CHAPTER III
RESEARCH METHODOLOGY

3.1 Study design

This thesis is based on the conventional and longitudinal study design for exposure study. The field work was carried out on 28 non-smoking participants in 14 shop houses in Bangkok. For each participating house, four types of PM-10 measurements; indoor air, near-by outdoor air, personal exposure monitoring, and ambient roadside air, were performed simultaneously and repeatedly for 3 consecutive days per season and only on weekdays. Measurements were conducted in all three seasons from December 2002 to August 2003 (winter: December to January, summer: March to May and the rainy season: June to August). All measurements were programmed to be collected for 24 hrs from 10:00 a.m. of the first day to 10:00 a.m. of the next day. Thus a total of nine measurements per subject/sampling location were obtained. Questionnaires and interviews were used to collect background information, household characteristics and the individual activities as well as the time spent for indoor and outdoor during the personal measurements.

3.2 Sampling site

Sukhumvit Road is one of the roads in Bangkok with both a large traffic burden and a representative distribution of building types and styles of life along its length. Along the road from Soi 1 to Soi 105 (which are side streets), a distance of approximately 11 km running from the inner zone to the outer zone of Bangkok, there are numbers of shop houses on both sides of the road. The Pollution Control Department of Thailand, PCD, has monitored the ambient air quality of the Sukhumvit area for years using both the general station at Bangna and the roadside station at On-Nuch. Based on their willingness to volunteer and the location of their homes, the occupants of 14 shop houses in which the owners and/or workmen live upstairs were invited to participate in this study, especially those residing in non-smoking households. All the houses are

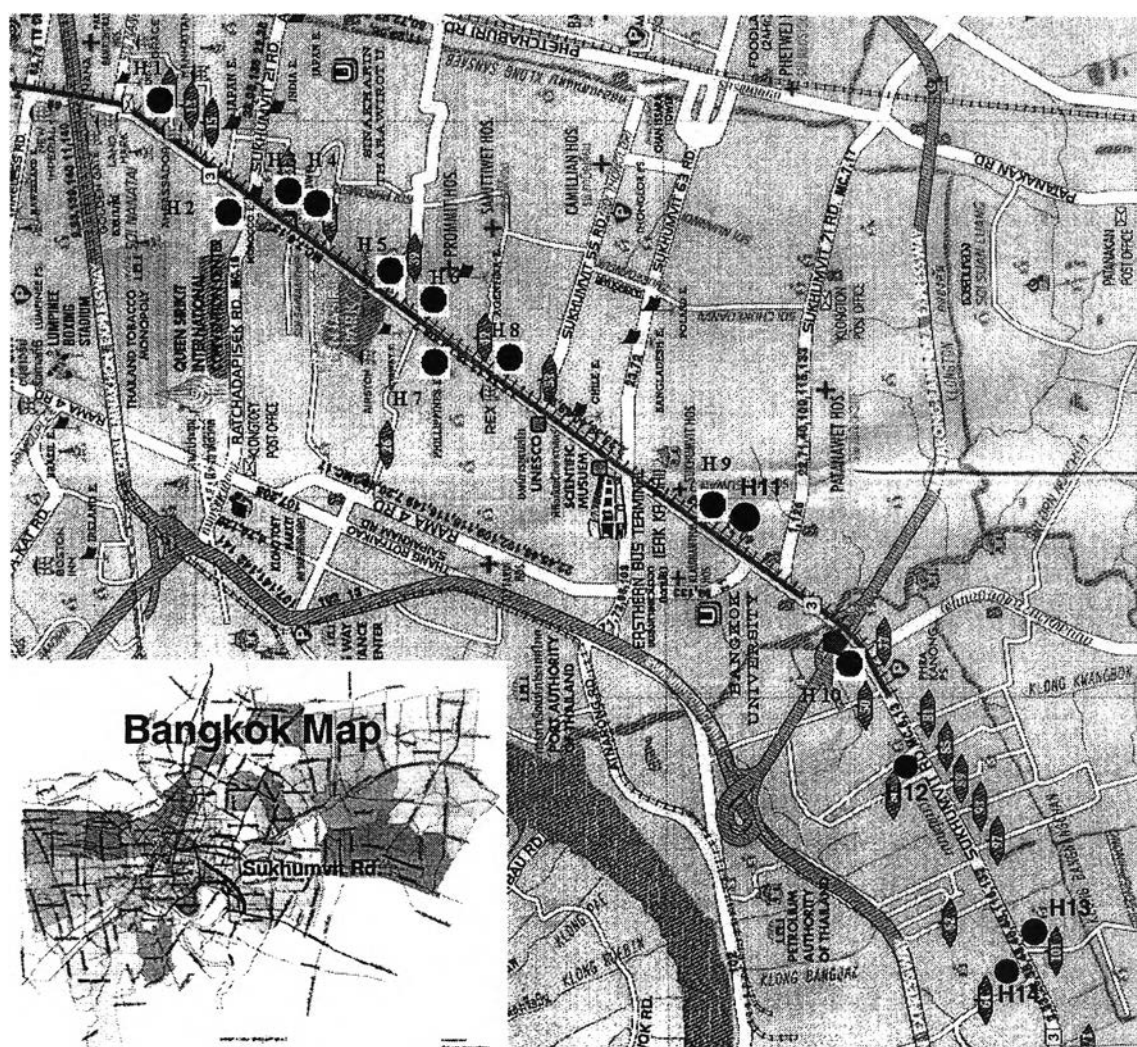within a radius of approximately 7 km from the On-Nuch ambient roadside station, as shown in Figure 3.1.

Figure 3.1 Location of the 14 shop houses: ● and the On-Nuch roadside station: ⬠

3.3 Measurements of PM-10

3.3.1 Indoor, outdoor, ambient, and personal PM-10 measurement

On each measurement day, only one shop house was measured for PM-10 concentrations, an approach directed by the available equipment. For each shop house, the measurements were conducted for 24 hr periods and for 3 consecutive days in each season. Four types of PM-10 measurements; indoor air, outdoor air, personal exposure monitoring, and ambient roadside air, were performed concurrently in each

measurement day. A schematic diagram of typical sampling locations in a measurement day is shown in Figure 3.2.

For indoor measurements, three sampling locations were selected in each shop house, at the 1st, 2nd and 4th floors. The measurements were taken by placing Personal Exposure Monitor (PEM) instruments at about 1.5 m height from the floor. The 1st floor or ground floor normally was the shop area, whereas the 2nd and 4th floor contained living or bedrooms. The outdoor measurement was made by placing a PEM outside the building at the 2nd floor balcony about 5 m above ground level. The ambient roadside measurement was taken at the On-Nuch station using a High Volume PM-10 Air Sampler.

To obtain personal PM-10 concentrations, two participants in each shop house were instructed to carry PEM instrument, which the air sampler set was in an acoustic leather bag, for a 24 hr period. They were instructed further to attach the impactor near their breathing zone during the daytime and to place the instrument near their beds during the night.
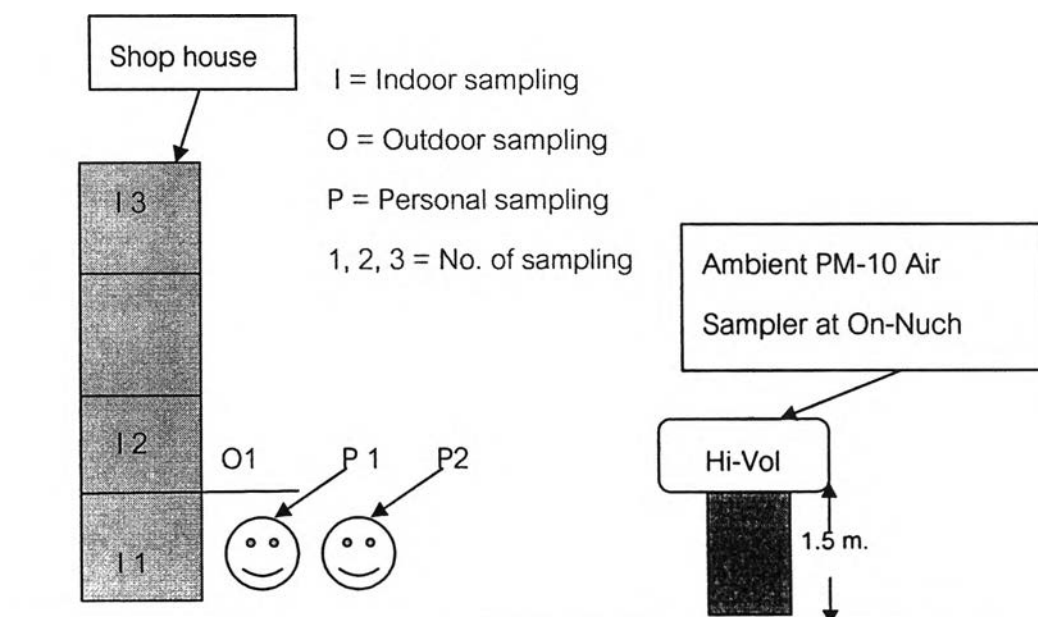

Figure 3.2 Types of sampling conducted in a shop house during a measurement day

Questionnaires were used to obtain information about household characteristics including floor plan, air conditioning usage, potential indoor sources of small particulates, cooking fuel and time-activity pattern of the participants. In addition, the subjects were interviewed after each day of measurements in order to record details of daily activities such as incense use, cooking, cleaning, time spent for outdoors, exposure to tobacco smoke and so forth.

3.3.2 Sampling equipment

3.3.2.1 Personal exposure monitor

A personal exposure monitor (PEM) consisted of a small impactor and a battery powered sampling system. A Personal Environmental Monitor Model 200 (PEM™, MSP Corporation, USA.), a single-stage impactor in which particles smaller than 10 µm are collected on a 37 mm filter (2 µm PTFE filter with PMP support ring, SKC Inc., USA.), was connected to a personal air sampler pump (model 224-PCXR 8, SKC) as shown in Figure 3.3. The operation is based on the inertial separation of airborne particles using a conventional impactor. The large particles, because of their inertia, impact on the ring, while small particles are carried along the air streamlines and collected on the filter.

To obtain a 24 hr integrated measurement while preventing filter overloading and battery failure, the sampler pumps were programmed for 23 hr 30 min of sampling periods with intermittent operation (1 min on and 1 min off). The batteries of the pumps were modified by using 3000 mAh metal hydride batteries to achieve sampling for an entire day without need for battery charging. The pump flow rate was calibrated with an automatic flow meter (Dry Cal, Bios.) to 4 ± 0.05 l/min before sampling and was also checked again after sampling. The average flow rate and the reading from an elapsed time meter were used to compute the sample volume.
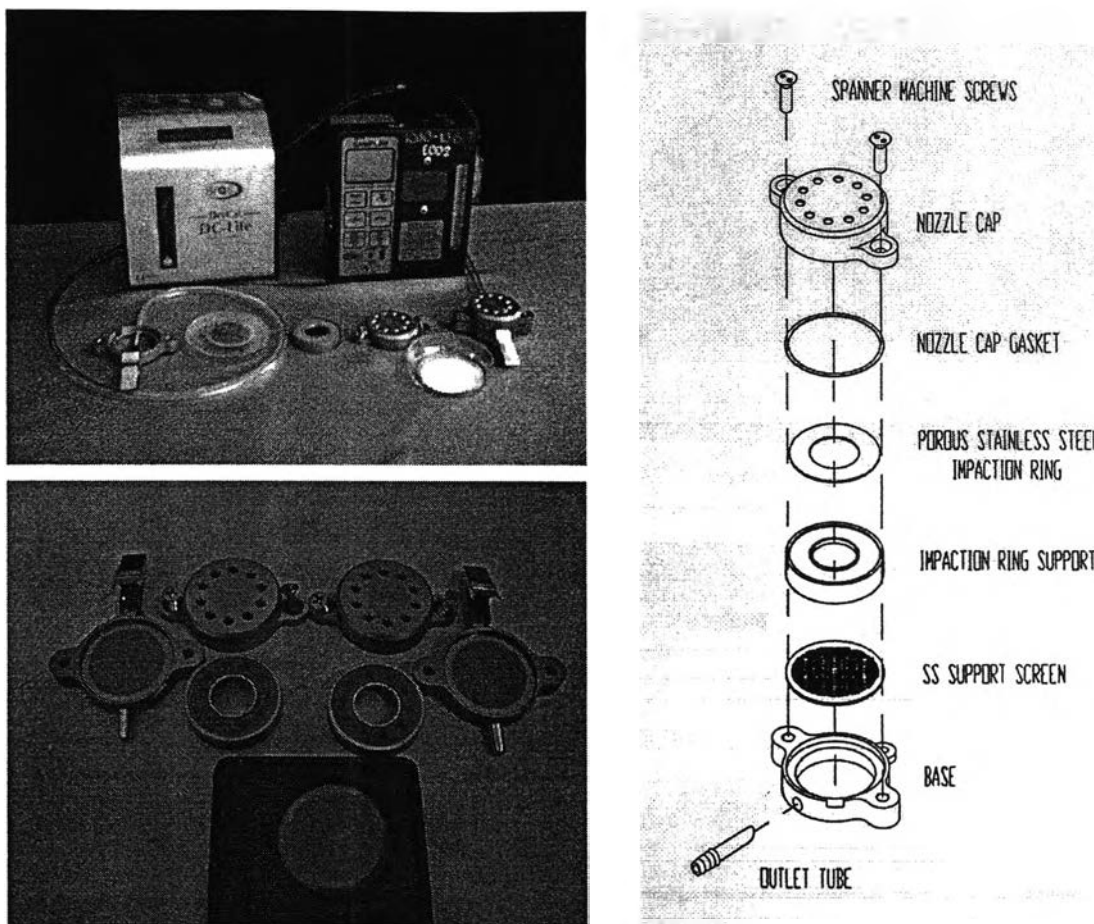
Figure 3.3 Pump and schematic diagram of Personal Environmental Monitor (PEM)

3.3.2.2 High volume air sampler

A High Volume Air Sampler for PM-10 (ASI/GMW Model 1200) with Volumetric Flow Controller (VFC) was used to collect ambient roadside PM-10 for 24 hr following the method of USA; 40 CFR 53, Appendix J Reference Method for PM-10 (Appendix A). The sampler was calibrated by an orifice transfer standard (GMW 25A) to ensure a flow rate of 1.13 m^3/min. The 8 x 10 inch quartz fiber filters (SKC), both before and after sampling, were conditioned for 24 hr in a desiccator and then weighed in a humidity and temperature-controlled room at the laboratory.

3.3.3 Filter weighing

All the sampling filters were transferred into a plastic container and then sealed with Parafilm® tape and foil and stored in an ice chest before transporting to the laboratory. All the samples were stored in the refrigerator at 4 °C for further analysis.

PM-10 mass was analyzed by a gravimetric method. Filters were weighed using a microbalance with 1 µg reading precision (Sartorius MC5, Germany). The filters, both before and after sampling, were desiccated for at least 24 hr before weighing. Stable weighing room condition and careful weighing procedures are required.

The weighing room condition was controlled at a temperature of 23 $\pm$ 5 °C and relative humidity of 45 $\pm$ 5% and the room should have reached at this condition for at least 24 hr before weighing begins. In the weighing procedure, every filter was weighed twice and the two weights of the same filter had to be less than 10 µg different in order to be recorded. In cases where the difference was more than 10 µg, the filter had to be reweighed twice.

3.3.4 Quality assurance and Quality control

3.3.4.1 Performance of the PM-10 sampling method

Because there were differences in two PM-10 measurement methods used, High volume PM-10 Sampler and PEM instruments, these two methods were assessed to determine the data comparability by placing a PEM instrument near the High Volume PM-10 sampler at On-Nuch station for a 24 hr collocation sampling study. In addition, a High Volume PM-10 Sampler from PCD and the identical one from this study were placed close together for 10 days.

The precision of the PEM instrument was also determined by placing 5 sets of the PEM sampling instruments close together in the same room and then performing the sampling and analysis procedure as in the sampling design. This operation was done for 3 times and the relative standard deviations of the results were calculated to determine the precision of the method.

Field blanks were performed to ensure effective sampling procedures. A field blank was obtained for each day of measurements by placing PTFE filter in the filter holder with no air sampler pump near the indoor sampling location for 24 hr. All PM-10 mass data were corrected with the corresponding field blanks.

3.3.4.2 Weighing Performance

Laboratory filter blanks, three of fifty filters were desiccated and used to control for weighing conditions and balance stability. Lab blanks were weighed

at the beginning and at the end of each weighing session and also periodically during weighing. In addition, a 100 mg stainless steel standard weight was weighed at the beginning and the end of each weighing session.

3.4 Elemental compositions of PM-10 analysis by ICP-MS

All Teflon filters for PEM instruments were acid digested on a hot-plate to solubilize the elements of interest and subsequently analyzed by ICP-MS. The extraction procedure and analysis procedure followed the compendium methods for the determination of inorganic compounds in ambient air: IO-3.1; selection, preparation and extraction of filter material and compendium method IO-3.5; determination of metals in ambient particulate matter using inductively coupled plasma – mass spectrometry, respectively (54). 18 species, Ag, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, In, K, Mg, Mn, Na, Ni, Pb, V, and Zn, were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; model: E-LAN 600, Perkin-Elmer, Germany) as shown in Figure 3.4. ICP-MS is a powerful technique for multi-element analysis and detection limit are in a range of part per billion (ppb). The detection limit was calculated individually for each element. The steps in elemental analysis are summarized below (54).

Figure 3.4 ICP/MS instrument

3.4.1 Using plastic forceps retrieve the filter and place it into a labeled 150 ml Griffin beaker.

3.4.2 Using an automatic dispensing pipette, add 10 ml of extracting acid (5.55% HNO_3/16.75% HCl) into the beaker. Ensure acid volume cover the entire filter as presented in Figure 3.5.

3.4.3 Place Beaker on the hot-plate, contained in a fume hood, and reflux gently while covered with a watch glass for 30 min. Do not allow sample dry. Remove the beaker from the hot-plate and allow it cool.
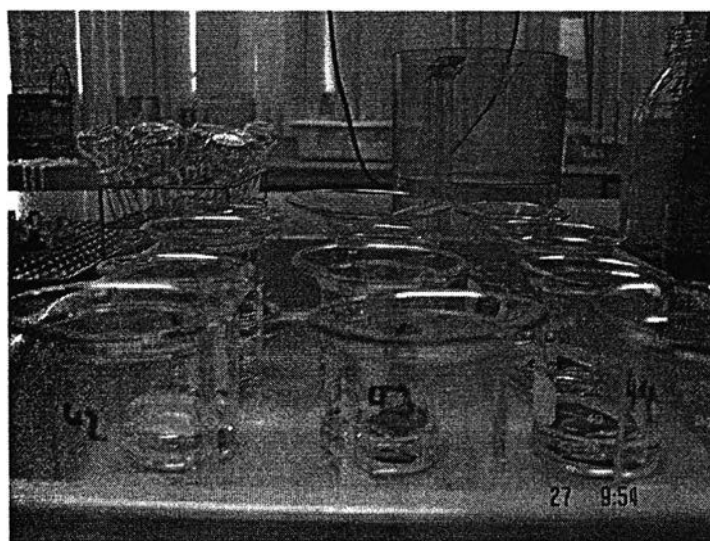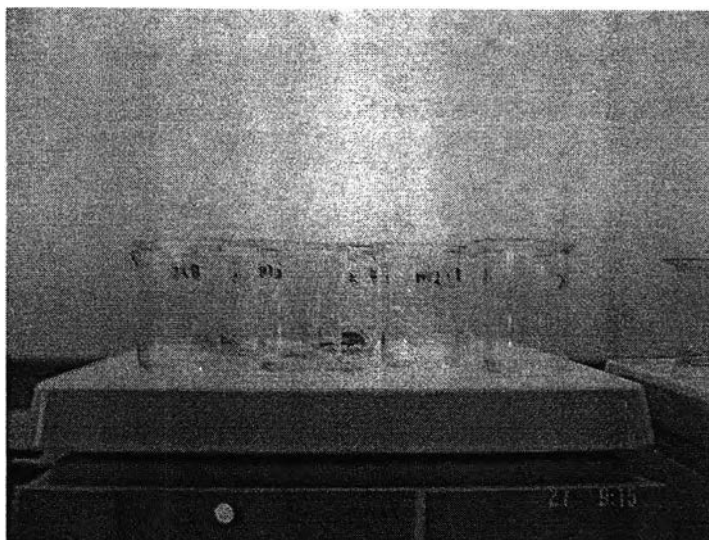
Figure 3.5 Hot acid digestions of filter samples

3.4.4 Rinse the beaker walls and wash with D.I. water (approximately 10 ml). Add approximately 10 ml reagent water to the remaining filter material in the beaker and allow it stand for at least 30 min. Transfer the extraction fluid from the beaker to a 25 ml volumetric flask. Rinse the beaker and any remaining solid material with type I water and add the rinse to flask. Dilute to the mark with type I water and shake through roughly.

3.4.5 The final extraction volume is 25 ml. Store in the refrigerator at 4 °C for subsequent analysis by ICP-MS.

3.4.6 ICP-MS analysis: The digested solution was pumped into the plasma with a peristaltic pump. All compounds in the sample stream are dissociated into their most basic components, elemental ions. From the plasma, the ion stream enters a vacuum through a pinhole. The ions are focused into the quadra-pole mass analyzer which allows ions of a single mass-to-charge ratio through at a time. Ions were directed into an electron multiplier to increase the signal and be detected.

3.4.7 Method detection limits (MDL) and percent recovery (% recovery) are established for all elements.

3.5 Factor analysis and multiple regression analysis

3.5.1 To determine the sources of PM-10, a varimax rotated Principle Component Analysis (PCA) was performed. Because each element concentration was considered as a variable, PCA was applied to the data set of elemental variables in order to reduce a large set of intercorrelated of elemental concentrations to be a smaller number of independent variables (components/factors). First, to prepare data matrix, elemental concentration with a unit of $\mu g/m^3$ was transformed into a dimensionless standardized form. Second, the correlations coefficients between the different elements were computed to analyze their relationship in order to create the correlation matrix. Then, a principle component analysis was carried out by eigenvalue decomposition of the covariance matrix and a varimax rotation was applied.

3.5.2 To consider the number of factors, only the common factors which the eigenvalue were more than 1 were retained. The element compositions with the factor loading more than 0.5 were grouped into the corresponding common factors. Supposedly, each common factor represented each source of PM-10 so that the probably source types were identified from the elemental compositions in those factors.

3.5.3 The absolute principle component score (APCS) were computed for each identified factors and for each sample which the procedures to calculate the APCS were the same as those purposed by Thurston and Spengler (50). Then they were used as independent variables, whereas, PM-10 exposure concentrations used as a response variable in multiple regression analysis. Then compute the regression equation and estimate the contributions of each source.

3.6 Data analysis

The descriptive statistical method was used to evaluate levels and distribution of outdoor, indoor and personal exposure concentrations.

Analysis of Variance and paired T- tests were applied for indoor and personal concentration comparisons.

The individual longitudinal correlations between personal exposure, indoor and outdoor PM-10 levels were investigated by simple linear regression.

Factors influencing personal concentrations were determined by multiple step-wise regression analysis.

Factor analysis and multiple linear regression analysis were applied to identify and quantify source categories and their contributions to PM-10 exposure concentrations.

All statistical tests and analysis applied in this thesis were computed with Statistical Package for Social Sciences (SPSS for Windows, SPSS Inc. Chicago, Illinois, USA) version 10.0