1. INTRODUCTION

Lead has been an important metal in human societies over many thousands of years. Lead pipes for water supply was used from the period of the Roman Empire. However, the use of lead has increased dramatically since the early days of the industrial revolution. Some uses of lead are construction material for tank linings, piping, and other equipment handing corrosive gas and liquids used in the manufacture of sulfuric acid, petroleum refining, some processes of halogenation, sulfonation, extraction, and condensation. It can also be used for x-rays and atomic radiation protection; in the manufacture of tetraethyllead as an anti-knocking agent in anti- explosion engines; pigments for paints; bearing metal and alloys; storage batteries; in ceramics, plastics, and other electronic devices. Lead has also been used over the years as a glaze on pottery, in cosmetics and as sweetening wine [1].

While lead is an important factor and widely used in our daily life. On the other hand, lead is considered to be one of the most common toxic heavy metals in the environment. Mining, smelting and refining of lead, as well as the production and use of lead-based products give rise to release of lead into the environment: the air, surface water and deposit on the land. Through food , drinking water, air , as well as a number of other sources, people are exposed to lead, and affected by this toxic heavy metal.

The Global Environmental Monitoring System (GEMS), in which UNEP, UNESCO, WMO and WHO cooperate, concentrates on major environmental features of climate and long-range pollution. Air pollution monitoring under GEMS is carried out in 60 cities in 50 countries. Due to the toxicity and most common use, lead was ascribed to be one of the heavy metals under this program , which includes the assessment, through biological monitoring, of air, water and food quality, and of the effects on humans of exposure to organochlorine compounds and certain heavy metals [2].

1.1 Properties of lead and Analytical methods

1.1.1 Properties of lead

Lead is a heavy metal in the IV A group of the periodic table. The atomic number of lead is 82 and atomic mass is 207.2. The physical properties of lead is flexible, malleable, easily melted, cast rolled, and extruded. Its color ranges from bluish-white, silvery, and grayish. Lead can slightly dissolve in water but fairly dissolve in nitric acid and hot sulfuric acid. The density of lead is 11.34 g/cm^3 and melting point and boiling point are 327.4 °c and 1740 °c, respectively[3].

1.1.2 Analytical methods

For quantitative determination of lead in environmental and biological samples, following methods are applied: atomic absorption spectroscopy (AAS), optical emission spectroscopy, X-ray fluorescence (XRF), isotope dilution mass spectrometry (IDMS) , colorimetric or spectrophtometric analysis using dithizone, and electrochemical methods(voltammetry). The majority of these methods is restricted to the measurement of the total lead and cannot directly identify various compounds of lead.

For AAS, lead atoms in the sample must be vaporized either in a precisely controlled flame or in a furnace. Furnace system in AAS applying graphite tubes or cups offer a high sensitivity and the possibility to analyze small samples. AAS currently is the preferred method for routine lead analyses in environmental and biological specimens [4,5].

Optical emission spectroscopy is based on the measurement of light emitted by element when they are excited in an appropriate energy medium. The technique has been used to determine the lead content in soils, rocks, minerals, and airborne dusts at 5- 10 μg/g level. The primary advantage of the method is that it allows a simultaneous measurement a larger number of elements in small samples. More

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recent activities have focused attention on the inductively coupled plasma(ICP) system as a valuable means of excitation and analysis [6]. The ICP system offers a high degree of sensitivity with less analytical interference than other typical emission spectroscopy systems.

X-ray fluorescence also allows the simultaneous identification of several elements using a high energy irradiation source. The method is based on the principal that an intense electron beam, which is directed on a sample, produces several forms of radiation, including X-rays, the wavelengths of which depend on the elements present in the material, and their intensities depend on the relative quantities of these elements. The technique offers the advantage that the sample degradation can be kept to a minimum. It has been used, e.g., for the in vivo determination of lead in teeth and bones[7,8].

Isotopic dilution mass spectrometry (IDMS) is the most accurate measurement technique presently known. No other technique serves more reliably as a comparative reference technique. IDMS has been used for analysis of subnanogram concentrations of lead in variety of sample types. The isotopic composition of lead produced from ores of different origin has been used as a means of tracing the origin and distribution of anthropogenic lead[9].

Colorimetric analysis of lead using dithizone as the reagent is a "classical" method which has been used for many years. Prior to the development of the IDMS method, it frequently served as a reference method. Differential pulse polargraphy (DPP) and anodic stripping voltammetry (ASV) offer sufficient analysis sensitivity for most lead measurement in environmental and biological samples. Current practice with commercially available equipment allows lead analysis at subnanogram concentration with a precision of about 5-10% on a routine basis.

1.1.3 Problems of lead analysis in environmental samples

A major source of error in the determination of lead in environmental and biological samples is the secondary contamination, which can occur during sampling and analysis. Failure to recognize the source of contamination (collecting containers, reagents, labware, laboratory atmosphere, hand contact) may result in the artificially high analytical results. It is therefore important that emphasis is placed on a careful control(10,11,12). It should be mentioned that the US National Bureau of Standard (NBS), the International Atomic Energy Commission (IAEC) and some other organizations offer reference material with certified metal concentrations. In part, such material are also commercially available. These materials should be used to control the accuracy of any analytical procedure[13].

1.2 Toxicity of lead

1.2.1 Metabolism of lead in man

The movement of lead from ambient air to the bloodstream is a two-part process: deposition of some fraction of inhaled air lead in the deeper part of the respiratory tract and absorption of the deposited fraction. The deposition rate mainly is determined by the particle size distribution of the inhaled particles and the ventilation rate. For adult humans, the deposition rate of particulate airborne lead occurring in rural and urban atmospheres is about 30-50%. All of the lead deposited in the lower respiratory tract appears to be absorbed so that the overall absorption rate is governed by the deposited rate. Respiratory uptake via respiratory tract in children, while not fully quantifiable, seem to be comparatively greater on a body-weight basis[14,15].

Gastrointestinal absorption of lead mainly involves lead uptake from food, drinking water, and beverages as well as lead deposited in the upper respiratory tract and swallowed. It is also includes uptake of non-food materials such as dust and paint chips, which may be unwittingly ingested by young children due to their mouthing activity and pica habits. The lead gastrointestinal lead absorption in human adult has been determined to in the order of 10-15%. The rate can be significantly increased under fasting conditions to 45% compared to lead ingested with food. For children, the fraction absorbed is much higher than in adults, ranging up to 50% [16].

Absorption of inorganic lead compounds through the skin is much less significant than through the respiratory and gastrointestinal tract [17].

Lead absorbed into human body enters the bloodstream initially, and rapidly attaches itself to red blood cells. Lead in the blood takes a further rapid distribution between blood, extracellular fluid and other storage sites, such that only about half of the fresh absorbed lead is founded in the blood after only a few minutes. The storage site for lead probably is in soft tissue, as well as bone. There appears to be a steady accumulation of lead in bone throughout life that the amount entering long-term storage increasing with uptake of lead. There is also evidence that not all of lead is immobile. Some will be continuously re-entering the bloodstream. The lead that remains in the bloodstream is lost steadily through excretion. And it is the lead circulating in the bloodstream able to exert adverse effects on the body. Hence, the concentration of lead in the bloodstream is an important parameter in the characterization of an individual's exposure to lead and in the relationship between exposure and occurrence of adverse consequences.

1.2.2 Biological and adverse health effects of exposure to lead

Lead has many adverse physiological and biochemical effects, which generally are of a deleterious nature. No evidence has been presented for an essential function of lead in the metabolism of human and animals. The adverse effects involved the central nervous system, kidney, cardiovascular system, and other organs and tissues, virtually every system in the body.

Very severe lead exposure in human can cause coma, convulsions, and even death. It is particularly harmful to the developing brain and nervous system of fetuses and young children, and neural damage due to lead poisoning may be irreversible.

Over recent years, there has been mounting concern about more subtle chronic adverse effects to health at low level of exposure[18]. Lower lead levels cause adverse effects on the central nervous system, kidney, and hematopoietic system. Blood lead levels as low as 10 µg/dl, which do not cause distinctive symptoms, are associated with decreased intelligence and impaired neurobehavioral development[19; 20]. Many other effects begin at these low blood levels, including decreased stature, decreased hearing ability to maintain a steady posture. Lead's impairment of synthesis of the active metabolite 1, 25-$(OH)_2$ vitamin D is detectable at blood levels of 10-15 µg/dl. Some studies have suggested harmful effects at lower levels. As yet, no threshold has been identified for the harmful effects of lead [18].

1.3 Lead in environment: air, water, and soils

1.3.1 Lead in air

1.3.1.1 Sources of lead in air

Emissions of lead into the atmosphere were estimated by the US Environmental Protection Agency (EPA) for the year 1975. By far the greatest source is emission from vehicles burning leaded petrol[21] although the relative importance of this sources in the US may have diminished in recent years due to the progressive introduction of lead-free petrol, and in some other countries due to reduction of lead content of petrol. Emissions from the lead industry and fossil fuel combustion are important as a sources in air but on a more local scale than vehicle emission[1] .

Lead is added to gasoline as the organic tetraalkyllead additives i.e. tetramethyllead, tetraethyllead; and mixed alkyls i.e. triethylmethyllead, diethyldimethyllead and ethyltrimethyllead. There are no lead additives in diesel,

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kerosene(paraffin) or fuel oil. In 1973, the UK consumption of lead antiknock additives was 12000 tones per year[22]. Of this, about 70-75% is emitted from the exhaust as inorganic salts of lead, and about 1 % is emitted unchanged as tetraalkyllead. Evaporative loss of fuel from fuel tanks and carburetors also contribution to tetraalkyllead compounds to the atmosphere. The remaining 20-25% of the lead remains trapped in the exhaust system and engine oil.

Concentration of lead in vehicle exhaust gases are typically 2 000-10 000 $\mu g/m^3$. The quantity of inorganic lead emitted as a proportion of that consumed by the engine is highly dependent upon the driving mode[23]. The vast variation, from 5% during stable speed driving to almost 2 000% during rapid acceleration, is due to the deposition and subsequesquent resuspension of lead from the vehicle exhaust system. The emission of tetraalkyllead is also dependent upon driving model, with from <0.1 to 5 % of input lead emitted in this form.

The organic tetraalkyllead compounds are volatile and exit into the air in the vapor phase, while the inorganic salts are emitted as particles. The primary exhaust particles are approximately 0.015 μm in diameter, and these particles will be subject to rapid growth in the ambient air by coagulation with other particles [24]. The largest vehicle-emitted particles of 300-3 000 μm diameter are subject to rapid gravitational setting, while the 5-50 μm fraction also settles close to sources [25]. The smaller particles of < 5 μm have a far longer atmospheric lifetime, and it is mainly these particles which reach atmospheric sampling equipment, and which present the greatest hazard to health. The are eventually removed from the atmosphere by dry deposition upon surface and by precipitation scavenging processes known as rainout and washout.

1.3.1.2 Concentration of lead in the ambient air

There is no simple relation between the sources strength and ambient concentration of an atmosphere, since dispersion of pollutant between the source and receptors is a process dependent upon meteorological conditions and is hence very variable. For this reason, concentrations measured over a short time period at only one site may not be representative of ambient concentration in that region, and longer-term average concentrations measured at carefully selected sites are to be greatly preferred [1].

Industrial sources of lead are typically point sources of emission. Such sources give rise to a narrow plume of pollution, and hence considerable temporal variation in pollution levels are encountered dependent upon the wind direction.

By far the major proportion of vehicle-emitted lead in air is inorganic, and hence exists in the air in particulate form. The fate of particulate pollution is highly dependent upon the particle size. Particles of $> 10\ \mu m$ diameter are subject to significant sedimentation rates as a result of gravitational forces. Consequently their atmospheric lifetime is severely limited by the gravitational settling process. Particles of $< 10\ \mu m$ diameter are removed only relatively slowly from the atmosphere. Estimates of the atmospheric lifetime of lead aerosol range typically between 7 and 30 days. This time is sufficient for transport over thousands of kilometers and consequently even the most remote sites may experience pollution by inorganic lead. It is hence valuable to consider inorganic lead pollution under two headings: roadside, and urban (close to sources)and rural (remote from sources) pollution. Mean air concentrations were related to traffic volume and distance from the highway [26, 27, 28]. The magnitude of such pollution will, of course, depended upon the sources strength (traffic volume, concentration of lead in petrol, driving model) and the prevailing meteorological conditions.

In an urban area, there are two separate effects. In addition to the lead arising from a nearby road, an urban background of perhaps 0.5 -1 $\mu g\ /m^3$ of lead exists arising from the network of roads in the area. The effect of one particular highway becomes difficult to discern beyond about 100 m from the carriage way, and the lead concentration is best described in terms of emissions within the whole urban area[1].

1.3.2 Lead in water

Elevated levels of lead in water principally from industrial discharges, highway runoff and weathering process in areas of natural lead mineralization. Once the lead has entered a water body its mobility and distribution will be closely controlled by its chemical forms. These will alter according to the nature of the particular water body.

During its transport by water, the lead may interact detrimentally with the aquatic life. Furthermore, it will become available for abstraction into public water supplies. In both cases behaviour and effects will be determined by the chemistry of the lead.

1.3.3 Lead in soils

1.3.3.1 Sources of lead in soil

1.3.3.1.1 Parent materials

The parent geological materials from which soils are derived are important contributors of lead. In immature soils, the lead content often relates well to that in the parent material, but in more developed soils this relationship may be lost as pedogenetic factors influence the distribution of lead in the soil profile. Thus the mean level of lead mineralization, substantially elevated levels of lead may be found in some local soils.

1.3.3.1.2 Deposition of airborne lead.

Deposition includes dry deposition and wet deposition. Airborne lead is subject to dry deposition by two major mechanism. The first is that of gravitational settling, and this significant for all particles of > 10 μm , but rapid only for the very larger particles(>50 μm). The second mechanism, which applied to particles of all size but is of greatest importance for the smaller particles, is deposition onto surface due to impaction, and for the extremely small particles due to Brownian diffusion. Wet deposition of airborne lead is scavenging by precipitation, it is an efficient means of removing particulate pollutants from atmosphere.

1.3.3.1.3 Disposal of sewage sludge to land

Sewage sludge are the solids separated during the treatment of waste water. As produced by the sewage treatment works, they are comprised of more than 90% water, and sometimes, dried or filtered prior to disposal. In the sewage treatment process, 80-100% of the input lead is typically incorporated in the sludge, along with other heavy metals present in the raw sludge. These sludge are rich in nitrogen and phosphorus, and so as to make use of these important plant nutrients and to ease the problems of sludge disposal, considerable volume of sludge are currently spread on the land.

1.3.3.2. Concentration of lead in soil

Lead in dust is considered to be one of the major sources of exposure that is probably highly significant for children living in central urban area and near smelter due to hand contamination and repetitive mouthing[29,30].

Mean concentration of lead in unpolluted soils relate closely to concentration in the parent geological material. In non-mineralization(most area, in practice) areas, concentrations of lead range from 2 to 200 mg/kg with most samples being in the range of 5 to 25 mg/kg [31]. Concentrations in excess of these are generally indicative of lead pollution or mineralization

Since soils are strong accumulators of lead, the analysis of lead in soil is an excellent indicator of accumulated deposition in the vicinity of a source of the metal. There have been numerous reports on the concentration of lead in the roadside soils.

Deposited lead is normally restricted to the first few centimeters of an undisturbed soil [32].

1.4 Rationale and Aim of the study

Pollution of lead was an inevitable byproduction of the development of the lead industry and with lead used as antiknock additives in the motor vehicles, the problem exacerbated. People are simultaneously exposed in varying degrees to lead in food, drink and air, as well as a number of other sources.

In the past decades, research on lead pollution has been expanded to look at the effects of the lead petrol pollution. Although non-lead petrol has already been used instead of lead-petrol in some developed countries, but at the present time lead-petrol is still used in most developing countries.

In Thailand, transportation system developed very fast in the past years. The number of motor vehicles in Thailand increased more than 10 times in 1990 than that in 1970[33]. Air pollution in some urban area became quite serious, especially in Bangkok. Thai government firstly started to control lead pollution by reducing the content of lead in regular gasoline from 0.84 to 0.45 g/L in 1984. Started from 1992, lead content in regular and premium gasoline was reduces to be 0.15 g/L, at the same time started using unleaded gasoline for premium gasoline. From January 1, 1996, all gasoline used in Thailand were changed to be completely leaded-free .

Chiang Mai is the biggest city in northern Thailand. During the period of time 1990 -1995, the average increased numbers of motor vehicles were 2,650 cars; 8,625 vans and trucks; and 18,497 motorcycles per year in Chiang Mai province and in 1995, the total numbers of vehicles reached 38,696 cars; 81, 134 vans and trucks; and 328,969 motorcycles. Therefore, in 1995, there were approximately 36 persons for one car, 17 persons for one van or truck, and 4.2 persons for one motorcycle; or about 3 persons for one motor vehicle in Chiang Mai Province. However, the number

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of persons per vehicle ratio in the urban area of Chiang Mai may be even higher and the number of vehicles is keeping increasing.

The present study was carried out in such areas with rather high number of motor vehicles and fairly heavy traffic volume. During such a period of time leaded gasoline leaded gasoline was going to be completely phased out. The aim of present study was to investigate the lead levels in roadside dusts as well as the levels of airborne lead and airborne suspended particulate matters in the atmosphere of Chiang Mai City. The present study was also to find out the relation between monitoring of lead and dust in the air using mask filter and the traditional method employed high volume air sampler.

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