行政院國家科學委員會補助專題研究計畫 □成果報告 ■期中進度報告

富含砷之沖積含水層的地質微生物與化學特性及其健康效應-(子計畫一)沖積含水層及泥火山地區之砷移動性及其與細菌及腐質物質之相互作用(1/3)
The biogeochemical and hydrogeological processes on the mobility of arsenic in the alluvial aquifers and mud volcano area

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執行單位：成功大學地球科學系
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Abstract

Major ion and trace element analyses were performed on groundwater samples collected in Chia-Nan plain, Ilan plain (Lanyang Plain), aquifers from India and Bangladesh to examine As mobilization in aquifers. The high concentrations of As, Fe and Mn in the groundwater is consistent with low Eh values (under moderately reduced state). The observed Na/Cl and SO₄/Cl molar ratios in groundwater demonstrate the influence of seawater intrusion. Seawater intrusion could provide required electron acceptors (i.e., SO₄) for bacterial sulfate reduction and promote reducing conditions that are favourable for As mobilization. Mud volcano fluids were also collected and analyzed to assess the possible source of As in the Chia-Nan plain groundwater. These high-As sediment samples are inferred to be the sinks where arsenic was precipitated from groundwater. Once environmental conditions, such as pH and Eh, change, these arsenic sinks may release arsenic into groundwater. The composition of major ion in fluid shows the dominance of Na and Cl contents.

Key word: Chia-Nan plain, Ilan plain, As, Eh, electron acceptors, mud volcano

Introduction

Natural contamination of groundwater by arsenic (As) has become a crucial water quality problem in many parts of the world, including economically developed countries like the USA, countries of the European Union and most importantly Taiwan for its unique blackfoot disease.
The prolonged consumption of groundwater with high As content emerged lately to be a serious global public health issue, leading to unprecedented environmental problems especially in parts of south and east Asia. Skin, lung, liver and prostate cancers as well as blackfoot disease (only in SW Taiwan) are common among the population to mention only a few of the most severe consequences of As poisoning. In order to mitigate the problem and to assure a sustainable groundwater supply, a thorough understanding of the biogeochemical process that lead to the occurrence of high As concentrations as well as toxicological effects is urgently required.

In Taiwan (NW and SE), India and Bangladesh, the stratigraphic variation of As concentration is heterogeneous, including varied distribution of As (total), As(III)/As(V) and Fe(II)/Fe(III) ratio. Following intensive field and laboratory research, the arsenic release mechanism is still remains a debate. Recent findings in Bangladesh revealed that arsenic was believed to be released up-gradient and transported to the aquifer at well depth, where arsenic can be found at highest level. It was observed higher amount of iron (hydr)oxides in oxidized upper sediments as well as in orange Pleistocene sediments, however iron (hydr)oxides do not appear widespread in the gray Holocene aquifer at depths of the highest As concentrations.

The Chia-Nan plain in SW Taiwan is well known for its high concentrations of arsenic and humic substances in groundwater, which are considered as a possible agent for the endemic blackfoot disease. Thus it is required to study the relationship between As concentration and depositional environments. This could be useful to understand the source of such contaminants in groundwater. Studies of the mud volcano areas in SW Taiwan found that mud samples including mud fluids contains considerable amount of arsenic and was hypothesized to be one of the primary source of arsenic. The weathering of slate from Central Mountain Range is also believed to be another source of As in these aquifers. Therefore, it is urgently required to study in detail about the relationship between mud volcano and As in Chia-Nan plain.

Objectives

Tracing the sources and understanding the mobilization mechanism of arsenic in groundwater from different alluvial aquifers (e.g., Chia-Nan plain, Ilan plain, India and Bangladesh) is one of the major objectives of this integrated project. To achieve this goal, we have collected and analyzed groundwater and cored sediment samples for concentrations of arsenic as well as other trace elements and major ions. The purpose is to evaluate whether these
Sediments can be the sources of groundwater arsenic.

**Sampling and analytical technique**

**Sampling of groundwater, fluids and sediments**

Groundwater samples were collected from different parts of the Chia-Nan plain, Ilan plain as well as arsenic-effected areas from India and Bangladesh; their major ions, trace element compositions were analyzed and compared. Electrical conductivity (EC), pH, Eh, temperature, total dissolve solids (TDS), salinity, alkalinity, dissolve oxygen (DO) was measured at the field sites. All these measurements were done in such a way to exclude contact with the atmosphere. Water samples were filtered on-site using 0.45 μm cellulose nitrate filters (Sartorius AG, Germany) and were preserved with 0.5 ml of 0.01 M HNO₃ of “suprapur” quality (Merck, Germany). Pre-cleaned (washed with HNO₃ followed by Milli-Q water) polypropylene bottles were used for the collection of water samples.

Fluid samples were also collected from the mud volcanoes (Yen-Shui-Keng and Kuan-Zih-Ling) located in the groundwater recharge areas east of the Chia-Nan plain. About 100 mL fluid samples were collected to measure different chemical parameters. After collection, the samples were shipped to the laboratory in an ice-box and analyzed for major ions and trace element concentrations. Eh and pH values of the fluid samples were measured in the field. The collected fluid samples represent the connate water originated from the deep earth crust, and could be one of the potential sources for As in the Chia-Nan plain.

Sediment samples were collected from two cores, which were both drilled from Budai and Jinghu at the western Chia-Nan plain where high arsenic concentrations of 0.35 ppm has been reported from groundwater. Both the Budai and Jinghu cores reached a depth of 250 m. Instead of sampling every fixed interval, samples were collected wherever lithological and grain size changes were identified. Fifty samples were collected from each core. To determine the largest amounts of arsenic that can be leached from these sediment samples, strong HF (24N), HNO₃ (7N), and HCl (6N) were used to leach these samples. Abundances of trace elements, including As, in leacheats were determined by ICP-MS. Several samples were analyzed with XRD to characterize constituent minerals. One high-As sample was separated into coarse-, medium-, and fine-grain aliquots. Each aliquot was analyzed with ICP-MS and XRD to very the host phases of arsenic in this samples.
Analytical techniques

Anion and cation concentrations of mud volcano fluids and groundwater from the Chia-Nan plain aquifers were analyzed using a Dionex DX 120 Ion Chromatograph (Dionex, CA, USA). Trace elements were measured with ICP-MS (Agilent 7500cs) using external calibration with certified multi-element standards. Accuracy was checked in each analytical batch by measuring the certified reference material ‘Trace Metal in Drinking Water’ (TMDW; Lot # 623609) from High Purity Standards (HPS, USA), and was found to be within ± 10% of the certified values. To correct instrumental drift and non-spectral effects, Bi and In were used as internal standards. Precision was evaluated by the standard deviation of three individual runs, and was typically better than 2%.

Summary of the results

Chemical characteristics of the Chia-Nan and Ilan plain groundwater, Taiwan

The distribution of trace metal in Chia-Nan plain, Ilan plain and Bangladesh is clearly distinct from the Figure 1. From this figure it clearly shows As and Fe is comparatively higher in Chia-Nan plain than the other parts of the study area. Mn is high in groundwater of Ilan plain it shows the reducing environment. Groundwater samples taken from water wells of Ilan plain contains as much sulfate as 0-3 mg/l, chloride 2-48 mg/l and nitrite 0.83-58 mg/l. Calcium, Na, Mg, K and NH₄ in groundwater samples ranges from 9.4 to 88, 26 to 441, 3.7 to 18, 1.0 to 40 and 0 to 14 mg/l, respectively. The chemical properties of Ilan plain are similar to Bangladesh water samples.
Chemical characteristics of the Bangladesh groundwater

The pH values of the groundwater ranging from 6.61 to 8.58 (mean: 7.59). Bangladesh groundwater contains high sulfate (range: 0-86 mg/l) and chloride (range: 4-136 mg/l), while low in nitrate (range: 0-8.3 mg/l) and nitrite (range: 1.5-9.6 mg/l). Most of the cases, the groundwater have been reduced, where nitrate gets reduced to nitrite. Calcium, Na, Mg, K and NH$_4$ in groundwater samples of Bangladesh ranges from 14 to 76, 12 to 80, 12 to 41, 3 to 41 and 0 to 18 mg/l, respectively. The concentration of As in water samples from Bangladesh is 1.5 to 141 µg/l (Table 1).
Table 1: Trace element concentrations in groundwater of Bangladesh

<table>
<thead>
<tr>
<th>Station No.</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Sr</th>
<th>Mo</th>
<th>Ba</th>
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<td>STN1</td>
<td>289.2</td>
<td>171</td>
<td>106.2</td>
<td>0</td>
<td>1.942</td>
<td>9.633</td>
<td>342.5</td>
<td>0</td>
<td>58.7</td>
</tr>
<tr>
<td>STN2</td>
<td>186.8</td>
<td>162.7</td>
<td>0.6784</td>
<td>0</td>
<td>17.91</td>
<td>8</td>
<td>345.4</td>
<td>0</td>
<td>87.75</td>
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<tr>
<td>STN3</td>
<td>0</td>
<td>130.5</td>
<td>0.4593</td>
<td>0</td>
<td>0</td>
<td>18.56</td>
<td>337.3</td>
<td>0</td>
<td>51.5</td>
</tr>
<tr>
<td>STN4</td>
<td>175.6</td>
<td>194.6</td>
<td>13.62</td>
<td>0</td>
<td>0</td>
<td>20.55</td>
<td>342.5</td>
<td>0</td>
<td>73.66</td>
</tr>
<tr>
<td>STN5</td>
<td>0</td>
<td>109.9</td>
<td>6.251</td>
<td>0</td>
<td>0</td>
<td>16.34</td>
<td>207.4</td>
<td>0</td>
<td>66.22</td>
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<tr>
<td>STN6</td>
<td>0</td>
<td>204.5</td>
<td>0</td>
<td>6.397</td>
<td>0</td>
<td>0</td>
<td>378.8</td>
<td>0</td>
<td>158.6</td>
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<td>STN7</td>
<td>8.625</td>
<td>169.3</td>
<td>0.9122</td>
<td>0</td>
<td>0</td>
<td>22.55</td>
<td>385.6</td>
<td>1.38</td>
<td>32.77</td>
</tr>
<tr>
<td>STN8</td>
<td>379.3</td>
<td>201</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>140.8</td>
<td>430.8</td>
<td>0</td>
<td>68.27</td>
</tr>
<tr>
<td>STN9</td>
<td>65.06</td>
<td>142.1</td>
<td>0</td>
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<td>0</td>
<td>17.61</td>
<td>254</td>
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<td>456.5</td>
<td>140.5</td>
<td>13.85</td>
<td>0</td>
<td>0.9666</td>
<td>85.43</td>
<td>217.5</td>
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<td>STN11</td>
<td>462.8</td>
<td>182.8</td>
<td>0</td>
<td>0.8223</td>
<td>12.39</td>
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<td>STN12</td>
<td>4.148</td>
<td>161.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>41.13</td>
<td>392.7</td>
<td>0</td>
<td>44.38</td>
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<tr>
<td>STN13</td>
<td>182.6</td>
<td>123.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>72.08</td>
<td>291.4</td>
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<td>34.19</td>
<td>129.6</td>
<td>0</td>
<td>0</td>
<td>0.5899</td>
<td>26.04</td>
<td>362.2</td>
<td>0</td>
<td>33.25</td>
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<tr>
<td>STN15</td>
<td>69.23</td>
<td>132.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>29.6</td>
<td>353.3</td>
<td>0</td>
<td>58.02</td>
</tr>
<tr>
<td>STN16</td>
<td>0</td>
<td>128.1</td>
<td>1.31</td>
<td>2.972</td>
<td>0.382</td>
<td>0</td>
<td>469</td>
<td>0</td>
<td>73.62</td>
</tr>
<tr>
<td>STN17</td>
<td>0</td>
<td>145.9</td>
<td>0</td>
<td>0</td>
<td>1.867</td>
<td>1.454</td>
<td>464.7</td>
<td>0</td>
<td>103.4</td>
</tr>
<tr>
<td>STN18</td>
<td>8.788</td>
<td>185.7</td>
<td>0</td>
<td>0</td>
<td>2.7</td>
<td>0</td>
<td>388.2</td>
<td>0</td>
<td>58.33</td>
</tr>
<tr>
<td>STN19</td>
<td>214.1</td>
<td>163.3</td>
<td>0</td>
<td>0</td>
<td>1.043</td>
<td>14.81</td>
<td>405.3</td>
<td>0</td>
<td>75.21</td>
</tr>
<tr>
<td>STN20</td>
<td>0</td>
<td>136.5</td>
<td>0</td>
<td>1.874</td>
<td>0</td>
<td>68.52</td>
<td>350.4</td>
<td>0.4245</td>
<td>40.65</td>
</tr>
</tbody>
</table>

Chemical characteristics of the Indian groundwater

The chemical characteristics of the analyzed groundwaters are summarized in Table 2. The characteristic chemical features of the anoxic groundwaters (mean Eh: -124 mV) include high values of electrical conductivity (mean: 670 µS/cm), alkalinity (mean: 409 mg/L), Ca (mean: 101 mg/L), Mg (mean: 24 mg/L), Cl (mean: 30 mg/L), and with low values of SO₄ (mean: 2.05 mg/L), NO₃ (mean: 21 mg/L), while the pH is slightly acidic to slightly alkaline (mean: 6.38). The As concentration with a mean of 116 ± 74 µg/L, greatly exceeding both the WHO (10 µg/L) and Indian (50 µg/L) guideline values for drinking water. The Fe concentrations (mean: 4.74 mg/L) also exceed drinking water guideline values. The concentration of Mn is typically lower
with means of 0.37 mg/L. The data shows that the reduced arsenic species (As-III) is dominant in this groundwater. The observed chemical characteristics favour the mobilization of arsenic through Fe-(oxy)hydroxide reduction.

Table 2. Chemical characteristics of the Indian groundwater.

<table>
<thead>
<tr>
<th></th>
<th>Chakdaha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>4.6</td>
</tr>
<tr>
<td>Eh (mV)</td>
<td>-154</td>
</tr>
<tr>
<td>HCO₃ (mg/L)</td>
<td>160</td>
</tr>
<tr>
<td>pH</td>
<td>6.0</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>242</td>
</tr>
<tr>
<td>Cl (mg/L)</td>
<td>6.0</td>
</tr>
<tr>
<td>NO₃ (mg/L)</td>
<td>0.1</td>
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<tr>
<td>SO₄ (mg/L)</td>
<td>bd</td>
</tr>
<tr>
<td>PO₄ (mg/L)</td>
<td>0.03</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>6.9</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>1.8</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>12</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>78</td>
</tr>
<tr>
<td>As (µg/L)</td>
<td>0.93</td>
</tr>
<tr>
<td>As(III) (µg/L)</td>
<td>0.26</td>
</tr>
<tr>
<td>As(V) (µg/L)</td>
<td>0.67</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Arsenic concentration in Budai sediments and its significance

All samples from the Budai core have been process ICP-MS analysis. All but 6 samples contain less than 15 ppm (mostly less than 10 ppm) strong-acid soluble arsenic (Fig. 2). This arsenic concentration range is lower than that of 20–30 ppm for sediments from Bangladesh and West Bengal, regions severely polluted by arsenic (e.g., Nickson et al. 2000). This implies that most of these sediments were either unaffected by high-As groundwater or not the sources of groundwater arsenic. Six of the 46 analyzed samples contain > 20 ppm arsenic. They were collected from the depths of 57.5, 66.1, 66.6, 93.8, 119.2, and 189.8 meter, corresponding to arsenic concentrations of 23, 48, 94, 274, 84, and 2033 ppm, respectively. These high-As sediment samples are inferred to be the sinks where arsenic was precipitated from groundwater. In the short depth interval of 55 to 67 meters, there are low-As samples intercalated with high-As samples, implying the changes in pH and/or Eh conditions that led to periodic As precipitation (or adsorption). Alternatively, such a scenario might reflect episodic groundwater supply to the sediments.

![Graph of arsenic concentration vs. depth](image)

Fig. 2. Arsenic concentration as a function of depth of the sediment core from BooDie in the western Chia-Nan Plain, Taiwan. Note that the vertical axis is in log scale. The horizontal dashed line indicates arsenic concentration of 20 ppm.
Mineral phases hosting arsenic

Most significant is the ultra-high arsenic concentration of 2033 ppm from samples collected at the depth of 189.8 meter. This sample was segregated into coarse (sandy; ~50 vol%), medium (silt and clay; ~47 vol%), and fine (clay; ~3 vol%) grain sizes for arsenic concentration determination and XRD analysis. The coarse-grain aliquot is mainly composed of quartz and has arsenic concentrations < 10 ppm, similar to most of the “normal” sediments. The medium- and fine-grain aliquots contain sub-equal amount of quartz and clay minerals with high arsenic concentration of ~2000 ppm. Based on mass balance calculation, these results confirm the high arsenic concentration of ~2000 ppm from bulk samples and further verify the accuracy of our ICP-MS analysis. Since quartz is unlikely the arsenic host, it can be inferred that most of the arsenic resides in clay minerals. XRD patterns showed that chlorite and illite are the constituent clay minerals (Fig. 3). Several documents have concluded that mica can contain high arsenic abundances (Dowling et al., 2002). Owing to the similarity in crystal structure between mica and illite, we suggest that illite is the major host of arsenic in the analyzed sediment samples. Other studies also documented that iron oxy-hydroxides is a strong absorber of arsenic (Nickson et al., 1998, 2000; McArthur et al., 2001; Dowling et al., 2002). However, our results show that iron oxy-hydroxides play no role in controlling the As abundance in this ultrahigh As sediment sample.

![XRD pattern](image)

**Fig. 3.** XRD pattern of the medium-grained aliquot of sample from the depth of 189.9. The sample contains high
arsenic concentration of 2033 ppm, two orders higher than that in Bangladesh and West Bengal sediments. Chlorite and illite are the major clay minerals with sub-equal amount of quartz.

Relationship between abundances of arsenic and other trace elements

In addition to that of arsenic, abundances of 25 other trace elements were also determined by ICP-MS. In general, there is no obvious correlation between the abundances of arsenic and other trace elements. However, some high-As samples have high U and Rb abundances. Since U and Rb are relatively mobile elements, it is inferred that As, Rb, and U were transported by water together and the high-As sediment samples can be considered as sinks of arsenic. Once environmental conditions, such as pH and Eh, change, these arsenic sinks may release arsenic into groundwater (Smedley et al., 2002).

Characterization of mud volcano fluid geochemistry

The chemical characteristics of the mud volcano fluids are shown in Table 3. The pH values (range: 6.8 to 8.2) demonstrate that the fluids are generally neutral to slightly alkaline, while negative Eh values (range: -36 to -77 mV) demonstrate reducing nature of the fluids. The concentrations of Na and Cl are generally high when compared with the Chia-Nan plain groundwater. However, the values are low when compared with standard seawater (Drever, 1997). The mud volcano fluids have Na/Cl molar ratios generally higher than seawater (0.86), but their SO₄/Cl molar ratios are lower than that of seawater (0.05), with some exceptions. The depletion of sulfate indicates that active bacterial sulfate reduction occurs in the mud volcano; this interpretation is in accordance with reducing nature of the fluids.
Table 3. Chemical characteristics of the mud volcano fluids.

<table>
<thead>
<tr>
<th>Mud volcano</th>
<th>Eh (mV)</th>
<th>pH</th>
<th>Na (mg/L)</th>
<th>K (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Cl (mg/L)</th>
<th>NO₃ (mg/L)</th>
<th>NO₂ (mg/L)</th>
<th>SO₄ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yen-Shui-Keng-01</td>
<td>-48</td>
<td>7.6</td>
<td>4,916</td>
<td>45</td>
<td>186</td>
<td>17</td>
<td>5,393</td>
<td>38</td>
<td>17</td>
<td>19</td>
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<td>Yen-Shui-Keng-02</td>
<td>-77</td>
<td>8.2</td>
<td>4,250</td>
<td>47</td>
<td>195</td>
<td>15</td>
<td>5,231</td>
<td>41</td>
<td>15</td>
<td>15</td>
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<tr>
<td>Kuan-Zih-Ling-01</td>
<td>-36</td>
<td>6.8</td>
<td>3,033</td>
<td>70</td>
<td>22</td>
<td>8.0</td>
<td>1,296</td>
<td>2.0</td>
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<td>19</td>
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<td>7.3</td>
<td>2,912</td>
<td>81</td>
<td>11</td>
<td>5.0</td>
<td>1,141</td>
<td>2.0</td>
<td>11</td>
<td>91</td>
</tr>
<tr>
<td>Kuan-Zih-Ling-03</td>
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<td>NA</td>
<td>82</td>
<td>4.4</td>
<td>113</td>
<td>13</td>
<td>372</td>
<td>0.53</td>
<td>11</td>
<td>28</td>
</tr>
</tbody>
</table>

Conclusion

Well water samples from the arsenicosis-affected areas (Chia-Nan plain, Ilan plain, India and Bangladesh) show common phenomena with respect to their physical and chemical properties. However, well water in the area is unsuitable for drinking in view of its high contents of As and other trace metals. High amount of arsenic and other trace elements were observed in the sediments collected from Chia-Nan plain. The chemical composition of mud volcano fluids and groundwater demonstrated the influence of seawater salinization. This may influence in arsenic mobilization process.

References


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