CHAPTER IV

METHODOLOGY

FIELDWORK

A successful survey must have at least two qualifications (Rose *et al.*, 1981). It must be based on valid principle and it must be efficiently carried out.

Establishing and confirming the validity of the principles, previously mentioned is the function of the survey. Selection of the field procedure for the survey is then only a matter of determining the cheapest and most efficient mean of gathering the required data. The fieldwork in this current research can be divided into 2 separated parts, such as on land and near-shore fieldwork. The former is designed for rock and soil sampling, and the latter are for collecting sediments in the river estuary.

Sampling Pattern

Selection of the sampling pattern is determined largely by size, shape, and topography of Mae Klong watershed. Since size and shape of the watershed is quite large and its topography is dominated by highly mountainous area, so sampling pattern is designed based primarily upon the percentage and aerial distribution of rocks and materials exposed in the study area (see Table 4.1). From these parameters, sampling can be made from accessibility to the area, such as along the transportation line and thus becomes the primary factor in sampling. In this study, sampling is randomly oriented along the main roads and accesscible tracts.

Table 4.1 Percentage of rock samples compared with percentage of rocks in the whole watershed.

Types of rocks	% of rocks in total area	% of rock samples
igneous rocks	12.63	3.57
limestone	54.73	46.42
shale	16.84	32
sandstone	9.47	10.7
metamorphic rocks	6.31	7.14

Percentage of rock types collected in this study compare favorably with the percentage of the whole watershed. However, percentage of shale and igneous rocks are slightly lower, this is because most of the igneous rocks which are regarded as plutonic rocks are distributed extensively at the top of mountain in the western parts of the area and cannot be easily accessed.

Collection of Samples

Types of materials collected in this research include rocks, soils, and sediments. For rock and soil samples, the method of selection for sample sites vary with scale of the survey, type of samples to be collected and availability of outcrop, drill core or other materials (Rose *et al.*, 1981).

Rock samples are usually broken from the outcrop with a hammer as large as can be conveniently carried and used in the field. Cloth or plastic bags are usually the most convenient container. As soil, 20-50 g of sample provides enough material after sieving for analysis. Soil samples in this study were collected with soil auger from the of depth 30 - 60 cm. Area for collection covers Kanchanaburi, Ratchaburi, and Samutsongkhram province. Fifty-six rock samples and six soil samples were collected.

These samples were collected during October 1994 to January 1995. Location of each sampling station is shown in Table 4.2 and Figure 4.1

Sediment samples in this study were collected from the Mae Klong estury in November 1994 with the cooperation of the Chula Research 1 vessel from Aquatic Resources Research Institute, Chulalongkorn University. Petersen grab sampler were used. Position of sediment sampling stations is shown in Table 4.3 and Figure 4.1.

LABORATORY

Preparation of Powdered Samples.

Considerable and intensive care must be taken in the preparation of samples in order to avoid contamination. Before grinding the samples, all such surficial contamination are removed by breaking off the affected portion. For rock samples, a jaw crusher, and a disc mill can be used to reduce the sample to powder that pass through a 100 mesh sieve (Shapilo, 1975). Soil and sediment samples are freeze-dried, thawed, homogenized, and passed through 63 micron sieve. These preparation steps were done at Department of Geology, Faculty of Sciences, Chulalongkorn University .

After initial prepartion, Three types of analyses were carried out. The first type is an XRF (X-Ray Fluorescence Spectrophotometry) analysis. The second type is atomic absorption spectrophotometry, using method as proposed by Shapiro, (1975). The third is spectrophotometry for the determination of aluminium with the method proposed by Shapiro, (1975).

XRF method

The elemental analysis by XRF (X-Ray Fluorescence) technique is aimed to be a preliminary estimation of concentration levels for both major and trace elements in samples. The full details of analysis is described by Sangsila (1996).

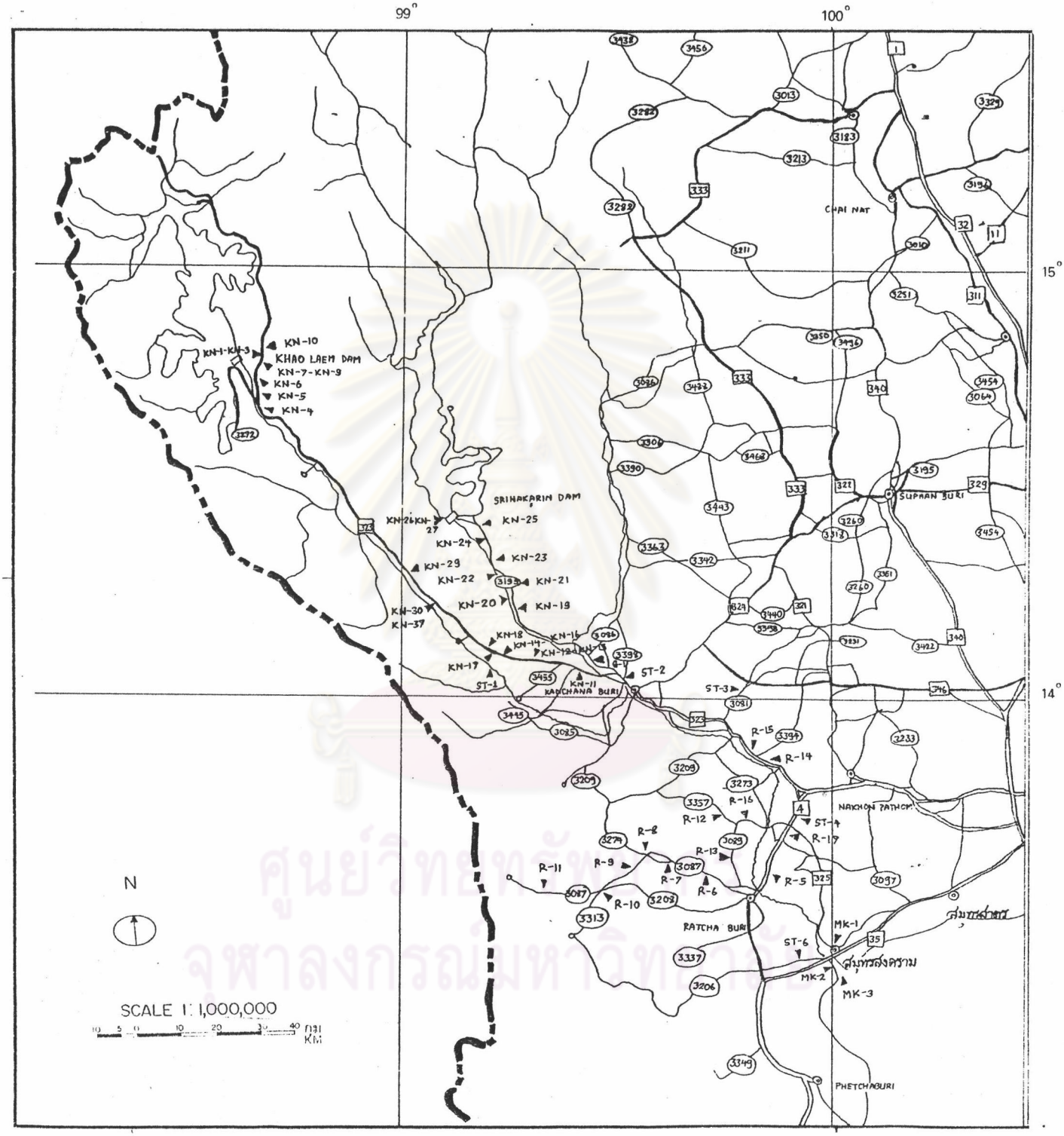

Figure 4.1 Sampling stations in Mae klong watershed area.

Table 4.2 Types and position of geological materials sampled in Mae Klong watershed area.

sample code	type	Road No.	Position
KN-1	sandstone	323	Khao Laem Dam
KN-2	limestone	323	Khao Laem Dam
KN-3	metamorphic	323	Khao Laem Dam
KN-4	sandstone	323	5 Km. from Khao Laem Dam
KN-5	shale	323	7 Km. from Khao Laem Dam
KN-6	shale	323	10 Km. from Khao Laem Dam
KN-7	shale	323	11 Km. from Khao Laem Dam
KN-8	shale	323	11 Km. from Khao Laem Dam
KN-9	limestone	323	12 Km. from Khao Laem Dam
KN-10	limestone	323	20 Km. from Khao Laem Dam
KN-11	limestone	323	15 Km. from Muang Kanchanaburi district
KN-12	limestone	3199	17 Km. from Muang Kanchanaburi district
KN-13	limestone	3199	17 Km. from Muang Kanchanaburi district
KN-14	limestone	3199	25 Km. from Muang Kanchanaburi district
KN-15	shale	3199	25 Km. from Muang Kanchanaburi district
KN-16	metamorphic	3199	25 Km. from Muang Kanchanaburi district
KN-17	metamorphic	3199	30 Km. from Muang Kanchanaburi district
KN-18	limestone	3199	35 Km. from Muang Kanchanaburi district

sample code	type	Road No.	Position
KN-19	limestone	3199	Ta Tung Na Dam
KN-20	shale	3199	15 Km. from Ta Tung Na Dam
KN-21	limestone	3199	21 Km To Erawan waterfall
KN-22	shale	3199	15 Km To Erawan waterfall
KN-23	shale	3199	12 Km To Erawan waterfall
KN-24	shale	3199	11 Km To Erawan waterfall
KN-25	sandstone	3199	7 Km To Erawan waterfall
KN-26	limestone	3199	Srinakarin Dam
KN-27	metamorphic	3199	Srinakarin Dam
KN-28	limestone	323	Sri Yok Noi Waterfall
KN-29	limestone	323	10 Km from Sri Yok Noi Waterfall
KN-30	limestone	323	Sai Yok district
KN-31	sandstone	323	Sai Yok district
KN-32	sandstone	323	Sai Yok district
KN-33	shale	323	Sai Yok district
KN-34	shale	323	Sai Yok district
KN-35	limestone	323	Sai Yok district
KN-36	limestone	323	Sai Yok district
KN-37	shale	323	Sai Yok district
R-1	limestone	3087	Khao Ngu, Rachaburi province
R-2	limestone	3087	Khao Ngu, Rachaburi province
R-3	limestone	3087	Khao Ngu, Rachaburi province
R-4	limestone	3087	Khao Ngu, Rachaburi province
R-5	shale	4	Muang Rachaburi district
R-6	shale	3087	14 Km to Chom Bumg district
R-7	limestone	3087	Khao Bin, Chom Bumg district

sample code	type	Road No.	Position
R-8	sandstone	3087	Khao Bin, Chom Bumg district
R-9	limestone	3087	Chom Bumg district
R-10	limestone	3087	Chom Bumg district
R-11	shale	3087	Chom Bumg district
R-12	shale	3089	Pho Tha Ram district
R-13	shale	3089	Pho Tha Ram district
R-14	shale	323	Ban Pong district
R-15	limestone	323	Ban Pong district
R-16	limestone	4	Pho Tha Ram district
R-17	limestone	4	Pho Tha Ram district
G-1	granite	323	Khon Chon Kai, Kanchanaburi
B-1	basalt	3086	Bo Ploi district, Kanchanaburi
ST-1	soil	323	Khon Chon Kai, Kanchanaburi
ST-2	soil	323	Muang Kanchanaburi district
ST-3	soil	323	Tha Ma Ka district
ST-4	soil	4	Pho Tha Ram district
ST-5	soil	4	Muang Rachaburi district
ST-6	soil	35	Pak Tho district, Samutsongkhram

Table 4.3 Sediment sampling position in Mae Klong estuary.

Sample code	Latitude	Longtitude
MK-1	13° 17.65′ N	100° 01′ E
MK-2	13° 17.1′ N	100° 01.45′ E
MK-3	13° 16′ N	100° 02.35′ E

Total digestion method

The solid samples are transformed to sample solution before determination of elemental concentration. A suitable ratio of reagent and sample is applied to help reducing time of digestion. The total samples (rock, soil, and sediment) are digested by the same method (same types of reagents , same ratio of reagent and sample , same weight of sample, and same condition). With this method two kinds of solution are produced. The first solution is called "solution A", which is used in determination of Al_2O_3 . The second solution is called "solution B" and used in determinations of total Fe, Mn, Zn, Cu and Pb.

During analysis, each bacth of samples is quality-controlled by using the certified reference materials. The standard reference materials for rocks and soils is the JDO-1 of GSJ (Geological Survey of Japan) provided by Department of Mineral Resources, and IAEA SD-M-2/TM of IAEA (International Atomic Energy Agency) for sediments..

Preparation of solution A

A portion of the sample is fused with NaOH at a comparatively low temperature in a nickel crucible for about 5 min. After cooling, the melt is leached with water, and the solution is acidified with 1+1 HCl acid.

Reagent : - 30 % NaOH solution
- 1+1 HCl

Procedure : Transfer 5 ml portion of 30% NaOH solution to a series of 75 ml nickle crucibles. Evaporate the solution in each crucibles to dryness over a hot plate. Accurately weigh 0.05 g of each sample powder of a solid, ground sample (e.g. silicate rocks, soils, and sediments or 0.2 g of sample powder of carbonate rocks) and transfer to the crucible containing the fused NaOH. Cover and heat the crucible in a furnace which is set at 800°C to dull redness for about 5 min. Leave it to cool down to room temperature. Place the crucible inside a 1 litre plastic beakers. Add about 980 ml deionized water to the beaker and stir by a plastic rod. Add 20 ml 1+1 HCl

while stirring. Then the crucible is removed and the solution is ready to be used for determination of Al_2O_3 .

The solution A was preprared in the Laboratory of Analysis Division, department of Mineral Resources.

Preparation of solution B

The sample is digested with a mixture of HF, H_2SO_4 , and HNO_3 . This procedure will effectively decompose most of the sample. Organic matter is destroyed by the addition of few drops of $HClO_4$ after the step of removing sulfuric acid fumes by heating.

Reagents : - a mixed solution of 454 ml of 48% HF + 165 ml H_2SO_4 + 40 ml HNO_3

- 72% $HClO_4$

Procedure : Transfer 0.2 g of each sample to 100 ml teflon beakers. Under the fume hood, add 5 ml of mixed-acid solution and swirl to wet the sample. Place the beaker on a hot plate and heat at 150°C until sulfuric acid fume evolve, then remove the beaker. Add about 4 drops of $HClO_4$ and replace the beakers on the hot plate. Heat each beaker until strong fume is evolved and any color (brown) caused by organic matter disappears. If color still persists, repeat this step. Remove the beakers from the hot plate, allow them to cool for a few minutes, and then make volume to 50 ml with 2 % nitric acid.

The solutiion B was prepared in the Laboratory of Department of Marine Sciences , Faculty of Sciences , Chulalongkorn University

Determination of elemental concentrations

Aluminium in the form of Al_2O_3 is determined by measuring the absorption of light at 475 nm of solution A in which aluminium has been converted to a calcium aluminium alizalin red-S complex

Reagent : - a complexing solution, prepared by mixing

- 880 ml of Deionized water
- 0.3 g of potassiumferricyanide
- 40 ml of 10% hydroxylamine hydrochloride
- 80 ml of calcium chloride solution
  - calcium carbonate 14 g.
  - HCl 30 ml make volume to 1 lit

- 0.3% Thioglycolic acid solution
- Buffer solution
  - sodium acetate 80 g.
  - glacial acetic 24 ml make volume to 1 lit
- 0.01% Alizalin red-S

Procedure : Transfer 3 ml each of the solution A , blank and the standard solution to 50 ml beakers using a high-precision automatic pipette. Add 5 ml of the complexing solution and add 5 ml of the thioglycolic acid solution. Allow to stand for 5 min. Add 5 ml of the buffer solution. Allow to stand for 10 min. Add 5 ml of the 0.01% Alizalin red-S and allow to stand for 45 to 70 min. Determine the percent transmission at 475 nm for each solution using the blank solution as a reference.

Determination of concentration of Al is carried out at the laboratory of EMDEC (Eastern Marine Fisheries Development Center).

Fe, Mn, and Zn in solution B are determined by a Flame Atomic Absorption of Perkin-Elmer series 5000 in the laboratory of Analysis Division, Department of Mineral Resources.

Cu and Pb in solution B are determined by a graphite furnace Atomic Absorption spectrophotometry of Hitachi series Z-8100 in the laboratory of EMDEC.

STATISTICAL ANALYSIS

Linear regression analysis is used to estimate model parameters for each metal with reference elements (Al, Fe, Mn), using reference elements as the independent variable (Schropp and Windom, 1988).