CHAPTER III

MATERIALS AND METHOD

3.1 Survey and Identification of Sampling Sites

In this study, the Geographic Grid System was used. This is a fundamental system specifying locations of the on the earth surface of the earth which have geographic coordinate,- latitude and longitude (e.g. the UTM Map of Chiang Mai) specified in Section 1.5 (Eastman, 1992). Usually, this is a rectangular grid of specified area (e.g. 1 sq. km) having two coordinates that meet at right angles and lie in the same plane.

There are 20 sampling grids identified in this study. Each sampling grid comprises an area of one square kilometer as shown in Figure 3. These 20 sampling grids cover the old Chiang Mai City which is surrounded by a moat and also the urbanizing surrounding areas. Each sampling grid was divided into two areas to constitute two replications as shown in Figure 4. A transect line was also made in the divided area as a reference line, where possible point for soil collection will be located. Along this transect line, sites were surveyed and identified based on the theory that an undisturbed soil could have possibly accumulated a certain lead level since it stayed

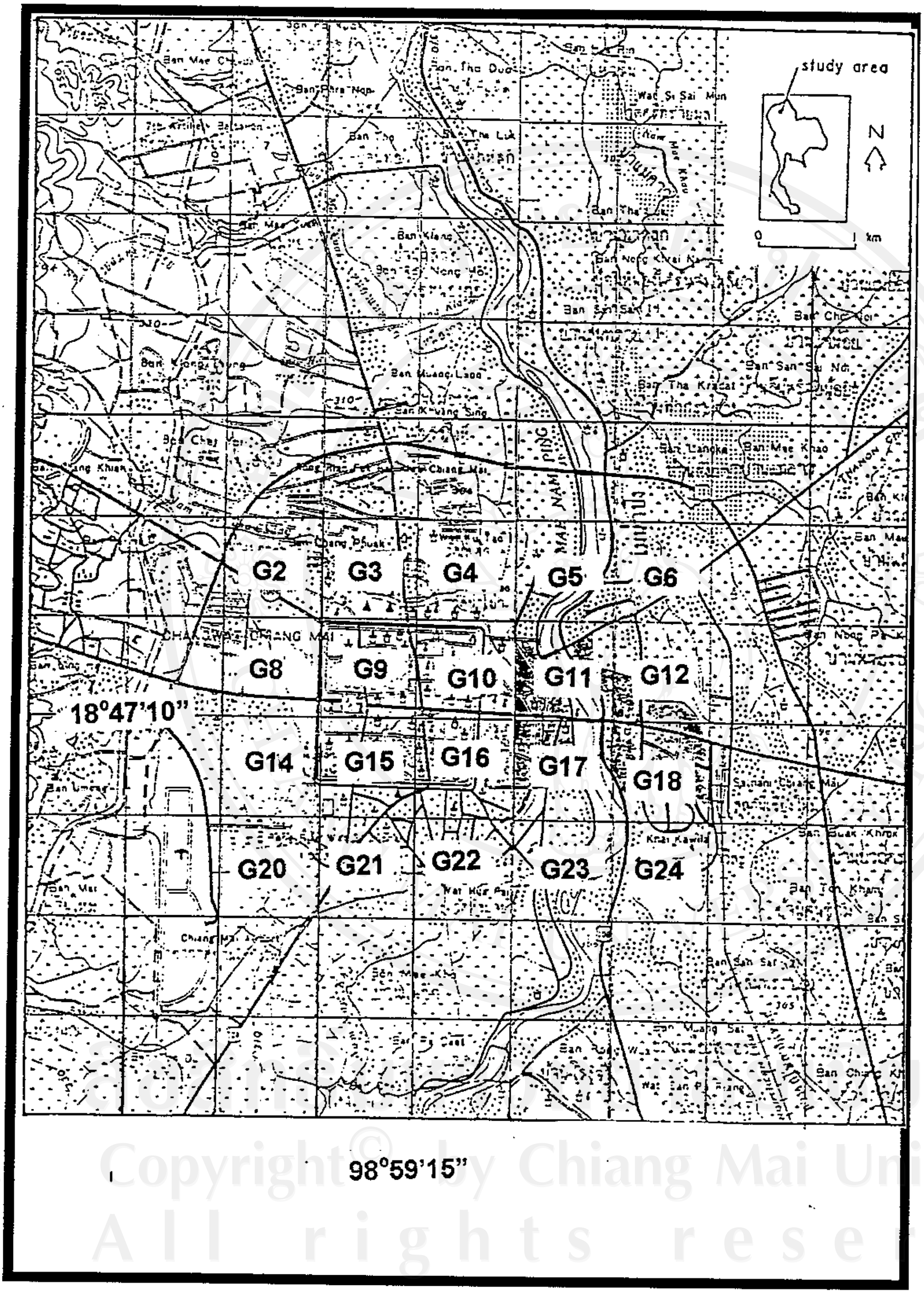


Figure 3. The topographic map of Chiang Mai City showing the different locations of the 20 sampling grids

there for a long period of time and was not a product of transport arising from urban development. These sites were usually situated in temples, government offices and old residential houses and lawns and were selected based on the above criteria.

3.2 Sample Collection

At least 6 sampling sites/units were identified in each grid with 3 sampling sites/units for each replication . Each sampling site comprises 10 sampling units as shown in Figure 4. At least 1 kg soil samples were collected from the 10 sampling units at a soil depth down to 2-3 cm. The collected soil samples from the three sampling sites were mixed to constitute one replication in each grid. Samples of at least three kg were obtained for each replication for analysis in the laboratory.

3.3 Soil Analysis

3.3.1 Determination of Lead in Soils by AAS

The German Standard Method of analysis for lead in soil by Atomic Absorption Spectrophotometry (AAS) modified after the method used by Institute of Environmental Studies, University of Toronto, Canada (van Loon, 1980) was used in this study (Figures 5 and 8). The trace metal (Pb) lead determination was as follows:

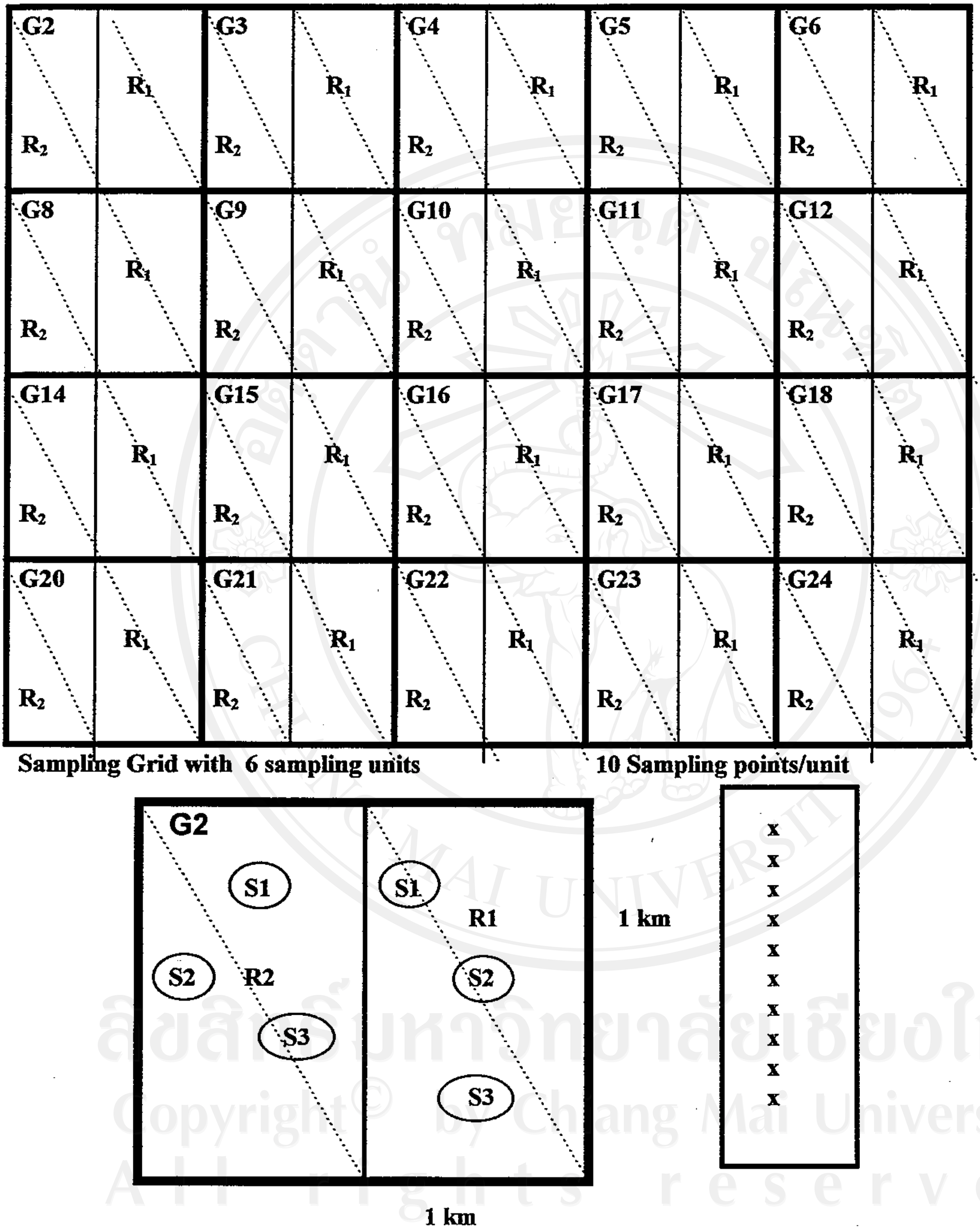


Figure 4. *Diagram of 20 sampling grids at 1 sq. km area, showing the different location of replications and sampling units*

3.3.2 Equipment and Glassware

- A Flame AAS, Perkin Elmer, Model 2380
- (Pb) Hollow cathode lamp, operated at 10 mA
- Rocklabs ring mill
- Jones riffle
- sieve # 2 mm aperture
- funnels and filter paper
- hotplate
- beakers, volumetric flasks, pipettes, stands
- electronic weighing balance
- oven

3.3.3 Reagents/ Standards:

- 1000 ppm lead standard solution (from Titrisol lead standard solution by
- MERCK, No. 9969, 1000g ±0.002 g Pb ($Pb(NO_3)_2$)$_2$ in water)
- concentrated nitric acid
- concentrated hydrochloric acid
- deionized distilled water
- IAEA Certified Reference Material - Soil 7
- IAEA Certified Reference Material - Soil 5

3.3.4 Preparation of Calibration Standard Solution

A set of calibration solutions at different concentrations was prepared from the 1000 ppm stock solution of Pb . The 1000 ppm stock solution was prepared from the Titrisol-lead standard No. 9969 by Merck containing 1.000g ±0.002 g Pb (Pb $(NO_3)_2$ in HNO_3. In the preparation of the 100 ppm stock solution 10 ml of concentrated nitric acid was placed first as stabilizer then water was added up to a volume of 1 liter.

From the intermediate stock solution of 100 ppm, five calibration solutions were prepared. The corresponding required and concentrations and volume to be taken from the stock solution of 100 ppm are shown in Appendix 1. Blank sample with zero analyte concentration was always included .

3.3.5 Preparation of Soil Samples

Samples are prepared according to the German Standard Method for Pb analysis in soil modified after the method used by Institute of Environmental Studies, University of Toronto, Canada (Van Loon, 1980) as shown in Figures 5 and 8. The 3 kg representative soil sample material from each replication were mixed thoroughly and dried at a temperature not exceeding 110 °C for a period of at least 1 day. After

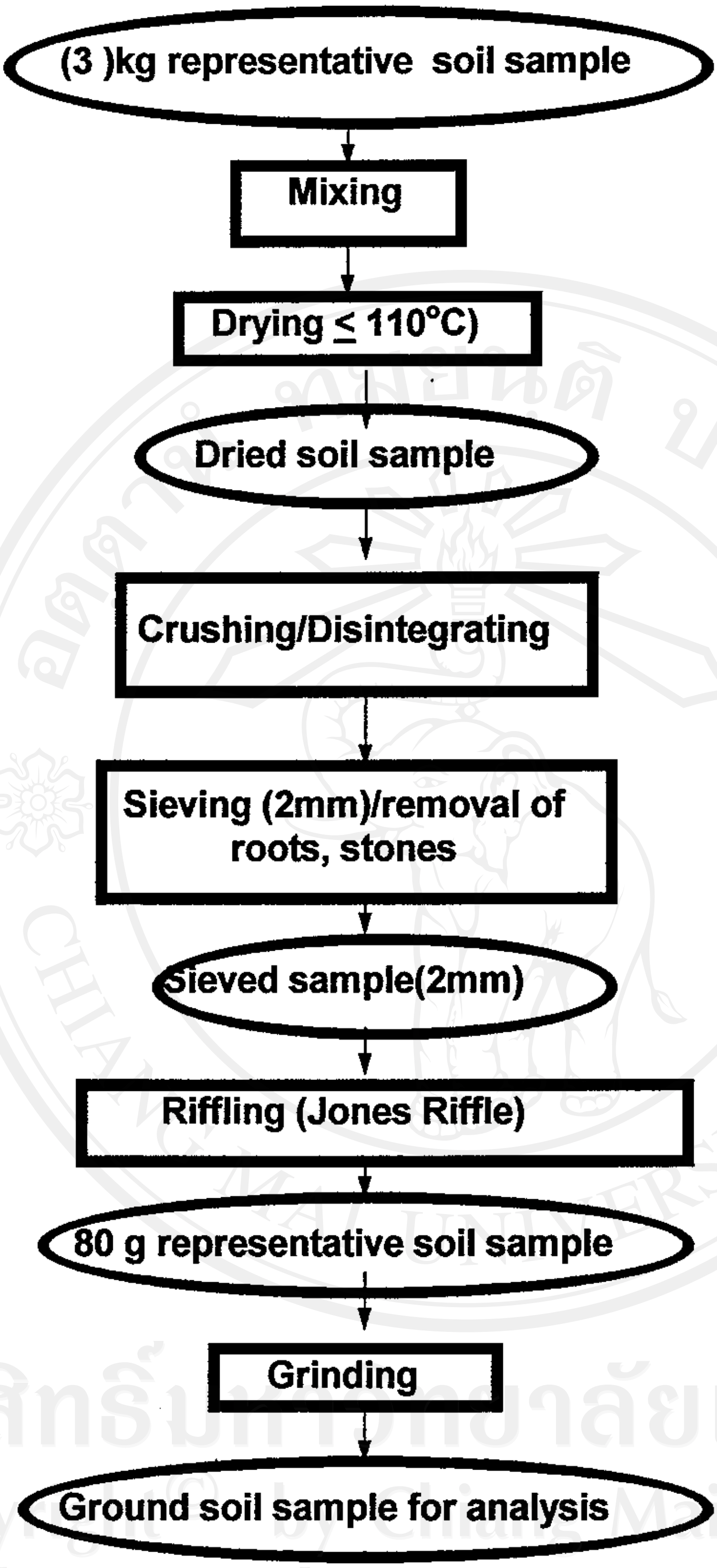


Figure 5. Diagram of the initial soil sample preparation

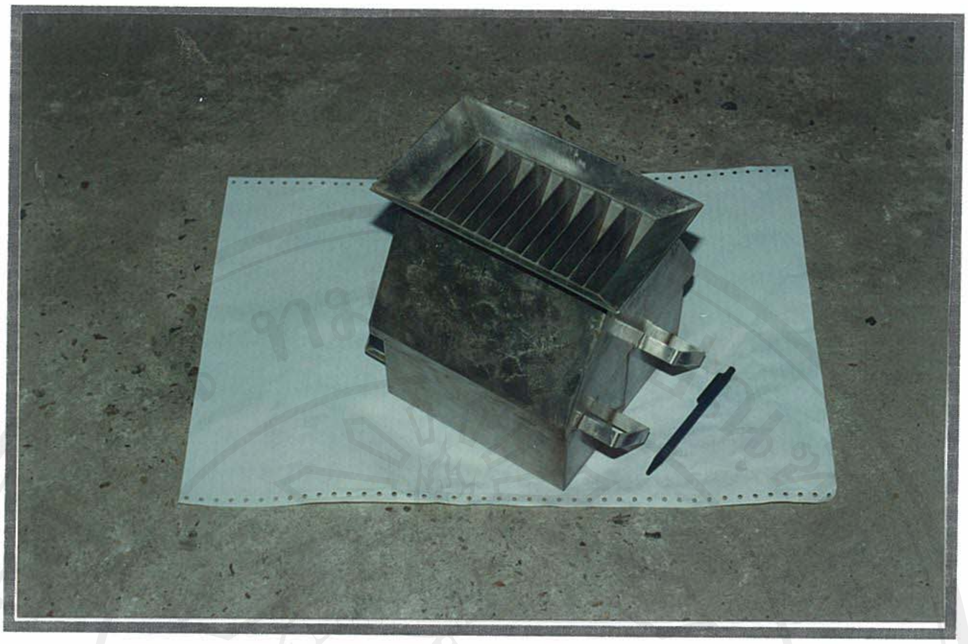
the drying process, soils were crushed and disintegrated to less than 2 mm size and sifted through a 2 mm aperture sieve. Roots, gravel, insects, etc. were removed as seen in the sifted material. The 2 mm representative soil sample obtained from sieving was riffled using a special separating equipment (Jones Riffle) as shown in Figure 6.

In the riffling process, soils are quartered until an approximately 80 g representative sample is obtained. The 80 gram 2 mm representative sample is then ground to impalpable powder for a period of about 15 minutes as a sample for laboratory analysis. A special grinding ring mill (Rocklabs ring mill) was used for this purpose as shown in Figure 7.

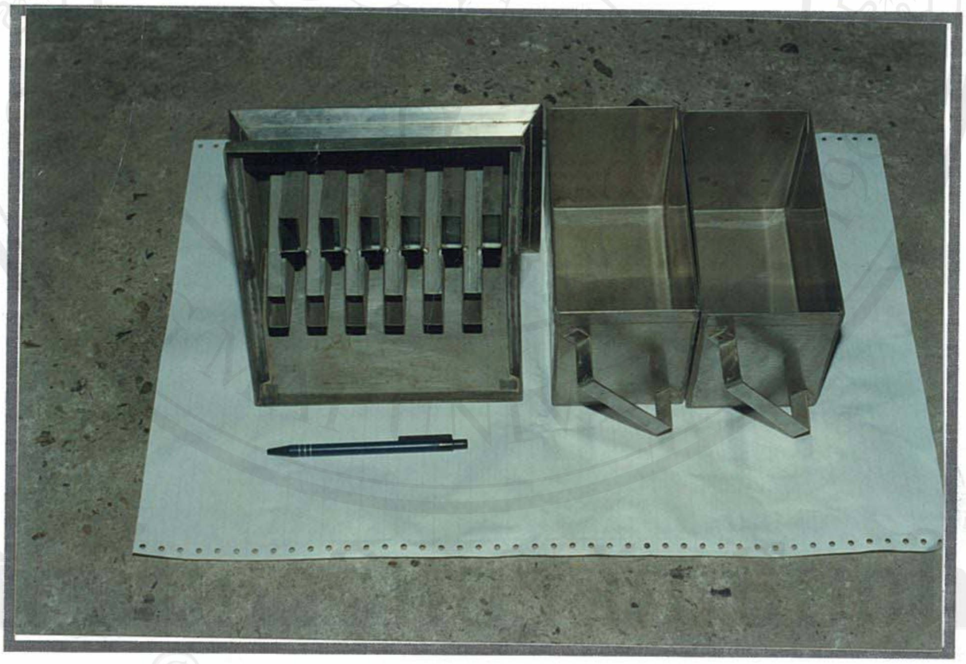
In order avoid contamination of samples, a compressed air was used to remove dust sticking to the sieve and the riffling equipment while the grinding mill was washed. All precautionary measures of possible sample contamination had always been maximized and controlled.

3.3.6 Preparation of Solutions of Samples and IAEA Reference Soil Materials

There are 46 samples that were prepared and analyzed in this study which include 40 samples from the 20 grids, two samples from the control site (located in Mae Rim District) and two IAEA Reference Materials (Soil 7 and Soil 5). Analysis



(a) Isometric view of riffling equipment



(b) Separating chamber c) Separating container

Figure. 6 Riffling equipment for separating representative soil sample for grinding

(a) Isometric view of the Rocklabs ring mill

b) Tungsten carbide grinding plate

Figure 7 The Rocklabs ring mill- grinding machine for soil samples were done were done at different times. Likewise the two IAEA Reference Materials (Soil5 and Soil 7) were also analyzed at different time together with analysis of sample solutions. In every set of analysis, a fresh set of calibration standard solutions was also prepared.

Specifically, the process of sample solution preparation is shown in Figure 8. The process started with the digestion shown in Figure 9a. The 3 gram portions of impalpably powdered representative soil sample were transferred into a 250 ml Erlenmeyer flasks. Ten ml concentrated nitric acid and 30 ml hydrochloric acid were added into each flask. Then, the flask was swirled until the sample was in suspension. A small beaker was used to cover the mouth of the flask which then was left on the balcony overnight to digest (Figure 9a).

On the second day, the digested soil samples were boiled for one hour at about 135°C (Figure 9b) then allowed to cool before filtration. In order to avoid damage of filter paper due to acid, distilled water (about equal to the sample) was added to the digested sample solution. The digested sample solution was filtered (Figure 9c) and the solid residue remaining in the flask are being washed with a wash solution (1 +99 V/V) HCl/H_2O. The filtrate was collected in a beaker and then transferred to a 50 ml volumetric flask. To make up the mark of 50 ml, distilled water was added. The flask was stopped and shaken to mix the contents ready for AAS analysis.

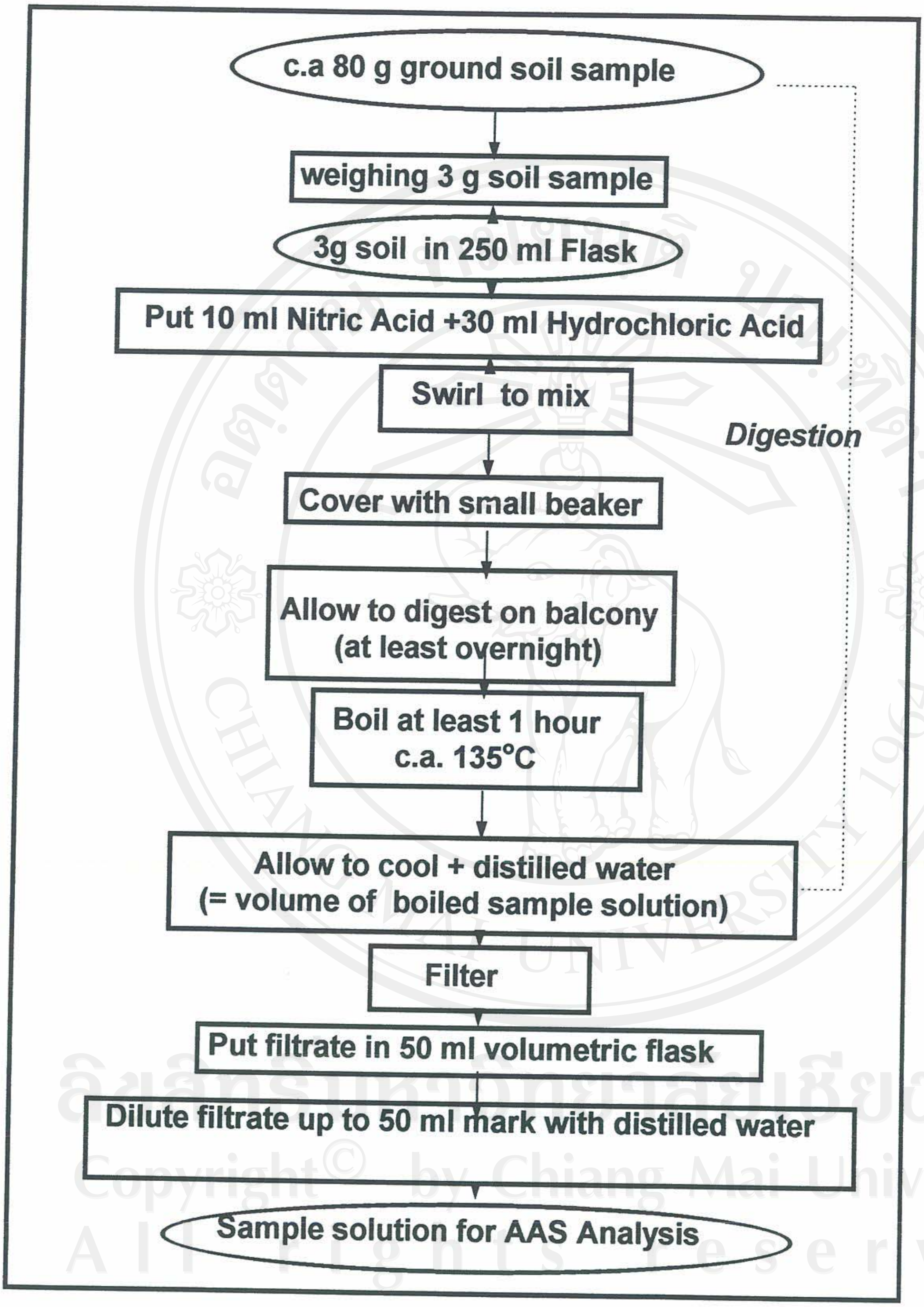
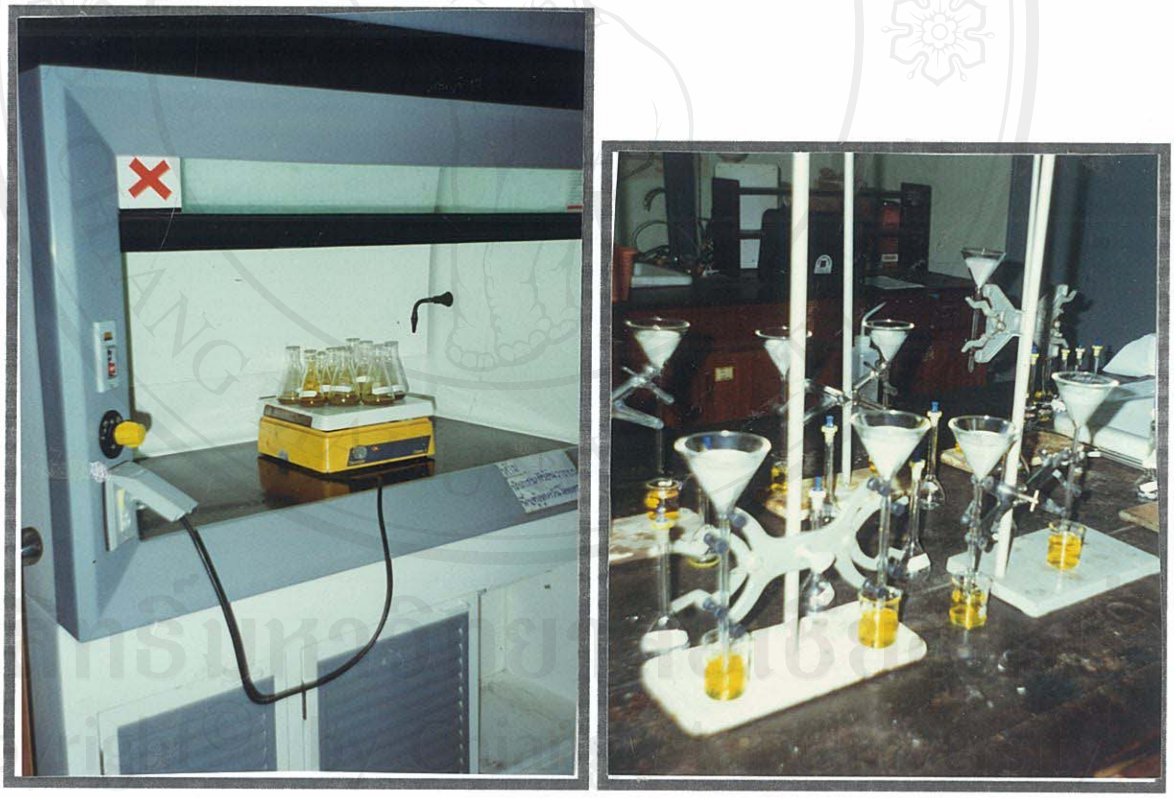


Figure 8 Diagram of sample solution preparation.

(a) Digestion process of soil sample solution allowed to stay in balcony



(b) Boiling process (c) Filtration process

Figure 9. Series of sample solution preparation

3.3.6 Analysis by Flame AAS, Perkin Elmer, Model 2380

Prior to aspirating a set of unknown samples and the calibration standard solutions, the Flame AAS, Perkin Elmer, Model 2380 (Figure 10) was first set of its optimum operating conditions. The procedure is described in Appendix 2. The wavelength was set at 283.3 nm as recommended for lead (Pb) in order to have a sensitivity (99%T) of 0.45 mg/L. In order to obtain accurate result, the background correction system using the D_2 lamp was operated. The AAS Perkin Elmer Model was set at BG-EN prior to absorbance reading in every set. After setting optimum conditions, calibration standard solutions were first aspirated and their initial absorbance were noted, then, the set unkonwn sample solutions. Two absorbance readings were obtained for the unknown sample solutions. Finally, the calibration standard solutions were again aspirated to obtain second absorbance readings

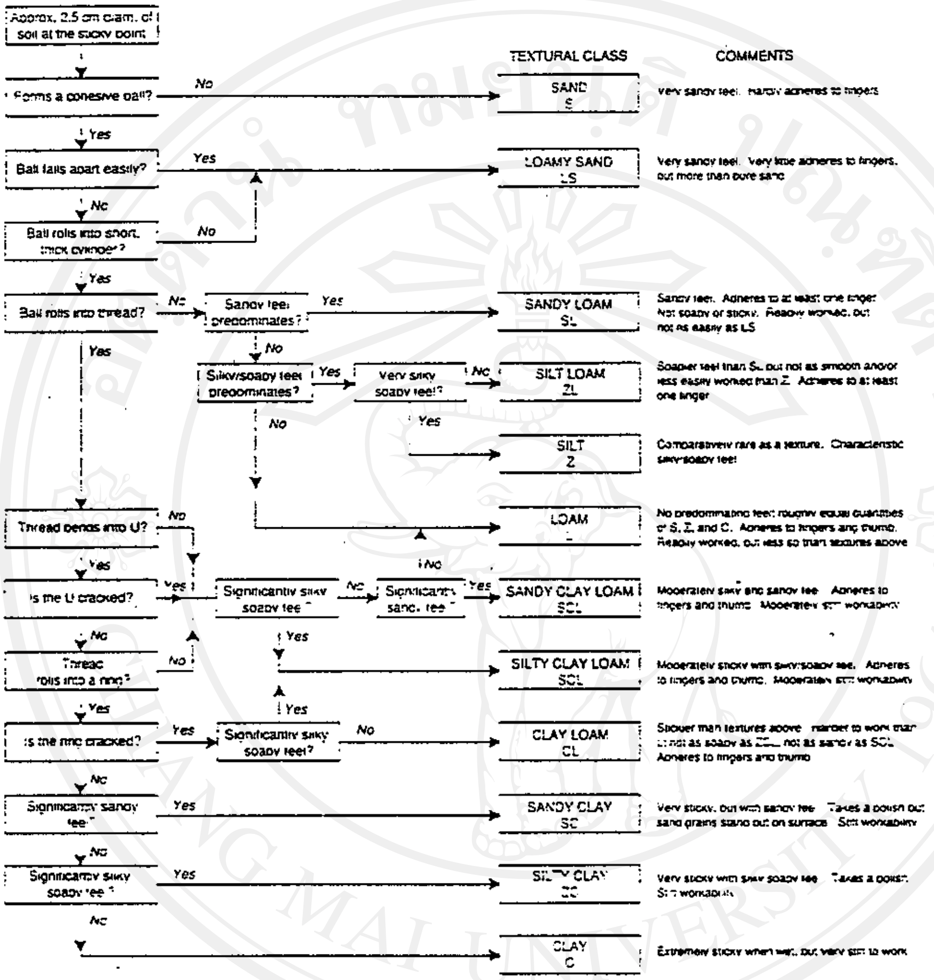
3.4 Soil Textural Analysis

The finger assessment of soil texture for mineral soils was used as the method in determining the soil texture of the samples collected. This method was adopted and introduced by S. Nortcliff and J.R. Landon (Rowell, 1994). The guide to the method is shown in Figure 11 and the recommended methodology described in Appendix 3.

(a) Front view of the Flame AAS Perkin Elmer Model 2380

(b) Researcher , optimizing the operating condition of the AAS Perkin Elmer Model 2380

Figure10. The flame AAS Perkin Elmer Model 2380 used in the analysis of lead



NOTES

Sticky point:	Moisture content at which a dry soil being wetted just begins to adhere to fingers
Workability:	Ease with which soil can be moulded between fingers. Because consistence varies greatly with moisture, samples must be properly and uniformly wetted up.
Cylinder :	Approx 5 cm long and 1.5 cm diameter
Thread .	Approx 13 cm long and 0.6 cm diameter
Ring :	Approx 2.5 cm diameter formed from about 5 cm of above thread

Figure 1.2 A guide to field assessment of texture for mineral soils. By S. Nortcliff, Reading University and J.R. Landon, Booker Agricultural International.

Figure 11. *A guide to field assessment of texture of mineral soils by finger probe method adopted andintroduced by S. Nortcliff, Reading University and J.R. Landon of Booker Agricultural International*

After the finger proof method of textural classification of soil , the classification of texture in terms of particle size-distribution was determined through the use of a triangular diagram shown in Figure 12. Various classifications had been devised. However, for this particular study, the USDA system shown in Figure 12 was used. The three variables are plotted in this way because they are related (sand + silt + clay = 100). The triangular diagram was used to determine texture if particle size distribution was known. In this particular study, the determination of clay content in the soil was given the emphasis since it was used in the risk assessment analysis.

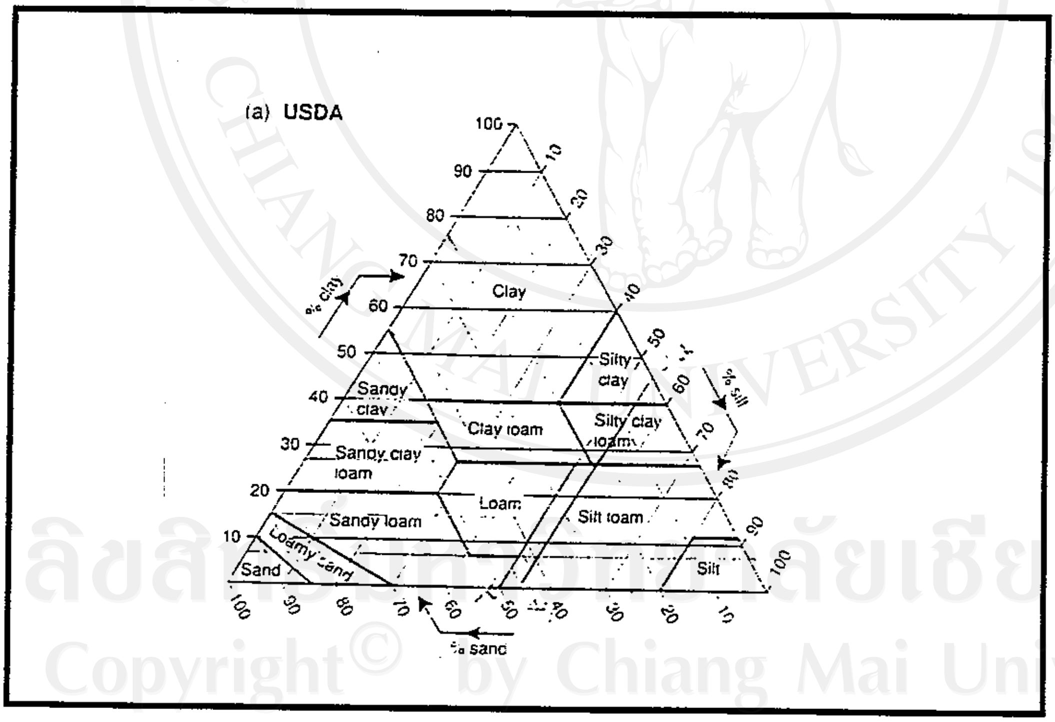


Figure 12. Soil textural classes and their particle-size distribution USDA System.

3.5 Determination of Soil pH.

3.5.1 Equipment/Glassware

- pH meter (Vibret Laboratory pH Meter)
- bottle with screw caps
- weighing balance
- shaker
- volumetric flask (100 ml)
- beaker
- wash bottle

3.5.2 Reagents

Buffer solution pH 4.0

- Dry potassium hydrogen phthalate ($COOHC_6H_4COOK$)
- distilled water

Buffer solution pH 6.9

- Dry potassium dihydrogen orthophosphate (KH_2PO_4)
- Disodium hydrogen orthophosphate (Na_2HPO_4)
- distilled water

3.5.3 Method

3.5.3.1 Calibration of the pH meter

The pH values of buffer solutions are temperature dependent and are supplied with the buffer tablets. However, for routine purposes, the above solutions were used and variation with temperature was neglected. Thus, the temperature control of the pH meter is set to be at ambient temperature.

Prior to measurement of soil pH, the pH meter (Vibret Laboratory pH Meter) was calibrated. First the electrode was washed with with distilled water and then gently dried with tissue. The electrode was placed in the pH 4.00 buffer solution and gently swirled. Swirling reduced the time required for the reading to stabilize. The meter was adjusted to pH 4.0 using the buffer control. The electrode was then removed and again rinsed with water and inserted into a buffer solution with pH 6.9 and likewise gently swirled. When the reading had stabilized, the slope control was adjusted until the reading of pH 6.9 was obtained. Then these adjustments were repeated until correct readings were obtained on both buffer solutions.

Once the pH meter was calibrated, it was ready for use to measure pH of any solution (e.g. soil suspension for soil pH) following the procedure below. However, during the series of measurements the correct pH reading was periodically checked on one of the buffer solutions. When the electrode was not in use, the porous plug were kept in potassium, chloride solution.

3.5.3.2 Measurement of Soil pH

A soil suspension was made by weighing about 10 grams ± 0.10 g air dry , - 2 mm soil sample. The soil sample was placed in a bottle with a screw cap and 25 ml water was added from a measuring cylinder. Then the soil suspension was shaken for at least 15 minutes using a shaking machine before the reading was made. Again the suspension was stirred, using the inserted electrode and swirled at the same time to get the final reading for a period of 30 seconds. However, it was noted that in neutral and alkaline soil suspension the reading was slow to stabilize. Thus, for precise chemical work, the longer period of more than 30 seconds was adopted.

3.6 Organic Matter Content Determination

Principally the percentage difference between the initial and final weight of soil sample before and after roasting is the amount of organic matter contained in the soil and burned during roasting. The organic matter content was determined using an oven-dry weight basis. At least 10 grams of 2 mm representative soil sample was taken and roasted in the furnace at more than $600^{O}C$ for a period of 1 hour. After roasting, the final weight was determined and the amount of organic matter content (%) was calculated using the equation below:

$$\boxed{(\%)\ \text{Organic Matter Content} = \frac{\text{Initial Wt (g). - Final Wt(g)}}{\text{Initial Wt. (g)}}\ (100\%)}\quad \text{Equation 2}$$

3.7 Statistical Analysis

The data collected from different parameters were analyzed with the use of the SPSS statistical program in order to determine its correlation, variability and significant differences among the different grids . There are at least two replications in each grid where consisting of 20 sampling grids, (1) control area and two international soil standard samples (Soil 5 and Soil 7). A Complete Randomized Design was used to compare the effects between different sites. To compare means among different grids the LSD test was used.

3.8 Mapping and Risk Assessment Using Lead Immobility Model

The lead immobility model after the Sewage -Sludge Regulation of Germany for water resources (DVWK Leaflet for Water Resources 212/1988) was used as the basis in the assessment of risk of lead in soil of Chiang Mai City. A suitability value range was obtained from the Muti-Criteria Evaluation (modeling) using the Voogd Weighted Linear Combinations (Voogd, 1983) which was the basis for formulating risk indices at a given threshold value for each parameter (lead, pH, organic matter content and clay content) recommended by the Sewage Sludge Regulation.

Voogd Weighted Linear Combination (Voogd, 1983)

$$\boxed{S = \Sigma W_i X_i} \qquad \text{Equation 3}$$

where : S = suitability value

W_i = weight of factor i

X_i = criterion score of factor i

Weight factor i was evaluated subjectively and a given percentage was assigned to each parameter based on its degree of risk towards water resources with reference to available literature. Such weighting constitutes 40 % for lead concentration, 30%

for organic matter content , 20 % for pH and 10 % for clay content . The summation of the products of each parameter will result in a suitability value, the risk indices of which will be assigned based on the above model. These suitability values will be the basis in formulating risk indices in different sites of this study using the Voogd Weighted Linear Combination Equation. The same weights will be used to compute the suitability values. Once indices had been assigned, data were mapped manually as well as by the use of a computer. The result from manual mapping was compared with that of the computer-based mapping of risk.

3.9 Computer- Based Risk Assessment by IDRISI GIS Program

In the computer-based risk assessment of lead accumulation in soil of Chiang Mai City, the IDRISI-GIS software was used. The system utilized the topographic map of Chiang Mai (UTM- Changwat Chiang Mai , Series L9013, Edition 3 - RTSD) as the resource map. The map of the study area was scanned and imported into the IDRISI- System to serve as the reference map for digitizing.

In the digitizing process, Identification Numbers (IDs) were assigned in each grid (e.g. ID1...ID20) and the vector files derived from digitizing were converted into an image file as a reference map for assigning attribute values for GIS analysis. In the same way, attribute value files for each parameter (lead, pH, organic matter content and clay content) were inputted into the database system of GIS. These value files were then assigned to the image file of the reference map (i.e. digitized map) and produced several unreclassified maps wiith different color codings.

Prior to overlay of all parameters, unreclassified maps were reclassified according to given range of threshold values for each parameter described in the lead immobility model (DVWK, 1988). The reclassified maps of each parameter were then overlaid and produced another unreclassified overlaid map. The unreclassified overlaid map is again reclassified according to the number of categories In this study, five categories were used such as: 5= very low, 4= low, 3= medium, 2= high and 1= very high. Color coding was used on these different categories to relay information of the condition of the area and final risk assessment map is produced. The output risk assessment map produced in this method was compared with the manual mapping by Multi-Criteria Evaluation using the Voogd Weighted Linear Combination (Voogd, 1983).