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The Science of the Total Environment 304 (2003) 231–256

**the Science of the  
Total Environment**

An International Journal for Scientific Research  
into the Environment and its Relationship with Man

www.elsevier.com/locate/scitotenv

## Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China

Milena Horvat<sup>a,\*</sup>, Nataša Nolde<sup>a</sup>, Vesna Fajon<sup>a</sup>, Vesna Jereb<sup>a</sup>, Martina Logar<sup>a</sup>, Sonja Lojen<sup>a</sup>, Radojko Jacimovic<sup>a</sup>, Ingrid Falnoga<sup>a</sup>, Qu Liya<sup>b</sup>, Jadran Faganeli<sup>c</sup>, Damjana Drobne<sup>d</sup>

<sup>a</sup>*Department of Environmental Sciences, Jozef Stefan Institute, Ljubljana, Slovenia*

<sup>b</sup>*Guizhou Institute for Environmental Protection, Guiyang, PR China*

<sup>c</sup>*Marine Biological Station, National Institute of Biology, Piran, Slovenia*

<sup>d</sup>*Department of Biology, University of Ljubljana, Vecna pot 111, Ljubljana, Slovenia*

Received 13 February 2002; accepted 15 October 2002

### Abstract

The province of Guizhou in Southwestern China is currently one of the world's most important mercury production areas. Emissions of mercury from the province to the global atmosphere have been estimated to be approximately 12% of the world total anthropogenic emissions. The main objective of this study was to assess the level of contamination with Hg in two geographical areas of Guizhou province. Mercury pollution in the areas concerned originates from mercury mining and ore processing in the area of Wanshan, while in the area of Quingzhen mercury pollution originates from the chemical industry discharging Hg through wastewaters and emissions to the atmosphere due to coal burning for electricity production. The results of this study confirmed high contamination with Hg in soil, sediments and rice in the Hg mining area in Wanshan. High levels of Hg in soil and rice were also found in the vicinity of the chemical plant in Quingzhen. The concentrations of Hg decreased with distance from the main sources of pollution considerably. The general conclusion is that Hg contamination in Wanshan is geographically more widespread, due to deposition and scavenging of Hg from contaminated air and deposition on land. In Quingzhen Hg contamination of soil is very high close to the chemical plant but the levels reach background concentrations at a distance of several km. Even though the major source of Hg in both areas is inorganic Hg, it was observed that active transformation of inorganic Hg to organic Hg species (MeHg) takes place in water, sediments and soils. The concentration of Hg in rice grains can reach up to 569  $\mu\text{g}/\text{kg}$  of total Hg of which 145  $\mu\text{g}/\text{kg}$  was in MeHg form. The percentage of Hg as MeHg varied from 5 to 83%. The concentrations of selenium can reach up to 16  $\text{mg}/\text{kg}$  in soil and up to 1  $\text{mg}/\text{g}$  in rice. A correlation exists between the concentration of Se in soil and rice, indicating that a portion of Se is bioavailable to plants. No correlation between Hg and Se in rice was found. Exposure of the local population to Hg may occur due to inhalation of Hg present in air (in particular in Hg mining area) and consumption of Hg contaminated food (in particular rice and fish) and water. Comparison of intake through these different routes showed that the values of Hg considerably exceed the USA EPA Reference Concentration (RfC) for chronic Hg exposure (RfC is 0.0004  $\text{mg}/\text{m}^3$ ) close to the emission sources. Intake of Hg through food consumption, particularly rice and fish, is also an important route of Hg exposure in study area. In general, it can be concluded that the

\*Corresponding author. Tel.: +386-611-885-386; fax: +386-811-885-346.

E-mail address: milena.horvat@ijs.si (M. Horvat).

population mostly at risk is located in the vicinity of smelting facilities, mining activities and close to the waste disposal sites in the wider area of Wanshan. In order to assess the real level of contamination in the local population, it is recommended that biomonitoring should be performed, including Hg and MeHg measurements in hair, blood and urine samples.

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*Keywords:* Guizhou; China; Mercury; Methylmercury; Selenium; Rice; Soil; Fish; Mining; Exposure

## 1. Introduction

Mercury is among the most highly bioconcentrated toxic trace metals in the human food chain, and many national and international agencies and organisations have targeted mercury for possible emission control. Mercury toxicity depends on its chemical form, among which alkylmercury compounds are the most toxic. The biogeochemistry of mercury has received considerable attention because of the toxicity of methylmercury compounds (MeHg), the accumulation of Hg in biota, and its biomagnification in aquatic food chains. Concerns about Hg are based on its effects both on ecosystems and human health. It is generally accepted that the principal pathway for general human exposure is the consumption of contaminated fish, though this study shows that other sources of mercury and MeHg should be seriously considered in special areas. Numerous recent studies (US EPA, 1997) have concluded that the majority, if not all, of the Hg that is bioaccumulated through the food chain is as MeHg. Therefore, knowledge of the concentration, transport, transformation and dynamics of MeHg in aquatic and terrestrial ecosystems is needed to predict its potential impact on humans, as well as on aquatic life.

The joint FAO/WHO Expert Committee on Food Additives (FAO/WHO, 1978; WHO-IPCS, 1990, 1991) provisionally recommended that total Hg intake should not exceed 5  $\mu\text{g}/\text{kg}$  of body weight per week, with no more than 3.3  $\mu\text{g}/\text{kg}$  per week as MeHg. Of 26 nations reviewed (WHO/IAEA/FAO, 1996) none showed mean dietary intakes approaching these values, most probably due to the limited number of population groups involved in the survey.

In the absence of occupational exposure, human intake of Hg is dominated by two sources; diet

and amalgam dental fillings. MeHg in fish and fish products is the major source of Hg and represents up to 85% in total intake of Hg from the diet (Parr et al., 1992). Typically less than 1% of total inorganic Hg intake is derived from drinking water. Amalgam fillings contain 50% of their weight as metallic Hg. Chewing causes a mechanical release of Hg(II) and volatilization of Hg<sup>0</sup>, part of which is inhaled and absorbed into the lungs and possibly directly into the brain via the nasal passage. This is the predominant source of inorganic Hg in the non-exposed population.

It is generally accepted that the consumption of contaminated fish is the primary route of exposure to MeHg for humans and wildlife. Public health regulations in the USA prohibit consumption of fish with tissue mercury concentrations of >1 mg/kg fresh weight, while some other countries regulate at the 0.5 mg/kg level.

In 1997, the US Environmental Protection Agency (US EPA) set a new guideline for methylmercury in the diet of 0.1 microgram of mercury per kilogram of body weight per day (0.1  $\mu\text{g}/\text{kg}/\text{day}$ ) (US EPA, 1997). This is 4.7 times as strict as the World Health Organization (WHO) standard of 0.47  $\mu\text{g}/\text{kg}/\text{day}$ . The average concentration of Hg in fresh and marine fish is approximately 0.2 mg/kg. In practical terms this means that an average person weighing 60 kg can only consume approximately 30 g of fish per day (Mahafey et al., 1997). This recommendation is based on epidemiological studies conducted in Iraq after the MeHg epidemic. The value for a reference dose is currently under review, before being officially adopted. Two large epidemiological studies in the Seychelles (Myers et al., 1995) and the Faroe Islands (Grandjean et al., 1997) that were designed to evaluate childhood development and neurotoxicity in relation to foetal exposures to MeHg will

provide more information for further refinement of reference dose values.

The Minimal Risk Level (MRL) is often used to identify contaminants and their potential health effects. An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure. These values are derived on the basis of No-Observed-Adverse-Effects-Level (NOAEL) and the uncertainty approach. Non-cancer risk values defined for MeHg and elemental mercury (through inhalation) by several organizations are given in Tables 1a and 1b.

Selenium is an essential element for humans. Worldwide, the probability of Se deficiency in human diet exceeds that of toxicity, with deficiency usually associated with monotonous vegetarian diets in areas with Se-deficient soils. In China, there are areas of Se deficiency as well as areas with elevated Se in soil leading to Se toxicosis (Mayland et al., 1989). Selenium has been found to play a role in the metabolism of mercury in man. Mercury and selenium accumulation in humans is already known and the results from different population groups, such as miners, dentists, and non-occupationally burdened individuals, suggest the formation of 1:1 Hg–Se compounds that may explain Hg detoxification by Se (Kosta et al., 1975; Byrne et al., 1995; Falnoga et al., 2000). It seems that the presence of accumulated endogenous Se can protect against harmful effects of accumulated and retained Hg. In recent studies it is hypothesized that the plasma selenoprotein P

Table 1b

Non cancer inhalation risk values for elemental Hg

	Organization name	
	AT SDR	US EPA
Risk value name	Chronic MRL	RfC
Risk value (mg/m <sup>3</sup> )	0.0002	0.0004
Year	1999	1995
Basis (EXP), (mg/m <sup>3</sup> )	LOAEL: 0.026	LOAEL: 0.025
Uncertainty factor	30	30
Critical organ	CNS	CNS

AT SDR—Agency for Toxic Substances and Disease Registry; US EPA—US Environmental Protection Agency; NOAEL—No-Observed-Adverse-Effects-Level; Basis ADJ—Bench mark dose identified in the critical study; RfD—Reference dose kg<sub>bw</sub>—per kg body weight; LOAEL—The Lowest-Observed-Adverse-Effects-Level; RfC—Reference concentration, CNS—Central Nervous System; I TER—International Toxicity Estimates for Risk.

together with a reduced metabolite of Se may play a role in Hg sequestration in the blood stream and consequent accumulation. Therefore, in the present study Se was determined in soil and rice grains in order to estimate the Se status as a possible co-factor in mercury toxicity.

### 1.1. Mercury contamination in Guizhou Province, China

The province of Guizhou (N24°30'–29°13', E103°1'–109°30', 1100 m above sea level, subtropical humid climate) in Southwestern China is one of the world's most important mercury production areas. The cinnabar deposits in Guizhou,

Table 1a

Non-cancer oral risk values for MeHg

	Organization name		
	AT SDR	ITER	US EPA
Risk value name	Chronic MRL	RfD	RfD
Risk value (mg/kg <sub>bw</sub> /day)	0.0003	0.0003–0.0004	0.0001
Basis (EXP) (mg/kg/day)	NOAEL 15.3 ppm in hair	21 ppm in hair	11 ppm in hair
Basis (ADJ) (mg/kg/day)	0.0013 estimated intake	0.0009–0.003 estimated intake	0.0011 estimated intake
Uncertainty factor	4.5	3	10
Critical organ	CNS	CNS	CNS

approximately 80 000 t of mercury, represents approximately 70% of the total in China. Emissions of mercury from the province to the global atmosphere have been estimated to be approximately 12% of the world total anthropogenic emissions (Nriagu, 1979; Nriagu and Pacyna, 1998). Guizhou has produced mercury for 600 years, and the total output was reported to be 26 000 t from 1949 to 1981, and the peak annual mercury emission from mining and refining to the atmosphere has reached 11 t (Tan et al., 1997, 1997a,b). In addition, Guizhou is one of the major coal production provinces in China. Approximately 80% of the total energy consumption by a population of 34 million (Tan et al., 1997, 1997a,b) results from coal combustion. In recent years annual coal burning was above  $8 \times 10^6$  t without flue gas cleaning or emission control actions. The concentrations of mercury in coal vary from 0.255–0.552 mg/kg (Xinbin et al., 1997).

An additional source of environmental Hg is emission from chemical industries where Hg is used as a catalyst for the production of acetaldehyde and other organic compounds. Hg is also used in agriculture, medicine, the electrical industry, extraction of gold and in traditional uses such as red pigments, etc., (Jingyi, 1997).

An inventory of anthropogenic mercury emissions from Guizhou and the atmospheric mercury deposition on Fanjing Mountain Nature Reserve of the province (Tan et al., 1997b; Lindqvist et al., 1996; Xiao et al., 1998; He et al., 1997, 1999; He and Tan, 1995; Tan et al., 2000) have been reported. These data show the seriousness of pollution, and strongly suggests much future research work is needed in order to understand Hg transport and transformation mechanisms in this karstic environment and in particular the possible health effects of Hg and its compounds.

Exposure of the local population to Hg may occur due to inhalation of Hg present in air and consumption of Hg contaminated food and water. In the air, the major form of Hg is volatile elemental Hg. The highest value of Hg in air in the city of Guiyang was reported to be  $0.566 \mu\text{g}/\text{m}^3$  (Liya and Hunyan, 1997, 1999), while the concentrations of Hg in air in the mercury mining area are even much higher. These values consid-

erably exceed the USA EPA Reference Concentration (RFC) for chronic Hg exposure ( $0.0004 \text{ mg}/\text{m}^3$ ). These values also exceed the Minimal Risk Level (MRL) as defined by the AT SDR (Tables 1a and 1b). Intake of Hg through food consumption is also an important route of Hg exposure. Major sources of Hg in human diet in the region are rice and fish consumption. For example, Hg concentrations in rice in the contaminated area of Wanshan may exceed  $0.3 \mu\text{g T-Hg}/\text{g}$ . With a daily consumption of 400 g of contaminated rice, the daily dose for a 60 kg person would mean  $2 \mu\text{g T-Hg}/\text{kg}$  body weight (assuming that 100% is retained in the body), which also exceeds the international recommendations for daily intake of Hg.

Another area of investigation is close to the city of Guiyang where two artificial lakes, namely Hongfeng and Baihua, are located. The lakes are connected by a channel. Lake Hongfeng was built in 1960 and is in general deeper with a maximum depth of 42 m. This lake is also a major source of drinking water for the city of Guiyang. In recent years various industries developed their activities and the number of people living in the area have also increased. Both lakes are therefore receiving a considerable amount of untreated domestic and industrial sewage. Apart from mass reproduction of zoo- and phyto- plankton and the presence of toxins due to cyanophytes and increased benthic flora and fauna, both lakes are subject to large-scale environmental problems. A chemical plant which is located in the vicinity of the city of Quingzhen and approximately 24 km from the capital city of Guiyang discharges waste waters into the channel and therefore contributes to the pollution problems of the lakes. The chemical plant was built in 1965 and became operational in 1971 (Liya and Hunyan, 1999). According to the published data over 140 t of Hg was discharged into the environment. Mercury is used as a catalyst for the production of acetic acid. As a by-product acetaldehyde is also produced. From 1971 to 1986 over  $12 \times 10^3$  t of acetic acid was produced and after 1987 the production exceeded  $20 \times 10^3$  t. It is estimated that for the production of 1 t of acetic acid 0.77 kg of Hg is used. Hg emissions to the environment were very high until 1986. Hg was

emitted (1) as a gas in emission amounting to of  $0.24 \times 10^6 \text{ m}^3/\text{year}$  (Hg conc.  $200 \mu\text{g}/\text{m}^3$ ); (2) as a solid residue, which was sent to the smelting house of the Hg mine for recycling of Hg; and (3) as waste water ( $0.12 \times 10^6 \text{ t}/\text{year}$ , concentration of T-Hg  $3\text{--}8 \mu\text{g}/\text{l}$ , of which organic Hg was approximately 15–30% and the rest was in the form of inorganic Hg. In the year 1986 cleaner technologies were installed in order to remove Hg from waste waters, particularly MeHg, which dropped to approximately 0.04% of the total Hg.

Elemental mercury was found at the bottom of Lake Baihua. The concentrations of Hg in the sediment of this lake were found to be very high (e.g.  $557 \mu\text{g}/\text{g}$  dry mass and MeHg of approx.  $0.048 \mu\text{g}/\text{g}$ ). The highest concentration of total Hg reported for rice was  $0.127 \mu\text{g}/\text{g}$  and for MeHg  $0.018 \mu\text{g}/\text{g}$ . Concentrations in fish of the lake were also reported to be high (total Hg  $0.955 \mu\text{g}/\text{g}$ ). Hg emissions from coal burning power plants also contribute to the contamination of this area (Liya and Hunyan, 1997, 1999).

The present report comprises results obtained during joint sampling in September 1999 performed by the Jozef Stefan Institute of Slovenia and the Guizhou Institute for Environmental Protection in cooperation with S&T Commission of Guizhou of China with the main objective to assess the level of contamination with mercury in various environments in Guizhou and to identify major sources of human exposure.

## 2. Experimental

### 2.1. Sampling areas

In the framework of the Slovenian–Chinese collaboration sampling was conducted in the period from the 21st to 23rd of September, 2000 in two areas of Guizhou Province (e.g. Wanshan in Quingzhen) presented in Figs. 1–3. The sample taken and some basic information for each sampling point are also given in Tables 2 and 3. In both cases the sampling points are located in typical karst areas with all its characteristics. Wanshan is a hilly karst site approximately 700 m above sea level, while the area of Quingzhen is

located in a valley. Sampling was performed during the rice-harvesting period.

#### 2.1.1. Wanshan (Fig. 2)

Samples from nine sampling stations were collected as described in Table 2. Three stations were located in the area of the city of Wanshan (W7–mining and flotation facilities, W8–smelting facilities, W9–former waste disposal site). The remaining stations were located in the valley of the river Xiaxihe, into which waters from mining and ignition residue disposal sites are leached. The river Xiaxihe joins the river Jin Jiang at Yangtou (not shown on the map). Some 25 km upstream along the river Jin Jiang another active Hg mine, is located at Tongren. The river Jin Jiang is a tributary of the Yuan Jiang river, which flows into lake Dongting Hu (some 250 km distant from Wanshan). This complex hydrological system is finally connected with the Jangtze Kiang river.

#### 2.1.2. Quingzhen (Fig. 3)

Samples from five different locations (Table 3) were selected representing both types of Hg pollution source such as the water discharge from the chemical plant (Q1) and areas directly influenced by this water (Q2 and Q3), and atmospheric pollution at the Beimen thermal power plant (Q5) and the control area at Lake Huaqiao.

## 2.2. Rice and fish species

### 2.2.1. Rice

In the study area rice is eaten with almost every meal and provides more calories than any single food. The rice grain is a seed that contains an embryonic rice plant. The hull, a hard protective covering, surrounds the bran, which consists of a layer of fibrous tissue that contains proteins, vitamins, minerals and oils. Beneath the bran is the endosperm, which makes most of the rice grain. The bran and endosperm are the edible portions of the grain. There are several thousand varieties of rice, all belonging to the family Gramineae. Asian rice is classified as *Oryza sativa*. Almost all species of rice require very moist soils. Rice fields in the region investigated are flooded during the growing season. Flooded rice is grown in paddies,



Fig. 1. Map of Guizhou province with study areas identified.

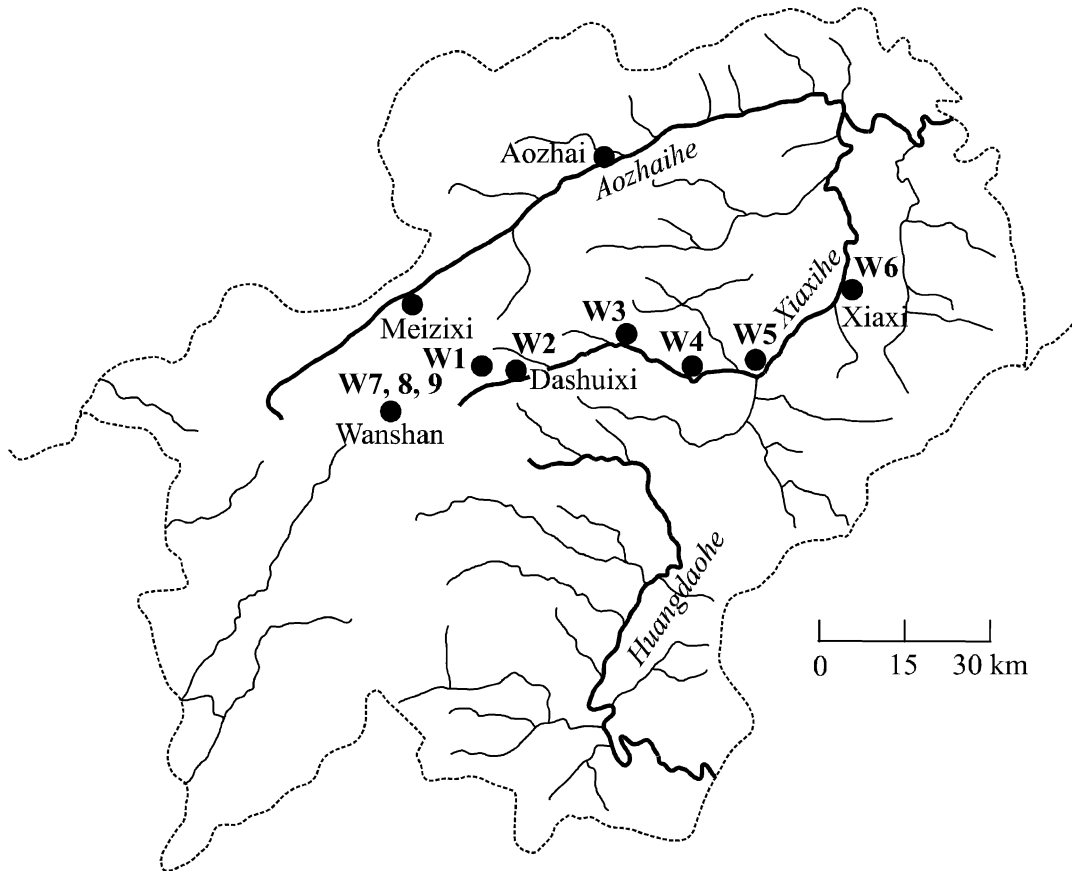


Fig. 2. Sampling sites in Wanshan. Sampling sites W7, W8 and W9 are located in the vicinity of the mine, W1 on mine residues, while the rest of the stations are located along the river Xiaxihe.

which are fields that contain water enclosed by low walls of earth called bunds. Paddy rice is fed by rainfall or/and a combination of rainfall and irrigation. Rice grains are normally ready for harvest from 3 to 6 months. When rice is processed, the hull is removed, exposing bran. Rice at this stage is brown rice. The fibrous bran of brown rice is rich in oil, proteins, the B vitamins, thiamin, riboflavin and niacin, and minerals such as Fe, P and K. To make white rice, the bran is removed. White rice is less nutritious. Polished rice is then made by processing white rice kernel through a machine with a brush that smooths and shines them. In this study rice with hull and brown rice were taken for analysis.

#### 2.2.2. Fish

Three fish species were collected in the channel connecting lake Baihua and Lake Hongfeng:

1. COMMON CARP (*Cyprinus carpio haematopterus* Linnaeus 1758): Common carp is a species belonging to the family Cyprinidae. Carp prefer slow moving rivers and streams and warm lake habitats with abundant vegetation. They feed on a wide variety of plant and animal food items from the water surface, from vegetation and rocks, and from stream and lake bottoms. Shallow sloughs and marshes, adjacent to stream channels or lakes, are preferred breeding habitats.

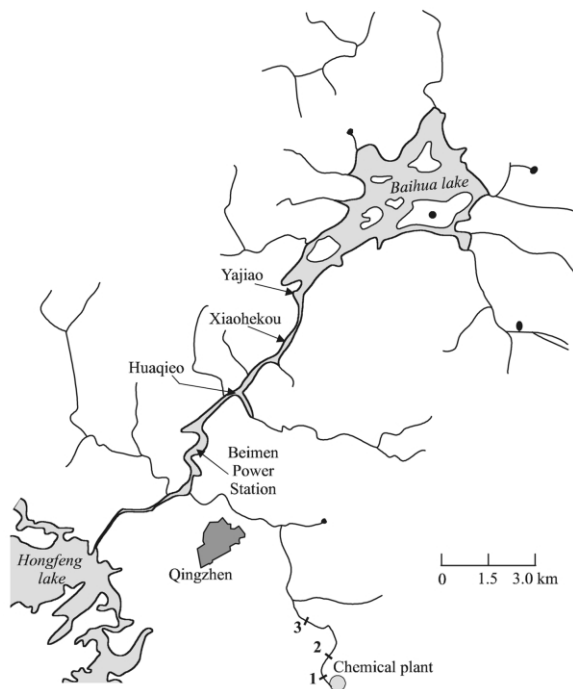


Fig. 3. Sampling sites in the area of Quingzhen.

2. **GRASS CARP (*Ctenopharyngodon idella Valenciennes 1844*):** The grass carp is a large, rather typical carp, with teeth designed for eating aquatic vegetation. They have large throat teeth which help cut and shred plant material. It is a fast swimmer and strong jumper. Grass carp will eat up to twice their weight in plants daily and grow approximately three times as fast as the common carp. Grass carp have attained weights of up to 30 kg and lengths to 125 cm. They are considered good food fish. They are extremely hardy and can survive low temperatures and relatively low oxygen concentrations.
3. ***Carassius auratus gibelio Bloch 1783*:** This carp also belongs to the family Cyprinidae and is a native of China. *Carassius auratus gibelio* lives in all kinds of water, but prefers slow moving and standing waters. It survives in low oxygen conditions, high temperatures and organic contamination. Adults can growth to a length of 45 cm. They reach sexual maturity at age 3 or 4

years. They feed mainly on microscopic plants (phytoplankton).

### 2.3. Sampling and sample preparation

All precautions were taken in order to avoid any contamination during sampling. Samples were stored in a refrigerator temporarily, until transported to Ljubljana, Slovenia for further processing.

Soil samples were taken from rice fields, and only the upper 5–10 cm were sampled; rice samples were taken from the same rice fields. Fish were caught by a local fisherman and prepared in the laboratories of the Institute for Environmental Protection, Guizhou. All samples, except water samples, were then frozen and as such transported to Ljubljana, Slovenia.

Samples were freeze dried at  $-52\text{ }^{\circ}\text{C}$  and a pressure of 0.05 bar (Christ, Loc-1, Alpha 1–4) to a constant weight. Rice was lyophilized for 24 h, while soils and sediments were dried for 48 h. The water content in samples was recorded. All the results are expressed on a dry weight basis.

#### 2.3.1. Rice

Rice was divided into two parts: (1) one part represented brown rice. The hull was removed from the grain and homogenized and (2) the other portion was left with the hull. The hull from the rice seeds was removed by a scalpel. Samples were then crushed and ground in a zirconium mortar with Zr ball in a Fritsch vibration micro-pulverizer. (Fritsch pulverisette planetary micro mill.) The lyophilised samples were weighed to determine the wet/dry ratio. The grinder was thoroughly cleaned after each sample. The first aliquot of ground material was discarded and then the bulk of each sample ground. Powdered samples were subsequently packed into plastic dishes, sealed in polyethylene bags and stored in a refrigerator. The results are expressed on a dry weight basis and were corrected for moisture content determined on separate aliquots by drying the material at  $85\text{ }^{\circ}\text{C}$  until constant weight.

#### 2.3.2. Soil and sediment samples

Bigger particles, e.g. stones and plant residues were removed and then the sample homogenized



Table 2  
Description of sampling sites in the area of Wanshan

ID No.	Description	Samples taken
W1	Mine and ignition residues Above sampling point W2	Soil Rice
W2	Mining and ignition residues. Water leached from waste deposited site; alkaline water An accumulation reservoir that was built is not operational at the moment.	Soil Ignition residues Rice Water
W2a	500 m below station W2. The upper part of the soil on a rice field consists of a layer of white precipitation. This indicates flooding of these fields with water leached from ignition and mining residues.	Soil Rice Water
W3	Flooded area along the river Xiaxihe.	Soil Rice Water
W4	Soil and rice from a field along the river Xiaxihe.	Soil Rice
W5	Soil and rice from a field along the river Xiaxihe.	Soil Rice River sediment
W6	Close to the town Xionxi located along the river Xiaxihe.	Soil Rice Water
W7	Location below the mercury mine in Wanshan. Water from the mine residue disposal site regularly floods the area.	Soil Rice
W8	Rice field close to the smelting house in the city of Wanshan.	Soil Rice
W9	Mine residues were disposed of until 1960; later agricultural activity developed including rice, corn and sweet potato fields. A fish pond is also located in this area.	Soil Rice Water Fish sediment from the fish pond

*Note:* Soil was always sampled from rice paddy fields.

Table 3  
Description of sampling sites in the area of Quingzhen

Sample ID No.	Description	Sample type
Q1	Quingzhen Chemical Plant, 100–150 m from waste water outfall; the water is used for irrigation of rice fields	Rice, Soil Water
Q2	1000 m from the Quingzhen Chemical Plant	Soil Rice
Q3	2500 m from the Quingzhen Chemical Plant, close to the city of Quingzhen	Water
Q4	Lake Huaqiao, the clean part of the lake, see photos	Water Fish
Q5	Close to the thermal power plant	Rice Soil Rice

in Zr containers with one Zr ball (Fritsch, Laborgerätebau). During the whole sample preparation procedure, special precautions were necessary to avoid cross-contamination of samples, including the sequence of sample treatment. Therefore, homogenization started with the control samples, followed by less contaminated and continued with more contaminated samples. The homogenizer was thoroughly cleaned after each sample. For each sample, the first aliquot ground was discarded, and then the bulk of the sample was ground. Homogenized samples were stored in plastic containers, sealed in polyethylene bags, and stored in a refrigerator until further processing. An aliquot taken for determination of moisture content was dried at 85 °C to constant weight. All data are expressed on a dry weight basis.

#### 2.3.3. Fish muscle

In the field samples were labeled and placed in polyethylene bags and temporarily stored at +4 °C in a refrigerator. Weight and length were recorded and the fish transferred to the laboratory for further preparation. Muscle tissue samples were carefully removed from the fish and stored in polyethylene vials and then stored deep-frozen (–25 °C). Before sample aliquots were taken for analysis, muscle tissues were macerated on sterilized glass plates using a clean scalpel. A homogeneous mass was obtained and aliquots of the mass sampled for total and Me–Hg determination. Laboratory tools and ware needed for preparation of samples were washed with an aqueous detergent solution, soaked in hot nitric acid, rinsed with double distilled Hg-free water and dried. To avoid changes in the tissue water content, the processing of the homogenized tissues was carried out immediately after maceration.

#### 2.3.4. Water samples

Water samples were collected at the surface (0.5 m depth) in 1 l acid-cleaned Teflon bottles. Samples were stored at 4 °C until further processing in the laboratory. Water samples were filtered (Whatman GFC-Glass fiber filter). Total Hg and MeHg were determined in filtered and non-filtered water samples.

#### 2.4. Analytical methods for determination of total Hg, MeHg and Se

Various analytical methods were used which are described elsewhere. A summary of the analytical methods is presented in Table 4 and the list of reference materials used in Table 5.

### 3. Results and discussion

The results for total Hg, MeHg and Se are presented and discussed in the present report. In addition to mercury analysis some representative samples were also analyzed for other elements including toxic heavy metals (HM) and some of the rear earth elements (REE) which are discussed in another paper (Lojen et al., in preparation).

Where available, data for critical values according to Slovenian legislation (which is harmonized with European legislation) are also reported and compared with measured data. Where appropriate a comparison of values with the Idrija mercury mining area in Slovenia are presented and discussed.

#### 3.1. Mercury and selenium in soils, sediment and mine residues

Data for total Hg, Se and MeHg are given in Table 6 and total Hg and MeHg presented graphically in Figs. 4 and 5. The critical value (10 mg/kg) on the graphs is presented as a horizontal dotted line. Evidently, concentrations for total Hg exceed this value at almost all-sampling stations. So far, legislation does not define values for MeHg, so no comparison with critical data is possible. In general there is no correlation between the concentrations of total Hg and MeHg, which reflects the well-known fact that the total mercury concentration is not the only factor influencing transformation mechanisms of Hg in different environmental conditions. The percentage of MeHg is rather low, except at the station close to the thermal power plant (Q5), where the percentage of Hg as MeHg of 1.3% was measured. According to literature data, the % of MeHg in soils very rarely exceeds 1%.

Table 4  
Summary of analytical methods used for the analysis of total Hg and MeHg and selenium

Sample/analyte	Methods			
	Pretreatment/extraction/ digestion	Detection	Limit of detection	Reference
Rice, total Hg	Acid digestion with HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub> in closed Teflon vials → reduction with SnCl <sub>2</sub> → amalgamation on gold trap	Cold vapor atomic absorption spectrometry (CV AAS)	0.01–1.0 ng/g	Horvat et al., 1991
Rice, MeHg	Acid leaching with KBr/H <sub>2</sub> SO <sub>4</sub> → extraction of MeHgBr into toluene → clean-up with aqueous solution of cysteine → re-extraction of MeHg into benzene	Gas chromatography with electron capture detector (GC ECD)	0.01–0.05 ng/g	Horvat et al., 1988 Horvat et al., 1989 Horvat, 1991
Fish, total Hg	Acid digestion with HNO <sub>3</sub> in sealed pyrex ampoules → reduction with SnCl <sub>2</sub> → amalgamation on gold trap	CV AAS	0.01–1.0 ng/g	Horvat et al., 1986 Horvat et al., 1991
Fish, MeHg	Acid leaching with HCl → separation of organic and inorganic ion-exchange column → UV oxidation of MeHg → reduction with SnCl <sub>2</sub> → amalgamation on gold trap	CV AAS	0.01–1.0 ng/g	May et al., 1987 Horvat et al., 1988
Soil, total Hg	Acid digestion with HNO <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub> in closed Teflon vials → reduction with SnCl <sub>2</sub> → amalgamation on gold traps	CV AAS	0.01–1.0 ng/g	Horvat et al., 1991
Soil, MeHg	Acid leaching with KBr/H <sub>2</sub> SO <sub>4</sub> → extraction of MeHgBr into toluene → clean-up with aqueous solution of cysteine → re extraction of MeHg into benzene	GC ECD	0.01–0.05 ng/g	Horvat et al., 1988 Horvat et al., 1991
Water, total Hg	Acidification with HCl and BrCl → irradiation with UV → reduction with SnCl <sub>2</sub> → amalgamation on gold traps	CV AAS	0.01–1.0 ng/g	Liang et al., 1996
Water, MeHg	Acidification with HCl → extraction of MeHgCl into CH <sub>2</sub> Cl <sub>2</sub> → back extraction of MeHgCl into water phase by evaporation of CH <sub>2</sub> Cl <sub>2</sub> → ethylation of ionic Hg species → room temperature adsorption on Tenax	Isothermal gas chromatography, pyrolysis, cold vapor atomic fluorescence spectrometry (CV AFS)	0.001–0.01 ng/g	Horvat et al., 1993  Liang et al., 1994a Liang et al., 1994b Liang et al., 1996 Logar et al., 2000 Logar et al., 2001
Selenium	Irradiation in nuclear reactor	<i>k</i> <sub>0</sub> -Instrumental neutron activation analysis (INAA), Gamma spectrometry		De Corte et al., 1993 De Corte, 1998

Table 5

List of Certified reference materials used in the present study and the results obtained. Data obtained are reported in italics and in brackets as a mean value and standard deviation of at least three independent determinations

Producer	CRM	Certified value and its uncertainty	
		T-Hg ( $\mu\text{g/g}$ )	Me-Hg ( $\mu\text{g/g}$ )
IAEA-MEL	IAEA-356 Polluted marine sediment*	$7.62 \pm 0.65$ <i>(7.45 ± 0.09)</i>	$0.0054 \pm 0.0008$ <i>(0.0049 ± 0.0002)</i>
NRCC	DORM-1 Dogfish muscle	$0.798 \pm 0.074$ <i>(0.787 ± 0.05)</i>	$0.731 \pm 0.060$ <i>(0.745 ± 0.050)</i>
IAEA	IAEA, H-9 Mixed human diet	$0.0048 \pm 0.0012$ <i>(0.0051 ± 0.0005)</i>	$0.0030 \pm 0.0002$ <i>(0.0032 ± 0.0002)</i>
NIST	SRM 2976 Mussel homogenate	$0.0610 \pm 0.0035$ <i>(0.068 ± 0.002)</i>	$0.0277 \pm 0.0020$ <i>(0.0257 ± 0.001)</i>
NBS (NIST)	SRM 1568 Rice flour	$0.0060 \pm 0.0007$ <i>(0.0058 ± 0.0005)</i>	No certified value available

IAEA-MEL: International Atomic Energy Agency—Marine Environmental Laboratory. NRCC: National Research Council Canada. NIST: National Institute of Standards and Technology. NBS: National Bureau of Standards, \*(Horvat et al., 1994).

Closer observation of the data in the area of Wanshan reveals some interesting features. The concentrations of total Hg in soils from the rice fields are very high in the vicinity of the smelting facilities (W8), where values of over 150 mg/kg were recorded. This value is comparable with values found in contaminated soil near the smelting house in the former Hg mine in Slovenia (Gnamuš

et al., 2000). It is assumed that most Hg in this area is deposited from the atmosphere in the form of Hg enriched aerosols. Interestingly, concentrations of Hg in soil close to the mercury mine (W7) are more than three times lower. The sampling point W7 represents an area close to the mercury mine and the facilities where Hg enriched particles are separated by the process of flotation.

Table 6

Concentration of Se, total Hg, MeHg and % of Hg as MeHg in soil, sediments and mine residues

Sampling points	Selenium ( $\mu\text{g/g}$ )	Total Hg ( $\mu\text{g/g}$ ) Mean $\pm$ S.D.	MeHg (ng/kg)	
			Mean $\pm$ S.D.	%MeHg
W1	<0.20	$78.9 \pm 12.9$	$21.9 \pm 0.50$	0.028
W2	0.17	$34.1 \pm 3.3$	$22.5 \pm 0.71$	0.066
W2, ignition residues	–	$33.2 \pm 0.8$	$2.71 \pm 0.01$	0.008
W2a	0.50	$35.4 \pm 2.4$	$3.21 \pm 1.05$	0.009
W3	5.17	$89.7 \pm 1.4$	$2.65 \pm 0.32$	0.003
W4	3.65	$36.9 \pm 2.8$	$1.27 \pm 0.04$	0.003
W5	0.42	$18.8 \pm 0.8$	$1.47 \pm 0.50$	0.007
W5, river sediment	–	$30.1 \pm 2.1$	$1.83 \pm 0.03$	0.006
W6	0.56	$8.10 \pm 0.5$	$1.43 \pm 0.20$	0.018
W7	0.17	$43.4 \pm 2.1$	$1.75 \pm 0.07$	0.004
W8	16.9	$156 \pm 0.01$	$11.9 \pm 0.01$	0.008
W9	<0.30	$16.3 \pm 0.01$	$4.33 \pm 1.17$	0.027
W9, sediment: fish pond	–	$115 \pm 7.1$	$19.3 \pm 1.20$	0.017
Q1-1999	0.32	$289 \pm 2.8$	$32.0 \pm 3.3$	0.011
Q1-1998	–	$354 \pm 15$	$67.0 \pm 1.2$	0.019
Q2	1.18	$14.3 \pm 0.1$	$13.2 \pm 0.50$	0.092
Q4	1.21	$0.25 \pm 0.04$	$1.77 \pm 0.01$	0.708
Q5	8.82	$0.27 \pm 0.01$	$3.59 \pm 1.42$	1.33

Mean  $\pm$  S.D. Mean standard deviation of at least 3 determinations

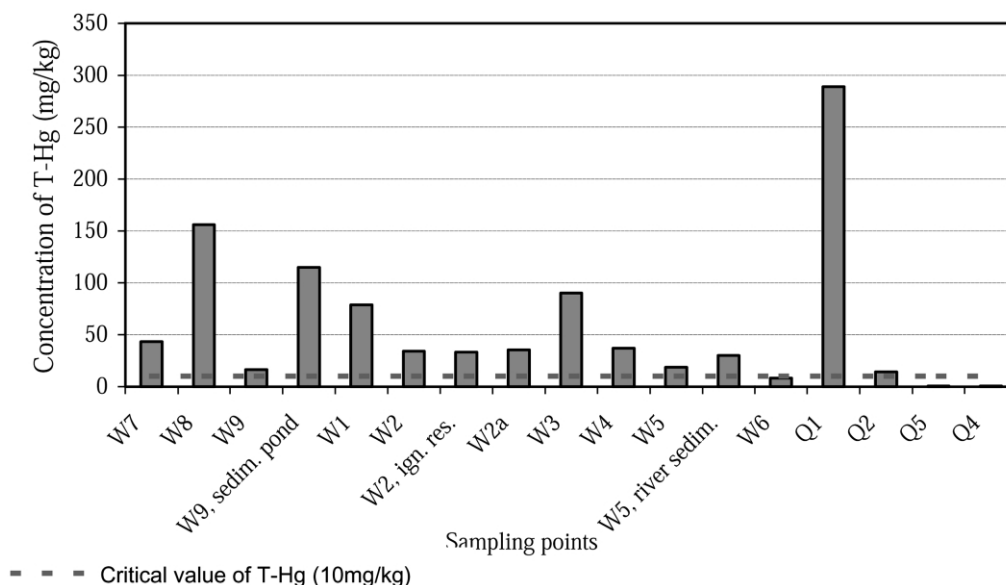


Fig. 4. Concentrations of total mercury in soil, sediments and mining residue samples.

The wastes from this process (mining residues) are then disposed of in the vicinity of the mine or elsewhere in the area. This indicates that smelting pollutes the local environment with mercury to a much greater extent than the mining operations. It is also interesting to note that the values of MeHg in the smelting area are much higher compared to the area impacted by mining activity alone. This may be explained by the lower reactivity of Hg at station W7, where Hg is present as mostly unreactive HgS.

Sampling area W9 is located close to the city of Wanshan. Until 1960 most of the mining and ignition residues were dispersed in this area. The total Hg concentration in this sample is lower than expected; however, the sediment of the fishing pond showed much higher values (over 100 mg/kg). This suggests that the sample taken from the field may be not representative of the whole area. Relatively high concentrations of MeHg were found in pond sediments as compared to MeHg values found in other sampling points of this area, indicating much more favorable conditions for mercury transformation in the aquatic environment as compared to the soil.

Sampling stations from W1 to W6 represent soil samples taken along the river Xiaxihe. The upper stations W1 and W2, where mining and ignition residues are disposed of, represent the major sources of Hg in the area. Evidently, the concentrations of total mercury decreased by a factor of 10 at station W6 as compared to station W1. A surprisingly high value of 90 mg/kg in soil was found at station W3. This sampling station is located on one of the biggest flood plains along the river Xiaxihe and therefore serves as an accumulation area for mercury enriched particles transferred from contaminated upstream areas during heavy rain events. However, the concentration of MeHg in this area is rather low, as compared to stations W1 and W2, indicating different behaviour of Hg in this rice field, possibly favoring demethylation over methylation processes.

The major source of mercury in sampling areas of Quingzhen is water contaminated with mercury originating from the chemical plant. Thermal power plants also contribute to the increased values of Hg in the atmosphere. Samples Q1 and Q2 were taken from rice fields along the stream into which wastewaters from the chemical plant are dis-

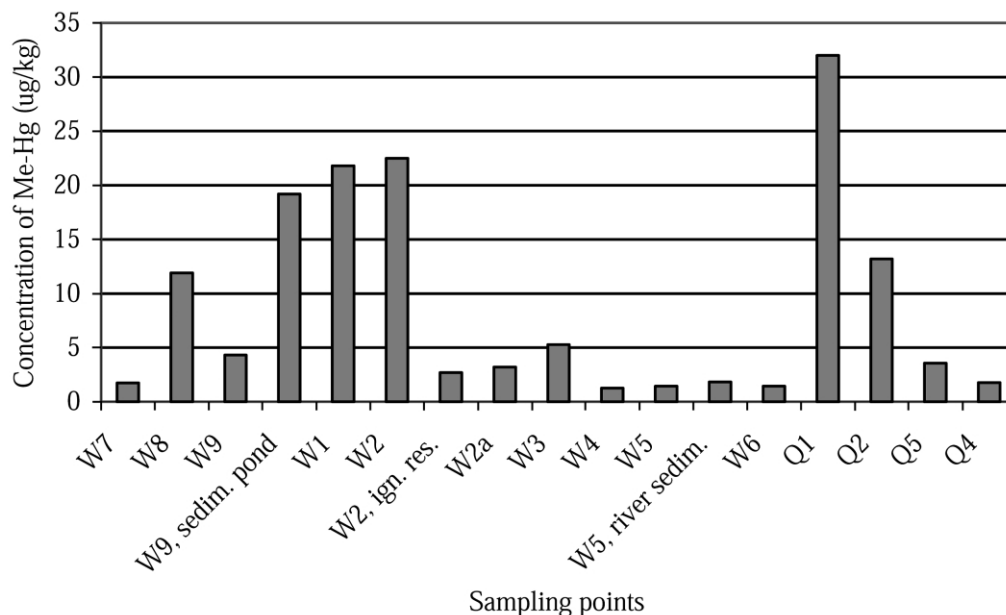


Fig. 5. Concentrations of MeHg in soil, sediments and mining residue samples.

charged. At station Q3 only a water sample was taken. Sampling area Q4 is located at Lake Huaqiao, while station Q5 represents an area close to the thermal power plant. Total Hg concentrations close to the chemical plant are very high (approx. 290 mg/kg) and even exceed values found in areas close to the smelting facilities in Wanshan (156 mg/kg). Results for total and MeHg clearly indicate that the concentrations rapidly decrease with the distance from the chemical plant. At a distance of approximately 1000-m from the chemical plant the concentrations of total Hg decreased by a factor of 20. However, the concentration of MeHg only decreased by a factor of 2, again demonstrating that total Hg concentration is not the only factor influencing Hg transformation in the environment. Values of total Hg at stations Q4 and Q5 are much lower than at other stations, probably representing background values of the area.

During sampling in March of 1998, samples of soil and some plants were also taken from sampling point Q1. The results obtained were similar to those reported in those found in October 1999, but MeHg values were twice as high (Table 6).

This may indicate spatial differences and/or more productive methylation processes affected by the soil moisture in the springtime.

Selenium levels in soil of both areas vary from 0.17 to 16.9 mg/kg (Table 6). These concentrations significantly exceed values known for urban soils, agricultural soils and stream sediments (Reiman and de Caritat, 1998) where the concentrations of Se rarely exceed 1 mg/kg. For example, a maximum concentration of 0.06 mg/kg was reported of Se in soil in paddy rice fields of the Yangtze river delta (Cao et al., 2001). The highest concentrations of Se in our study were found at station W8 and Q5, with values of 16.9 and 8.82 mg/kg, respectively. Both stations are impacted by smelting facilities (e.g. W8: Hg ore smelting and at Q5: coal burning). Relatively high values of Se were also found in paddy field soils at stations W3 and W4 impacted by frequent flooding and deposition of particles eroded from mining and ignition waste disposal sites. Ignition residues alone are most probably not the source of Se, as the values at ignition residue disposal site (stations W2 and W2a) were much lower. It is well known that Se can be volatilized during combustion, and

Table 7  
Concentration of total Hg and MeHg in filtered and non-filtered water samples

Sampling point	Non-filtered water			Filtered water		
	T-Hg (ng/l)	Me-Hg (ng/l)	% Me-Hg	T-Hg (ng/l)	Me-Hg (ng/l)	% Me-Hg
W2, leached water	10 580	0.410	0.004	655	0.057	0.009
W2a leached water from the accumulation reservoir	550	0.035	0.006	15.8	0.006	0.038
W3 river Xiaxihe	310	0.210	0.068	12.2	0.114	0.934
W4 river Xiaxihe	60.0	0.012	0.020	3.81	<0.005*	
W5 river Xiaxihe	20.0	0.059	0.295	4.53	0.04	0.883
W9 fish pond	1500	0.766	0.051	38.1	0.242	0.635
Q1 stream from chemical plant	1830	0.053	0.003	12.7	0.023	0.181
Q3 2.5 km from chemical plant	450	0.083	0.018	16.1	0.012	0.075
Q4, Lake Huaqiao	30.0	0.094	0.313	3.19	0.069	2.163
Q4, rice field	6.0	0.223	3.72	0.66	0.023	3.484

\* Below the limit of detection.

concentration in ignition residues are expected to be lower. It is also well known that high concentrations of Se in soils are frequently related to its natural occurrence, while the process of irrigation may redistribute and concentrate Se (Mayland et al., 1989; McLaughlin et al., 1999) which, most probably, is the case in the areas investigated in the present study.

### 3.2. Mercury in water samples

Water samples from 10 stations were taken. The results are given in Table 7. It is well known that water samples represent only information under the particular hydrological conditions during the time of sampling and the data are therefore of limited value only.

The data confirm the well-known fact that mercury tends to be bound to particulate matter in water samples (much higher concentrations in non-filtered water samples). There seems to be very little correlation between total and MeHg concentrations in water samples, reflecting environmental differences affecting the transformation of Hg in various aquatic environments.

In the area of Wanshan the highest concentrations of Hg were found at station W2 where water leached from the mining and ignition residues enters the river Xiaxihe. The dissolved fraction of Hg is also relatively high, indicating high solubility of Hg in leached water at this high pH. Relatively

high concentrations of MeHg (0.4 ng/l) were also recorded in this sample. This concentration is quickly diluted by the less polluted Xiaxihe River at station W2a. The concentrations at other stations decrease with distance from the source of pollution; however the values remain elevated even at station W5, some 20 km downstream.

The data clearly show that Hg concentrations follow the same trend as concentrations found in soils (Table 6). Only in one case (W2: 10.85  $\mu\text{g}$  T-Hg/l) did the concentration in water exceed the limit value for wastewaters according to Slovenian legislation (10  $\mu\text{g}$  T-Hg/l).

The water of the fish pond (W9) in Wanshan contains the highest concentrations of MeHg (0.77 ng/l) found. It is generally known that in stagnant waters mercury is more easily methylated than in well-aerated river waters. This may well explain the MeHg values in the waters of this fish pond.

Total Hg and MeHg in the area of Quingzhen are in general lower than in Wanshan. The highest concentrations were found at station Q1 that is heavily affected by wastewaters of the chemical plant. With distance from the chemical plant the concentrations of Hg decrease. At station Q4 two water samples were taken, one from the lake and one from the neighboring rice field. Higher values for total Hg were recorded for the lake water but MeHg was much higher in water from the rice field, an indication of active transformation of Hg in this microenvironment. To our knowledge the

Table 8  
Concentration of total Hg, MeHg and Se in rice samples

Sampling station	Rice with hull				Rice without hull			
	Total Hg (ng/g)	MeHg (ng/g)	%Hg as MeHg	Se ( $\mu\text{g/g}$ )	Total Hg (ng/g)	MeHg (ng/g)	%Hg as MeHg	Se ( $\mu\text{g/g}$ )
W1	155	59.6	38.5	<0.3	183	51.7	28.3	<0.4
W2	710	117	16.5	<0.3	569	144	25.2	<0.4
W2a	40.6	8.40	20.7	0.32	38.9	11.0	28.3	–
W3	107	15.2	14.2	0.17	92.5	20.4	22.1	–
W4	10.0	9.73	98.7	<0.3	11.1	8.03	72.6	–0.65
W5	14.4	11.7	81.5	0.37	16.0	11.3	70.8	–
W6	18.9	12.4	65.6	0.13	18.9	12.4	65.6	<0.4
W7	265	59.7	22.6	<0.3	152	59.7	39.3	<0.4
W8	1451	18.6	1.28	1.02	337	18.4	5.46	1.06
W9	87.7	41.4	47.2	0.056	74.1	51.6	69.6	–
Q1	35.3	18.6	52.8	0.19	33.5	28.0	83.7	0.24
Q2	17.7	13.2	74.3	0.36	17.6	14.5	82.6	0.41
Q4	5.62	1.85	32.9	0.2	4.63	1.94	42.0	0.5
Q5	9.81	4.00	40.7	0.91	2.53	0.71	28.1	1.01
Commercial rice from Italy	–	–	–	–	5.21	0.86	16.5	<0.05

only study that addressed MeHg in drainage water of rice paddy fields was made in the Sacramento river basin (Domagalski, 1998) where MeHg was of the same order of magnitude as in this study. Domagalski also reported that concentration of MeHg was not significantly different from other drainage water, but was rather seasonally dependent.

### 3.3. Mercury and selenium in rice

Concentrations of mercury and MeHg in rice are presented in Table 8 and Figs. 6 and 7. At each sampling station the sample was divided into two portions. The hull was removed from the grain to give brown rice. It should be mentioned, however, that local population further process the rice to obtain white rice, which is easier to store. Rice grains with hull were also analyzed in order to examine surface contamination, particularly in areas where atmospheric Hg and Se was expected to be high. In general, the concentrations of MeHg in rice with and without hull are similar at all stations, probably indicating that atmospheric (or external) sources of MeHg are minimal. However, significant differences were observed at the following stations:

- W8: Close to the smelting house, where the concentrations of Hg in air can be very high and consequently leading to surface contamination of the rice seeds.
- W7: Below the mercury mine where elevated concentrations in air are mostly due to Hg bound to aerosols.
- Q5: In the vicinity of the thermal power plant in Quingzhen, where Hg is also elevated in the atmosphere due to emission of Hg in the stack gas. Evidently, the concentrations in absolute values are much lower than in Wanshan, but the difference between the rice with and without hull is significant, reflecting elevated concentrations of Hg in air.

The general observation is that the concentrations of total and MeHg decrease with distance from the source of contamination. The correlation between total Hg and MeHg in rice is presented in Fig. 8. There is a positive trend, except at station W8, where this relation is altered by high atmospheric Hg deposition. Interestingly, the concentration of MeHg in this sample is relatively low, which may also indicate that high levels of elemental mercury present in the area may interfere with the net formation and/or transport of MeHg into the rice grain.



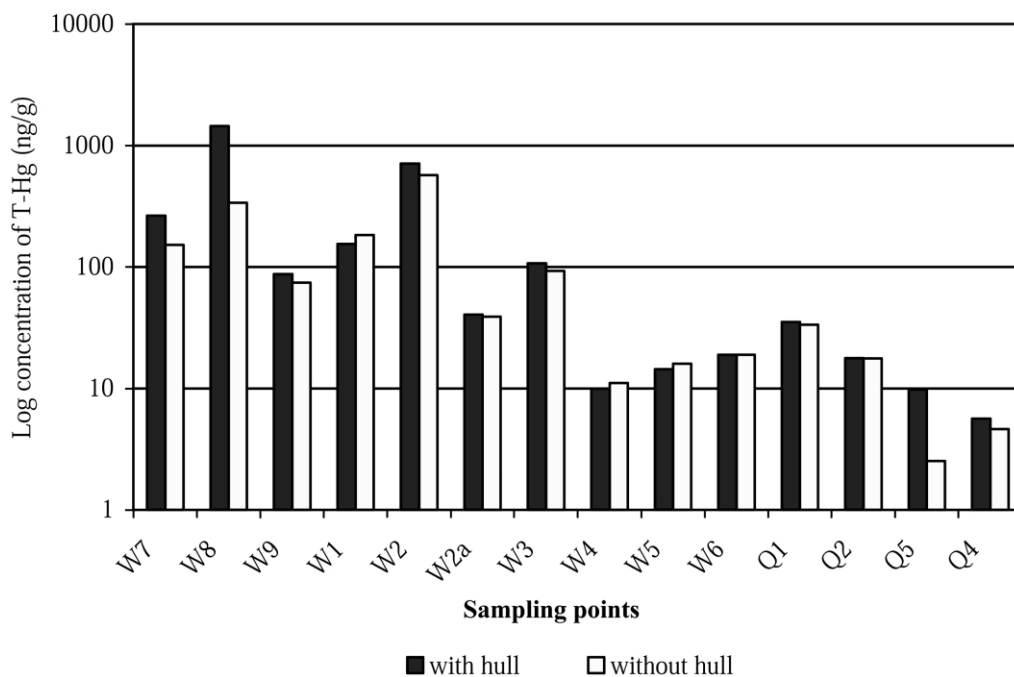


Fig. 6. Concentrations of total Hg in rice.

Concentrations of total Hg and MeHg in the area of Wanshan are generally much higher than in the area of Quingzhen. Mercury in the Wanshan area is spread over a larger geographical area due to active transport through the atmosphere and deposition of Hg over a larger geographical region.

Most probably Hg in rice in this area reflects combined uptake of Hg from the soil and from the atmosphere through absorption by plant leaves (Patra and Sharma, 2000). It is difficult to interpret the concentrations in rice vs. Hg in soil. There is no correlation between total Hg or MeHg in soil and in rice. This clearly indicates that the uptake and retention of Hg in rice is influenced by a number of factors, of which the concentration of total Hg in soil may only be one, and not the most important, of the variables. This can also be demonstrated by comparing Hg concentrations in rice from stations in Wanshan and Quingzhen with similar concentrations of Hg in soil (W8 and Q1) but distinct differences in Hg concentrations in rice, for both total and MeHg. One of the stations in the Wanshan area, W2, deserves a very special

attention. The concentrations in soil are between 33 and 37 mg/kg, but concentrations in rice seeds (rice without hull) are relatively high at 569 ng/g total Hg and 144 ng/g of MeHg. On the other hand, the much more contaminated soil at station Q1 in Quingzhen with 289 mg/kg of total Hg resulted in less than 30 ng/g of MeHg.

Sampling stations in Quingzhen were chosen based on the distance from the source of pollution—the chemical plant. The main mechanism of transport of Hg into other areas is through water flow and the use of this water for the irrigation of rice fields. As presented in Fig. 9 a positive correlation between total MeHg in soil and rice can be observed for the area of Quingzhen. This also applies to the correlation between concentrations in rice, water and soils in the area. This also confirms the conclusion that the absence of a positive correlation between soil and rice, where elevated concentrations in the atmosphere are to be expected (e.g. Wanshan area), is most probably related to the combined uptake, but the relationships still need to be understood. One should also

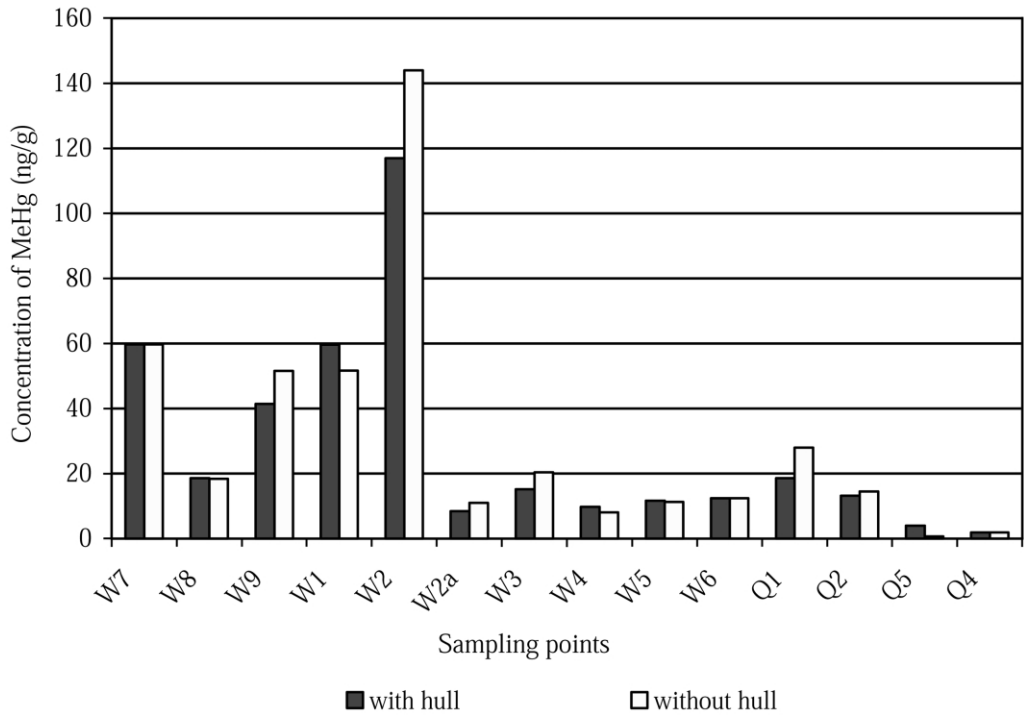


Fig. 7. Concentrations of MeHg in rice.

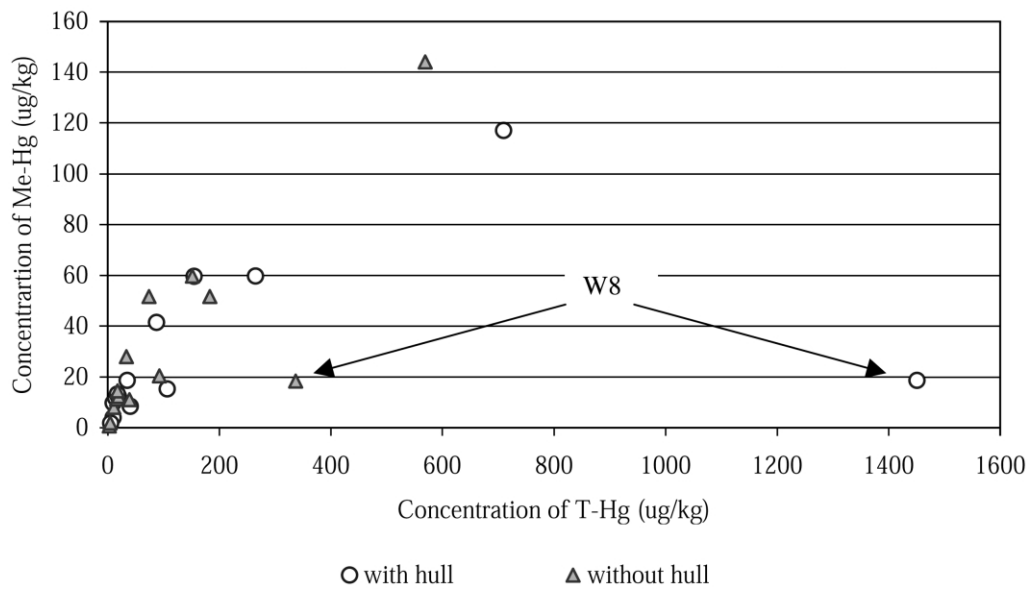


Fig. 8. Correlation between total and MeHg in rice samples.

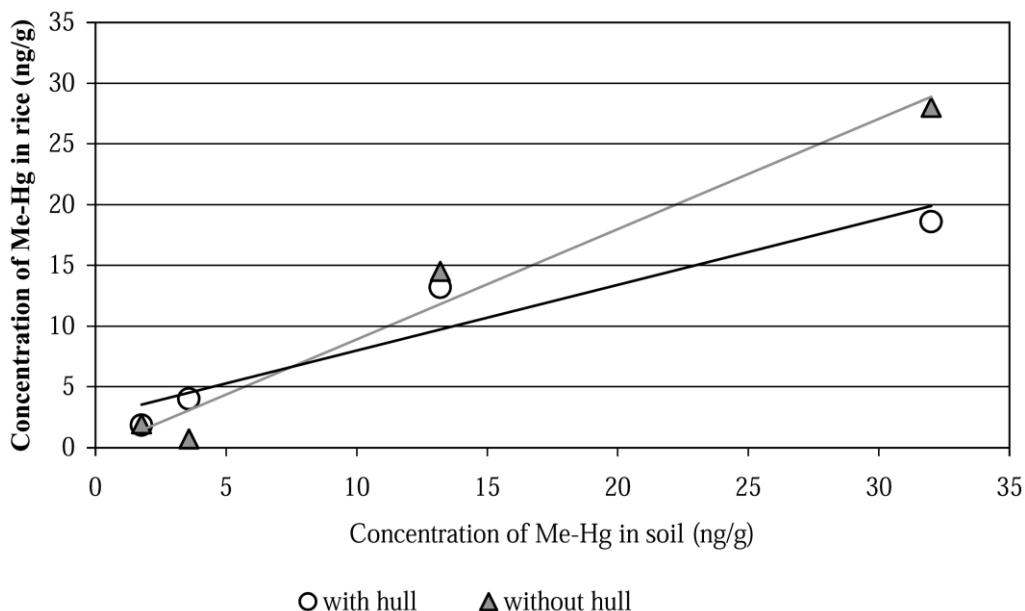


Fig. 9. Correlation between MeHg in soil and rice in sampling areas of Qingzhen.

not neglect the well known genetic control by the rice genotype (Patra and Sharma, 2000).

Concentrations of Hg in rice taken from the area of the lake Huaqiao are rather low and are comparable to values that are found in rice on the Western market originating from Italy (Rice Zlato polje) (Table 8).

In order to check the strength of binding and solubility of Hg in rice an aliquot of rice grains from station W2 (with a total Hg content 596 ng/g) was homogenized in a ratio of 1.10 w/v with 10 mM Tris-HCl (pH 7.6 ml) and 0.1 mM dithiothreitol. After homogenization in a Teflon homogenizer and ultracentrifugation (1 h at 4 °C and 100 000×g rpm) the water soluble phase contained only 13.7% of total Hg, indicating that Hg is strongly bound in rice and is most probably not lost with evaporation during cooking.

It should be noted that in general it is believed that Hg in rice does not pose a significant source of exposure in humans. Indeed in a few studies in which Hg was determined in rice the levels were rather low. In Saudi Arabia the range of concentrations were between <LOD to 43.5 µg/kg (Al-Saleh and Shinwari, 2001) while in the mercury

polluted area of Niigata, Japan, levels below 1 mg/kg were reported (Nakagawa and Yumita, 1998). A study in Ganjam, India, an area impacted by the chlor alkali industry, the levels of Hg in rice reached up to 8 µg/kg; however, elevated Hg was found in some other vegetables, contributing significantly to the daily load of mercury in some localized areas close to chlor alkali plant (Lenka et al., 1992). This suggests that in mercury contaminated sites, the source of mercury is not primarily related to fish consumption, but other foods needs to be evaluated as well. To the best of our knowledge, the concentrations of MeHg have not been reported previously in rice samples.

### 3.3.1. Selenium in rice

Concentrations of Se in rice are given only for some samples, due to spectral interferences in INAA caused by high concentrations of zirconium in the ground rice (contamination in Zr mill during homogenization). Concentrations of Se are highest (approx. 1 mg/kg) at stations W8 and Q5 where the highest Se levels in soils were found. Interestingly, at stations W3 and W4 the levels in rice were significantly lower, although Se in soil is

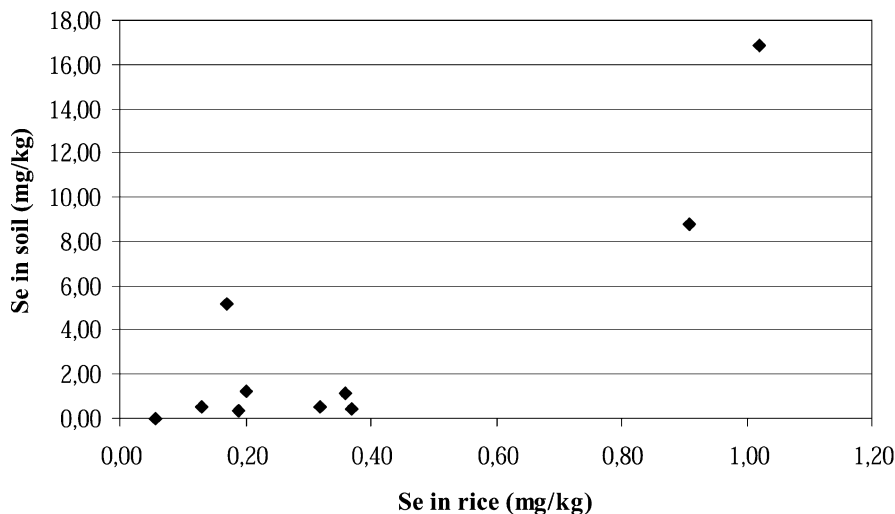


Fig. 10. Correlation between concentration of selenium in rice and soil.

relatively high as well. It is generally well known that Se in soils and plants are poorly correlated due to the complex chemistry of Se in soils affecting its bioavailability and uptake (Reilly, 1996; Suzuki et al., 1980). The correlation between the concentration of Se in rice and soil is presented in Fig. 10, where a positive correlation is observed. Although, the Se concentration in the soil in some of the samples is very high, levels of Se in rice corresponds to values typical of crops grown on selenium adequate soils (Reilly, 1996) with values of up to 1 mg/kg. For example, concentrations in the seleniferous region of Enshi county in China, levels of up to 2.5 mg/kg were reported in rice (Reilly, 1996). In general, Se concentrations in rice are much lower, such as for example in the Yangze river delta, where values of up to 0.035 mg/kg were reported (Cao et al. 2001). The concentration of Se in control rice samples from Italy (Table 8) was also very low. Only five pairs of rice samples (e.g. with and without hull) were compared, with the finding that the Se concentration in grain alone is slightly higher, indicating that the concentration of Se is mostly from uptake by the plant with little additional atmospheric deposition and uptake close to smelting/coal burning facilities. There is no correlation between Hg

and Se in rice samples, showing that Se most probably does not play a role in Hg uptake and retention in the rice grain.

#### 3.4. Mercury in fish

In order to examine a possible relation between size and concentration, a number of fish samples of different weight and size were taken from Lake Huaqiao. Also, the three most common fish species consumed by the local population were sampled. The concentration ranges of Hg are presented in Fig. 11. The percentage of MeHg in fish samples is presented in Fig. 12, confirming retention and accumulation of this toxic Hg compound in fish tissues. No correlation between the length or the weight of fish with total Hg and MeHg concentrations was found. In comparison to other similar lakes the concentrations of both total and MeHg are relatively low. For example, fish in the marine environment impacted by mercury mining activity in Slovenia have approximately 10 times higher Hg concentrations (Horvat et al., 1999). Moreover, concentrations of Hg in less contaminated (1–2 ng of Hg/l in water) lakes in the USA and Canada are much higher, mostly exceeding 0.2 mg/kg (Hecky et al., 1991).

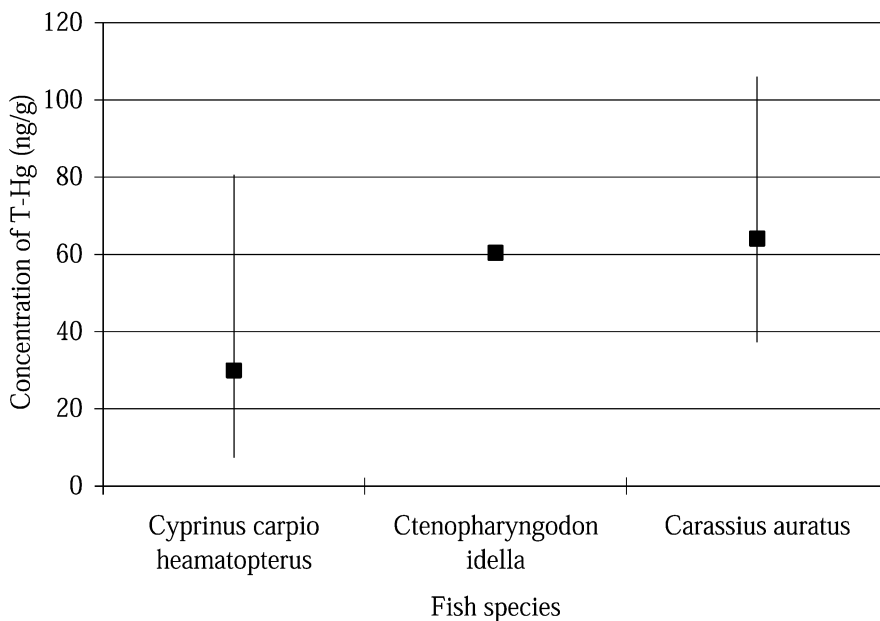


Fig. 11. Total mercury in three different fish species, Quingzhen.

### 3.5. An assessment of mercury exposure in man

In this study we could not conduct a dietary survey, but we assumed that the major route of exposure is contaminated rice and fish from the studied areas and inhalation of elemental Hg in

the area of Wanshan. It was assumed that the daily consumption of rice is 400 g, and of fish 100 g. For the assessment of Hg intake through inhalation it was assumed that a person inhales approximately 20 m<sup>3</sup> of air per day. It should be noted, however, that in the present study brown, unpolished rice

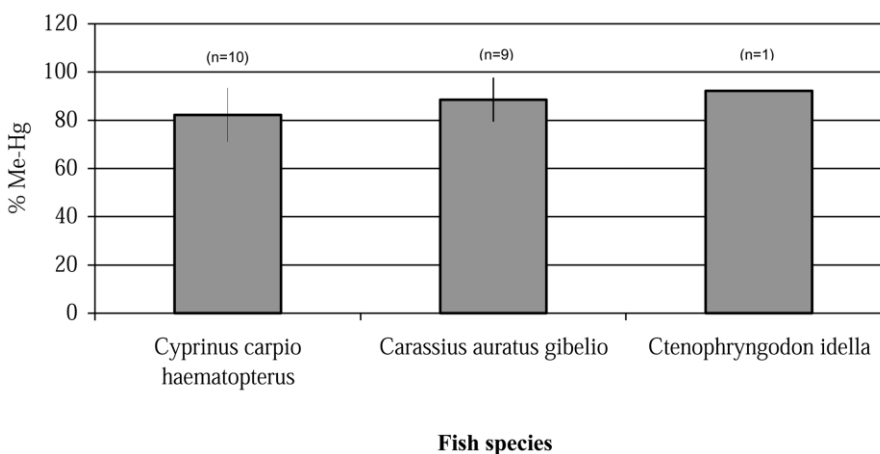


Fig. 12. Percentage of mercury as MeHg in fish muscle samples.

Table 9

Estimated total daily intakes of total Hg and MeHg in adult population in the area of Wanshan and Quingzhen. All intake values are calculated as  $\mu\text{g}/\text{kg}$  body weight of 60 kg person

	WANSHAN		QUINGZHEN	
	Inorganic Hg*	MeHg	Inorganic Hg*	MeHg
Rice (400 g per day)	0.003–0.227	0.05–0.96	0.001–0.003	0.005–0.019
Fish (100 g per day)	No data	No data	0.000–0.003	0.01–0.13
Air	Elemental Hg** 0.13–0.40	MeHg Not significant	Elemental Hg** 0.001–0.100	MeHg Not significant

\* Conc. of inorganic Hg = (conc. of total Hg - conc. of MeHg). The intake values are corrected for the low absorption of inorganic Hg (cc. 8%).

\*\* For calculation of daily intake by inhalation we assumed that the levels of Hg in air in Wanshan are in the range from 500 to 1500 ng T-Hg/m<sup>3</sup>, and in the area of Quingzhen from 5–500 ng T-Hg/m<sup>3</sup>.

was analyzed. In practice, white rice is mainly consumed by the local population. Though white rice is less nutritious than brown rice, it is more convenient for storage and is cooked faster. In order to provide more realistic daily doses of Hg, rice as consumed should be analyzed in the future.

Estimated daily intakes are presented in Table 9. Concentrations of Hg in air fluctuate considerably depending on the temperature, wind direction, humidity, vicinity of the sources of Hg, etc., of a particular area. For the calculation of exposure through the inhalation route, average Hg concentrations in air were used. The same applies to the estimation of the daily uptake of Hg through food consumption, where the limited absorption of inorganic Hg (difference between total and MeHg concentrations) should be taken into account. In man this proportion is approximately 8% of inorganic Hg and 100% for MeHg.

In comparing the routes of intake, as shown in Table 9, it was found that inhaled Hg represents a considerable fraction of total Hg intake in Wanshan and Quingzhen as compared to that from food consumption.

According to the recommendations of FAO/WHO the daily intakes are considerably exceeded for MeHg in the area of Wanshan. A significant portion to the total daily intake is also due to inhaled Hg. In the Quingzhen area these values are not exceeded. However, if the new US EPA recommended values are considered, then the intakes in some of the population groups in Quingzhen are also exceeded.

Populations heavily exposed to elemental Hg through inhalation and MeHg through food consumption live close to the smelting facilities (W8), mining activities (W7) and areas close to the disposal sites for mining residues (W1 and W2) in the Wanshan area. Population groups along the river Xiaxihe (W3–W6) are not heavily exposed to Hg and are not considered as a population at risk due to exposure to mercury. Similar conclusions can be drawn for most parts of Quingzhen with the exception of inhabitants close to the chemical plant, where the highest values of total Hg and MeHg were found.

The Minimal Risk Level (MRL) for chronic exposure to Hg<sup>0</sup> is 0.2  $\mu\text{g}/\text{m}^3$ , while the LOAEL was found to be 26  $\mu\text{g}/\text{m}^3$ . Taking these values into consideration, the MRL is considerably exceeded in Wanshan. The same applies to the area in Quingzhen in the vicinity of thermal power plant where concentrations of elemental Hg may reach up to 0.5  $\mu\text{g}/\text{m}^3$ .

Based on the above assumptions the daily intake of selenium through rice consumption would reach up to 400  $\mu\text{g}$  per day, which exceeds the recommendations of US National Academy of Sciences of 50–200  $\mu\text{g}/\text{day}$  as safe and adequate (McLaughlin et al., 1999; Reilly, 1996). It should be noted, however, that the rice is not the only source of Se in this population and it should be recommended that Se is further addressed and investigated. Due to the well known antagonistic effects of co-accumulated Se in mercury exposed populations (Falnoga et al., 2000; Kosta et al., 1973,

1975; Byrne et al., 1995) elevated Se in rice and probably in other foods may play an important protective role against Hg toxicity in local populations.

**4. Conclusions**

The results of this study confirmed heavy contamination of Hg in soil, sediments and rice in the Hg mining area in Wanshan. High levels of Hg in soil and rice were also found in the vicinity of the chemical plant in Quingzhen. With distance from the main sources of pollution the concentrations of Hg decreased considerably. The general conclusion is that Hg contamination in Wanshan is geographically more widespread, due to deposition and scavenging of Hg from contaminated air and deposition on land. In Quingzhen Hg contamination of soil is very high close to the chemical plant but the levels reach background concentrations at a distance of several km.

Even though the major source of Hg in both areas is inorganic Hg, we observed that active transformation of inorganic Hg to organic Hg species (MeHg) takes place in water, sediments and soils. The transformation rates depend on several factors, which cannot be addressed in this study, due to limited information available on the soil type, pH, redox conditions, pedological properties, water quality parameters, etc.

An interesting outcome of this study is the observation that the percentage of MeHg in rice is rather high and represents the major source of this toxic Hg form to the local population. The percentage of mercury as MeHg in fish is even higher. This clearly confirms the well-known fact that MeHg is accumulated and biomagnified in trophic food chains in the aquatic and terrestrial environments. Fig. 13 shows the increase in %MeHg from total Hg in different samples analyzed in the studied areas, confirming the above observations. An interesting observation was also the fact that

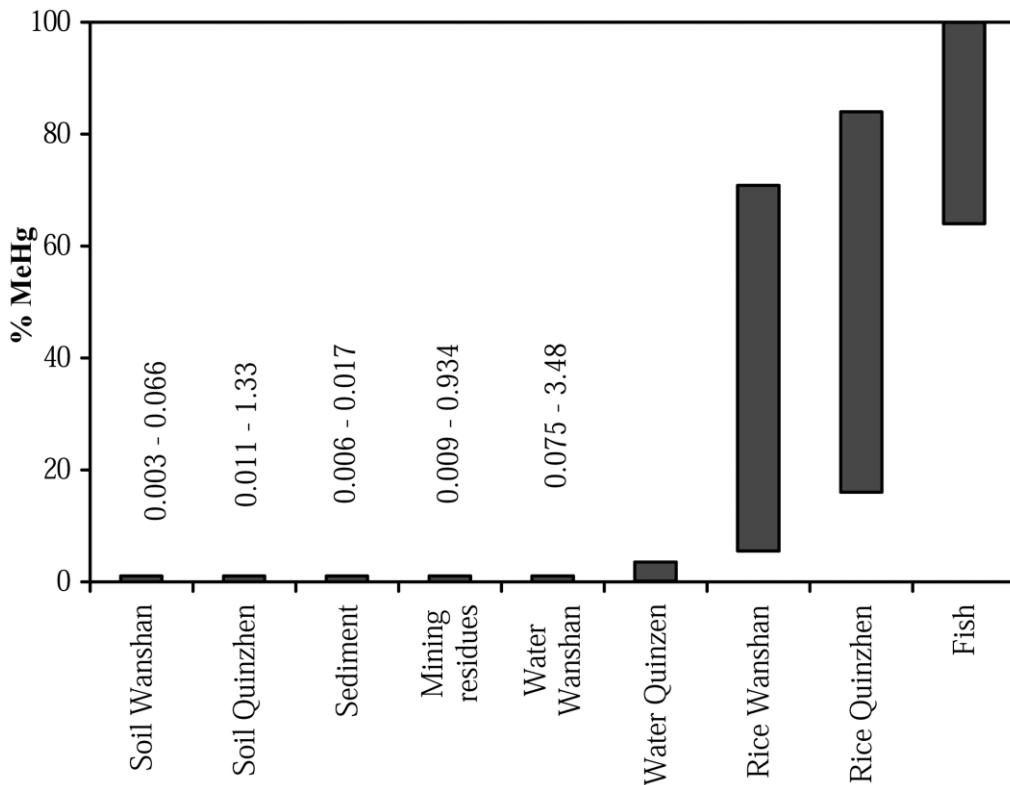


Fig. 13. Percentage mercury as MeHg in different environmental compartments.

levels of Hg in fish are of the same order of magnitude as the rice samples. The reason for this probably lies in the fact that MeHg in alkaline lake water is much less available to fish than in the acidic lakes of the northern hemisphere studied extensively in Europe and North America.

The estimated daily intakes for the adult population in the areas studied revealed interesting conclusions. It was assumed that the major routes of exposure are consumption of contaminated food (mainly rice and fish) and through inhalation of air contaminated with Hg. Daily intakes through food consumption are much higher than inhalation in both studied areas. In the area of Wanshan, daily intakes for MeHg considerably exceed the FAO/WHO recommendations, while in the area of Quingzhen the daily intakes are below these recommendations. In addition, the Minimal Risk Level (MRL) for chronic exposure to elemental Hg of  $0.2 \mu\text{gHg}/\text{m}^3$  (proposed by the AT SDR) is also exceeded in the vicinity of the Beimen thermal power plant near Quingzhen.

Taking into consideration the new recommended daily intakes for total Hg and MeHg proposed by the US EPA, the intakes of Hg are exceeded in both studied areas. In general, it can be concluded that the population most at risk is located in the vicinity of smelting facilities, mining activities and close to the waste disposal sites in the wider area of Wanshan. In order to assess the real level of contamination in the local population, it is recommended that biomonitoring should be performed, including Hg and MeHg measurements in hair, blood and urine samples, similar to the study conducted by Drasch et al., 2001 in the Philippines. In addition, a number of biomarkers of possible effects, such as peroxidation and functional damage in target organ tissues should also be done. Elevated levels of Se in most soils and rice samples also need to be addressed in the future study, in particular with respect to the possible protective role of Se in populations highly exposed to mercury.

### Acknowledgments

This work was conducted in the framework of Scientific and Technological Cooperation between

the Republic of Slovenia and the People's Republic of China, Project Number 03-3-01. The cooperation of the S&T Commission of Guizhou of China as highly acknowledged as well, in particular assistance during the sampling campaign. The work was also conducted in the framework of the program on Biological and Geochemical Cycling P 531 and the financial support of the Ministry of Science and Technology of Slovenia is sincerely acknowledged. Dr A.R. Byrne is acknowledged for his editorial expertise.

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