CHAPTER II

LITERATURE REVIEW

2.1 Ambient air quality standards

The air quality is one of the most environmental concerns especially in developing countries. Airborne particulate matter can come in the form of solid particles as dust, liquid droplets suspended as fume or in a gaseous form. The particulate matter can be the physical like dust, ash, soot, smoke, or biological like pollen, spores, algal cells, and many other forms. Particulates are the most apparent for of air pollution because they reduce visibility and leave dirty deposits on construction and properties. Thai standards for ambient air quality are illustrated in Table 2-1. These standards are similar to those recommended by the World Health Organization, and adopted in other countries such as the US, but adjusted for local socio-economic, technology, health and environmental concerns. Thai standards for 24 hour and annual average concentrations total suspended particulate (TSP) are 330 and 100 $\mu g/m^3$, respectively.

Table 2.1 Thai standards for ambient air quality

	1-hr average		8-hr average		24-hr average		Annual average	
	mg/m^3	ppm	mg/m^3	ppm	mg/m^3	ppm	mg/m^3	ppm
CO	34.2	30	10.26	9	-	-	-	-
NO$_2$	0.32	0.17	-	-	-	-	-	-
SO$_2$	0.78	0.3	-	-	0.30	0.12	0.10*	0.04
TSP	-	-	-	-	0.33	-	0.10*	-
PM10	-	-	-	-	0.12	-	0.05*	-
Ozone	0.20	0.1	0.14	0.07	-	-	0.10	0.04
Lead	-	-	-	-	-	-	0.0015**	-
* annual arithmetic mean **monthly average								

(Pollution Control Department, 2006)

2.2 SEM (Scanning electron microscope)

Radiological and Environmental Management, Purdue University (2008) give the details about the SEM. SEM stands for scanning electron microscope. The SEM is a microscope that uses electrons instead of light to form an image. Since their development in the early 1950's, scanning electron microscopes have developed new areas of study in the medical and physical science communities. The SEM has allowed researchers to examine a much bigger variety of specimens. The scanning electron microscope has many advantages over traditional microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today (Radiological and Environmental Management, Purdue University, 2008).
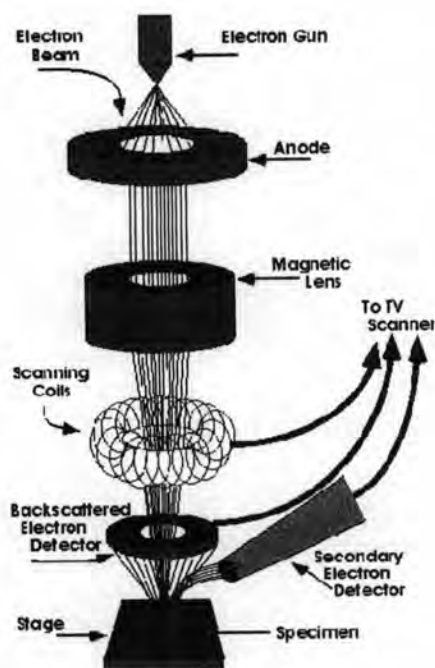
Figure 2.1 Diagram of scanning electron microscope (SEM)

(Radiological and Environmental Management, Purdue University, 2008)

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample (Radiological and Environmental Management, Purdue University, 2008)
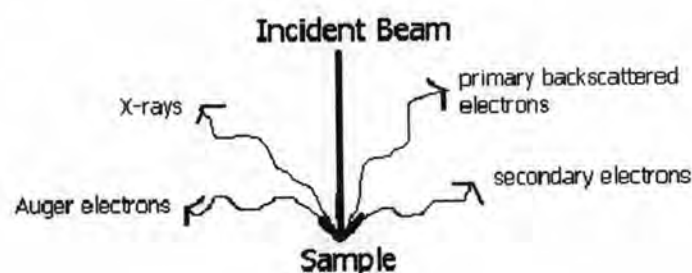

Figure 2.2 The electron beam

(Radiological and Environmental Management, Purdue University, 2008)

Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image. Sample preparation of the SEM utilizes vacuum conditions and uses electrons to form an image, special preparations must be done to the sample. All water must be removed from the samples because the water would vaporize in the vacuum. All metals are conductive and require no preparation before being used. All non-metals need to be made conductive by covering the sample with a thin layer of conductive material. This is done by using a device called a "sputter coater." The sputter coater uses an electric field and argon gas. The sample is placed in a small chamber that is at a vacuum. Argon gas and an electric field cause an electron to be removed from the argon, making the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions knock gold atoms from the surface of the gold foil. These gold atoms fall and settle

onto the surface of the sample producing a thin gold coating (Radiological and Environmental Management, Purdue University, 2008).

2.3 ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry)

Alloway and Ayres (1997) explain the finction of ICP-AES as the argon plasma that serves as an atomic excitation source is driven by a 40.68 MHz free-running RF generator, which sends an alternating current through water-cooled coils around the quartz torch (Figure 2.3) that supports the plasma. After initiation by sparks from a Tesla coil, the oscillating magnetic field around the coils accelerates electrons in the plasma and collisions with argon atoms cause further ionization. When recombination occurs, the emitted radiation raises temperatures and the geometry directs the plasma into a doughnut-shaped volume at 7000-9000 K. The system is supported by outer, intermediate and inner quartz tubes, which introduce argon into the torch. The inner tube carries the sample aerosol through a zone at c. 4000-5000 K, which ensures that solvent is stripped and atomization occurs prior to entering the viewing zone at 6000 K; at low-power operation this lies at 10-20 mm above the coil. The tangential outer flow serves to maintain and stabilize the plasma while thermally insulating the outer envelope. Gas flow through the intermediate tube is not essential to the operation of the torch, but is useful when the sample includes a high concentration of organic compounds. The conditions in the viewing zone are not suitable for AA spectroscopy and so emission is determined (ICP-OES). This has become a technique of first importance and has the advantages of:

1 speed, precision and simplicity of operation

2. intensity of emission is lineal and is not attenuated

3. freedom from matrix effects

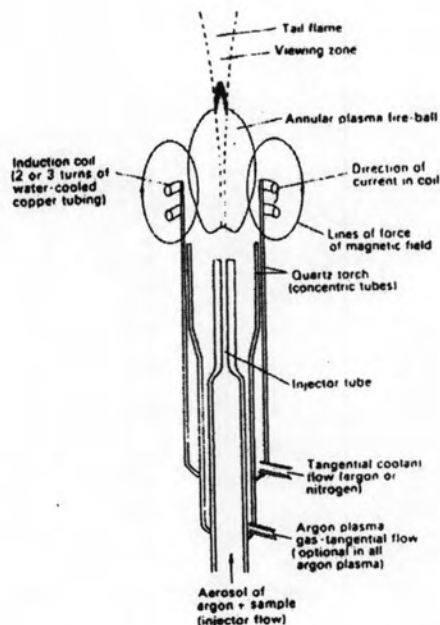4. refractory elements such as uranium and boron are atomized.

(Alloway and Ayres,1997)

Figure 2.3 Diagram of the inductively coupled plasma torch
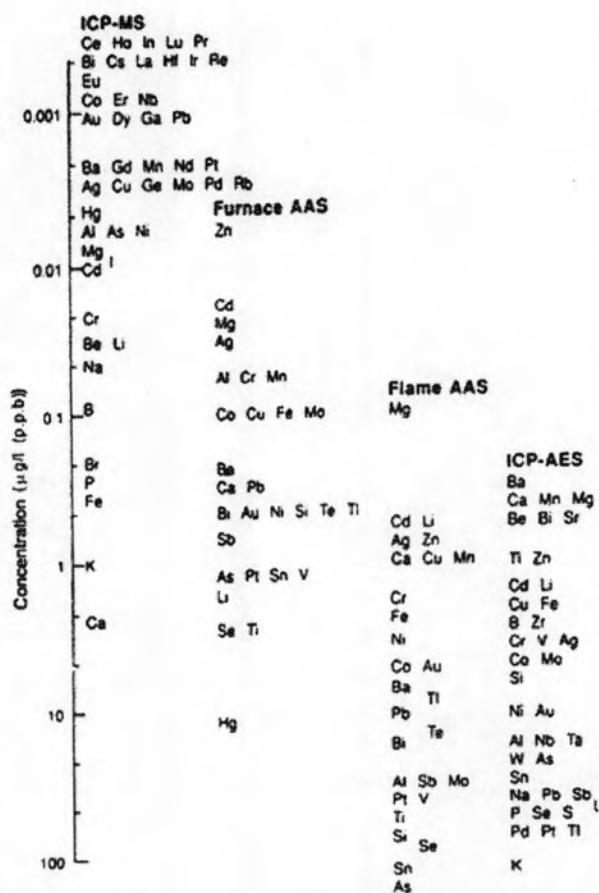
(Alloway and Ayres,1997)

Figure 2.4 Compares detection limits by various spectroscopic techniques

(Alloway and Ayres,1997)

The sample is introduced following formation of the aerosol by the more common gas nebulizer or else by ultrasonic nebulization. For general purposes, a Gem Tip cross-flow nebulizer is used, which resists HF and is not clogged, provided the solution contains less than 5% salts. For higher salt concentrations, a cone spray nebulizer is preferred, while for solution concentrations below 1 % a Meinhard type gives good sensitivity. Such low concentrations are necessary if the more expensive ultrasonic nebulizer is used, but as a result the sensitivity is increased by a factor of 10 to 50 for most elements compared with that of pneumatic nebulization. At the higher sensitivity, the use of a graphite furnace may be avoided (Alloway and Ayres, 1997).

The high excitation temperature results in spectra with many emission lines and interference may well result from other elements, especially those which aie line-rich. These include Fe, Co, Ni, V, Cr, Ti, W, Mo and rare earth elements; evaluation becomes most difficult when these are major components or when interference arises from elements such as Ca and Mg with intense emissions. In the absence of interference, one may select the most intense line from the tabulated literature, otherwise a compromise must be accepted and measurement becomes dependent on a weaker line in an emission window. For good performance, it is necessary to optimize the power input to the ICP, the gas flow rates and the observation height above the coil. These parameters will vary with both the type of nebulizer and the sample solvent (Alloway and Ayres, 1997).

Table 2.2 Typical ICP operating parameters

	Nebulization / sample solvent		
	Pneumatic/ aqueous	Ultrasonic/ aqueous	Pneumatic/ organic
RF power (kW)	1.1	1.2	1.5
Plasma argon flow (1/min)	15	15	15
Auxiliary argon flow	0.75	0.85	1.0
Nebulizer argon flow	0.5	0.5	0.7
Sample solution uptake (ml/min)	1.0	2.5	0.7
Observation height above coil (mm)	15	15	15

(Alloway and Ayres,1997)

The parameters will also vary somewhat from element to element and for different lines in the same spectrum. This presents no problem if individual elements are measured in sequence, but when analytes are determined simultaneously a compromise will again have to be accepted. Furthermore, ICP-OES is mainly used to determine many elements simultaneously, and in this event the recommended parameters for the Perkin Elmer Optima instrument are as given in Table 2.2 When calibrating instruments for simultaneous measurements, commercial standards are employed which contain the analytes at concentrations of about 500-1000 times their detection limits. It is usual to employ only one such standard for each analyte. The samples are mostly in 2-5% (by vol.) nitric or hydrochloric acid. Sulphuric and phosphoric acids are best avoided because many metals form insoluble sulphates and phosphates and clear, filtered, solutions need to be fed to the nebulizer (Alloway and Ayres, 1997).

2.4 Receptor Methods

Brook *et al.* (2004) describe the receptor methods as receptor methods for source attribution or apportionment include the interpretation of physical and chemical measurements of ambient particles and their precursors to infer possible or probable sources and to quantify contributions from these sources. Source attribution implies that individual PM emitters are identified (e.g., a specific power plant), while apportionment identifies general source types or categories (e.g., vehicle exhaust, fugitive dust) responsible for the observed PM. Receptor methods encompass a variety of observationally based techniques that use differences in chemical composition, particle size, and concentration patterns in space and time, as well as ratios among specific compounds (particles and/or gases), to identify source types and limiting precursors, and to quantify source contributions affecting particle mass concentrations, light extinction, or deposition. "Receptor models" are receptor methods that provide the theoretical and mathematical framework for quantifying source contributions. Receptor Model Types, such as the Chemical Mass Balance (CMB) model and its derivatives, are derived from the same physical principles as source models. Others, such as eigenvector analysis, are statistically based, showing associations between variables from which causative factors may be inferred (Brook, *et al.*, 2004).

Multivariate receptor models require a large number of PM samples with chemical characterization. These models derive information from the temporal and spatial variability in the chemical concentrations and inter-relationships between the different chemical concentrations. At least 50 samples are needed, and more than 100 samples from many locations and/or one location over a long time period are preferred, Samples should include high and low contributions from the suspected sources, usually requiring <24-hr averages. Sampling sites should be most densely located along strong concentration gradients for a pollutant or source. Network adequacy (Chow *et al.*, 2002) is not usually evident until after the measurements have been acquired.

2.4.1 Chemical Mass Balance

The CMB model expresses that the ambient chemical concentrations as the sum of products of species abundances and source contributions. These equations are solved for the source contributions when ambient concentrations and source profiles are supplied as model input. Source profiles consist of the mass fractions of selected particle properties in source emissions. The CMB is the only receptor air-quality model that calculates quantitative uncertainty values for source-contribution estimates. It provides the basic structure for other receptor models that can be derived from physical principles. The CMB model has been applied to evaluate PM control effectiveness (Chow *et al.*, 1990) determine causes of high concentrations (Schauer and Cass, 2000; Vega *et al.*, 1997), quantify contributions to light extinction and to estimate sources of particle deposition (Feeley and Liljestrand, 1983). Several different CMB solution methods have been applied, but the multivariate effective-variance, least- squares estimation method is most commonly used because it incorporates precision estimates for all of the input data into the solution and propagates these errors to the model outputs. The tracer solution, in which a single chemical component or particle property is used to represent a single source or source type, is also in common use, but source-contribution estimates are more uncertain than with the multivariate solution because they are highly dependent on the variability of the tracer-to-mass ratio. Artificial tracers (injected markers), such as rare-earth elements, sulfur hexafluoride, and halocarbon gases have been released with normal emissions and used in a CMB tracer solution to estimate contributions

from many sources using the same fuel and from individual emitters (Horvath *et al.*, 1988; Ondov *et al.*, 1992).

The accuracy and precision of CMB source-contribution estimates depend on the variability of chemical abundances in the source profiles. Source profiles should represent source compositions as they would be perceived at a receptor. Profiles are most often measured at the source, and changes that take place during transport are not realized. These "fresh" profiles do not account for secondary PM formation and particle volatilization that may take place from source to receptor. Source profiles also must contain several chemical components, which differ greatly in their abundances among different source types. Profiles often have not been measured on representative sources, or on enough different sources, to obtain reasonable estimates of profile variability. The propagated standard errors associated with CMB source-contribution estimates underestimate the true uncertainties of the apportionment in these cases. The CMB attempts to explain the ambient chemical concentrations selected for its calculation with the source profiles provided. Excessive differences between calculated and measured concentrations usually indicate that profiles are insufficient, or that a contributing profile is missing. It is the responsibility of the modeler, not the CMB model, to evaluate the CMB uncertainties and performance measures, along with other data such as emission inventories. This is all receptor- and source-oriented models as illustrated in Table 2.3 (Brook *et al.*, 2004).

Table 2.3 Summary of receptor model source-apportionment models

Receptor Model (Example Applications)	Data Requirements	Strengths	Weaknesses
Chemical Mass Balance	-Source and receptor measurements of stable aerosol properties that can distinguish source types. -Source profiles (mass abundances of	-Simple to use, software available. -Quantifies major primary source contributions with element, ion, and carbon measurements.	-Completely compatible source and receptor measurements are not commonly available. -Assumes all observed mass is due to the sources selected

	physical and chemical properties) that represent emissions pertinent to the study location and time. -Uncertainties that reflect measurement error in ambient concentrations and profile variability in source emissions. -Sampling periods and locations that represent the effect (e.g., high PM, poor visibility) and different spatial scales (e.g., source dominated, local, regional)	-Quantifies contributions from source sub-types with single particle and organic compound measurements. -Provides quantitative uncertainties on source contribution estimates based on input data uncertainties and colinearity of source profiles. -Has potential to quantify secondary SO_4 contributions from single sources with gas and particle profiles when profiles can be "aged" by chemical transformation models.	in advance, which involves some subjectivity. -Does not directly identify the presence of new or unknown sources. - Typically does not apportion secondary particle constituents to sources. Must be combined with profile aging model to estimate secondary aerosol. -Much colinearity among source contributions without more specific markers than elements, ions, and carbon.
Injected Marker CMB Tracer Solution	-Non-reactive marker(s) added to a single source or set of sources in a well-characterized quantity in relative to other emissions. Sulfur hexafluoride, perfluorocarbons,	-Simple, no software needed. -Definitively identifies presence or absence of material from release source(s). -Quantifies primary emissions	-Highly sensitive to ratio of marker to PM in source profile; this ratio can have high uncertainty. -Marker does not change with secondary aerosol formation — needs

	andrare earth elements have been used.	contributions from release source(s).	profile aging model to fully account for mass due to "spiked" source. -Apportions only sources with injected marker. -Costly and logistically challenging.
Enrichment Factor (EF)	-Inorganic or organic components or elemental ratios in a reference source (e.g., fugitive dust, sea salt, primary carbon). -Ambient measurements of same species.	-Simple, no software needed. -Indicates presence or absence of emitters. -Inexpensive. -Provides evidence of secondary PM formation and changes in source profiles between source and receptor.	-Semi-quantitative. More useful for source/process identification than for quantification.
Multiple Linear Regression (MLR)	-100 or more samples with marker species measurements at a receptor. -Minimal covariation among marker species due to common dispersion and transport.	-Operates without source profiles. -Abundance of marker species in source is determined by inverse of regression coefficient. -Apportions secondary PM to primary emitters when primary markers are	-Marker species must be from only the sources or source types examined. -Abundance of marker species in emissions is assumed constant with no variability -Limited to sources or source areas with markers. -Requires a large

		independent variables and secondary component $(e.g. SO_4^=)$ is dependent variable -Implemented by many statistical software packages.	number of measurements.
Eigenvector Analysis	-50 to 100 samples in space or time with source marker species measurements. -Knowledge of which species relate to which sources or source types. -Minimal covariation among marker species due to common dispersion and transport. -Some samples with and without contributing sources.	-Intends to derive source profiles from ambient measurements and as they would appear at the receptor. -Intends to relate secondary components to source via correlations with primary emissions in profiles. -Sensitive to the influence of unknown and/or minor sources.	-Most are based on statistical associations rather than a derivation from physical and chemical principles. -Many subjective rather than objective decisions and interpretations -Vectors or components are usually related to broad source types as opposed to specific categories or sources.
Time Series	-Sequential measurements of one or more chemical markers. -100s to 1000s of individual measurements.	-Shows spikes related to nearby source contributions. -Can be associated with highly variable wind directions. -Depending on sample duration,	-Does not quantify source contributions. -Requires continuous monitors. Filter methods are impractical.

		shows diurnal, day-to day, seasonal, and inter-annual changes in the presence of a source.	
Aerosol Evolution	-Emissions locations and rates. -Meteorological transport times and directions. -Meteorological conditions (e.g.. wet, dry) along transport pathways.	-Can be used parametrically to generate several profiles for typical transport/ meteoro logical situations that can be used in a CMB.	-Very data intensive. Input measurements are often unavailable. -Derives relative, rather than absolute, concentrations. -Level of complexity may not adequately represent profile transformations,
Aerosol Equilibrium	-Total (gas plus particle) SO_4^-, NO_3^-, NH_4^+ and possibly other alkaline or acidic species over periods with low temperature and relative humidity variability. -Temperature and relative humidity.	-Estimates partitioning between gas and particle phases for NH_3, HNO_3, and NH_4NO_3. -Allows evaluation of effects of precursor gas reductions on ammonium nitrate levels.	-Highly sensitive to T and RH. Short duration samples are not usually available, -Gas-phase equilibrium depends on particle size,which is not usually known in great detail. -Sensitivity to aerosol mixing state not understood/quantified.

(Brook *et al.*, 2004)

2.4.2 Factor Analysis

Karar *et al.* (2006) define the factor analysis as "multivariate analysis technique, factor analysis called principal component analysis (PCA) has been widely used to identify possible sources of ambient particles. Among multivariate techniques, PCA is often used as an exploratory tool to identify the major sources of air pollutant

emissions (Guo *et al.*, 2004). The great advantage of using PCA as a receptor model is that there is no need for a priority knowledge of emission inventories. Factor analysis is a statistical technique that can be applied to a set of variables in order to reduce their dimensionality.

In factor analysis, set of variables is first normalized as X_{it} as shown in Equation

(1) so that their variances are unity.

$$X_{it} = (C_{it} - C_i)/d_i \qquad (1)$$

where C_{it} is the concentration of the variable i in the sample t, C_i and d_i are the arithmetic mean and standard deviation of the variable i for all samples included in the analyses. These common factors are typically characterized as pollutant source types in air pollution studies. The factor analysis model applied in the field of air pollution is given in Equation (2).

$$X_{it} = \sum_{j=1}^{N} L_{ij} S_{jt} + E_{it} \qquad (2)$$

where L_{ij} is the factor loading of the variable i in the source j with N number of sources, S_{jt} is the factor score of the source j for sample t and E_{it} is the residual of variable i in the sample t not accounted by the j sources or factors.

The two vectors L and E are unknown in factor analysis (FA) and are obtained by assuming various covariance relationships between the vectors S and E and finally solving the covariance matrix as an eigenvalue-eigenvector decomposition problem. In this study, FA was carried out on seven toxic trace metals and PM. The factors that have been determined is rotated to transform the initial matrix to easily interpret. The sum of the eigen values is not affected by rotation but rotation will alter the eigenvalues of particular factors and will change the factor loadings.

The varimax rotation of the matrix was selected which attempts to minimize the number of heavy metals that have high loadings on a factor. This enhanced the interpretability of the factors. Unusual events or errors in sampling and analysis results in very high or very low values (outliers) of one or more variables. These outliers have to be removed before analysis to avoid propagation of errors, since they do not represent the normally observed situation (Kumar *et al.*, 2001).

Factor analysis determines factor F in such a way so as to explain as much of the total variation in the data as possible with as few of these factors as possible. In factor analysis, F_i is the ith factor as calculated by Equation (3).

$$F_i = \sum_{i=1}^{p} w_{ij}X_j = w_{i1}X_1 + w_{i2}X_2 + \cdots + w_{ip}X_p \qquad (3)$$

where the w's are the factor weights (to be estimated from the data) chosen so as to maximize the quantity and the X's are the original variables in standardized form.

The second factor F_2 is such that weighted linear combination of the variables which is uncorrelated with F_1 and which accounts for the maximum amount of the remaining total variation not already accounted for by F_1. The higher the factor weight for a given variable, the more that variable contributes to the overall factor score and the higher the factor loading. Higher factor loadings of particular element can help in identifying the possible sources (Henry *et al.*, 1984). The factors obtained are rotated to achieve the meaningful underlying vectors with more interpretability.

The former study investigate the seven toxic trace metals (Cr, Zn, Pb, Cd, Ni, Mn, and Fe) have been included for PCA with 45 number of samples. Henry *et al.* (1984) suggested that the minimum number of samples (n) for factor analysis should be such that n > 30 + (V + 3)/2, where V represents the number of variables. Several researchers have applied PCA study for identification of sources with limited number of elements. In Czech Republic performed PCA with only nine variables of toxic elements and identified possible emission sources. In another study by Banerjee (2003) in Delhi, India, an attempt has been made to define the possible origin of six toxic trace metals from street dust using Principal Component Analysis" (Karar *et al.*, 2006).

2.5 Anthropogenic sources of elements

The dominant anthropogenic sources of trace elements to the environment are believed to be oil, gasoline and coal combustion, smelting, and refuse incineration. These emissions and their worldwide import are relatively recent phenomena. As reported by Hong *et al.* (1997), Greenland ice cores dated for the period from 7,760 to 471 years ago showed no significant difference in cadmium and zinc content. Rock and soil dust and continental biogenic sources were the most important contributors to

natural zinc and cadmium in these ice cores. Metal working was performed by humans previous to 471 years ago, but the extent was only large enough to cause worldwide contamination with copper and lead. A recent investigation of deposition rates, employing Pb measurements, indicates that the overall deposition of metals has continued to increase over the last 150 years (Jensen, 1997).

Another consideration is the rapidity at which contaminant levels can increase in the environment. For example, wintertime lead in soils increased from 60 to 90 to 100 to 140 mg/kg in just 2 years after completion of a new roadway. Another example is the now widespread appearance of the fuel additive methyl-tert-butyl ether (MTBE) (Korte, 1999).

Elements that are particularly enriched by anthropogenic activities are cadmium, copper, nickel, lead, and zinc. For example, an investigation of floodplain surface soils in Germany revealed that lead and zinc contents are twice the preindustrial level, and copper is 1.5 times higher (Korte, 1999). Similarly, Chester *et al.* 1991 measured aerosols over the Indian Ocean and reported enrichment of zinc, lead, and cadmium especially, with some copper, nickel, vanadium, and chromium. One of the reasons these elements are so widely distributed by human activity is their high concentrations in power plant fly ash.

Many investigations have shown that the primary sources and sinks of anthropogenic elemental contamination reside in urban areas. Moyers *et al.* (1977) showed that airborne dust in Tucson, Arizona, was generated primarily from within the urban area and not undeveloped desert. Some study observed that lead was four times higher at the urban end, and copper and nickel were twice as high at the urban versus the rural end. Nevertheless, trace elements are distributed widely to less-polluted locales as a result of atmospheric deposition. For example, principal component analysis of trace element data from mosses determined that bismuth, lead, antimony, molybdenum, cadmium, vanadium, arsenic, zinc, thallium, mercury, and gallium were enriched in Norwegian soils because of long-range atmospheric transport (Berg *et al.*, 1995).

Motor Vehicles

Motor vehicles are such a major source of trace element contamination. Lead contamination has always been related to the automobile because of its former widespread use as an engine antiknock compound. Now that lead is not used so much

for this purpose, long-range transport of lead has apparently decreased. There are, however, a number of other elements emitted by motor vehicles (Table 2.4).

Table 2.4 Some Elements Found in Motor Oil

Element	Concentration, mg/L
Antimony	0.028 ±0.015
Bromine	0.098 ± 0.04
Chromium	0.31±0.16
Cobalt	0.031 ±0.012
Iron	11 ±5
Zinc	890 ±180

(Huang *et al.*, 1994)

The relatively high concentration shown in Table 2.4 illustrates why zinc is so widespread in the environment. Although the concentrations of the other elements are low, the quantities emitted to the environment are high because such an enormous amount of oil is used. Perhaps, any of the elements in Table 2.4 could be used to trace motor vehicle emissions. Barium also results from automobiles and has been suggested as a means of tracing vehicle emissions now that lead is being phased out (Monaci and Bargagli, 1997).

Road Dust

The considerable quantity of metals related to motor vehicles, many studies have looked at contamination near roads. As expected, values can be very high and typically correlate with the age of adjacent buildings and the nearby traffic volume (Tong, 1990). The latter study reported ~1,125 mg/kg of lead and ~600 mg/kg of copper in soil near a busy highway. In a nearby residential area, one-way streets or cul-de-sacs showed levels of lead near 887 mg/kg and copper of 378 mg/kg. Similarly, lead in residential soils in New Orleans, Louisiana, was related to urban geography with values >600 mg/kg in the inner city dropping to 150 to 300 mg/kg in outlying residential areas (Mieike, 1991).

Lee *et al.* (1997) used EFs to evaluate particles settling out along a roadway. They normalized the data to iron and reported EFs for lead (to 18), zinc (to

27), and cadmium (to 14). The upper limit that has been reported for road and house dust can be as much as one to two orders of magnitude larger than the median, especially for lead, copper, and zinc (Harrop et al.,1990).

Urban

Runoff metals are contributed to urban runoff primarily by vehicle emissions, tire wear, road salt, paints, and road dust. These sources increase with the amount of traffic and impervious cover in the area and can account for 40 to 70% of the metal input to a receiving stream (Bubb and Lester, 1991).

As with road dust, lead, zinc, and copper represent the major pollutant load in urban runoff. The mobility of these elements and Cd is enhanced when leached with sodium chloride applied as a de-icing salt (Norrstrom and Jacks, 1998). It should be illustrated that most of the data represent average values and that much higher concentrations have been reported. For example, zinc has, been reported in concentrations to almost 5,000 mg/kg (Korte, 1999).

High metal concentrations in suspended solids can result in significant dissolved concentrations as noted by Morrison et al. cited in Korte (1999) that the concentration of dissolved zinc in runoff from an urban area was approximately 0.16 to 0.23 mg/L. Ellis and Revitt (1982) also reported that zinc is relatively soluble in road dusts and gutter sediments. They found up to 1 mg/L in road dust leachate. Zinc's solubility is apparently a consequence of its ability to exist as carbonate and hydroxyl complexes in aerobic waters.

These investigators saw little arsenic, cadmium, mercury, nickel, antimony, or selenium and essentially no thallium and silver. Traces of antimony were observed only when copper and lead were very high. The latter observation illustrates the fact that rarer metals such as antimony, silver, and thallium and to some extent cadmium are usuall found only when the more common metals (copper, lead, and zinc) are present in very high concentrations (Korte, 1999).

House Dust

Fergusson and Kim (1991) reported that house dusts were enriched in lead, zinc, copper, cadmium, arsenic, antimony, chromium, calcium, sodium, gold, chlorine, and bromine and reported that the following elements have sources within the home: copper, cobalt, arsenic, antimony, zinc, cadmium, gold, chlorine, and lead.

Finally, it should be recognized that there can be a correlation to work activities. Construction workers, who often work in urban areas and are always exposed to motor vehicle emissions, were found to have lead concentrations of 220 to 640 mg/kg in their homes.

2.6 Source apportionment studies

Fang *et al*. (2002) studied on the ambient suspended particulate in Taichung, central Taiwan. Metallic species (Fe, Zn, Pb, Ni) were also analyzed in the study. The results showed that the concentrations of particulate mass are higher in the traffic site than the other sampling sites in this study. Also, the fine particle (PM2.5) concentration is the dominant species of the total suspended particles in Taichung, central Taiwan.

Kumar *et al*. (2001) studied on the source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India. In this study, very high concentration of suspended particulate matter (SPM) is observed at traffic junctions in India. Factor analysis-multiple regression (FA-MR), a receptor modelling technique has been used for quantitative apportionment of the sources contributing to the SPM at two traffic junctions (Sakinaka and Gandhinagar) in Mumbai, India. Varimax rotated factor analysis identified (qualitative) five possible sources; road dust, vehicular emissions, marine aerosols, metal industries and coal combustion. A quantitative estimation by FA-MR model indicated that road dust contributed to 41%, vehicular emissions to 15%, marine aerosols to 15%, metal industries to 6% and coal combustion to 6% of the SPM observed at Sakinaka traffic junction. Due to limitation in source marker elements analysed about 16% of the remaining SPM at these two traffic junctions could not be apportioned to any possible sources by this technique. Of the observed lead in the SPM, FA-MR apportioned 62% to vehicular emissions, 17% to road dust, 11% to metal industries, 7% to coal combustion and 3% to marine aerosols at Gandhinagar traffic junction and about a similar apportionment for lead in SPM at Sakinaka traffic junction.

Shah *et al.* (2006) studied on characterization, source identification and apportionment of selected metals in TSP in urban area at Islamabad, Pakistan. The purpose of his study is to understand the metal distribution characteristics in the atmosphere of urban Islamabad. Total suspended particulate (TSP) samples were collected on daily 12 h basis, at Quaid-i-Azam University campus, using high volume sampler. The TSP samples were treated with $HNO_3/HClO_4$ based wet digestion method for the quantification of eight selected metals; Fe, Zn, Pb, Mn, Cr, Co, Ni and Cd by FAAS method. The monitoring period ran from June 2001 to January 2002, with a total of 194 samples collected on cellulose filters. Effects of different meteorological conditions such as temperature, relative humidity, wind speed and wind direction on selected metal levels were interpreted by means of multivariate statistical approach. Enhanced metal levels for Fe (930 ng/m3), Zn (542 ng/m3) and Pb (210 ng/m3) were found on the mean scale while Mn, Cr, Co and Ni emerged as minor contributors. Statistical correlation study was also conducted and a strong correlation was observed between Pb-Cr (r = 0.611). The relative humidity showed some significant influence on atmospheric metal distribution while other meteorological parameters showed weak relationship with TSP metal levels. Regarding the origin of sources of heavy metals in TSP, the statistical procedure identified three source profiles; automobile emissions, industrial/metallurgical units, and natural soil dust. The metal levels were also compared with those reported for other parts of the world which showed that the metal levels in urban atmosphere of Islamabad are in exceedence than those of European industrial and urban sites while comparable with some Asian sites.

Salvador *et al.* (2004) identified and characterized sources of PM10 in Madrid (Spain) by statistical methods. In this study, the source apportionment was performed to characterize PM10 sources in the urban area of Madrid. Receptor modeling techniques were applied to obtain the different source contributions, identifying four main sources that contribute to most of the analyzed PM10 mass, namely: road traffic, crustal/mineral, secondary and marine aerosol. PM10 mean concentration and chemical profile were obtained for each source category by multilinear regression analysis. Road traffic was found to be the major contributor to the PM10 mass (48%), together with crustal (26%) and secondary particles (18%). A minor contribution has been associated to marine aerosol (3%), while 5% of the PM10 mass has been

attributed to non-identified sources. An analysis of the geographical origin was performed for remote sources. Residence time probability values were calculated based on air mass back trajectories information. Different elements have been selected as tracers of the sources. Desertic regions from North Africa have been identified as the most significant source area for crustal particles, with a high content of Al and Ti. Atlantic Ocean regions have been identified as weak to intermediate source areas of Na, supporting the marine source identified by the factor analysis. Then the influence of remote natural sources on the PM10 levels in central Spain has been detected by the use of single components as tracers, even at urban sites highly affected by traffic.

Lee and Hills (2003) conducted a research on cool season pollution episodes in Hong Kong during 1996–2002 and found that high concentrations of As, Mn, V, non-sea-salt sulphate and ammonium N on the episode days indicate the significant impact of fossil fuel burning, while enhanced Al, Ca, Fe and Mn concentrations show the effect of mineral dusts and crustal materials.

Sternbeck *et al.* (2002) studied metal emissions from road traffic in two heavily trafficked tunnels in Gothenburg, Sweden. Aerosol concentrations of larger particles and of several metals are apparently dominated by resuspended matter, rather than by emissions from vehicles. The vehicle-derived metals (Cu, Zn, Cd, Sb, Ba and Pb) mainly derive from wear rather than from combustion; Cu, Ba and Sb are probably dominated by brake wear. There are also indications that heavy duty vehicles are stronger emitters of Ba and Sb, but not of Cu, than light duty vehicles.

Hitchins *et al.* (2000) had shown that the exposure to submicrometer particles, particulate concentration is significantly higher within the investigated distance from 15 to 150m from a major road, when compared to the urban average exposure levels. Thus, the particulate problem is much more severe in roadside microenvironment.

Hussein *et al.* (2004) have previously investigated the daily, monthly and seasonal variations of the aerosol particle number size distributions in Helsinki during 1996–2003. The temporal variation of the particle number concentration showed good correlations with traffic activities. The highest total number concentrations were observed in Helsinki during workdays, especially on Fridays; and the lowest

concentrations occurred during weekends, especially on Sundays. Seasonally, the highest total number concentrations in Helsinki were observed during winter and spring, and the lowest number concentrations were observed during June and July.

Al-Masri *et al.* (2006) studied on the speciation of Pb, Cu and Zn determined by sequential extraction for identification of air pollution sources in Syria. Speciation of three trace elements (Zn, Pb, Cu) in air particulates of two Syrian cities (Tartous and Darya) with different climate conditions and industrial emissions had been studied. Approximately 60% of lead in air particulates of both cities was found to be associated with organic materials produced by incomplete burning of vehicles fuels and residential heating. Zinc was found (28–65%) collected in Tartous city, indicating that the Tartous cement factory and phosphate loading cargoes are the main source of emissions. In the Darya filters, zinc associated with organic materials (28–49%) was related to the presence of plastic molding industries and corroding car tires. In addition, copper was also found to (19–46%) in both cities in the summer periods, while 13–25% and 35% are associated with organic materials and silicates, respectively. Differences in chemical forms of the studied trace elements in air particulates were found to be related to differences in air pollution sources and differences in human behaviour throughout the year. Therefore, chemical fractionation of trace elements in air particulates using sequential leaching can be used for identification of air pollutions sources in urban and industrial areas.

2.7 Source apportionment and profiles inventory in Thailand

JICA(1991) studied on the atmospheric aerosol around Samutprakarn industrial district for the air quality planning in that area. Total suspended particulate matter (TSP) samples were collected by high volume and majority of the elemental composition was measured by neutron activation analysis. Lead (Pb) was determined by X-ray fluorescence and carbons were measured by thermal analysis. The soil and road dust were also investigated, and the chemical profiling is displayed in Table 2.6 The CMB model had been applied to estimate the contribution of emission sources of PM for the air quality planning in that area.

Table 2.5 The compositions of emission sources in Samutprakarm district (% mass)

Element	Soil	Road dust
EC	0.325	1.690
OC	0.100	0.060
Na	0.650	0.720
Al	5.550	5.000
K	3.150	2.100
Ca	0.175	2.600
Sc	0.00045	0.00045
TI	0.270	0.230
V	0.004	0.005
Cr	0.003	0.003
Mn	0.037	0.061
Fe	1.200	1.800
Ni	0.003	0.0025
Zn	0.002	0.0130
Se	0.001	0.0006
Br	0.002	0.0150
Sb	0.0002	0.0003
Pb	0.007	0.0130

(JICA,1991)

Radian (1998) studied on the particulate matter in Bangkok urban area. Samples were collected from four monitoring sites during two separate sampling periods (November 1995 and January 1996). A source apportionment using the CMB receptor model was done in the study. The Chemical Mass Balance (CMB) receptor model uses the chemical and physical characteristics of particles measured at the source and receptor to both identify the presence of and to quantify source contributions to pollutants measured at the receptor. The results are displayed in the Figure 2.5
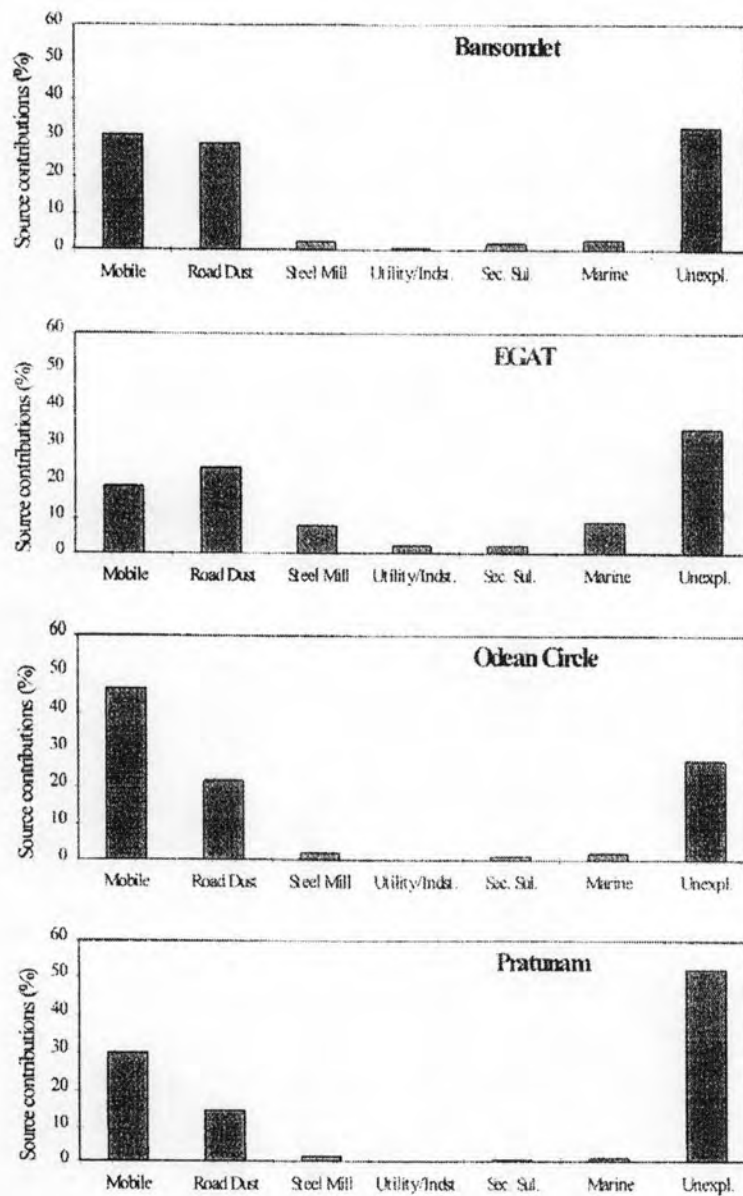
Figure 2.5 Average source contributions to TSP at four Bangkok sites

(Radian, 1998)

Wangkiat (2003) characterized the atmospheric aerosol in Mae Moh Thailand, and identified its sources using source apportionment. Thirty-one samples of PM10 were collected by Dichotomous air samplers during January-April 2001. Ambient samples were analysed by ICP-MS. The results showed that organic carbon and soluble potassium were highest in biomass burning aerosol. Of biomass burning samples, it was found that agricultural aerosol contained significantly high K. Truck

aerosol contained highest elemental carbon (EC). However, Earth's crust related samples (soil, road and fly ash) contained high amounts of Al, K, Mg, Ca. and Fe. Fine aerosol of stack samples contained high Na and Zn.

Tanguraiwan (2006) studied on mass concentrations and chemical compositions of particulate matter in atmosphere at Samutprakarn province. The result of ambient PM10 concentrations was showed that its depend on sources of particulate matter. The industrial, constructive, and traffic activities caused higher PM10 concentrations than agricultural activity. Furthermore, the PM10 concentrations in dry season were higher than rainy season. The average of PM10 mass concentration during dry season was 60.86 $\mu g/m^3$, whereas rainy season was 39.29 $\mu g/m^3$. It was decreased approximately 14-51% because of precipitation removal. From the study of chemical composition, the composition fractions of Na, Si, Fe, S, Cl. K, Zn, OC, EC, SO_4^{2-}, NO_3^-, Cl^-, Na^+, and K^+ were more than 1% of PM10 total mass. These might be occurred from industrial sources such as fuel burning or production process, vehicles, incineration, biomass burning, dust, and sea spray. This study also found that most of ambient PM10 of Samutprakarn province was originated from industrial activities.

Hongsresawat (2006) determined the apportionment of various pollution sources that affect the air quality of Samutprakarn province Thailand. Particulate matters were captured at four monitoring stations in 2005. Major possible sources for collected PM 10 particles were classified as marine aerosols, soil and road aerosols, motor-vehicle aerosols, industrial boiler aerosols, refuse-burning aerosols and biomass-burning aerosols. The calculated PM 10 source apportionment yielded soil and road aerosols 0 - 36.7%, motor-vehicle aerosols 0 - 32.9%, industrial boiler aerosols 14.9 - 61.6%, industrial-related aerosols 0 - 26.8%, marine aerosols 0 - 4.8%, and suspended aerosols from unknown sources. From CMB method, the resulted PM 10 source apportionment was road aerosols 0 - 25.0%, light diesel truck aerosols 0 - 12.1%, 4-cycle engine motorcycle aerosols 3.3 - 14.3%, refuse-burning aerosols 0 - 13.6%, biomass-burning aerosols 0 - 18.9%, oil fuel industrial boiler aerosols 0 - 29.0%, lignite coal fuel industrial boiler aerosols 0 - 17.3%, saw-dust fuel industrial boiler aerosols 0 - 4.7%, lumber industry aerosols 0 - 22.9%, ceramic industry aerosols 7.1 - 15.4%, steel industry 0 - 18.5%, and marine aerosols 2.8 - 4.7%.

Suwanthanee (2002) identified the contribution from TSP major sources in Bangkok Metropolitan Area using chemical mass balance and study TSP concentration variations in ambient and source contribution in northeast monsoon, southwest monsoon and all of the year 2002. The TSP was sampled at 4 stations. There were 8 major sources used in this model as follows, diesel vehicle and motorcycle emission, biomass burning, soil and road dust, marine aerosol, ammonium sulfate, sodium nitrate, heavy oil combustion and steel mill. The result showed that ambient 24-hour TSP concentrations in northeast monsoon were between 128-280 $\mu g/m^3$. Chemical mass balance receptor modeling showed source contribution as follows, diesel and motorcycle emission 17-41% (22-114 $\mu g/m^3$), biomass burning 33-43% (48-91$\mu g/m^3$), soil and road dust 2-5% (2-11 $\mu g/m^3$), marine aerosol 1-3% (2-4 $\mu g/m^3$), ammonium sulfate 4-10%(12-13 $\mu g/m^3$) and sodium nitrate 5-7% (8-15 $\mu g/m^3$). Heavy oil combustion and steel mill were not identified at any stations. Ambient 24-hour TSP concentrations in southwest monsoon were between 52-143 $\mu g/m^3$. Chemical mass balance receptor modeling showed source contribution as follows, diesel and motorcycle emission 18-35% (14-48 $\mu g/m^3$), biomass burning 19-40% (14-57 $\mu g/m^3$), soil and road dust 0.5-3% (1-2 $\mu g/m^3$), marine aerosol 4-17% (7-9$\mu g/m^3$), ammonium sulfate 1-3% (1-3 $\mu g/m^3$) and sodium nitrate 2-6% (2-5 $\mu g/m^3$), heavy oil combustion 3-11% (5-6 $\mu g/m^3$) and steel mill 3-10% (5-6 $\mu g/m^3$). The study also revealed that diesel and motorcycle emission was the most important source at Dindeang and Junkasem and biomass burning was the most important source at Bansomdet and Ratburana in northeast monsoon. Biomass burning and diesel and motorcycle emission were equally important sources at all stations in southwest monsoon. Moreover, it was also found that marine aerosol was the minor source.