Journal of Hazardous Materials 221–222 (2012) 28–34

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A human health risk assessment of mercury species in soil and food around compact fluorescent lamp factories in Zhejiang Province, PR China

D.D. Shao[a,b,c], S.C. Wu[b], P. Liang[a,b], Y. Kang[b], W.J. Fu[a], K.L. Zhao[a], Z.H. Cao[a], M.H. Wong[a,b,*]

[a] School of Environmental and Resource Sciences, Zhejiang Agriculture and Forestry University, Linan, PR China
[b] Croucher Institute for Environmental Sciences, and Department of Biology, Hong Kong Baptist University, Hong Kong SAR, PR China
[c] Foreign Economic Cooperation Office, Ministry of Environmental Protection of China, PR China

ARTICLE INFO

Article history:
Received 30 November 2011
Received in revised form 16 February 2012
Accepted 22 March 2012
Available online 1 April 2012

Keywords:
CFLs
Mercury
Mud skipper
Bioaccessibility

ABSTRACT

This study investigated total mercury (THg) and methylmercury (MeHg) contamination in a major production center of compact fluorescent lamps (CFLs) located in Gaohong, Zhejiang Province, China. This was a result of the growing concern associated with the release of mercury into the environment from such components. The results of the study included the following mean concentrations for THg and MeHg of 157 ± 11 (61–518) ng/g dw and 0.28 ± 0.07 (0.07–0.67) ng/g dw in agricultural soil, respectively, and 18.6 ± 6.5 (3.2–47.8) ng/g ww and 0.11 ± 0.03 (0.02–0.37) ng/g ww in vegetable samples, respectively. A significant correlation was observed between THg in vegetables and corresponding soil samples ($r = 0.64$, $p < 0.01$). THg and MeHg in sediment samples had respective concentrations ranging from 28 to 1019 ng/g dw and 0.11 to 3.15 ng/g dw. Mud skipper bought from the local market contained the highest Hg (THg: 170 ± 45 ng/g ww, MeHg: 143 ± 37 ng/g ww) amongst all fish species (THg: 14–170; MeHg: 11–143 ng/g ww) of the study. The risk assessment indicated that fish consumption should not result in a MeHg EDI exceeding the RfD (0.1 μg/kg bw/d) for both adults and children, when MeHg bioaccessibility is taken into account.

1. Introduction

Compact fluorescent lamps (CFLs) are a type of fluorescent lamp, which relies on mercury (Hg) as a source of ultraviolet radiation, for the production of visible light. The amount of Hg contained within each bulb, in 1994, was relatively small, ranging from 0.72 to 115 mg with an average Hg content of about 30 mg [1]. In 2003, however, CFLs of the same brand contained as little as 1.4–2.7 mg Hg per lamp, with Hg contents increasing slightly with wattage [2]. CFLs have been extensively used for house lighting because they are energy-efficient and have a longer rated life [3]. Much of the current and projected growth for them is associated with their domestic use, in that consumers are offered approximately 75% reduction in energy usage and 10-fold increase in lifetime, relative to incandescent bulbs. Federal legislation already passed in the USA signifies the phasing out of the use of incandescent bulbs by 2012, with CFLs being the likely replacement [3].

Nevertheless, individuals can still often be directly exposed to the dangers of Hg vapor emissions from CFLs, such as when they are damaged or broken during shipping, handling, retailing, and while in use. This is of potential concern particularly in scenarios involving multiple lamps, confined spaces and young children [4]. Concerns also arise with regard to Hg exposure *via* inhalation, where 80% of it is physiologically absorbed [5]. This vapor being a well-documented neurotoxin easily penetrates the blood–brain barrier, with elemental Hg also shown to be oxidized to the inorganic divalent form in body tissues [6]. Consequently, exposure to Hg can result in neurological and behavioral disorders including: tremors; emotional lability; insomnia; memory loss; neuromuscular changes; and headaches.

The THg released into the environment from fluorescent lamps is estimated to be about 15 t in China [7]. Gaohong Town (30°19′N, 119°40′E) is located within the northeastern part of Lin'an District in Hangzhou City in northern Zhejiang Province, China. It also commonly known as the "town of CFLs" because of the central role it plays in CFL production, spanning a total area of 110 km^2 with a population of 35,000 including 21,000 migrants (Statistics Bureau of Zhejiang Province, 2010) and in 2003, there was in excess of 70 factories manufacturing CFLs in Gaohong, which accounted for a third of the country's production (Statistics Bureau of Zhejiang Province, 2010). However, the region also has a major industry for agricultural production, vegetable, tea and fruit produces, therefore, Hg contamination resulting from CFL production can have potentially negative and significant impacts on the growth and safety of such produce.

* Corresponding author. Tel.: +852 3411 7746; fax: +852 3411 7743.
E-mail address: mhwong@hkbu.edu.hk (M.H. Wong).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.03.061

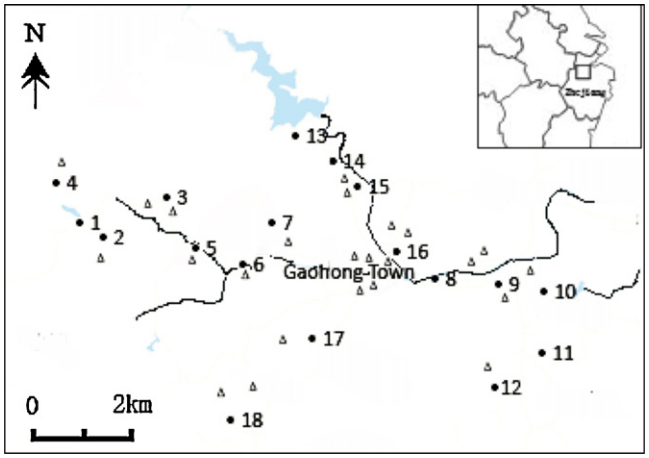

Fig. 1. Locations of the sampling sites in Gaohong. No. 1: Daxi reservoir, No. 2: Xiafeng village, No. 3: Changqing village, No. 4: Daxi village, No. 5: Huoshan village, No. 6: Nanshanwu village, No. 7: Chenjiakan village, No. 8: Shang'an village, No. 9: Xiaan village, No. 10: Tangxia village, No. 11: Chalukou village, No. 12: Taiping hill, No. 13: Shuitaozhuang reservoir, No. 14: Northern Xinde village, No. 15: Xinde village, No. 16: Hongqiao village, No. 17: Maling village, No. 18: Wuma village, △: locations of CFL companies.

This is the first study dealing with Hg contamination in environmental matrices around CFL manufacturing sites in China. The main objectives of the present study were: (1) to investigate the THg and MeHg contamination in soil and vegetables collected from farms in Gaohong; (2) to investigate THg and MeHg contamination in sediments and fish collected in Gaohong; and (3) to evaluate the health risk of dietary MeHg exposure from different food items.

2. Materials and methods

2.1. Sampling and pretreatment

The samples were collected, during January 2011, from 18 sampling sites located around Gaohong (Fig. 1). Soil samples acting as the control were obtained from both the Daxi (No. 1) and Shuitaozhuang reservoirs (No. 13), while sediment samples (0–10 cm, $n=3$) were collected using a grab sampler from the former and its branch streams. The other 16 soil samples (10–40 cm) and vegetable samples (Chinese white cabbage (*Brassica campestris* L.), xuelihong (*Brassica juncea* var. *crispifolia*), Chinese radish (*R. sativus* var. *longipinnatus*), spinach (*Spinacia oleracea*), and lettuce (*Lactuca sativa*) were collected from farmland in close proximity to CFL factories (triplicate samples for each site). Two species of freshwater fish (bighead carp (*Aristichthys nobilis*) ($n=4$), crucian carp (*Carassius carassius*) ($n=6$) were caught from the Daxi reservoir (No. 1), while 5 species of fish (grass carp (*Ctenopharyngodon idellus*) ($n=6$), northern snakehead (*Channa argus*) ($n=4$), oriental weatherfish (*Misgurnus anguillicaudatus*) ($n=20$), mud skipper (*Periophthalmus argentilineatus*) ($n=25$) and yellowhead catfish (*Pelteobagrus fulvidraco*) ($n=5$) were bought from the local markets. After collection, all soil and sediment samples were immediately transported to the laboratory in polyethylene zippered bags in cold boxes, and stored under −20 °C prior to freeze-drying. While, dorsal muscles of fish were placed in polyethylene bags, stored at 0 °C and transported to the laboratory within the same day.

2.2. Sample analyses

Sediment and soil samples were freeze dried, ground into fine powder and passed through a 0.154 mm sieve. Fish (dorsal muscles) and vegetable samples were freeze-dried, crushed, and ground into powder. All glassware was soaked in 50% (v/v) HNO_3 for 24 h and rinsed with deionized water before use.

The analytical protocol for MeHg in sediment and soil was based on the method applied in Liang et al. [8]. MeHg was extracted from sediment (1 g) and soil (1 g) using 25% HNO_3 (1 mL), 1 M $CuSO_4$ (1 mL) and CH_2Cl_2 (8 mL) in 50 mL centrifugal tube. The tube was shaken for 30 min, centrifuged for 20 min at 3000 rpm, and filtered. The organic phase was made up to 40 mL by adding Milli-Q water to the 50 mL centrifugal tubes. The tubes were placed in a water bath at 50 °C and purged with N_2 to remove excess dichloromethane (DCM) (60 °C, 10 min). The solution (30 μL) was added to 40 mL vials (ensured to be absent of air by filling with Milli-Q water) with Teflon lined septa caps. Samples were buffered (300 μL) to pH 4.9, ethylated with the addition of $NaBEt_4$ (40 μL), and made up to volume with Milli-Q water, capped, shaken and loaded into the auto sampler of the MeHg analyzer. The MeHg analyses of fish and vegetables were conducted according to the Brooks Rand LLC Standard Operating Procedures (SOPs). Sample weighing 0.1–0.2 g was digested with 25% KOH methanol (2.5 mL) in an oven at 70 °C for 3 h. The solution was diluted to 20 mL with methanol after cooling. The solution (30 μL) was added to 40 mL vials (ensured to be absent of air by filling with Milli-Q water) with Teflon lined septa caps. Samples were buffered (300 μL) to pH 4.9, ethylated with the addition of $NaBEt_4$ (40 μL), and made up to volume with Milli-Q water, capped, shaken and loaded into the auto sampler of the MeHg analyzer.

The THg concentration was analyzed by the direct mercury analyzer DMA-80 (Milestone, USA) following the USEPA Method 7473 [9]. Measurements of MeHg were conducted using the automated modular mercury system from Brooks Rand (MERX, Brooks Rand Labs, USA).

2.3. Quality control

The accuracy of the THg and MeHg measurements for each analytical batch was determined using 3 certified reference materials: TORT-2 (Lobster hepatopancreas, National Research Council of Canada); NIES No. 13 (Human hair, National Institute for Environmental Studies, Japan); and NIST 1570a (Spinach leaves, National Institute of Standards and Technology, USA). The recoveries of the standard reference materials for THg and MeHg ranged from 96–105% to 92–106%, respectively.

2.4. Oral bioaccessibility determination of Hg in fish and vegetables

The *in vitro* digestion test was performed according to the one used in Ruby et al. [10] Gastric solution for the test was prepared by adding 8.8 g of NaCl, 0.5 g of citrate, 0.5 g of malate, 0.4 mL of lactic acid, 0.5 mL of acetic acid, and 1.25 g of pepsin in to 1 L of deionized water, which was adjusted to pH 1.5 with 12 M HCl. The pH of the intestinal solution was adjusted to 7.0 using a saturated solution of $NaHCO_3$, followed by the addition of 15 g pancreatin, 5 g α-amylase, 1.5 g bile salt and 7 g lipase to 1 L of deionized water. Samples of either fish or vegetables weighing 1–2 g were added to 10–20 mL gastric solution and the mixture shaken at 37 °C for 4 h. Afterwards, the mixture was centrifuged at 3000 rpm for 20 min and the resulting supernatant filtered through 0.45 μm filter paper. Then 10 mL intestinal solution was added to suspend the pellet in the centrifuge tube. After shaking at 37 °C for 4 h, the mixture was centrifuged at 3000 rpm for 20 min and filtered. Hg in the extracts and pellets were measured. The bioaccessibility (% BA) of Hg (stomach and intestine) was calculated as:

$$\%\ \mathrm{BA} = \frac{[\mathrm{Hg\ \ in\ \ bioaccessible\ \ fraction}]}{[\mathrm{Hg\ \ in\ \ food}]} \times 100$$

To test the recovery, certified reference materials of TORT-2, NIST 1566b and NIST-1570a were analyzed in parallel with each batch of 5 fish samples. The recovery rate was obtained by calculating the ratio of the sum of Hg in digestible and indigestible fractions to the Hg concentration in the certified reference materials. The recovery rates of MeHg and THg ranged from 64 to 83% and 89 to 115%, respectively. If the recovery rate was below 75% (a small proportion), the reported data was adjusted by the recovery rate.

2.5. Risk assessment of fish and vegetable consumption

To estimate the daily intake of MeHg *via* the consumption of freshwater fish, the following equations [11] were used:

$$\mathrm{EDI} = \frac{\text{MeHg concentration } (\mu g/g\,\text{ww}) \times \text{consumption rate } (g/d)}{\text{body weight } (kg)}$$

$$\mathrm{EDI_{bio}} = \frac{\text{MeHg concentration } (\mu g/g\,\text{ww}) \times \text{consumption rate } (g/d) \times \%\ \text{BA}}{\text{body weight } (kg)}$$

whereby EDI and EDI_{bio} represented the estimated daily intake of MeHg and estimated daily intake of bioaccessible MeHg, respectively, BA% was bioaccessibility of MeHg in fish, MeHg concentration in fish tissue was based on wet weight, body weights for adults and children were 55.9 [12] and 21.8 kg, respectively [13], and the consumption rate was 32.1 g/d for adults and 18.3 g/d for children, respectively, in Zhejiang Province [14]. The oral reference dose (RfD) for MeHg recommended by the USEPA 2010 [16] was 1×10^{-4} mg/kg/d. The acceptable daily intake (ADI) established by the Joint Expert Committee on Food Additives (JECFA) was 0.23 μg/kg bw/d (2006) [17]. To estimate the daily intake of THg *via* the consumption of vegetables, the same equations were used as the ones for fish. The consumption rate was 465 g/d and 265 g/d for adults and children, respectively, in Zhejiang Province [14]. Both the fish and vegetable consumption rate for children were estimated as 57% of that of adults [15]. The RfD for $HgCl_2$ recommended by the USEPA 1995 [18] was 0.3 μg/kg bw/d.

2.6. Statistical analyses

All of the data were analyzed using the Statistical Package for Social Sciences (SPSS). The one-way ANOVA test was used to determine any significant differences in terms of Hg concentrations in soil, vegetable, sediment and fish samples. While, independent two-sample *t*-test was used to determine differences between Hg concentrations for sampling and control sites and linear regression used to identify relationships between Hg levels in soil and vegetables. The data was log-transformed prior to linear regression and one-way ANOVA analysis with the level of significance set at $p < 0.05$ for all analyses.

3. Results and discussion

3.1. Soil Hg levels

THg and MeHg concentrations in soil samples are shown in Fig. 2, with the mean concentration of THg being 157 ± 11 ng/g dw, ranging from 61 to 518 ng/g dw. While, the mean concentration of MeHg was 0.28 ± 0.07 ng/g dw, ranging from 0.07 to 0.67 ng/g dw, with MeHg contributing to 0.19% of THg. The highest THg and MeHg values were observed in Wuma Village (No. 18) and Hongqiao Village (No. 16). The mean THg and MeHg concentrations in soil samples collected from CFL manufacturing sites were significantly higher ($p < 0.05$) than those of the control sites (THg: 48 ± 2 (17–56) ng/g dw; MeHg: 0.07 ± 0.02 (0.02–0.12) ng/g dw).

THg levels from 2 sites (No. 16 and No. 18) exceeded grade II (0.3 mg/kg; grade II classification deems agricultural soil suitable for growing paddy rice and vegetables) of the Chinese Soil Environmental Quality Standard (GB 15618-1995) for Hg concentrations. When compared with other studies, the concentrations of Hg obtained in the present study were lower than those in the topsoils around the Diss Mere weaving industry of the UK (THg: 200–600 ng/g dw) [19] and agricultural soil around zinc smelting areas in Liaoning (THg: 0.51–18 μg/g) [20]. The Hg levels in the present study were also lower than those in Guangzhou urban soils, which ranged from 0.013 to 12 μg/g with an average of 0.61 μg/g [21], as well as, in Foshan and Nanhai farmland soil, which ranged from 0.12 to 1.3 μg/g with an average of 0.71 μg/g [22]. This may be due to the long industrial history of Guangzhou involving electronics, ceramics, and printing and dyeing, [21] and the increasing application of agrochemicals (fertilizers, pesticides, and animal manures) on farmland of Foshan and Nanhai [22]. In comparison with Hg contamination caused by coal combustion, THg concentrations in agricultural soil obtained in the present study were slightly higher than those found under the same experimental set up conducted in Korea (11–192 ng/g dw) [23]. But slightly lower than those found around a coal-fired power plant in Baoji, China (197–2105 ng/g dw) [24] and Wuhu, China (25–1696 ng/g dw) [25].

When compared with samples collected from abandoned Hg mines in Wanshan District of Guizhou Province, high THg and MeHg concentrations were obtained from riparian soil mined areas (Aozhai River and Xiaxi River), ranging from 5.1 to 790 mg/kg and 0.13 to 15 ng/g, respectively [26]. Wanshan in Guizhou Province was the largest conglomeration of Hg mines and refining plants in China, with mining dating back to the Qin Dynasty (221 B.C.) but all of this ceased in 2001. When large-scale Hg mining and retorting were shut down, approximately 22,000 t of Hg and 6000 t of cinnabar had been produced [26], which may have caused the most severe Hg contamination in Guizhou Province. The THg concentration in the rice paddy soil samples ranged from 8.0 to 130 mg/kg [27]. The highest level was observed in soil samples collected from Guizhou, followed by Guangdong and Zhejiang when comparing Hg concentrations. It appears Hg mining can be attributed as a factor more serious to Hg contamination in soil than other industrial activities, including CFL factories.

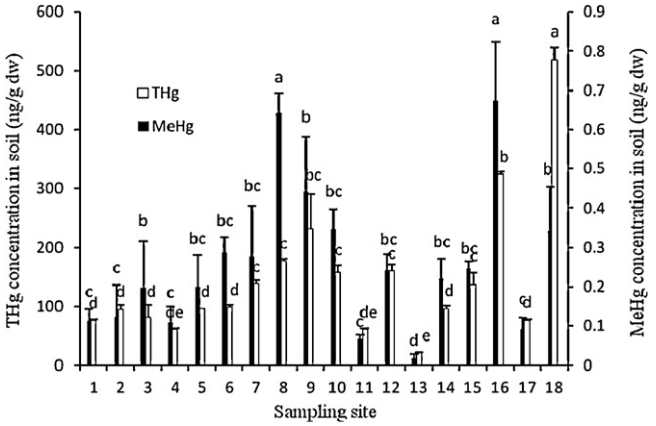

Fig. 2. THg and MeHg concentrations in soil samples. Columns with the same letter are not significantly different ($p < 0.05$) according to the results of one way ANOVA test.

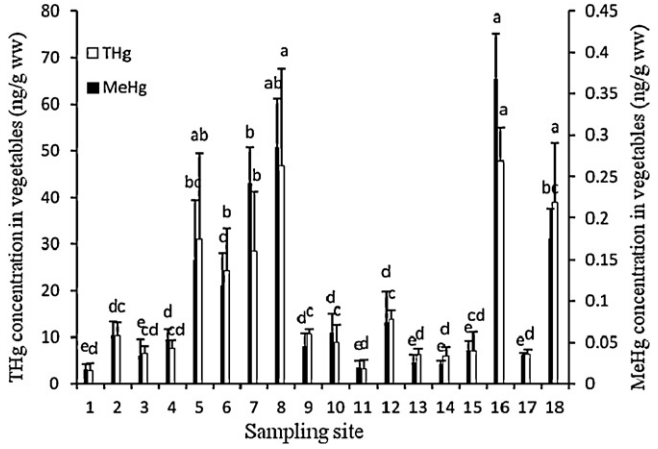

Fig. 3. THg and MeHg concentrations in vegetable samples. Columns with the same letter are not significantly different ($p < 0.05$) according to the results of one way ANOVA test.

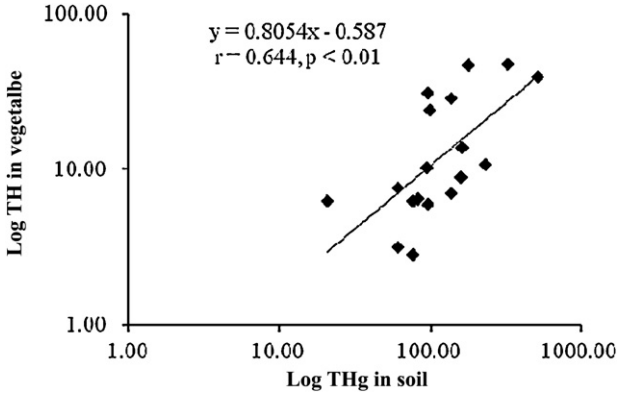

Fig. 4. The relationship between THg concentrations in vegetable samples and corresponding soils. The data was log-transformed prior to linear regression.

3.2. Vegetable Hg levels

Fig. 3 shows the THg and MeHg concentrations in vegetable samples. The mean concentration of THg was 18.6 ± 6.5 ng/g ww, ranging from 3.2 to 47.8 ng/g ww, while the mean concentration of MeHg was 0.11 ± 0.03 ng/g ww, ranging from 0.02 to 0.37 ng/g ww, with the ratio of MeHg to THg being 0.58%. The highest THg and MeHg values were observed in the villages of Shang'an (No. 8) and Hongqiao (No. 16), respectively, which may be due to the higher density of CFL manufacturing plants relative to the other sites (Fig. 1). The mean THg and MeHg concentrations in vegetable samples collected from CFL manufacturing sites were significantly higher ($p < 0.05$) than those from the control sites (THg: 4.5 ± 1.4 (1.9–7.2) ng/g ww; MeHg: 0.02 ± 0.01 (0.01–0.09) ng/g ww). In addition, THg concentrations in 50% of the vegetables were higher than China's National Standard (10 ng/g ww), which indicates that Hg released from CFL manufacturing was a source of Hg pollution.

THg levels of vegetables (Chinese white cabbage, xuelihong, Chinese radish, spinach, and lettuce) obtained in the present study were higher than those collected from the PRD (1.32 ± 0.57 ng/g ww) [28]. But lower than those from the Wanshan area (130 ng/g ww) [29], Dashuixi (346 ng/g ww), Xiachangxi (87 ng/ ww) and Baoxi (109 ng/g ww) villages in Wanshan town [30], and the vicinity of five Hg mines including Laowu, Gouxi, Dashui, Sikeng and Gaolou (8.92–1160 ng/g dw) [31] in Guizhou Province. For MeHg, similar levels were observed from these three regions (PRD: 0.03 ± 0.01 ng/g ww [28]; Wanshan: 0.097 ng/g ww [29]). In addition, there were significant correlations between THg in vegetable and corresponding soil samples ($r = 0.64$, $p < 0.01$) (Fig. 4). These results indicate that vegetable samples can accumulate inorganic Hg from farmland soil, and Hg contamination in soil may be the source of Hg pollution in vegetables. In addition, previous studies showed that plants can take up elemental Hg from the air and inorganic Hg (II) and MeHg from the soil [32,33]. The Hg released from industrial activities settles on the surface of vegetables and in turn causes the increase in Hg concentrations. Further investigation is needed in order to obtain a more in-depth explanation of the results.

3.3. Sediment Hg Levels

Sediment samples were collected from 9 sites around CFL manufacturing plants (No. 3, 8–12 and 16–18), with THg and MeHg concentrations ranging from 28 to 1019 ng/g dw and 0.11 to 3.15 ng/g dw, respectively. The mean Hg concentrations in sediments collected from CFL manufacturing sites (THg: 322 ± 30 ng/g dw, MeHg: 0.85 ± 0.14 ng/g dw) were higher than those from the control site (No. 1) (THg: 77.9 ± 2.0 ng/g dw, MeHg: 0.15 ± 0.05 ng/g dw). The highest Hg level was observed in samples from Hongqiao Village (No. 16), which contained 1019 ± 54 ng/g dw of THg and 3.15 ± 0.14 ng/g dw of MeHg. This may have resulted due to the higher density of CFL manufacturing plants existing at this location relative to the other sampling sites.

THg and MeHg concentrations in sediments (Gaohong) of the present study were slightly higher than the Hg levels of freshwater fish pond sediments in the PRD (33–386 ng/g dw of THg, 0.18–1.3 ng/g dw of MeHg) [34]. Furthermore, when comparing with Hg pollution caused by coal combustion, the present study's Hg concentrations were higher than those found around a coal-fired power plant in Xiamen (THg: 55–201 ng/g dw; MeHg: 0.017–0.26 ng/g dw) [35]. However, both Hg concentrations in sediments from Gaohong and the PRD were lower than those collected from areas of mining in Wanshan (THg: 1.1–480 μg/g dw) [27], zinc smelting in Liaoning (THg: 0.15–15.4 μg/g dw) [20] and weaving industry in Diss Mere (average THg: 3000 ng/g dw) [19] and a sodium pentachlorophenate manufacturing plant in Taiwan (THg: 0.8–157 μg/g dw; MeHg: 2–12.7 ng/g dw) [36]. In addition, the concentration of MeHg in stream sediments was generally higher than that of agriculture soils for the corresponding locations (Fig. 5). This result is in line with the study conducted in Wanshan, which obtained higher Hg concentrations in sediments than those in associated soil samples [27]. This may be explained by the fact that Hg evaporates more readily in soil than in sediment. In addition, sediments under aerobic conditions when compared to soils are known to be more favorable for Hg methylation by anaerobic bacteria, with optimal conditions occurring at the sediment/water interface [37].

3.4. Fish Hg levels

Two fish species were collected from the Daxi reservoir, with higher Hg concentrations observed in bighead carp (57.0 ± 16.9 ng/g ww of THg and 50.8 ± 14.8 ng/g ww of MeHg) than in crucian carp (83.7 ± 29.0 ng/g ww and 64.9 ± 18.3 ng/g ww, respectively). Five fish species were bought from the local market, with the highest Hg concentrations observed in the descending order as follows: the dorsal muscle of mud skipper (THg: 170 ± 45 ng/g ww, MeHg: 143 ± 37 ng/g ww); yellowhead catfish (THg: 41.2 ± 16.3 ng/g ww, MeHg: 32.6 ± 11.8 ng/g ww); northern snakehead (THg: 31.2 ± 6.4 ng/g ww, MeHg: 25.3 ± 5.83 ng/g ww); grass carp (THg: 23.6 ± 10.9 ng/g ww, MeHg: 18.6 ± 7.2 ng/g ww); and oriental weatherfish (THg: 14.1 ± 4.3 ng/g ww, MeHg:

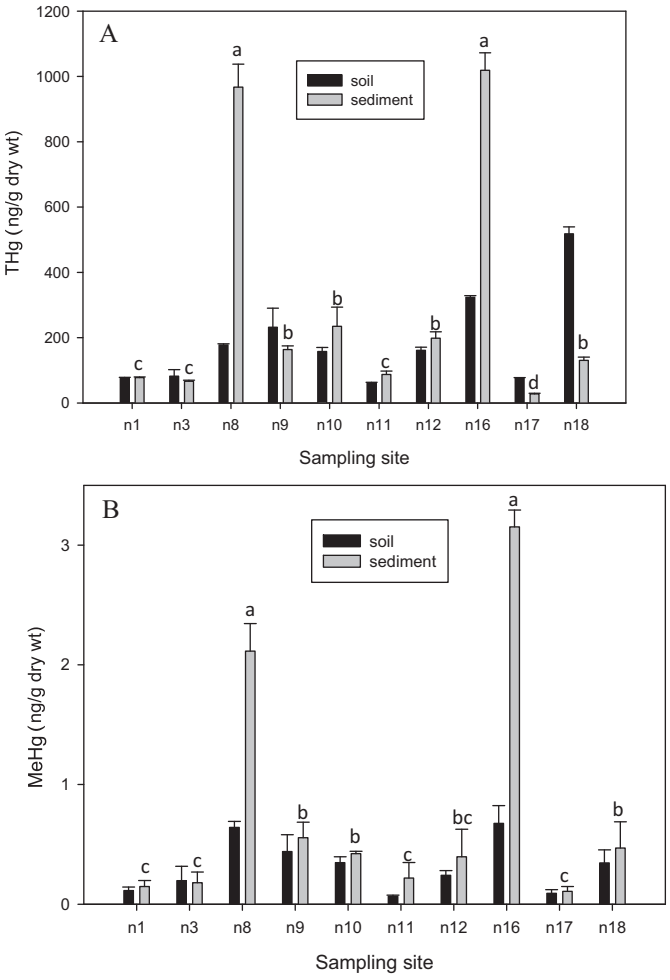

Fig. 5. Comparison of Hg concentrations in soil and sediment samples collected from the same sites. (A): THg; (B): MeHg. Columns with the same letter are not significantly different ($p < 0.05$) according to the results of one way ANOVA test.

10.5 ± 3.5 ng/g ww) (Fig. 6). The Hg concentrations observed in all fish samples did not exceed the USEPA 2010 health guideline of 0.30 mg/kg [16] and China's National Standard for THg concentrations of 0.5 mg/kg ww), which is the acceptable Hg level for fish.

Table 1 compares the THg and MeHg concentrations of different fish species collected from Gaohong, the PRD and Wanshan.

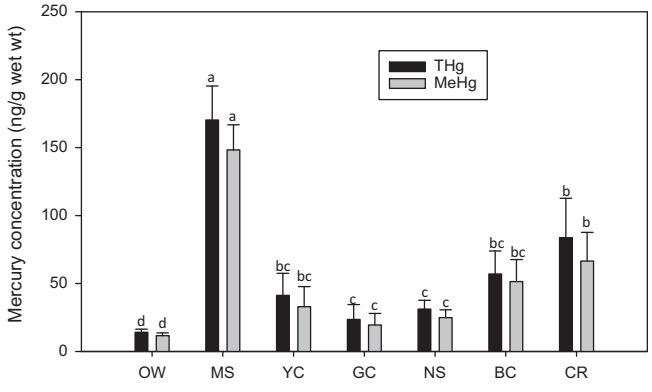

Fig. 6. Mercury concentrations in different fish species. OW, MS, YC, GC, NS, BC, and CR represent oriental weatherfish, mud skipper, yellowhead catfish, grass carp, northern snakehead, bighead carp and crucian carp, respectively. Columns with the same letter are not significantly different ($p < 0.05$) according to the results of one way ANOVA test.

The grass carp collected from Dashuixi in Wanshan and the mud skipper collected from Gaohong market (present study) contained the highest THg and MeHg concentrations, respectively. In general, fish trophic level influences the concentration of Hg, with the highest levels found in fish at the top of the predatory food chain [38]. It is commonly acknowledged that grass carp feed on hydrophytes, therefore, they usually contain lower Hg than other fish species. However, in our study the highest THg in fish was observed in grass carp from Wanshan, which may be explained by the severely Hg contaminated water of the Wanshan Hg mining area (THg: 15–9300 ng/L, MeHg: 0.31–25 ng/L) [39]. The high MeHg noted in the mud skipper from Gaohong market may be attributed to the extensive periods of time they spend in the mud, and thus, resulting in the bioaccumulation of Hg *via* their skin and gills as well as dietary intake of predominantly small fish and insects [40].

3.5. Human health risk assessment

Table 2 shows the EDI of MeHg *via* fish consumption for both adults and children in Zhejiang Province, which indicates that consumption of mud skipper at 32% would result in an EDI exceeding the USEPA RfD (0.1 μg/kg bw/d) for adults. The MeHg EDIs of adults for all other sampled species including: northern snakehead; grass carp; crucian; bighead carp; yellowhead catfish; and oriental weatherfish were lower than the RfD (Table 2). For children, higher MeHg EDIs when compared to RfD were found for 60% of mud skippers but lower than the RfD for six other fish species. However, the MeHg EDI of all the samples did not exceed the ADI set by the JECFA (0.23 μg/kg bw/d) [17] for both adults and children (Table 2). The present results are inconsistent with the findings of our earlier study in that consumption of freshwater fish including bighead carp, northern snakehead and grass carp around the PRD resulted in a higher EDI of Hg than the RfD for adults [34]. These differences were due to the high rate of fish consumption by PRD residents, 93 g/d for adults and 50 g/d for children [34].

The USEPA established the RfD of 0.3 μg/kg bw/d for $HgCl_2$ in 1995 [18]. In the present study, MeHg accounted for less than 1% of THg found in vegetables, which infers that THg is mostly composed of inorganic Hg [41]. However, inorganic Hg can consist of elemental Hg and divalent Hg (Hg^{2+}). With the assumption that all Hg forms in vegetable samples exist as $HgCl_2$, the EDI *via* vegetable consumption for three sampling sites (No. 8: 0.39 μg/kg bw/d, No. 16: 0.40 μg/kg bw/d and No. 18: 0.33 μg/kg bw/d) would be expected to exceed the RfD of $HgCl_2$ (0.3 μg/kg bw/d) for adults and five sampling sites (No. 5: 0.38 μg/kg bw/d, No. 7: 0.35 μg/kg bw/d, No. 8: 0.57 μg/kg bw/d, No. 16: 0.58 μg/kg bw/d and No. 18: 0.47 μg/kg bw/d) for children.

It should be noted that the assessment results may be influenced by other factors such as fish ingestion rates and bioavailability of MeHg in fish to humans. Considering the limitations of *in vivo* studies (expensive, laborious and ethical issues) [42], the *in vitro* method was used instead for this study to estimate the bioaccessibility of MeHg in fish. Table 3 shows the MeHg bioaccessibility of different fish species collected from Gaohong. The total bioaccessibility of MeHg in different fish ranged from 37.5% (yellowhead catfish) to 56.5% (bighead carp). The average gastric and intestinal bioaccessibility of MeHg in fish ranged from 14.2% to 22.2% and 29.4% to 38.2%, respectively. The present data were higher than those observed in Cabanero et al. [43] (gastric: 9–20%; intestinal: 9–17%; fish species: tuna, swordfish, sardine). This may be due to differences in the fish species studied, which might affect the solubility of Hg and/or the release of Hg from each sample during digestion [43]. Table 2 shows the EDI_{bio} of bioaccessible MeHg *via* the consumption of freshwater fish for both adults and children in Zhejiang Province. The results indicate that the consumption of any of the sampled fish species should not result in a MeHg EDI exceeding

Table 1
THg and MeHg levels in different fish species collected from Gaohong, the PRD and Wanshan.

Fish species	THg (ng/g ww)	MeHg (ng/g ww)	Location	Sample size (*n*)
Grass carp	13.1 ± 6.9	8.1 ± 2.6	PRD, market[a]	16
	10.1 ± 5.1	8.6 ± 4.4	PRD, fish pond[b]	33
	61–680	24–98	Wanshan, mining[c]	–
	23.6 ± 10.9	18.6 ± 7.2	Gaohong, market[d]	6
Bighead carp	45.9 ± 4.8	40.4 ± 3.3	PRD, market[a]	16
	44.5 ± 11.0	42.5 ± 12.3	PRD, fish pond[b]	17
	57.0 ± 16.9	50.8 ± 14.8	Gaohong, reservoir[d]	4
Northern snakehead	80.4 ± 19.6	70.4 ± 18.6	PRD, market[a]	15
	25.2 ± 6.8	24.4 ± 7.3	PRD, fish pond[b]	24
	31.2 ± 6.4	25.3 ± 5.8	Gaohong, market[d]	4
Crucian carp	43.5 ± 38.0	34.7 ± 30.1	PRD, market[a]	15
	83.7 ± 29.0	64.9 ± 18.3	Gaohong, reservoir[d]	6

[a] [28].
[b] [32].
[c] [37].
[d] Present study.

Table 2
Estimated daily intake of MeHg or bioaccessible MeHg *via* freshwater fish consumption for adults and children in Zhejiang Province(μg/kg bw/d).

Fish species	Adult	$Adult_{bio}$	Children	$Children_{bio}$
Oriental weatherfish	(2.76E−03–9.36E−03, 6.09E−03)	(1.54E−03–5.24E−03, 3.41E−03)	(4.03E−03–1.37E−02, 8.90E−03)	(2.26E−03–7.66E−03, 4.98E−03)
Mud skipper	(4.34E−02–1.12E−01, 8.34E−02)	(1.95E−02–5.05E−02, 3.75E−02)	(6.35E−02–1.64E−01, 1.22E−01)	(2.86E−02–7.39E−02, 5.48E−02)
Grass carp	(5.74E−03–1.64E−02, 1.04E−02)	(2.99E−03–8.54E−03, 5.39E−03)	(8.39E−03–2.40E−02, 1.52E−02)	(4.36E−03–1.25E−02, 7.88E−03)
Yellowhead catfish	(1.04E−02–2.78E−02, 1.83E−02)	(3.95E−03–1.06E−02, 6.94E−03)	(1.52E−02–4.06E−02, 2.67E−02)	(5.77E−03–1.54E−02, 1.01E−02)
Northern snakehead	(1.20E−02–1.94E−02, 1.34E−02)	(6.60E−03–1.06E−02, 7.34E−03)	(1.75E−02–2.83E−02, 1.95E−02)	(9.65E−03–1.56E−02, 1.08E−02)
Bighead carp	(2.00E−02–3.96E−02, 2.86E−02)	(1.14E−02–2.26E−02, 1.63E−02)	(2.93E−02–5.78E−02, 4.18E−02)	(1.67E−02–3.30E−02, 2.38E−02)
Crucian carp	(2.13E−02–5.08E−02, 3.81E−02)	(1.11E−02–2.64E−02, 1.98E−02)	(3.11E−02–7.43E−02, 5.56E−02)	(1.62E−02–3.86E−02, 2.89E−02)
Reference dose	0.1 μg/kg bw/d			
Acceptable daily intake	0.23 μg/kg bw/d			

Table 3
Bioaccessibility of Hg in different fish species and vegetables.

Fish and vegetable	Stomach (%)	Intestine (%)	Total (%)
Oriental weatherfish (MeHg)	19.30 ± 2.10	36.70 ± 3.20	56
Mud skipper (MeHg)	15.40 ± 1.60	29.50 ± 3.00	44.9
Yellowhead catfish (MeHg)	14.20 ± 1.60	23.30 ± 2.20	37.5
Grass carp (MeHg)	18.30 ± 1.90	33.20 ± 3.10	51.5
Northern snakehead (MeHg)	16.30 ± 1.80	38.20 ± 4.10	54.5
Bighead carp (MeHg)	21.10 ± 2.40	35.40 ± 3.70	56.5
Crucian carp (MeHg)	22.20 ± 2.50	29.40 ± 3.40	51.6
Chinese white cabbage (THg)	29.30 ± 3.10	17.55 ± 2.10	46.85
Xuelihong (THg)	21.20 ± 2.10	13.20 ± 1.40	34.4
Chinese radish (THg)	27.20 ± 1.50	23.30 ± 2.50	50.5
Spinach (THg)	22.30 ± 2.50	21.20 ± 1.30	43.5
Lettuce (THg)	33.10 ± 2.90	21.50 ± 2.40	54.6

the USEPA RfD (0.1 μg/kg bw/d) for both adults and children, when MeHg bioaccessibility was taken into account.

The bioaccessibility of THg in vegetables is shown in Table 3. The total bioaccessibility of THg in different vegetables ranged from 34.4% (xuelihong) to 54.6% (lettuce). While, the gastric bioaccessibility in different vegetables ranged from 21.2% to 33.1%, which was lower than the intestinal bioaccessibility range of 13.2–23.3%. The results of EDI_{bio} indicate that the consumption of vegetables of all sampling sites should not result in EDI_{bio} exceeding the RfD of $HgCl_{2Cha}$ (0.3 μg/kg bw/d) for adults and children, when THg bioaccessibility is considered.

4. Conclusion

Soil and vegetable samples collected from CFL manufacturing sites showed higher Hg concentrations than those of the control sites, and thus indicating that the Hg released from CFL production processes does actually affect the surrounding environment. A significant correlation ($p < 0.05$) was observed between vegetables and corresponding farmland soil. Mud skipper bought from the local market contained the highest Hg amongst all the fish species studied, possibly due to its habit of being in close contact with mud the majority of time. The risk assessment indicates that the consumption of fish should not result in a MeHg EDI exceeding the RfD (0.1 μg/kg bw/d) for both adults and children, when MeHg bioaccessibility is taken into account.

Acknowledgment

The authors are grateful to the Research Grants Council of the University Grants Committee of Hong Kong (Central Allocation, Group Research, no. HKBU 1/07C and Special Equipment Grant, no. HKBU09) and Hong Kong Baptist University (Mini-AoE, Area of Excellence, RC/AOE/08-09/01) for their financial support.

References

[1] M. Jang, S.M. Hong, J.K. Park, Characterization and recovery of mercury from spent fluorescent lamps, Waste Manag. 25 (2005) 5–14.
[2] Y. Li, L. Jin, Environmental release of mercury from broken compact fluorescent lamps, Environ. Eng. Sci. 28 (2011) 1–5.
[3] N.C. Johnson, S. Manchester, L. Sarin, Y. Gao, I. Kulaots, R.H. Hurt, Mercury vapor release from broken compact fluorescent lamps and in situ capture by new nanomaterial sorbents, Environ. Sci. Technol. 42 (2008) 5772–5778.
[4] M.J. Eckelman, P.T. Anastas, J.B. Zimmerman, Spatial assessment of net mercury emissions from the use of fluorescent bulbs, Environ. Sci. Technol. 42 (2008) 8564–8570.
[5] M. Cherian, J. Hursh, T. Clarkson, J. Allen, Radioactive mercury distribution in biological fluids and excretion in human subjects after inhalation of mercury vapor, Arch. Environ. Health 33 (1978) 109–114.
[6] UNEP, Global Mercury Assessment, UNEP Chemicals, Geneva, Switzerland, 2002.
[7] Y.P. Yan, The assessment for heavy metal contamination in economic fish in Chinese offing, Mar. Environ. Sci. 12 (1993) 99–103.

[8] L. Liang, M. Horvat, X. Feng, L. Shang, H. Li, P. Pang, Re-evaluation of distillation and comparison with HNO_3 leaching/solvent extraction for isolation of methylmercury compounds from sediment/soil samples, Appl. Organomet. Chem. 18 (2004) 264–270.
[9] USEPA, Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry, Draft Method 7473, United State Environmental Protection Agency: Washington, DC, 1998.
[10] M.V. Ruby, A. Davis, R. Schoof, S. Eberle, C.M. Sellstone, Estimation of lead and arsenic bioavailability using a physiologically based extraction test, Environ. Sci. Technol. 30 (1996) 422–430.
[11] USEPA, Guidance for assessing chemical contaminant, data for use in fish advisories, United State Environmental Protection Agency, Washington, DC, 2000.
[12] X.L. Wang, T. Sato, B.S. Xing, S. Tao, Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish, Sci. Total Environ. 350 (2005) 28–37.
[13] S. Leung, S. Chan, S. Lui, W. Lee, D. Davies, Growth and nutrition of Hong Kong children aged 0–7 years, J. Paediatr. Child Health 36 (2000) 56–65.
[14] M. Zhang, C.W. Binns, A.H. Lee, Dietary patterns and nutrient intake of adult women in south-east China: a nutrition study in Zhejiang province, Asia Pac. J. Clin. Nutr. 11 (2002) 13–21.
[15] USFDA, CSFII Total diet study 1994–96, 1998: TDS Diets Version 3; CFSAN/Office of Plant and Dairy Foods and Beverages, US Food and Drug Adminstration, Washington, DC, 2003.
[16] USEPA, Guidance for implementing the January 2010 Methylmercury Water Quality Criterion. United State Environmental Protection Agency, Washington, DC, 2010.
[17] JECFA, Summary and conclusions of the sixty-seventh meeting of the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives, JECFA/67/SC, Rome, 5, July 2006.
[18] USEPA, Integrated Risk Information System, United State Environmental Protection Agency, Washington, DC, 1995.
[19] H.D. Yang, Historical mercury contamination in sediments and catchment soils of Diss Mere, UK, Environ. Pollut. 158 (2010) 2504–2510.
[20] N. Zheng, J.S. Liu, Q.C. Wang, Z.Z. Liang, Mercury contamination due to zinc smelting and chlor-alkali production in NE China, Appl. Geochem. 26 (2011) 188–193.
[21] W. Yin, Y. Lu, J.H. Li, C.X. Chen, C. Zhang, F. Dong, Distribution characteristics and pollution assessment of mercury in urban soils of Guangzhou, Chin. J. Soil Sci. 5 (2009) 1185–1188.
[22] Y. Liu, G.T. Kong, Q.Y. Jia, F. Wang, R.S. Xu, F.B. Li, Y. Wang, H.R. Zhou, Effects of soil properties on heavy metal accumulation in flowering Chinese cabbage (*Brassica campestris* L. *ssp. chinensis var. utilis Tsen et Lee*) in Pearl River Delta, China, J. Environ. Sci. Health B 42 (2007) 219–227.
[23] K.E. Lee, H.T. Chon, M.C. Jung, Contamination level and distribution patterns of Hg in soil, sediment, dust and sludge from various anthropogenic sources in Korea, Mineral. Mag. 72 (2008) 445–449.
[24] X.P. Yang, L.Q. Wang, Spatial analysis and hazard assessment of mercury in soil around the coal-fired power plant: a case study from the city of Baoji, China, Environ. Geol. 53 (2008) 1381–1388.
[25] F. Fang, D. Yang, L. Wang, B. Jiang, Distribution of arsenic and mercury in soil around coal-fired power plant in Wuhu, J. Soil Water Conserv. 24 (2010) 109–113.
[26] G.L. Qiu, X.B. Feng, S.F. Wang, L.H. Shang, Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China, Appl. Geochem. 20 (2005) 627–638.
[27] Y. Lin, T. Larssen, R.D. Vogt, X. Feng, Identification of fractions of mercury in water, soil and sediment from a typical Hg mining area in Wanshan, Guizhou province, China, Appl. Geochem. 25 (2010) 60–68.
[28] D.D. Shao, Human Risk Assessment Based on Mercury Contamination in Food and Environmental Matrix at Two Regions in Guangdong and Zhejiang Provinces, PhD thesis, Hong Kong Baptist University, 2011.
[29] H. Zhang, T. Larssen, G.L. Qiu, R.D. Vogt, In inland China rice, rather than fish, is the major pathway for methylmercury exposure, Environ. Health Perspect. 118 (2010) 1183–1188.
[30] X.B. Feng, P. Li, G.L. Qiu, S. Wang, G.H. Li, L.H. Shang, B. Meng, H.M. Jiang, W.Y. Bai, Z.G. Li, X.W. Fu, Environ. Sci. Technol. 42 (2008) 326–332.
[31] G. Qiu, X. Feng, P. Li, S. Wang, G. Li, L. Shang, X. Fu, J. Agric. Food Chem. 56 (2008) 2465–2468.
[32] A.C.P. Heaton, C.L. Rugh, N. Wang, R.B. Meagher, Phytoremediation of mercury- and methylmercury- polluted soils using genetically engineered plants, J. Soil Contam. 7 (1998) 497–510.
[33] D.Y. Wang, S.S. Mou, C.L. Qing, The effect of atmospheric mercury on the accumulation of mercury in soil plant system, Acta Sci. Circumst. 2 (1998) 194–198.
[34] D.D. Shao, P. Liang, Y. Kang, H.S. Wang, Z. Cheng, S.C. Wu, J.B. Shi, S.C.L. Lo, W.X. Wang, M.H. Wong, Mercury species of sediment and fish in freshwater fish ponds around the Pearl River Delta, PR China: human health risk assessment, Chemosphere 83 (2011) 443–448.
[35] Y. Liang, X. Liu, D. Yuan, Z. Gong, Z. Zhang, Mercury species in seawater and sediment of Xiamen western sea area adjacent to a coal-fired power plant, Water Environ. Res. 82 (2010) 335–341.
[36] T.N. Wu, Distribution of methylmercury in a mercury-contaminated ecosystem, Pract. Periodical Hazard. Toxic Radioactive Waste Manag. 10 (2006) 192–197.
[37] M. Roulet, J.R.D. Guimaraes, M. Lucotte, Methylmercury production and accumulation in sediments and soils of an amazonian floodplain – effect of seasonal inundation, Water Air Soil Pollut. 128 (2001) 41–60.
[38] H.Y. Zhou, M.H. Wong, Mercury accumulation in freshwater fish with emphasis on the dietary influence, Water Res. 34 (2000) 4234–4242.
[39] G.L. Qiu, X.B. Feng, S.F. Wang, X.W. Fu, L.H. Shang, Mercury distribution and speciation in water and fish from abandoned Hg mines in Wanshan, Guizhou province, China, Sci. Total Environ. 407 (2009) 5162–5168.
[40] B.E. Al-Behbehani, H.M.A. Ebrahim, Environmental studies on the mudskippers in the intertidal zone of Kuwait bay, Nat. Sci. 8 (2010) 79–89.
[41] WHO, Environmental Health Criteria 118, Inorganic Mercury, World Health Organization, Geneva, 1991.
[42] L.G. Danielsson, A. Zarpen, A.W. Glynn, Aluminum fractionation in simulated rat stomach: an in vitro study, Analyst 120 (1995) 713–720.
[43] A.I. Cabanero, Y. Madrid, C. Camara, Selenium and mercury bioaccessibility in fish samples: an in vitro digestion method, Anal. Chim. Acta 526 (2004) 51–61.