DETERMINATION OF ARSENIC CONTENT IN WASTEWATER-FED FISH POND IN HOANG MAI DISTRICT, HANOI, VIETNAM

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ABSTRACT

Aquaculture in pond fed with wastewater has been practiced since the 1960s in Hoang Mai and Thanh Tri districts in Hanoi, Vietnam. Wastewater after directly discharged into Kim Nguu and To Lich rivers is currently used for cultivation of vegetables and fishes. According to the previous studies, the content of some heavy metals in water and sediments from Kim Nguu and To Lich rivers exceeded the Vietnamese standard values. In this study, arsenic concentration in water, sediment, fish and plant collected from a wastewater fed-fish pond in Hoang Mai district, Ha Noi, Vietnam were determined by graphite furnace atomic absorption spectrometry (GF/AAS). Arsenic concentration in water collected from inlet and outlet sites of the pond were of 45.86 and 23.22 µg/L, respectively and those levels were higher than the Vietnamese standard. About 14% of arsenic entered the fish pond was in the suspended particulate matter (SPM) form. Arsenic concentration in the sediment ranged from 12.26 to 23.87 mg/kg (dry weight). The highest levels of arsenic found in the sediment near the pond outlet were probably caused by the movement of the sediment and heavy metals with the water flow. Based on the Vietnamese standards for agriculture soils, the studied pond sediment is not safe for crop application. Arsenic contents of 0.20 and 0.06 mg/kg (dry weight) were found in tissues of common carp and tilapia. The lower As contents in the outlet water in comparison to the inlet water showed that part of As was removed in the fish pond by different processes including the sedimentation and bio-adsorption. The As contents in the coarse stems/leaves of the water spinach samples were about 2.6 times higher than those in the shoot tips/younger leaves. As the findings, the water spinach and fish in this wastewater–fed fish pond were considered safe for human consumption with respect to arsenic content and Vietnamese standard.

Keywords: arsenic, common carp, tilapia, wastewater fed-fish pond, water spinach.
1. INTRODUCTION

Rapid population growth, urbanization and the looming fresh water crisis have increased the need for wastewater reuse in agriculture and other purposes in many countries [1]. The fact is that being a low-income countries, wastewater has been used for centuries by farmers as a cheap and reliable source of water and nutrients for agriculture and aquaculture [2]. In Ha Noi capital, Vietnam, aquaculture in pond fed with wastewater has been a common practice since the 1960s in Hoang Mai and Thanh Tri district. Wastewater after directly discharged into Kim Nguu and To Lich river is being used for aquatic vegetables and fish cultivating. In the past 13 years, the land area used to produce fish increased from 2,060 ha to 3,350 ha and the associated yield was increased 10-30% [1]. However, using untreated wastewater for food production may pose certain environmental issues and health risks to producers and consumers.

According to the previous studies, the content of some heavy metals in Kim Nguu and To Lich river water and sediments were above the Vietnamese standard [1]. Due to mixing of industrial and domestic wastewater streams, wastewater often contains potentially toxic elements (PTEs). Marcussen et al. [7] found that sediment in the wastewater exposed rivers of Hanoi had high Pb and Sb concentrations and was severely polluted with As, Ba, Cd, Cu, Ni and Zn. Especially the Cd concentrations in Tolich river with a maximum of 427 mg/kg d.w. was of concern to the environment and humans. Marcussen et al. [] also described that liver of tilapia harvested in wastewater-fed fish pond Hanoi had high Cd and Pb concentrations with a mean of 0.366 and 0.31 mg/kg f.w., respectively. The As concentrations were high in skin of tilapia from Hanoi with a mean concentration of 0.15 mg/kg f.w. The tradition of wastewater reuse for aquaculture in general and for fish culture in particular is now under threat of the actual and the potential risk for the environment and the human health. In this study, arsenic concentration in water, sediment, fish and plant collected from a wastewater-fed fish pond in Hoang Mai district, Ha Noi, Vietnam were analyzed to assess the quality and safety of this reused water source.

2. SAMPLING AND ANALYSIS METHODS

2.1. Sampling time and sites

The study site is a wastewater fed-fish pond located in Bang B hamlet, Hoang Liet village, Hoangmai district, Hanoi where high rate of wastewater reuse for irrigation and aquaculture has been reported. The wastewater from the To Lich river being used for aquaculture activities in Bang B commune is a mixture of last four polluted river waters (To Lich, Kim Nguu, Set and Lu rivers). Sampling of pond water and sediment sites include inlet, outlet and in the pond centre.

In dry season, wastewater is pumped from the Tolich river into the fish pond in Bang B hamlet every two days per week lasting 2 hours each time with the capacity of 150m³/hr. The fish pond has a square shape with an area of about 1 ha each, the pond’s depth of 1.2 to 2 m. The most popular fish species grown there are common carp (Cyprinus carpio), grass carp (Ctenopharyngodonidellus), Indian carps (Cirrhinusmrigala) and Nile tilapia (Orechromis niloticus) with the average stock densities of 3 and 2 fishes/m² for tilapia and common/Indian carp, respectively.

The sampling time was during dry season (from September to November) when river water pumping will be more frequency. Sampling of pond water, sediment and water spinach was carried out in two campaigns; and one campaign for fish when they are harvested. The samples...
were collected according to the procedure described in Vietnamese standard TCVN 6663-1:2011/ISO 5667-1:2006.

2.2. Sample preparation and analysis methods

2.2.1. Water samples

Water samples were preserved by addition of 1.5 mL 70 % HNO₃ per 500 mL and stored at 4 - 5 °C for further analysis. Filtered water samples were used for determination of As concentration in dissolved and SPM forms (using 0.45 µm porous filter).

2.2.2. Sediment samples

Sediment samples were mixed thoroughly and dried at 45 °C in an oven until reaching constant weight. The samples then were grinded and sieved through 2mm siever. The sediment samples were put into zip lock bag and kept in the desiccators for analysis.

2.2.3. Fish samples

Fish samples were rinsed with double distilled water and divided in two parts: the eaten (consisting of muscle and skin) and the non-eaten (consisting of the remaining parts such as stomach, bone, intestine, etc.). Both parts of the fish sample were grounded separately till obtaining fine mass then were put into zip lock bags and frozen immediately. The dried fish samples were digested according to the procedure for microwave assisted acids digestion of fish [].

2.2.4. Water spinach samples

Water spinach samples were washed by distilled water. The fresh weight (f.w.) of each plant part was determined. The shoot tips/younger leaves and coarse stems/leaves were blended in a food processor until a fine mass was obtained then were put into zip lock bag and frozen immediately.

2.2.5. Arsenic content analysis

As content in all samples was analyzed by GF/AAS (using AAS Perkin Elmer 5100, HGA-600 graphite furnace, Perkin Elmer, USA). Arsenic was reduced to the As (III) in the form of AsH₃ (arsin ) by reaction with NaBH₄ reagent at the temperature 800 °C. AsH₃ was then transported to the atomic absorption flow throw cell (AAC) and absorbed monochromatic light source lamp by hollow cathode discharge lamps nonpolar at a wavelength of 193.7 nm.

Quality assurance was conducted by including an analytical blank and a certified reference material. Calibration was carried out at each run. LOD was calculated as three times the standard deviation (SD) of a minimum for eight replicates of the calibration (CRM) in every digestion. The CRM recoveries were high (in the range of 93 – 114 %).

3. RESULTS AND DISCUSSION

3.1. Arsenic concentration in pond water
As can be seen in Figure 1, no significant differentiates of As content between two collection campaigns (P > 0.05) was observed. Elevated As levels were encountered in the pond water were ranged from 23.22 to 45.86 µg/L. However, the reduction of As concentration in water outlet was remarkable (around 40-50%). That was probably due to part of As that existed in settable form was removed as sediment. The As concentrations were much higher than those previous reported of Toan (2008) (3.96 to 3.09 µg/L). However, the differentiate of As concentrations collected in inlet and outlet sites found similar. Similar result was also observed by Nejmeddine et al. [1].

![Figure 1. As content in pond water at different sampling sites.](image)

Since the As concentrations in the outlet water were still higher than the Vietnamese standards (QCVN 38/2011/BTNMT) [1], it is recommended that this water sources should not be used for irrigation. The As concentrations in dissolved and SPM forms was compared to assess the risk for fish aquaculture in the pond (Table 1).

**Table 1.** As concentrations in the non-filtered, filtered water and SPM.

<table>
<thead>
<tr>
<th>Sample point</th>
<th>Non-filtered water</th>
<th>Filtered water</th>
<th>SPM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg/L</td>
<td>%</td>
<td>µg/L</td>
</tr>
<tr>
<td>Inlet water (n=3)</td>
<td>44.33</td>
<td>100</td>
<td>38.10</td>
</tr>
<tr>
<td>Outlet water (n=3)</td>
<td>21.33</td>
<td>100</td>
<td>17.65</td>
</tr>
<tr>
<td>Inside pond water (n=15)</td>
<td>30.73</td>
<td>100</td>
<td>26.84</td>
</tr>
<tr>
<td>QCVN 38/2011/BTNMT [12]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The findings showed that As existed most in soluble form (around 86%). This phenomena could be due to many reasons such as the adsorption of As in SPM was depending on pH and the availability of particulate surfaces and total dissolved metal content [1].

### 3.2. Arsenic content in pond sediment

As content in pond sediment samples were found in both sampling campaigns with As content in the range of 12.30-23.77 mg/kg d.w. (Table 2). The high As content near outlet point...
could be explained by the movement of the sediment and heavy metals with the water flow in fish pond.

*Table 2. As contents in sediment samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st sampling campaign</th>
<th>2nd sampling campaign</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sed_{inlet} (n=3)</td>
<td>12.34 ± 0.128</td>
<td>12.26 ± 0.071</td>
<td>12.30 ± 0.057</td>
</tr>
<tr>
<td>Sed_{outlet} (n=3)</td>
<td>23.87 ± 0.045</td>
<td>23.66 ± 0.110</td>
<td>23.77 ± 0.15</td>
</tr>
<tr>
<td>Sed_{pond center} (n=9)</td>
<td>15.81 ± 0.067</td>
<td>16.13 ± 0.086</td>
<td>15.97 ± 0.229</td>
</tr>
</tbody>
</table>

QCVN 03/2015/BTNMT

The As concentrations in pond sediment were lower than those reported in soil in Thailand/Malaysia, the Dutch target/intervention value, however they were much higher than the Thailand soil standard and slightly higher than the Danish soil criteria [7]. The As content in the pond sediment found higher than the pond water which was similar to number of previous studies since most heavy metals in wastewater tend to associate with particular matter and deposit in the pond sediment [7].

The As contents in the pond sediment were also higher than the background and the aquaculture soil value according to Vietnamese standards and slight greater than that in the study of Marcussen [7] which reported about the aquatic soil in Hanoi and the sediment of the Kim Nguu and To Lich rivers. Due to its high total As content, this sediment is considered may cause the risks to crops and should not be applied to agricultural fields.

### 3.3. Arsenic content in fish

As was detected in all analyzed fish samples. The ranges of the As content in the fish samples are showed in Table 3. The mean As concentrations in tissues of tilapia and common carp were 0.17 and 0.20 mg/kg d.w., respectively, while in the non-eaten parts were much lower, around 0.06 and 0.09 mg/kg d.w. The results was consistent to those observed by Abdul Q. S. et al [7], in which the As content in different tissues were varied greatly(ranged from 2.12 to 15.2 mg/kg d.w.). However in the study of A. Takatsu et al. [7], the contrast result was reported, showing lower levels of arsenic content in muscles samples.

The differences of As contents in the eaten part and non-eaten part were probably due to the soft tissue of the eaten part which has higher metal absorption capacity than the non-eaten part which mainly bone and scales.

*Table 3. As contents in fish samples

(n = 9 for each part of each species fish, LOD < 0.0011).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eaten part</th>
<th>Non-eaten part</th>
<th>Average</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d.w</td>
<td>f.w</td>
<td>d.w</td>
<td>d.w</td>
</tr>
<tr>
<td>Tilapia</td>
<td>0.17±0.008</td>
<td>0.046±0.002</td>
<td>0.06 ± 0.013</td>
<td>0.023±0.005</td>
</tr>
<tr>
<td>Common carp</td>
<td>0.20±0.018</td>
<td>0.054±0.005</td>
<td>0.09 ± 0.021</td>
<td>0.033±0.007</td>
</tr>
</tbody>
</table>
| Vietnamese threshold limits [7] 2 mg/kg d.w.
Through the As content was lower than Vietnamese threshold limit (see Table 3), long term exposure to the contaminated fish is still considered posing health risk to the consumers. It is clear that contaminants in fish pond can be bioaccumulated in fish and may be a significant intake source to dietary exposure to these compounds [1].

3.4. Arsenic content in water spinach

As can be seen in Figure 2, no difference in the As contents between the two sampling campaigns for both shoot tips/younger leaves and coarse stems/leaves of water spinach (P > 0.05). This insignificant difference could be explained by both the sampling times were in dry season so they were grown in the similar weather conditions including As content loading to the pond. However, significant differences in the As contents were attained in the shoot tips/younger leaves and coarse stems/leaves of the water spinach (P < 0.05). The contents of As in the coarse stems/leaves were about 3.71 times higher than that in the tips/younger leaves (P<0.05). The obtained results showed the tendency to accumulate of As in the stem and root of water spinach which could be due to the long exposure time of the roots with the contaminated pond water and the plant uptake mechanism [2]. The As content in the coarse stems/leaves (3.64 mg/kg d.w.) was higher than the Vietnamese threshold limits (1mg/kg d.w.). Therefore, additional risk probably may occur since these parts are often used for animal fodder.

![Graph showing As contents in water spinach samples.](image)

Figure 4. As contents in water spinach samples.

5. CONCLUSIONS

The total As concentration in the water samples ranged from 23.22 to 45.86 µg/L. The highest levels were found in the inlet water and the lowest were in the outlet water. About 14% of As entered the fish pond in the SPM form. The lower As contents in the outlet sampling point may result from some natural removal processes such as sedimentation and adsorption in the fish pond.

The ranges of As contents in the pond sediment samples were 12.26-23.87 mg/kg d.w.. The highest contents of As were found near the pond outlet probably caused by the movement of the sediment containing As with the water flow. Based on the Vietnamese standards for agriculture soils (QCVN 03/2015/BTNMT, As ≤15 mg/kg d.w. soil), this pond sediment is not safe for crop application with respect of As content.
Concerning to the risks for human, the As contents in the eaten parts of both fish and water spinach samples were found below the Vietnamese threshold limits. Therefore, it is supposed still safe for the consumers. However, the bioaccumulation through the food chain and long term exposure should be considered in further studies. In addition, the factors that affect on the As fate and transport in the fish pond such as dissolved organic and inorganic ligands, physical or chemical adsorption, precipitation and co-precipitation reactions or ingestion by plankton organisms, etc. should be studied.

REFERENCES


