

CHAPTER III

MATERIALS AND METHODOLOGY

3.1 Field investigation

3.1.1 Water sample collection

The water samples were collected from 16 public shallow groundwater wells in the study area as shown in Figure 3.1. The collection was divided into two seasons, dry season during April 30, 2013 – May 3, 2013 and rainy season during August 29 – 30, 2013.

Before collecting the water samples, the water had been pumped out for 15 minutes through a flow-through cell (Figure 3.3). The water temperature, pH, electrical conductivity (EC) and Redox potential (Eh) were continuously monitored during the purging. Then, these parameters were stable; the water samples were collected and stored in plastic bottles. Moreover, all samples were percolated immediately via the filter no.47 mm (Figure 3.4) before preserving and taking back to the laboratory. The conservation of chemical parameters of water sample is shown in Table 3.1.



Table 3.1 Conservation of chemical parameters of water samples

Parameter	Conservation	Maximum holding time and Method
pH, Temp, EC, O ₂ , ORP	Field measurement in a flow cell	
Cation: <ul style="list-style-type: none"> • Calcium (Ca²⁺) • Magnesium (Mg²⁺) • Potassium (K⁺) • Sodium (Na⁺) 	Acidify with nitric acid to pH < 2	< 6 months; 7 days without acidifying sample.
Anions: <ul style="list-style-type: none"> • Bicarbonate (HCO₃⁻) • Carbonate (CO₃²⁻) • Chloride (Cl⁻) • Sulfate (SO₄²⁻) 	Cool to 4 °C	28 days. For HCO ₃ ⁻ and CO ₃ ²⁻ , recommend 24 hours, but 14 days acceptable.
Metals: <ul style="list-style-type: none"> • Arsenic (As) • Aluminum (Al) • Cadmium (Cd) • Iron (Fe) • Lead (Pb) • Manganese (Mn) • Zinc (Zn) 	Acidify with nitric acid to pH < 2	< 6 months
Other: <ul style="list-style-type: none"> • Total hardness • Phosphorus(total) • Nitrogen 	Acidify with nitric acid to pH < 2 Acidify with H ₂ SO ₄ to pH < 2 Acidify with H ₂ SO ₄ to pH < 2	< 6 months 28 days. 28 days.



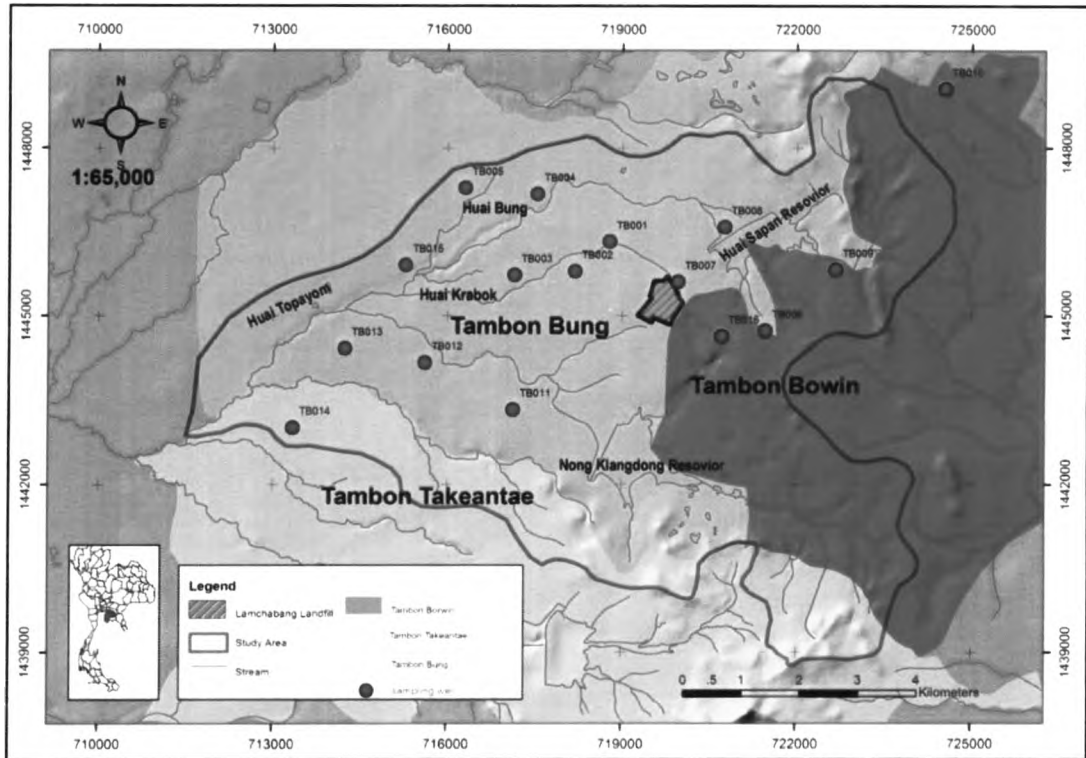


Figure 3.1 Map showing location of the study area and water sampling stations

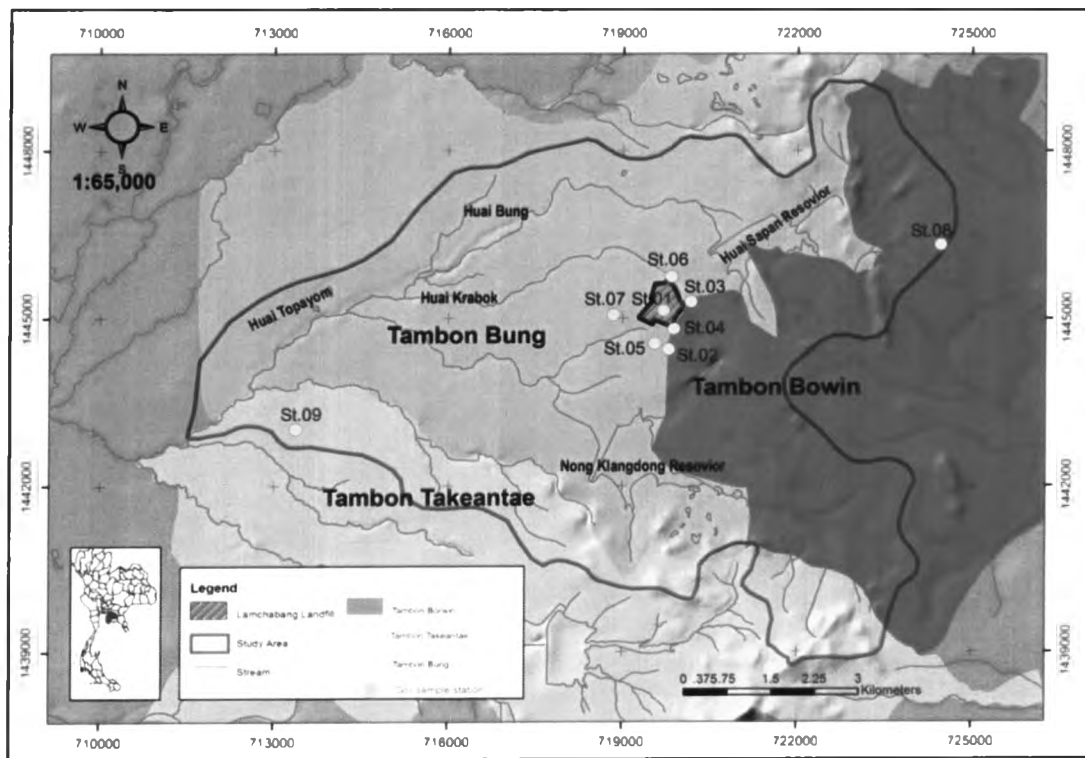


Figure 3.2 Map showing location of the study area and soil sampling stations



Figure 3.3 A flow-through cell



Figure 3.4 Field filtering of water samples

3.1.2 Soil sample collection

Soil samples were collected from a depth between 0 and 200 cm below the ground surface from Laem Chabang sanitary landfill, Changwat Chonburi where located between latitudes $13^{\circ} 0' N$ to $13^{\circ} 6' N$ and longitudes $100^{\circ} 96' E$ to $101^{\circ} 07' E$ as shown in Figure 3.2 and Soil samples were packed and transported back to the laboratory as Figure 3.5.

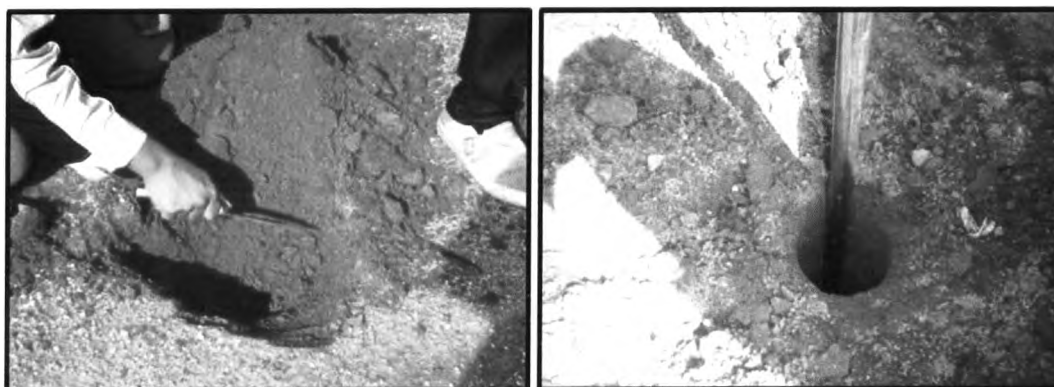


Figure 3.5 Soil samples collection



3.2 Laboratory analysis

3.2.1 Chemical properties of shallow groundwater

The water samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), arsenic (As), cadmium (Cd), iron (Fe), lead (Pb), manganese (Mn) and zinc (Zn) by using the Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS) at the Bureau Environmental Health.

Sulfate (SO_4^{2-}) and Chloride (Cl^-) were analyzed by using Turbidimetric Method 4500- SO_4^{2-} E and Potentionmetric Method 4500- Cl^- D, respectively, at The Environmental Research Institute Chulalongkorn University.

Bicarbonate (HCO_3^-) and Carbonate (CO_3^{2-}) were done at geochemical laboratory of Geology Department, Faculty of Science, Chulalongkorn University by using Indicator Method.

3.2.2 Physical and chemical properties of soil

The soil texture was characterized by using sieve analysis as show in Figure 3.6. The soil samples were air dried, crushed and sieve by mechanical shaker on a column of six sieves: 5, 10, 35, 60, 120 and 200 mm. The chemical compositions of soil samples determined by using X-ray fluorescence spectrophotometer and the mineralogical composition of the raw material components determined by using X-ray diffraction spectrophotometer for both qualitative and quantitative analysis. The sample analyses are conducted at geochemical laboratory of Geology Department, Faculty of Science, Chulalongkorn University.

The chemical properties of soil such as pH, cation exchange capacity (CEC), electrical conductivity (EC), organic matter content (OM), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), iron (Fe) and manganese (Mn) were analyzed at Agriculture Production Science Research and Development Office.





Figure 3.6 A mechanical shaker used for sieve analysis

3.2.3 Point of zero charge (PZC)

Point of zero charge (PZC) was determined in this study according to Van Raij and Peech (1972). The samples of 2 g of soil were placed in a 20 ml solution of NaCl (at concentrations of 1.0, 0.1, 0.01 and 0.001 M) and then agitated for 1 h. At 2-min intervals, 2 ml of 0.001-M NaOH was added to half the samples and 2 ml of 0.001-M HCl was added to the rest of the samples with the pH being measured after each addition (Jorge, 2003).



3.3 Column experiment and modeling

3.3.1 Column experiment

All samples were dried, crushed and sieved through mesh No.10. Firstly, the solution for tracer was prepared by diluting 1.0 M of NaBr to 0.12 M of NaBr and adjusted the volume to 1,000 ml in volumetric flask. The secondly, background solution was prepared by dissolving 0.336 g of NaHCO₃ in distilled water and adjusted the volume to 1,000 ml in volumetric flask. The last solution, sodium arsenate dibasic heptahydrate (HAsNa₂O₄.7H₂O) was used as the source of As⁵⁺. Stock solutions were prepared by dissolving 0.01 g of sodium arsenate dibasic heptahydrate in background solution and adjusted the volume to 1000 ml.

The columns were made from acrylic tubing, which were a length of 10.00 cm and an inner diameter of 2.50 cm. A wet packing technique was used for packing the soil into the columns with an approximate effective porosity and bulk density of 0.44 and 1.35 g/cm³. The flow rate of the influent was maintained approximately 9.5 ml/hr using a piston pump and collected the effluent by using the fraction collector. The schematic of saturated packed soil columns and columns set up as shown in Figure 3.7 and Figure 3.8.

The soil column was first saturated by flushing at least six pore volumes (PVs) of distilled water. After the saturation procedure, 30 mg/L of bromide solution was injected and then the test was carried out, until the bromide breakthrough curves were fitted by hydrous 1-D program.

After the tracer was tested, the column was rinsed by flushing 3 pore volumes (PVs) of distilled water and least 3 pore volumes of NaHCO₃ with fixed pH value of 5.5 - 6.0 to establish chemical conditions of arsenic transportation.

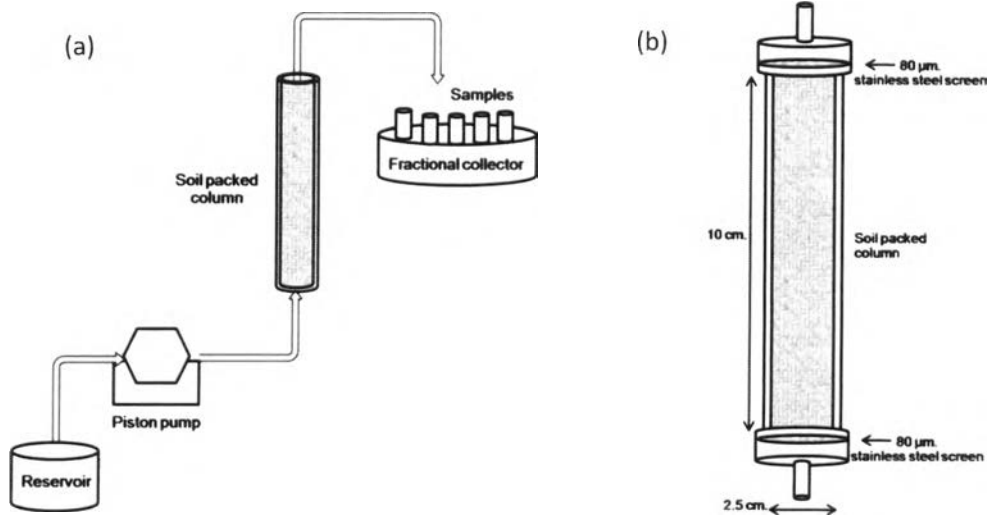


Figure 3.7 (a) A schematic diagram of the column flow apparatuses for conducting saturated soil experiment and (b) packed soil column apparatus

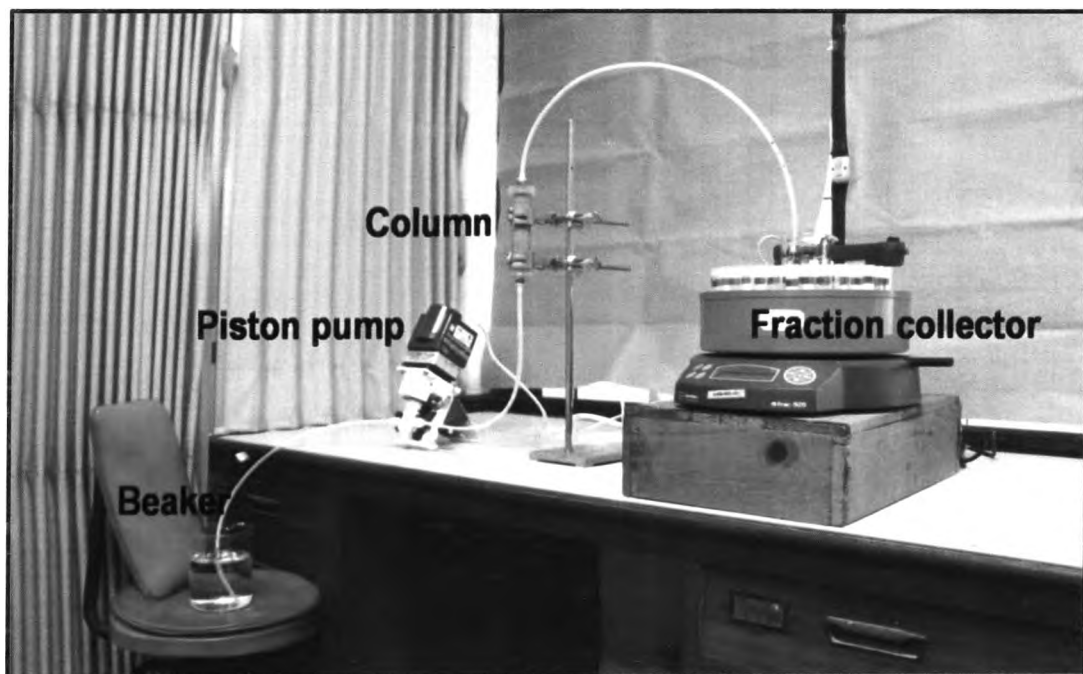


Figure 3.8 Experimental setup

3.4 Groundwater flow and arsenic transports modeling

3.4.1 Boundary setting

For boundary setting, the y coordinates are 1438640 – 1449447 N from south to north, and x coordinates are 711455 – 724875 E from west to east. The total area is about 74.97 square kilometers. The layers were 100 rows and 100 columns. The numbers of grid cells were 20,000 cells.

Furthermore, one of the most important steps in defining a model is to define the layer elevations. The layer elevations include a top elevation, a bottom elevation and starting head. Each condition was specified as below:

- The top layer grid cells were used the data from DEM (Digital Elevation Model). Dem and topography in the study area were used by the GIS program for calculating.
- Each of bottom layer grid cells were estimated from lithological well-log and conceptual model information. The bottom condition in the study area based on geologic setting which has the depth of the layer varied from 0 to 50 meters.
- The starting head were used the data from the water level which collected in the field work and elevation in the study area.

3.4.2 Parameter input

1. Recharge Rate

It was estimated from the average annual rainfall, land use and topography. The 30-year average of rainfall was calculated during 1961-1990 of Changwat Chonburi is as 1,314 mm/y.



Table 3.3 The percentage of the average annual rainfall as the soil materials

Materials	Percentage (%)
Granite	0-3
Qcp and Qc	3-18

2. Hydraulic Conductivity

It is the most important parameter for groundwater simulation. The evaluations of hydraulic parameters of the aquifers are considered from the hydrogeologic formation (Spitz and Moreno, 1996).

Table 3.4 The hydraulic conductivity of soil materials

Materials	Hydraulic Conductivity (m/d)
Granite	0.29-1.40
Qcp and Qc	8-200

3. River

In groundwater flow simulation, river package (RIV) is used to specify head-dependent flux boundaries. Following the topography of the study area, the hydraulic conductivity was set on default as 0.1-0.3 m/day, and assumed that the river bedding was a thickness as 1 meter along the river.

4. Porosity

In solute-transport modeling, effective porosity and total porosity were used in MT3D module to determine the temporal average linear groundwater velocities per path line. In this study, the porosity was specified as 0.30, which is default value for each aquifer.

3.4.3 Calibration and validation

The parameters were applied to a groundwater model until the output from the model matches with an observed data set. In this study, the model calibration was in the steady-state condition. The data of sixteen groundwater wells from field investigation were used in the process. The hydraulic conductivity (K) and recharge rate were the major parameters which were calibrated in this step by Trial and Error method.

3.4.4 MT3D

Mass transport of total dissolved solids has been investigated by using MT3D. The boundary conditions for the transport model are no-mass-flux at the bottom. The landfill was assumed to be the source of contamination. The initial recharge concentration of arsenic was 0.25 mg/L from the leachate. The model was run for three periods: 15 years, 25 years and 50 years and 2 scenarios; sorption and no sorption for comparing arsenic contamination distribution.



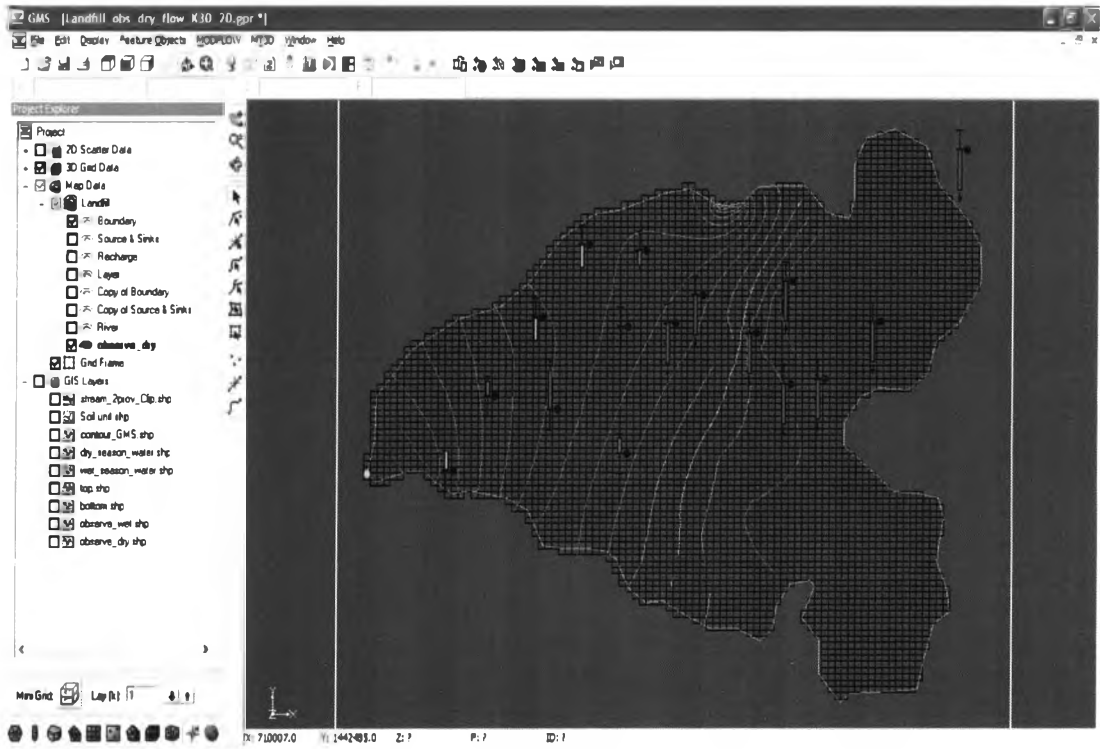


Figure 3.9 Model calibration and validation

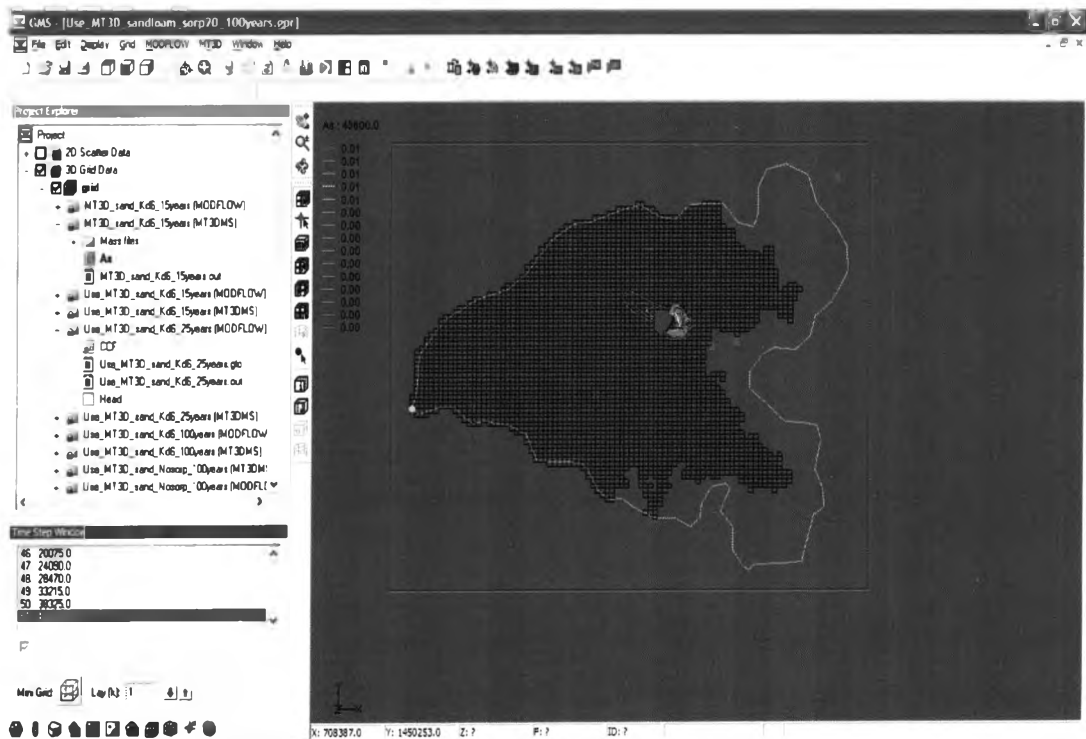


Figure 3.10 MT3D for arsenic transpotation