plants, insects, insect larvae, bottom invertebrates, algae.	2.2 – 2.8 (2.5±0.1)	L. Balkyldak
Siberian dace	*Leuciscus baicalensis*	*C*	Herbivore/omnivore. Feeds on insect larvae, terrestrial insects, cladocerans, copepods, algae and higher aquatic plants.	2.2 – 2.8	L. Balkyldak
Tench	*Tinca tinca*	*C*	Omnivore/carnivore. Feeds on bottom invertebrates and aquatic insect larvae; young also feed on algae. In winter, it stays in the mud without feeding itself.	3.5 – 3.8	L. Balkyldak
River perch	*Perca fluviatilis*	*P*	Piscivore. Juveniles feed on zooplankton, bottom invertebrate fauna and other perch fry, adults feed on invertebrates and fish.	3.2 – 4.4 (3.6±0.2)	L. Balkyldak, River Irtysh
Pikeperch	*Lucioperca lucioperca*	*P*	Piscivore. Adults feed largely on other fish.	3.3 – 4.3 (3.9±0.1)	River Irtysh
Northern Pike	*Esox lucius*	*E*	Piscivore. Adults feed mainly on fish, also feed heavily on frogs and crayfish. Cannibalistic as juveniles.	3.8 – 4.5 (4.4±0.1)	River Irtysh

[†]Source: Froese and Pauly (2006). TL=trophic level, ranges were estimated from diet data. Values in brackets denote means±SE.
Family: *C=Cyprinidae, P=Percidae, E=Esocidae.*

Mercury concentrations in carp (*Carassius gibelio*), the most frequently encountered fish species in the lake, ranged from 0.54 to 1.39 mg kg^{-1}, with a mean of 0.96 mg kg^{-1}. These concentrations represent very high levels of contamination for a bottom feeder. We do not have background data on Hg concentrations in carp in Kazakhstan, but in various studies in the U.S. that were based mainly on data from uncontaminated sites, mean Hg concentrations in carp ranged from 0.05 to 0.11 mg kg^{-1} (U.S. EPA, 1997; U.S. EPA, 2001b after Bahnick et al., 1994). Higher Hg levels were reported for carp from contaminated rivers and reservoirs in Siberia and the Czech Republic (Koval et al., 1999; Svobodova et al., 1999; Rehulka, 2002). In slightly impacted Czech water reservoirs, mean Hg concentrations for 5-6 year old carp (*Carassius auratus*) were 0.219 mg kg^{-1} compared to 0.153 mg kg^{-1} at relatively unpolluted control sites (Svobodova et al. (1999), for example, and Hg levels between 0.08 and 4.2 mg kg^{-1} (mean 1.0 mg kg^{-1}) were reported for unaged *Carassius auratus* near the Usolie-Sibirskoe chlor-alkali plant on the Angara River (Koval et al., 1999). Raldua and Pedrocchi (1996) found that Hg concentrations in common carp (*Cyprinus carpio*) collected from two rivers downstream of a chloralkali-plant in NE Spain ranged between 0.30-1.36 mg kg^{-1} (GM 0.74 mg kg^{-1}) and 1.05-2.59 mg kg^{-1} (GM 1.44 mg kg^{-1}), respectively. Mercury concentrations in carp from Lake Balkyldak are similar to Hg levels determined in carp at these chlor-alkali contaminated sites (Raldua and Pedrocchi, 1996; Koval et al., 1999). However, in both the Russian and the Spanish study, Hg levels in water were <0.1 μg L^{-1} and mean Hg concentrations in sediments were ≤3 mg kg^{-1}, i.e. much lower than Hg concentrations measured by us in sediments and water from Lake Balkyldak (cf. part I of this paper).

(a)



(b)

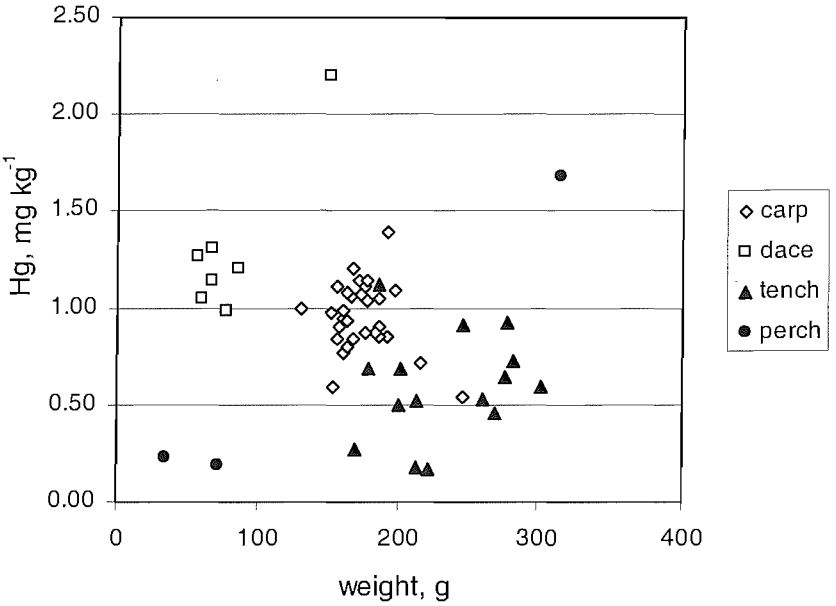


Fig. 1 a and b. Mercury concentrations in fish caught from Lake Balkyldak in relation to fish age and weight.

Mercury concentrations in dace (*Leuciscus baicalensis*) from Lake Balkyldak (Table 2) are similar to levels reported by Koval et al. (1999) for the Angara River near Usolie-Sibirskoe (1.5-2.2 mg kg^{-1}, mean 1.77 mg kg^{-1}, n=3), while Hg levels in tench (*Tinca tinca*) are significantly higher than levels in tench (0.163-0.217 mg kg^{-1}, age 5-8, n=3) from a slightly impacted water reservoir in the Czech Republic (Rehulka, 2002). Interspecies comparisons indicate that Hg is accumulated to different degrees by the four fish species (Fig. 1ab). We found that dace had significantly more Hg in their tissue than carp (mean 1.31 mg kg^{-1} vs. 0.96 mg kg^{-1}), and both dace and carp accumulated significantly more Hg than tench (mean 0.59 mg kg^{-1}). The comparison is not straightforward, however, because the sampled fish species also differed in their age and size distribution. Dace, although on average 30-35% younger and smaller than tench, had about twice as much Hg in their tissue. Dace also had higher tissue Hg concentrations than carp, who were on average ~50% older and had more than twice the weight of dace. Tench was on average 15% older and 34% heavier than carp. Some of the observed differences in bioaccumulation may be attributable to growth dilution with increasing age, as dace were younger than carp and particularly tench (Table 2). However, mean Hg concentrations for carp at age 4 years (0.96 mg kg^{-1}, n=24) and tench at age 4 years (0.62 mg kg^{-1}, n=5) were also significantly different ($p<0.05$), and there was no trend of diminishing Hg concentrations with increasing age in any of the investigated species. Growth dilution effects are therefore more likely to be connected with interspecific differences in growth rates. Our data indicates that Hg is accumulated in the order dace > carp > tench, i.e. in inverse order to their observed growth rates (dace had the lowest body weight at any given age, tench the highest). Data from other studies that found higher mean Hg concentrations in dace than in carp (Koval et al., 1999) and in carp compared to tench (Rehulka, 2002) would appear to be in agreement with this, although in both cases the sample size was rather small. Apart from interspecific differences in growth rates, the different net Hg bioaccumulation rates are also likely to reflect differences in feeding strategies, varying degrees of sediment ingestion, and different MeHg assimilation efficiencies (Bowles et al., 2001; and others). It is well known that the Hg content of aquatic organisms generally increases with increasing level in the food chain (Becker and Bigham, 1995; Boudou and Ribeyre, 1997; Watras et al., 1998; Mason et al., 2000; Bowles et al., 2001). Carp and tench are both omnivorous bottom feeders, but tench occupies a slightly higher trophic level in the aquatic food web and would thus be expected to contain comparatively more Hg in their tissue (Table 1). However, tench stays dormant in the mud in the winter without feeding itself, which may partly explain the lower Hg concentrations found in tench in this study. Furthermore, several studies have found that inorganic Hg decreased with increasing trophic level, whereas only the percentage/proportion present as MeHg increased (Watras et al., 1998; Mason et al., 2000).

Table 2. Summary data on age, weight, length and Hg content of fish caught from Lake Balkyldak and the River Irtysh, including oxbow lakes

	n	age (years)		weight (g)		length (mm)		Hg (mg kg^{-1})		
		range	mean	range	mean	range	mean	range	mean±SE	med
Lake Balkyldak										
Carp	30	3-5	4.1	130-246	174	153-189	171	0.54-1.39	0.96±0.03	0.96
Dace	7	2-6	3.3	57-151	81	143-203	161	0.98-2.20	1.31±0.16	1.21
Tench	15	3-6	4.7	169-302	233	180-230	205	0.16-1.12	0.59±0.07	0.59
River Perch	3	3-5	3.7	35-316	141	125-235	173	0.19-1.68	0.70±0.49	0.23
TOTAL	55	2-6	4.1	35-316	177	115-235	179	0.16-2.20	0.89±0.05	0.91
River Irtysh										
Pike[†]	22	1-2	1.8	39-640	346	165-410	312	0.091-0.159	0.117±0.004	0.110
Pikeperch	3	2-4	3	150/170[‡]		235-345	273	0.113-0.115	0.114±0.001	0.114
River Perch[†]	5	4-5	4.4	88-185	120	160-210	176	0.075-0.125	0.091±0.009	0.085
TOTAL	30	1-5	2.4	39-640	294	160-410	286	0.075-0.159	0.112±0.004	0.110

n – number of specimens; length (mm) – given values represent the length of the fish without the caudal fin

[†] mostly caught from oxbow lakes of the river

[‡] weight info lost for one specimen

Mercury levels in fish are usually the highest in predatory fish species such as pike and perch (e.g. Grieb et al, 1990; Raldua and Pedrocchi, 1996; Koval et al., 1999; Svobodova et al., 1999; Rehulka, 2002). However, for perch (*Perca fluviatilis*) from Lake Balkyldak there was too little data to make meaningful comparisons with the other fish species in the lake (n=3). Increasing levels of Hg are generally noted in perch with increasing age, weight and/or length (e.g. Grieb et al, 1990; Haines et al., 1992; Driscoll et al., 1994; Szefer et al., 2003). In Lake Balkyldak, Hg concentrations in muscle tissue were 0.19 and 0.23 mg kg^{-1} for three year old perch (n=2) and 1.68 mg kg^{-1} for five year old perch (n=1). The high Hg concentration in the oldest specimen most likely reflects a dietary shift to piscivory with increasing age, as previously reported for yellow perch (*Perca flavescens*) above 200 mm length in the Adirondack lakes (Driscoll et al., 1994). Mercury concentrations in perch from Lake Balkyldak appear to be similar to levels detected at other Hg-impacted sites, e.g. in a Czech drinking water reservoir (Rehulka, 2002) and in rivers downstream of chlor-alkali plants (Koval et al., 1999; Zlabek et al., 2005).

Preliminary studies on aquatic ecosystem health were carried out by local investigators following our survey of fish Hg concentrations. A survey of the biological characteristics of dace (n=34, 14 females and 20 males) in August 2002 revealed that despite their high Hg content, dace from Lake Balkyldak appear to be of good nutritional status and display a normal growth rate. However, disturbances in reproductive ability were noted, and >75% of females were carrying unreleased eggs in the middle of August, whereas spawning typically takes place in April/May, or at the latest by the end of June (S.S. Galushak, unpublished data). For carp, there appeared to be a reduction in growth rates with increasing age (V.A. Skakun, unpublished data). Signs of mutagenesis (phenodeviants) were also noted, and the proportion of males to females was highly skewed (1:15).

Mercury concentrations in fish caught from Lake Balkyldak are much higher than Hg concentrations in fish from the Irtysh (Table 2). However, the only species that can be compared directly due to its occurrence in both ecosystems is river perch (*Perca fluviatilis*). Mercury concentrations in perch from Lake Balkyldak (0.19-1.68 mg kg^{-1}, age 3-5, n=3) appear to be significantly higher than in perch from the Irtysh (0.075-0.125 mg kg^{-1}, age 4-5, n=5), however not enough fish were collected to allow statistically meaningful comparisons to be made.

3.1.2 River Irtysh

Fish from the River Irtysh and its oxbow lakes contained significantly less Hg in their tissue than fish from Lake Balkyldak (Table 2). Most fish were caught from the Irtysh oxbow lakes close to Pavlodarskoye village. At the time of the spring flood, the oxbow lakes are connected with the river, before progressively drying up over the summer. Mercury concentrations in fish

caught from the Irtysh side channel and the oxbow lakes are therefore not expected to differ significantly.

Fish length and weight were well correlated for both pike ($r=0.966$, $p<0.001$) and perch ($r=0.994$, $p<0.001$). In contrast to fish caught from Lake Balkyldak, Hg concentrations in fish tissue were significantly correlated with length (measured without the caudal fin, $r=0.560$ at $p<0.002$) and weight ($r=0.515$, $p<0.005$) for all fish irrespective of the species. Because of the strong covariation of the Hg content with fish weight and length, interspecies comparisons have to be made between fish of similar size.

Pike is a predator at the top of the aquatic food chain and is a sensitive indicator of aquatic Hg contamination. Because pike are already piscivorous as juveniles, they are able to accumulate substantial amounts of Hg, and increasing tissue Hg concentrations are commonly found with increasing age, weight or length of the fish (Grieb et al, 1990; Lodenius, 1991; Rask and Metsala, 1991; Rehulka, 2001). Pike are also known to be cannibalistic, and we found a small pike (40 g, 165 mm, 94.3 mg Hg kg^{-1}) in the stomach of a larger specimen (635 g, 410 mm, 117.3 mg Hg kg^{-1}). Overall, Hg concentrations in pike ranged from 0.091-0.159 mg kg^{-1} ($n=22$) and were significantly correlated with both weight and length ($r=0.433$ and $r=0.442$ at $p<0.05$).

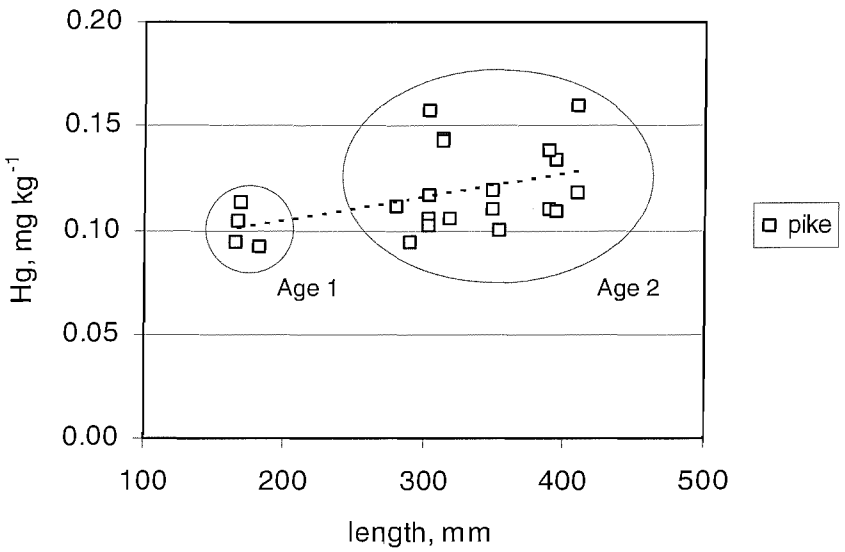


Fig. 2. Mercury concentrations in one and two-year-old pike from the Irtysh side channel and oxbow lakes ($r=0.442$, $p<0.05$).

Fig. 2 illustrates the variation in Hg concentrations with increasing body size (length without caudal fin) for one and two year old pike from the Irtysh. Details on the observed means and ranges of Hg concentrations, body weight and length for the two age groups are given in Table

3. Despite the small sample size, it was evident that Hg concentrations in 2-year-old pike were significantly higher than in 1-year-old pike ($p<0.05$). Nevertheless, pike from the Irtysh can be considered as uncontaminated compared to background concentrations in other geographic regions. For example, Grieb et al. (1990) reported similar albeit slightly higher concentrations for pike from non-impacted lakes in northern Michigan and Wisconsin: Hg concentrations ranged from 0.07-0.41 mg kg^{-1}, with 0.08 mg kg^{-1} in year-1 pike (n=1) and a mean of 0.23 mg kg^{-1} in 2-year-old pike (n=16). Overall mean Hg concentrations in northern pike from 43 U.S. states were 0.36 mg kg^{-1} (U.S. EPA, 2001b after NLFWA 2001). Mercury concentrations in pike from the Irtysh are also considerably lower than Hg concentrations for similar age/size fish from Finnish forest lakes and a Czech drinking water reservoir (Rask and Metsala, 1991; Rehulka, 2002). For comparison, on rivers directly impacted by chlor-alkali plants, Hg concentrations in pike ranging from 1.20-2.87 mg kg^{-1} have been observed (Raldua and Pedrocchi, 1996).

Table 3. Mercury concentrations observed in different age classes of pike (*Esox lucius*) from the River Irtysh

		Hg concentration (mg kg^{-1})			weight (g)		length* (mm)	
	n	mean±SE	med	range	mean±SE	range	mean±SE	range
Y1 pike	4	0.101±0.005	0.099	0.091-0.113	43±2.5	39-50	171±3.8	165-182
Y2 pike	18	0.120±0.005	0.114	0.094-0.159	413±36.8	235-640	344±10.5	280-410

*measured without the caudal fin

Mercury concentrations in perch from the Irtysh ranged between 0.075 and 0.125 mg kg^{-1} and do not appear to be elevated beyond natural levels (Table 2). For example, they are similar to or lower than average levels of 0.1 – 0.3 mg kg^{-1} reported for perch in undisturbed Russian lakes (Haines et al., 1992 and 1995), in Swedish lakes (Sonesten, 2003), and in Baltic coastal waters (Szefer et al. 2003). In the U.S., perch and other predatory fish had mean tissue Hg levels between 0.12 and 0.52 mg kg^{-1} (U.S. EPA, 1997; U.S. EPA, 2001b after Bahnick et al., 1994, Kidwell et al., 1995, NESCAUM 1998, and NLFWA 2001). Average Hg concentrations in 3 to 6 year old yellow perch (*Perca flavescens*) from lakes in upper Michigan and Wisconsin were more than twice as high as levels in perch from the Irtysh, ranging between 0.20 and 0.28 mg kg^{-1} (Grieb et al., 1990).

Pike generally have higher Hg concentrations in their tissue than perch as they are top level predators. For example, Grieb et al. (1990) investigated Hg levels in fish from 35 lakes in upper Michigan and Wisconsin and found that pike had higher mean Hg concentrations than perch when the same age classes were compared. Average Hg concentrations in pike from the Irtysh

are also significantly higher than Hg levels in perch ($p<0.05$), despite the pike being much younger, but the two species cannot be compared directly as the captured fish were not in the same size and age range (Table 2). The mean body weight of pike was almost three times higher than for perch, and due to the small sample size for perch, mean Hg concentrations in pike and perch are not significantly different when either fish length or weight are factored out in a covariance analysis.

3.1.3 Bioaccumulation factors

The accumulation of Hg by aquatic biota is influenced by a large range of factors that can directly or indirectly affect Hg uptake rates, such as water chemistry, pH, DOC, and temperature, as well as by species-specific differences in MeHg assimilation efficiencies, growth rates, feeding habits, and trophic position in the aquatic food web (Grieb et al., 1990; Haines et al., 1992 and 1995; Watras et al., 1995 and 1998; Bowles et al., 2001; Paller et al., 2004). Many of these factors are interlinked, and most are likely to be site specific. Bioaccumulation factors are ratios relating aqueous Hg concentrations to Hg concentrations in biota, and provide a measure of the magnitude of Hg bioconcentration in a particular aquatic ecosystem. Species-specific bioaccumulation factors (BAFs) for Lake Balkyldak and the river Irtysh were calculated according to the formula

$\mathrm{BAF} = \frac{C_t}{C_w}$ where C_t is the concentration of Hg in the wet tissue and C_w is the concentration of Hg in water. For Lake Balkyldak, the average aqueous THg concentration of 0.14 $\mu g\ L^{-1}$ determined in unfiltered water samples from the less contaminated northern part of the lake was used, which was considered to be more representative of the lake as a whole than the overall mean and median concentrations of 0.38 and 0.23 $\mu g\ L^{-1}$ (cf. part I of this paper). In the case of the Irtysh, the average measured aqueous THg concentration of 4.2 $ng\ L^{-1}$ was used for the oxbow lakes, and a mean Hg concentration equal to half the detection limit (1 $ng\ L^{-1}$) was assumed for the side channel.

Table 4 illustrates the calculated BAF values for fish from Lake Balkyldak. Overall, log BAF values for THg varied from 3.06 to 4.20 and were the lowest for tench, and the highest for dace. For the Irtysh, log THg-BAF values ranged from 5.04 to 5.16 for the side channel, and from 4.25 to 4.58 for the oxbow lakes. The higher BAF values obtained for the side channel compared to the oxbow lakes are purely the result of the lower aqueous Hg concentrations for the river, however, and Hg concentrations in fish from the two locations do not differ significantly.

It should also be noted that whenever unfiltered THg concentrations are used for the calculation of BAFs, as is the case here, this is likely to result in an underestimation of the 'true'

Table 4. Estimated site-specific bioaccumulation factors (BAF, $L \cdot kg^{-1}$) for fish from Lake Balkyldak, the River Irtysh and oxbow lakes. LogBAF values are also given in brackets, to facilitate comparison with other studies.

		THg BAF			MeHg BAF		
	n	GM	GSD	range	GM	GSD	range
Lake Balkyldak							
carp	30	6.7×10^3 (3.83)	1.22 (1.02)	$3.8 \times 10^3 - 9.9 \times 10^3$ (3.58 – 4.00)	9.2×10^4 (4.96)	1.22 (1.02)	$5.3 \times 10^4 - 1.4 \times 10^5$ (4.72 – 5.14)
dace	7	9.0×10^3 (3.95)	1.28 (1.03)	$7.0 \times 10^3 - 1.6 \times 10^4$ (3.85 – 4.20)	1.2×10^5 (5.09)	1.28 (1.02)	$9.6 \times 10^4 - 2.2 \times 10^5$ (4.98 – 5.33)
tench	15	3.7×10^3 (3.56)	1.73 (1.07)	$1.2 \times 10^3 - 8.0 \times 10^3$ (3.06 – 3.90)	1.2×10^5 (5.06)	1.73 (1.05)	$3.6 \times 10^4 - 2.5 \times 10^5$ (4.56 – 5.40)
perch	3	–	–	$1.4 \times 10^3 - 1.2 \times 10^4$ (3.13 – 4.08)	–	–	$4.2 \times 10^4 - 3.7 \times 10^5$ (4.63 – 5.57)
River Irtysh side channel							
pike	2	–	–	1.1×10^5 / 1.4×10^5 (5.04 / 5.16)	–	–	7.9×10^6 / 1.0×10^7 (6.90 / 7.01)
pikeperch	3	–	–	1.1×10^5 (5.05 – 5.06)	–	–	$8.1 \times 10^6 - 8.2 \times 10^6$ (6.91)
oxbow lakes							
pike	20	2.7×10^4 (4.43)	1.17 (1.02)	$2.1 \times 10^4 - 3.8 \times 10^4$ (4.34 – 4.58)	8.5×10^5 (5.93)	1.17 (1.01)	$6.8 \times 10^5 - 1.2 \times 10^6$ (5.83 – 6.07)
perch	5	2.1×10^4 (4.33)	1.19 (1.02)	$1.8 \times 10^4 - 3.0 \times 10^4$ (4.25 – 4.47)	6.6×10^5 (5.82)	1.19 (1.01)	$5.6 \times 10^5 - 9.3 \times 10^5$ (5.75 – 5.97)

Notes: Means were not computed if the sample size was less than 5. EPA Draft National MeHg-BAFs for trophic levels 2 to 4 (combined values for lentic and lotic ecosystems) are BAF_2: 1.2×10^5, BAF_3: 6.8×10^5, BAF_4: 2.7×10^6 (U.S. EPA, 2001a).

BAFs, since not all of the aqueous THg can be deemed to be available for uptake by aquatic biota. Southworth et al. (2004) found that BAFs based on unfiltered THg concentrations were highly variable and decreased with increasing THg concentration, which they attributed mainly to a reduction in the ratio of aqueous MeHg to THg with increasing THg. BAFs based on THg are therefore lower for contaminated systems than for uncontaminated waters.

BAFs based on measured MeHg concentrations are less variable and are independent of THg (Southworth et al., 2004), and are generally preferred. However, as we did not determine MeHg concentrations in this study, we could only make a relatively crude estimation of MeHg-BAFs, based on measured THg concentrations and published conversion factors for MeHg in water and fish tissue. The U.S.EPA recently published draft national BAFs for MeHg for each trophic level of the aquatic food chain, based on empirical field data collected mostly from non point source-impacted sites (U.S. EPA, 2001a). We converted THg concentrations measured in water and fish tissue to tentative MeHg concentrations using the same methodology as applied by the EPA in deriving the draft national MeHg-BAFs: For trophic level 2 fish (carp and dace) from Lake Balkyldak, the conversion factor of 0.44 applicable to lentic aquatic systems was used, i.e. it was assumed that 44% of the Hg in fish tissue was MeHg. For fish at trophic levels 3 and 4 (tench, perch, pikeperch, and pike), all Hg was considered to be present in the MeHg form. Mercury concentrations in water were converted to tentative MeHg concentrations using a translation factor of 0.032 for lentic ecosystems (Lake Balkyldak and Irtysh oxbow lakes), and a factor of 0.014 for lotic ecosystems (Irtysh side channel). Estimated MeHg-BAFs are listed in Table 4, together with the THg-BAFs. In accordance with other studies, the estimated MeHg-BAFs were 1-2 orders of magnitude higher than those based on THg (Mason et al., 2000; Southworth et al., 2004). The mean estimated MeHg-BAF for dace is in line with the draft criterion value published by the EPA for trophic level 2 fish (1.2×10^5). The estimated MeHg-BAF for carp (9.2×10^4) is somewhat lower than this, but is in good agreement with the directly measured BAF_2 for lentic ecosystems of 8.6×10^4 established in the same study (U.S. EPA, 2001a). To achieve an MeHg-BAF of 1.2×10^5 for carp, a MeHg content of 55-60% would have had to be assumed.

Becker and Bigham (1995) observed unusually high log MeHg-BAF of ~6.2 for benthivores such as carp (*Cyprinus carpio*) from Onondaga Lake, despite major Hg inputs from the chloralkali industry having ceased 25 years earlier. This is presumably due to a combination of high residual tissue Hg concentrations in the fish and comparatively low aqueous Hg and MeHg concentrations in this system, and illustrates the highly site-specific nature of Hg bioaccumulation. Default BAFs whilst being a useful guide are therefore of limited usefulness, and field-measured site-specific BAFs based on local data should be obtained whenever possible. Furthermore, Southworth et al. (2004) cautioned that in highly contaminated systems, aqueous MeHg concentrations may be significantly lower than in uncontaminated waters,

therefore the application of default values for %MeHg as in the EPA methodology may overestimate aqueous MeHg concentrations in highly contaminated streams and lead to lower calculated BAFs.

Methyl mercury concentrations, the proportion of total Hg present as MeHg, and MeHg-BAF values generally increase with increasing trophic level (Becker and Bigham, 1995; Watras et al., 1998; Mason et al., 2000; Bowles et al., 2001; U.S.EPA, 2001a). The estimated log MeHg-BAFs for 4-5 year old perch from the Irtysh ranged between 5.75 and 5.97, with a mean of 5.82 ($6.6x10^5$). This is very similar to the default MeHg-BAF of $6.8x10^5$ (log BAF 5.83) suggested by the EPA for trophic level 3 fish (U.S. EPA, 2001a), and is also in good agreement with other studies (Bloom et al., 1991; Driscoll et al.; 1994). For example, in the Adirondack lakes, log MeHg-BAF values for age 3+ to 5+ yellow perch (*Perca flavescens*) which occupies a similar trophic level to river perch ranged from 5.73 to 7.03 (Driscoll et al., 1994). Average log BAF for MeHg in non-impacted Wisconsin lakes were 6.0 to 6.5 for yearling yellow perch (Bloom et al., 1991).

Estimated log MeHg-BAFs for pike from the Irtysh ranged from 5.83 to 7.01, with a mean of 6.02. This is similar, although slightly lower than the EPA default MeHg-BAF for trophic level 4 fish ($2.7x10^6$, log BAF 6.4), probably due to the fact that only one and two year old pike were sampled in our study (U.S. EPA, 2001a). Bowles et al. (2001) reported very similar log MeHg-BAF values of 5.84-7.25 for piscivores in a tropical lake system with average Hg concentrations in water and surface sediments that are almost the same as Hg concentrations in the Irtysh (1.42 ng L^{-1} and ~0.1 mg kg^{-1}, respectively).

3.1.4 Risk

The frequency distribution of Hg concentrations in fish caught from Lake Balkyldak is shown in Fig. 3. The maximum permissible concentration of Hg in freshwater fish in Kazakhstan is 0.3 mg kg^{-1} (w.w.) and a maximum level of 0.6 mg kg^{-1} applies for predatory fish. However, the allowable residue concentration in fish intended for human consumption is 0.5 mg kg^{-1}. The same value is in force for fishery products marketed in Europe, with the exception of certain long-lived predatory species such as pike for which a limit value of 1 mg kg^{-1} is applicable (European Commission, 2005).

It is generally accepted that the consumption of contaminated fish is the main route of exposure to MeHg for humans (e.g. Clarkson et al., 2003). Maximum intake values have therefore been suggested to protect human health (U.S. EPA 2001a,b; JEFCA, 2003). The Joint FAO/WHO Expert Committee on Food Additives recommends a provisional tolerable weekly intake (PTWI) for MeHg of 1.6 μg per kg body weight per week (JEFCA, 2003). On the basis of studies showing possible neurodevelopmental effects, the U.S.EPA recommends a stricter oral reference dose (RfD) of 0.1 μg per kg b.w. per day, and a fish tissue residue criterion of 0.3

mg MeHg kg^{-1} fish (U.S. EPA, 2001a). U.S.EPA also recommends that the assumption be made that all Hg is present as MeHg in order to be most protective of human health (U.S. EPA, 2001b). If the 0.3 mg kg^{-1} criterion is applied to our results and assuming that 100% of the Hg is MeHg, only 5 of the 55 fish caught from Lake Balkyldak can be considered fit for human consumption (3 tench and two young perch), whilst 91% of the fish exceed the permissible level. On the other hand, all 31 specimens of fish caught from the River Irtysh and floodplain oxbow lakes are well below this value.

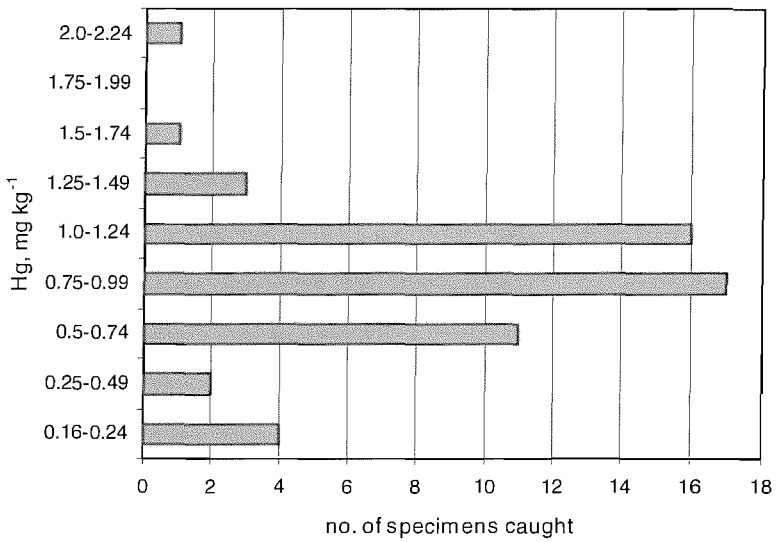


Fig. 3. Frequency distribution of Hg concentrations in fish caught from Lake Balkyldak. (Dotted line indicates the maximum acceptable level of Hg in fish intended for human consumption that applies in Kazakhstan and the EU.)

Using the above criteria, U.S.EPA has calculated consumption limits for fish, defined as the number of allowable fish meals per month based on MeHg concentrations in fish tissue (U.S. EPA, 2001b). The risk based consumption limit for fish tissue concentrations between 0.48 – 0.97 mg kg^{-1} MeHg (w.w.) which would apply to the majority of fish from Lake Balkyldak is one fish meal per month. However, the calculations are based on a consumer adult body weight of 70 kg and may thus not be sufficiently protective of children. Considering that due to the contamination history of the lake, toxic substances other than Hg are also likely to be present in the fish tissue, it would be prudent not to consume any fish from the lake at all.

3.2 Soils

Atmospheric emissions from chlor-alkali plants are important sources of Hg to soils (Wallin, 1976; Biester et al., 2002). Mercury levels in soils usually decline rapidly with increasing distance from the industry, however (Shaw and Panigrahi, 1987; Biester et al., 2002). We found

that Hg concentrations in the 24 soil samples collected in Pavlodarskoye village, located at 4-5 km distance from PCP, ranged between 0.10 and 3.30 mg kg^{-1} (mean 1.04 mg kg^{-1}, median 0.90 mg kg^{-1}). These concentrations are significantly elevated compared to reported regional Hg background concentrations in soils of 0.004 mg kg^{-1} (Kamberov et al.,1999), and represent enrichment factors between 25 and 825 (mean 260, median 225). They are also elevated compared to other published studies of soil contamination near chlor-alkali plants. For example, Shaw and Panigrahi (1987) reported Hg levels in soils of approximately 0.7 mg kg^{-1} at a distance of 2 km from an Indian chlor-alkali plant, and Biester et al. (2002) reported average concentrations between 0.442 and 0.696 mg kg^{-1} within 1 km of three chlor-alkali plants in Europe. In the latter study, enrichment factors calculated from median Hg concentrations (0.157 and 0.571 mg kg^{-1}, respectively) ranged between 2 and 5.8, with a maximum of 56. It is possible that apart from atmospheric Hg emissions, the soils in Pavlodarskoye also received additional Hg inputs from the application of Hg-containing agricultural pesticides such as Granosan (cf. section 3.3.2 in part I of this publication). About 50% of the soils showed topsoil enrichment, whereas the other 50% showed higher concentrations in the subsoils. Because of this and since garden soils are prone to mixing, it is not meaningful to discuss differences between topsoils and subsoils.

Mercury in soils is typically strongly attached to organic matter (Schuster, 1991; Lodenius, 1994) and is therefore not thought to be readily accumulated by vegetables. The detected Hg concentrations in soils from Pavlodarskoye most likely do not pose a significant risk to human health. Nevertheless, a preliminary risk analysis carried out by our co-workers for the soil contamination pathway indicated that potential health risks to the local population from the consumption of homegrown vegetables and the ingestion of attached soil particles cannot be excluded (Woodruff and Dack, 2004). It is therefore recommended that vegetable uptake be studied further.

3.3 Water

3.3.1 Groundwater

Mercury concentrations in all groundwater samples collected from Pavlodarskoye village were below the limit of detection (5 ng L^{-1}). Groundwater quality is therefore fully compliant with CCME, EU and WHO drinking water standards (1 µg L^{-1}), as well as with Kazakhstan water standards (0.5 µg L^{-1}), and drinking water contamination is currently not a pathway of concern.

3.3.2 Spot sampling of surface waters

Kamberov et al. (1999) noted that Hg concentrations in water-filled depressions and small ponds near PCP can be quite high, despite relatively low Hg concentrations in soils/sediments (e.g. 0.5 μg L^{-1} in surface water and 0.053 mg kg^{-1} in the associated sediment). This is most likely due to contaminated surface runoff from the surrounding soils which are impacted by past atmospheric emissions from PCP. We determined 0.05 and 0.53 μg Hg L^{-1} in two water-filled depressions, and between 0.37 and 3.3 μg Hg L^{-1} in former clay pits (pH 7.5-8.0, 0.4-0.9 g Cl^- L^{-1}). Water samples taken from a deep pond adjacent to the waste lagoons contained between 27.1 and 53.4 μg Hg L^{-1} (pH 8.9, 2 g Cl^- L^{-1}), and water accumulated in one of the lagoons which were uncovered at the time of our investigation contained 46927 μg Hg L^{-1} (pH 10.2, 135 g Cl^- L^{-1}).

Contaminated surface waters pose a risk to cows that are grazing the land around the plant. The upper limit for Hg in livestock drinking water suggested by the FAO is 10 μg L^{-1} (Ayers and Westcot, 1985), but stricter guideline values of 2-3 μg L^{-1} apply in Australia and Canada (CCME). We determined 17.9 μg Hg L^{-1} in unfiltered surface water samples taken from an open ditch between the plant and the lake where cows were drinking. The soils at the watering place were severely disturbed by hooves and additional surface water contamination by transfer of contaminated soil was likely. In an undisturbed area of the same ditch, ~400 m from the habitual watering place, 2.2 μg Hg L^{-1} were determined in the water.

3.4 Plants

Terrestrial plants can accumulate Hg via several routes: through root uptake of dissolved Hg from the soil, by direct absorption of vapor-phase Hg from the atmosphere, and from atmospheric deposition (Stein et al., 1996). Factors affecting root uptake into plants include e.g. soil type, pH, organic content, redox potential, and dissolved metal content (Lodenius, 1994). However, the availability of soil Hg to plants is generally considered to be low, and the absorbed Hg has a tendency to remain in the roots and is not readily translocated to aboveground parts of the plant (Schuster, 1991). Mercury present in the atmosphere or Hg vapor re-emitted from contaminated soils can be absorbed via the stomata (Stein et al., 1996). Similarly to Hg concentrations in soils, Hg levels in plants near chlor-alkali complexes are generally highest near the electrolytic cells and decline rapidly with increasing distance from the industry (Wallin, 1976; Shaw et al., 1986; Gonzalez, 1991; Maserti and Ferrara, 1991).

The soils between PCP and Lake Balkyldak are densely covered with pickleweed (*Salicornia* spp., saltwort). Salicornia is a perennial, leafless plant with short, succulent stems and is a typical salt marsh plant that tolerates arid conditions as well as seasonal flooding. Total Hg concentrations measured by us in the aerial parts of Salicornia and underlying topsoils

within 1 km from PCP are given in Table 5. To our knowledge this is the first time Hg levels in Salicornia are reported in the literature. Plants collected at site 1, located 1 km north-west of PCP, contained slightly less Hg compared to site 2, which was about 650 m further north than site 1 and 500 m further away from the factory, but concentrations were in the same order of magnitude. However, Hg concentrations in the topsoil at site 1 were about 20 times higher than at site 2.

Table 5. Total mercury concentrations in aerial parts of *Salicornia* spp. and underlying soils

			Hg concentration in soils		Hg concentration in plants	
	Location	*n*	mg kg^{-1} (d.w.)	RPD	mg kg^{-1} (d.w.)	RPD
Site 1	1 km NW of plant	2	22.38	2.2%	1.09	7.6%
Site 2	1.5 km NW of plant	2	0.93	4.3%	1.66	9.1%

n, number of samples analysed; RPD, Relative percent difference (precision of duplicate samples)

Unfortunately, no data on background concentrations of Hg in Salicornia is available, but the plants have clearly accumulated significant amounts of Hg. Total Hg concentrations in Salicornia are considerably higher than Hg levels found by us in cattail (*Typha angustifolia*) in another Hg-contaminated region in Kazakhstan. Mercury concentrations in cattail leaves ranged from 0.63 mg kg^{-1} in the most polluted section of the river Nura to 0.03 mg kg^{-1} at a distance of ca. 60 km downstream (Ullrich et al., *in preparation*). Mercury concentrations in perennial grasses, wildflowers and other terrestrial plants collected near chlor-alkali complexes in Italy and India ranged from 0.02 to 2.12 mg kg^{-1}, compared to natural background levels of 0.04-0.08 mg kg^{-1} (Shaw et al., 1986; Maserti and Ferrara, 1991). Gonzalez (1991) reported mean Hg concentrations of 2.23 mg kg^{-1} in perennial herbs within ½ km from a Cuban chlor-alkali plant. Background concentrations of 0.03 mg kg^{-1} were reached at 5 km distance.

According to Kazakhstan sanitary norms, maximum allowable levels of Hg are 0.1 mg kg^{-1} for fodder grain and 0.05 mg kg^{-1} for rough and enriched fodder and roots. The European Commission (2002) has proposed a maximum Hg content of 0.1 mg kg^{-1} in feedstuffs intended for animal nutrition with a relative moisture content of 12% (equivalent to 0.11 mg kg^{-1} d.w.), and 0.2 mg kg^{-1} for complementary feedstuffs. From the limited sample size taken by us in the current study, it would appear that Hg concentrations in Salicornia plants exceed maximum allowable levels of Hg in animal feedstuffs by about one order of magnitude.

3.5 Bovine tissue and milk

Between the middle of April and the end of October when there is no stable snow cover, the contaminated land between the factory and the lake is used for grazing cattle herds on a daily basis. Salicornia plants form a major part of the cows' diet. The cows also drink contaminated surface water and are likely to ingest contaminated soil particles together with plants. There is therefore potential for contamination of the agricultural food chain, and human exposure to Hg through the ingestion of contaminated beef products (milk, muscle, liver, kidneys). Shaw and Panigrahi (1986) found that sheep and goats grazing on contaminated soils close to a chlor-alkali plant had accumulated high levels of Hg in their tissues. However, Hg concentrations in plant leaves were higher in that study than the levels measured by us in pickleweed (cf. section 3.4).

Of the three bovine tissues that are commonly analysed (muscle, liver, and kidney), the kidney is considered the best indicator organ for detecting Hg residues, followed by the liver (Stevens, 1992). We determined Hg concentrations in both kidney and liver tissue from a 2-year old cow. The results are given in Table 6 and are consistent with the fact that Hg accumulates preferentially in the kidneys. In all four control samples from south-east Kazakhstan (Almaty), Hg was below the limit of detection. To put our results into context, the available literature data on Hg concentrations in bovine tissue has been summarized in Table 7. Our results for Hg in kidney and liver tissue are in good agreement with values reported for cattle in Belorussia, the Czech Republic, Sweden, and northern Poland (Zarski et al., 1997; Raszyk et al., 1998; Jorhem et al., 1991; Falandysz, 1993). The kidney concentrations are also very similar to values for cattle from a predominantly rural area in NW Spain, but liver tissue concentrations are lower in the Spanish study (López Alonso et al., 2003a,b). Mean Hg concentrations in bovine muscle tissue (data not included in table) generally vary between 0.4 and 11 $\mu g\ kg^{-1}$, but are more typically between 1 and 5 $\mu g\ kg^{-1}$ w.w. (Vreman et al., 1986; Jorhem et al., 1991; Niemi et al., 1991; Falandysz, 1993; Kottferová and Korénekovà, 1995; Zarski et al., 1997; Raszyk et al., 1998; Larsen et al., 2002; López Alonso et al., 2003a; Miranda et al., 2003).

Table 6. Total mercury concentrations in kidney and liver tissue of a 2-year old cow from Pavlodarskoye village

		Hg concentration in tissue samples			Hg in control samples
Tissue type	*n*	$\mu g\ kg^{-1}$ (w.w.)	SE	RPD	$\mu g\ kg^{-1}$ (w.w.)
Kidney	2	10.96	0.55	10.1%	ND
Liver	2	5.74	0.08	2.7%	ND

n, number of samples analysed; RPD, Relative percent difference (precision of duplicate samples); ND, not detected

Table 7. Comparison of literature data on mercury levels in bovine tissue (μg kg^{-1} w.w.)

Kidney			Liver				
n	mean	range	*n*	mean	range	Details	Reference
184	12.2† calves	ND – 89.4	184	0.85† calves	ND – 93.8	rural area in NW Spain (Galicia) with two large coal-fired power plants and other point sources	López Alonso et al. (2003a,b)
56	10.8† cows	ND – 87.4	56	1.01† cows	ND – 26.4		
100	3.40† 8.10 calves	ND – 45.9	100	0.77† 1.67 calves	ND – 27.1	industrial area and mining region in NW Spain (Asturias), no dominant Hg point sources	López Alonso et al. (2003a,b), Miranda et al. (2003)
26	<7 calf	7 – 17	26	<7 calf	<7	Danish Food Monitoring Programme	Larsen et al. (2002)
49	17 ox	7 - 391	24	<7 ox	<7 - 12		
21	12.1		21	8.7		Czech cattle farms	Raszyk et al. (1998)
19	18.1	6.6 – 32.4	19	5.0	1.6 – 9.9	Grodno, Belorussia	Zarski et al. (1997)
10	6.1	5.1 – 13.0	10	1.7	0.5 – 2.1	Bialystok region, Poland	
≥6		31 – 60‡	≥6		8 – 44‡	farms near metallurgical industry, East Slovakia	Kottferová and Koréneková (1995)
292	11	0.49 – 91 8.4 – 12‡	291	4.2	0.22 – 66 3.4 – 4.9‡	cattle in Northern Poland	Falandysz (1993)
100	15		114	12		Finnish cattle	Niemi et al. (1991)
68	10		30	6		Swedish cattle	Jorhem et al. (1991)
2138	20 cattle	ND - 280	2138	10 cattle	ND - 140	Canadian slaughter animals	Salisbury et al. (1991)
209	20 veal	ND - 50	210	10 veal	ND - 20		
9	24 – 79		9	9 – 26		long-term feeding study, daily intake 1.2-3.1 mg Hg (0.2 mg for controls)	Vreman et al. (1986)
6		controls:‡ 5 and 9	6		controls:‡ 3 and 7		

† geometric mean
‡ range of means from several sub-groups
ND – not detected

Simpson et al. (1997) reported kidney Hg concentrations in the range of 58 to 91 mg kg^{-1} w.w. in dairy heifers suffering from acute Hg poisoning. These values are more than three orders of magnitude higher than Hg concentrations determined by us in kidney tissue from the cow from Pavlodarskoye. The Hg contamination around the plant is therefore unlikely to pose a health risk to the cattle themselves. Regulatory limits for Hg in beef products set by some countries vary between 30 and 500 μg kg^{-1} fresh weight for liver and kidney (López Alonso et al., 2003a). The Hg levels we determined in bovine tissue are well below the most stringent criteria. From this very limited data it would therefore appear that the terrestrial pathway is not a significant exposure route compared to the consumption of fish by humans. However, further studies would be advisable to clarify whether there may be an increased risk for individuals who ingest large amounts or frequent meals of beef liver and kidney.

Table 8. Estimated biotransfer factors (BTF) for mercury to bovine liver, kidney and milk

BTF	Liver	Kidney	Milk	Source
daily dose-to-tissue[1)]				
'steady-state'	1.5 x 10^{-2} day kg^{-1}	4.9 x 10^{-2} day kg^{-1}		Stevens (1992)
after 100 days	3.5 x 10^{-3} day kg^{-1}	2.8 x 10^{-2} day kg^{-1}		Crout et al. (2004)
after 1000 days	7.8 x 10^{-3} day kg^{-1}	6.4 x 10^{-2} day kg^{-1}		Crout et al. (2004)
daily dose-to-milk[2)]				
'steady-state'			1.1 x 10^{-5} day L^{-1}	Stevens (1991)
after 100 days			1.3 x 10^{-5} day kg^{-1}	Crout et al. (2004)
after 1000 days			1.9 x 10^{-5} day kg^{-1}	Crout et al. (2004)
feed-to-tissue[3)]				
'steady-state'	3.1 x 10^{-1}	9.9 x 10^{-1}		Stevens (1992)
feed-to-milk[4)]				
'steady-state'			1.7 x 10^{-4} kg L^{-1}	Stevens (1991)

1) ratio of (steady-state) bovine tissue Hg concentration to average daily intake of Hg
2) ratio of (steady-state) bovine milk Hg concentration to average daily intake of Hg
3) ratio of (steady-state) bovine tissue Hg concentration to average feed concentration of Hg
4) ratio of (steady-state) bovine milk Hg concentration to average feed concentration of Hg

Biotransfer factors (BTFs) can be used to relate estimated daily exposure levels or feed levels of chemicals to tissue concentrations. BTFs for Hg in bovine tissue and milk have been estimated from long-term feeding studies and bolus dose experiments (Stevens, 1992; Crout et al., 2004) and are summarized in Table 8. We used these values to make a broad estimate of the average daily oral dose of Hg the cow may have received, and the average Hg feed concentration it may have been exposed to. Using the daily dose-to-tissue BTFs published by Stevens (1992) and Crout et al. (2004) and substituting the Hg concentrations we measured in kidney and liver tissue for the steady-state Hg tissue concentration gives an estimated daily oral dose for the cow ranging between 0.2 and 1.6 mg day^{-1}. Using the steady-state feed-to-tissue BTF published by Stevens (1992), we calculated an estimated average Hg feed concentration of 0.01-0.02 mg kg^{-1}. This is two orders of magnitude lower than the maximum tolerable concentration of 2 mg kg^{-1} dietary Hg recommended for cattle by the National Research Council (NRC, 1980).

Since Hg is capable of translocating into bovine milk, the ingestion of contaminated milk is another potentially important exposure pathway for humans (Stevens 1991). Using the daily dose-to-bovine milk BTFs published by Stevens (1991) and Crout et al. (2004) and substituting our calculated average daily dose of between 0.2 and 1.6 mg day^{-1} indicates that Hg concentrations in cow's milk could be in the order of 2 to 20 ng L^{-1}. Maximum Hg concentrations in cows' milk reported in the literature range from 2.4 to 7 μg kg^{-1} (Vreman et al., 1986; Raszyk et al., 1998; Cerkvenik et al., 2000). Raszyk et al. (1998) reported an average Hg concentration of 0.9 μg kg^{-1} (maximum 3 μg kg^{-1}, n=27) for cows' milk from two cattle farms in the Czech Republic at similar mean kidney Hg levels to the one determined by us. In the Czech study, average Hg concentrations in feed mixtures and bulk fodders were 0.0025 and 0.0115 mg kg^{-1}, respectively, and Hg in drinking water was <0.1 μg L^{-1}. According to the BTFs published by Stevens (1991) and Crout et al. (2004), the corresponding maximum Hg concentrations in cow's milk would be 6.4 and 32 ng L^{-1}, respectively. Real concentrations were two orders of magnitude higher than predicted, however. If this experience is transferred to the calculated concentration range for Hg in cow's milk from Pavlodarskoye, then Hg concentrations in milk could possibly be in the region 0.2 – 2 μg kg^{-1}.

Unfortunately, due to accidental overdilution of the milk samples during the analytical procedure, our detection limit for the determination of Hg in bovine milk was very high (2 μg kg^{-1}), therefore no Hg was detected in any of the 15 milk samples we collected in the village and Hg concentrations in milk could not be established. Maximum residue levels for Hg in cows' milk have not been set in the EU or Kazakhstan, but are 10 μg kg^{-1} in the Czech Republic (Raszyk et al., 1998) and 30 μg kg^{-1} in Slovenia (Cerkvenik et al., 2000). As Hg in cows' milk samples from Pavlodarskoye village was consistently below 2 μg kg^{-1} we would conclude that there does not appear to be a risk for humans from the consumption of milk.

4. Summary and conclusions

Fish collected from Lake Balkyldak were found to be seriously contaminated by Hg and are unfit for human consumption. Total Hg concentrations determined in fish tissue are similar to concentrations detected at other contaminated sites that have been impacted by emissions from the chlor-alkali industry (e.g. Raldua and Pedrocchi, 1996; Koval et al., 1999). Our data indicates that Hg is accumulated in the order dace > carp > tench, i.e. in inverse order to their observed growth rates, however there was not enough data to allow for rigorous statistical modeling. Mercury concentrations in pike, perch and pikeperch from the Irtysh were found to be at background levels.

The consumption of contaminated fish from the lake presents a significant health risk and fishing should be prohibited with immediate effect. Because of the past and present usage of the lake as a wastewater settling pond, the fish are also likely to contain other pollutants, such as

POPs and heavy metals. Unfortunately, in our experience risk communication alone is unlikely to achieve the desired effect of stopping people from fishing in the lake. It may thus become necessary to consider eliminating the current fish population. This could be achieved e.g. by using rotenone, a naturally occurring fish poison that has a short environmental lifetime and is rapidly broken down in water. The use of this substance, although it is widely employed in fisheries management, remains somewhat controversial, however (Rotenone Stewardship Program, 2002).

Further studies are needed to determine the environmental and human health impacts associated with cattle grazing on the contaminated land around the plant and drinking contaminated surface waters. However, Hg levels in a small number of bovine tissue and milk samples were well below regulatory limits and it would appear that the terrestrial pathway is not a significant exposure route compared to the consumption of fish. Mercury uptake from vegetables grown in contaminated soil has not been studied and may warrant further investigation.

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Chapter 4

Mercury distribution and transport in a contaminated river system in Kazakhstan and associated impacts on aquatic biota

ABSTRACT: The River Nura in Central Kazakhstan has been heavily polluted by mercury (Hg) originating from an acetaldehyde plant. A number of studies were undertaken to investigate the transport, fate and bioavailability of Hg in this river system. The sediments within a 20 km section of the river downstream of the effluent outfall canal are highly polluted and are acting as a strong source of surface water contamination. Mercury transport in the river is dominated by the remobilization of contaminated bed sediments and river bank erosion during the annual spring flood. Peak Hg concentrations in unfiltered surface water samples during a larger than usual flood event in 2004 were in the order of 1600 – 4300 ng L^{-1}. The majority of the particulate-bound Hg appears to be sedimented in the shallow Intumak reservoir ~75 km downstream of the source of the pollution, leading to a drop in aqueous Hg concentrations by one order of magnitude. Nevertheless, background concentrations of Hg in surface water are not reached until at least 200 km downstream, and during the flood period Hg is also detected in the terminal wetlands of the river.

Mercury concentrations in sediment cores taken from the river bed in the most contaminated section of the Nura ranged from 9.95 to 306 mg kg^{-1}. Methylmercury (MeHg) levels in shallow sediment cores were highest in surface sediments and ranged between 4.9 and 39 μg kg^{-1}, but were generally less than 0.1% of total Hg (THg). A significant inverse relationship was found between THg concentrations and the percentage of MeHg formed in the sediments, irrespective of the sampling depth. The observed relationship was confirmed by comparison with results from a different river system, indicating that it may be true also for other highly contaminated aquatic systems. We hypothesize that at high THg levels in severely contaminated sediments, the accumulation of MeHg may be limited by increasingly efficient demethylation processes, and that this underlying trend in sediments is the reason why MeHg levels in surface water are often found to be higher at less contaminated sites compared to upstream sites.

Mercury concentrations in biota in the most contaminated section of the river were 15 – 20 times higher than background levels. Fish were found to be impacted for more than 125 km downstream from the source, indicating significant transport of dissolved MeHg to downstream areas and/or in-situ MeHg production in less contaminated downstream reaches. There were also indications that impoundments may increase the bioavailability of Hg.

1. Introduction

The 978 km long River Nura is the main river of the central Kazakhstan plain, an area of some 200 000 km^2 that is rich in mineral and coal resources but lacks water resources for industrial and agricultural development (Tanton et al., 2001). The river rises in the mountainous terrain in the east of the country and flows westward through the heavily industrialised Karaganda region, before entering the terminal lakes of the internationally important Kurgaldzhino nature reserve (Fig. 1). A severe case of mercury (Hg) pollution occurred at the city of Temirtau,

approximately 20 km west of Karaganda. A chemical plant similar to the infamous Chisso plant at Minamata in Japan (D'Itri, 1991; Kudo and Miyahara, 1991; Fujiki and Tajima, 1992) operated in Temirtau for more than 40 years, using mercuric sulphate as a catalyst for the production of acetaldehyde and discharging untreated and partially treated wastewater to the Nura. More than 150 t of Hg are thought to have entered the river since the 1950s, most likely in dissolved and elemental form (Yanin, 1997). Mercury emissions have mostly ceased since the closure of the plant in 1997, but the river sediments and floodplain downstream of Temirtau are highly contaminated (Heaven et al. 2000a,b). About 300 km downstream of Temirtau lies the new capital city Astana, with a rapidly expanding population and increasing water demand. A link canal between the Nura and the smaller Ishim river is intended to supply additional water to Astana, although some concerns remain over the upstream Hg contamination. About 150 km south west of Astana, the Nura discharges into the Kurgaldzhino wetlands and Lake Tengiz, one of the most important wetland sites in Central Asia which is currently being considered as a UNESCO World Heritage Site.

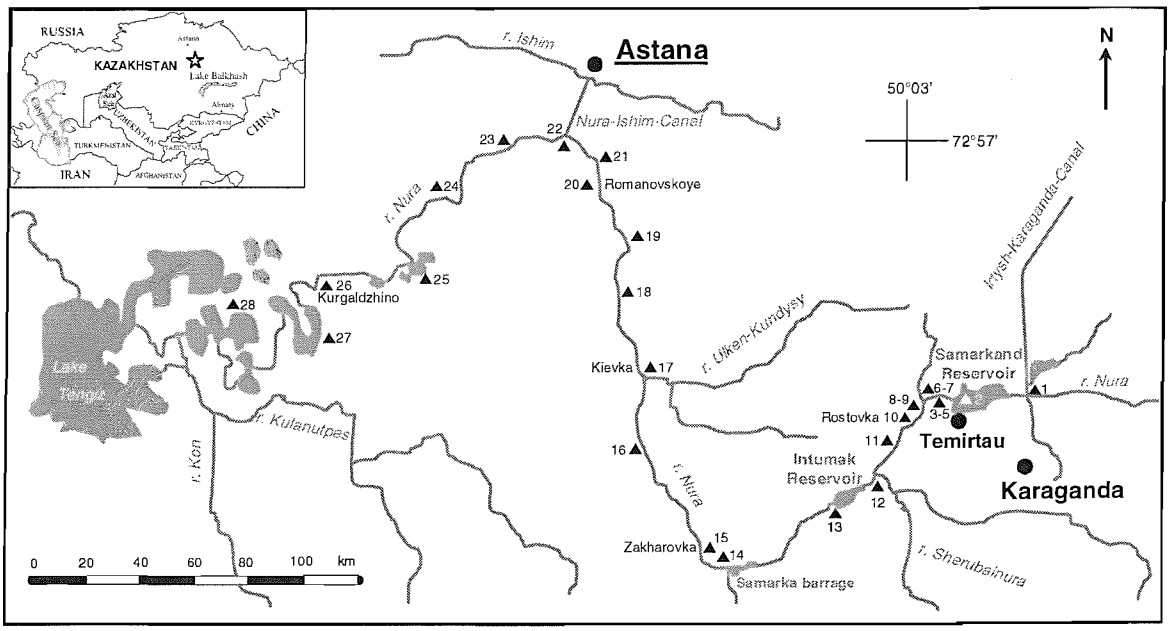

Fig. 1. Map showing the geographic location of the study site within Kazakhstan and the location of water sampling points along the river Nura. The 200 km upstream section of the river is not shown.

Mercury is a persistent, bioaccumulative, and toxic pollutant (USEPA, 1997; UNEP, 2002). Inorganic Hg that is discharged into aquatic systems is mostly incorporated into sediments, owing to its high affinity to particulate matter (Mason et al., 1993; Coquery et al., 1997; Le Roux et al., 2001). However, although sediments generally act as an efficient sink for Hg, they can also be a source of Hg species and particularly methylmercury (MeHg) to the water column

(Covelli et al., 1999; Gill et al., 1999; Mason et al., 1999; Hines et al., 2000; Faganeli et al., 2002; Macleod et al., 2005; Merritt and Amirbahman, 2007). Sediment-water partitioning, fluvial transport, and species transformation processes of Hg are controlled by a large number of physical, chemical and biological factors (Parks et al. 1989; Suchanek et al., 1998; Waldron et al. 2000; Ullrich et al., 2001; Bonzongo et al., 2006; Hissler and Probst, 2006). Inorganic Hg in aquatic systems is readily converted to organic MeHg in a process that is thought to be mediated by sulfate-reducing bacteria, and surficial sediments are regarded as the primary sites of microbial MeHg production (Ramlal et al., 1993; Gilmour et al., 1998; Benoit et al., 2003). MeHg is a potent neurotoxin (Clarkson, 1998) that is readily accumulated by aquatic biota and biomagnified along the food chain (Watras and Bloom, 1992; Watras et al., 1998; Mason et al., 2000). Its presence in the aquatic environment can therefore pose risks of reproductive and neurological impairment to piscivorous birds and mammals even at low concentrations (Henny et al., 2002; Scheuhammer et al., 2007). The consumption of contaminated fish is regarded as the main route of exposure for humans to MeHg (Clarkson et al., 2003).

This paper summarizes the results of several field campaigns that were undertaken between 1998 and 2005 to study the transport, fate and bioavailability of Hg in the Nura catchment. While earlier studies focused on the most polluted section of the river, post 2001 surveys covered a more than 500 km long section of the river between an upstream reference point and the terminal wetlands at Kurgaldzhino. We also report here previously unpublished data on MeHg levels in sediments. This is the first time MeHg concentrations have been investigated in this heavily contaminated river system. Mercury levels in biota were also studied, to assess the extent of contamination downstream and identify potential sources of human exposure.

2. Study area

The Nura drains an area of almost 55,000 km^2 and is the main perennial watercourse in the semi-arid steppe of central Kazakhstan. The climate of the region is sharply continental and is characterized by dry, hot summers (mean July temperature +20°C), cold winters (mean January temperature -15°C), and little precipitation (~250 mm per year) which falls mainly as winter snow and spring rains. The river freezes on average for a period of 140-150 days, and a stable ice cover is generally established by the end of November. Because of the climatic conditions, 85-90% of the flow of the Nura occurs as snowmelt in spring, while the summer/autumn period accounts for 10-15% and the winter period for less than 1% of the annual flow volume. Estimated average naturalised flow is 5.9 $m^3 s^{-1}$ just upstream of Temirtau and 19.6 $m^3 s^{-1}$ near Astana, but is subject to significant seasonal and inter-annual fluctuations.

The spring flood usually starts in the first decade of April. Peak discharge is extremely variable and can range from 40 $m^3 s^{-1}$ in upstream reaches to 980 $m^3 s^{-1}$ near Astana. Maximum flows at Temirtau are typically less than 150-200 $m^3 s^{-1}$, but in April 2004 a disproportionately

high discharge of flood water from Samarkand reservoir led to a sudden increase in flow from 5 to 640 $m^3 s^{-1}$, causing the river to break its banks and inundate several villages. During the summer/autumn low-water period between June and October, average flow rises from 1.6 $m^3 s^{-1}$ at the entrance of Samarkand reservoir to 5.9 $m^3 s^{-1}$ at Romanovskoe (~280 km downstream). The lowest water levels are generally recorded at the end of August. During the winter low-water period (November to April), the average discharge is 0.2-1.3 $m^3 s^{-1}$. Because of the strong seasonality of the flow patterns, surface water sampling was undertaken during the spring flood as well as in the summer and winter low-water periods.

There are two major reservoirs on the Nura, Samarkand reservoir in Temirtau and the unfinished Intumak reservoir ~75 km further downstream, as well as a number of smaller dams and barrages. Below Samarkand reservoir, the Nura receives inputs of industrial wastewater from various metallurgical and chemical plants, domestic and agricultural wastewater, and mine waters carried by the Sherubainura, the largest tributary to the Nura which joins the river about 60 km downstream of Temirtau. The main water quality problem is posed by Hg emitted from the former acetaldehyde plant at Temirtau. According to our previous studies, bottom sediments of the river between Temirtau and the Intumak reservoir contain ~10 t of Hg, and more than 110 t of Hg have been deposited in the floodplain and on the river banks at times of flood (Heaven et al. 2000a,b). The predominant vegetation growing on the river banks is narrow-leaf cattail (*Typha angustifolia*). The river strongly meanders and the bed is often branched into two or three channels. There are a lot of backwaters, oxbow lakes and old river beds, and the banks tend to be steep with heights up to 4 m or more. Water enters the flood plain on average once every 3-5 years, in downstream reaches near Astana the land is fully flooded once every 5-6 years.

The Nura terminates in the Tengiz-Kurgaldzhino Lake System, an area comprising up to 50 lakes with varying levels of salinity. Large parts of the wetlands are covered by dense thickets of reed (*Phragmites communis*) and are not easily accessible. The wetlands are of great importance as breeding, moulting and resting grounds for migratory waterfowl. Nearly 300 species of birds have been recorded at Lake Tengiz; many of them are endangered. Breeding species include the Greater Flamingo (*Phoenicopterus ruber*), Dalmatian Pelican (*Pelecanus crispus*) and White-headed Duck (*Oxyura leucocephala*). The area was declared a Zapovednik (State Nature Reserve) and was added to the list of wetlands of international importance by the former Soviet Union in the 1970s and has recently become Kazakhstan's first designated Ramsar site.

3. Materials and methods

3.1 Sampling

Sediments

Two deep sediment cores were taken from the river bed in August 1998 to a depth of 1.5 and 2.5 metres, using purpose-made sediment augers. The sampling sites were located at 600 m and 9.5 km distance from the outfall. Six shallow sediment cores (sampling depth 25 – 30 cm) including one field duplicate core were taken from the effluent outfall canal, the river bed at 1.9 km, 9.4 km and 13 km distance from the outfall, and the head of the Intumak Reservoir, located ~75 km downstream. Additional shallow sediment cores with duplicates were taken in March 2001 at 2.4 km, 8.5 km and 19.7 km distance from the outfall. Shallow sediment cores were taken close to the river bank (0.5 – 1 m) and the distance between duplicate cores was no more than 1– 1.5 m. The cores were collected by pushing acid-cleaned plastic tubes (ø 5 cm) into the sediment until the hard stratum was reached. The sampling tubes were carefully lifted up and closed at both ends with acid-cleaned rubber bungs, placed in a cool-box (4°C), frozen on the same day and shipped to the laboratory. In July 2005, surface sediment samples (0-5 cm layer) were collected in duplicate from 16 locations along the river, focusing on the less contaminated reaches and covering a distance of up to 470 km down to the terminal wetlands. A reference sample was taken ~30 km upstream of Temirtau. Sediment samples were stored frozen in acid-cleaned HDPE bottles until analysis.

Water

Surface water samples were collected between Temirtau and the terminal wetlands (including an upstream reference point) in November 2001, April 2002, August 2002, April 2004 and July 2005. Samples were generally taken from the main river channel by lowering a bathometer fitted with a disposable 1 or 2 litre PET bottle from a bridge, dam, or other accessible structure. The sampler was moved steadily up and down the water column until the bottle was filled. Sampling bottles were rinsed three times with river water before the final sample was collected. Where sampling from a bridge or dam was not possible, samples were taken from the river bank by immersing a sampling bottle into the water to a depth of ~0.5 m. Water from the sampling bottle was transferred into labelled single-use 0.5-litre PET bottles which were rinsed three times with sample beforehand. The suitability of PET bottles for the sampling and storage of waters containing Hg in the low ng L^{-1} range has been demonstrated by Fadini and Jardim (2000) who found no significant difference compared to Teflon. Water samples were generally unfiltered, but in April 2002 additional samples were taken for determination of dissolved and suspended Hg content. In this case, 0.5 l water samples were filtered through 0.45 µm

membrane filters immediately after sampling and the filters were stored in clean zip-lock PE bags. All water samples were taken in duplicate. Clean protocols were adopted to avoid contamination during sample collection, handling and storage, and daily field blanks were included in every sampling campaign to check for potential contamination. Samples were immediately preserved with 0.5% v/v conc. HCl to avoid losses of Hg, double-bagged in clean PE bags, and placed in a cool-box for delivery to the laboratory.

Aquatic plants

Samples of narrow-leaf cattail (*Typha angustifolia*) growing on the river banks were collected in August 1998 between the outfall canal and Intumak Reservoir. Only leaf tips of 5-7 cm length were collected. The samples were combined to give integrated samples for 12 river sections. The approximate length of the river sections was 3 – 6 km within the first 25 km from the outfall; thereafter samples were combined for each 15 km interval. The leaves were put in clean PE bags and dried at room temperature with no direct sunlight. Common reed (*Phragmites communis*) was sampled in the Kurgaldzhino wetlands in June/July 2004. The aboveground biomass was separated into leaf tissue and stem tissue. Plants were rinsed thoroughly first with tap water, then with distilled water. Plant roots were scrubbed clean to remove any adhering particulate matter. Roots and stems were oven dried to constant weight at <70°C, leaves were air dried. All plant samples were pulverized before analysis.

Fish

130 specimens of fish were caught by local fishermen from seven sampling locations between the outfall canal and Sabyndy (~370 km downstream) in April/May 2002. The fish were double-wrapped in clean PE bags, temporarily stored at +4°C in a refrigerator, frozen within 2 days and transported to the laboratory in Almaty for further processing. Twenty additional fish were collected in July 2005, mostly from Gagarinskoye (~9 km downstream of the outfall) and from the terminal lakes. Six specimens were purchased on the local market in Temirtau and were analysed for comparison with the river fish. All fish were identified and their weight, fork length and standard length were recorded. Fish age was estimated from scale samples.

3.2 Analysis

Sediments

Deep sediment cores taken in 1998 were analysed for total Hg in 10 cm layers. Samples were dried at room temperature in the dark to avoid losses of Hg due to evaporation. Shallow sediment cores were kept frozen until analysis. The partially defrosted cores were sectioned into

0-2 cm, 2-5 cm, and thereafter into 5 cm portions, using a stainless steel knife. Shallow cores taken in 1998 were analysed for both total Hg and MeHg.

Total Hg in 1998 and 2001 sediment cores was determined by CV-AAS after acid digestion. Sediment samples (1 g) were digested by hot refluxing in a 1:1 mixture of 30% HNO_3 and 30% H_2SO_4 (Hatch and Ott, 1968; Adeloju et al., 1994). Total Hg was determined on a Perkin-Elmer AAnalyst 100 with mercury hydride system MHS-10, after $NaBH_4$ reduction (MDL 5 ng g^{-1}). No reference materials were available in 1998, but quality assurance included daily instrument calibration, analysis of reagent blanks and duplicate samples. In 2001, accuracy was assessed using the certified reference materials CRM023 and CRM024 (R.T. Corporation, Wyoming, USA). The recovery was 96.4% (n=1) for CRM-023 (certified value 77.78±6.25 mg kg^{-1}) and 101.4% (n=1) for CRM-024 (certified value 0.71±0.05 mg kg^{-1}).

Methylmercury in 1998 sediment cores was determined by capillary gas chromatography with electron capture detection (GC-ECD). Sediment samples (2 g) were treated with 5*M* HCl and extracted with benzene and cysteine acetate solution, following a modified Westöö procedure (Westöö, 1968) adapted from Chiba et al. (1983) and Hintelmann et al. (1997). The estimated MDL was 0.1 ng g^{-1}. Quality assurance included daily calibration with MeHg and EtHg standard solutions, analysis of reagent blanks and duplicate samples, and spike additions of MeHg. Recovery of spiked MeHg was very variable, however, and could not be reliably estimated. This problem was previously noted by Horvat et al. (1990 and 1993) who also found that acid leaching alone was not sufficient to extract MeHg from sediments quantitatively. Since no reference materials were available in Kazakhstan at the time, sub-samples of the top 2 cm sediment layer were analysed at the ESWE Institute for Water Research and Technology in Germany for interlaboratory comparison. MeHg in these samples was determined by microwave digestion, distillation, and aqueous phase ethylation, followed by HPLC separation and ICP-MS detection (Horvat et al., 1993; Wilken et al., 2003). The results were validated with estuarine sediment CRM-580 (Community Bureau of Reference, Brussels; certified value 70.2±3.4 μg kg^{-1}), with an average recovery of 92.4±4.15% (n=3).

Surface sediment samples collected in 2005 were digested in a 3:1 mixture of HCl and HNO_3 (aqua regia) at 95°C (PSA, 1998). After dilution with distilled water, samples were oxidized with BrCl and set aside overnight. Excess bromine was destroyed with hydroxylamine hydrochloride and total Hg was determined by CV-AFS after $SnCl_2$ reduction, with an MDL of 0.002 mg kg^{-1}. Accuracy was assessed using River Sediment NCS DC 78301 (China National Analysis Center for Iron and Steel, Beijing; certified THg content 0.22±0.04 mg kg^{-1}), which gave an average recovery of 94.0±4.18% (n=2). All sediment results are quoted as dry weight concentrations.

Water

Water samples for total Hg determination were oxidized with BrCl immediately after delivery to the laboratory and were left standing overnight for complete digestion. Excess bromine was destroyed with hydroxylamine hydrochloride and total Hg was determined by CV-AFS after $SnCl_2$ reduction (Jones et al., 1995; PSA, 2001) on a PSA 10.025 Millenium Merlin System (PS Analytical, U.K.) with an MDL of 2 ng L^{-1}. For the determination of Hg in suspended solids, filter papers were digested with conc. H_2SO_4 on a water bath at 70°C until the filters were completely dissolved. The resulting solution was then treated in the same way as described for water samples. Quality assurance included daily instrument calibration, replicate analyses, spike additions, analysis of reagent blanks and field blank samples. Calibration standards were prepared fresh every day from two working solutions (50 and 100 µg L^{-1}) prepared by dilution of a mercury standard solution (1000 mg L^{-1}, Merck SpectrosoL). Ultra-pure water (Fistreem Multipure, Fisher Scientific) was used for all dilution purposes. Two field blanks were prepared daily and were analysed in the same way as ordinary water samples. All water samples were analysed in duplicate; the quoted results therefore represent the means of duplicate analyses. Analytical precision of replicate water samples was on average 4.1±0.34%. The relative percent difference between unfiltered field duplicate samples averaged 8.6-11.5% in the low water periods, and 15.0% and 20.8% during the high water periods. The sometimes large variation between field duplicates is mainly attributable to the variable suspended solids content of the samples.

Aquatic plants

Dried cattail leaves collected in 1998 were ground and 250 – 300 mg sub-samples were digested with 7 ml conc. HNO_3 and 3 ml conc. H_2SO_4 on a water bath at 95°C for 1 hour. The mixture was cooled and the volume was made up to 100 ml with distilled water. Hg was determined by CV-AAS on a 'Rtut-101' mercury analyzer (instrumental DL 0.05 µg), after $SnCl_2$ reduction. Reed samples (roots, stems, and leaves) collected in 2004 were digested by the same procedure, but the heating time was extended to 2 hours. After cooling the mixture was treated with BrCl in the same way as described for water samples and Hg was determined by CV-AFS after $SnCl_2$ reduction (Jones et al., 1995). QC included reagent blanks and duplicate samples.

Fish

Samples of fish muscle tissue were taken with a stainless steel knife from the posterior part of the fish on the left hand side of the body. Tissue samples (1 g) were digested in a mixture of 7 ml conc. HNO_3 and 3 ml conc. H_2SO_4 for 1 h (Adeloju et al., 1994). After cooling, 1.0 ml of H_2O_2 was added and the digestion was continued for another hour (PSA Application note 019). The solution was chilled, diluted with ultra-pure water to 100 ml and oxidized with BrCl in the

same way as water samples. Samples were set aside overnight for complete digestion. Excess bromine was destroyed with hydroxylamine hydrochloride and total Hg was determined by CV-AFS after $SnCl_2$ reduction (Jones et al., 1995). The MDL was 2 ng g^{-1} and quality assurance included method blanks, duplicate digestions, matrix spikes, and analysis of reference materials. Accuracy was assessed using the certified reference materials DORM-2 (dogfish muscle tissue; National Research Council Canada), BCR-422 (cod muscle tissue; Community Bureau of Reference, Belgium), and ERM-CE278 (mussel tissue; Institute for Reference Materials and Measurements, Belgium). Rates of recovery expressed as means±SE for samples taken in 2002 and 2005, respectively, were 98.2±1.96% (n=5) and 99.5±1.22% (n=2) for DORM-2 (certified value 4.64±0.26 mg kg^{-1}), 96.7±1.73% (n=3) for BCR-422 (certified value 0.559±0.016 mg kg^{-1}), and 93.4±0.12% (n=2) and 100.6±1.960% (n=2) for ERM-CE278 (certified value 0.196±0.009 mg kg^{-1}). The relative percent difference (%RPD) between duplicate sample digests averaged 5.7% for fish collected in 2002 and 6.5% for fish collected in 2005. All tissue concentrations are reported as wet weight concentrations.

3.3 Data analysis

Data was analyzed using standard statistical procedures such as linear correlation and regression. Parametric tests were preferred, and differences between sample means were assessed using *t*-Tests and one-way analysis of variance (ANOVA). Because fish Hg content was often significantly correlated with fish length and weight, site-specific differences between Hg concentrations in fish tissue were assessed using one-way analysis of covariance (ANCOVA).

4. Results and discussion

4.1 Sediments

4.1.1 Total mercury

The river Nura downstream of Temirtau is strongly contaminated, and the first 20 km of the river bed below the effluent outfall canal are thought to contain ~8.5 t of Hg (Heaven et al., 2000a). A large part of the Hg is associated with power station fly ash that was discharged to the river during the same period. The distribution of the contaminated sediments is highly heterogeneous and is strongly determined by the morphology of the river. Total Hg (THg) concentrations in shallow (0 – 30 cm) sediment cores taken from the river channel and backwaters ranged from 9.95 to 242 mg kg^{-1}. Mercury concentrations were highest in the canal sediments and in river sediments within 2 km from the outfall, as well as near the village of Old

Gagarinskoye at ~9 km from the outfall. Thereafter Hg concentrations generally decreased with increasing distance downstream. The vertical distribution of Hg concentrations showed great variability, and there was no consistent gradient with increasing depth (Fig. 2). This is typical for Hg-contaminated sediments and has also been found e.g. by Bloom et al. (1999) for cores taken in Lavaca Bay.

Our results show that Hg concentrations in surface sediments are often lower than in deeper-lying layers, indicating coverage by less contaminated sediments in recent years. Nevertheless, the contamination in surface sediments is severe. Average Hg concentrations in the upper 5 cm sediment layer were 120 mg kg^{-1} (n=2) at 1.9 km distance from the outfall, 55.1 mg kg^{-1} (n=4) at 2.4 km, 35.6 mg kg^{-1} (n=8) at ~9 km, and 14.2 mg kg^{-1} (n=4) at 19.7 km. In a large backwater at 13 km distance where significant amounts of silts had been deposited, the top 5 cm sediment layer contained 70.1 mg kg^{-1} of Hg. The detected levels of contamination show that the Nura is one of the most severely impacted fluvial systems known to date. Mercury concentrations in the Nura are higher than e.g. in stream sediments in Hg mining districts in Nevada and Slovenia, or on the Sudbury River in Massachusetts that suffered Hg contamination from an industrial complex (Wiener and Shields, 2000; Gray et al., 2002; Hines et al., 2006). The levels of Hg in the Nura are comparable to those reported for the river Elbe in Germany in the 1990s (Hintelmann and Wilken, 1995; Wilken and Wallschläger, 1995). However, in contrast to the Nura which is a closed semi-arid river basin, contamination in the Elbe has been much reduced in recent years due to its high average annual discharge of 712 – 850 m^3 s^{-1} that flushes contaminants to the North Sea.

Sediment cores taken at Old Gagarinskoye show a large variation in sediment deposition patterns within a 900 m section of the river (Fig. 2, 8.5 and 9.4 km). Although Hg concentrations in the upper 5 cm sediment layer are very similar for the two sets of cores, only one set shows strong Hg enrichment in the 5 – 15 cm layer. Backwaters are sinks for contaminated particles transported from upstream areas and it could be that the contaminant peak has been covered by cleaner sediments. On the other hand, it is also possible that the observed subsurface peak reflects past riverbank erosion, as these cores were taken relatively close to the shore. The profile of a deep core taken in the middle of the river channel 100 m downstream at 9.5 km reveals a profound maximum of 306.5 mg kg^{-1} at ~1 m depth, reflecting the peak of the historic deposition and subsequent coverage by cleaner sediments (Fig. 3). The data from this core also shows that the sediments are contaminated to a depth of at least 2.5 m. Above the peak of the contamination which resides at 0.5 – 1.1 m depth, Hg concentrations vary between 49.9 and 69.7 mg kg^{-1}, whereas below 1.1 m they range from 18.7 – 109.6 mg kg^{-1}, presumably as a result of the downward leaching of contaminated pore water. The core taken closest to the outfall canal showed altogether lower Hg concentrations and did not display the pronounced subsurface maximum seen at Gagarinskoye (Fig. 3). It may be that the flow

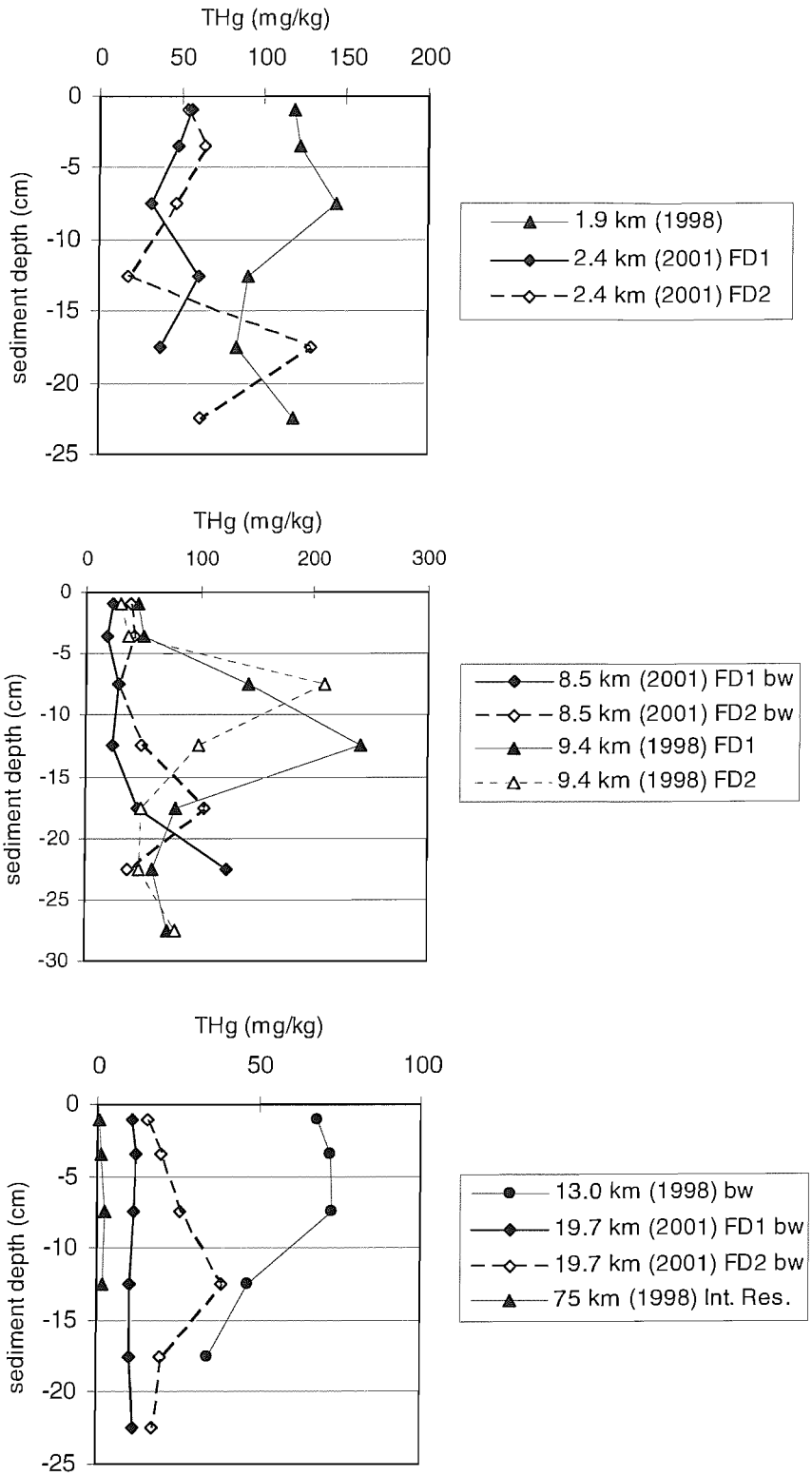

Fig. 2. Depth distribution of total mercury concentrations in sediment cores taken between the outfall and Intumak Reservoir in 1998 and 2001.
(FD = field duplicates, bw = backwater sediment).

dynamics in the section close to the outfall are such that contaminants are carried downstream rather than being deposited, or the contaminant peak could have been buried at greater depth due to high overall amounts of suspended matter in the canal which receives effluents from several industrial enterprises.

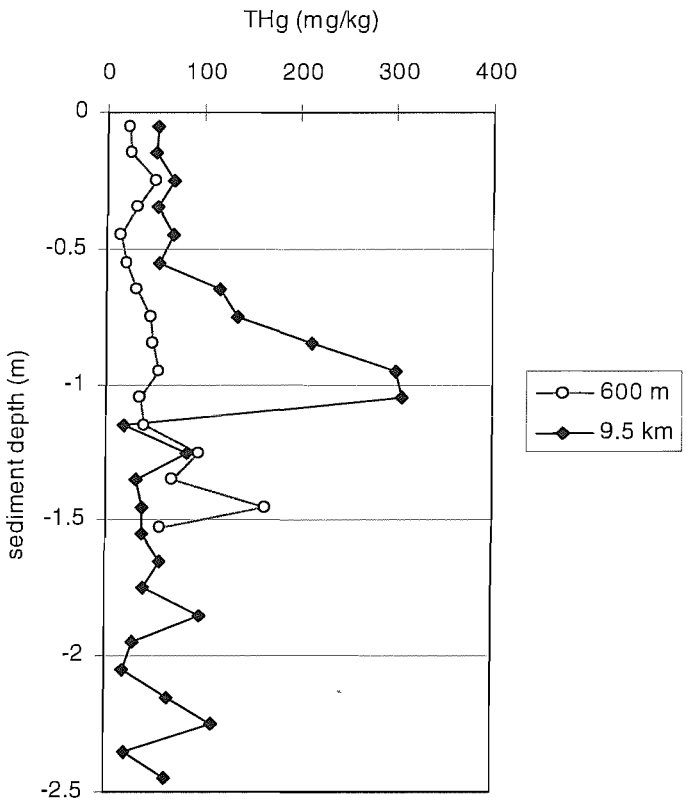

Fig. 3. Deep sediment cores taken near the pollutant outfall (600 m) and near Old Gagarinskoye village (9.5 km).

The results of the 2005 surface sediment survey indicate that Hg concentrations in the upper 5 cm sediment layer have been reduced by about a third to 11.8 mg kg^{-1} at Old Gagarinskoye and 4.5 mg kg^{-1} near Tegis-Zhol (Table 1). This is most likely due to the large flood in 2004 which appears to have led to the deposition of cleaner sediments from upstream areas. On the other hand, the slightly increased Hg concentrations found in surface sediments at sampling points 11 and 12 compared to an earlier investigation seem to suggest that the 2004 flood has transferred sediments from the highly contaminated reach between the outfall and Gagarinskoye to the section below Rostovka (Table 1).

In a shallow core taken at the head of the Intumak reservoir, THg ranged from 0.64 mg kg^{-1} in the top 2 cm sediment layer to a maximum of 2.1 mg kg^{-1} at 5-10 cm depth (mean 1.45 mg kg^{-1}). Additional surface sediment samples taken along the shore of the reservoir contained

<0.005 mg kg^{-1} and 0.038 mg kg^{-1} of Hg (0-1 cm and 1-5 cm sediment layer). These results are in good agreement with the findings of a recent (unpublished) study of Hg contamination in the reservoir which indicated that the sediments are more contaminated in the upper half of the reservoir where the highest Hg concentrations appeared to be associated with fly ash particles, and that less contaminated materials have been deposited recently (Deckwer and Leonhäuser, 2005). Below the Intumak reservoir, Hg concentrations in surface sediments decrease by almost two orders of magnitude to levels <0.1 mg kg^{-1} (Table 1), confirming our previous hypothesis that the reservoir is acting as a settling pond for contaminated particles (Heaven et al., 2000b). However, although Hg concentrations in surface sediments gradually decrease downstream of the reservoir, they do not approach background levels until the Uyalyshalkar group of lakes at the entrance to the terminal wetlands. Mercury concentrations in surface sediments taken from various sites in the wetlands ranged from 0.003 to 0.012 mg kg^{-1}, whereas control sediment samples taken at a reference site upstream of Temirtau contained <0.005 mg kg^{-1} and 0.006 mg kg^{-1} of Hg (Table 1).

4.1.2 Methylmercury

Environmental MeHg concentrations reflect the net sum of MeHg production and degradation processes. Rates of MeHg formation depend on the amount of Hg that is available for methylation reactions, rather than on THg concentrations, and are influenced by a large number of physico-chemical and biological factors (Ullrich et al., 2001). The percentage of MeHg formed is generally less than 1% and is more typically in the region of 0.1% or less of THg content (Bubb et al., 1991; Bloom et al., 1999; Hines et al., 2000; Zelewski et al., 2001; Niessen et al., 2003), although higher levels up to 2% and 13% have also been reported (Gilmour et al., 1998; Mikac et al., 1999; Fischer and Gustin, 2002). In the most contaminated section of the Nura, MeHg levels in sediments ranged between 4.9 and 39 μg kg^{-1} and were generally less than 0.1% of THg. The highest MeHg concentrations were measured in the top 2 cm surface sediments (33 – 39 μg kg^{-1}), corresponding to 0.01 – 0.11% of THg. It was surprising, however, that the MeHg content in these samples was very similar, despite the large variation in THg concentrations. The lowest MeHg concentration in surface sediments (1.7 μg kg^{-1}, corresponding to 0.27% of THg) was determined at the moderately contaminated Intumak reservoir. No other studies of MeHg have been carried out on the Nura to date.

Methylmercury concentrations in sediments from the river Nura are higher than levels reported for many uncontaminated and contaminated aquatic systems (Gilmour et al., 1998; Bloom et al., 1999; Mikac et al., 1999; Hines et al., 2000; Zelewski et al., 2001). In these studies, MeHg concentrations generally did not exceed 10 μg kg^{-1} and were more typically <5 μg kg^{-1}, at THg levels that were mostly <2 mg kg^{-1}, except for the Gulf of Trieste where THg ranged between 0.77 and 47.8 mg kg^{-1} (Hines et al., 2000). Higher MeHg levels up to 33.4 μg

kg^{-1} were found on the River Yare (Bubb et al., 1991 and 1993), and in particular on the River Elbe where maximum MeHg concentrations in sediments downstream of an acetaldehyde factory and several chlor-alkali plants were 35 μg kg^{-1} at 12 mg kg^{-1} total Hg content, and 119 μg kg^{-1} at 112 mg kg^{-1} of THg (Hintelmann and Wilken, 1995; Wilken and Wallschläger, 1995). It should be noted that in the case of Hg contamination arising from acetaldehyde production, some of the detected MeHg may not have been formed in situ, but could have been discharged by the plant itself. Following the catastrophe at Minamata Bay in Japan, it became known that under certain conditions MeHg can be formed in a side reaction of the manufacturing process (UNEP, 2002). For example, Horvat et al. (2003) recently reported that until the mid 1980s the Quingzhen acetic acid plant in China emitted wastewater containing 3 – 8 μg Hg L^{-1} of which 15 – 30% was organic Hg.

Although MeHg concentrations in the sediment cores were variable, in general there was a trend for concentrations to decrease with increasing depth. Fig. 4 illustrates the variation of MeHg concentrations and the methylation rates (expressed as the percentage of total Hg) with increasing depth. Methylation rates are usually highest in the upper 2 cm of sediments where the microbiological activity is highest (Bubb et al., 1991 and 1993; Croston et al., 1996; Gilmour et al., 1998; Bloom et al., 1999; Mikac et al., 1999; Hines et al., 2000; Zelewski et al., 2001), but in this study relatively high MeHg concentrations were also found at depth in some of the cores (Fig. 4). Secondary subsurface peaks in methylation activity are not unusual, however, and have also been found in other studies (Hintelmann and Wilken, 1995; Zelewski et al., 2001; Hines et al., 2006). For example, Zelewski et al. (2001) reported that high MeHg concentrations at a depth of 30 cm coincided with maximum THg concentrations.

4.1.3 Relationship between total Hg and MeHg

The most significant of our findings is that Hg methylation rates were inversely related with total Hg concentrations (Fig. 5). Most studies report that there is no or just a weak correlation between total Hg and MeHg concentrations in sediments (e.g. Jackson 1986; Ramlal et al., 1993; Wilken and Wallschläger 1995). Although THg concentrations were not directly correlated with MeHg concentrations in sediments, we found that there was a significant inverse relationship between the THg content and the percentage of MeHg formed ($r=0.761$ for $n=29$, $p<0.001$, Fig. 5). If one potentially outlying result close to the detection limit is disregarded, the correlation is further improved ($r=0.930$ for $n=28$ at $p<0.001$). It would appear that this relationship has so far been overlooked, as most workers tend to compare THg and MeHg concentrations directly. However, when the results of Wilken and Wallschläger (1995) for the Hg-contaminated river Elbe were plotted for comparison, they were found to be in good agreement with our data (Fig. 5). We therefore suspect that a similar relationship may also exist for other Hg-contaminated rivers, which would warrant further investigation.

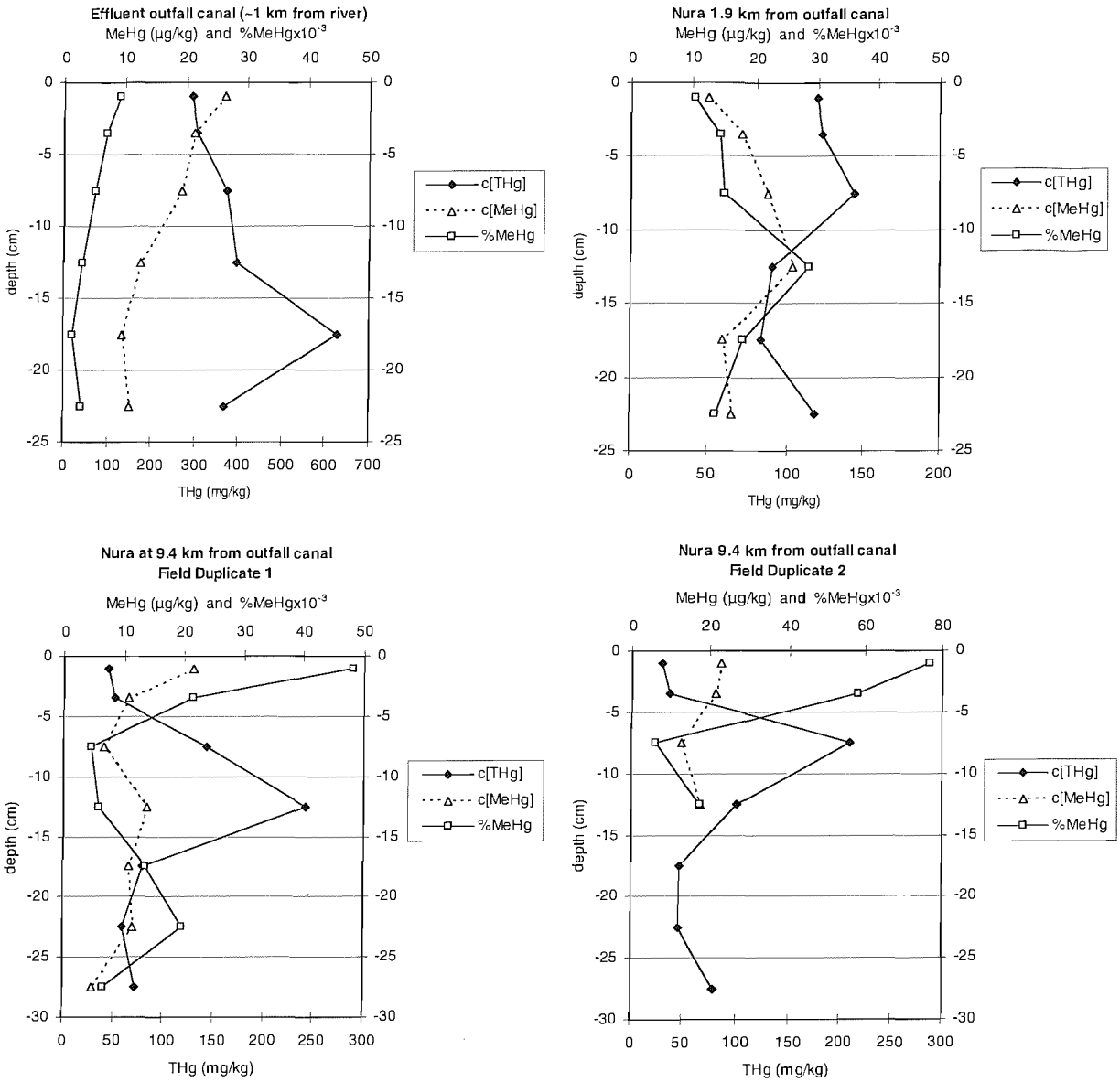

Fig. 4. Methylmercury concentrations and percentage of methylmercury formed in relation to total mercury content in shallow sediment cores.

Our findings are analogous to the observation by Schaefer et al. (2004) that a lower proportion of THg appears to be present as MeHg in highly contaminated as compared to pristine surface waters. Schaefer et al. (2004) found a significant inverse relationship between the proportion of THg as MeHg (%MeHg) and the concentration of THg which they attributed to increased MeHg degradation rates in Hg-contaminated waters. They suggested that in Hg-contaminated surface waters, the amount of MeHg that accumulates is limited by high rates of reductive demethylation by Hg-resistant bacteria, whereas in environments with low levels of THg where microbial communities are not adapted to Hg, the concentration of bioavailable Hg may be

insufficient to induce the expression of mercury-resistance (*mer*) operons that regulate reductive demethylation. Marvin-DiPasquale et al. (2000) had previously shown that reductive degradation (*mer*-detoxification) dominates in sediments at severely contaminated sites, whereas in less contaminated ecosystems demethylation rates are lower and are governed by oxidative demethylation. In studies on the Carson river, the highest degradation rates were observed at the most strongly impacted sites where THg ranged from 4.5 to 21.3 mg kg^{-1} (Oremland et al., 1995; Marvin-DiPasquale et al., 2000).

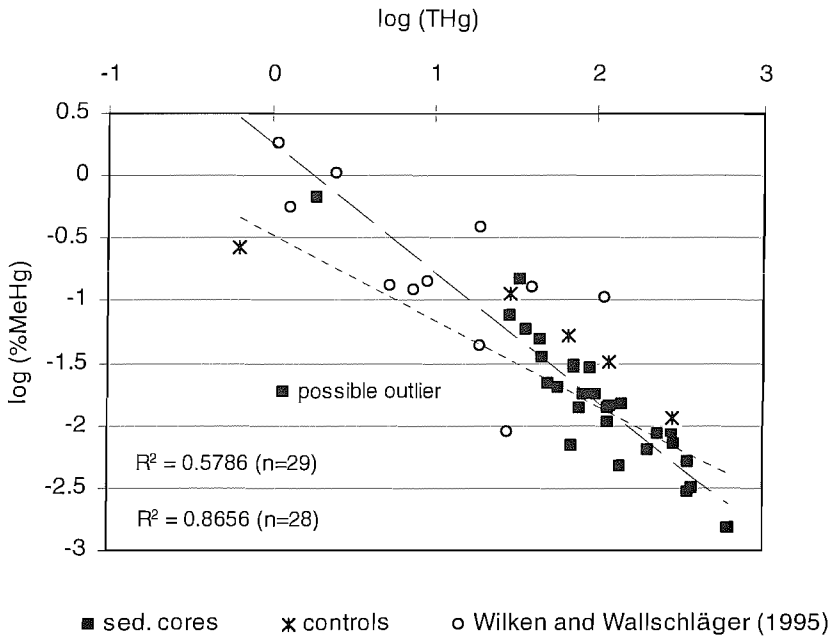

Fig. 5. Relationship between total mercury and methylmercury content in 29 sediment samples taken at varying depths (0 – 30 cm) and distances from the outfall. Data from Wilken and Wallschläger (1995) is plotted for comparison.

We first suspected a possible inverse relationship of net MeHg production with THg concentrations when investigating the factors that influence Hg methylation in aquatic systems, and speculated that this may be the reason why MeHg levels in sediments rarely exceed 1% (Ullrich et al., 2001). On the basis of the above results, we can now refine this hypothesis further and propose that net MeHg production is controlled by different processes at high compared to low environmental Hg concentrations. While Hg availability appears to be the limiting factor for MeHg production and accumulation at low ambient Hg concentrations, at high concentrations the amount of MeHg that accumulates in sediments appears to be limited by efficient degradation. For example, data from recent Hg amendment studies (Orihel et al., 2006) suggests a linear response of MeHg production at low Hg loading rates and low ambient Hg

concentrations (0.004 – 0.007 mg kg^{-1} of THg and 0.03 – 0.1 μg kg^{-1} of MeHg). Rudd et al. (1983) also found that MeHg production in surficial sediments was directly related to concentrations of added $^{203}Hg^{2+}$ over 2 orders of magnitude, but leveled off at 5 – 10 mg Hg kg^{-1} sediment. Benoit et al. (2003) examined data from a wide range of ecosystems and reported that MeHg and THg in surficial sediments appear to be correlated up to about 0.5 mg kg^{-1}, whereas higher THg concentrations had little increased impact on MeHg production at contaminated sites. Our results agree with the observations by Benoit et al. (2003) for contaminated sites and we hypothesize that there may be a threshold concentration of bioavailable Hg beyond which *mer*-detoxification is effectively induced in bacteria and MeHg begins to be actively degraded in sediments. Such a threshold concentration would most likely be site-specific and depend on the nature of the microbial community, the amount of bioavailable Hg, and other environmental factors such as redox conditions. For example, Schaefer et al. (2002) found higher Hg(II) concentrations were required to induce the expression of Hg resistance operons in anaerobic compared to aerobic environments.

Total Hg concentrations in sediments and waters generally decrease rapidly with increasing distance from point sources of pollution, but this is not necessarily the case for MeHg. On the contrary, a number of studies on contaminated fluvial systems have found that aqueous MeHg concentrations and/or the ratio of MeHg : THg in water actually increased with increasing distance downstream, while THg concentrations strongly decreased (Parks et al., 1989; Hill et al., 1996; Hines et al., 2000; Bonzongo et al., 2006). This is in line with the findings of Schaefer et al. (2004) that the percentage of THg as MeHg is inversely related to the concentration of THg in surface waters. However, as Hg methylation takes place primarily in surface sediments (Ullrich et al., 2001), MeHg concentrations in the water column are ultimately controlled by processes that occur in sediments rather than in the water phase. Suchanek et al. (1998) found that while both THg and MeHg in sediments declined exponentially as a function of distance from the Sulphur Bank Mercury Mine at Clear Lake, California, the ratio of MeHg : THg increased with increasing distance from the mine. Furthermore, it has frequently been reported that MeHg concentrations or percentages are lowest at the most contaminated sites and higher in uncontaminated areas (Hill et al., 1996; Gilmour et al., 1998; Hines et al., 2000). These observations are in agreement with the inverse relationship proposed by us between THg concentrations and the percentage of MeHg formed in highly contaminated sediments.

4.2 Surface water

Mercury concentrations in surface water are highly influenced by the flow regime of the river. The annual spring flood leads to the remobilization of Hg from bed sediments, river bank silt deposits and flood plain soils (Heaven et al., 2000a,b). Similar processes of bed sediment

resuspension during the spring snow melt have also been observed for other river systems, e.g. the Thur river in France (Hissler and Probst, 2006) and the Carson river in Nevada, U.S.A. (Bonzongo et al., 1996). Table 1 summarizes the surface water monitoring data for the Nura and distinguishes between low-water periods (November 2001, May 2002, July 2005) and flood periods (April 2002 and April 2004). Mean THg concentrations in surface sediments are given for comparison.

4.2.1 Upstream sites

No Hg was detected in any of the surface water samples taken at the upstream reference site, irrespective of the sampling period. At Samarkand reservoir within Temirtau city centre, Hg concentrations were slightly elevated above background in the low-water period (up to a maximum of 16.1 ng L^{-1} in July 2005), but were below the detection limit at the undeveloped shore of the reservoir opposite the city centre. The elevated concentrations near the city centre are likely due to dispersed pollution from the Alash chemical-metallurgical plant that discharges process water to the reservoir. Stratiyenko et al. (2004) found that effluents discharged between April and October 2004 had an average Hg concentration of 170 ng L^{-1}, giving clear evidence that the plant contributes Hg to the reservoir. Additional surface water samples taken by us close to the discharge point in July 2005 contained 627 ng Hg L^{-1} (data not included in table), and surface sediment samples also show that the reservoir is impacted (Table 1). In the 2002 flood period, Hg concentrations in the reservoir were mostly below the detection limit, but ranged between 2.6 and 6.9 ng L^{-1} during the large flood in April 2004.

Mercury concentrations in river water 2.5 km upstream of the outfall (sampling point 3) were only very slightly elevated during the low-water periods, but higher concentrations were noted in the flood periods. During the receding flood in 2002, Hg concentrations ranged from <DL to 10.5 ng L^{-1} here, compared to 16-61 ng L^{-1} at the rise and peak of the large flood in 2004 and 6 ng L^{-1} after the peak had passed.

4.2.2 Downstream of the outfall

Downstream of the effluent canal, Hg concentrations in river water were severely elevated, with maximum concentrations in the order of 1600 – 4300 ng L^{-1} during the exceptionally large flood in 2004 (Table 1). These concentrations are of a similar magnitude as the peak values of 1500-2100 ng Hg L^{-1} observed downstream of mine tailings piles on the Carson river (Bonzongo et al., 1996). Horvat et al. (2003) investigated Hg concentrations near an acetic acid plant at Quingzhen city in the province of Guizhou, China. The Quingzhen plant is of the same type as the plant in Temirtau and emitted an estimated 140 t of Hg into the environment. Mercury concentrations near the wastewater outfall (1830 ng L^{-1}) and 2.5 km downstream from the plant (450 ng L^{-1}) were very similar to the concentrations found in the Nura.

Table 1. Total mercury concentrations in unfiltered surface water samples and sediments

	Sampling location and distance from outfall canal	km	period sampled	THg concentration in water, ng/L range	mean	med	SE	n	THg in sediments, mg/kg*
1	Nura upstream of Samarkand reservoir (reference site)	-35	A, C, E B	<DL <DL				6 6	0.006 *(<0.005)*
2	Samarkand reservoir, Temirtau	-3.5	A, C, E B, D	2.7 - 16.1 <DL - 6.9	8.3	6. 7	2.3	6 9	0.24/3.27 *(0.026**)*
3	Nura 1.5 km downstream of Samarkand reservoir	-2.5	A, C, E B, D	2.1 - 3.3 <DL - 61.3	2.7	2.6	0.18	6 16	*(0.92)*
4	inflow point of the effluent outfall canal to the Nura	0	A, C, E B, D	655 - 1650 44.1 - 884	1023 354	769 317	199 69.1	6 14	
5	Nura 1.8 km downstream of the effluent outfall canal	1.8	A, C, E B, D	205 - 380 57.9 - 4258	314 751	345 173	27.9 397	6 14	*(96.3)*
6	Nura near New Gagarinskoye village (formerly Kalininskoye)	4.6	A, C, E B, D	112 - 560 227 - 1640	272 651	141 436	88.2 141	6 12	
7	Nura near Old Gagarinskoye village	8.4	A, C, E B	111 - 383 190 - 3873	257 484	288 350	48.6 125	6 8	11.8 *(43.4)*
8	Nura at Mill house dam, downstream of Oshagandy inflow	14.2	A, C, E B	77.1 - 502 198 - 833	260 385	236 254	71.4 96.2	6 8	
9	Nura near Tegis-Zhol village	18.1	A, C, E B, D	94.2 - 347 121 - 3778	234 1351	270 1235	46.1 340	6 14	4.51
10	Nura near Rostovka village	30.0	A, C, E B, D	41.8 - 128 86.8 - 2345	93.1 664	113 449	16.1 197	6 14	*(2.38)*
11	Nura near Molodetskoye village	52.5	A, C, E B, D	27.0 - 184 62.4 - 749	96.3 282	80.9 143	28.2 77.3	6 12	5.15 *(1.95)*
12	Nura near Aktobe village (upper reach of Intumak reservoir)	70	A, C, E B, D	19.4 - 60.5 17.5 - 307	40.4 106	45.8 81.6	6.9 28.6	6 12	2.81 *(2.26)*
13	Intumak reservoir, tail water	85	A, C, E B, D	2.3 - 5.5 5.4 - 21.7	3.7 10.5	3.2 7.9	0.58 1.93	6 10	0.012 *(0.142)*
14	Samarka barrage, tail water	125	A, C, E B	3.3 - 35.2 7.6 - 13.8	20.0 9.6	21.4 8.2	5.8 1.05	6 6	0.069
15	Nura near Akhmeshet village (formerly Zakharovka)	150	E D	19.8 / 22.5 12.6 / 12.7	21.2 12.6		1.34 0.02	2 2	
16	Nura near Tassuat village	180	C, E B	<DL - 13.1† 2.5 - 9.2	5.0	3.6	1.18	4 6	
17	Nura near Kievka village	205	A, C, E B, D	<DL - 11.7‡ <DL - 8.7				6 8	0.048
18	Nura near Chernigovka village	235	D	6.0 / 9.8	7.9		1.89	2	
19	Nura near Akhmet-Aul village (formerly Entuziast)	255	C, E B, D	<DL - 6.0† 2.5 - 13.9	6.2	5.0	1.52	4 8	
20	Nura near Romanovskoye village	280	C, E B, D	<DL - 6.0† 2.1 - 19.0	6.3	3.3	2.33	4 8	0.019
21	Nura near Rozhdestvenka village	285	A	<DL				2	
22	Preobrazhensky dam, tail water	295	C, E B	<DL - 3.7† 2.2 - 8.0	4.1	2.9	0.97	4 6	
23	Nura near Birlik village	335	E B	<DL <DL - 5.0				2 6	0.026
24	Nura near Sabyndy village	370	E B	<DL <DL - 10.5				2 6	
25	Uyalyshalkar Lake	420	E	3.1 / 4.2	3.6		0.52	2	0.003
26	Nura near Kurgaldzhino village	450	E B, D	<DL <DL - 13.2				2 8	0.006
27	Shalkar Lake	480	E	<DL				2	0.012
28	Sultankeldy Lake near Karazhar	550	E	<DL				2	0.011

Notes: DL = 2 ng/L, n = no. of individual samples. Sampling periods: A) 4-6 November 2001, B) 7-13 April, 17-22 April, 29 April - 5 May 2002, C) 22/23 August 2002, D) 4-10 April 2004, E) 18-22 July 2005.
†<DL in period E, ‡<DL in period A. *2005 data (1998 and/or 2001 data in italics). **sample taken from tail water pool.

The highest Hg concentrations in surface water are generally noted during the rising flood when large amounts of the contaminated sediments downstream of the outfall canal are resuspended. This is illustrated by the monitoring data of April 2004 shown in Fig. 6. At the peak of the flood, Hg levels usually drop, presumably because of dilution effects, and then gradually decrease further as the flow stabilises, while the contaminant peak shifts further downstream. In 2002, the spring flood started earlier than expected and the peak discharge had already passed when our measurements began on 7 April (Fig. 6). Mercury concentrations at the outfall and 1.8 km downstream were 834 and 305 ng L^{-1} in period 1 and dropped by 40-60% during more stable flow conditions in period 2 and 3.

The proportion of Hg in dissolved and suspended forms was only investigated in April 2002 (period 1 – 3), in the effluent canal and at three locations on the river between the inflow point and Molodetskoye, ~50 km downstream. Relatively high values of dissolved Hg (up to 10% and 15% of total Hg) were measured in the outfall canal where on average 91% of THg was associated with suspended matter. In the river water, 93 – 99% of THg (mean 97%) was associated with suspended matter at sampling points 5, 9, and 11, whereas dissolved Hg was only 1.3 – 6.6%. This confirms that Hg in surface waters is mainly adsorbed to particulates (Coquery et al., 1997; Hissler and Probst, 2006) and is also in good agreement with the findings of Horvat et al. (2003) who reported 0.7% and 3.6% of dissolved Hg in water samples taken near the Quingzhen plant. However, our results are in strong contrast to an earlier study on the Nura where the majority of Hg downstream of the outfall was found to be in dissolved form (Heaven et al., 2000a). Stratiyenko et al. (2004) also state that dissolved Hg predominates in the section between the effluent canal and the Intumak reservoir, except during the spring flood. As our samples were taken exclusively during the flood period, the results reflect the presence of large amounts of suspended particulates in the water, while dissolved Hg entering the river via the outfall canal has a lesser influence at this time of the year due to the high volume of water in the river.

4.2.3 Seasonal variations

Between the outfall canal and Intumak reservoir, mean Hg concentrations were consistently higher during the flood periods, with the exception of the inflow point of the effluent canal to the Nura where Hg concentrations were significantly higher during the low-flow period (Table 1). This is likely due to the influence of Hg entering the river from the effluent canal being more pronounced in the low-water period. Due to the lack of precipitation and high water losses through evaporation, the water level in the Nura severely decreases over the summer months and generally reaches its lowest level in August. Fig. 7 shows that in the contaminated section of the river, Hg concentrations in the summer low-water period are comparable to Hg concentrations during the receding spring flood, and a significant decrease is only noted during

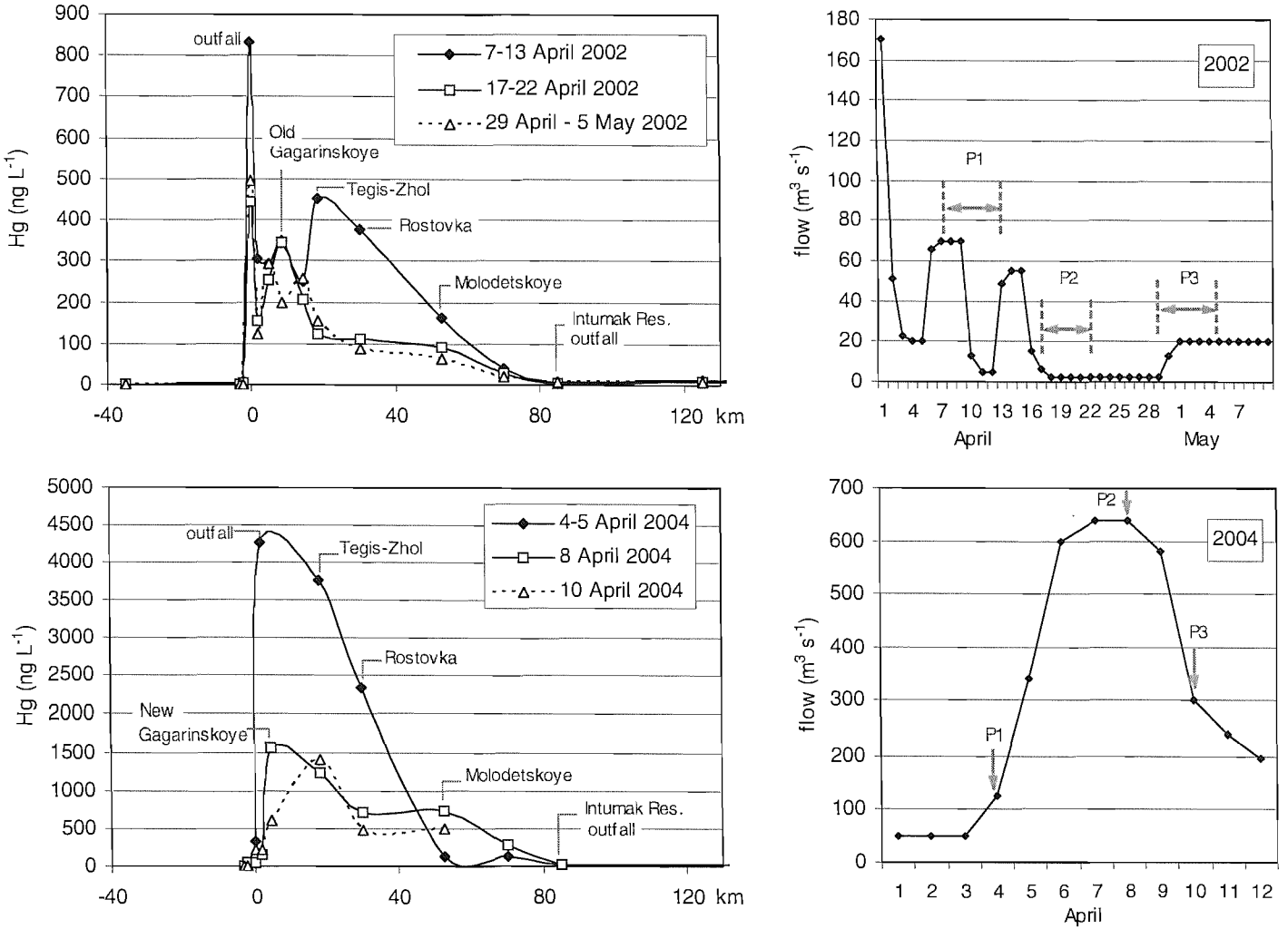

Fig. 6. Mercury concentrations in unfiltered surface water samples taken in three different periods towards the end of the 2002 spring flood and during the exceptionally large flood in April 2004. Discharge data is given for Samarkand Dam, located 3.5 km upstream of the effluent outfall canal (point zero). Peak flow in March 2002 was between 170-200 $m^3 s^{-1}$, compared to 640 $m^3 s^{-1}$ in April 2004.

the winter low-water period (Fig. 7). Stratiyenko et al. (2004) reported that contamination of the alluvial aquifer occurs during the flood period through the infiltration of river water. Groundwater seepage into the river under baseflow conditions in summer could thus contribute to the high Hg concentrations observed in the low-water period. This was also thought to be the reason for seasonally elevated Hg concentrations in the East Fork of the Upper Carson River (Fischer and Gustin, 2002).

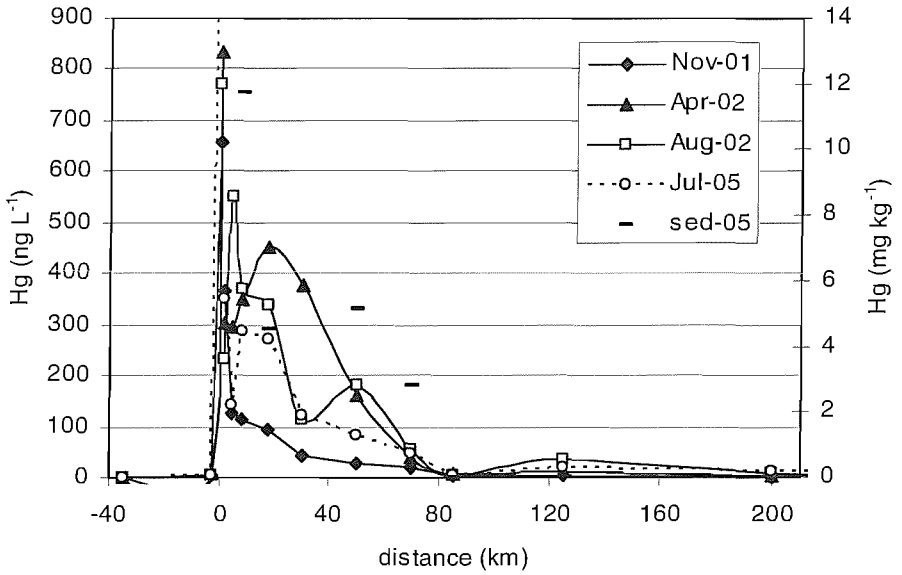

Fig. 7. Seasonal variation in Hg concentrations in unfiltered surface water samples. Only period 1 is shown for April 2002. Note that the Hg concentration at the outfall in July 2005 is off scale (1640 ng L^{-1}).

Seasonal changes in hydrological conditions are likely to affect not only the magnitude of Hg concentrations in the river water, but also Hg speciation and particle-partitioning, through changes in the water chemistry (Babiarz et al., 1998; Bonzongo et al. 2006; Hissler and Probst, 2006). Bonzongo et al. 2006 reported that periods of low water flow in the Carson River correspond to high water pH (8.1 – 8.3) and relatively high concentrations of Group VI oxyanions, which could interfere with microbial sulphate reduction and Hg methylation, while periods of high flow result in lower circumneutral pH (7.3 – 7.5), reduced concentrations of oxyanions and higher Hg methylation potential. Surface water pH in the Nura is generally above 8.0, but is depressed to about 7.5 near the inflow point of the effluent canal (Fig. 8). Pronounced seasonal effects are also noted, and the pH of the river water was found to be 0.6 – 1.5 units lower in April 2002 than in July 2005 at all measured points (Fig. 8), while the pH in the effluent canal remained nearly constant (7.3 – 7.4). The general pH depression in April is in

agreement with the observations of Bonzongo et al. (2006) and is most likely due to the effect of acidic snow melt. It is well known that the export of acidic solute such as sulphate and nitrate from watersheds during spring snowmelt can lead to a short-term decrease in surface water pH (Davies et al., 1987). High concentrations of NO_3^- and SO_4^{2-} were noted in river water (Stratiyenko et al., 2004), and the Nura between Temirtau and Birlik is classed as a nitrate sensitive zone. The small Oshagandy inflow that joins the Nura ~14 km from the outfall had a surface water pH of 7.1 in April 2002, but this did not appear to have a noticeable effect on the pH of the Nura which was already depressed to a similar level. The slight drop in pH after sampling point 11 at 52.5 km in July 2005 could be due to the Sherubainura inflow that joins the Nura at this point and carries water from mining districts (Fig. 8).

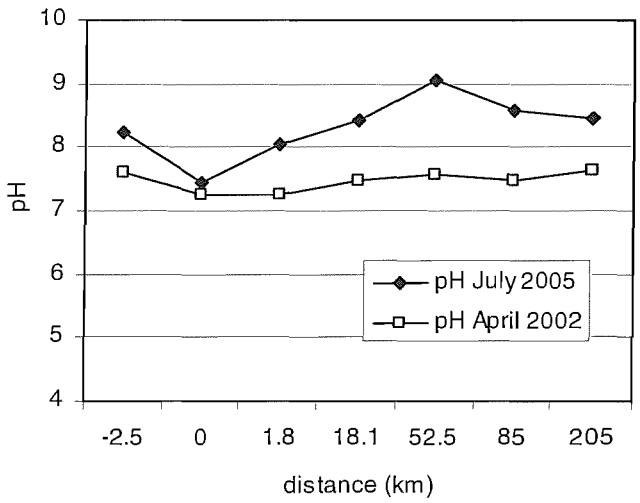

Fig. 8. Surface water pH between Temirtau and Kievka in April 2002 and July 2005. The outfall enters the river at point zero.

4.2.4 Intumak Reservoir

The large and shallow Intumak reservoir serves as a settling pond for contaminated particles, resulting in a drop in aqueous THg concentrations by one order of magnitude between the upper reach of the reservoir and the tail water basin (Table 1). During the flood period in April 2002 (P1 – P3), we observed a reduction in suspended load of 50 – 83% between sampling points 11 and 13 (Molodetskoye and Intumak tail water), and an 88 – 92% decrease in Hg bound to suspended particles. Reservoirs on the Sudbury river in eastern Massachusetts were also found to be depositional sinks for THg and removed about 23% of the THg load by sedimentation (Waldron et al., 2000; Wiener and Shields, 2000). Natural burial processes gradually decreased the quantity of Hg available for methylation, and Hg release from the contaminated reservoir sediments was minimal. Significant losses of Hg from the water column were also observed in

the Lahontan reservoir on the Carson river in Nevada (Bonzongo et al., 1996). In addition to sedimentation losses of particulate-bound Hg, volatilization of dissolved gaseous Hg was thought to be a potentially important removal pathway. In view of the similarity in climatic conditions, this might also be relevant to the Intumak reservoir.

Sedimentation of particulate-bound Hg in the Intumak reservoir results in reduced THg inputs to downstream locations, but dissolved Hg forms including MeHg could be exported from the reservoir (Schetagne et al., 2000). Deckwer and Leonhäuser (2005) found that Hg concentrations in the reservoir water generally varied from 2 – 20 ng L^{-1} in October 2004, with the highest concentrations nearest to the inlet. The methylation potential in the reservoir has to date not been assessed, but the water appears to be well-oxygenated in all seasons, with a pH between 7.4 and 8.2 (Deckwer and Leonhäuser, 2005). These conditions are considered to be less favourable for Hg methylation than e.g. anaerobic conditions and acidic pH values (Ullrich et al., 2001). Nevertheless, even small amounts of MeHg could be of concern because of the associated bioaccumulation risk. Furthermore, there are plans to increase the height of the Intumak dam (which at present is unfinished) to its full design height. It is well known that flooding stimulates microbial activity, leading to increased MeHg formation in newly-created reservoirs (Bodaly et al., 1997; Kelly et al., 1997; Montgomery et al., 2000; St. Louis et al., 2004; Hall et al., 2005; Hylander et al., 2006). It is therefore likely that an increase in the overall flooded area associated with the construction of the dam would lead to increased methylation and could result in higher MeHg levels in fish both in the reservoir itself and downstream

4.2.5 Downstream reaches

Mercury concentrations in unfiltered surface water samples taken at the Samarka barrage were always slightly higher than concentrations at the outfall of the Intumak reservoir, both in the low-water periods and during all three sampling campaigns in April 2002 (Table 1 and Fig. 7). Note that as the Samarka barrage was not monitored during the 2004 flood, the means and ranges of Hg concentrations quoted for Intumak and Samarka in Table 1 cannot be directly compared for the high-water period. It is not clear what was causing the persistent increase in aqueous THg concentrations at the Samarka barrage. On the Soča river downstream of the Idrija mercury mine, elevated THg levels were also noted just downstream of a dam (Hines et al., 2000), leading the authors to suspect that impoundments may enhance Hg mobilisation by increasing MeHg concentrations. This was confirmed in a subsequent study which found that the freshwater impoundment sediments were highly active Hg transformation sites (Hines et al., 2006). Surprisingly high Hg concentrations were found in fish at Samarka, despite the comparatively low THg levels in sediments and water (section 4.5). This would appear to indicate increased methylation activity at this site and requires further investigation.

Between Samarka and Kievka, Hg concentrations decline further and beyond Kievka, almost no Hg was detected in the low-water periods. The Ulken-Kundysy inflow at Kievka may provide further dilution in periods of low flow. With the exception of the Uyalyshalkar Lake (sampling point 25), no Hg was detected downstream of Kievka in July 2005. Data for the lower reach beyond Romanovskoye is scarce, but the results indicate that small amounts of Hg get transferred down to the wetlands during the flood period (Table 1). Between 3.4 and 10.5 ng Hg L^{-1} were detected between Akhmet-Aul and Kurgaldzhino (sampling points 19 – 26) on 11 and 12 April 2002. This corresponded to ~1 week after the peak of the flood had passed the section between Romanovskoye and Birlik, while flood waters were still rising at Kurgaldzhino. In the second and third sampling episode of the 2002 flood, no Hg was detected beyond the Preobrazhensky dam (sampling point 22). In 2004, points beyond Kievka were only sampled on 5 April which corresponded to the rising flood in the downstream reaches. In this year, the downstream section near Romanovskoye already experienced the first flood at the beginning of April, ahead of the main flood wave from Samarkand reservoir, due to large amounts of snow melt runoff from the Ulken-Kundysy river and smaller inflows. Mercury concentrations in the Nura ranged from 6 – 19 ng L^{-1} between Kievka and Kurgaldzhino. It is not known whether Hg concentrations kept rising after this date, as the flood peak reached Romanovskoye on 15 April, after our survey.

Mercury levels in downstream reaches of the Nura are comparable to levels reported by other researchers for non-impacted rivers. Hurley et al. (1995) reported mean unfiltered THg concentrations of 3.5 ng L^{-1} in the autumn and 7.9 ng L^{-1} in spring for 39 Wisconsin rivers with contrasting physical and geological characteristics. Bonzongo et al. (1996) found background concentrations of Hg upstream of mining activity in the Carson river were 4 ng L^{-1}, and on the Sudbury river, mean THg was about 2 ng L^{-1} at reference sites (Waldron et al., 2000). However, Hg levels in the downstream reaches of the Nura are higher than at the upstream site where no Hg was detected in any of the sampled seasons (Table 1).

It is not clear whether Hg detected downstream of Kievka during the flood periods originates from contaminated upstream reaches of the river and reflects fluvial transport of Hg, or whether it could be attributable to runoff from the floodplain with snowmelt. It is well known that snow actively scavenges contaminants from air, and Dommergue et al. (2003) have shown that most Hg is removed from the snow pack during the first days of snowmelt. This could explain why at the sampling points downstream of Kievka, Hg was detected only in the first of the three monitoring periods in April 2002, and almost no Hg was detected in the low-water periods. Whatever the source of the Hg, even small amounts transferred to the wetlands could be of potential concern, as numerous studies have shown that wetlands are active sites of MeHg production (StLouis et al., 1996; Kelly et al., 1997; Gilmour et al., 1998; Waldron et al., 2000; Wiener and Shields, 2000). Proposed limit values for the protection of aquatic wildlife

populations, expressed as THg in unfiltered water, are in the order of 0.9 – 1.3 ng L^{-1} (Nichols et al., 1999). A small number of fish sampled from the wetlands in 2005 indicate that at present, aquatic biota do not appear to be impacted to a significant degree (cf. section 4.5).

4.3 Hg mass flow

The effluent canal is still a significant source of pollution to the river water. Water samples taken from the canal at Chkalovo village (~1.5 km from the Nura) contained 577 ng L^{-1} in November 2002, 159 – 260 ng L^{-1} in April 2002, and 843 ng L^{-1} in July 2005. At the inflow point to the Nura, the Hg concentration was even higher and ranged from 444 ng L^{-1} in April 2002 up to 1.64 µg L^{-1} in July 2005, possibly due to the desorption of Hg from highly polluted canal sediments. At an average flow rate of ~1 m^3 s^{-1}, the canal is likely to still contribute several kilograms of Hg per year to the river. Stratiyenko et al. (2004) estimated that the amount of Hg discharged to the Nura was 1.8 kg in 2002, 2.5 kg in 2003, and 4.7 kg between April and October 2004. Higher amounts in recent years were attributed to the start of remediation work at the plant which led to additional pollution via the storm drains.

Stream discharge data and average Hg concentrations were used to estimate annual mean loads of Hg for different river sections in the large 2004 flood. For the most contaminated reach between the outfall and Rostovka (0 – 30 km), monthly flow data was available for sampling points 3 and 9, and annual discharge data was available for points 5 and 10 from which the flood flow could be estimated. For points 3 and 9, the April 2004 flow volume was 76% of the annual flow for the year. Assuming the same percentage for the nearby sampling points 5 and 10 and using the mean Hg concentrations determined during the 2004 flood for the high-water period and data from Table 1 for the low-water period gives an estimated flux in the order of 520 – 1100 kg Hg through these three river sections for the year 2004, based on data from sampling points 5, 9 and 10. The estimate decreases to 140 – 950 kg if median values of Hg concentrations are used. Due to the scarcity of data this is only a very crude approximation of possible Hg fluxes. The higher estimate concurs with Stratiyenko et al. (2004) who state that between 584 and 1243 kg of Hg were mobilised between the outfall and Rostovka in 2004.

The average annual discharge at the Intumak reservoir is in the order of 420 million m^3. Assuming that 80% of the flow occurs in April/May and using the mean Hg concentrations of 10.5 ng L^{-1} for the flood period and 8 ng L^{-1} for the rest of the year (Table 1), the annual export of Hg to downstream reaches of the river could be in the order of 4.2 kg per year (3.5 kg in the flood period and 0.7 kg during the remainder of the year). During the large flood in 2004, the combined discharge for April and May was 687 million m^3 (79.6% of the annual flow), and the measured average Hg concentration in April was 16.5 ng L^{-1}, giving a total flux of 11.3 kg Hg for the flood period and 0.5 kg for the remainder of the year. The true figure is likely to be

somewhat lower than this, however, as we assumed that Hg concentrations in May (not measured) were as high as the values determined in April. Our estimates differ significantly from those of Stratiyenko et al. (2004) who calculated an annual export of 122 kg THg and 14.6 kg dissolved Hg for the river section at Intumak, using an average Hg concentration of 17.5 ng L^{-1}.

Average long-term runoff at Romanovskoye is 619 million m^3 per year. The average discharge in April 2002 was 205 m^3 s^{-1}, giving a total discharge of 531 million m^3 for that month. Using the average Hg concentration of 2.9 ng L^{-1} determined in April 2002 gives an estimated export of 1.5 kg of Hg through this section in the 2002 flood. During the exceptionally large flood in April 2004, discharge was 591 million m^3. Assuming the average THg concentration of 16.7 ng L^{-1} measured in Romanovskoye during the rising flood on 5 April was representative for the whole month, an estimated 10 kg of Hg could have been transported through this watershed. Compared to the flood periods, Hg transport at other times of the year is probably negligible in this section. Stratiyenko et al. (2004) calculated an annual export of 80 kg THg and 4.4 kg dissolved Hg for the river at Romanovskoye, using an average annual Hg concentration of 4 ng L^{-1}. However, our data which was obtained using clean techniques shows that this concentration might be more representative of the flood period, and that Hg is not detected in this section of the river during all seasons (Table 1). The Hg budget calculated by Stratiyenko et al. (2004) would therefore seem excessively high.

4.4 Aquatic plants

Terrestrial and aquatic plants can accumulate Hg from contaminated soils and sediments. The uptake and retention of Hg is plant-specific and is influenced by a large number of factors (Crowder, 1991; Patra and Sharma, 2000). Mercury concentrations in narrow-leaf cattail (*Typha angustifolia*) growing on the banks of the river ranged from 0.63 mg kg^{-1} near the effluent outfall canal to 0.03 mg kg^{-1} at a distance of ca. 60 km downstream. The highest concentrations are similar to levels reported by Szymanowska et al. (1999) for common cattail (*Typha latifolia*) from lakes receiving untreated sewage (0.31 – 0.60 mg kg^{-1}), although Hg concentrations in the corresponding lake sediments ranged between 0.25 and 0.54 mg kg^{-1} and were therefore much lower than Hg levels in soils and sediments on the Nura. Fig. 9 illustrates the decline in Hg concentrations in cattail along the river, in relation to Hg levels in river bank soils and bed sediments (Heaven et. al., 2000ab). In general, Hg concentrations in cattail leaves mirrored Hg concentrations in river bank soils surprisingly well and appeared to respond even to localised increases in soil Hg. Apart from the first 5 km and the section between Tegis-Zhol and Rostovka (ca. 20-30 km downstream), Hg concentrations were below 0.1 mg kg^{-1}. Stratiyenko

et al. (2004) reported background concentrations of 0.02 mg kg^{-1} for cattail upstream of Samarkand Reservoir, and 0.21 mg kg^{-1} at Tegis-Zhol.

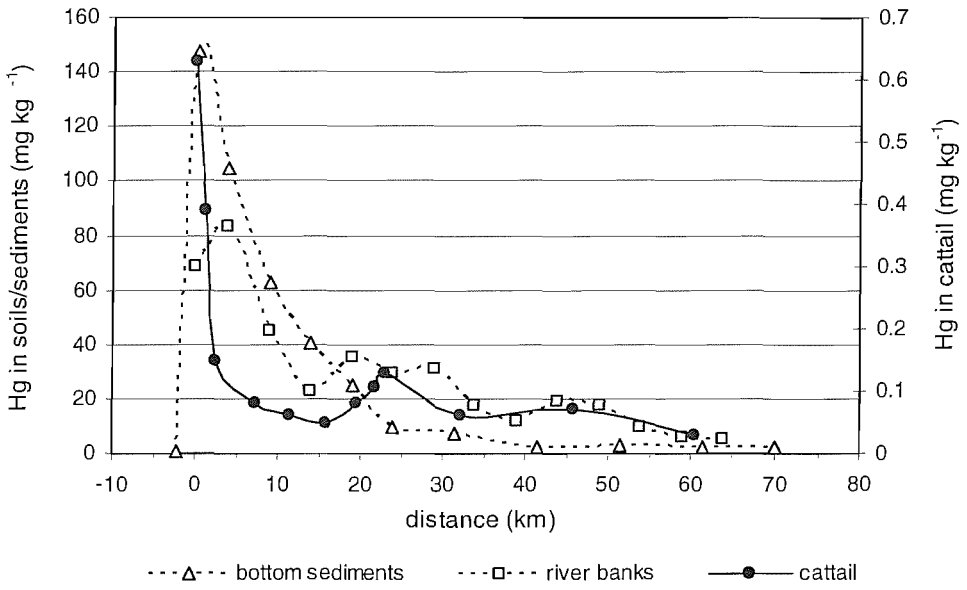

Fig. 9. Mercury concentrations in narrow-leaf cattail (*Typha angustifolia*) and corresponding Hg concentrations in river bank soils and sediments (Heaven et al., 2000b).

Mercury in river bank soils between Tegis-Zhol and Rostovka (THg 30 – 35 mg kg^{-1}) appeared to be more available for plant uptake than at Old Gagarinskoye (THg ~45 mg kg^{-1}). The reason for this is unclear. Bonzongo et al. (2006) found that Hg-rich river-bank materials on the Carson river became sites of Hg methylation as their water content increased during periods of high flow. It could be that the river banks in the section between Tegis-Zhol and Rostovka are less steep and are more frequently in contact with water, which may provide more favourable conditions for methylation.

Another interesting observation is that Hg concentrations in cattail at the upper reach of the Intumak reservoir were close to background concentrations (0.03 mg kg^{-1}), whereas Stratiyenko et al. (2004) reported 0.10 mg kg^{-1} for cattail growing at the tail water pool of the reservoir. Similarly, Deckwer and Leonhäuser (2005) found up to 0.025 mg kg^{-1} in reeds growing at the headwater of the reservoir, whereas reeds at the tailwater pool contained 0.05-0.17 mg Hg kg^{-1} (Stratiyenko et al., 2004). Increased Hg concentrations were also found in fish downstream of the reservoir (section 4.5). It could be that the area just downstream of the dam is a site of enhanced MeHg production, and this would warrant further investigation.

Mercury concentrations in common reed (*Phragmites communis*) from Kurgaldzhino were significantly higher in roots (3.5 mg kg^{-1}) than in stalks and leaves (0.05 mg kg^{-1} and 0.77 mg kg^{-1}, respectively). These Hg concentrations are an order of magnitude higher than levels reported by Stratiyenko et al. (2004) for reeds sampled at Kurgaldzhino in the same year (0.07 mg kg^{-1}), and are also higher than concentrations reported in the same study for the contaminated section of the river at Tegis-Zhol (0.22 mg kg^{-1}). Background concentrations of Hg in leaves of reeds growing upstream of Samarkand Reservoir were 0.01 mg kg^{-1} (Stratiyenko et al., 2004). The large difference found for reeds from Kurgaldzhino could be due to the selection of sampling locations with different hydrological and biogeochemical characteristics, as the wetlands cover an extensive area. The high Hg concentrations accumulated by plant roots despite the very low Hg concentrations in sediments (Table 1) indicate that Hg is in a highly bioavailable form compared to the upstream site at Tegis-Zhol where Hg concentrations in sediments and river bank soils are more than three orders of magnitude higher than in the wetlands. This would concur with the fact that wetlands are sites of MeHg production (StLouis et al., 1996; Kelly et al., 1997; Gilmour et al., 1998; Waldron et al., 2000; Wiener and Shields, 2000), but is somewhat at odds with our observation that Hg concentrations in fish caught from the lakes were low (section 4.5). Further studies are needed to establish MeHg concentrations in sediments and plants in the wetlands.

4.5 Fish

Fish are sensitive indicators of aquatic Hg pollution, but it is generally acknowledged that THg in waters or sediments is not a good predictor of Hg in fish tissue. Methylmercury is the species that is bioaccumulated and commonly accounts for >90% of THg in fish tissue, depending on the trophic level (Bloom, 1992; Watras et al., 1998; Mason et al., 2000). Although MeHg is thought to be less available for uptake in alkaline surface waters (Haines et al., 1992; Lange et al., 1993), fish in the Nura are clearly impacted by the high Hg concentrations in this river system. Table 2 summarises the data on Hg in fish caught between the outfall canal at Temirtau and the terminal wetlands. For comparison, a smaller survey carried out by Stratiyenko et al. (2004) cites near background concentrations of Hg for fish from the slightly impacted Samarkand reservoir as 0.03 mg kg^{-1} for bottom feeders, and 0.04 – 0.06 mg kg^{-1} for predatory fish species, while two specimens of roach from a 'true' reference site 100 km upstream contained 0.01 and 0.02 mg kg^{-1} of Hg. We found that crayfish bought on the local market in Temirtau contained 0.026 mg kg^{-1} of Hg, whereas crayfish from the reservoir contained about twice as much Hg (0.043 mg kg^{-1}).

Bottom feeding fish (roach, carp, bream and gudgeon) were predominant in the most contaminated section of the river and contained on average between 0.3 and 0.5 mg kg^{-1} of Hg.

Table 2. Summary data on age, weight, length and total Hg content of fish caught from the River Nura

Location and species	n	age (years)		weight (g)		length (mm)		Hg (mg kg^{-1})			distance
		range	mean	range	mean	range	mean	range	mean±SE	med	
Nura at Temirtau											*-2.5 km*
Perch	1	3+			93		156		0.15		
Effluent outfall canal											---
Roach	2	2+ / 3+	2.5	38/68	53	135/150	143	0.41/0.56	0.49±0.07	0.49	
Gudgeon	1		2		15		96		0.36		
Bream	2	2+ / 2+	2	95/116	106	170/175	173	0.27/0.38	0.32±0.06	0.32	
Inflow of canal to river											*0 km*
Roach	19	2+ - 4+	3.2	44-111	75	128-180	150	0.22-0.81	0.38±0.04	0.34	
Gudgeon	16	2+ - 4+	3.0	17-47	27	98-130	111	0.20-0.64	0.44±0.03	0.45	
Bream	3	2+ - 3+	2.3	85-139	112	163-185	174	0.31-0.70	0.51±0.11	0.50	
Dace	1				100		165		0.09		
Nura near Gagarinskoye											*5 - 9 km*
Roach	3				(23)†		(130)†	0.20-0.31	0.24±0.03	0.22	
Gudgeon	1				(12)†		(120)†		0.34		
Bream	1								0.39		
Carp	3	(1+)†			(14)†		(103)†	0.10-0.52	0.36±0.13	0.46	
River Perch	1								0.18		
Pikeperch	1								0.40		
Nura at Mill House dam											*14 km*
Roach	6	1+ - 3+	2.2	16-66	45	99-146	130	0.19-0.63	0.42±0.06	0.43	
Gudgeon	2	2+ / 3+	2.5	13/20	16	88/102	95	0.42/0.44	0.43±0.01	0.43	
Bream	7	2+ - 3+	2.6	100-193	133	168-200	182	0.15-1.07	0.56±0.13	0.70	
River Perch	5	2+ - 3+	2.2	26-42	36	115-137	121	0.64-1.15	0.94±0.12	1.09	
Nura near Tegis-Zhol											
Roach	5	3+ - 4+	3.4	64-170	95	140-177	153	0.32-0.50	0.38±0.03	0.36	*18 km*
Carp	1								0.38		
River Perch	1	1+			15		96		0.70		

Location and species	n	age (years)		weight (g)		length (mm)		Hg (mg kg^{-1})			distance
		range	mean	range	mean	range	mean	range	mean±SE	med	
Intumak reservoir outfall											*85 km*
Roach	5	1+ - 3+	2.2	9-67	43	79-144	124	0.38-0.58	0.48±0.03	0.47	
River Perch	14	1+ - 4+	2.5	15-87	47	88-165	128	0.35-1.32	0.54±0.06	0.50	
Dace	1				8		81		0.31		
Samarka barrage outfall											*125 km*
Roach	7	1+ - 2+	1.7	20-50	33	104-140	121	0.28-0.59	0.41±0.04	0.43	
Carp	6	2+ - 4+	3.0	75-163	107	135-175	152	0.02-0.05	0.03±0.003	0.03	
River Perch	6	2+ - 4+	2.7	19-106	50	103-180	134	0.23-0.86	0.50±0.09	0.50	
Ruffe	1	3+			45		122		0.68		
Nura near Sabyndy											*370 km*
Carp	20	2+ - 3+	2.3	50-114	73	115-160	132	0.007-0.09	0.03±0.006	0.03	
Uyalyshalkar Lakes											*420 km*
Pike	2	2+ / 3+	2.5					0.09/0.29	0.19±0.098	0.19	
Pikeperch	2	3+	3					0.08/0.10	0.09±0.011	0.09	
Lakes near Karazhar											*480-550 km*
Pike	2	3+ / 6+	4.5					0.045-0.079	0.062±0.017	0.062	
Pikeperch	1	4+							0.054		

n – number of specimens; length (mm) – given values represent the length of the fish without the caudal fin
[†]age / weight / length info for one specimen only

This is higher than the maximum permissible concentration of Hg in freshwater fish in Europe and Kazakhstan which is set at 0.3 mg kg^{-1} (w.w.). Mercury levels in predatory fish species such as perch were even higher than in bottom feeders and reached up to 0.94 mg kg^{-1} at the Mill house dam (14.2 km from the outfall). The results of a biomonitoring survey conducted by us in several villages along the river in 2005 show that people who regularly consume fish from the river have elevated Hg concentrations in their hair (Hsiao and Ullrich, *in preparation*). Mercury concentrations in human hair were higher in Rostovka than in the most contaminated reach at Gagarinskoye, indicating that people in downstream villages are more at risk, which may be pointing to a higher MeHg content in fish downstream from the source of the pollution (Hill et al., 1996).

Fig. 10 illustrates mean Hg concentrations in bottom feeders (*Cyprinidae*) compared to predatory species (*Percidae*) for the 125 km section of the river between the outfall canal and Samarka. Mercury levels in carp (*Carassius carassius*) at Gagarinskoye (mean 0.36 mg kg^{-1}, n=3) and Tegis-Zhol (0.38 mg kg^{-1}, n=1) were elevated by about one order of magnitude compared to background levels. However, carp on the Nura is not as highly contaminated as in Lake Balkyldak in northern Kazakhstan, where Hg concentrations ranged from 0.54 – 1.39 mg kg^{-1} (Ullrich et al., 2007). Information on perch (*Perca fluviatilis*) and pikeperch (*Sander lucioperca*) in the first 14 km from the outfall is limited, unfortunately, as only one specimen each was collected. In the section near the Mill House dam and Tegis-Zhol (combined mean 0.90 mg kg^{-1}), Hg levels in perch were significantly higher ($p<0.01$) than at the outfall of the Intumak and Samarka reservoirs (means of 0.54 mg kg^{-1} and 0.50 mg kg^{-1}). Only one specimen of perch was collected near Tegis-Zhol (0.7 mg kg^{-1}), but Stratiyenko et al. (2004) reported 0.56 mg kg^{-1} and 0.69 mg kg^{-1} for perch of the same age at this sampling point, which is in fairly good agreement. Tissue levels of Hg in perch at Intumak and Samarka were significantly correlated with both weight and length of the fish ($r= 0.625$ and 0.910 at $p<0.05$).

It is remarkable that apart from carp and perch, there was no discernible trend of diminishing Hg concentrations in fish tissue with increasing distance from the source of the pollution (Fig. 10). Mean Hg levels in roach (*Rutilus rutilus*) between the effluent outfall canal and Samarka barrage ranged from 0.24 to 0.49 mg kg^{-1}, but did not differ significantly. Mercury concentrations in roach at the outfall of the Intumak reservoir (0.48 mg kg^{-1}, n=5) appeared to be as high or even higher than concentrations in and near the effluent canal (0.49 mg kg^{-1}, n=2, and 0.38 mg kg^{-1}, n=19). Concentrations at Samarka were also high (0.41 mg kg^{-1}, n=7). Schaefer et al. (2004) suggested that at high aqueous THg concentrations, higher MeHg degradation rates reduce bioaccumulation, leading to similar MeHg levels in biota.

Due to the small sample sizes, there were no significant differences in Hg accumulation between individual species of bottom feeders. However, it is interesting that while Hg levels in carp (*Carassius carassius*) were similar to levels in other bottom feeders at Gagarinskoye and

Tegis-Zhol, Hg concentrations in carp at Samarka barrage appeared to have decreased to background levels of 0.03 mg kg^{-1}, whereas Hg levels in roach were still elevated and were more than an order of magnitude higher. The reason for this is unclear, as both species occupy a similar trophic position in the aquatic food web, but it most likely reflects differences in feeding strategies.

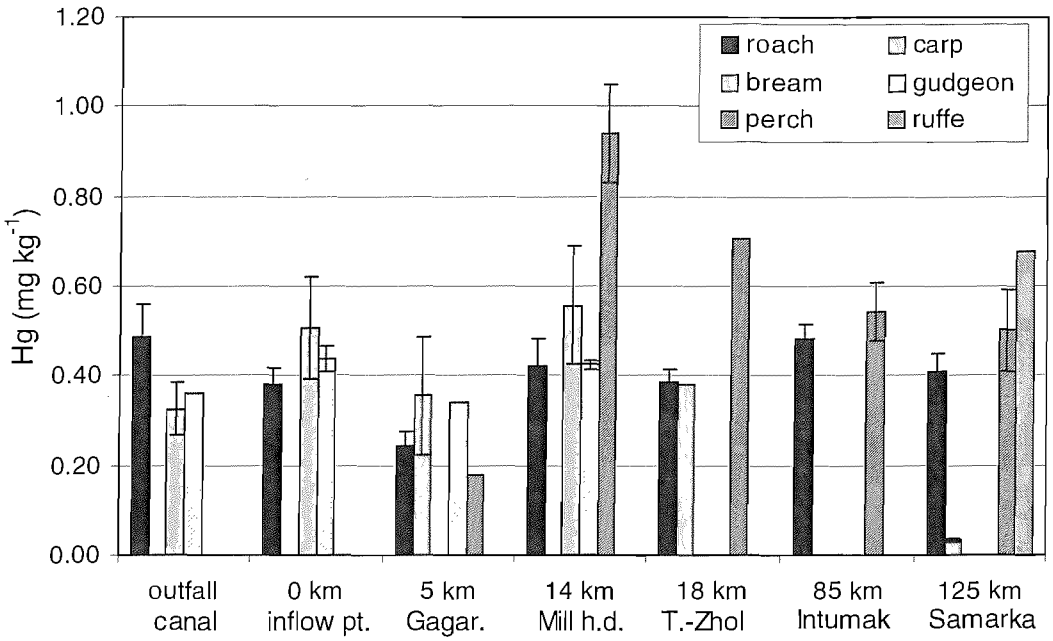

Fig. 10. Mean mercury concentrations in muscle tissue of bottom feeders (roach, carp, bream, gudgeon) and predatory fish species (perch, ruffe).

It is surprising that Hg concentrations in fish are still elevated at a distance of more than 100 km from the source and after significant quantities of contaminated particles have settled in the Intumak reservoir. Mercury concentrations in waters and sediments are 1 – 3 orders of magnitude lower beyond Intumak compared to upstream sites. However, increased Hg concentrations were found in aquatic plants downstream of the Intumak reservoir (section 4.4), and a small increase in aqueous THg concentrations was noted at Samarka in all seasons (section 4.2.5). There is a lack of data on Hg concentrations in biota between Samarka barrage and Sabyndy, 370 km downstream. Stratiyenko et al. (2004) sampled 4 specimens of fish near Kievka at 205 km and found that 5-year-old perch and pikeperch had accumulated ~0.6 mg kg^{-1} of Hg (n=2), whereas 2 specimens of carp had tissue levels of 0.07 – 0.12 mg kg^{-1} and two samples of caddis fly larvae contained 0.1 mg kg^{-1} of Hg. The fact that Hg levels in biota are still elevated above background in this section indicates that the river is impacted at least up to Kievka. It could be that the slight but persistent increase in aqueous THg concentrations

immediately downstream of the Samarka barrage is attributable to dissolved MeHg and that this is causing an increase in fish Hg concentrations downstream. Reservoirs are known to have downstream effects on Hg concentrations in fish by exporting MeHg in water and invertebrates (Bodaly et al., 1997; Schetagne, 2000). Hines et al. (2000 and 2006) also observed that impoundments on the Soča river enhanced Hg methylation and mobilization. More data is needed for the section between Intumak and Sabyndy to corroborate this assumption.

The elevated Hg concentrations found in fish in downstream reaches could reflect fluvial transport of MeHg from upstream sites, or increased in-situ production of MeHg at less impacted sites. The spring thaw is thought to mobilize largely non-methyl forms of Hg (Babiarz et al., 1998). However, it could be that Hg transport at the time of the flood transfers 'fresh' Hg to downstream reaches that may be more available for methylation. A number of recent Hg amendment studies have shown that newly deposited or freshly added Hg is more readily methylated than ambient Hg (Hintelmann et al., 2000; Branfireun et al., 2005; Orihel et al., 2006). In East Fork Poplar Creek in Tennessee, 'fresh' Hg contributed by upstream sources was also found to be more available for bioaccumulation compared with pre-existing Hg in pond sediments (Southworth et al., 2002). Furthermore, as methylation activity is usually highest in spring/summer (e.g. Bubb et al., 1993; Hintelmann and Wilken, 1995; Bloom et al., 1999), the annual input of 'fresh' Hg on the Nura happens at a time that would be conducive to MeHg formation.

In the terminal wetlands of the Nura, Hg concentrations in pikeperch (*Sander lucioperca*) ranged from 0.05 – 0.10 mg kg^{-1} (mean 0.079, n=3), compared to 0.015 mg Hg kg^{-1} in pikeperch bought on the market. Similarly, Hg levels in pike (*Esox lucius*) ranged between 0.045 – 0.29 mg kg^{-1} (mean 0.127, n=4), while pike from the market contained 0.054 mg kg^{-1} of Hg. These concentrations are close to background levels. Although the sample size was very small, the data seems to indicate that Hg concentrations in the two fish species were slightly higher in the first group of lakes (Uyalyshalkar) between Sabyndy and Kurgaldzhino, compared to the lakes near Karazhar which are at the centre of the wetlands (Table 2). During the spring flood, the Uyalyshalkar lakes slowly fill up with water and only gradually pass on the flood waters to the rest of the wetlands. It is possible that small particulates with Hg adsorbed to them that have been transported from upper reaches settle out here, and that this causes the slight difference in tissue Hg concentrations. Mercury concentrations in pike and pikeperch from the lakes near Karazhar are ~0.06 mg kg^{-1} and are very close to background. On the basis of this limited set of data, we would conclude that there is probably no significant impact of Hg on wildlife at the terminal lakes, but further studies are recommended.

5. Conclusions

Mercury concentrations in surface water in the river Nura are largely controlled by seasonal hydrological conditions. The majority of Hg mass flow takes place during the annual spring flood which leads to the remobilization of contaminated bed sediments and causes extensive river bank erosion. However, high Hg concentrations were also found under base flow conditions during the summer low-water period when the water level in the river is severely decreased.

At the Intumak reservoir, Hg concentrations in surface water are reduced by one order of magnitude, indicating that the major part of particulate Hg is removed by sedimentation. Our estimates of Hg mass flow at Intumak and Romanovskoye differ significantly from those of Stratiyenko et al. (2004) and show that these workers most likely overestimated the Hg flux in downstream sections of the river.

A significant inverse relationship was found between THg concentrations in sediments and the percentage of MeHg formed. This may be the underlying reason why higher MeHg levels are often observed in waters at less contaminated compared to contaminated sites, and could explain why in fluvial systems MeHg concentrations in water and fish have frequently been found to increase rather than decrease with increasing distance from a point source.

Aquatic biota in the Nura were found to be impacted by Hg for more than 125 km downstream and for most species there was no significant decrease in Hg tissue levels over this distance. More data is needed for the section of the river between Samarka and Sabyndy. Elevated Hg concentrations in water, fish and aquatic plants near impoundments appear to indicate that the availability of Hg for methylation may be increased in these areas.

A project to clean up the most polluted section of the river has recently been initiated and remediation work is planned to start in spring 2008 (World Bank, 2003). However, experience to date has shown that it is not certain how quickly Hg concentrations in fish will respond to the decrease in aquatic Hg contamination in the upper reach of the river (Munthe et al., 2007). It is therefore likely that further monitoring activities will have to be carried out on the river for a considerable period of time.

The terminal wetlands of the Nura do not appear to be impacted at present, but further studies are advisable and further transport of Hg to downstream reaches of the river should be prevented. Future work should focus on investigating the methylation capacity at the Intumak reservoir and the Samarka barrage. There are indications that these structures are causing localised increases in fish Hg, and may also transfer dissolved MeHg further down the river. The dynamics of MeHg formation at these impoundments is presently not clear and this would be an interesting and useful subject for further research.

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