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RESEARCH ARTICLE

# Mercury human exposure through fish consumption in a reservoir contaminated by a chlor-alkali plant: Babeni reservoir (Romania)

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**Abstract**
*Purpose* Chlor-alkali plants are one of the most important point sources of mercury to aquatic environment. The problem of Hg contamination has been studied in a region, Rm Valcea (Romania), impacted by the wastewater discharge of a chlor-alkali plant. The purpose of the present study is to evaluate the current status of mercury pollution in the Babeni reservoir (Olt River) and the exposure of local population via fish consumption to mercury originating from the chlor-alkali plant.
*Methods* Sediments were collected from Valcea, Govora and Babeni reservoirs. Grain size distribution, organic content and total mercury (THg) concentrations were analysed in sediments. Fish were purchased from local anglers, and the scalp hair was collected from volunteers. THg in sediment, fish and hair samples was determined using an atomic absorption spectrophotometer for Hg determination. Monomethylmercury (MMHg) was analysed in the muscle and liver tissues by species-specific isotope dilution and capillary gas chromatography hyphenated to inductively coupled plasma mass spectrometer.
*Results* High mercury concentrations were found in the sediments and in fish from Babeni reservoir, with a median of 2.1 mg/kg (IQR=3.2) in sediments and a mean value of 1.8±0.8 mg/kg_ww in fish muscle. MMHg concentrations in fish were well above the WHO guidelines for fish consumption. Local population consuming fish from the Babeni reservoir had THg concentrations in hair significantly higher than those consuming fish from upstream reservoirs and/or from the shops and reached a median value of 2.5 mg/kg (IQR=3.6).
*Conclusions* The remnant pollution in the fish of this reservoir, and probably many other lakes and reservoirs receiving Hg polluted wastewater, represents a considerable health risk for the local fish consumers.

**Keywords** Mercury · Human exposure · Fish consumption · Chlor-alkali

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## 1 Introduction

Mercury (Hg) is a trace metal which environmental cycling has strongly enhanced by mining, coal burning and industrial uses (Mason and Sullivan 1998; Boening 2000). Industry is an important source of Hg pollution in the environment (Pacyna and Munthe 1991; UNEP 2002) specially chlor-alkali industry, the releases of which represent severe problems of Hg contamination in Canada (Gilbertson 2004), Kazakhstan (Ullrich et al. 2007), Colombia (Olivero-Verbel et al. 2008), Sweden (Lindeström 2001), Czech Republic (Marsalek et al. 2005), Taiwan (Huang et al. 2008), China (Yan et al. 2008), and other countries (UNEP 2002).

European chlor-alkali industry accounts for 21% of the world Hg consumption and around 50% of the total European Hg consumption is used in mercury cells (Maxon 2006). In 2006, some 40% of total capacity to produce chloride and caustic soda in Europe still used Hg-cell technology (Eurochlor 2007). Hg released from chlor-alkali plants can enter the aquatic systems, oxidise, bind easily to suspended particles, and be deposited in the bottom sediments, where it can be partly methylated by specific bacteria activities (Gilmour and Riedel 1995; Pak and Bartha 1998; Gray et al. 2004; Fleming et al. 2006).

The consumption of Hg-contaminated fish is the most common exposure pathway of monomethylmercury (MMHg) for humans (WHO-IPCS 1990). Despite the worldwide recognition of the risk of MMHg intoxication (Amin-Zaki et al. 1974; Clarkson 1993, 1998; Harada 1995; Ninomiya et al. 1995; Ekino et al. 2007), the high Hg concentrations found recently in sediments and biota from different lakes and reservoirs contaminated by chlor-alkali plants (Lindeström 2001; Gilbertson 2004; Marsalek et al. 2005; Ullrich et al. 2007; Yan et al. 2008) highlight the importance to study the impact of Hg contamination in the sites located close to this known source of pollution.

The problem of Hg contamination has been studied in the framework of the ESTROM project (see Acknowledgements) in a region, Rm Valcea (Romania), impacted by the wastewater discharge from a chlor-alkali plant. Since 1974, the plant has been discharging Hg into the Olt River, the largest Romanian tributary of the Danube River. In a previous study, we examined the contamination history inferred from sediment records in the Babeni Reservoir, located downstream from the wastewater releases (Bravo et al. 2009a).

The present study reveals the transfer of Hg from the Babeni reservoir to human via fish consumption. Here, we demonstrate that the severe Hg contamination of sediment and fish in this reservoir results in a high Hg concentration in the hair of a population consuming fish from the Babeni reservoir.

## 2 Materials and methods

### 2.1 Study area

Rm Valcea is a large urban area of 90 km$^2$ with a population of 110,000. An industrial platform was built in the 1950s, including salt processing and chemical and thermal power plants. The company with the largest chlor-alkali production in central and Eastern Europe is settled in Rm Valcea.

Rm Valcea is located in the middle reaches of the Olt River, a 615-km-long tributary of the Danube. The water discharge of the Olt River is 160 m$^3$ at the confluence with the Danube. The Babeni Reservoir (Fig. 1) is one of the 19 reservoirs built during the 1970s in the Olt River for flood prevention and power generation. Hence, the hydroelectric plants regulate the river flow regime.

The mean yearly flows of the Olt River during the period 1995–2004 were in the range of 101–191 m$^3$/s at the entrance to the Babeni reservoir. The mean reservoir volume is 35.3 million m$^3$; it has a surface area of 905 thousands m$^2$ and a mean depth of 3.9 m. Three Olt River tributaries join the Babeni Reservoir (Fig. 1): the Govora (0.15–1.01 m$^3$/s), the Bistrita (1.3–5.7 m$^3$/s), and the Topolog (1.0–4.6 m$^3$/s).

Babeni reservoir is a warm-temperate waterbody which can reach 25°C in surface waters during summer (August 1995–2004). Oxygen, conductivity and pH vary along the reservoir. Oxygen content can decrease in water column below 2 m deep during summer; for example, in August 2003, water column showed 75% of oxygen saturation at 2 m and 62% at 8 m deep, at a site close to the dam. Similar values were measured in October 2000. Conductivity and pH vary monthly along the reservoir and with depth. In general, conductivity increases with depth and from upstream part of the reservoir to downstream. An opposite trend has been observed for pH measurements. Conductivity and pH varied from 661 to 1,201 µS/cm and from 7.9 to 8.6, respectively, in August 2003. Similar values were measured during summer periods between 1995 and 2004 (Data of Apele Romana Olt, see acknowledgements).

### 2.2 Sampling

#### *2.2.1 Sediments*

In the preliminary stage in August 2005, ten sediment samples were collected with Ponar-type grab sampler from Valcea, Govora, and Babeni reservoirs and from the channel discharging wastewater from the chlor-alkali plant. These samples were analysed for THg, grain size and loss on ignition (LOI). One year later, two, 17 and 52 sediment samples were collected in the Valcea, Govora and Babeni reservoirs, respectively. Approximately 300 g wet weight (ww) from the top (2 cm) was subsampled from the centre of the grab to avoid metal contamination.

In October 2007, sediments from the Govora, Bistrita and Topolog Rivers were sampled, with the same sampling method, in order to verify other possible fluvial sources of Hg for the Babeni reservoir.

#### *2.2.2 Fish*

Although there is no professional fishing in the reservoirs, angling is very popular and provides a considerable food

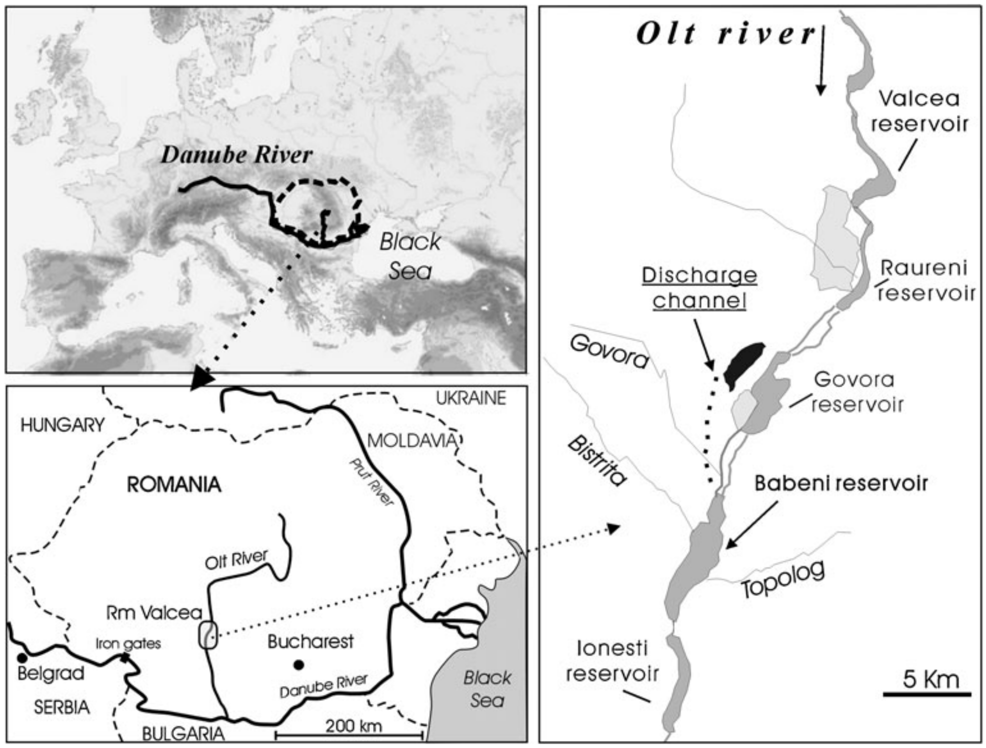


**Fig. 1** Localization of the Olt river Romania and Europe

resource for numerous families. The sampling strategy was chosen to determine the mercury level in the fish groups actually consumed by the local population; consequently fish samples were purchased from local anglers.

In October 2007, 24 fish from Babeni reservoir and 31 fish from upstream reservoirs were collected, among which eight species were identified: bleaks (*Alburnus alburnus*), asps (*Aspius aspius*), Prussian carps (*Carassius gibelio*), European carps (*Cyprinius carpio*), Euroasian ruffes (*Gymnocephalus cernus), European perchs (Perca fluviatilis), roachs (Rutilus rutilus) and pikeperchs (Stizostedion lucioperca). The fish were placed in polyethylene bags and kept frozen until analyses.*

Once in the laboratory, the weight and the length were recorded. A portion of the dorsal muscle tissue and liver from each fish were dissected and freeze-dried for THg and MMHg analyses. The concentrations are presented in ww calculated with an average value of 75% of water content in fish muscle. The age was determined using the scales and/or the otoliths (Morales-Nin 1992; Ombredane and Bagliniere 1992).

### 2.2.3 Hair

A total of 75 hair samples were collected from volunteers. Volunteers came from a great diversity of social groups including workers, housewives and unemployed people living in houses or in various vehicles or carts stationed at the banks of the reservoir. All participants were informed about the target of the study. A questionnaire including gender (F: female; M: male), age (c: children from 1 to 12 years old; a: adult: > 12 years), weight, activity (i: chlor-alkali plant; an: anglers; o: other), frequency of fish consumption (number of fish meals per week), and origin of the eaten fish (s: shop; babeni: Babeni Reservoir; olt: other reservoir of the River Olt) was completed by each person. Hair samples were cut close to the scalp, put in polyethylene bags and kept in dark conditions. The scalp-side 2 cm hair sections were subsampled for THg analyses in order to assess the recent exposure.

### 2.3 Laboratory analyses

In general, river sediments are much coarser than lake sediment, thus the separation and measurement of grain size distribution are different. The coarse river sediments were sieved at 1 mm and 0.063 mm, separated in the three major size classes according to their diameter ($\Phi$; clays and silts, $\Phi$<0.063 mm; fine-coarse sand, 0.063 mm<$\Phi$<1 mm; very coarse sand and gravels, $\Phi$>1 mm) and then dried at 60°C to a constant weight for analyses.

The analyses of particle size of lake sediments were performed on wet sediment in deionised water with a LS-100 analyser (Beckman Coulter, Fullerton, CA, USA), following Loizeau et al. (1994) method. This method allows calculating the volume percentage of particles according to their diameter: clay ($\Phi$< 0.002 mm), silt (0.002<$\Phi$<0.063 mm), and fine-coarse sand (0.063<$\Phi$<1 mm) fractions.

All sediment subsamples were powdered and homogenised with an agate mortar and stored in dark conditions until analysis. The scalp hair and freeze-dried samples of fish muscle were homogenised by cutting them with cleaned scissors and kept in dark conditions.

The LOI, a surrogate of organic matter content (Dean 1974), was measured by heating dried sediments at 550°C for 1 h. The THg in sediment, fish and hair samples was determined using an atomic absorption spectrophotometer for Hg determination (Advanced Hg Analyser; AMA 254, Altec s.r.l., Czech Rep.). The accuracy of Hg measurements in lake sediment and fish measurements was frequently checked by analyzing two reference materials WQB-3 and TORT-2, respectively (National Water Research Institute, Canada). The measured values were in the certified range for all analyses. Precision determined by replicate analysis in each run was better than 4% for sediments, 6% for fish and 3% for hair.

MMHg was only measured in the muscle and liver tissues of the most numerous fish groups from each reservoir (Table 1): common bleaks from the Babeni reservoir and European perch from the upstream reservoirs. The Hg species extraction was achieved with a focused microwave method (4 min, 80 W, CEM) from 100 mg of fish tissue in 5 ml of a tetramethylammonium hydroxide solution (25%, Fluka; Martin-Doimeadios et al. 2002), and remaining particles were removed by centrifugation. The extracts were analysed by species-specific isotope dilution and capillary gas chromatography (Focus GC, ThermoFinnigan) hyphenated to inductively coupled plasma mass spectrometer (X7 II, ThermoElectron) to correct for species inter-conversion if necessary (Monperrus et al. 2008). Briefly, the extracts were buffered at pH 4 and isotopic-enriched Hg species $^{199}$IHg and $^{201}$MMHg were then added. Species were then ethylated with sodium tetraethyl borate and recovered in isooctane. Each sample was injected three times, and blanks were checked to control for contamination. The accuracy of the of MMHg measurements was checked by analyzing certified reference material BCR 464 and DOLT-4m, and recoveries of MMHg were found to be 89% for each reference material used to calculate MMHg concentrations in fish. MMHg concentrations are presented as mgHg/kg fish wet weight (ww).

## 2.4 Statistical analysis

Kolmogorov–Smirnov test was used to evaluate the normality of the data. The centre and dispersion of the samples following a non-normal distribution are represented by the median and the inter-quartile range (IQR). THg concentrations, the percentage of clay in the surface sediments of Govora and Babeni reservoirs and the THg concentrations in fish and hair did not follow a normal distribution. Several transformations were tested ($f^2$, $\ln(f)$, $\ln(f+1)$, $f^{1/2}$), but the distributions did not follow a normal distribution. Consequently, the non-parametric test, Mann–Whitney, was used to compare the THg concentrations in sediments of the Govora and Babeni reservoirs. Kruskal–Wallis test was used for multiple sample comparison: (1) THg concentration in hair vs activity of the people and (2) THg concentrations in hair vs origin of the eaten fish. Rho–Spearman test was used to analyse the correlation (1) THg vs LOI, clay, silt and sand contents and (2) fish consumption vs THg in hair. Correlation between the age of fish and

**Table 1** Latin name of sampled fish and Hg concentration in fish muscle from the different reservoirs

Mercury concentration (mg/kg_ww) in the fish muscle

| Name | Common name | Babeni | | | Upstream | | |
|---|---|---|---|---|---|---|---|
| | | N[1] | Hg[2] | MMHg[3] | N | Hg | MMHg |
| *A. alburnus* | Bleak | 7 | 2.8±0.5 | 2.6±0.4 | 3 | 0.12±0.03 | |
| *A. aspius* | Asp | | | | 4 | 0.142±0.003 | |
| *C. gibelio* | Prussian carp | 7 | 1.6±0.4 | | 9 | 0.06±0.02 | |
| *C. carpio* | European carp | 1 | 0.5 | | | | |
| *G. cernus* | Eurasian ruffe | 2 | 1.1±0.3 | | 4 | 0.17±0.10 | |
| *P. fluviatilis* | European perch | 4 | 1.6±0.4 | | 11 | 0.17±0.04 | 0.14±0.03 |
| *R. rutilus* | Roach | 2 | 1.7±0.5 | | | | |
| *Stizostedion lucioperca* | Zander/pike-perch | 1 | 0.4 | | | | |
| | Total and mean | 24 | 1.8±0.8 | | 31 | 0.10±0.05 | |

[1] Number of individuals

[2] Mean ± SD of Hg concentrations (mgHg/kg_ww) measured by AMA-254

[3] Mean ± std of MMHg concentrations (mHg/kg_ww) measured by GC-ICPMS and species-specific isotope dilution

THg concentration could not be established because there were not enough available data to perform a robust test. Mean and standard deviation (mean ± SD) summarised the sub-group data of THg concentration in fish, which followed a normal distribution and the comparisons of the distributions were performed with the *t* test (sub-groups of THg concentration in fish according to their reservoir of origin).

All the statistical tests and images were performed using SPSS (17.0) software, and a *p* value of 0.05 was chosen to indicate the statistical significance.

## 3 Results

### 3.1 Reservoir sediments

The THg concentrations measured in the samples collected during in the summer 2005 revealed high values in the Babeni reservoir (5 mg/kg, $n=5$) and reached 21 mg/kg in the discharge channel of the chlor-alkali plant. Lower values (0.11–0.66 mg/kg, $n=4$) were found in Govora and Valcea reservoirs. The median THg concentration in surface sediment sampled in 2006 in the Babeni reservoir was 2.1 mg/kg (IQR=3.2 mg/kg, $n=52$). The highest concentration exceeded the 6 mg/kg in one sample collected in the upstream part of the reservoir. Seventy-five percent of the collected samples exceeded 0.74 mg/kg, and the 25% exceeded the 3.9 mg/kg. High concentrations (4 mg/kg) were measured in the area close to the dam. Significantly lower concentrations were found in Valcea and Govora reservoirs a median value of 0.15 mg/kg (IQR=0.06 mg/kg, $n=17$).

Sediments from Govora and Babeni reservoirs had similar grain size distribution. Silt was the predominant fraction, around 75±2%. The sand fraction was around 20±3% for both reservoirs and the remaining was clay. In the Babeni reservoir, the sand fraction decreased from 95% in the upstream part of the reservoir to 0.2% in the downstream part. The clay followed an opposite trend and reached a maximum value of 7% in the downstream part of the reservoir. A significant correlation was found between clay percentage and THg concentration in sediments. The LOI values measured in the Govora reservoir was smaller and less variable than those measured in the Babeni reservoir, with mean values of 6±2% ($n=17$), and 9±7% ($n=52$), respectively.

### 3.2 River sediments

The THg concentrations measured in the different fractions of the river sediments were two orders of magnitude smaller than those found in sediments of the Babeni reservoir. The THg concentrations were higher in the silt and clays ($\Phi<$ 0.063 mm) than in the fine sand (0.063 mm$<\Phi<$1 mm), and very coarse sand ($\Phi>$1 mm). The THg concentrations were 0.019, 0.025 and 0.069 mg/kg for the different grain fractions in Govora River, from the larger to the finer fraction. The highest concentration was measured in the fine fraction in the Bistrita River, with a value of 0.091 mg/kg in the fine fraction.

### 3.3 Fish

Kolmogorov–Smirnov test revealed a normal distribution in the sub-groups of THg concentration in fish according to their reservoir of origin. Table 1 shows the mean and standard deviation of the mercury concentrations in the fish coming from non-contaminated reservoirs and from the Babeni reservoir. Fig. 2 represents the distribution of THg concentration in all purchased fish in a boxplot. The age of the sampled fish ranged between <1 and 3 years old, length from 9 to 27 cm weight from 8 to 253 g, and they were mainly omnivorous, including the juvenile pike-perch fish caught, which is piscivorous when adult.

The mean THg concentration in the fish from the Babeni reservoir was 1.8±0.8 mg/kg ww ($n=24$). The lowest THg concentration found among the fish caught in the Babeni reservoir was in a juvenile pike-perch (0.4 mg/kg ww). The bleaks showed the highest concentrations, with a mean THg of 2.8±0.5 mg/kg ww ($n=7$) and a maximal value of 3.4 mg/kg ww.

Other cyprinids also show high level of THg, like roach or Prussian carp (Table 1). For European perch, the same range of value was observed.

The mean THg concentrations were significantly higher in fish caught in the Babeni reservoir than in those found in the upstream reservoirs, which presented a mean value of 0.10±0.05 mg/kg ww ($n=31$). The lowest concentration

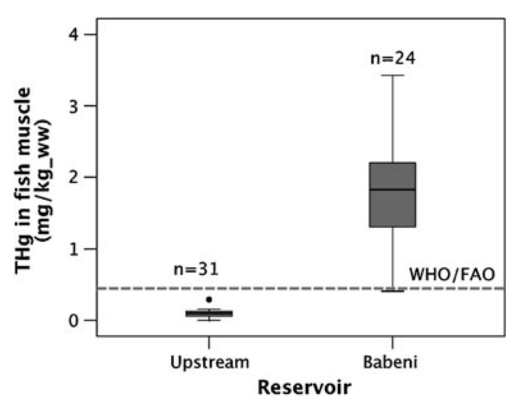


**Fig. 2** Boxplots of THg concentration in muscle of fish (mg/kg ww) collected in the upstream reservoirs and in the Babeni reservoir. *Dotted line* represents the threshold value of 0.5 mg of THg/kg of fish ww established by the WHO (WHO 2004) for non-carnivorous fish

was measured in one Prussian carp with a concentration of 0.06±0.02 ($n$=9) mg/kg ww (Table 1).

The MMHg in perch collected in upstream reservoirs accounted for 83±5% ($n$=11) of the THg. MMHg in the liver of the perch was one order of magnitude (0.038 mg/kg ww) lower than those measured in their fish muscle. However, MMHg represented 97±1% ($n$=7) of the THg in the muscle of bleaks collected in the Babeni reservoir. MMHg concentrations measured in the liver tissue of bleaks were in the same range as those measured in the muscle.

### 3.4 Hair

The median of THg concentrations in hair of all screened individuals was 1.1 mg/kg (IQR=2.7, $n$=75). Twenty-five percent of the sampled hair exceeded 2.9 mg/kg; 10% was above 5 mg/kg, and in three samples (4%), the concentration exceeded 10 mg/kg. THg concentrations were not significantly different between women (median=0.95 mg/kg, IQR=2.38, $n$=38) and men (median=1.46 mg/kg, IQR=2.98, $n$=37), and between children (median=1.04, IQR=1.83, $n$=24), and adults (median=1.38, IQR=3.14, $n$=51). The THg concentrations found in the individuals grouped according to their activity, fish consumption and origin of fish in their diet are presented in the Fig. 3.

#### *3.4.1 Hg concentration in hair versus the origin of the fish in their diet*

THg concentration in hair is significantly higher for people eating fish from the Babeni reservoir (median=2.5 mg/kg dw, IQR=3.6) than for the people who purchase fish from shops or from anglers fishing in the upstream reservoirs (Fig. 3a). THg concentrations were not significantly different between people eating fish from shops or from an upstream reservoir of the Olt River ($p$ value=0.6). For this reason, results of the THg concentration in hair according to people's activity or fish consumption were treated separately for population eating regularly fish from the Babeni reservoir and from shops and upstream reservoirs in Fig. 3b, c.

#### *3.4.2 Hg concentration in hair versus human activities*

Among the 75 volunteers, 42 consumed fish from the Babeni reservoir. Among these 42, 15 were anglers or family's anglers, ten workers in the industry, and 17 had other activities. The medians of THg concentrations of their hair were 3.4 mg/kg dw (IQR=7.5), 2 mg/kg dw (IQR=2.8), and 1.4 mg/kg dw (IQR=2), respectively (Fig. 3b) and were significantly different ($p$ value<0.001). In general, fisherman families presented higher THg concentrations,

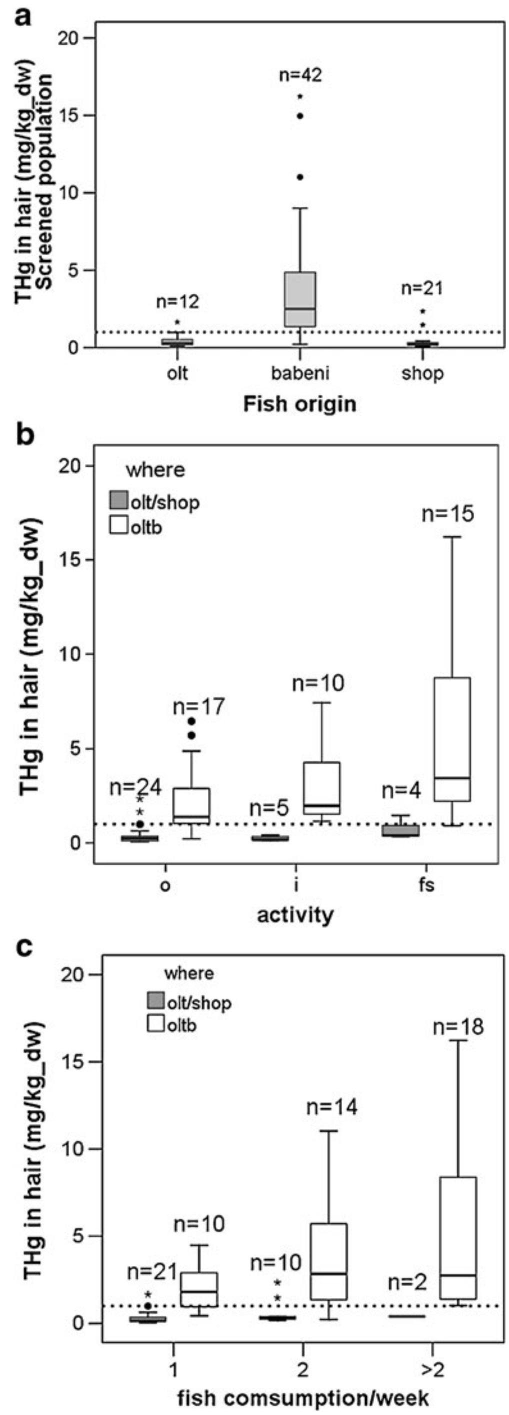


**Fig. 3** *Box plots* of mercury concentrations in scalp hair of individuals grouped according to their activity (i: chlor-alkali plant; an: anglers; o: other), their fish consumption per week and origin of the consumed fish (oltb: Babeni reservoir; olt: upstream reservoirs in Olt River; shop: shop or markets). The mercury concentrations in hairs of screened people consuming fish from the Babeni reservoir are represented by *white boxplots* and the others in *grey boxplots* (b, c plots). *Dotted line* represents reference concentration of 1 mg THg/kg in hair (USEPA 2001)

including families consuming fish from shops or from upstream reservoirs.

*3.4.3 Hg concentration in hair versus fish consumption*

Rho–Spearman test showed ($\rho$=0.53, $p$ value<0.001) a significant correlation between fish consumption and THg concentration in hair. The median concentrations in scalp hair of people consuming fish one or less per week from shops or from upstream reservoirs was 0.l4 mg/kg dw (IQR=0.25, $n$=21; Fig. 3c). Among the volunteers, only two people eat fish more than twice per week from shops or upstream reservoirs, and their THg concentrations did not exceed 0.4 mg/kg dw. However, this value exceeds 2.7 mg/kg dw (IQR=7, $n$=18) if fish from Babeni reservoir were consumed more than twice a week (Fig. 3c).

The fish consumption per week was significantly higher for anglers. Lower fish consumption was found for the group having other activities. THg concentration in the hair of the group eating fish from the Babeni reservoir more than twice a week was significantly higher than for the group eating fish from this reservoir once a week or less (Fig. 3c). One angler reported the highest fish consumption with seven meals per week. However, the THg concentration measured in his hair did not exceed 0.4 mg/kg dw. This individual catches the fish mainly from the upstream reservoir.

## 4 Discussion

### 4.1 Sources of Hg contamination

*4.1.1 Constraining the main Hg source*

The results of THg concentration from the surface sediment confirm that the Babeni reservoir is currently Hg-contaminated by the chlor-alkali plant discharge. The median of THg concentrations in the surface sediments in 2006 was in the same range as those found in top section of sediment cores collected in the same year (Bravo et al. 2009a). The median THg concentration was one order of magnitude higher in the Babeni reservoir than in the upstream reservoirs (Govora and Valcea) and exceeded 1.06 mg/kg, which is the concentration above which harmful effects for life will probably be observed in freshwater ecosystems (probable effect concentration; MacDonald et al. (2000)).

The highest values of THg concentration were found close to the discharge channel and in the upstream part of the reservoir. The THg concentrations and the maxima of clay content measured close to the dam indicate a transport of Hg along the whole reservoir (Colman et al. 1999), probably due to the clay–Hg association, as suggested by a significant correlation found between clay percentage and THg concentrations in the sediments from Babeni ($\rho$=042, $p$ value=0.007). Govora, Bistrita and Topolog tributaries do not represent a notable source of Hg for the reservoir, as testified by a low THg content in the fine fraction of the sediments collected at the mouth of these rivers.

*4.1.2 Hg in sediments and Hg emissions from the chlor-alkali plant*

According to the Romanian Ministry of Environment and Water Management (MEWM 2006), the Oltchim chlor-alkali plant operates at present a unit of 120,000 tonnes/year chlorine capacity based on membrane technology and another unit of 210,000 tonnes/year with Hg cells. The World Chlorine Council, (WCC 2006) has calculated a mean value of 0.09 g THg emitted into the water per tonne of chlorine capacity, in European countries. Thus, the total amount of THg emitted into the Babeni reservoir should not exceed 20 kg per year, which means that an amount of 0.022 μg THg/($cm^2$ y) would deposit (following WCC 2006), if we assume a homogenous deposition of this emitted Hg in the Babeni reservoir.

However, considering a constant sediment accumulation rate of 3.5 g/($cm^2$y) (Bravo et al. 2009a) and taking the Q25–Q75 of THg concentration measured in sediments in 2006 as a range of THg concentration in the reservoir, the THg deposited in the Babeni reservoir would be in the range of 2.6–13.7 μg THg/($cm^2$y). This estimated flux of THg is two orders of magnitude higher than the assumed 0.022 μg THg/($cm^2$y) calculated with the WCC data (WCC 2006). Therefore, it is important to note that this chlor-alkali plant (and possibly others) working with a similar technology might exceed the estimated emission of THg in water given by WCC and Eurochlor (Eurochlor 2007).

### 4.2 Mercury concentrations in fish and fish consumption advisories

*4.2.1 Contamination in fish from Babeni reservoir and advisories*

The widespread occurrence of Hg contamination in fish led to recommendations issued by the World Health Organisation (WHO 2004) and the Food and Agriculture Organization of the United Nations (FAO) for concentration limits at 1 mg of Hg/kg ww of fish for predatory fish and 0.5 mgHg/kg ww of fish for the other kind of fish. Ninety-two percent of the fish from the Babeni Reservoir, examined in this study, exceeded the threshold of 0.5 mg/kg established by the WHO (WHO 2004) for non-carnivorous fish. Moreover, the WHO (WHO 2004) also suggested a Provisional Tolerable Weekly Intake (PTWI) of 1.6 μg MMHg per kg of human body weight. Applying the 0.8 MMHg/THg ratio (Jensen and Jernelov 1969; Fitzgerald and Clarkson 1991; Bloom 1992) to all purchased fish from the Babeni reservoir, the calculated mean of MMHg concentration would be 1.4± 0.6 mg/kg ww. Similar results would be obtained for the MMHg/THg ratio measured in this study for bleaks. Hence, a standard meal (227 g, WHO 2004) of fish from the Babeni reservoir contains 318 μg MMHg. Therefore, a meal of fish coming from the Babeni reservoir exceeds by a factor of 3 the most restrictive PTWI of 112 μg MMHg for a 70-kg person. Additionally, the MMHg concentration in fish from Babeni is higher than 1.9 mg/kg with a probability of 25%, the recommended limit proposed for its consumption (USEPA 2001).

Similar risk of fish consumption has been found in Rosignano Solvay region (Tyrrhenian coast), where a chlor-alkali plants operate since 1940 (Gibicar et al. 2009). The calculated mean of MMHg concentrations in fish from Piombino market is 1.07±0.86 mg/kg ww ($n$=6). Thus, a standard meal (227 g) of fish contains 243 μg MMHg, exceeding also the PTWI (WHO 2004).

n the Babeni reservoir, the three most highly contaminated species are cyprinids: bleak, roach and Prussian carp. Moreover, MMHg measured in bleaks represents 97% of THg. This proportion is higher than the 80% generally reported for non-predatory species (Bloom 1992). Bleaks mainly feed on plankton, drifting insects or invertebrates fallen on the water surface (Kottelat and Freyhof 2007). This high level of contamination, especially for bleaks, could indicate a high bioavailability of Hg and, consequently, high bioaccumulation of MMHg in this contaminated reservoir. It is probable that Hg-contaminated sediment trapped in the Babeni reservoir becomes a perfect compartment for methylation. Preliminary results indicate that the MMHg/THg percentage might reach 10% in surface sediments (Bravo et al. 2009b). To understand this high MMHg values in sediments and biota, further research should investigate the methylation rate in sediments and in the water column of the Babeni reservoir. Geochemical data furnished by Apele Romana indicated a decrease of oxygen content in the water column in summer conditions. Hg methylation could be enhanced in the Babeni reservoir during these periods.

It should be also noted that the reservoir contamination in the past was even worse, as testified the concentration up to 40 mg/kg of THg measured in deeper layers in a sediment core corresponding to 1987 (Bravo et al. 2009a). Although not necessarily proportional, the concentrations in fish were probably much higher in the past than they are today, and thus, the long-term exposure of population could be higher than at present time.

#### *4.2.2 Comparison of Hg concentrations in fish from reservoirs contaminated by industry using mercury cells technology*

Some region of the Great Lakes, Lake Balkyldak (Kazakhstan), Lake Vänern (Sweden), Skalka (Czech Republic) and Tainan (Taiwan) reservoirs have been contaminated by chlor-alkali plants since the early 1970s, while Baihua reservoir (China) receives wastewaters from a chemical plant using mercury cells in acetic acid production process. THg concentration measured in fish from the Babeni reservoir were in the same range or higher than those measured in the most contaminated groups of fish found in the lakes or reservoirs mentioned above (Table 2). It is important to remark that THg concentration in sediments of the Baihua reservoir in Guizhou and Babeni reservoir were in the same range, while THg concentrations in fish are two orders of magnitude higher in the Babeni reservoir (Table 2). In closed water bodies, located near industrialised regions or mining areas, Hg chemical discharges impact the fish concentration (Dorea 2008), but the bioaccumulation is variable from one lake to another (Simonin et al. 2008).

### 4.3 Human exposure

The THg concentrations in hair of the group eating fish from the Babeni reservoir is one order of magnitude higher than those getting fish from the upstream reservoirs or from shops. Consequently, the origin of the consumed fish is the predominant factor (Fig. 3a) for high Hg exposure of the local population. It is an alarming problem because among the 75 volunteers, 42 consume frequently fish from the Babeni reservoir (Fig. 3). Anglers (and their families) eat fish more often than the other groups, and thus they are more exposed to Hg. THg concentration in hairs collected from three individuals exceeded the safety limit (10 mg/kg) established by the WHO (2004) and 50% of the screened people exceeded a concentration of 1 mg/kg of THg in the scalp hair, which corresponds to the reference dose (USEPA 2001). The influence of the fish consumption and the dietary habits on the THg concentrations in hair has been observed in the Rm Valcea (Fig. 3) as in several countries all over the world such as Cambodia (Agusa et al. 2005), Bangladesh (Holsbeek et al. 1996), USA (Knobeloch et al. 2005), Amazonian areas (Dorea et al. 2006), Japan (Akira et al. 2004), Sweden (Johnsson et al. 2004), Malaysia (Hajeb et al. 2009), and Italy (Diez et al. 2008; Gibicar et al. 2009).

Plant workers had significantly higher THg concentration in hair than people of other professions (Fig. 3b). It could indicate a local exposure pathway different from fish consumption, contributing significantly to THg content in hair, as it was the case of population living near a chlor-

**Table 2** THg (mg/kg_ww) concentrations in fish muscle from contaminated freshwater systems

THg mg/kg ww concentrations in fish muscle

| | Reservoir/Lake | Mean ± std | Max | *N* | Country | Reference |
|---|---|---|---|---|---|---|
| Mercury cells | Canadian Great lakes | | | | Canada | Weis 2004 |
| | *Jackfish Bay* | 1 | 1.3 | 28 | | |
| | *Severn Sound* | 1.2 | 1.4 | 14 | | |
| | *Cornwall* | 1.4 | 1.9 | 13 | | |
| | Vanern Lake[1] | 0.52 ±0.07 | 2.2 | 10 | Sweden | Lindeström 2001 |
| | Skalka Reservoir | 3.1±0.2[2]<br>0.96±0.22 | | 30 | Czech Republic | Marsalek et al. 2005 |
| | Baihua Reservoir | 0.028 | | | Guizhou China | Yan 2006 |
| | Balkyldak Lake | 0.89±0.05 | 2.2 | 55 | Kazakhstan | Ullrich et al. 2007 |
| | Tainan Reservoir | 0.43±0.36 | 2.1 | 236 | Taiwan | Huang et al. 2008 |
| | Babeni Reservoir | 1.8±0.8 | 3.4 | 24 | Romania | *This study* |

[1] Exos luscious (pike) collected in 1999 in the Kattfjorden.

[2] The highest measured concentrations in the predatory fishes

alkali plant in Ribera d'Ebre, north-eastern Spain (Montuori et al. 2006).

The current view is that the Hg problem through fish consumption in Europe is, in general, limited (Pirrone et al. 2001). However, this study reveals a point source of Hg, a chlor-alkali plant, with a high impact on the hair Hg concentration of the local population through the fish consumption. The emissions of Hg from the chlor-alkali industry have decreased during the last years (Pirrone et al. 2001). Nevertheless, this study demonstrates that contaminated reservoirs are still a source of Hg exposure for the local population and that the fish consumption patterns are a tool to assess this Hg exposure. Of special importance would be the examination of lakes and reservoirs in which contaminated sediments can be active sources of MMHg, long time after implementation of mercury-free technology in chlor-alkali plants.

### 4.4 Recommendations

Future monitoring programmes should include not only water column measurements, but first of all surface sediments and fish. As the Hg contamination in the Babeni reservoir was even worse in the past (Bravo et al. 2009a), an epidemiological study could possibly detect a damage by Hg-intoxication in the population of Rm Valcea. Moreover, as long as the results of monitoring in fish do not demonstrate a decrease of mercury content below an acceptable level (WHO recommendations), the local population should be warned against the risk related to the systematic and frequent fish consumption from the Babeni reservoir while fishing in the upstream reservoirs can be recommended as an acceptable alternative.

## 5 Conclusion and recommendations

THg concentrations in sediments of the Babeni reservoir indicated that the use of Hg as an electrode in the Oltchim chlor-alkali plant contributed to the contamination of the aquatic environment in the Rm Valcea region. The present study (1) identified the source of Hg in Rm Valcea region, (2) showed the current status of mercury pollution in sediments, (3) proved the high Hg content in fish, and (4) informed about the exposure degree of local population to this contamination trough the fish consumption.

Even if the present releases from the chlor-alkali plant are much lower than in the past, the remnant pollution in the sediment of this reservoir, and probably many other lakes and reservoirs receiving Hg polluted wastewater, can present a considerable risk for the health of the local fish consumers. The sediments are highly contaminated and received more Hg than the amount which chlor-alkali plants in Western European countries were entitled to emit. The elevated Hg concentrations in fish suggest high bioaccumulation and biomagnification of this pollutant through the aquatic chain food in the Babeni reservoir.

More studies would be necessary to better understand the methylation, bioaccumulation and biomagnification processes in this highly Hg-contaminated reservoir and evaluate the probable health effects of a long-term Hg exposure in a part of the Rm Valcea population.

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