LEAD DISTRIBUTION AND ITS POTENTIAL ENVIRONMENTAL RISKS DERIVED FROM A BATTERY RECYCLING PLANT

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Thesis

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Naruemol Jongkolrat

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LEAD DISTRIBUTION AND ITS POTENTIAL ENVIRONMENTAL RISKS DERIVED FROM A BATTERY RECYCLING PLANT

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ABSTRACT

Lead contaminations were assessed in the environment in the vicinity of a battery recycling plant in Saraburi Province, Thailand. Lead concentrations were determined in soil, sediment and plant samples to investigate potential environmental risks within a radius of 1 km from the plant using the hazard quotient equation (HQ).

The results revealed that lead contaminations in the soil decreased with increasing distance from the battery recycling plant (r^2=0.73, $p<0.001$). High lead contaminations were found within distances of 50 m from the plant. The concentrations of lead in soil collected in all transect lines with distances of 50, 100 and 250 m from the battery recycling plant exceeded background value ($p<0.001$, $p<0.01$ and $p<0.005$, respectively). Then, lead concentrations decreased to the background level at stations located farther than 500 m distance away ($P<0.05$).

Lead concentrations in sediment collected downstream from the effluent discharge point (625-18,621 mg/kg dw) were much higher than those collected upstream (29-174 mg/kg dw), and gradually decreased with distance.

In addition, lead concentrations in most of plant samples from contaminated areas (18-1,601 mg/kg dw) were much higher than those from uncontaminated areas (0.01-10 mg/kg dw). As the maximum allowance of lead contamination in grass utilized for grazing animal consumption is only 7 mg/kg dw, these lead contaminations might affect to health of animals in this area, and consequently enter to food chain through human consumption of meat and dairy products. For potential environmental risks consideration, HQ values in soil samples at a radius of 50 m and an area about 100 m northward from the plant were in the range of 1.4 to 17.5. Also, HQ values in sediments and edible plants collected in the vicinity of the battery recycling plant were in the range of 1.7 to 186.2 and 3.6 to 228.7, respectively. These HQ results indicate potential environmental risks in the study area.

It can then be concluded that lead has been distributed from the battery recycling plant and has contaminated soils, sediments and plants in its vicinity.

KEY WORDS: LEAD / BATTERY RECYCLING PLANT/ POTENTIAL ENVIRONMENTAL RISK

133 pp.

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การกระจายตัวของตะกั่วจากโรงงานหลอมตะกั่วจากแบตเตอรี่เก่าและศักยภาพความเสี่ยงทางสิ่งแวดล้อม (LEAD DISTRIBUTION AND ITS POTENTIAL ENVIRONMENTAL RISKS DERIVED FROM A BATTERY RECYCLING PLANT)

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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อประเมินการปนเปื้อนของตะกั่วในบริเวณรอบโรงงานหลอมตะกั่วจากแบตเตอรี่เก่าของจังหวัดสระบุรี โดยการเก็บตัวอย่าง ดิน, ดินตะกอน และพืช ในรัศมี 1 กิโลเมตรรอบโรงงานเพื่อประเมินความเสี่ยงทางสิ่งแวดล้อมโดยใช้สมการ Hazard Quotient (HQ)

ผลการศึกษาพบว่าระดับการปนเปื้อนตะกั่วในดิน ลดลงตามระยะห่างจากโรงงาน (r^2 = 0.73, $p<0.001$) โดยมีระดับการปนเปื้อนค่อนข้างสูงในตัวอย่างดินที่จุดเก็บห่างจากโรงงาน 50 เมตร ทั้งนี้ปริมาณการปนเปื้อนของตะกั่วที่พบในตัวอย่างดินทั้ง 5 แนวทิศรอบโรงงานที่ระยะทาง 50 , 100 และ 250 เมตรจากโรงงาน มีระดับสูงกว่าในดินตามธรรมชาติปกติ ($p<0.001$, $p<0.01$, $p<0.005$, ตามลำดับ) และมีค่าเริ่มใกล้เคียงกับตัวอย่างดินในธรรมชาติปกติที่จุดเก็บห่างจากโรงงานมากกว่า 500 เมตร ($p>0.05$)

สำหรับตัวอย่างดินตะกอนจากทางระบายน้ำหน้าโรงงาน พบว่าปริมาณตะกั่วในตัวอย่างจากจุดเก็บบริเวณใต้จุดปล่อยน้ำทิ้ง (625-18,621 มิลลิกรัม/ กิโลกรัม น้ำหนักแห้ง) มีระดับสูงกว่าตัวอย่างจากจุดเก็บบริเวณเหนือจุดปล่อยน้ำทิ้ง (29-174 มิลลิกรัม/ กิโลกรัม น้ำหนักแห้ง) ค่อนข้างมากและปริมาณตะกั่วในตัวอย่างดินตะกอนมีระดับลดลงตามระยะห่างจากโรงงาน

นอกจากนี้พบว่าปริมาณตะกั่วในพืชที่เจริญอยู่ในบริเวณที่มีการปนเปื้อน (18-1,601 มิลลิกรัม/ กิโลกรัม น้ำหนักแห้ง) มีระดับที่สูงกว่าพืชทั่วไป (0.01-10 มิลลิกรัม/ กิโลกรัม น้ำหนักแห้ง) และอาจส่งผลกระทบต่อสุขภาพสัตว์กินพืชในบริเวณนั้นได้เนื่องจากค่าสูงสุดที่ยอมให้ตะกั่วปนเปื้อนในพืชมีค่าไม่เกิน 7 มิลลิกรัม/ กิโลกรัม น้ำหนักแห้ง และตะกั่วยังอาจปนเปื้อนเข้าสู่ห่วงโซ่อาหารของมนุษย์ที่กินเนื้อสัตว์หรือผลิตภัณฑ์จากสัตว์ดังกล่าวได้ สำหรับการประเมินความเสี่ยงทางสิ่งแวดล้อมพบว่าดินที่จุดเก็บห่างจากโรงงาน 50 เมตรทุกทิศทางและจุดเก็บที่ห่างจากโรงงาน 100 เมตรด้านทิศเหนือมีระดับความเสี่ยงทางสิ่งแวดล้อมสูงกว่าค่าที่ยอมรับได้ 1.4–17.5 เท่า ส่วนดินตะกอนและพืชบริเวณใกล้โรงงานมีระดับความเสี่ยงทางสิ่งแวดล้อมสูงกว่าค่าที่ยอมรับได้ 1.7–186.2 และ 3.6–228.7 เท่า ตามลำดับ แสดงให้เห็นว่าพื้นที่บริเวณรอบโรงงานนี้มีความเสี่ยงทางสิ่งแวดล้อมจากการปนเปื้อนของตะกั่ว

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LIST OF ABBREVIATIONS

CEC	=	Cation Exchange Capacity
cm	=	Centimeter
DIW	=	Department of Industrial Works
dw	=	Dry weight
km	=	Kilometer
m	=	Meter
mm	=	Millimeter
OM	=	Organic matter
Pb	=	Lead
PCD	=	Pollution Control Department
US EPA	=	United States Environmental Protection Agency

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CHAPTER I
INTRODUCTION

1.1 Statement of the Problem

For many years, lead has been extracted from ores for many purposes of use and more than half of these are used for battery production. Other major uses include semi-finished sheet metal and pipes, alloys, cable sheathing, additives in gasoline and other compounds, and ammunition. The largest use of lead about 90% in Thailand total goes to automotive and industrial lead acid battery. Nowadays, lack of considerable lead resources cause amount of lead from ores is not enough for use in lead production. So, more than 80 % of lead produced in Thailand is recycled from scrap automobile batteries.

In the western world today lead is produced by recycling more than by mining. Recycling is important for waste management, because it generally saves money, resources and energy. Lead is recycled because it is easy to collect and requires less energy than extracting primary metal from its ore. However, recycling of lead gives rise to some environmental problems, mainly air pollution due to the emission of sulfur dioxide and chloridized fumes and lead discharges (Lave et al., 1996). The battery recycling processes can potentially harm people and the environment in local areas and frequently situated close to human settlements. The battery recycling plants are well known to create pollution problem including transportation, workplace and ambient air emissions, storage and handling of scrap batteries, slag disposal and wastewater discharge. In lead smelting industries, the main hazard are the lead dust produced during the crushing and dry grinding operations, lead fumes and lead oxide during furnace reduction and refining.

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Lead is recognized as one of the most toxic heavy metals in the environment. Like other heavy metals, it is stable and persistent environmental contaminant because it cannot be degraded or destroyed. Therefore, it tends to accumulate in different environmental media such as soils, seawater, fresh water and sediments. Excessive levels of lead are known to have adverse effects on the natural environment and human health. It has various effects on human nervous and circulatory systems especially, it is harmful to young children even at low concentrations (ICPS, 1995).

Several studies showed that pollution in the surroundings of lead smelters had been severe enough to produce an increase in the intake of lead by people living nearby. Areas near lead smelting establishments may be enriched by aerial deposition of particles. As a consequence, soil pollution and quality deterioration of edible portions of vegetation can be produce due to metal enrichment. In Thailand, lead contaminations become severe in certain areas, especially from small to medium industry of smelter factories. A drastic increase of lead concentration on the surface soils to the range of 1,500-7,000 mg/kg was observed within 1-2 km surrounding those factories less than ten year operating (Parkpian, 1999).

In this study, battery recycling plant has been operated twenty years more and is located very close to residential areas and grazing animal farms. As the results, the migration of lead off site is of major concern for the people and ecological systems located within the possible contamination area incase of inadequate environmental management practices. Thus surface soils, sediments and plants were used to establish the lead distribution in vicinity of the battery recycling plant as well as to assess the current levels of lead contamination that might be potential hazards. The results of this study can then be used to prevent pollution from the future operations.

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1.2 Research Objectives

1.2.1 General objective

The aims of the study were to evaluate the lead distribution and its potential environmental risks focusing on lead in surface soils and sediments in the vicinity of the battery recycling plant in Saraburi Province.

1.2.2 Specific objectives

1.2.2.1 To determine the levels of lead concentrations in surface soils around the battery recycling plant and vicinity area.

1.2.2.2 To determine the levels of lead concentrations in sediments along the drainage system adjacent to the battery recycling plant.

1.2.2.3 To evaluate potential environmental risks of lead in surface soils and sediments around the battery recycling plant using hazard quotient equation (HQ).

1.3 Research Hypotheses

1.3.1 The lead concentrations in soils decrease as the distances from the battery recycling plant increase.

1.3.2 The lead concentrations in sediments at the stations downward from the effluent discharge point decrease as increasing distance away from the battery recycling plant.

1.4 Scope of the Study

The battery recycling plant in this study is located in Saraburi province, in Central Region of Thailand, and was selected as the source of lead contamination. The study area is within radius around 1 km in the vicinity of the battery recycling plant including both residential areas and grazing animal farms. Surface soils, sediments and plants were used to establish the extent of the contaminated area around the battery recycling plant. The uncontaminated locations in the remote area with the same soil

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characteristic as the contaminated site were used as background/reference sites in this study. The samples were collected in both wet season (August to September 2006) and dry season (February 2007).

1.5 Definition of Keywords

1.5.1 Secondary lead smelter means any plant or factory in which lead-bearing scrap or lead-bearing materials, other than lead-bearing concentrates (ores) derived from a mining operation, is processed by metallurgical or chemical methods into refined lead, lead alloys or lead oxide.

1.5.2 Lead smelting means a high-temperature metallurgical process in which lead concentrates and fluxes such as silica and limestone are processed in one or more steps to separate molten metal from a calcium/iron silicate slag containing impurities.

1.5.3 Lead-acid battery means any battery with a capacity of six or more volts which contains lead and sulfuric acid and which is used as a power source in a vehicle.

1.5.4 Contaminated site means a site at which hazardous substances occur at concentrations above background levels and where assessment indicates it poses, or is likely to pose an immediate or long-term hazard to human health or the environment.

1.5.5 Background/reference site means a site at which naturally occurring substances are present in environmental medium as a results of natural geologic process, not influenced by the site contamination and should have the same basic characteristics as the site sample.

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1.6 Conceptual Framework

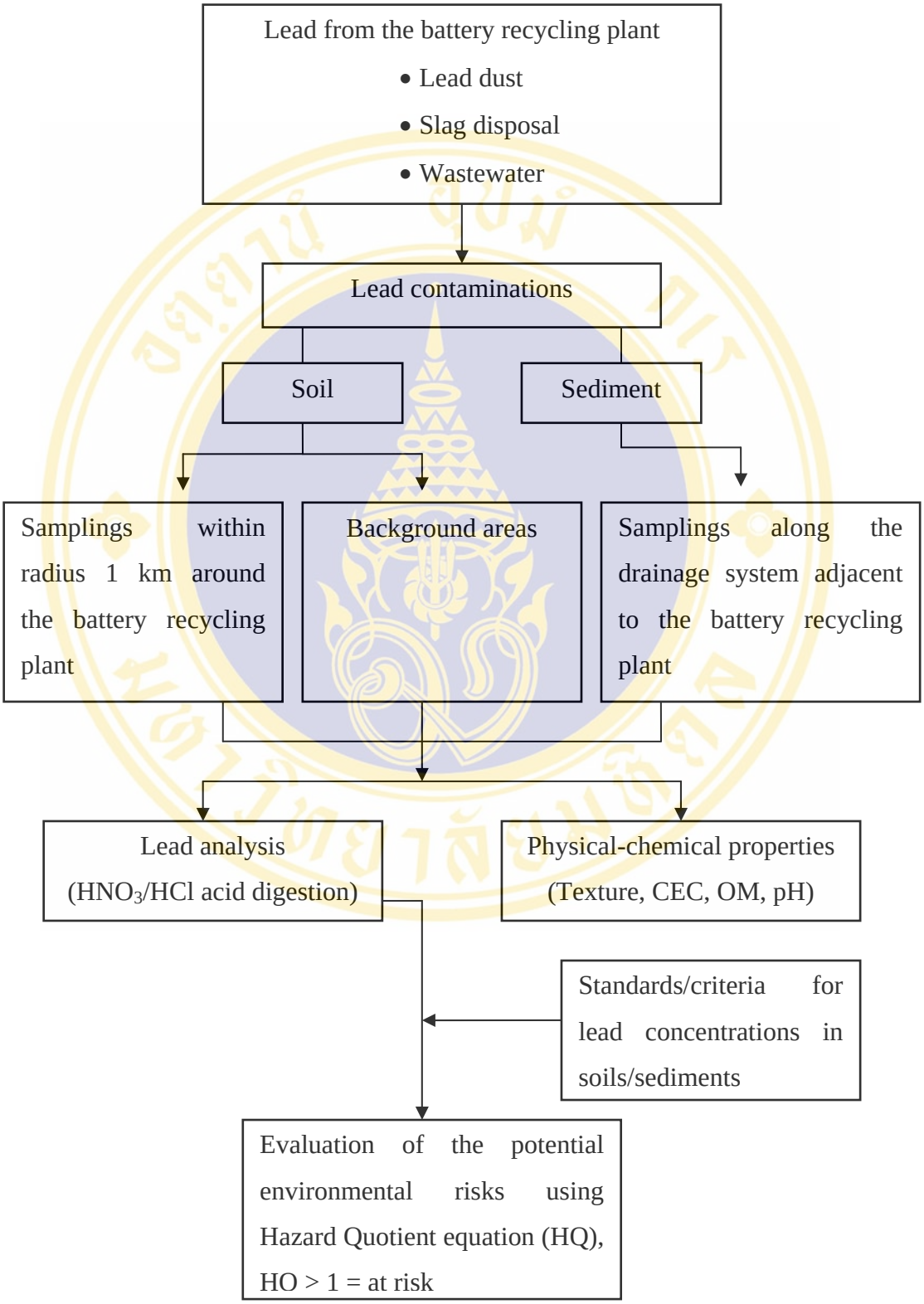

Figure 1.1 Conceptual framework

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CHAPTER II
LITERATURE REVIEWS

2.1 Lead Properties

2.1.1 Physical properties

Lead is an element in a member of group 14 (IVA) of the periodic table. Lead is a bluish-white lustrous metal that occurs naturally in the environment as well as being produced by variety of human activities. Lead possesses the general physical properties of metals; it is a conductor of electricity and heat, has a metallic luster, albeit a dull one, and has high density. It has a very low melting point, compared with most other metals and different isotopes exist in nature. The physical properties of lead were shown in Table 2.1.

Table 2.1 The physical properties of lead

Properties	Lead
Density (g/cm^3)	11.34
Melting point (^oC)	327.5
Boiling point (^oC)	1,750
Atomic number	82
Atomic weight	207.19
Isotopes	^{208}Pb, ^{206}Pb, ^{207}Pb, ^{204}Pb

Source: ATSDR (2005)

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2.1.2 Chemical properties

Lead exists in three oxidation states: Pb(0), Pb(II) and Pb(IV). Metallic lead, Pb(0) exists in nature, but its occurrence is rare. In the environment, lead primarily exists as Pb(II). Lead most commonly occurs as the mineral galena (PbS), and is sometimes found in other mineral forms, which are of lesser commercial importance, such as anglesite ($PbSO_4$) and cerussite ($PbCO_{3)}$. Pb(IV) is only formed under extremely oxidizing conditions and inorganic Pb(IV) compounds are not found under ordinary environmental conditions. While organolead chemistry is dominated by the tetravalent (+4) oxidation state (ATSDR, 2005).

Lead is excellent corrosion resistance in the environment. When exposed to air and water, films of lead sulfate, lead oxides, and lead carbonates are formed; these films act as a protective barrier that slows or halts corrosion of the underlying metal. Lead is amphoteric, forming plumbous and plumbic salts in acid and plumbites and plumbates in alkali (King and Ramachandrian, 1995; ATSDR, 2005).

2.2 Application of Lead

In Thailand lead application was about 135,500 tons/year for many purposes of use and the major uses of lead are lead metal and lead compounds (Yanyongsawat, 2005). Present uses of lead metal and lead compounds are:

2.2.1 Lead metal

(1) Lead-acid storage batteries

The manufacture of electric storage batteries is responsible for the largest consumption of lead about 90% of total lead. This industry uses both metallic lead in the form of a lead-antimony alloy and lead oxides in about equal proportions. The metallic lead is in the grids and lugs.

(2) Constructional uses

Lead piping is now a minor application, as it is no longer used for domestic water supplies because of concerns that lead slowly dissolves in soft water and may pose a risk to health and because of improvements in alternative materials. New lead pipes are used in the chemical industry. Lead sheet is widely used on roofs

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for flashings and weatherproofings, and is often used for complete roofs on both historic and modern buildings.

(3) Cable sheathing

Lead sheaths are used to protect underwater and some underground power cables. This is now a minor application of lead.

(4) Radiation screening

Lead is the most effective of the commonly available materials for screening from X-rays and some other types of radiation. It is widely used in hospitals as part of X-ray equipment and also in nuclear power stations.

(5) Lead alloys

Lead-tin solder is widely used, particularly by the electronics industry. Small additions of lead are made to some steels, brasses and bronzes to improve machinability.

(6) Miscellaneous products

Lead is widely used in shot and other munitions. Some alternatives are available, and are used in situations where lead poses a particular risk to wildlife, especially to birds, as a result of ingestion. Lead is also used extensively in weighting application.

2.2.2 Compounds of lead

(1) Batteries

This is a major use of lead oxide. Lead dioxide is pasted on to the battery grids and is the active material in the electrochemical reaction.

(2) Pigments and other paint additives

Lead compounds were widely used until a few decades ago. They have been replaced in certain applications following concerns about potential impacts to human health. Leaded paints are still used in specialized outdoor applications as coatings for commercial vehicles and other industrial applications because of excellent rust-proofing properties. Lead dryers are still used in alkyd-based air drying paints as very efficient and cost effective through-dryers.

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(3) Glasses and glazes

Lead additions improve the appearance and cutting properties of crystal glass. Small additions are also made to optical and electrical glass. The major application of leaded glass is in television screens and computer monitors, to protect viewers from the harmful X-rays generated by these appliances. Lead containing glazes are used for some pottery, tiles and tableware.

(4) Functional ceramics

Lead titanates/zirconates are used in the electronics industry in various functions.

(5) Additions to PVC

Small additions of organic lead compounds to some grades of PVC improve durability and heat resistance, both in manufacture and in service.

2.3 Sources of Lead in the Environment

2.3.1 Natural sources

In the natural cycle, lead is released to the earth's surface through a variety of processes that include weathering of rocks, volcanic activity, and uptake and subsequent release by plants. The weathering of rocks releases lead to soils and aquatic systems. This process plays a significant role in the global lead cycle, but only rarely results in elevated concentrations in any environmental compartment.

(1) Lithosphere/Geosphere

Lead, like all other metals, occurs naturally in small concentrations in all rocks and soils. Lead is naturally present in all soils generally in the range of 15 to 40 mg/kg. Its average concentration in the Earth’s crust is estimated to be approximately 16 mg/kg (Thornton, 1995), though it is not evenly distributed. Natural weathering processes, such as abrasion and attack by water and air, slowly break down the rock into grits, sand and eventually finer particles, and biological activity assists in the transformation of the resulting particles into soil.

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(2) Hydrosphere

Natural waters can dissolve minerals from soils and rocks. Concentrations of lead in river waters are dependent on local inputs as residence times are short. However, unlike some other elements, such as cadmium and arsenic, most lead compounds have low solubilities in water, and high concentrations of lead in water are rare. However, they can occur in acidic drainage from mine wastes (Alloway and Ayres, 1997), in areas of lead mineralisation, rivers can contain as much as ten times more lead than in unmineralised areas.

(3) Atmosphere

Dusts and vapors of metals can enter the air from natural as well as man made processes. It has been estimated that global natural emissions of lead to the atmosphere are in the range of 18.6 to 29.5 million kg per year. Out of this, 60-85% is believed to be windblown material, 5-10% from vegetation, and the remainder from volcanoes, sea spray and meteorites (Nriagu and Pacyna, 1988; Thornton, 1995). These amounts are small compared to the historical anthropogenic flux of lead in the atmosphere.

2.3.2 Anthropogenic sources

Human activities remove lead from the earth's crust and transfer it to environmental media, where it’s potential for resulting in both human and ecosystem exposure is greatly increased. While uses of lead have been known since ancient times, industrialization has vastly accelerated its transport into human and environmental exposure pathways.

(1) Lead derived from vehicle exhausts

The development of lead fuel additives in the 1920s and the increasing use of the automobile greatly escalated the rate at which lead was released to the atmosphere. The majority of lead emissions occur following the combustion of leaded gasoline in the engine, although some lead is also released with gasoline vapors during refueling. But now, the amount of lead emitted from this source has decreased because lower given the reduction in the use of tetraethyl lead.

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(2) Lead derived from agricultural material

Agricultural practices constitute very important non-point sources of lead that make significant contributions to their total concentrations in soil in many parts of the world, especially in regions of intensive farming. The main sources are: impurities in fertilizers, sewage sludge, manure from intensive animal production, pesticides and refuse derived composts (not widely used in agriculture). Most agriculture and horticultural soil in technologically advanced countries are regularly amended with fertilizer and many also receive organic manure and lime. The typical lead concentrations found in these materials are given in Table 2.2 where it can be seen that phosphate fertilizer, lime and refuse-derived composts can be important source of lead.

Table 2.2 Typical ranges of lead concentrations (mg/kg dw) in fertilizers, farmyard manure, lime and composts

Type	Lead (mg/kg dw)
P fertilizers	7-225
N fertilizers	2-27
Farmyard manure	1.1-27
Lime	20-1,250
Composted refuse	1.3-2,240

Source: Alloway (1995)

(3) Mining and smelter

Mining involves extracting minerals from the ground, breaking or grinding them down to a suitable size for further processing, and separating the mineral of interest from other material. Lead dust or spillage of concentrates and tailings can contaminate environment near ores. Old smelting wastes can include slags (non-metallic solid material) with high metal contents. Historical smelting in uncontrolled conditions has resulted in considerable quantities of lead being lost as vapor, which would have condensed onto dust particles to be deposited on to soil and

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water. This has caused local contamination of land around historical smelting operations.

The high elevated concentrations of lead in contaminated area and around industrial smelting and refining operations were shown in Table 2.3.

Table 2.3 Lead concentrations (mg/kg dw) in soils

Study Site	Lead (mg/kg dw)	References
Near metal smelter	1,200–2,700	Beyer et al. (1985)
Control site	99–490	
Near factory	210–485	Edwards and Clay (1977)
Reference site (1,000 m)	10–30	
Industrial Smelting Complex		US EPA (1979a)
Distance from stack (km)		
0.65	1,525	
1.3	925	
4.0	190	
7.3	85	
control	16	

In Thailand, lead contaminated soils become severe, especially from small to medium industry of metal smelted factories. A filed survey that conducted in 1999 by Department of Industrial Works, in developing data based on metal distribution and potential contaminated ground and ground waters, had been found that of all 10 selected sites, 4 of these were found to be severe polluted by lead and surface soils collected from the area within radius of 1-2 km were contaminated with the lead concentration level ranging from 1,500-7,000 mg/kg dw (Parkpian, 1999).

(4) Lead derived from sewage sludge

Sewage sludge is significant source of plant nutrients and organic matter and some specially treated sludge, such as those containing lime or cement kiln

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dust, as well as limiting properties. However, the beneficial properties of sludge are limited by their contents of potentially harmful substances such including lead. Although all sludge contain a wide range of metal and other contaminants in varying concentrations, those from industrial catchments generally have higher metal contents than those from mainly suburban domestic areas. Staelens et al. (2000) reported that 258 mg/kg dw or 14% of total lead in the raw industrial sewage sludge was presented in potentially bioavailable forms, being associated with the exchangeable and acid extractable phases. Poonpolwatanaporn (2000) studied on potential leachability of toxic heavy metals in Bangkok of Thailand sewage sludge and reported that lead content in sewage sludge from Si-Phaya central wastewater treatment plant were in the range of 97-194 mg/kg dw, which 48% leachability reduced by zeolite-sewage sludge mixture. The ranges of lead concentrations in sewage sludge are given in Table 2.4.

Table 2.4 The ranges of lead concentrations (mg/kg dw) in sewage sludge and various maximum permitted concentrations in European Union, USA and AIT- Thailand

Metal	Minimum value	Maximum value	Maximum permitted concentrations (mg/kg dw)		
			EU	USA	AIT
Lead	29	3,600	750-1,200	840	1,000

Sources: Alloway (1995); AIT (1998)

(5) Chemicals and other industrial sources

Other significant sources of lead pollution in the environment can be the manufacture and/or use and disposal of the following: batteries, pigments and paints, catalysts, polymer stabilizers, pollution from incineration of plastics, printing and graphics.

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2.4 Environmental Fate of Lead

2.4.1 Lead in the atmosphere

Industrial lead emissions and automotive emissions are in the form of particles of inorganic compounds of lead. Lead forms were emitted to the atmosphere from automobile exhaust consist of the lead halides; lead bromide ($PbBr_2$), lead chloride ($PbCl_2$), lead bromochloride (PbBrCl) and double salt lead bromochloride ammonium chloride ($2PbBrCl \cdot NH_4Cl$) (NSF, 1977). After 18 hours, approximately 75% of the bromine and 30-40% of the chlorine was released, and lead carbonates, oxycarbonates and oxides were produced. These lead oxides are subject to further weathering to form additional carbonates and sulphates (Olson and Skogerboe, 1975). Studies have shown that 95% of the particles emitted from secondary lead smelting operations are less than 5 μm in diameter. The chemical forms most often detected are lead sulfide (PbS), lead sulfate ($PbSO_4$) and elemental lead (NSF, 1977). Another form emitted from mining operations and smelters is lead oxide·lead sulfate ($PbO \cdot PbSO_4$) (ATSDR, 1999). These forms are less water-soluble than automotive emissions, but will become more available through environmental weathering processes. A water-soluble form will be both more mobile in the environment and more readily absorbed by the human body.

Lead particles were emitted from vehicle exhaust comprises particles of around 0.015 μm in diameter and may be attached to particles of carbon of similar dimensions (Chamberlain et al., 1979). Particles arising from industrial process emissions cover a variety of sizes mostly 0.1-5.0 μm are typical (Bennett and Knapp, 1989) and lead from other sources, such as windblown road dust and fugitive losses from stockpiles, are substantially larger in size, typically 5-50 μm. Particles of 10 μm and larger are subject to rather rapid settling due to gravity and have a very short atmospheric lifetime.

Lead may be removed from the atmosphere by either wet or dry deposition. The consequence of the removal is the contamination of surface waters and soils. The most efficient clearing system is rain (wet deposition). Wet deposition appears to be more important than dry deposition for the removal of atmospheric lead. Depending

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upon geographical location and the level of emissions in the area between 40 and 70% of atmospheric lead is removed by wet deposition (IPCS, 1995).

2.4.2 Lead in soil

The predominant lead species in soils contaminated with auto battery wastes to be carbonates, hydroxides, oxides and sulfates [$PbCO_3$, $Pb(OH)_2$, PbO, $PbSO_4$] are transformed by chemical and biotic processes to adsorbed forms in soil (Chaney et al., 1988). The transformation process involves the formation of lead complexes with binding sites on clay minerals, humic acid and other organic matter and hydrous iron oxides (Chaney et al., 1988; Chuan et al., 1996; Sauve et al., 1997). The ability of soils to bind lead is dependent on soil pH and the cation exchange capacity of the soil components (e.g., hydrous iron oxides on clay and organic matter) (Chaney et al., 1988; US EPA, 1986). Only a small fraction (0.1–1%) of lead appears to remain water-soluble in soil (Khan and Frankland, 1983). The solubility of lead in soil is dependent on pH, being sparingly soluble at pH 8 and becoming more soluble as the pH approaches 5 (Chuan et al., 1996). Between pH 5 and 3.3, large increases in lead solubility in soil are observed. These changes in lead solubility appear to correlate with the pH-dependent adsorption and dissolution of Fe-Mn oxyhydroxides. In addition to pH, other factors that influence lead solubility in soil are total lead content and the concentrations of phosphate and carbonate in soils (Pardo et al., 1990; Sauve et al., 1997).

Evidence exists that atmospheric lead enters the soil as lead sulfate or is converted rapidly to lead sulfate at the soil surface. Lead sulfate is relatively soluble, and thus could leach through the soil if it were not transformed. In soils with pH of ≥ 5 and with at least 5% organic matter, atmospheric lead is retained in the upper 2-5 cm of undisturbed soil (Johnson, 1995).

The downward movement of elemental lead and inorganic lead compounds from soil to groundwater by leaching is very slow under most natural conditions except for highly acidic situations (NSF, 1977). The conditions that induce leaching are the presence of lead in soil at concentrations that either approach or exceed the CEC of the soil, the presence of materials in soil that are capable of forming soluble chelates with lead, and a decrease in the pH of the leaching solution (e.g., acid rain)

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(NSF, 1977). Leaching of soluble lead from contaminated soils into groundwater may be minimized by the presence of lead carbonate in the soil and by maintaining a soil pH of 8–10 (Mundell et al., 1989).

2.4.3 Lead in water

The chemistry of lead in aqueous solution is highly complex because this element can be found in a multiplicity of forms. Lead has a tendency to form compounds of low solubility with the major anions found in natural waters. The amount of lead dissolved in surface waters is dependent on the pH and the dissolved salt content of the water. In the environment, the divalent form (Pb^{2+}) is the stable ionic species of lead. Hydroxide, carbonate, sulfide, and more rarely, sulfate may act as solubility controls in precipitating lead from water. At pH<5.4, the formation of lead sulfate limits the concentration of soluble lead in water, while at pH>5.4, the formation of lead carbonates limits the amount of soluble lead (US EPA, 1979b).

The speciation of lead was found to differ in fresh water and sea water. In fresh water, lead may partially exist as the divalent cation (Pb^{2+}) at pH below 7.5, but complexes with dissolved carbonate to form insoluble $PbCO_3$ under alkaline conditions (Long and Angino, 1977). Lead chloride and lead carbonate are the primary complexes formed in seawater (Long and Angino, 1977). The speciation of lead in water is also dependent on the presence of other ligands in water. Lead is known to form strong complexes with humic acid and other organic matter (Denaix et al., 2001; Guibaud et al., 2003). Lead-organic matter complexes are stable to a pH of 3 with the affinity increasing with increasing pH, but decreasing with increased water hardness (Callahan et al., 1979). In sea water, there is the presence of lead complexed to Fe-Mn oxides, which is due to the content of these oxides in sea water (Elbaz-Poulichet et al., 1984). Sorption of lead to polar particulate matter in fresh water and estuarine environments is an important process for the removal of lead from these surface waters.

2.4.4 Lead in sediment

The forms of lead in the aquatic environment are organic and inorganic lead. Both organic and inorganic forms of lead pose serious health risks to all forms of

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life. Inorganic lead compounds (sulfide, carbonate, and sulfate) have low solubilities in natural water. Soluble lead is little affected by redox potential (Gambrell et al., 1991). Lead is tightly bound under strongly reducing conditions by sulfide mineral precipitation and complexion with insoluble organic matter, and is very effectively immobilized by precipitated iron oxide minerals under well-oxidized conditions (Gambrell et al., 1991). Lead bioaccumulation is primarily dependent on the amount of active lead compounds (predominantly aqueous species) in the environment and the capacity of animal species to store lead (Prosi, 1989). A study of bottom dwelling organisms suggests that iron-rich sediment inhibits lead bioavailability (Luoma, 1989). In a study of lake and fluvial sediment, most lead was bound to a carbonate fraction or to iron-manganese oxide minerals, both of which respond to chemical changes at the sediment-water interface, and are susceptible to remobilization in water (Schintu et al., 1991).

2.4.5 Lead uptake into plants

Lead may be taken up in edible plants from the soil via the root system, by direct foliar uptake and translocation within the plant, and by surface deposition of particulate matter. The amount of lead in soil that is bioavailable to a vegetable plant depends on factors such as cation exchange capacity, pH, amount of organic matter present, soil moisture content and type of amendments added to the soil.

Although the bioavailability of lead in soil to plants is limited because of the strong adsorption of lead to soil organic matter, the bioavailability increases as the pH and the organic matter content of the soil are reduced. Plants grown in lead contaminated soils were shown to accumulate low levels of lead in the edible portions of the plant from adherence of dusts and translocation into the tissues (Finster et al., 2004).

2.4.6 Pathways of human and animal exposure to lead

The primary routes of human and animal exposure to lead are inhalation and ingestion (of water, food, paint, soil and/or dust). In addition, the amount of lead taken up into the body is believed to vary depending on the concentration and composition (for example, particle size, chemical form) of the lead inhaled or

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ingested. The pathways of human and animal exposure to lead were shown in Figure 2.1.

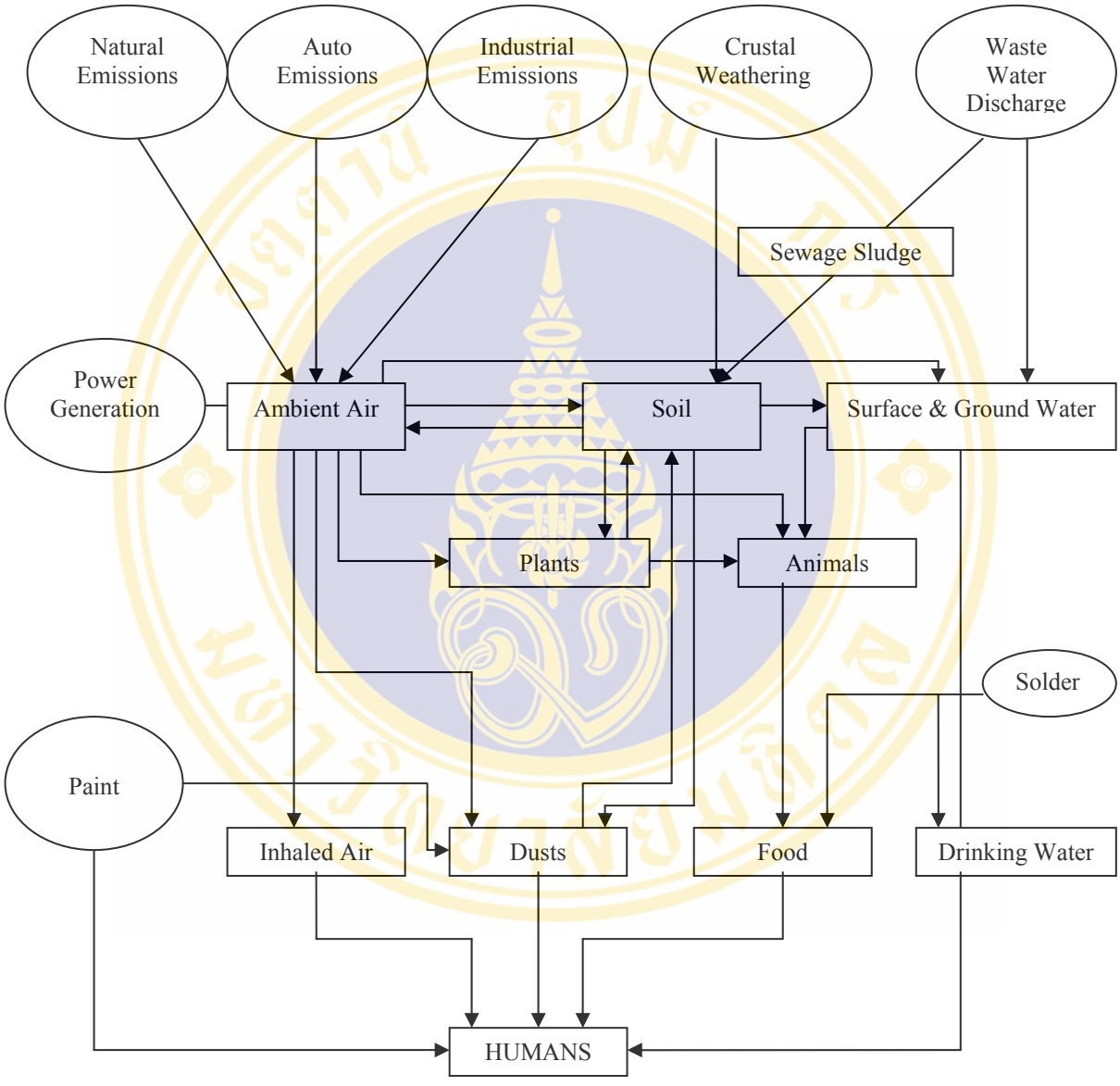

Figure 2.1 The pathways of human and animal exposure to lead (OECD, 1993)

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2.5 Toxicological Effect

2.5.1 Effect on human health

Lead is one of the most ubiquitous toxic metals. It has no known nutrition, biochemical or physiological function, and because there is no demonstrated biological need, and because it is toxic to most living things, the major concern of the moment is at what dose does lead become toxic (Goyer, 1996). The toxic effects of lead are the same, irrespective of whether it is ingested or inhaled, and blood levels as low as <10-100 ug/dl in children, and 10-100 ug/dl in adults have been associated with a wide range of adverse effects.

Ninety-nine percent (99%) of the lead that enters the adult human body and 33% that enters a child's body are excreted in about 2 weeks (ATSDR, 1999). Because of this, lead poisoning is a greater concern in children. Most of the accumulated lead is sequestered in the bones and teeth. This causes brittle bones and weakness in the wrists and fingers. Lead that is stored in bones can reenter the blood stream during periods of increased bone mineral recycling (i.e., pregnancy, lactation, menopause, advancing age, etc.). Mobilized lead can be redeposited in the soft tissues of the body and can cause musculoskeletal, renal, ocular, immunological, neurological, reproductive and developmental effects (Todd et al., 1996; ATSDR, 1999).

Replacement of calcium in the bone and muscle tissue by lead can impair normal bone growth and bone density and calcium content can decrease. High exposures (i.e., > 30 mg/kg/day) to lead cause muscle weakness, cramps and joint pain. Impaired kidney function and a weakened immune system can also result from over-exposure to lead. Various reproductive effects including decreased pregnancy rate, ovarian damage, testicular damage, testicular atrophy, cellular degeneration and irregular estrous cycles have been shown in animal studies (ATSDR, 1999). Renal toxicity is now used as a biochemical and physiologic marker of chronic subclinical lead toxicity (Todd et al., 1996).

2.5.2 Effects on plants

Lead is not essential to plants and can prove to be toxic to both if taken up in certain forms and at high enough concentrations. Some plants are able to

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accumulate lead at a level that although harmless to the plant itself, can be harmful to animals and humans if ingested by them. This situation poses a risk to the human food chain particularly if animals destined for human consumption, graze on the contaminated plants.

Lead in soil – effect on test plant (radish): inhibition of germination or growth is observed at concentrations of 125 μg/g in sandy soils, but no effects are observed in chalk soils up to concentrations of 200 μg/g. Solution of lead nitrate – disturbances in the development of the root systems are found at concentrations of 13.1 mg/L. Excessive concentrations of lead in plants have been found to cause a number of biochemical effects, including upon the processes of respiration, photosynthesis, transpiration and the proper functioning of dark green leaves. Normal concentrations of lead generally found in plant leaves (in the range 5-10 μg/g) are not far below concentrations that cause toxic effects (30-300 μg/g) (Kabata-Pendias and Pendias, 1984).

2.5.3 Effects on animals

Lead is also toxic to all aquatic biota and even though it is not considered one of the most environmentally mobile of metals, there is still appreciable evidence showing the bioavailability of sediment-bound lead to deposit feeding species. In addition, lead can be accumulated directly from sea and fresh waters, especially in organisms that utilize gill tissue as the major nutrient uptake route (Sadiq, 1992). Toxicological studies have reported sub-lethal effects in fish including changes in morphology, metabolism and enzymatic activity. Avoidance behavior has also been observed in adult fish exposed to levels ranging from 10-100 mg/L (WHO, 1989).

It is doubtful whether the term “toxic dose” has any real meaning when applied to lead, as it is affected by many factors. These include; environment, nutrition, disease and, most importantly, age, with young animals being considerably more sensitive than adults. Lead is cumulative and ubiquitous, and all living creatures are continually absorbing it, the toxic dose is only the amount necessary to bridge the gap between normal intake and a potentially dangerous level. Animals feeding close to smelting, mining and recycling facilities, have often ingested levels of lead that have resulted in poisoning and death (Henny et al., 1991).

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Lead poisoning in sheep and horses living on farmland in the vicinity of non-ferrous metal smelters in Baiyin of Gansu province in China illustrates that the apported lead through the ingestion of vegetation growing in the closest sites to the smelters were approximately surpassing the fatal dosages for horses of 1.7 mg/kg body wt./day and sheep of 4.4 mg/kg body wt./day (Liu, 2003).

Tissues and blood lead levels associated with chronic intoxication in horses were 18 mg/kg dw for liver and 16 mg/kg dw for kidney (Buck et al., 1973) and 0.2–0.5 mg/L for blood (Knight and Burau, 1973). Lead concentrations greater than 10 mg/kg dw in liver, 15 mg/kg dw in kidney cortex are indicative of lead poisoning, provided the clinical history and pathological effects (Humphreys, 1991).

2.6 Lead Production

2.6.1 Lead mining

The common minerals in lead ores are galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Galena is the most common mineral and is usually found with other sulphide ores most frequently those of zinc, copper and silver. Ore bodies near the surface are mined by open-pit methods, while those that occur at depth must be extracted. Ore is first drilled, then blasted, crushed and carried by trucks and/or conveyors to a mill. There the metal-bearing sulphides are finely ground, separated by froth flotation from waste (iron and minerals that are not metal-bearing), and concentrated into separator bulk lead, zinc and copper concentrates. The concentrates are often dried to specific moisture content, and then shipped for smelting. The lead content in concentrate typically ranges from 50-70 % (Yanyongsawat, 2005).

Thailand has a long history of lead mining and smelting and concern has been expressed over environmental levels of lead in the area. The smelter has operated for long time, originally as a primary lead smelter utilizing lead ores mined in the area as a raw material. But now, lead mining and smelting has ceased in Thailand because lack of considerable lead resources and amount of minerals has not enough to use as raw material (Yanyongsawat, 2005).

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2.6.2 Smelting and refining

Smelting and refining is classified as primary or secondary, the former producing refined lead from concentrates (primary lead); the latter recovering lead from scrap (secondary lead). The raw materials for secondary lead are process (new) scrap arising during manufacturing processes and recycled (old) scrap which arises when lead-containing manufactured goods are discarded (LDAI, 2002).

A large proportion of lead waste is recovered and recycled in secondary lead smelters. Concerning lead storage batteries the recovery is more than 90% in some countries. The major sources of raw material for lead recycling are starter batteries from motor vehicles. At least three-quarters of all lead used goes into products that are suitable for recycling. The use of secondary metal makes some important contributions to the environment: Firstly, the recovery of lead from scrap requires far less energy than smelting from ore. Secondly, recycling keeps unwanted products out of the waste stream and put them to good use. Thirdly, recycling conserves our natural resources for the benefit of future generations (LDAI, 2002). Lead produced by secondary smelting accounts for more than half of the lead produced in Thailand. There were 6 companies operating plants with individual capacities ranging from 6,000 to 15,600 tons per year.

Table 2.5 Lists of battery recycling plants in Thailand

Company	District	Province	Production capacity (tons/year)
1.Thai China Nonferrous Metal International Co.,Ltd.	Nong bua	Nakhon sawan	9,000
2.Bergsoe Metal Co.,Ltd.	Kaeng Khoi	Saraburi	11,000
3.Leang Houd Lor Lorm Loha Co.,Ltd.	Mueang	Samut prakan	6,000

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Table 2.5 Lists of battery recycling plants in Thailand (continued)

Company	District	Province	Production capacity (tons/year)
4.Wong Trakul Loha Thai Co.,Ltd.	Nakhonchaisri	Nakhon pathom	12,600
5.Thai Nonferrous Metal Co.,Ltd.	Plaeng yao	Chachoeng sao	15,600
6.Udsahakam Lorm Loha Thai Co.,Ltd.	Mueang	Rachaburi	14,000

Source: Yanyongsawat and Yongnate (2006)

2.7 Battery Recycling Process

The battery recycling plant in this study has operated more than twenty years ago and main raw materials are used lead acid batteries in production process. Other types of lead-bearing raw materials recycled by secondary lead smelters include drosses (lead-containing byproducts of lead refining), battery plant scrap, such as defective grids or paste and scrap lead. The plant has lead production capacity about 50 tons/day and has produced soft lead and lead alloys (TESCO, 2000).

2.7.1 The material composition of lead-acid batteries

Lead-acid battery means any battery that consists of lead and sulfuric acid, is used as a power source and has a capacity of six volts or more. The majority of lead-acid batteries are used as SLI batteries (starting, lightning and ignition) for the purpose of starting the engines of cars and lorries (Jacobs, 1985).

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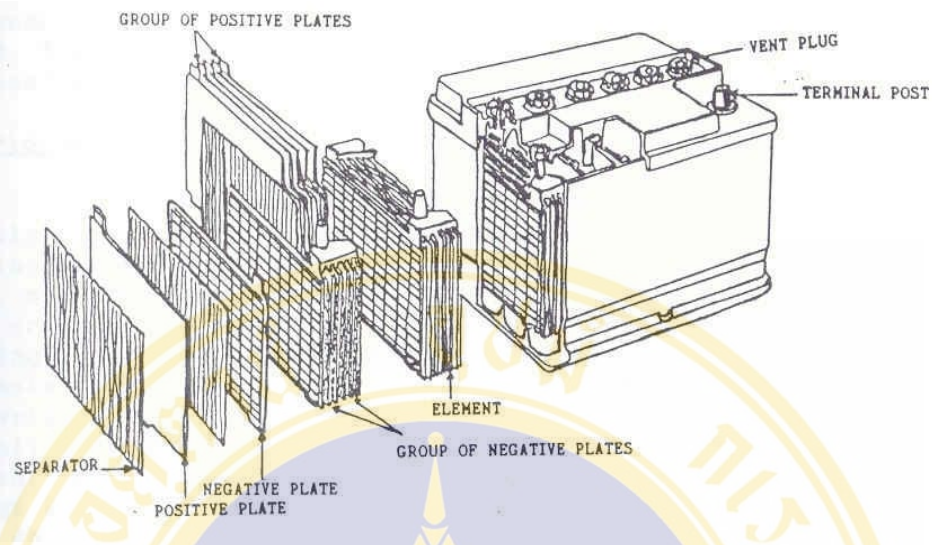

Figure 2.2 Structures of a lead-acid battery (Jacobs, 1985)

The main components of a lead-acid battery are:

- Active mass or lead paste which includes:
  - cathode (positive pole) which consists of lead oxides (PbO_2).
  - anode (negative pole) which consists of metallic lead (Pb).
- Grids and connecting bridges made of suitable lead-/antimony, lead-calcium (tin) (aluminum) alloys with additives in negligible quantities such as copper, arsenic, tin and selenium.
- Electrolytes (liquid filling of sulfuric acid) in which lead-antimony plates are immersed.
- Casing usually made of polypropylene and less frequently of hard rubber, ebonite, bakelite etc.
- Other components such us paper, rubber, fiberglass and wood

Batteries normally consist of multiple cells that are electrically connected. For example, a 12-volt automobile battery consists of six 2-volt lead-acid cells connected in series. All lead batteries, or rather their cells, work on the same set of reactions and use the same active materials. At the positive electrode, lead dioxide (PbO_2) is converted to lead sulfate ($PbSO_4$) and at the negative electrode, sponge metallic lead is also transformed to lead sulfate. The electrolyte is dilute sulfuric acid that provides the sulfate ion for the discharge reactions.

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The chemical reaction during discharge and recharge is normally written:

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_20$$

The cell system is closed, i.e. for every electron generated in an oxidation reaction at the negative electrode, there is an electron consumed in a reduction reaction at the positive electrode. As the process continues, the active material (i.e. the paste of lead oxides) becomes depleted and the reaction slows down until the battery is no longer capable of supplying electrons. The major part of the paste of lead oxides is converted into lead sulfate (Jacobs, 1985).

2.7.2 Battery recycling processes

The battery recycling processes includes 3 major operations: scrap pretreatment, smelting and refining.

(1) Scrap Pretreatment

Scrap pretreatment is the partial removal of metal and nonmetal contaminants from lead bearing scrap and residue. Processes used for scrap pretreatment include battery breaking, crushing. Those batteries were crushed in an M.A. battery breaker.

The crushed scrap is screened to remove the paste slurry that contains lead oxide and lead sulfate and the oversized grid metal and plastics are screwed to a gravity separator where the heavy grid metal sinks and is collected. The plastics are then washed and further separated into polypropylene and the heavier separator fraction. The polypropylene chips are sent to a washing plant for final rinsing with fresh water and draining. The polypropylene will then be bagged and sold to plastic recyclers. The rubber is separated from the polypropylene for use as fuel in the rotary furnace. Wastewater filtrate from the paste filtering process is collected and recycled back to the plant. Any excess wastewater is sent to the effluent treatment plant.

Paste and grid metal, Anthracite reductant, fluxes and mixed fume dust and drosses will be stockpiled in the enclosed building. All of the materials will be fed

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by an overhead grab into hoppers for feeding into the smelting furnace (TESCO, 2000). The battery scraps pretreatment process are shown in Figure 2.3.

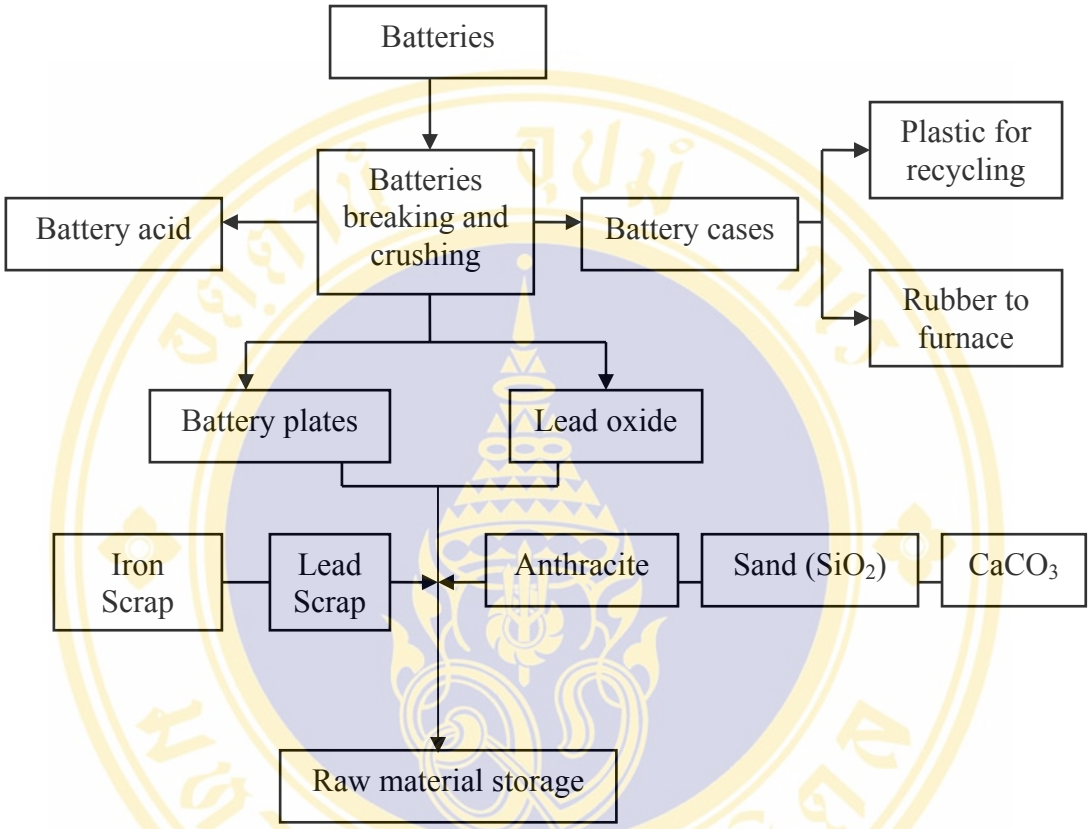

Figure 2.3 Battery scrap pretreatment process (Modified from TESCO, 2000)

(2) Smelting

Smelting produces lead by melting and separating the lead from metal and nonmetallic contaminants and by reducing oxides to elemental lead. Smelting is carried out in rotary furnaces. After removing the lead components from the batteries, the lead scrap is combined with other charge materials, such as refining drosses and flue dust and is charged to a furnace.

Charge materials are typically placed in the furnace using a retractable conveyor or charge skip. Lead-bearing raw materials charged to rotary furnaces include broken battery components, flue dust and drosses. Fluxing agents for rotary furnaces may include iron, silica, limestone and anthracite. The fluxing agents are

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added to promote the conversion of lead compounds to lead metal. Anthracite is used as a reducing agent rather than as a primary fuel. A typical charge may consist of 160 kg of $PbSO_4$, 160 kg of wet battery scrap, 520 kg of electrode plates , 160 kg of lead scrap , 240 kg of dross , 100 kg of lead dust , 120 kg of iron scrap, 40 kg of FeO , 28 kg of Anthracites, 56 kg of $CaCO_3$, 80 kg of sand (SiO_2) and will yield approximately 1,000 kg of lead product. Each batch takes 5 to 10 hours to process, depending on the size of the furnace. Smelting furnaces are used to produce crude lead bullion which is refined and/or alloyed into final lead products. Mass balance of lead production process is shown in Figure 2.4.

Chemical reaction processes of secondary lead smelting

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

$$2PbO + C \longrightarrow 2Pb + CO_2$$

$$PbO + CO \longrightarrow 2Pb + CO_2$$

$$PbSO_4 + 2C \longrightarrow PbS + 2CO_2$$

$$CO_2 + Fe \longrightarrow FeO + CO$$

$$CaO + 3SiO_2 + 2FeO \longrightarrow CaO.(FeO)_2.(SiO_2)_3 \text{ ….. Slag}$$

Finally PbS is converted into Pb through the following reactions:

$$PbS + Fe \longrightarrow Pb + FeS$$

or

$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$

$$PbS + PbO_2 \longrightarrow 2Pb + SO_2$$

The reactions take place in the melting furnace at high temperature (900-1,200°C) and need additives, which are carbon (in the form of Anthracite) and iron (in the form of iron scrap). Impurities are collected in the slag. The product of the smelting operation is crude lead, which needs subsequent refining, and slag as residue (TESCO, 2000).

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(3) Refining

Refining and casting the crude lead from the smelting furnaces can consist of softening, alloying, and oxidation depending on degree of purity or alloy type desired. These operations can be performed in kettle-type furnaces are most commonly used. Remelting process is usually applied to lead alloy ingots that require no further processing before casting. Kettle furnaces used for alloying, refining, and oxidizing are usually oil-fired. Refining and alloying operating temperatures range from 400 to 500 ^{o}C. Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper and nickel are the most common alloying materials (TESCO, 2000). The details of production processes are shown in Figure 2.5.

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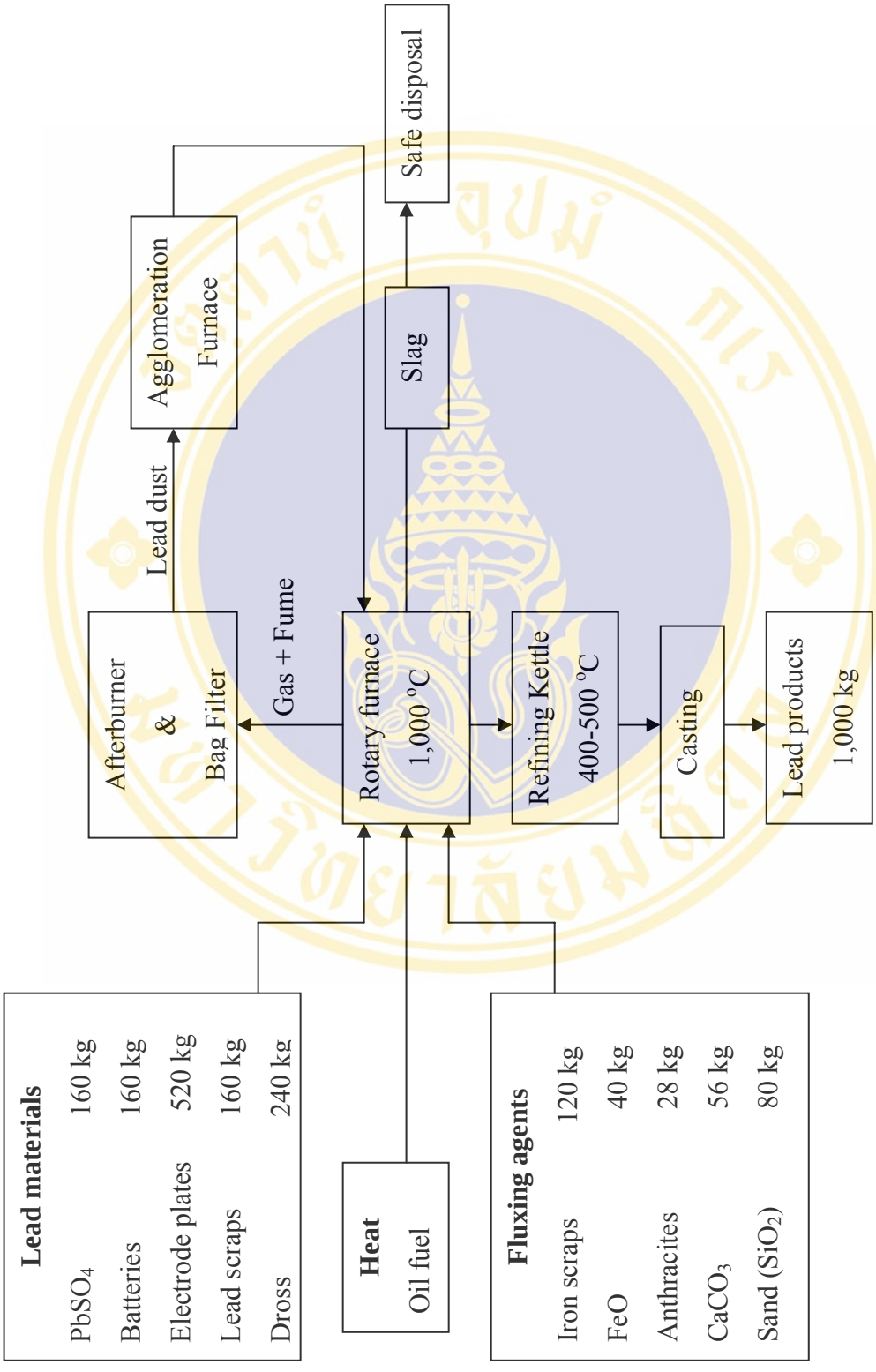

Figure 2.4 Mass balance of lead production process (Modified from TESCO, 2000)

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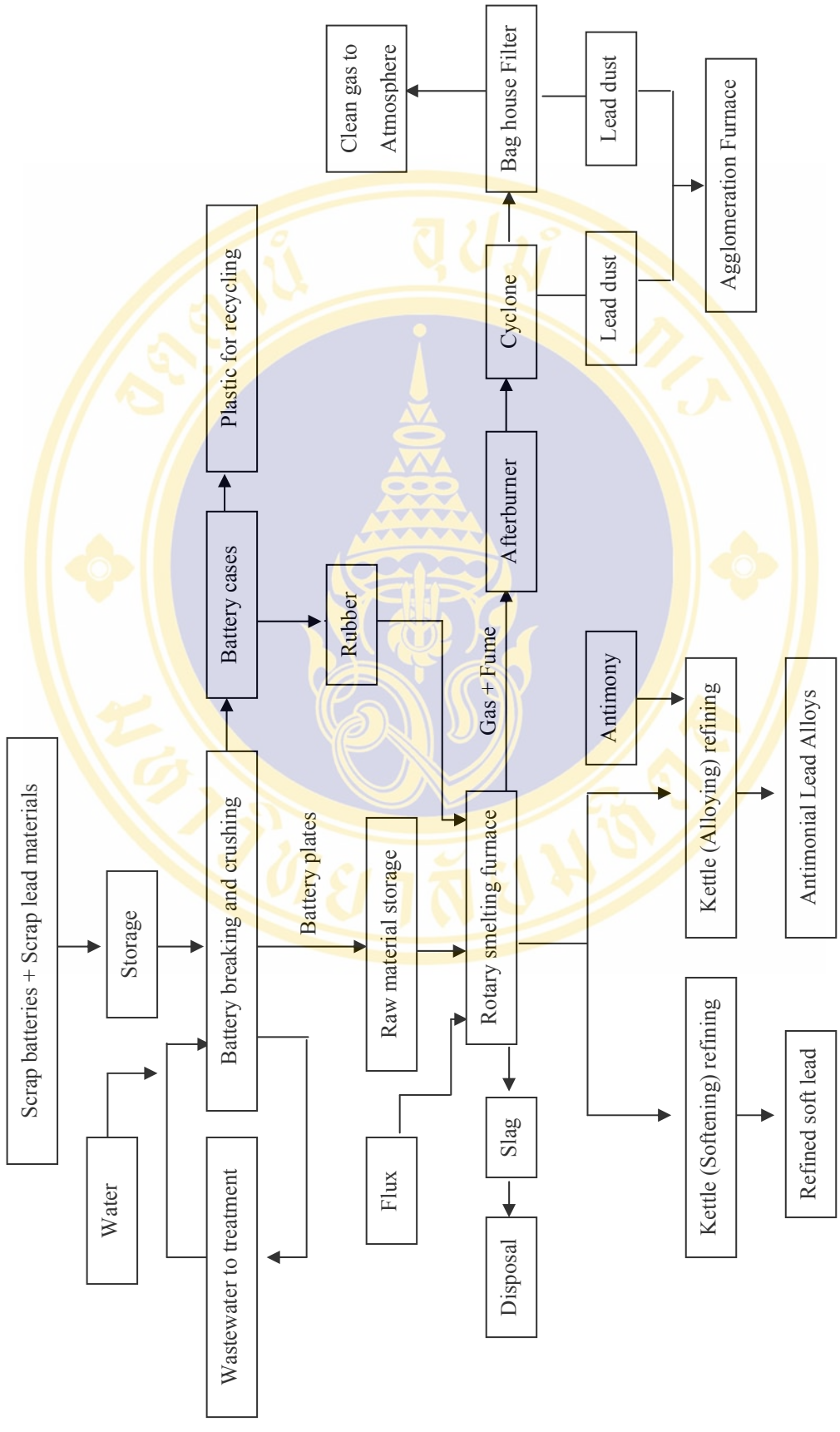

Figure 2.5 Production process and toxic waste handling of the plant (Modified from TESCO,Ltd., 2000)

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2.7.3 Environmental pollution from battery recycling process

The wastes generated by the battery recycling process are:

(1) Solid wastes

Slags may contain up to a few percent of lead (typically less than 5%) if slags contain more than 5% of lead are recycled back through the smelting process. Slags may also contain other contaminants such as arsenic and antimony. Since soda slag is water soluble and therefore hazardous when brought to landfills, modern lead recycling plants use silica slag, which is water insoluble. Silica slags mainly comprise glassy and crystalline phases which are subject to varying degrees of weathering.

Dusts from pollution control equipment and drosses may contain lead and other metals in relatively active forms; these are usually recycled, though a small proportion containing for example arsenic and cadmium may be disposed of in landfill (TESCO, 2000).

(2) Airborne emissions

Lead begins to fume significantly at temperatures above around 500 °C. Vapors and dusts of lead and lead oxide, together with other materials present in the raw materials (such as acidic sulphur-containing gases, arsenic and other metals) can be present in air, both within the plant and the external environment. The furnace stack gases are routed through a bag house, where particulates are collected in bag filters. These fumes are recycled to the furnaces. Stack gas emissions consist of the gaseous emissions from both the secondary lead refining and the bullion refining operations of the plant. In addition, fugitive emissions from secondary lead smelting are released with almost all stockpiling, transferring, charging and discharging processes (TESCO, 2000).

(3) Water borne emissions

The major sources of wastewater are generated from washing floor, equipment and batteries breaking. Electrolyte from the lead acid batteries and wastewater from the process area were treated using chemicals and flocculants. Metals such as lead, cadmium, copper, iron and tin are all collected in the filtered sludge and were recycled to the furnace for metal recovery. Not only that, they are the waters coming from roofs and roads inside the plant area were cleaned before discharged into the natural environment. Wastewaters were drained into a nearby drainage system,

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which eventually ends up in natural surface water (TESCO, 2000). If runoff has been carrying lead off the plant in the direction of the drainage system, then logically there would be an accumulation of lead in the sediment of this drainage system.

2.8 Study Area

2.8.1 Study location

This battery recycling plant has been operated more than twenty years ago, and now is one of the largest lead recycling plants in Thailand. The battery recycling plant has area of approximate 81,988 m^2 including 41,988 m^2 that separated for office and production area, 40,000 m^2 for slag disposal site. Separated types of raw material and products are kept in a storage place with roof building and closed building. The plant is separated from surrounding environment by the concrete fence. The battery recycling plant is located on flat land in residential areas of Central Region near the Mitraparb highway that leading to the Northeast of Thailand. The land use in the immediate vicinity of the plant within study area is a mixture of residential areas, hospital, personal land uses, agricultural areas and grazing animal farms (TESCO, 2000). The boundaries of the plant with adjacent areas are:

West: Adjacent to the residential areas and hospital
North: Adjacent to personal land uses and Mitraparb highway
South: Adjacent to the milling animal bones factory, residential areas and hill
East: Adjacent to the residential areas and grazing animal farm

Injudicious sitting of battery recycling plant can seriously affect the environmental features such as air, water, land, flora, fauna, human settlements and health of people. In sitting battery recycling industries, care should be taken to minimize the adverse impact of the industries on the immediate neighborhood as well as distant places.

According to the announcement of Ministry of Industry, volume 2 (B.E.2535), The Factories Act B.E. 2535 (1992), section 4 in the act, has prescribed criteria for consideration the establishment of battery recycling plant as follows:

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1. Must not have pond and natural reservoir inside the plant area, must not situate in flood plain areas and must have distance from pond, river and surface waters at least 1 kilometer.

2. Must situate in areas which have underground water levels from surface soil at least 10 m.

3. Must have a distance not less than 2 km from the hospital, school and temple.

4. Must not locate in areas which have land use for agricultural and animal farm.

The plant has situated on this site for long times before this announcement to enforce. Thus it can create pollution problem to local area with respects of inadequate environmental management practices. Lead can be distributed to surrounding environment from 3 sources; there are lead emission from stack and fugitive lead dust from lead production process, discharged wastewater and slag that dumped directly on to land. This leaks to local contamination of lead in both biotic and nonbiotic compartments in the area of concern, around smelting operations.

2.8.2 Physical environments

(1) Climates

From the meteorological records of Lopburi station for thirty years period (1971-2000), the study area is located within tropical zone which is under the influence of monsoon winds of seasonal character i.e. southwest monsoon and northeast monsoon. Southwest monsoon usually starts in May and ends in October while northeast monsoon normally starts in October and ends in February. The climates are classified to 3 seasons: summer season from March to April, rainy season from May to October, and winter season from November to February. The climatic features are characterized by the following:

- The annual mean air temperature is approximately 28.1 °C and the average monthly temperature reaches its maximum value in April (30.4 °C) and its minimum value in December (10.2 °C)

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- The average annual relative humidity is about 85%, and average monthly relative humidity reaches its maximum value in September (93%) and its minimum value in December (72%)
- The average annual rainfall is approximately 94 mm. The majority of the rainfalls are 6 months (May through October), with the highest in September.
- The dominant winds over the winter season trend NE. The dominant winds over the rainy season trend S. In transitional season (summer), the winds trend dominantly in S directions. The meteorological records of Lopburi station were shown in Table 2.6 (The Meteorological Department of Thailand, 2006).

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Table 2.6 Meteorological records of Lopburi province

Climate Parameters	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Average
Mean Daily Temperature (°C)	26.2	28.0	29.5	30.4	29.6	28.8	28.4	28.2	27.8	27.7	26.8	25.6	28.1
Minimum (°C)	9.8	15.0	16.4	19.7	21.4	21.7	21.7	21.4	20.5	17.0	13.0	10.2	9.8
Maximum (°C)	38.4	38.6	39.8	41.4	40.8	39.5	38.3	37.5	35.9	35.6	35.8	36.2	41.4
Mean Daily Relative Humidity (%)	78	83	85	86	88	89	90	91	93	89	78	72	85
Average Wind Speed (km/h)	3.7	4.1	4.8	4.6	3.9	3.9	3.7	3.3	2.2	2.8	5.0	5.4	4.0
Prevailing Wind direction	NE	S	S	S	S	S	S	S	S	NE	NE	NE	S
Monthly Rainfall (mm)	4.7	11.6	25.5	74.3	147.2	113.6	126.6	166.2	263.7	151.1	34.9	4.4	1,123.8
Mean rain days (days)	1.0	1.4	2.2	5.7	12.4	12.9	13.8	16.8	18.3	12.4	3.7	0.8	101.4

Source: The Meteorological Department of Thailand (2006)

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(2) Geology characteristics

Geologic map scale 1:50,000 and geological data use to identify the geology of the study area. The study area is located within the area of soil being classified into 3 groups as shown in Figure 2.6. Each group of soil is divided into various series which have difference of textures and characteristics as shown in Table 2.7, 2.8 and 2.9.

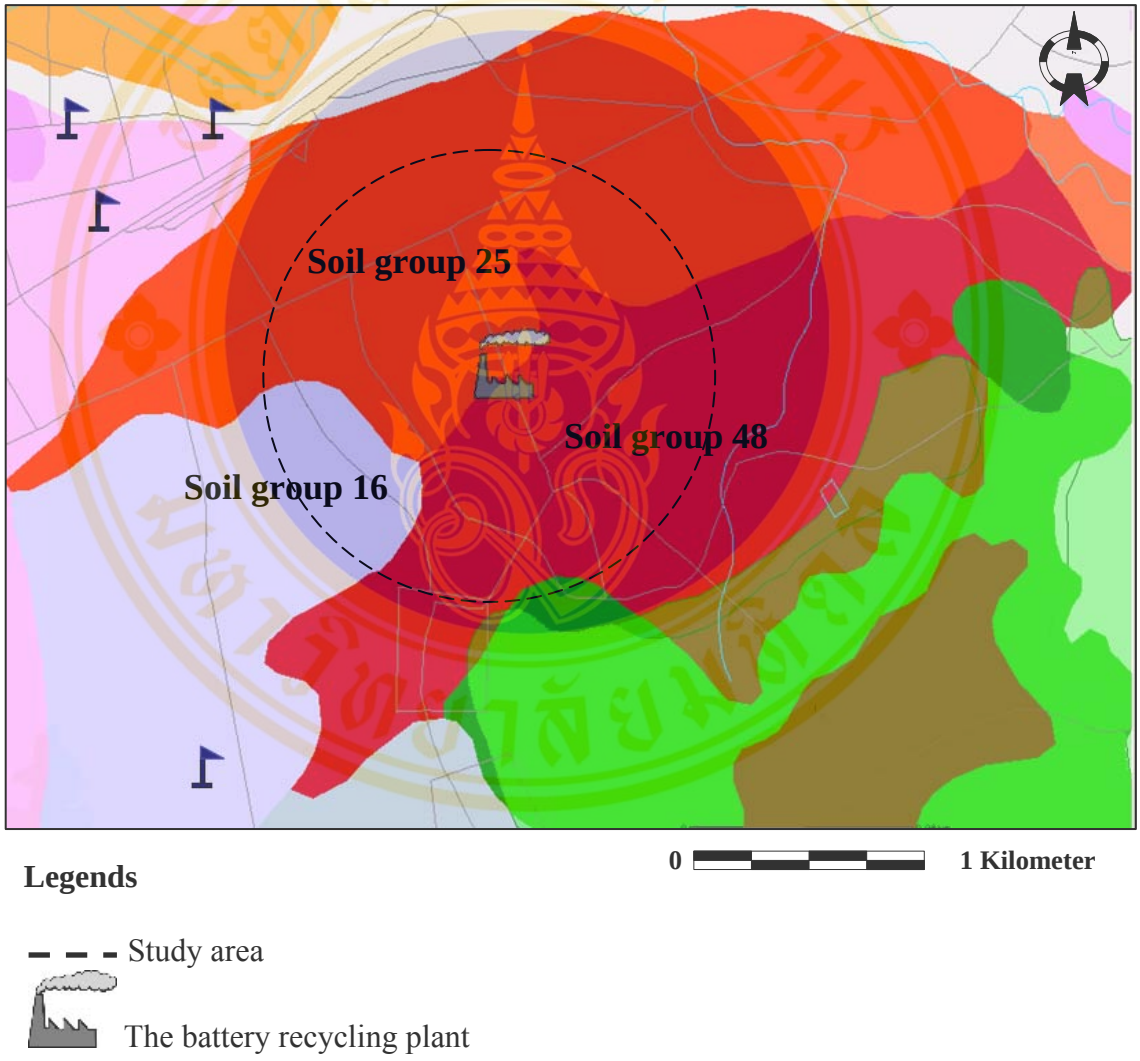

Figure 2.6 The groups of soil in study area

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Table 2.7 Characteristics of soil surface group 16 at a depth of 30 cm

Soil series Group 16	**CEC** (Meq/100 g soil)	**OM** (%)	**OC** (%)	**pH**	**Soil texture**	**Sand** (%)	**Silt** (%)	**Clay** (%)
Hinkong	4.45	0.76	1.06	5.0-6.0	Silt Loam	5.10	78.10	16.80
Si Thep	4.00	0.27	0.97	5.0-5.5	Silt Loam	20.00	74.00	6.00
Lampang	6.00	1.62	1.2	4.5-5.0	Silt Loam	26.00	62.00	12.00
Phan Thong	14.43	0.8	0.83	6.0-6.5	Silty Clay Loam	9.00	64.00	27.00
Koayai	13.30	4.36	2.86	6.0-6.5	Silt Loam	1.50	83.50	15.00

Source: Land Development Department (2006)

Table 2.8 Characteristics of soil surface group 25 at a depth of 30 cm

Soil series Group 25	**CEC** (Meq/100 g soil)	**OM** (%)	**OC** (%)	**pH**	**Soil texture**	**Sand** (%)	**Silt** (%)	**Clay** (%)
Kantang	3.90	2.16	1.19	4.5-5.0	Sandy Loam	54.50	45.00	0.50
Thung Kai	5.20	4.34	1.21	6.0-6.5	Silt Loam	24.50	70.50	5.00
Phayom Ngam	6.00	3.15	2.41	4.5-5.5	Silt Loam	31.50	53.50	15.00
Phen	5.20	0.56	0.85	4.5-5.5	Loam	40.80	43.30	15.90
Yan Ta Kao	4.30	3.97	1.67	4.5-5.5	Silt Loam	32.50	63.50	4.00
Sathon	3.20	1.09	0.88	4.5-5.5	Sandy Loam	61.50	37.00	1.50
On	2.40	0.72	0.61	4.5-5.5	Sandy Loam	67.00	18.20	14.80

Source: Land Development Department (2006)

Table 2.9 Characteristics of soil surface group 48 at a depth of 30 cm

Soil series Group 48	**CEC** (Meq/100 g soil)	**OM** (%)	**OC** (%)	**pH**	**Soil texture**	**Sand** (%)	**Silt** (%)	**Clay** (%)
Tha Yang	4.20	1.31	1.18	5.0-6.5	Loam	43.80	39.90	16.30
Nam Chun	4.40	1.72	0.35	6.0-7.0	Loamy Sand	79.30	15.70	5.00
Phayao	5.00	1.28	0.8	4.5-5.0	Sandy Loam	62.00	28.50	9.50
Mae Rim	6.20	1.03	0.94	4.5-6.5	Sandy Loam	69.10	15.40	15.50

Source: Land Development Department (2006)

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2.9 Guidelines and Standards for Lead in Soil and Sediment

Several countries set health-based and ecologically based investigation levels for lead, where an investigation level is the concentration of a contaminant above which further appropriate investigation and evaluation will be required. Guidelines and standards for lead in soil and sediment of Thailand and other countries were shown in Table 2.10.

Table 2.10 Lead concentrations (mg/kg dw) of background and maximum allowable values in soils and sediments

Organization	Background /Maximum allowable values		References
	Soil	Sediment	
Pollution Control Department, Thailand	400-750	-	PCD (2004)
Department of Agriculture, Soil Science Division, Thailand	Background level 17.5 Investigation level 55	-	Bernhard et al. (2004)
Department Industrial Work, Thailand	100	-	DIW (1997)
National Environmental Protection Agency, China	300	-	Liu et al. (2005)

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Table 2.10 Lead concentrations (mg/kg dw) of background and maximum allowable values in soils and sediments (continued)

Organization	Background /Maximum allowable values		References
	Soil	Sediment	
National Environmental Protection Agency, China	Background level 35	-	Liu et al. (2005)
Canadian Council of Ministers of Environment	-	Threshold effects 35 Probable effects 91.3	Andrews and Sutherland (2004)
Ontario Ministry of Environment and Energy	-	Lowest effect 31 Severe effect 250	Peramaki and Decker (1999)
ANZECC & ARM-CANZ	-	Trigger value 50 High value 220	Gale et al. (2006)
Soil, Water and Chemical Substances Department, Netherlands	Background level 50 Further investigation 150 Clean up level 600	-	VROM (1983)

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2.10 Evaluation the Potential Environmental Risks

Lead contaminations were detected in soil and sediment on site at levels that could cause environmental problems if people were repeatedly exposed to these contaminants over a long period of time. Evaluation the potential environmental risk can be estimated numerically using the Hazard Quotient (HQ) approach (US EPA, 2006). The HQ is a ratio, which can be used to estimate if risk to harmful effects is likely or not due to the contamination in site. The HQ is calculated using the following equation:

$$HQ = \frac{EEC}{\text{Screening Benchmark}}$$

EEC = Estimated (Maximum) environmental contaminant concentration in the soil, sediment, or water at site.

Screening Benchmark = Maximum allowable of lead concentration; if the contamination concentration is below this level, the contaminant is not likely to cause harmful effects.

After the calculation…

If HQ > 1.0 Then harmful effects are likely due to the contaminant in site.

If HQ = 1.0 Then contaminant alone are not likely to cause harmful effects.

If HQ < 1.0 Then contaminant are not likely to cause harmful effects.

2.11 Related Researches

The possible contaminations of soil and vegetation from a lead smelter were investigated in 1995 by Oyedele et al. Samples of soil and edible vegetables were collected at the distance of 10, 50, 100, 150 and 200 m from a smelting plant in the abandoned tin mine of Nigeria. The results found that total lead contents of the surface soils were in the range of 10,268, 1,163, 5,704, 730 and 365 mg/kg dw, respectively. Likewise, lead contaminations in edible vegetables collected at distance of 100, 150 and 200 m were in the range of 918.63, 612.43 and 1,224.82 mg/kg, dw respectively.

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The results were found that lead concentrations were exceeded the critical toxic levels, in both soils and vegetations around the smelting plant.

The distribution of lead in various environmental samples (water, sediments and soils) near the Shing-Yie storage battery recycling plant in Taiwan was investigated before and after amelioration. An exceedingly high lead concentration was found in the downstream river water of the Tawulum River passing by the plant. The concentrations of lead 418 and 372 mg/kg dw in the downstream river sediments were higher than that of 158 and 123 mg/kg dw in the upstream river sediments before and after amelioration, respectively. Maximum lead concentration of 2,402 mg/kg dw in dust was found in the surface soil from the station that closed to the plant and much higher than those from the other stations by about 18 times before amelioration. However, the maximum value dropped to 1,155 mg/kg dw after amelioration. On the whole, the lead concentrations in the surface soil closed to the plant was more than 1,000 μg/g and decreased to 100 mg/kg dw or less at the 15–30 cm depth about 2 km away from the plant (Yeh et al., 1995).

The distribution of lead and some other metals (Zn, Cu, Ni, Cr, Cd) in the topsoil and vegetation around a manufacturing lead batteries factory in Ibadan , Nigeria, was investigated and found to be contaminated with high lead elevated concentration, with average level of about 2,000 mg/kg dw. Whereas the station that closed to the fence with the distance of 750 m away the lead concentration declined gradually. Lead levels in soil around a primary school located about 500 m from the factory was found to be polluted at the concentration of 1,450 mg/kg dw. Lead levels were equally elevated in the vegetation, though average levels in vegetation were slightly lower than in the soil (Onianwa and Fakayode, 2000).

It had also been found that surface soil (0-15 cm) and plant samples had very high elevated lead levels only in the stations those closed to the facility and a clear decrease with increasing distance was found. Total lead levels in soil samples were ranged from 127 to 5,657 mg/kg dw, with more than 70% of lead extractable by EDTA

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in the most polluted soils. Lead levels in the aerial part of plant samples were in the range of 113-4,741 mg/kg dw (Palacios et al., 2002).

In 2003, lead poisoning was investigated in grazing animals living on farm in the vicinity of non-ferrous metal smelters in Baiyin of Gansu province, China. Soil and herbage samples were collected at five sampling sites situated at 100 m to 30 km from the smelter. The results showed that lead concentrations in soil sampled areas were in the range of 33 to 313 mg/kg dw (mean 55 mg/kg dw) and higher than those found in control area (mean 9 mg/kg dw) and found clear decrease with increasing distance to the smelter. The concentrations of lead in herbage samples were in the range 34 to 180 mg/kg dw (mean 59 mg/kg dw) and higher than those of control areas (mean 6 mg/kg dw) (Liu, 2003).

It was also found that, soils near a smelter in Nanning, southern China was contaminated and levels of lead in soils were measured. Results showed that soils from 2 villages located at the distance of 500 and 1,500 m from the smelter were heavily contaminated as compared with a village located at the distance of 50 km from the smelter (background area). Geometric means of lead concentrations in soils were 992, 74 and 16 mg/kg dw for the nearest and the farther villages, respectively (Cui et al., 2004).

In 2005, the contamination and distribution of lead in the vicinity of the battery recycling factory in Nahkonsawan province had been found in soil both at the depth of 0-20 and 20-40 cm at the distance of 100 m from the factory with much more contamination than those at the distance of 200 and 300 m. The concentrations of lead in the South direction were higher than those in the direction of North, East and West. Moreover, lead concentrations in all directions were found to increase with the exposure time from June to August and from June to October. Also, lead contaminations were found to decrease as increasing depth of soil and the concentrations of lead in soils were not exceeded the acceptable value (Santi, 2005).

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In 2006, heavy metal pollution in sediments derived from the Deule canal was investigated. Sediments were sampled at various stations not far from a smelting plant to assess the sediment quality. The total concentrations of lead in sediment samples were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). This investigation has revealed that lead pollution is readily apparent in the studied sediments. Furthermore, the lead contents in sediments were largely exceeding those in the background soils (The value of lead for background sediment was not available) and maximum values are obtained for sediments collected near the industrial zone. Total lead concentrations in these sediments ranged from 27 to 10,079 mg/kg dw (Boughriet et al., 2006).

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CHAPTER III
MATERIALS AND METHODS

This study included field survey and samples collection for lead concentrations determination in the laboratory of the Department of Sanitary Engineering, Faculty of Public Health, Mahidol University.

3.1 Sampling Locations

The battery recycling plant in Saraburi province was considered for this study due to it operated more than twenty years old before the law prescribed criteria for consideration the establishment of battery recycling plant to enforce. Then, injudicious sitting of battery recycling plant could be affected the environment around the plant from lead pollution as resulting from production process.

Topographic map scale 1:50,000 (series L7018, map sheet 5238 III, Amphoe Muak Lek) was prepared for study area at approximate horizontal grid reference of 1611000 to 1615000 and vertical grid reference of 716000 to 720000. Also, geological map scale 1:50,000 and geological data were prepared to identify the geology of the study area. Based on landscape analysis using aerial photographs and field survey, the study area can be divided into two geographic terrains including both hill and plain terrains. The location of study area is shown in Figure 3.1. Within this study area, the battery recycling plant is considered as the major anthropogenic source of lead contamination in this area.

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Figure 3.1 The topographic map of the study area

3.2 Sampling Designs

The battery recycling plant could be created pollution problem to local area with respects of inadequate environmental management practices. Lead from a battery recycling process together with crushing and dry grinding, smelting and refining had caused amount of lead emitted into the air. Likewise, lead from washing floor, equipment and batteries breaking process was remained in wastewater and discarded mainly to the drainage system near the plant. This discharge of lead in wastewater and atmospheric deposit on surface soil could be accumulated onto soil and sediment.

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After that lead could be absorbed to plants which grown in that area. These plants could be reached by grazing animal through ingestion, then lead were absorbed in blood, hair, milk and tissues of the affected grazing animals and transfer to humans by consumption grazing animal products.

Lead can be distributed from the smelter to surrounding environment from 3 sources; there are lead emission from stack and fugitive lead dust from lead production process, discharged wastewater and slag that dumped directly on to land. This leaks to local contamination of lead in both biotic and nonbiotic compartments in the area of concern, around smelting operations. The linkages of lead in various compartments from diverse lead smelting activities to surrounding environment were concluded as shown in Figure 3.2.

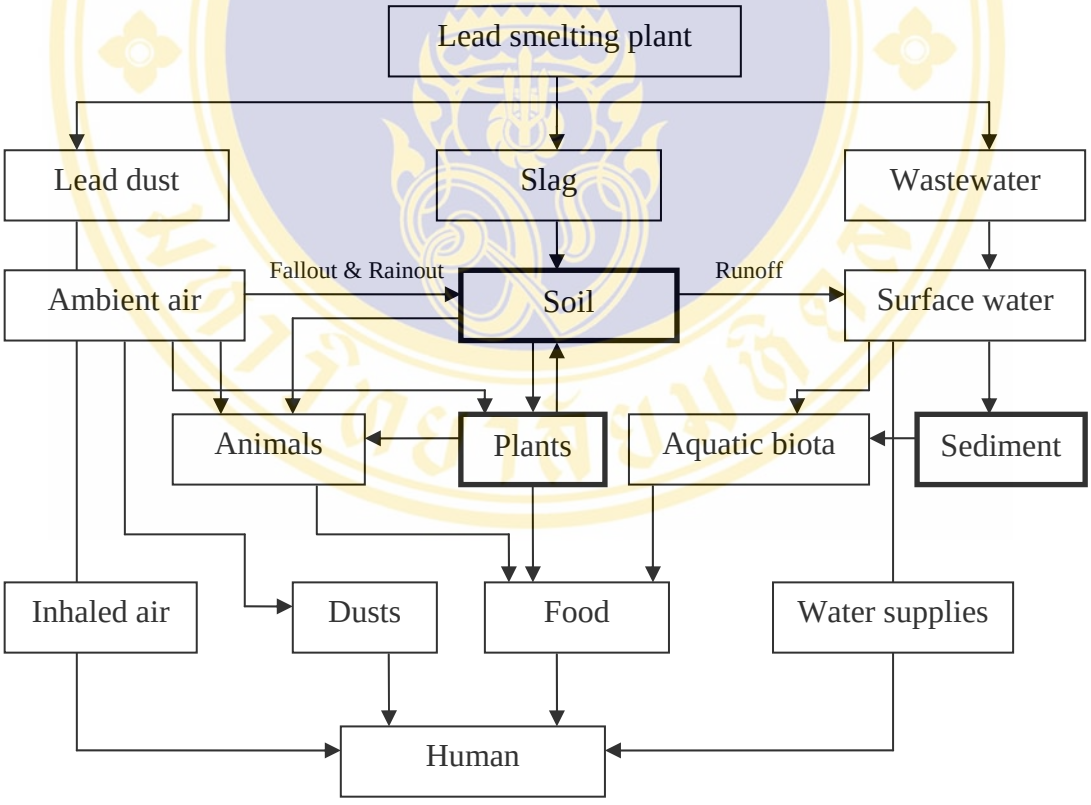

Figure 3.2 Ecological and food chain cycle of lead (Modified from Adriano, 1986)

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3.2.1 Sampling design for soil samples

The study area around the battery recycling plant were divided into five transect lines in the directions of north, east, west , south and south-west of the plant for soil sampling. Sampling stations were chosen at various distances from the plant along each transect line. Samplings were carried out within radius 1 kilometer from the plant at the distance of 50, 100, 250, 500 and 1,000 m. The soil samples were collected two times: First time, soil samples were collected at the depth of 10 cm in rainy season (August and September, 2006). Second time, soil samples were collected at three depths (0-10, 10-20, 20-30 cm) in high lead contaminated areas in dry season (February, 2006).

Background/reference sites were selected in areas of lead concentrations present in soil as a result of natural geologic process, not influenced by the plant activities. The background soils from 5 stations were collected at a distance about 2 km from the plant and soil characteristics were the same type/group to those in the contaminated area. The soil samples were collected at the depth of 0-10 cm in rainy season (August and September, 2006). Soil sampling stations were shown in Figure 3.3.

Figure 3.3 Soil sampling stations

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3.2.2 Sampling design for sediment samples

Sediment samples were collected along the drainage system adjacent to the plant. The drainage system flows through the effluent discharge point from the south to the north of the plant with end up at the receiving pond near Mitraphab high way. The length of the drainage system is about 600 m. The drainage system was full of water in rainy season and almost run dry in dry season. The samples were collected upstream and downstream from the effluents discharge point of the plant along the drainage system at various distances. Three sediment samples were collected upstream from the effluents discharge point at the distance of 100, 200 and 300 m. And five sediment samples were collected downstream from the effluents discharge point at the distance of 100, 200, 300, 350 and 400 m from the point source. The sediment samples were collected two times: First time, sediment samples were collected at the depth of 0-10 cm in rainy season (August and September, 2006). Second time, sediment samples were collected at three depths (0-10, 10-20, 20-30 cm) in high contaminated areas in dry season (February, 2006). Sediment sampling stations were shown in Figure 3.4.

Figure 3.4 Sediment sampling stations

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3.2.3 Sampling design for plant samples

Plant samples were collected from the same location as did for soil and sediment samples. The plant sampling stations were collected from the soil located within radius 50 m from the battery recycling plant and sediment located downstream from the effluent discharge point. Each plant species were randomly collected within the sampling area (Table 3.1).

Table 3.1 Plant sampling stations of each plant species

Sample No.	Sampling locations	Plant species	Edible part of plants
1	At sediment station 8 (Dry season)	*Ipomoea* spp.	Shoot, leaf
2	At sediment station 7 (Dry season)	Cyperaceae	Shoot, leaf
3	At sediment station 5 (Dry season)	*Brachiaria* spp.	Shoot, leaf
4	At soil station 19 (Rainy season)	*Brachiaria* spp.	Shoot, leaf
5	At soil station 6 (Rainy season)	Cyperaceae	Shoot, leaf
6	At soil station 11 (Rainy season)	Cyperaceae	Shoot, leaf
7	At slag heap (Rainy season)	*Leucaena glauca*	Pods
8	At slag heap (Rainy season)	*Leucaena glauca*	Branch, leaf
9	At soil station 16 (Rainy season)	Cyperaceae	Shoot, leaf
10	At soil station 16 (Rainy season)	*Brachiaria* spp.	Shoot, leaf

The plant samples were collected two times: First time, plant samples were collected at surface soil areas in rainy season (August and September, 2006). Second time, plant samples were collected at sediment areas in dry season (February, 2006). Plant sampling stations were shown in Figure 3.5.

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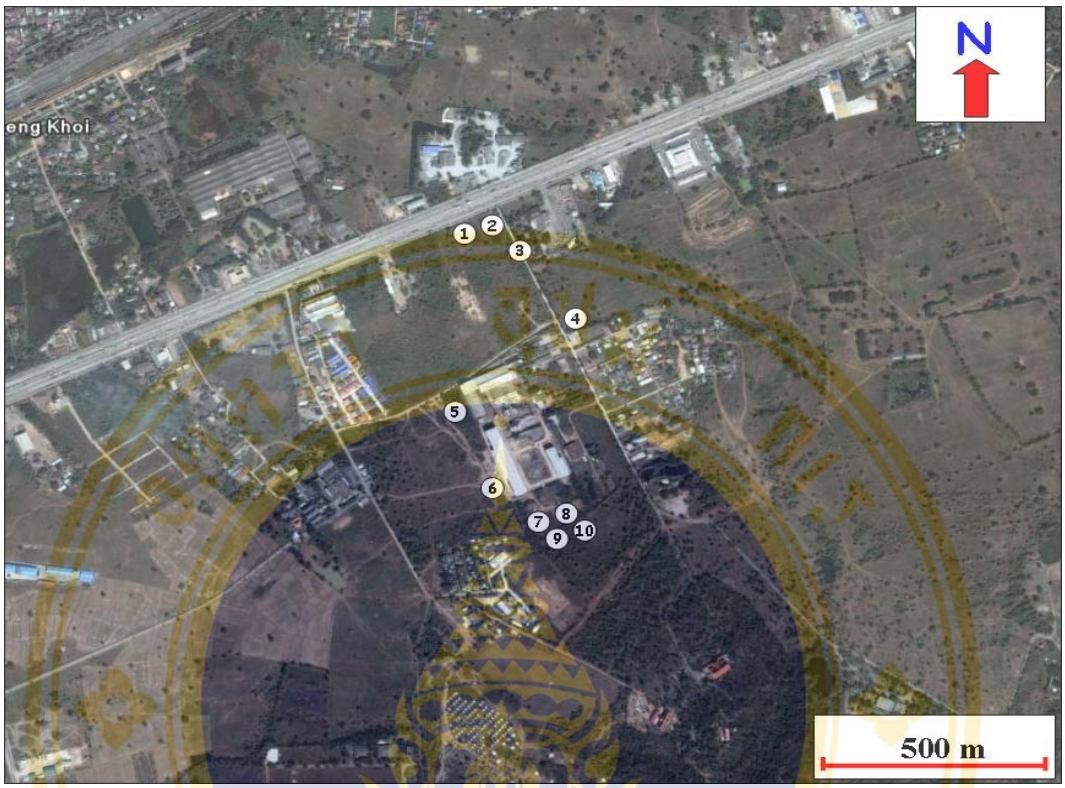

Figure 3.5 Plant sampling stations

The sampling design was considered based on the linkages of lead accumulation in various compartments. In this study it was designed for collecting samples of soil, sediment and plant to appraise lead contaminations in these areas, that lead could be transported to grazing animal and human in vicinity of the battery recycling plant. Soil, sediment and plant sampling designs were shown in Figure 3.6.

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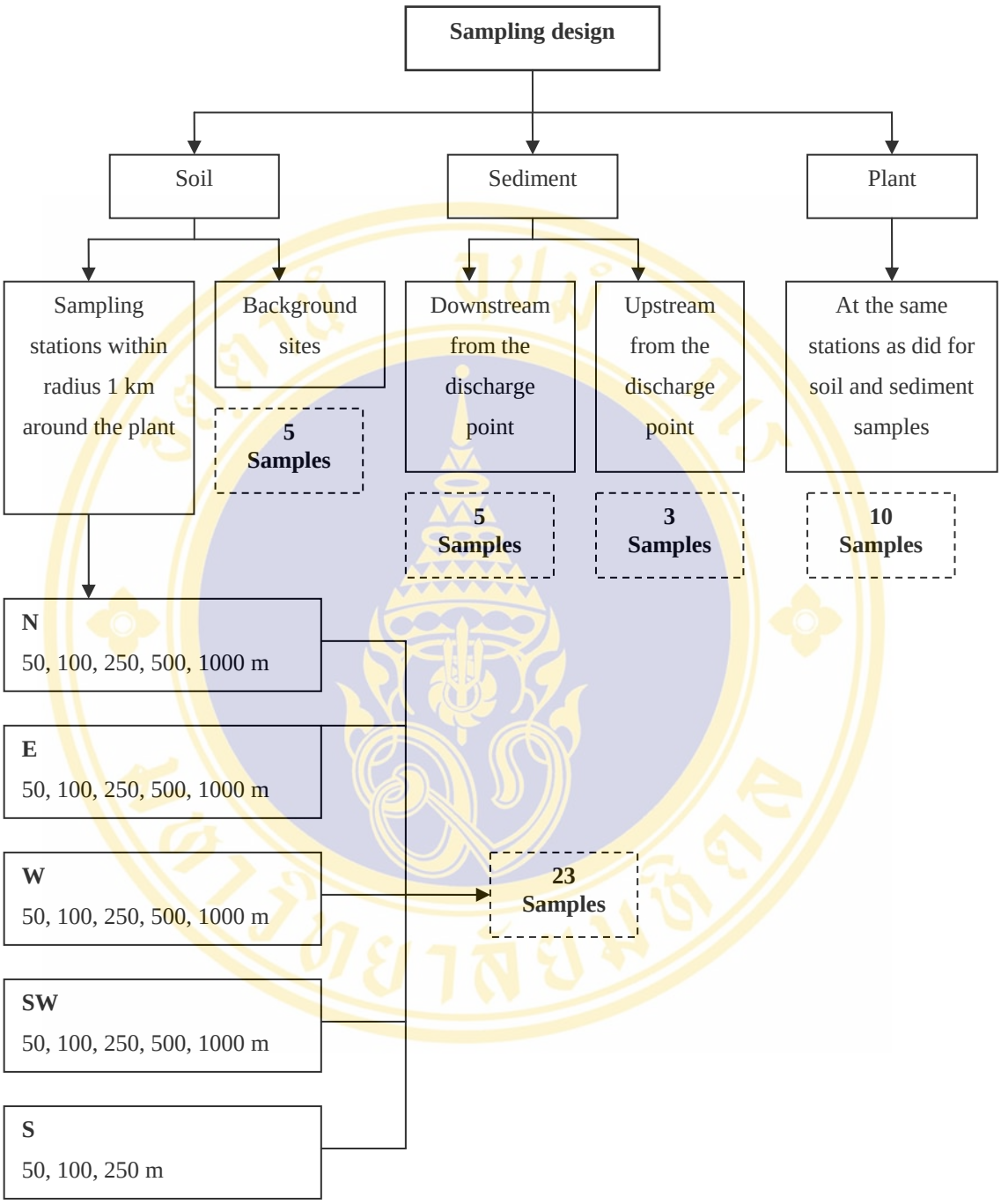

Figure 3.6 Soil, sediment and plant sampling designs

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3.3 Sampling Method

3.3.1 Equipment

1) Spoon and spade

2) Indelible ink marker, black or blue and label

3) Plastic bucket

4) Ziploc bags, trash bags

5) Topographic map 1:50,000, aerial photograph, GPS

3.3.2 Sampling procedure for soil, sediment and plant

Label number of samples on new ziploc bag for use as a sample collection container and record information of the sampling stations.

3.3.2.1 Soil sampling

1) Surface soil samples were collected using a spade at the depth of 10-30 cm. Vegetation and debris were removed and discarded.

2) Soil samples were collected in five replicates in a sampling station from an area of approximately 10 x 10 m^2. Each replicate of soil samples were collected 1 kg in plastic bucket.

3) All replicate samples from sampling stations were thoroughly mixed together then subsampled and one sample retained about 1 kg for analyses. All soil samples were kept in ambient air prior to laboratory.

3.3.2.2 Sediment sampling

1) Sediment samples were collected from the bottom of the drainage system using a spade at the depth of 10-30 cm.

2) Sediment samples were collected about 1 kg in five replicates in a sampling station. Vegetation and debris were removed and discarded. Thoroughly mixed together then subsampled and one sample retained about 1 kg for analyses.

3) All sediment samples were kept in ice box temperature of 4 ^{o}C and transport to the laboratory.

3.3.2.3 Plant sampling

1) Plant samples were collected from the same location as for soil and sediment samples within radius 50 m from the battery recycling plant.

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2) Each plant species were randomly collected within the sampling area. Edible parts of the each plant species were collected about 200 g for analyses.

3) All plant samples were kept in ice box temperature of 4 ^{o}C and transport to the laboratory.

3.4 Sample Preparation

3.4.1 Preparation for soil and sediment samples

Soil and sediment samples were air dried under shade around 2 days, crushed by using a porcelain pestle and mortar and sieved to remove the particles greater than 2 mm, using stainless sieve. This is because, more than 90 % of contaminants are expected to present in the particles smaller than 2 mm (Wasay et al., 2001). All soil and sediment samples were dried at 103 °C for 24 hours prior to digestion.

3.4.2 Preparation for plant samples

Each plant sample was thoroughly washed in running tap water after that samples was rinsed again with deionized water. The sample were then oven dried at 60-70 °C for 48 hours, cut and ground to a small pieces prior to digestion.

3.5 Sample Analysis

3.5.1 Physical and chemical analysis of soil and sediment

The physical and chemical characteristics of soil and sediment samples were analyzed in laboratory of soil and science at the Office of Science for Land Development, Department of Agriculture, Ministry of Agriculture and Cooperatives, Thailand. The parameters analysis methods were shown in Table 3.2.

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Table 3.2 Physical-chemical parameters and analysis methods

Parameter	Unit	Analysis method	Reference
pH	-	Soil:Water 1:1 pH meter	Peech (1965)
Organic matter (OM)	%	Wakley & Black titration	Wakley and Black (1947)
Cation Exchange Capacity (CEC)	cmol/kg	Extraction with 1 N NH_4OAc pH 7.0	Chapman (1965)
Soil Texture	% (sand, silt, clay)	Pipette method	Reynolds (1993)

3.5.2 Total lead analysis for soil and sediment

3.5.2.1 Apparatus

1) Hot plate
2) Hot air oven
3) 100, 1,000 mL Beakers
4) 10 mL Pipettes
5) 125 mL Erlenmeyer flasks
6) Glass filter funnels
7) Whatman No.42 filter paper
8) Analytical balance

All glassware were cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed again with deionised water and dried in clean room.

3.5.2.2 Reagents

1) Deionised water
2) Concentrated 65 % nitric acid (HNO_3)
3) Hydrochloric acid (HCl)

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3.5.2.3 Digestion of soil and sediment samples

Total lead content of soil and sediment samples were determined using method of Nitric/Hydrochloric acid wet digestion (Roy and Duncan, 1977) as following procedure:

1) Soil samples 2 g were accurately weighed into 125 mL Erlenmeyer flask.

2) Add 10 mL of deionised water, followed by 10 mL of concentrated nitric acid.

3) The samples were digested on hot plate and refluxed at 95 °C for 1 hour without boiling. Allow the sample to cool.

4) Add 10 mL of concentrated nitric acid again to ensure complete oxidation for 1 hour without boiling.

5) Allow the sample to cool, rinse the material back into the Erlenmeyer flask with a minimum amount of deionised water and then add 10 mL of hydrochloric acid. Continue reflux the digest solution for 1 hour until it becomes clear with light colored.

6) After cooling to ambient temperature, the solutions were filtered into Erlenmeyer flasks, diluted with deionised water. A volume was made up to 50 mL and mixed well.

7) Each soil sample was analyzed in three replicates. Retain the solution for lead analysis by Flame Atomic Absorption Spectrophotometry (FAAS). The analytical procedure is summarized in Figure 3.7.

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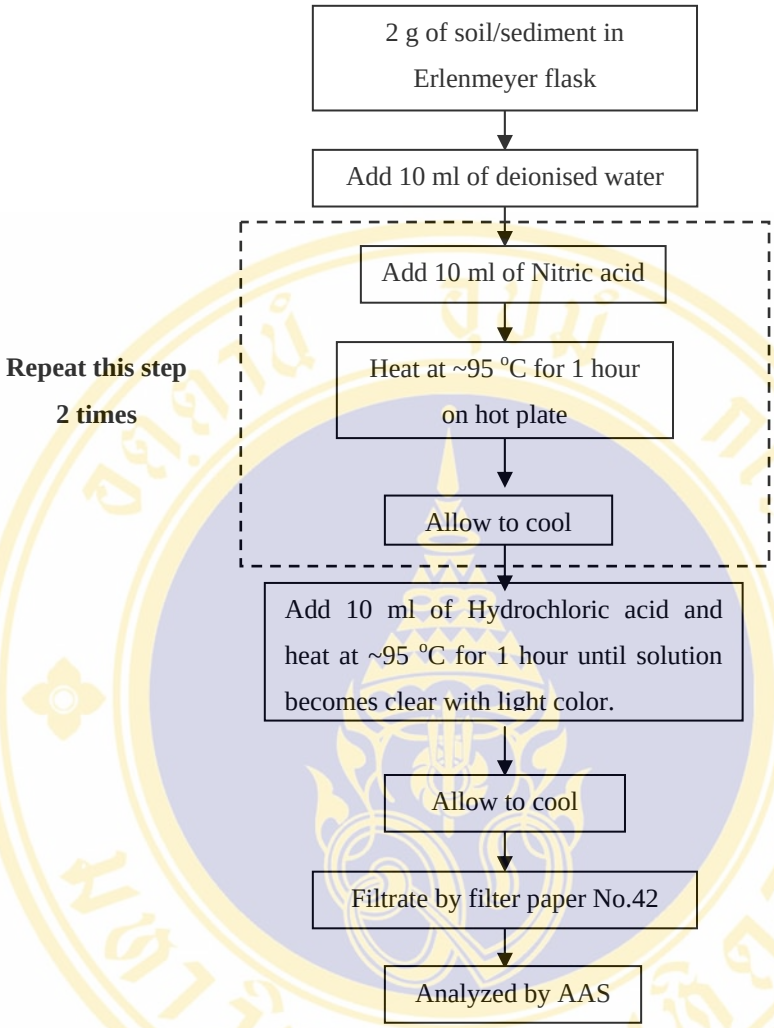

Figure 3.7 Procedure for acid digestion of soil using Nitric/Hydrochloric acid method

3.5.2.4 Digestion of plant samples

Total lead content of plant samples were determined using method of Nitric acid wet digestion (Rotkittikhun et al., 2006) as following procedure:

1) Plant sample 0.5 g was accurately weighed into 125 mL Erlenmeyer flask.

2) Add 10 mL of deionised water, followed by 10 mL of concentrated nitric acid.

3) The samples were digested on hot plate and refluxed at 95 °C for 1 hour without boiling. Allow the sample to cool.

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4) Add 10 mL of concentrated nitric acid again to ensure complete oxidation for 1 hour without boiling.

5) Allow the sample to cool, rinse the material back into the Erlenmeyer flask with a minimum amount of deionised water and then add 10 mL of nitric acid and reflux continue for 1 hour. Until solution becomes clear with light colored.

6) After cooling to ambient temperature, the solutions were filtered into Erlenmeyer flasks, and diluted with deionised water. A volume was made up to 50 mL then mixed well.

7) Each plant sample was analyzed in three replicates. Retain the solution for lead analysis by Flame Atomic Absorption Spectrophotometry (FAAS). The analytical procedure is summarized in Figure 3.8.

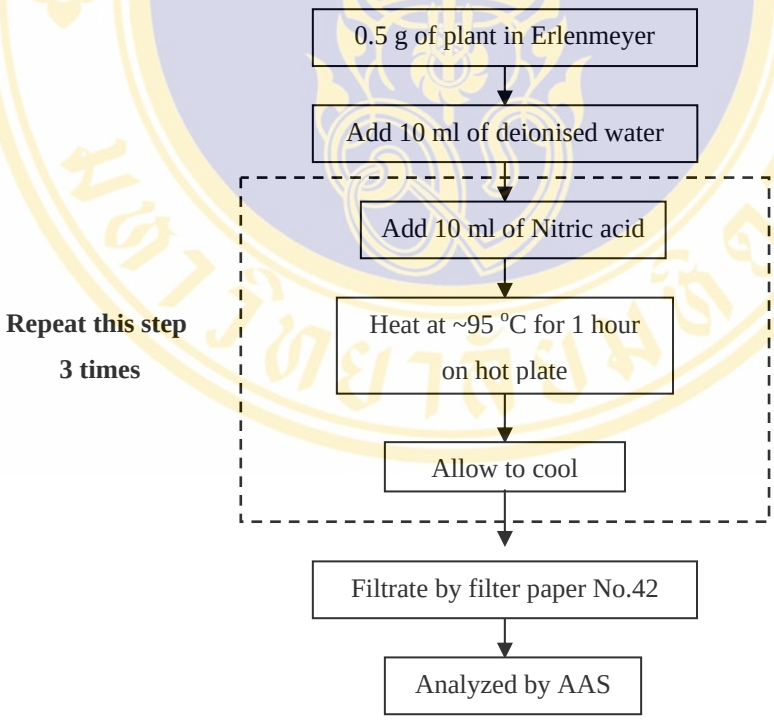

Figure 3.8 Procedure for the acid digestion of plants using Nitric acid method

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3.5.3 Quality control of laboratory

The accuracy of analytical procedure for lead determination was calibrated against two standard reference materials, SRM 2710 (Montana Soil Moderately Elevated Traces) for soil samples and SRM 8704 (Buffalo River Sediment) for sediment samples from the National Institute of Standards & Technology (NIST). The results of lead analysis were found to be close to the certified value as shown in Table 3.3. Whereas method detection limit (MDL) was at 0.006 mg/L with the percentage recovery ranged from 93.89-96.91.

Table 3.3 Analysis of standard reference materials for lead (n = 3)

SRM	Certified value (mg/kg dw)	Measured value (mg/kg dw)	Recovery (%)
2710 (Montana Soil)	5,532	5,361.53±81.10	96.91
8704 (Buffalo River Sediment)	150	140.84±6.47	93.89

*Recovery (%) = (Mean $_{\text{measured value}}$/ Mean $_{\text{certified value}}$) × 100%

3.5.4 Lead concentrations calculation

The total lead concentrations in soil, sediment and plant samples were determined and reported on a dry weight basis in mg/kg from the following equation:

$$\text{Lead concentration (mg/kg)} = \frac{\text{Result from AAS (mg/L in digest)} \times \text{final volume (mL)}}{\text{Weight of dried sample (g)}}$$

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3.6 Data Analysis

Descriptive analyses were used to describe lead concentrations as mean, maximum, minimum and standard deviation (S.D).

Non parametric (Kruskal-Wallis) was used to describe the differences observed in the lead concentrations in soil among the various directions and distances around the battery recycling plant ($p<0.05$), a multiple comparisons (Dunnett T3) test was performed. Regression analysis was used to describe the relationship between the distance from the battery recycling plant and lead concentrations in soil ($p<0.05$). These statistical analyses were calculated using statistical software SPSS version 15.0.

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CHAPTER IV
RESULTS AND DISSCUSSION

This chapter presents the results from laboratory analysis of lead contamination in soil, sediment and plant samples collected from the study area. The aims of the study are to evaluate the lead distribution and its potential environmental risk in vicinity of the battery recycling plant.

4.1 Characterization of Sediment and Soil in the Study Area

The sampling stations for physical and chemical characteristics of sediments and soils in the study area were shown in Figure 4.1.

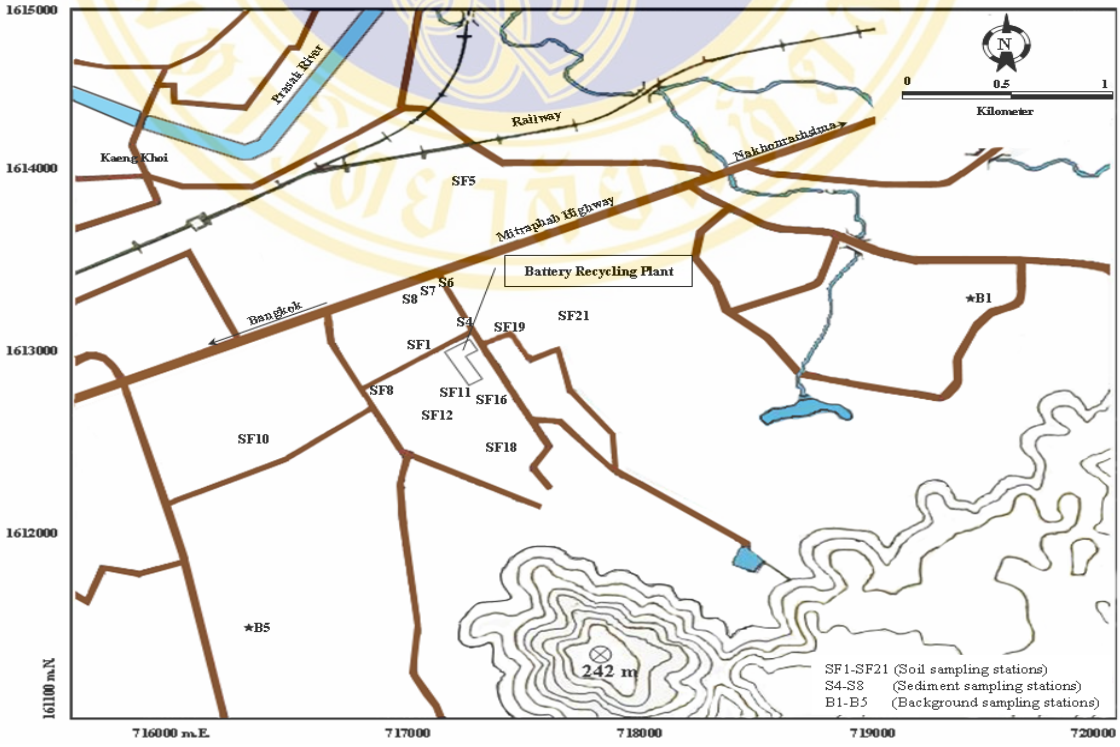

Figure 4.1 Sampling stations for sediment and soil

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The textures of sediments along the drainage system downstream from the effluent discharge point (S4-S8) were varied from sandy loam, clay loam, silty clay loam and silty loam. The percentages of clay contents were within the range of 14.4 to 38.8 with pH ranged from 4.4 to 6.8. The percentages of organic matter (OM) contents were varied from medium to very high within the range of 1.84 to 6.99. Also, the cation exchange capacity (CEC) were varied from medium to high within the range of 13.85 to 23.95 cmol/kg (Table 4.1).

Table 4.1 Characterization of sediments

Sampling stations	CEC (cmol/kg)	pH	OM (%)	Sand (%)	Silt (%)	Clay (%)	Soil texture
S4	18.12	6.8	6.99	32.6	52.3	15.1	Silty Loam
S6	13.85	6.7	4.17	59.7	25.9	14.4	Sandy Loam
S7	22.26	4.8	4.52	9.3	60.8	29.9	Silty Clay Loam
S8	23.95	4.4	1.84	27.0	34.2	38.8	Clay Loam

*S4-S8 = Sediment sampling stations along the drainage system near the battery recycling plant

At soil sampling stations within radius 1 km from the plant (SF1-SF21) and background areas (B1-B5), almost textures among the sampling stations were loam and sandy loam. The percentages of clay contents were within range of 8.9 to 25.6. The pH of soils in most of the stations were neutral to strongly acid ranged from 5.1 to 7.0. Furthermore, the percentages of OM content varied from 0.77 to 3.13. Whereas, the CEC varied within the range of 6.67 to 18.53 cmol/kg (Table 4.2).

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Table 4.2 Characterization of soils

Sampling stations	CEC (cmol/kg)	pH	OM (%)	Sand (%)	Silt (%)	Clay (%)	Soil texture
SF1	9.97	7.0	2.86	35.1	47.7	17.2	Loam
SF5	18.53	6.7	3.13	31.6	42.8	25.6	Loam
SF8	10.96	6.4	2.60	48.5	42.6	8.9	Loam
SF10	9.26	6.1	1.15	45.3	41.4	13.3	Loam
SF11	6.67	6.9	0.77	52.8	34.0	13.2	Sandy Loam
SF12	8.02	6.2	2.48	50.7	39.0	10.3	Loam
SF16	7.46	5.1	2.54	57.4	29.2	13.4	Sandy Loam
SF18	10.44	6.2	2.64	57.1	33.5	9.4	Sandy Loam
SF19	11.28	6.9	2.65	30.5	49.7	19.8	Loam
SF21	9.11	6.5	1.97	45.4	42.3	12.3	Loam
B1	10.35	6.1	2.95	50.1	40.1	9.8	Loam
B5	9.40	6.3	1.25	46.3	42.4	11.3	Loam

*SF1-SF21 = Soil sampling stations within radius 1 km from the battery recycling plant

*B1-B5 = Soil sampling stations in background areas

The results were found corresponding to those data in previous studied with pH values ranged from 4.5 to 7.0, the soil textures were silt loam, silty clay loam, sandy loam, loam and loamy sand, the percentages of clay contents ranged from 0.5 to 27.0, the percentages of OM contents of soils ranged from 0.27 to 4.36, and the CEC of soils ranged from 2.4 to 14.43. The characteristics of soils from the study area were wide range of variation depending on the group of soil that divided into various soil series (Land Development Department, 2006). Thus, the physical and chemical characteristics of soils and sediments in this study were variable depending on the sampling stations.

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4.2 Lead Concentrations in Surface Soils and Sediments

4.2.1 Lead concentrations in surface soils

Lead concentrations in surface soils were investigated both from the background areas and the contaminated areas around the battery recycling plant. The background soils were collected at the distance about 2 km from the plant and lead concentrations were in the range of 8 to 26 mg/kg dw (mean 15 mg/kg dw) (Table 4.3).

Table 4.3 Lead concentrations (mg/kg dw) in surface soil from background areas (August-September, 2006)

Sampling stations	Lead (mg/kg dw)		
	Minimum	Maximum	Mean (SD)
B1	19	20	19±0.2
B2	23	27	26±2
B3	9	11	10±1
B4	10	13	11±2
B5	7	9	8±1
Average			15±8
Background value (Bernhard et al., 2004) = 18 mg/kg dw			

Lead concentrations of background soils at various background areas were varied due to the different characteristics of soil parent materials and were generally closed to the other studies. They were consistent with the report of Parkpian et al. (2002) that lead concentrations in agricultural soil at various locations in Saraburi province, Thailand were in the range of 6 to 15 mg/kg dw. Also, Kabata-Pendias and Pendias (1992) found that lead concentrations in non-polluted soil in the worldwide were in the range of 10 to 70 mg/kg dw. Likewise, the mean of lead concentration in agricultural soils was of 18 mg/kg dw in Thailand region (Bernhard et al., 2004).

The study area were divided into five transect lines in the directions of north, east, west, south and west-south of the plant. Soil samples were collected within

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radius 1 km from the plant at the distance of 50, 100, 250, 500 and 1,000 m from the point source. The lead concentrations in all soil sampling stations were found within the range of 7 to 1,750 mg/kg dw (Table 4.4 and Figure 4.2).

Table 4.4 Lead concentrations (mg/kg dw) in surface soils at the depth of 10 cm (August-September, 2006)

Transect lines	Location descriptions	Distance from the plant (m)	Sampling stations	Lead (mg/kg dw)
				Mean (SD)
N	The north of the plant near Mitraphab highway including residential areas	50	SF1	1,750±84
		100	SF2	144±3
		250	SF3	62±8
		500	SF4	21±3
		1,000	SF5	17±1
W	The west of the plant including residential areas and hospital	50	SF6	340±14
		100	SF7	79±1
		250	SF8	43±14
		500	SF9	14±0.4
		1,000	SF10	10±1
WS	The west-south of the plant including residential areas	50	SF11	613±87
		100	SF12	43±5
		250	SF13	37±10
		500	SF14	8±1
		1,000	SF15	7±0.7
*S	The south (behind) of the plant near the forest and the hill	50	SF16	1,475±175
		100	SF17	31±4
		250	SF18	21±3
		500	-	-
		1,000	-	-
E	The east of the plant including residential areas and grazing animal farms	50	SF19	1,523±139
		100	SF20	27±1
		250	SF21	19±2
		500	SF22	13±0.6
		1,000	SF23	14±1
Background value (Bernhard et al., 2004) = 18 mg/kg dw				

*S = Soil samples at the distances of 500 and 1,000 m from the plant could not be collected due to its locations in forest.

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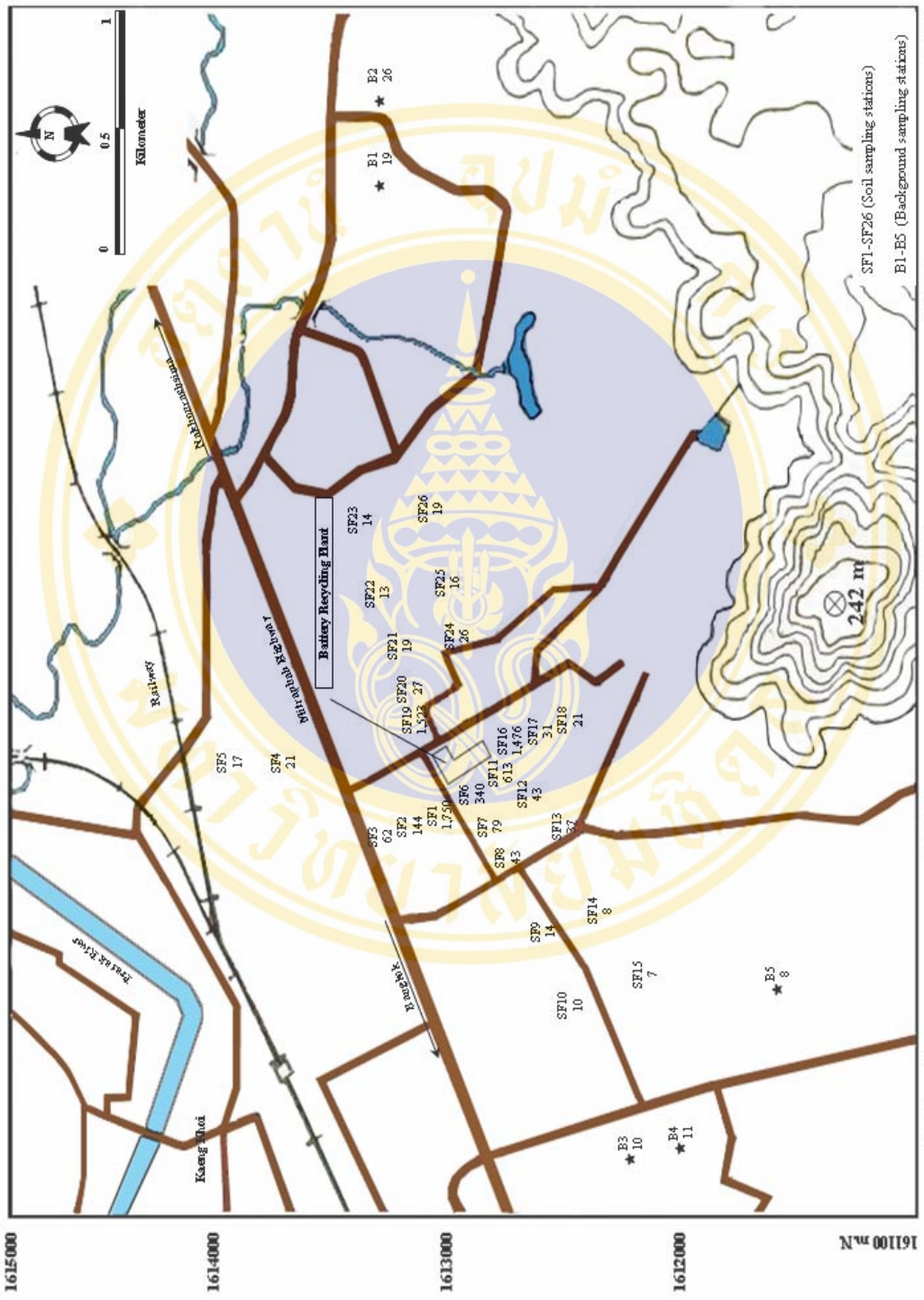

Figure 4.2 Lead concentrations (mg/kg dw) in surface soil sampling stations around the plant

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The results revealed that lead concentrations in soil decreased with increasing distance of 50, 100, 250, 500 and 1,000 m from the plant in all transects. In the north of the plant at the distance of 50, 100, 250, 500 and 1,000 m, lead levels were found to be at the concentrations of 1,750, 144, 62, 21 and 17 mg/kg dw, respectively. Likewise, in the east of the plant at the distance of 50, 100, 250, 500 and 1,000 m, lead levels were found to be at the concentrations of 1,523, 27, 19, 13 and 14 mg/kg dw, respectively. At the distances of 50, 100, 250, 500 and 1,000 m in the west of the plant, lead levels were found to be at the concentrations of 340, 79, 43, 14 and 10 mg/kg dw, respectively. Whereas in the west-south of the plant at the distances of 50, 100, 250, 500 and 1,000 m, lead levels were found to be at the concentrations of 613, 43, 37, 8 and 7 mg/kg dw, respectively. Also, at the distances of 50, 100 and 250 m in the south of the plant, lead levels were found to be at the concentrations of 1,475, 31 and 21 mg/kg dw, respectively.

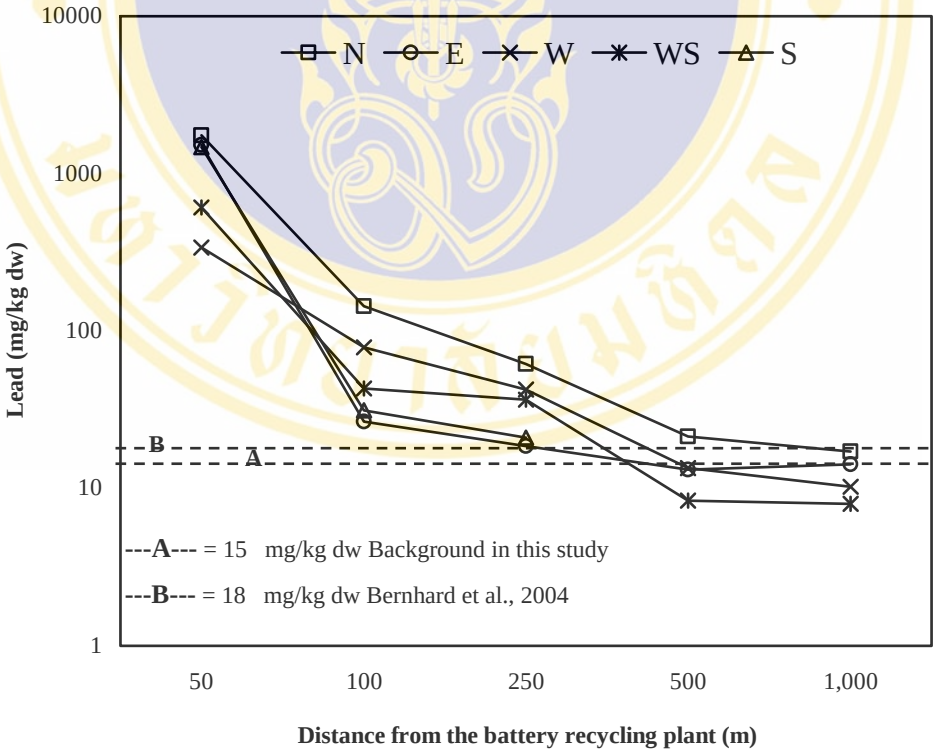

Figure 4.3 Lead concentrations (mg/kg dw) in surface soils around the battery recycling plant

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Lead concentrations in surface soil at most various sampling stations were found to be exceeded the background value (indicated by the dotted line in Figure 4.3). The results also showed that lead concentrations decreased in all of transect lines and lead levels were found to be exceeded background value only at distances of 50, 100 and 250 m from the plant. Furthermore, lead levels in the areas closed to the plant at the distance of 50 m in all transect lines were found to be elevated high. At the distances of 500 and 1,000 m from the plant lead levels found to decrease in all directions with the values that closed to the background one (Figure 4.3).

The results also showed that the high elevated concentrations of lead in soils were found at the distances less than 250 m from the battery recycling plant and exceeded background value. Lead distribution in all of transect lines indicated that the contamination was not migrate over large distances. The maximum lead contaminations were largely shown in soil surface at 50 m from the plant. At the distance more than 500 m from the plant lead concentrations were found to be closed to those generally found in the local soil background.

The statistical analysis at 0.05 level of significant showed that the lead concentrations of soil samples in study area at the distances of 50, 100 and 250 m away from the plant were significantly higher than soil samples in background area ($p<0.001$, $p<0.01$, $p<0.005$, respectively). Whereas at the distances more than 500 m from the plant lead concentrations were not significantly different from the background value ($p>0.05$).

This indicated that lead resulting from the battery recycling plant activities might have the potential adverse effects on ecosystems and habitats located within radius of 250 m from the plant.

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Lead concentrations in soil had tendency to decrease with increasing distance from the battery recycling plant (Figure 4.4). Regression analysis was used to confirm the negative nonlinear relationship between existed distance from the battery recycling plant and lead concentrations in soil. Also, lead concentrations in soil could be predicted with a nonlinear combination of the distance from the battery recycling plant ($p < 0.001$). The regression line that gave the best fit for lead was a power function of the following equation.

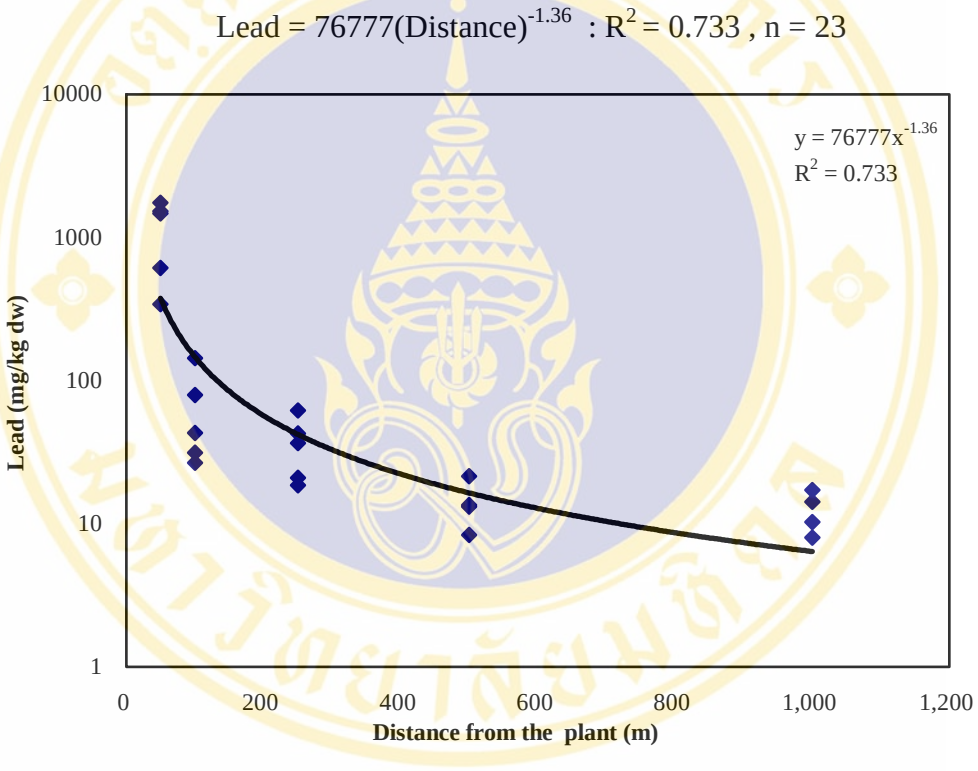

Figure 4.4 Lead concentrations (mg/kg dw) vs. distance from the battery recycling plant as defined by the calculated distribution function

This indicated that increasing distance from the battery recycling plant (range = 50-1,000 m), decreased soil lead concentrations (range = 1,750-7 mg/kg dw). The lead concentrations of surface soil were very high at the areas closed to the battery recycling plant and the concentrations in soil decreased significantly as the distances increased (Figure 4.4). The high elevated lead concentrations above background value would be indicative of soil contaminated concern due to lead pollution. Therefore, lead from battery recycling plant was the major anthropogenic source of lead in this study

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area concerning battery recycling plant activities.

The distribution of lead with distance from the plant in this study was corresponded to the study by Skinner and Saline (1995) that levels of lead obtained from the area around the battery recycling plant in Canada were found to be as high as 51,000 mg/kg dw and declined to 120 mg/kg dw in the area of 1 km away. This distribution tendency has already been observed in other studies about lead pollution from battery recycling and smelting industries surrounding areas and indicated dispersion of lead particles from the plants as a source of lead contamination in the soils.

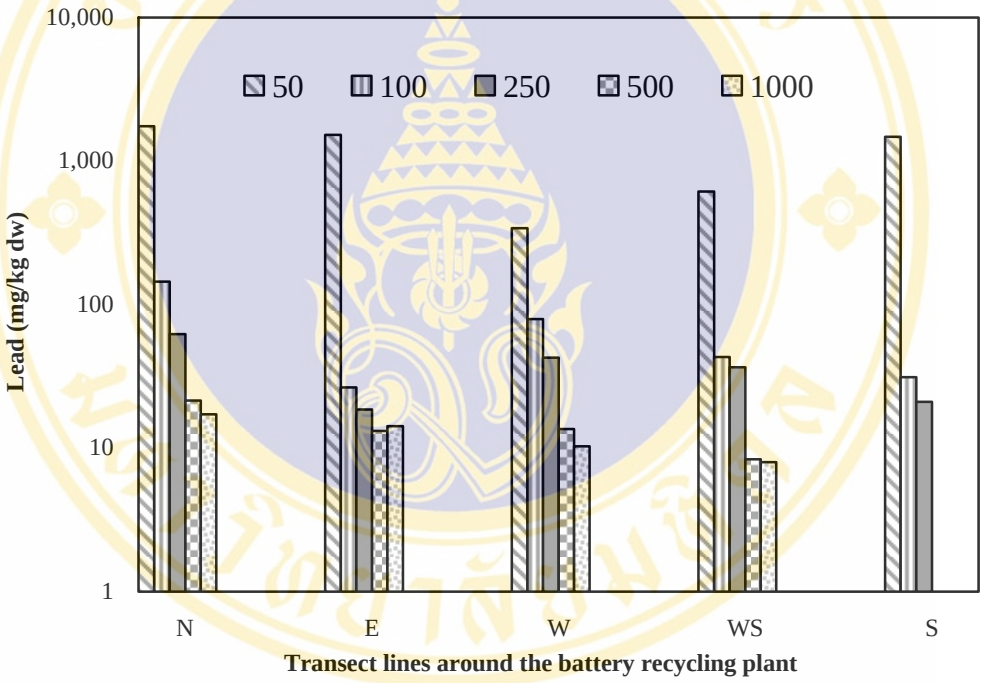

Figure 4.5 Lead concentrations (mg/kg dw) in surface soils at different transect lines around the battery recycling plant

Lead concentrations in surface soil at different transect lines around the battery recycling plant found to be a clear decrease with increasing distance from the recycling plant along the various transect lines. However, levels of lead concentrations in the north transect line appeared to be slightly higher than the other transect lines (Figure 4.5).

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The Kruskal-Wallis non-parametric analysis of variance on ranks ($p > 0.05$) showed that the lead levels among the different transect lines were not significantly different. With the respect of predominant wind direction (west-south directions) and topography (flatland), lead distribution was probably associated with wind movements. It can be concluded that, the levels of lead concentrations in soils were probably due to several factors, such as lead leaching from slag heap and atmospheric lead deposition, including wind movements as well as the major contribution of lead from the battery recycling plant.

4.2.2 Lead concentrations in sediments along the drainage system adjacent to the battery recycling plant

The sediment samples were collected from both upstream and downstream from effluent discharge point along the drainage system of the plant at various distances (Figure 4.6).

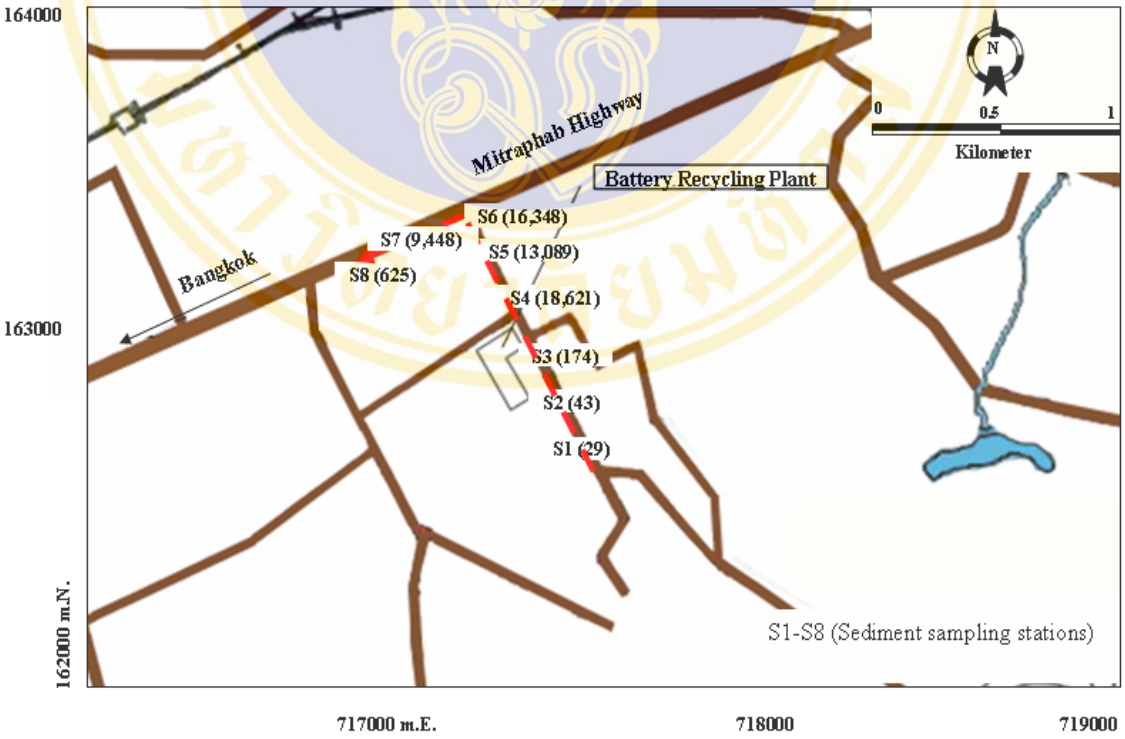

Figure 4.6 Lead concentrations (mg/kg dw) in sediment sampling stations along the drainage system

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Lead concentrations in sediment for the stations at the distance of 300, 200 and 100 m upstream from the effluent discharge point were ranged from 29, 43 and 174 mg/kg dw, respectively. Likewise, lead concentrations in sediment collected downstream from the effluent discharge point at the distance of 100, 200, 300, 350 and 400 m were 18,621, 13,089, 16,348, 9,448 and 625 mg/kg dw, respectively (Table 4.5).

Table 4.5 Lead concentrations (mg/kg dw) in sediments along the drainage system (August-September, 2006)

Sampling stations	**Station descriptions**	**Distance from the effluent discharge point (m)**	**Lead (mg/kg dw)**		
			Minimum	**Maximum**	**Mean (SD)**
S1	Upstream from the effluent discharge point	300	21	33	29±6
S2		200	39	45	43±4
S3		100	151	202	174±26
S4	Downstream from the effluent discharge point	100	17,270	20,209	18,621±1,484
S5		200	12,133	14,577	13,089±1,306
S6		300	15,717	16,738	16,348±551
S7		350	9,272	9,750	9,448±263
S8		400	600	640	625±23
Background value (Parkpian et al., 2002) = 6-15 mg/kg dw					

The results also found that lead concentrations in sediment downstream from the effluent discharge point was very high with the concentration of 18,621 mg/kg dw and the concentrations gradually decreased as the distance away from the effluent discharge point. Furthermore, the farthest station for sediment was about 400 m downstream at the end of drainage system with the lead concentrations at the level of 625 mg/kg dw which much higher than the background value. The higher elevated lead concentrations found in station S6 might due to the character of terrain itself. As the elevation of the drainage system at sampling station 6 was lower than the other

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stations. When wastewater flows through that station the flows might be slow down resulting in lead particulate settling down to sediment (Figure 4.7).

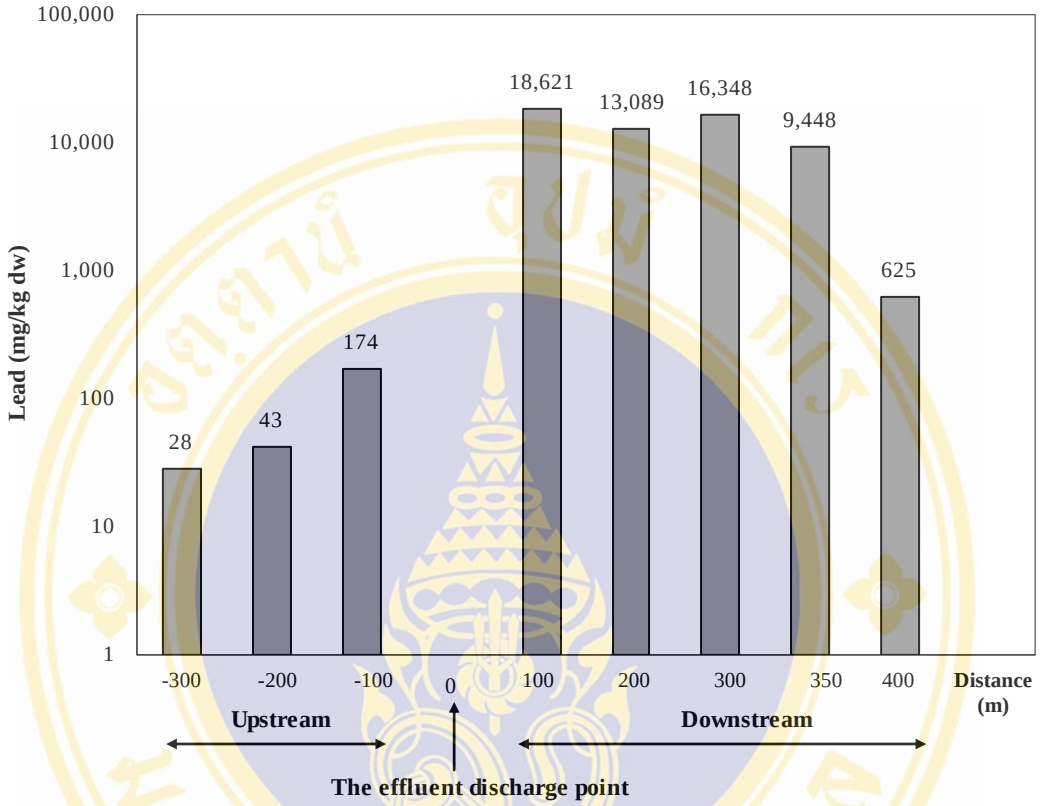

Figure 4.7 Lead concentrations (mg/kg dw) in sediment along the drainage system

Lead concentrations of sediment at the upstream and downstream stations from the effluent discharge point along this drainage system were considerably elevated higher than those found in unpolluted or background sediment. The elevated high concentrations of lead were probably due to the lead contaminated in soil surface in areas at close proximity to the plant resulting from atmospheric deposition from the battery recycling plant. And subsequently surface run off might be transported soil particles containing adsorbed lead and run to the drainage system. However, the major source of lead contaminated sediments in downstream stations was battery recycling plant discharged wastewaters which run into the drainage system.

The results of lead concentrations in sediment were corresponded to the study of Boughriet et al. (2006) in investigation of heavy metal pollution in sediments derived from the Deule canal near the smelting plant. It revealed that total lead

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concentrations in sediments were in the range of 27 to 10,079 mg/kg dw. The investigation had also concluded that lead pollution was readily apparent in the sediments, with the lead contents largely exceeded those of background soils with maximum values of lead in sediments obtained near the plant.

4.3 Lead Concentrations in Soil and Sediment Profiles at High Contaminated Stations

The lead concentrations in soil and sediment profiles at high contaminated stations at three depths of 10, 20 and 30 cm were investigated.

4.3.1 Lead concentrations in soil profiles

Lead concentrations in soil samples collected from high contaminated stations (1, 11, 16, 19) were varied within the range of 740 to 1,657 mg/kg dw, 181 to 698 mg/kg dw and 122 to 245 mg/kg dw for the first layer (0-10 cm), the second layer (10-20 cm) and the third layer (20-30 cm) of soil, respectively (Table 4.6).

Table 4.6 Lead concentrations (mg/kg dw) in the soil profiles at high contaminated stations (February, 2007)

Sampling stations	Distance from the plant (m)	Lead (mg/kg dw)		
		Soil depth (cm)		
		0-10	10-20	20-30
SF1	50 m up to the north	1,657	528	122
SF11	50 m up to the west-south	740	181	126
SF16	50 m up to the south	1,134	439	125
SF19	50 m up to the east	1,353	698	245

The highest elevated concentrations of lead were found in the first layer of soil and the lead concentrations decreased as increasing depth. At each sampling station, lead was found to migrate downward into the subsurface soil. Although, these

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stations, the high elevated concentrations of lead were found at the 30 cm depth with the levels that exceeded background value. This indicated that lead had migrated downward more than 30 cm below the surface soil resulting from exposure to lead for long period of time more than 20 years (Figure 4.8).

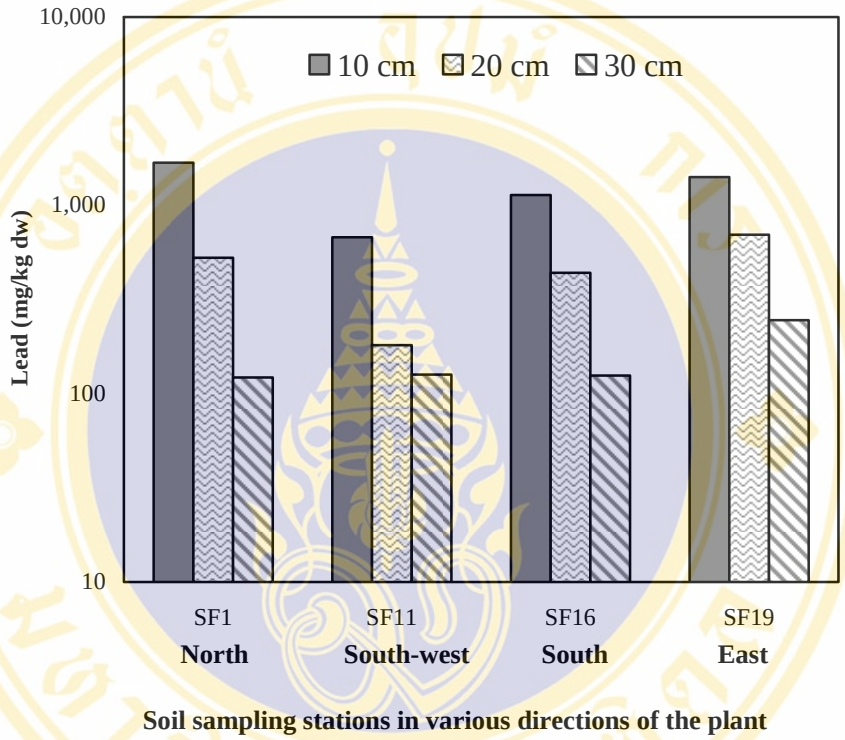

Figure 4.8 Lead concentrations (mg/kg dw) in the soil profiles at three depths

4.3.2 Lead concentrations in sediment profiles

The lead concentrations in sediment samples at high contaminated stations (4, 6, 7, 8) were varied within the range of 869 to 24,142 mg/kg dw, 125 to 15,842 mg/kg dw and 111 to 6,947 mg/kg dw for the first layer (0-10 cm), the second layer (10-20 cm) and the third layer (20-30 cm) of sediment, respectively (Table 4.7).

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Table 4.7 Lead concentrations (mg/kg dw) in the sediment profiles at high contaminated stations (February, 2007)

Sampling stations	Distance from the effluent discharge point (m)	Lead (mg/kg dw)		
		Sediment depth (cm)		
		0-10	10-20	20-30
S4	100 m downstream	24,142	15,842	6,947
S6	300 m downstream	13,539	6,872	3,952
S7	350 m downstream	5,407	2,963	2,032
S8	400 m downstream	869	125	111

Also, as the results found in contaminated soil, the very high elevated concentrations of lead were found in the first layer of superficial sediment and the concentrations decreased as increasing. Likewise, lead was found to migrate deeper into the subsurface sediment. At the 30 cm depth high elevated concentrations were found at all stations except at the station 8. Although, these stations the high elevated concentrations of lead were found at the 30 cm depth with the levels that exceeded background value of this area. This indicated that lead had migrated downward more than 30 cm below the surface of sediment resulting from exposure to lead for long period of time more than 20 year (Figure 4.9).

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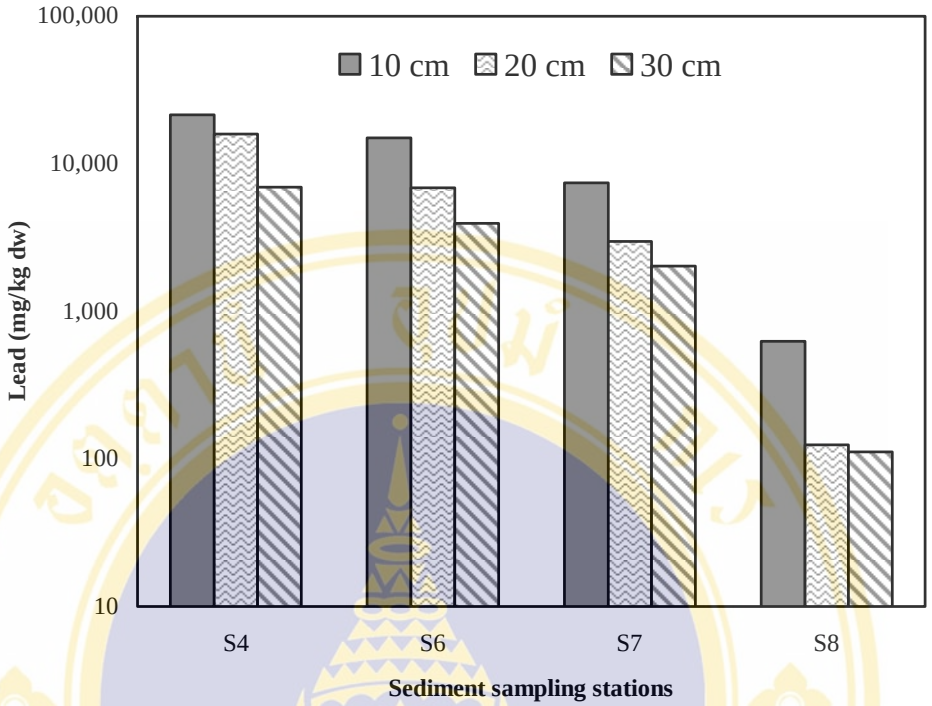

Figure 4.9 Lead concentrations (mg/kg dw) in the sediment profiles at three depths

In the vicinity of the battery recycling plant soils and sediments have been affected from lead emissions more than twenty years. Although, lead migration downwards and accumulations in the depth of soil and sediment profiles at the level above natural background, high elevated lead concentrations were also found in surface of soil and sediment as the major part of the contamination which is restricted to the upper 10 or 20 cm and decreased as increasing depth. The study of lead migration in old lead smelting sites has found to be very little, even where surface soils and slags contaminated with the high elevated levels of 10% lead. Vertical penetration of lead through a sandy rock-soil matrix, during a period of over 200 years, was found to be less than 70 cm (Maskell and Thornton, 1993). Furthermore, various reports on the vertical distribution of metals in soil also showed a superficial accumulation of non-indigenous metals, whether these originate from the spreading of waste or from atmospheric fallout of industrial contamination (Sterckeman et al., 1999).

Moreover, the investigations showed that lead contaminations of soil and sediment among these sampling stations were found to be very high elevated and

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exceeded the maximum limits established for soil and sediment. Although lead concentrations decreased with the increasing depth of soil and sediment profile, the high elevated concentrations of lead were found to be more than 100 mg/kg dw at the depth of 30 cm of some sampling stations (DIW, 1997). This indicated that lead might be migrated vertically (at least 30 cm) through the soil depth. The results was consistent with the theory that soil lead concentrations in excess of 200 mg/kg dw were found at a depth of 0.9 to 1.0 m in the areas of peak surface soil lead concentrations (Murray et al., 1997).

In the case of the locality heavily contaminated by lead might be migrated vertically through the soil profile into the groundwater, hazardous wastes which containing lead from the slag land fill and also wastewater discharged directly to the land in local areas near the battery recycling plant were the cause of lead contamination in these areas. Leaching of lead from the landfill contaminated with lead might directly flow downwards to ground water. Generally, soil and sediment characteristics have the effects on the spread of lead downward to the depth at contaminated area. The mobility of lead depends upon many factors such as soil texture, soil pH (acidity), CEC and OM (Reed et al., 1996).

The downward movement of elemental lead from soil to groundwater by leaching is very slow under most natural conditions except for highly acidic situations (NSF, 1977). Chuan et al. (1996) found that the solubility of lead in soil depended on pH which being sparingly soluble at pH 8 and becoming more soluble as the pH approached 5. Between pH 5 and 3.3 lead solubility was increasing in soil largely. Leaching of soluble lead from contaminated soils into groundwater may be minimized by the presence of lead carbonate in soil and by maintaining a soil pH of 8 to 10 (Mundell et al., 1989). It had been reported that adjusting the pH of any one soil had a major impact on soil ability to retain heavy metals (Scokart et al., 1983). From Table 4.1 and 4.2, pH of sediment and soil at these stations were found to be slightly acid to neutral with the pH of 4.4 to 7.0. Then, it indicated that lead could be soluble and migrate downward to the depth of soil and sediment. In addition to pH, the mobility of lead depends upon the other factors such as soil texture, CEC, OM and presence of lead contamination at those stations.

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The conditions that induce leaching are the presence of lead in soil at concentrations that either approach or exceed the CEC of the soil, the presence of materials in soil that are capable of forming soluble chelates with lead, and a decrease in the pH of the leaching solution (e.g., acid rain) (NSF, 1977). The CEC is determined by the amount of negative surface charge on soil surfaces and is correlated with soil surface area. Generally, soil CEC capacity increases with increasing pH up to neutral to slightly alkaline conditions (Dempsey, 1991). The results found that the presence of lead concentrations in all soil and sediment at high contaminated sampling stations exceeded the CEC of the soil and sediment (6.67-23.95 cmol/kg) indicated that lead had a tendency to be leached downward to the depth of soil and sediment.

Furthermore, lead in soil has a strong tendency to be adsorbed onto particles of clay or OM and in this form lead is largely immobile and biologically inert with very long half life. The mobility of clay metal complexes is generally limited and exhibits a high degree of adsorption on clay-rich soil. In addition, the complex lead interactions with the soil components show a higher accumulation capacity for loamy soils than for sandy soils (Griffiths, 1995). With the respect of the texture of sediment and soil at high contaminated sampling stations, percentages of clay (13.4-29.9 %) were found at most of sampling stations. The higher percentages of clay (38%) found at station S8 indicated that lead has a high tendency to be adsorbed onto soil particles. Likewise, percentages of OM at most sediment and soil sampling stations were found to be varied from low to high except station S4 that OM were found to be higher (6.99%) than the other stations. Even, at high contaminated sampling stations where high percentages of clay and OM occurred in soil/sediment, lead could be leached downward deeper resulting form the high concentrations of lead that exceeded the capacity of soil and sediment to absorb.

4.4 Potential Environmental Risks

Lead contaminations in soil and sediment at the study stations were investigated at the levels that could cause environmental problems. Hazard quotient (HQ) values were used to represent the potential risks to soil and sediment from lead contaminated in study areas. The HQ values were calculated by dividing the concentrations of lead

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by its associated benchmark soil and sediment guideline values. The evaluation HQ values were used to estimate the potential risks if the maximum concentrations of lead found at the sampling stations exceeded the screening benchmark value (HQ > 1), then there are the potential for risks and further study is needed to clarify that risk (US EPA, 2006).

4.4.1 Potential environmental risks of soil at contaminated sites

The lead concentrations in soil at different distances and directions around the battery recycling plant were shown in Figure 4.10. The extents of soil contamination were appraised by comparing the concentrations of lead from the study stations with the maximum allowable concentration of lead in soil which was established by Department of Industrial Works, Thailand at the concentration of 100 mg/kg dw. Lead concentrations in soil at all stations located about 50 m from the plant found to be exceeded the maximum allowable value. Whereas, lead concentrations in soils of the most stations located at distance of 100, 250, 500 and 1,000 m from the plant were found to be lower than the maximum allowable value.

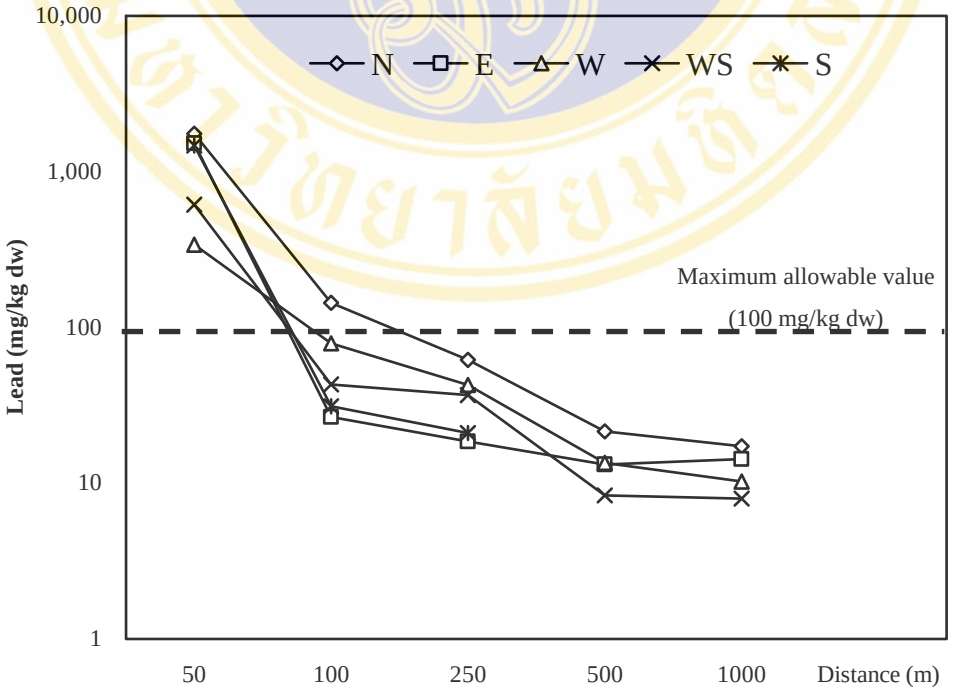

Figure 4.10 Lead concentrations (mg/kg dw) in soil around the battery recycling plant compared to the maximum allowable value

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The potential environmental risks using hazard quotient (HQ) values were estimated for soil contamination at site and proposed maximum allowable concentration of lead in soil as screening benchmark value was set up. The HQ values were then calculated for each soil stations in area around the battery recycling plant. The results found that HQ values in stations at distance of 50 m from the battery recycling plant in all transect lines were found at risks with the HQ value in the range of 3.40 to 17.50. The HQ values of lead in stations at distance of 100 m from the battery recycling plant in all transect lines were not at risks (HQ < 1) except the station of the north transect line with the HQ value of 1.44. Likewise, at all stations at the distance of 250, 500 and 1,000 m from the battery recycling plant in all transect lines, the HQ value were found to be not at risk (HQ < 1) (Table 4.8).

Table 4.8 Hazard quotients (HQ) of soil around the battery recycling plant

Directions	HQ of soil at different distances (m)				
	50	**100**	**250**	**500**	**1,000**
N	17.50	1.44	0.62	0.21	0.17
E	15.23	0.27	0.19	0.13	0.14
W	3.40	0.79	0.43	0.14	0.10
WS	6.13	0.43	0.37	0.08	0.07
S	14.75	0.31	0.21	-	-
Screening benchmark value for soil in this study = 100 mg/kg dw (DIW, 1997)					

The high potential environmental risks of soil resulting from lead contamination were found at the stations of concern at the distance of 50 m from the battery recycling plant in all directions. The HQ values in those stations that exceeded 1.0 indicated the soils in those stations were at risks. The remaining stations were not to be at risk with the HQ values less than 1.0 except the one station about 100 m from the plant up to the north. Thus the soils in the area out of the radius about 100 m from the point source were not at risk (Figure 4.11).

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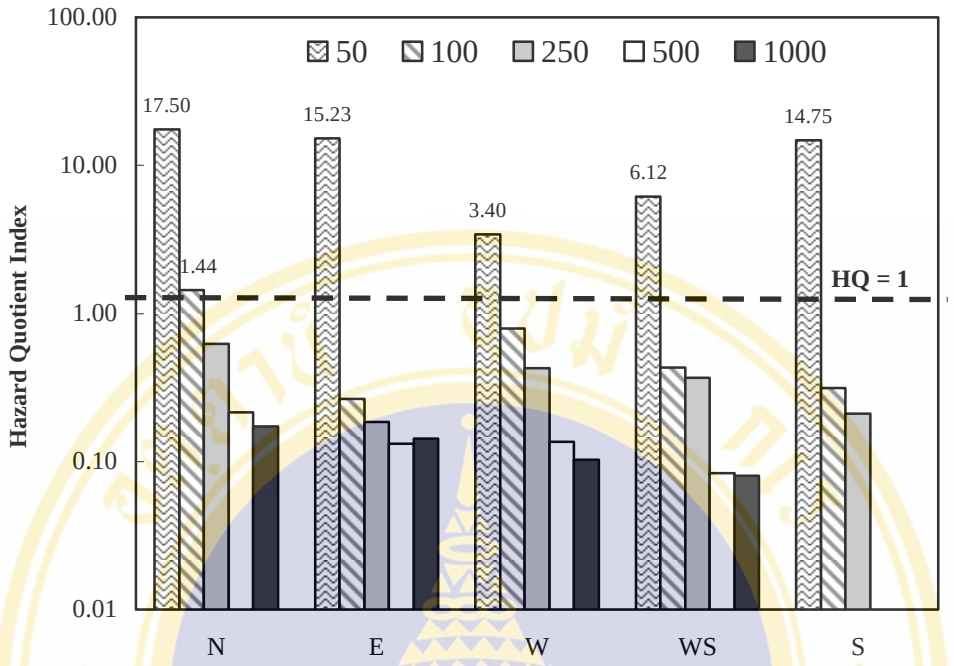

Figure 4.11 Hazard quotients (HQ) of soil around the battery recycling plant

The lead concentrations in soils at stations which exceeded the maximum allowable concentration demonstrated that the potential environmental risks of soil were at risk with adverse effects of lead on soils and soil biota. The study indicated that the soils within the radius of 50 m from the battery recycling plant in all directions and another one station at distance of 100 m from the plant up to the north were unsuitable for land use with concerning people, animals and plants of being exposure to those contaminated soils.

4.4.2 Potential environmental risks of sediment at contaminated site

The extent of sediment contamination along the drainage system near the point source was appraised by comparing the concentrations of lead from each station with the maximum allowable concentration of lead in soil that established by Department of Industrial Works, Thailand at 100 mg/kg dw (DIW, 1997), as screening benchmark value for sediment. Lead concentrations in sediment located downstream from the effluent discharge point within the distance of 400 m were extremely exceeded maximum allowable concentration of lead in sediment. On the other hand, those concentrations located upstream from the effluent discharge point were less than

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maximum allowable concentration of lead in sediment except the sediments at the stations located next to the effluent discharge point (Figure 4.12).

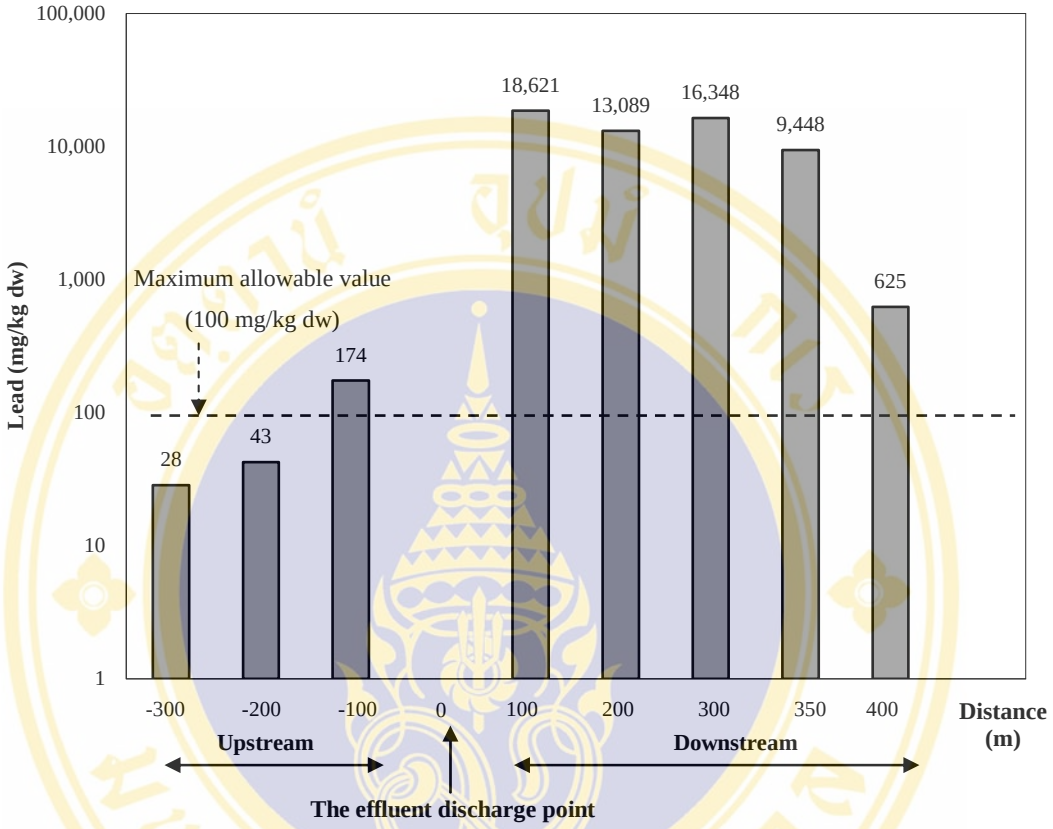

Figure 4.12 Lead concentrations (mg/kg dw) in sediment along the drainage system near the battery recycling plant compared to the maximum allowable value

The hazard quotients of the sediments located downstream of the effluent discharge point were in the range of 6.25 to 186.21. Whereas, hazard quotients values of sediments located upstream from the effluent discharge point were lower within the range of 0.28 to 1.74 (Table 4.9).

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Table 4.9 Hazard quotients (HQ) of sediment along the drainage system of the battery recycling plant

Station descriptions	Sampling stations	Distance from the effluent discharge point (m)	Lead (mg/kg dw)	HQ
			Mean	
Upstream from the effluent discharge point	S1	300	29	0.29
	S2	200	43	0.43
	S3	100	174	1.74
Downstream from the effluent discharge point	S4	100	18,621	186.21
	S5	200	13,089	130.89
	S6	300	16,348	163.48
	S7	350	9,448	94.48
	S8	400	625	6.25
Screening benchmark value for sediment in this study = 100 mg/kg dw (DIW, 1997)				

The high potential environmental risks of lead contaminated sediments at site were found at stations located downstream from the effluent discharge point and upstream station next to the effluent discharge point. The hazard quotients values in those stations were found to be exceeded 1.0. These revealed that the lead contaminated sediments in those areas were at risks. In contrast, the hazard quotient (HQ) values of sediments at the stations upstream from the discharge point were not exceeded the standard value of 1.0. These indicated that lead contaminated sediment in those stations were not at risk (Figure 4.13).

The lead concentrations in sediments at stations that exceeded the maximum allowable concentration revealed that the high potential environmental risks of lead and have had the harmful effects on those sediments. Whereas, the stations which lead concentrations were not exceeded the maximum allowable concentration were not at risk. It can be concluded that the sediment in area located downstream of the effluent discharge point of the battery recycling plant and another one station next to the effluent discharge point were unsuitable for land use which concerning people,

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plant and animals were exposure to.

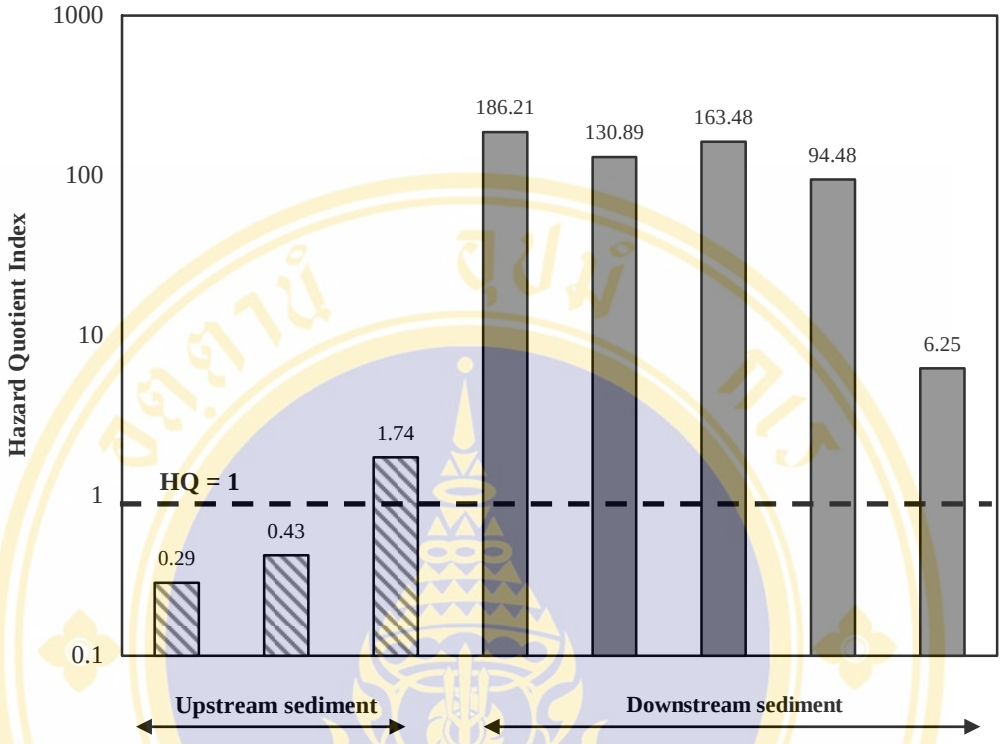

Figure 4.13 Hazard quotients (HQ) of sediment along the drainage system near the battery recycling plant

Although, the maximum allowable of lead value used in this study (DIW, 1997) was corresponding to the theory that lead concentrations in soil and sediment found at this level had inhibitory effects on germination or growth of plant and critical for soil in agricultural area (Kataba-Pendias and Pendias, 1984). Then, those areas were needed to clarify that risk further. Furthermore, soils and sediments in the areas that were at risks and lead polluted area, might not safe for people or animal living in those areas for long exposure. When increasing time, lead contaminations in soil and sediment at those areas might be at risks.

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4.4.3 Evaluation of present lead contaminations state

The distribution of lead in soils within radius 1 km from the battery recycling plant was analyzed using GIS methods. Lead concentrations were interpolated with the Kriging method. The contour map was obtained using GIS software (Surfer 8) and lead contaminations in surface soils were classified as shown in Figure 4.14.

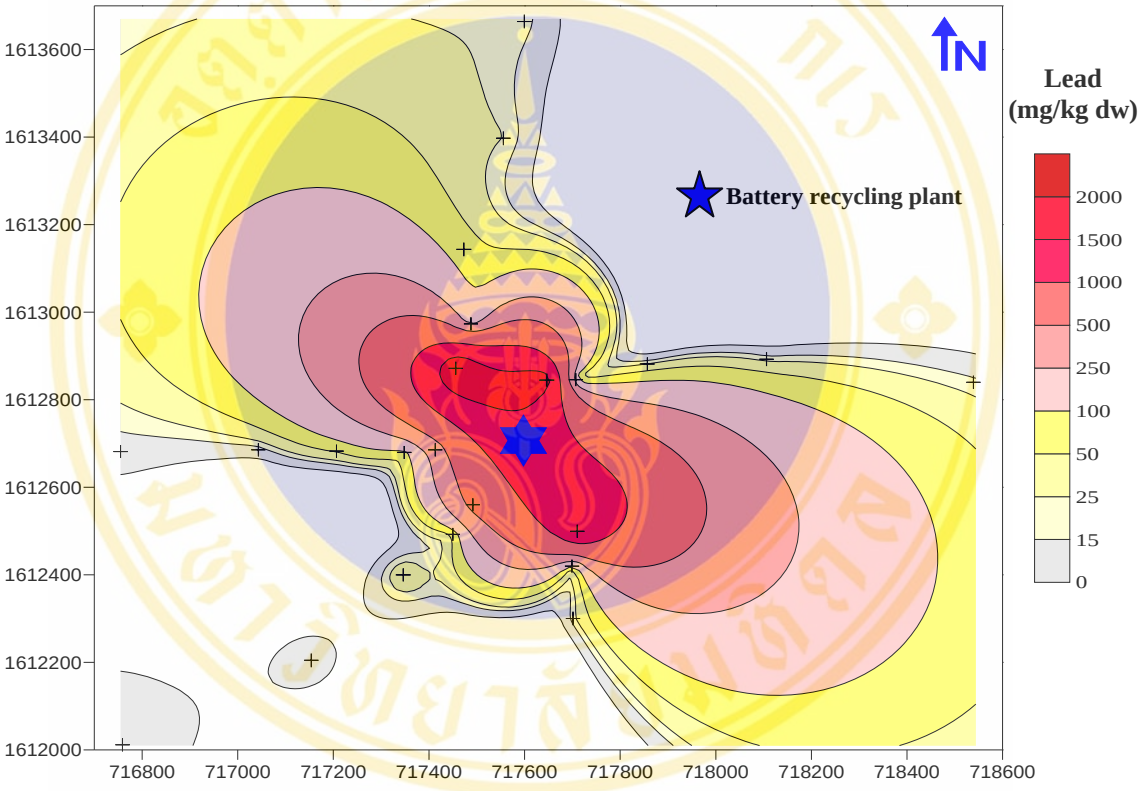

Figure 4.14 Contour plots of lead contaminations in surface soils around the battery recycling plant.

Contour map of lead contaminations in surface soils in the vicinity of the battery recycling plant indicated that lead contamination levels were different in each area. The high elevated concentrations of lead were found largely in soil at the distance of 50 m from the plant as well as the distance of 100 m from the plant up to the north (indicated by the pink to red zone). Lead concentrations of soil in these areas exceeded the background value (15 mg/kg dw) and the maximum allowable

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concentrations (100 mg/kg dw). Lead distribution in the north direction was farther than any other directions resulting from wind movements (west-south) in monsoon season that exists 8 months a year. The potential environmental risks of soil were at risks and indicated that lead distributed from the battery recycling plant activities might have the potential adverse effects on ecosystems and habitats located in these areas and might not safe for people or animal living in those areas for longer exposure.

Furthermore, lead concentrations in soil at the distance of 250 m from the battery recycling plant were found exceeded background value (15 mg/kg dw) but did not exceed the maximum allowable concentrations (100 mg/kg dw) (indicated by the yellow zone). The potential environmental risks at almost areas were not to be at risks except the one station about 100 m up to the north from the plant. Even, those areas were not to be at risks, with increasing time, lead contaminations in soil at those areas might be at risks and might have the potential adverse effects resulting from the distribution of lead from the battery recycling plant.

Likewise, away from the plant at distance more than 500 m (indicated by the gray zone) lead concentrations were found to be closed to those generally found in the soil background which were classified as low lead contamination and were not at risks.

4.4.4 Lead bioaccumulation in plants at contaminated areas

In the high lead contaminated areas around the battery recycling plant, samples of various kinds of plants were collected for lead analysis. Analytical results found that lead concentrations in plants were within the range of 0.79 to 1,601 mg/kg dw. Lead bioaccumulations in the plants were presented in Table 4.10.

Lead concentrations in most of plants in this study area concentrations largely exceeded the normal level in plant leaves with the range of 5-10 mg/kg dw (Djingove et al., 1993) and corresponded to the study of Kabata-Pendias and Pendias (1984) that lead in plants naturally growing in uncontaminated and unmineralized areas appears to be between 0.01 and 10 mg/kg dw with average value of 2 mg/kg dw. The results were compared to the background value of the grass growing in grazing land and farm near the major high way in Saraburi province, Thailand (Parkpian et al., 2002) that lead concentrations were found to be in the range of 0.8 to 7 mg/kg dw.

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Table 4.10 Lead bioaccumulations (mg/kg dw) in plants

Sampling stations	Lead in soils (mg/kg dw)	Plant species	Lead in plants (mg/kg dw)	HQ
S5*	13,089	*Brachiaria* spp. (Shoot, leaf)	1,601	228.7
S7*	9,448	Cyperaceae (Shoot, leaf)	105	15.0
S8*	625	*Ipomoea* spp. (Shoot, leaf)	18	-
Slag heap	3,829	*Leucaena glauca* (Pods)	0.79	-
Slag heap	3,829	*Leucaena glauca* (Edible part)	0.97	-
SF6**	340	Cyperaceae (Shoot, leaf)	132	18.9
SF11**	613	Cyperaceae (Shoot, leaf)	129	18.4
SF16**	1,476	Cyperaceae (Shoot, leaf)	65	9.3
SF16**	1,476	*Brachiaria* spp. (Shoot, leaf)	25	3.6
SF19**	1,523	*Brachiaria* spp. (Shoot, leaf)	27	3.9
Maximum benchmark value for grass = 7 mg/kg dw (Parkpian et al., 2002)				

* Plant samples were collected at the same stations as did for sediment

** Plant samples were collected at the same stations as did for soil

The maximum of lead concentration in grass in this study was considered to be compared with the maximum benchmark value and to estimate the potential of risks (HQ) in grass. Due to lead concentrations in grass of these areas it can be concluded that the grass were safe for grazing animal consumption. Within this study area lead concentrations in grass were compared with the maximum allowance value of lead concentration (7 mg/kg dw) and they were greater than 3.6-228.7 times. Then,

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lead concentrations in most plants were exceeded the maximum allowance value for grass consumption. It is therefore recommended that the lead concentrations in most grasses might be accumulated in animal product such as milk. Due to lead concentrations that found in Saraburi province the grass in this area were safe for grazing animal consumption and the levels of lead in raw milk from those sites (0.014 mg/L) were below the Codex Alimentarius Commissions Draft (1997) for the maximum level of lead in milk which has been set at 0.02 mg/L by FAO/WHO.

Moreover, plant samples collected from high lead contaminated area next to the point source were found to contain high lead levels and this result corresponded to the report of Kabata-Pendias and Pendias (1984) that lead concentrations for grass shoots grown at metal processing industry sites were in the range of 229 to 2,717 mg/kg dw. Also, it had been reported that the level of lead in the edible parts of the vegetation growing in those areas was the cause of animal death with the range of 113 to 4,741 mg/kg dw (Palacios et al., 2002). Likewise, the levels of lead concentration in plants in most this study area (105-1,601 mg/kg dw) were consistent to those reported for grazing animal death in lead intoxication.

4.4.5 Evaluation of lead intake by grazing animals

In the prevailing pastoral grazing land use environment, uptaken of lead by grass allows lead to enter the food chain. In order to assess the risk for grazing animal, the potential consumption of lead from contaminated areas near the battery recycling plant was considered. A few assumptions were made (Aslibekian and Moles, 2002).

1. Cattle on average consume 15–20 kg grass/animal/day.

2. Lead may cause different degrees of poisoning depending on the method of intake.

a. Lethal poisoning in cattle results from ingestion of about 10 g of lead.

b. The same result occurs when animals receive feed with lead concentrations of 300–400 mg/kg dw for a period of over two weeks.

c. Symptoms of intoxication in ruminants can be expected in the case of feed concentrations over 50 mg/kg dw over a period of several months.

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On this basis, the amounts of lead, which may be consumed by cattle during grazing, were estimated. Calculations of dietary lead intakes by grazing animal were shown in Table 4.11.

Table 4.11 Dietary lead intake by grazing animals

Sampling stations	Grass species	Dietary lead intake		
		Lead in grass (mg/kg dw)	Consumption (kg/day)	Lead intake (mg/day)
S5*	*Brachiaria* spp.	1,601	15-20	24,015-32,020
S7*	Cyperaceae	105	15-20	1,575-2,100
SF6**	Cyperaceae	132	15-20	1,980-2,640
SF11**	Cyperaceae	129	15-20	1,935-2,580
SF16**	Cyperaceae	65	15-20	975-1,300
SF16**	*Brachiaria* spp.	25	15-20	375-500
SF19**	*Brachiaria* spp.	27	15-20	405-540
Dietary lead intake (mg/day) = Lead in grass (mg/kg dw) × Grass consumption (kg/day)				

* Grass samples were collected at the same as stations as did for sediment

** Grass samples were collected at the same as stations as did for soil

Lead concentrations in grasses collected from high contaminated areas might be caused different degrees of lead poisoning in grazing animal depending on the method of intake. In some grass sampling stations cattle may consume a lethal dose of lead (>10 g/day) during a single day of grazing and the other stations have the potential to cause lethal dose over a two week period. Assessment of the sequential effects on grazing animals indicated that lead posed the greatest risks due to its high toxicity and high concentrations in soil. Within high contaminated areas grazing cattle might be intake a lethal dose of lead. So, the plants grown in this area were not appropriated for grazing animal consumption.

With the respect of high elevated lead concentrations found in the study area; among soil, sediment and plant tissue, health risk assessment should be further investigated. The exposure of lead contaminated grass in this area is of concern as it can pass up food chains, increasing to levels via bioaccumulation which pose a threat

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to those organisms which feed at the top of the food web. Organisms which are at risk of lead exposure include herbivorous cattle and goats and certainly, humans.

4.4.6 Linkages of lead for battery recycling plant and vicinity area

The linkages of lead in various environmental compartments from diverse battery recycling activities in study area can be concluded as shown in Figure 4.15.

From this study, it clearly shown that lead from a battery recycling process together with crushing and dry grinding, smelting and refining had caused significant amount of lead distributed into the air. Based on the findings in areas within radius 250 m from the plant operations, these areas have been contaminated by lead from battery recycling activities over the past 20 years. Likewise, lead from washing floor, equipment and batteries breaking process was remained in wastewater and discarded mainly to the drainage system near the plant. This discharge of lead in wastewater and atmospheric deposit on surface soil could be further washed out mainly by rain and its runoff then run to the drainage system and end up at the receiving pond located nearby. Then, lead distribution from both atmospheric lead and wastewater discharge affected plants and biota which grown in contaminated areas.

Lead distributed from the point source had been transported and up taken by the plants near the plant operations. Thus process was confirmed by elevated concentrations of lead accumulated in plants which corresponded to the quite high lead concentrations in soil and sediment. In this study, lead concentrations in most plants were exceeded the maximum allowance value for grass consumption that would be a health hazard for animal consumption. Likewise, lead concentrations in grasses collected from high contaminated areas might be caused different degrees of lead poisoning in grazing animal. If grazing animals intake vegetation growing in high lead contaminated areas, then lead could be absorbed in blood, hair and tissues of the affected grazing animals in this region and could be transferred to humans by consumption grazing animal products.

Other lead exposure pathways derived from this study included inhalation of lead contaminated air resulting from crushing and dry grinding, smelting and

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refining at the plant, dermal contact by lead contaminated soil and unintentional ingestion of soil polluted by lead at the plant operations.

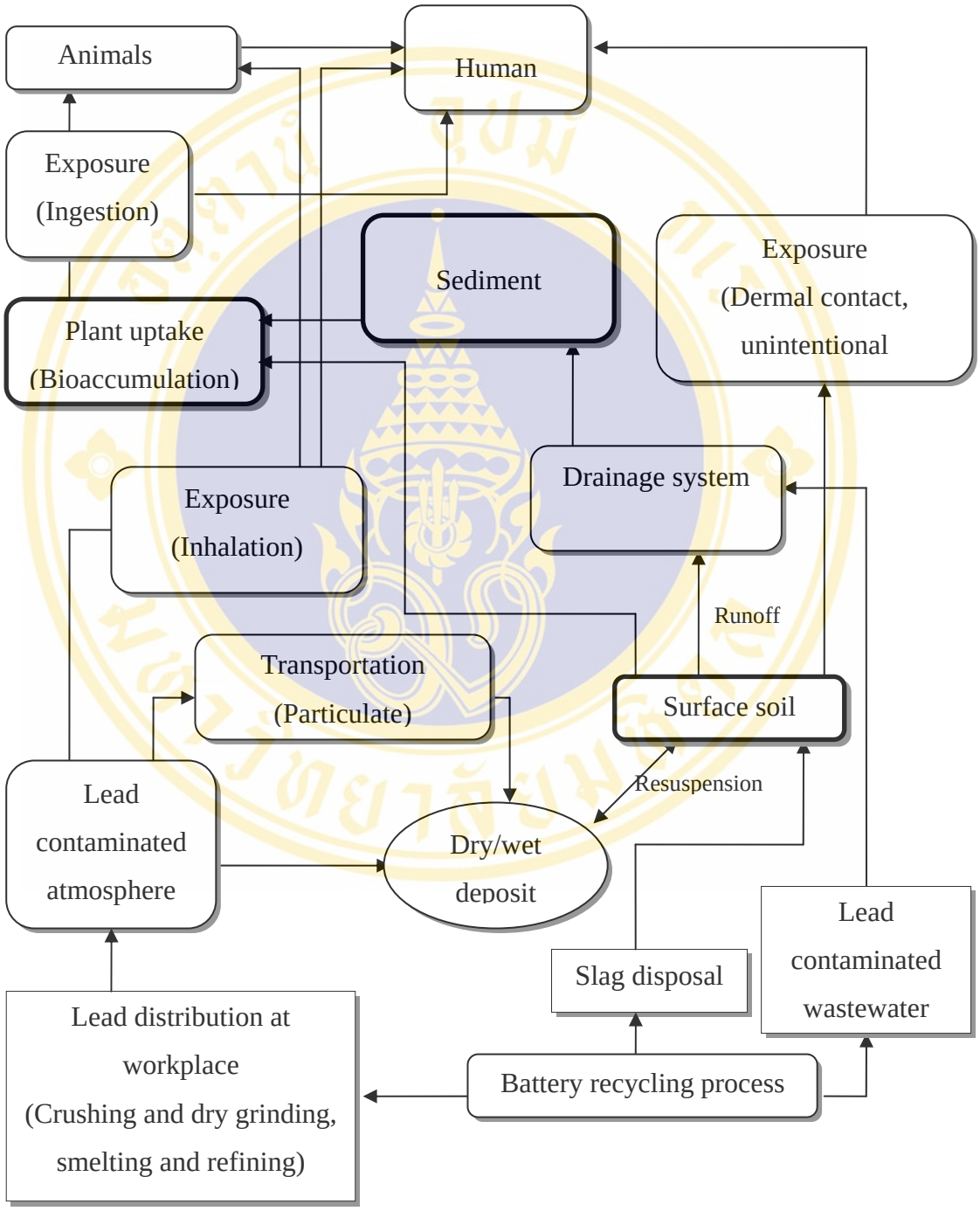

Figure 4.15 Conceptualization of linkages comprising the movement of lead release in the environment up through bioaccumulation in biota at battery recycling plant

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CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The effects of lead distribution from battery recycling activities on residential areas and grazing animals in vicinity of the battery recycling plant were investigated. The samples of soil, sediment and plant were collected at various sampling stations around the battery recycling plant to evaluate the lead contaminations and potential environmental risks, including the far away distance sites as reference/background area. The conclusions of this study as follow:

5.1.1 Lead concentrations in soil at various sampling stations within radius 1 km around the battery recycling plant decreased with increasing distance from the point source.

5.1.2 Lead contamination levels in soil at distances of 50, 100 and 250 m from the plant were exceeded background value, and at the distance of 50 m lead contamination levels in all directions were very high. Furthermore, lead contamination levels at distances of 500 and 1,000 m from the plant were closed to those in background area.

5.1.3 Lead concentrations in soil along the different transect lines around the point source were clearly shown to decrease along each transect line as increasing distance.

5.1.4 Lead distribution in the north direction was reached to the distance of 100 m, farther than any other directions resulting from the downwind in monsoon season that exists 8 months a year.

5.1.5 Lead concentrations in the sediment at various stations along the drainage system were slightly higher than those of soil background values. Likewise, the lead concentrations in sediment located downstream from the effluent discharge point were

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higher than the sediment located upstream and the concentrations decreased gradually as the distance away from the effluent discharge point.

5.1.6 Lead concentrations of both soil and sediment profiles at high contaminated stations at three different depths (0-10, 10-20 and 20-30 cm) were very high in the first layer and decreased with increasing depth. Although, at certain stations lead was found to migrate downward to the profiles depth of 30 cm or more and exceeded background value for natural soil in local area.

5.1.7 The hazard quotients (HQ) values in soil at the distance of 50 m in all directions and at the distance of 100 m from the battery recycling plant up to the north were at risks with the HQ value exceeded 1. Furthermore, the hazard quotients values in sediments located downstream from the effluent discharge point and another one station located upstream next to the effluent discharge point were also at risks. Thus, indicated these areas had potential environmental risks.

5.1.8 Lead concentrations in most of plants from contaminated area around the battery recycling plant were higher than those presented in plants growing in uncontaminated areas. Moreover, the lead concentrations in those grasses were greater than the maximum value for grass that safe for grazing animal consumption and that might affect to health of animal consumption.

5.2 Recommendations

Recommendations for further study

5.2.1 The total lead contents in soils did not provide much informations for its bioavailability. Thus, better correlations should be obtained form the extractable forms of lead.

5.2.2 Further investigations are to be needed to determine for ecological risk assessment incorporated additional variables such as lead in surface water, ground water, edible plants, milk of grazing animal, animal and human blood samples in vicinity of public concerned area around of battery recycling plant.

5.2.3 In the case of the locality heavily contaminated by lead might be migrated vertically through the soil profile into the groundwater, further study will be needed to

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investigate lead migration downward to subsurface of soil and sediment in the areas around the battery recycling plant at the depths below 30 cm.

5.2.4 From this study lead pollution found in the area around the battery recycling plant might have the adverse effects on residential areas nearby. Thus, environmental prevention of lead pollution will be designed and set up for the better operations and management in this plant.

5.2.5 Further investigations are to be needed to determine lead particulate deposition rate in the vicinity of the battery recycling plant in both 2 seasons (dry/wet deposition) due to the influence of wind direction variation in each monsoon season.

5.2.6 In sensitivity areas, such as residential areas and the hospital located near the battery recycling plant, lead concentrations in the air should be investigated to evaluate lead intake by inhalation.

5.2.7 For human health protection, lead distributions and evaluation of environmental risks in vicinity of the other battery recycling plants in Thailand should be studied.

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APPENDIX

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APPENDIX A
DATA FROM THE EXPERIMENT

Table A-1 The instrumental blank of FAAS and method blank of Nitric/Hydrochloric acid digestion

Instrumental blank

Blank	Lead (ppm)
Deionized water	N.D
Deionized water	N.D
Deionized water	N.D
N.D	<0.001

Method blank (Nitric/Hydrochloric acid digestion)

Blank	Lead (ppm)
Blank 1	0.015
Blank 2	0.012
Blank 3	0.010
Blank 4	0.013
Blank 5	0.010
Blank 6	0.009
Average	0.012

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Table A-2 Calculation for lead concentrations (mg/kg dw) in surface soil samples (August-September, 2006)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
SF1	2.0570	50	73.100	1,776.86	1612874	0717458	101° 01’ 06.5”	14° 34’ 49.2”
SF1	2.0236	50	76.080	1,879.82				
SF1	2.0225	50	69.310	1,713.47				
SF2	2.0839	50	6.131	147.10	1612976	0717490	101° 01’ 07.5”	14° 34’ 52.5”
SF2	2.0463	50	5.796	141.62				
SF2	2.0842	50	5.981	143.48				
SF3	2.0477	50	2.329	56.87	1613147	0717475	101° 01’ 03.8”	14° 34’ 58.1”
SF3	2.0766	50	2.964	71.37				
SF3	2.0497	50	2.372	57.86				
SF4	2.0723	50	0.872	21.04	1613402	0717558	101° 01’ 16.7”	14° 35’09.2”
SF4	2.0221	50	0.743	18.37				
SF4	2.0052	50	0.997	24.86				
SF5	2.0216	50	0.672	16.62	1613670	0717602	101° 01’ 14.9”	14° 35’ 15.0”
SF5	2.0168	50	0.660	16.36				
SF5	2.0331	50	0.757	18.62				

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Table A-2 Calculation for lead concentrations (mg/kg dw) in surface soil samples (August-September, 2006) (continued)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
SF6	2.0573	50	14.660	356.29	1612687	0717415	101° 01’ 05.0”	14° 34’ 43.1”
SF6	2.0553	50	13.630	331.58				
SF6	2.0222	50	13.480	333.30				
SF7	2.0174	50	3.232	80.10	1612681	0717350	101° 01’ 00.5”	14° 34’ 42.3”
SF7	2.0427	50	3.217	78.74				
SF7	2.0270	50	3.165	78.07				
SF8	2.0870	50	1.123	26.91	1612684	0717208	101° 01’ 58.1”	14° 34’ 41.8”
SF8	2.0546	50	1.920	46.72				
SF8	2.0258	50	2.197	54.23				
SF9	2.0422	50	0.538	13.17	1612683	0716755	101° 00’ 49.7”	14° 34’ 34.2”
SF9	2.0516	50	0.550	13.40				
SF9	2.0438	50	0.573	14.02				
SF10	2.0141	50	0.370	9.19	1612687	0717044	101° 00’ 36.1”	14° 34’ 24.4”
SF10	2.0066	50	0.444	11.06				
SF10	2.0189	50	0.426	10.55				

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Table A-2 Calculation for lead concentrations (mg/kg dw) in surface soil samples (August-September, 2006) (continued)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
SF11	2.0100	50	24.48	609.00	1612561	0717494	101° 01’ 07.6”	14° 34’ 39.0”
SF11	2.0171	50	29.66	735.21				
SF11	2.0286	50	23.13	570.10				
SF12	2.0309	50	1.726	42.49	1612493	0717452	101° 01’ 06.2”	14° 34’ 36.8”
SF12	2.0234	50	1.561	38.57				
SF12	2.0469	50	1.968	48.07				
SF13	2.0523	50	1.972	48.04	1612400	0717348	101° 01’ 02.7”	14° 34’ 33.8”
SF13	2.0333	50	1.223	30.07				
SF13	2.0745	50	1.314	31.67				
SF14	2.0315	50	0.405	9.97	1612010	0716759	101° 00’ 57.9”	14° 34’ 32.3”
SF14	2.0448	50	0.399	9.76				
SF14	2.0285	50	0.310	7.64				
SF15	2.0080	50	0.297	7.40	1612204	0717155	101° 00’ 55.8”	14° 34’ 24.0”
SF15	2.0398	50	0.356	8.73				
SF15	2.0455	50	0.319	7.80				

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Table A-2 Calculation for lead concentrations (mg/kg dw) in surface soil samples (August-September, 2006) (continued)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
SF16	2.0220	50	61.730	1,526.46	1612500	0717713	101° 01’ 14.9”	14° 34’ 36.8”
SF16	2.0673	50	52.950	1,280.66				
SF16	2.0970	50	67.900	1,619.00				
SF17	2.0281	50	1.358	33.48	1612420	0717702	101° 01’ 14.5”	14° 34’ 31.9”
SF17	2.0780	50	1.405	33.81				
SF17	2.0400	50	1.077	26.40				
SF18	2.0110	50	0.977	24.29	1612300	0717704	101° 01’ 19.2”	14° 34’ 34.4”
SF18	2.0678	50	0.777	18.79				
SF18	2.0038	50	0.794	19.81				
SF19	2.0069	50	57.040	1,421.10	1612847	0717649	101° 01’ 12.9”	14° 34’ 51.5”
SF19	2.0745	50	69.760	1,681.37				
SF19	2.0343	50	59.720	1,467.83				
SF20	2.0569	50	1.136	27.61	1612848	0717710	101° 01’ 14.9”	14° 34’ 52.6”
SF20	2.0403	50	1.023	25.07				
SF20	2.0658	50	1.112	26.92				

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Table A-2 Calculation for lead concentrations (mg/kg dw) in surface soil samples (August-September, 2006) (continued)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
SF21	2.0604	50	0.800	19.41	1612884	0717860	101° 01’ 19.1”	14° 34’ 55.9”
SF21	2.0180	50	0.775	19.20				
SF21	2.0100	50	0.802	19.95				
SF22	2.0474	50	0.491	11.99	1612895	0718110	101° 01’ 23.2”	14° 34’ 57.4”
SF22	2.0312	50	0.382	9.40				
SF22	2.0312	50	0.550	13.15				
SF23	2.0435	50	0.707	17.30	1613176	0718513	101° 01’ 42.9”	14° 35’ 02.8”
SF23	2.0358	50	0.612	15.03				
SF23	2.0096	50	0.599	14.90				
SF24	2.0130	50	1.247	30.97	1612657	0717941	101° 01’ 23.6”	14° 34’ 46.2”
SF24	2.0690	50	1.023	24.72				
SF24	2.0212	50	0.843	20.85				
SF25	2.0736	50	0.665	16.04	1612842	0718544	101° 01’ 30.3”	14° 34’ 52.9”
SF25	2.0243	50	0.523	12.92				
SF25	2.0748	50	0.737	17.76				

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Table A-2 Calculation for lead concentrations (mg/kg dw) in surface soil samples (August-September, 2006) (continued)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
SF26	2.0584	50	0.806	19.58	1612843	0718456	101° 01’ 40.6”	14° 34’ 51.9”
SF26	2.0179	50	0.777	19.25				
SF26	2.0131	50	0.781	19.40				
Slag heap	2.0403	50	122.600	3,004.46	1612378	0717509	101° 01’ 09.1”	14° 34’ 37.2”
Slag heap	2.0600	50	183.400	4,451.46				
Slag heap	2.0253	50	163.300	4,031.50				

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Table A-3 Calculation for lead concentrations (mg/kg dw) in surface soil samples from background areas (August-September, 2006)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
B1	2.0600	50	0.806	19.56	1613150	0719836	101° 02’ 26.7”	14° 35’ 03.5”
B1	2.0100	50	0.707	17.59				
B1	2.0131	50	0.821	20.39				
B2	2.0268	50	0.924	22.80	1613018	0719754	101° 02’ 24.3”	14° 34’ 57.4”
B2	2.0403	50	1.107	27.13				
B2	2.0062	50	1.079	26.90				
B3	2.0600	50	0.351	8.52	1611891	0716298	101° 00’28.5”	14° 34’ 21.7”
B3	2.0280	50	0.448	11.05				
B3	2.0410	50	0.370	9.06				
B4	2.0401	50	0.406	9.95	1611891	0716298	101° 00’28.5”	14° 34’ 21.7”
B4	2.0403	50	0.525	12.87				
B4	2.0203	50	0.399	9.88				
B5	2.0080	50	0.297	7.40	1611113	0716728	101° 00’ 42.6”	14° 33’ 56.3”
B5	2.0398	50	0.356	8.73				
B5	2.0455	50	0.319	7.80				

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Table A-4 Calculation for lead concentrations (mg/kg dw) in sediment samples (August-September, 2006)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
S1	2.0380	50	0.862	21.15	1612481	0717766	101° 01’ 17.7”	14° 34’ 40.5”
S1	2.0133	50	1.332	33.08				
S1	2.0564	50	1.284	31.20				
S2	2.0657	50	1.564	37.86	1612647	0717670	101° 01’ 14.6”	14° 34’ 46.0”
S2	2.0150	50	1.844	45.76				
S2	2.0500	50	1.811	44.17				
S3	2.0967	50	7.062	168.41	1612866	0717564	101° 01’ 11.1”	14° 34’ 53.1”
S3	2.0750	50	8.405	202.53				
S3	2.0654	50	6.268	151.74				
S4	2.0328	50	747.500	18,385.97	1613000	0717498	101° 01’ 08.9”	14° 34’ 57.5”
S4	2.0513	50	708.500	17,269.54				
S4	2.0177	50	815.500	20,208.65				
S5	2.0355	50	511.200	12,557.11	1612945	0717526	101° 01’ 09.8”	14° 34’ 55.6”
S5	2.0519	50	598.200	14,576.73				
S5	2.0510	50	497.700	12,133.11				

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Table A-4 Calculation for lead concentrations (mg/kg dw) in sediment samples (August-September, 2006) (continued)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)	UTM		Latitude/Longitude	
					N	E	E	N
S6	2.0029	50	670.500	16,738.23	1612892	0717556	101° 01’ 10.8”	14° 34’ 53.9”
S6	2.0026	50	629.500	15,717.07				
S6	2.0077	50	666.100	16,588.63				
S7	2.0274	50	377.900	9,319.82	1613016	0717446	101° 01’ 7.8”	14° 34’ 58.0”
S7	2.0348	50	396.800	9,750.34				
S7	2.0382	50	378.000	9,272.89				
S8	2.0559	50	26.320	640.11	1613000	0716900	101° 01’ 6.8”	14° 34’ 48.0”
S8	2.0331	50	25.890	636.71				
S8	2.0520	50	24.570	598.68				

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Table A-5 Calculation for lead concentrations (mg/kg dw) in soil and sediment samples at a depth of 10 cm (February, 2007)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)
S4	2.0266	50	971.000	23,956.38
S4	2.0315	50	976.000	24,021.66
S4	2.0410	50	998.000	24,448.80
S6	2.0475	50	557.800	13,621.49
S6	2.0295	50	565.600	13,934.47
S6	2.0176	50	527.000	13,060.07
S7	2.0325	50	226.400	5,569.50
S7	2.0202	50	210.900	5,219.78
S7	2.0191	50	219.300	5,430.64
S8	2.0559	50	36.320	883.31
S8	2.0331	50	35.890	882.64
S8	2.0520	50	34.570	842.35
SF1	2.0351	50	64.07	1,574.1
SF1	2.0286	50	71.34	1,758.4
SF1	2.0498	50	67.21	1,639.4
SF11	2.0214	50	28.460	703.97
SF11	2.0163	50	36.080	894.71
SF11	2.0349	50	25.320	622.14
SF16	2.0193	50	48.190	1,113.57
SF16	2.0410	50	42.380	1,038.22
SF16	2.0141	50	49.880	1,238.27
SF19	2.0398	50	53.060	1,300.62
SF19	2.0336	50	54.420	1,338.02
SF19	2.0027	50	56.840	1,419.08

*S4-S8 = Sediment sampling stations

*SF1-SF19 = Soil sampling stations

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Table A-6 Calculation for lead concentrations (mg/kg dw) in soil and sediment samples at a depth of 20 cm (February, 2007)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)
S4	2.0223	50	636.200	15,729.61
S4	2.0068	50	632.700	15,763.90
S4	2.0154	50	646.200	16,031.56
S6	2.0205	50	276.500	6,842.37
S6	2.0280	50	279.600	6,893.49
S6	2.0140	50	277.200	6,879.34
S7	2.0134	50	116.900	2,903.05
S7	2.0132	50	122.000	3,030.00
S7	2.0093	50	118.800	2,956.25
S8	2.0049	50	4.820	120.21
S8	2.0102	50	5.011	124.64
S8	2.0195	50	5.190	128.50
SF1	2.0126	50	21.173	529.14
SF1	2.0181	50	21.179	529.21
SF1	2.0158	50	21.009	525.03
SF11	2.0051	50	6.791	169.34
SF11	2.0177	50	7.400	183.38
SF11	2.0179	50	7.706	190.94
SF16	2.0140	50	17.679	438.90
SF16	2.0148	50	17.616	437.16
SF16	2.0142	50	17.659	438.36
SF19	2.0268	50	28.935	713.81
SF19	2.0083	50	29.055	723.37
SF19	2.0201	50	28.906	715.46

*S4-S8 = Sediment sampling stations

*SF1-SF19 = Soil sampling stations

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Table A-7 Calculation for lead concentrations (mg/kg dw) in soil and sediment samples at a depth of 30 cm (February, 2007)

Sample No.	Mass (g)	Final Vol. (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)
S4	2.0050	50	277.300	6,915.21
S4	2.0202	50	276.800	6,850.81
S4	2.0008	50	283.100	7,074.67
S6	2.0060	50	172.400	4,297.11
S6	2.0075	50	135.500	3,374.84
S6	2.0093	50	168.100	4,183.05
S7	2.0103	50	84.700	2,106.65
S7	2.0150	50	79.530	1,973.45
S7	2.0064	50	80.890	2,015.80
S8	2.0312	50	4.500	110.77
S8	2.0189	50	4.542	112.49
S8	2.0070	50	4.429	110.34
SF1	2.0318	50	4.957	123.55
SF1	2.0400	50	4.910	122.30
SF1	2.0203	50	4781	119.33
SF11	2.0058	50	4.780	119.15
SF11	2.0244	50	7.918	195.56
SF11	2.0034	50	2.584	64.49
SF16	2.0218	50	5.038	124.59
SF16	2.0108	50	4.982	123.88
SF16	2.0423	50	4.730	155.80
SF19	2.0112	50	9.915	246.50
SF19	2.0052	50	10.265	255.96
SF19	2.0122	50	9.915	246.37

*S4-S8 = Sediment sampling stations

*SF1-SF19 = Soil sampling stations

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Table A-8 Calculation for lead concentrations (mg/kg dw) in plant samples (August-September, 2006 and February, 2007)

Plant Species	Mass (g)	Final Vol (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)
(S5) *Brachiaria* spp.	0.5347	50	14.840	1,387.70
(S5) *Brachiaria* spp.	0.5098	50	19.160	1,879.17
(S5) *Brachiaria* spp.	0.5056	50	15.540	1,536.79
(S7) Cyperaceae	0.5608	50	1.215	108.33
(S7) Cyperaceae	0.5104	50	1.078	105.60
(S7) Cyperaceae	0.5199	50	1.052	101.17
(S8) *Ipomoea* spp.	0.5149	50	0.195	18.94
(S8) *Ipomoea* spp.	0.5078	50	0.176	17.33
(S8) *Ipomoea* spp.	0.5379	50	0.191	17.76
(Slag heap) *Leucaena glauca*	0.5180	50	0.009	0.87
(Slag heap) *Leucaena glauca*	0.5121	50	0.005	0.49
(Slag heap) *Leucaena glauca*	0.5469	50	0.011	1.01
(Slag heap) *Leucaena glauca*	0.5251	50	0.007	0.67
(Slag heap) *Leucaena glauca*	0.5340	50	0.015	1.40
(Slag heap) *Leucaena glauca*	0.5298	50	0.009	0.85
(SF6) Cyperaceae	0.5121	50	1.260	123.02
(SF6) Cyperaceae	0.5326	50	1.505	141.29
(SF6) Cyperaceae	0.5224	50	1.3825	132.32
(SF11) Cyperaceae	0.5153	50	1.308	126.92
(SF11) Cyperaceae	0.5277	50	1.237	117.21
(SF11) Cyperaceae	0.5521	50	1.562	141.46

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Table A-8 Calculation for lead concentrations (mg/kg dw) in plant samples (August-September, 2006 and February, 2007) (continued)

Plant Species	Mass (g)	Final Vol (mL)	AAS (mg/L)	Calculated lead (mg/kg dw)
(SF16) Cyperaceae	0.5479	50	0.724	66.07
(SF16) Cyperaceae	0.5075	50	0.544	53.60
(SF16) Cyperaceae	0.5603	50	0.831	74.18
(SF16) *Brachiaria* spp.	0.5733	50	0.285	24.86
(SF16) *Brachiaria* spp.	0.5688	50	0.295	25.93
(SF16) *Brachiaria* spp.	0.5711	50	0.290	25.39
(SF19) *Brachiaria* spp.	0.5020	50	0.248	24.78
(SF19) *Brachiaria* spp.	0.5115	50	0.295	29.29
(SF19) *Brachiaria* spp.	0.5068	50	0.272	27.05

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APPENDIX B
STATISTICAL ANALYSIS

Table B-1 Statistical analysis of lead concentrations in surface soil at various distances around the battery recycling plant and background areas

Tests of Normality

	Distance (m)	Shapiro-Wilk		
		Statistic	df	Sig.
Lead	50	.856	15	0.021
	100	.787	15	0.003
	250	.895	15	0.081
	500	.970	12	0.913
	1,000	.900	12	0.159
	Background	.864	15	0.028

NPar Tests

Kruskal-Wallis Test

	Distance (m)	N	Mean Rank
Lead	50	15	77.00
	100	15	57.53
	250	15	48.20
	500	12	23.08
	1,000	12	18.67
	Background	15	21.87
	Total	84	

Test Statistics [a,b]

	Lead
Chi-Square	66.317
df	5
Asymp. Sig.	<0.001

a Kruskal Wallis Test
b Grouping Variable: Distance

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Table B-2 Multiple comparisons between lead concentrations in surface soil at various distances around the battery recycling plant and background areas

Multiple Comparisons

Post Hoc Tests

Dunnett T3

Dependent Variable: Lead concentration

(I) Distance (m)	(J) Distance (m)	Mean Difference (I-J)	Sig.	95% Confidence Interval	
				Lower Bound	Upper Bound
50	100	1088.69827(*)	<0.001	564.6502	1612.7463
	250	1117.25620(*)	<0.001	593.6750	1640.8374
	500	1138.64785(*)	<0.001	615.1434	1662.1523
	1,000	1140.67243(*)	<0.001	617.1711	1664.1738
	Background	1138.85313(*)	<0.001	615.3437	1662.3626
100	50	-1088.69827(*)	<0.001	-1612.7463	-564.6502
	250	28.55793	0.363	-13.1834	70.2993
	500	49.94958(*)	0.011	9.5135	90.3857
	1,000	51.97417(*)	0.008	11.5807	92.3677
	Background	50.15487(*)	0.010	9.6474	90.6623
250	50	-1117.25620(*)	<0.001	-1640.8374	-593.6750
	100	-28.55793	0.363	-70.2993	13.1834
	500	21.39165(*)	0.006	5.1027	37.6806
	1,000	23.41623(*)	0.002	7.2637	39.5687
	Background	21.59693(*)	0.005	5.0737	38.1201
500	50	-1138.64785(*)	<0.001	-1662.1523	-615.1434
	100	-49.94958(*)	0.011	-90.3857	-9.5135
	250	-21.39165(*)	0.006	-37.6806	-5.1027
	1,000	2.02458	0.987	-4.1202	8.1694
	Background	.20528	1.000	-7.3889	7.7995
1,000	50	-1140.67243(*)	<0.001	-1664.1738	-617.1711
	100	-51.97417(*)	0.008	-92.3677	-11.5807
	250	-23.41623(*)	0.002	-39.5687	-7.2637
	500	-2.02458	0.987	-8.1694	4.1202
	Background	-1.81930	0.999	-8.9213	5.2827
Background	50	-1138.85313(*)	<0.001	-1662.3626	-615.3437
	100	-50.15487(*)	0.010	-90.6623	-9.6474
	250	-21.59693(*)	0.005	-38.1201	-5.0737
	500	-.20528	1.000	-7.7995	7.3889
	1,000	1.81930	0.999	-5.2827	8.9213

*The mean difference is significant at the .05 level

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Table B-3 Statistical analysis of lead concentrations at various directions around the battery recycling plant

Tests of Normality

	Directions	Kolmogorov-Smirnov			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
Lead	N	.441	15	<0.001	.563	15	<0.001
	W	.353	15	<0.001	.668	15	<0.001
	WS	.450	15	<0.001	.577	15	<0.001
	S	.409	9	<0.001	.662	9	0.001
	E	.480	15	<0.001	.525	15	<0.001

NPar Tests

Kruskal-Wallis Test

	Directions	N	Mean Rank
Lead	N	15	42.93
	W	15	33.13
	WS	15	29.33
	S	9	41.89
	E	15	30.47
	Total	69	

Test Statistics [a,b]

	Lead
Chi-Square	5.499
df	4
Asymp. Sig.	0.240

a Kruskal Wallis Test
b Grouping Variable: Directions

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Table B-4 Regression analysis of lead concentrations in soil and distances from the battery recycling plant

Model Summary

R	R Square	Adjusted R Square	Std. Error of the Estimate
.856	.733	.721	.912

The independent variable is Distance.

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	47.993	1	47.993	57.714	<0.001
Residual	17.463	21	.832		
Total	65.456	22			

The independent variable is Distance.

Coefficients

	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta	B	Std. Error
ln(Distance)	-1.360	.179	-.856	-7.597	<0.001
(Constant)	76776.690	74748.967		1.027	0.316

The dependent variable is ln(Lead).

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APPENDIX C
PHYSICAL AND CHEMICAL ANALYSIS OF SOIL

Soil pH
(pH H_2O)

Equipments

1. pH meter
2. 50 mL Beaker
3. Stirring rod
4. 10 mL Measuring cylinder

Reagents

1. Standard buffer solution pH 4 and 7
2. Deionized water

Procedures

1. Weight 10 g of soil into a 50 mL beaker.
2. Add 10 mL of deionized water. Thoroughly mix the solution with a stirring rod and allow it to sit for a minimum of 30 minutes and a maximum of 2 hours.
3. The pH meter should be adjusted pH reading with a pH 7 and 4 of standard buffer solutions before being used to measure pH of soil solution.

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Organic Matter
(Walkley and Black Method)

Equipments

1. 250 mL Erlenmeyer flasks
2. 10 mL pipette
3. 25 and 50 mL Measuring cylinder
4. 50 mL burette
5. Analytical balance

Reagents

1. Concentrated of sulfuric acid (H_2SO_4)
2. Potassium dichromate ($K_2Cr_2O_7$) 1 N
3. Ferrous Ammonium Sulphate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] 0.5 N
4. O-phenanthroline indicator 0.025 M

Procedures

1. Weigh 1 g of dried soil and transfer to a 250 mL Erlenmeyer flask.
2. Add 10 mL of 1 N $K_2Cr_2O_7$ by means of a pipette.
3. Add 15 mL of concentrated H_2SO_4 and swirl gently to mix. Avoid excessive swirling that would result in organic particles adhering to the sides of the flask out of the solution.
4. Place the flasks on an insulation pad and let stand 30 minutes.
5. Dilute the suspension with about 50 mL of deionized water and allow to cool.
6. Add 5 drops of O-phenanthroline indicator. The indicator should be added just prior to titration to avoid deactivation by adsorption onto clay surfaces.
7. Titrate with 0.5 N Ferrous Ammonium Sulphate to a burgundy endpoint. The color of the solution at the beginning is yellow-orange to dark green, depending on the amount of unreacted $Cr_2O_7^{2-}$ remaining, which shifts to a turbid gray before the endpoint and then changes sharply to a wine red at the endpoint. This will eliminate uncertainty in determining the endpoint by color change.

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8. Run a reagent blank following the above procedure without soil. The reagent blank is used to standardize the Ferrous Ammonium Sulphate solution daily.

9. Calculate organic carbon and organic matter percentages:

a. Percentage easily oxidizable organic carbon:

$$\% \text{ Organic carbon} = \frac{(B-T)N}{B} \times \frac{100}{77} \times 3 \times \frac{100}{10^3} \times \frac{10}{W}$$

B = mL of Ferrous Ammonium Sulphate solution used to titrate blank

T = mL of Ferrous Ammonium Sulphate solution used to titrate sample

N = Concentration of Potassium dichromate (N)

W = Weight of sample (g)

b. Percentage of organic matter (OM):

$$\% \text{ Organic matter} = \frac{\% \text{ Organic carbon}}{0.58} = \% \text{ Organic carbon} \times 1.724$$

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Cation Exchange Capacity (CEC)
(Ammonium Replacement Method)

Equipments

1. 125 mL Erlenmeyer flask
2. Buchner funnels vacuum flasks and source of vacuum
3. 500 mL Filtering flask
4. Whatman No. 42
5. 100 mL Volumetric flask
6. 800 mL Kjeldahl flask
7. 50 mL Burette
8. pH meter
9. Distillation equipment
10. Analytical balance

Reagents

1. Deionized water
2. Ammonium acetate (NH_4OAc)1 N pH 7
3. Ethanol, 95%
4. Hydrochloric acid, 0.1 N
5. Ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$], 10%
6. Ammonium hydroxide (NH_4OH), 50%
7. Ammonium chloride (NH_4Cl_2), 1 N
8. Ammonium chloride (NH_4Cl_2), 0.25 N
9. Silver nitrate ($AgNO_3$), 0.01 N
10. Soduim hydroxide (NaOH), 40%
11. Boric acid (H_3BO_3), 3%
12. Mixed indicator (Bromo glycerol and Methyl red)
13. Sodium Chloride (NaCl), 10%

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Procedures

1. Weigh 5-10 g of dry soil pulverized to pass 10 mesh sieve (< 2.0 mm) soil into a 125 mL Erlenmeyer flask. Add 60 mL of ammonium acetate solution and close the flask, and then swirl gently to mix and let stand overnight.

2. Connect a 1 L vacuum extraction flask to a Buchner funnel fitted with a Whatman No. 42. Moisten the filter paper with 2 mL deionized water

3. Transfer the soil suspension into the Buchner funnel and leach the sample with 175 mL of 1 N ammonium acetate. The soil extract may be analyzed for extractable K, Ca, Mg, and Na.

4. Leach the soil sample in the Buchner funnel by leaching with 1 N of Ammonium chloride 4 times and 0.25 N of Ammonium chloride 1 time after that rinse with 95 % of ethanol to remove chloride and discard the leachate.

5. Rinse the soil sample with 10% of NaCl , Na^+ to replace the exchangeable ammonium. Bring leachate to a final volume of 225 mL volumetric flask using deionized water.

6. Pour the soil solution in step 5 into Kjeldahl flask and add a little amount of Pumice stone.

7. This determination can also be made using the Kjeldahl distillation method. Add 25 mL of 40% NaOH into soil solution in Kjeldahl flask to increase pH of soil solution to remove NH_4^+.The vapor of NH_3 from distillation is trap in 50 mL of 3% boric acid.

8. Add 5 drops of mixed indicator into solution from step 7 until solution change color from violet to green. Titrate with 0.1 N Hydrochloric aid to a burgundy endpoint. The color of the solution at the beginning is green to violet at the endpoint.

9. Run a reagent blank following the above procedure without soil.

10. Calculate CEC

$$\text{CEC (cmol/kg)} = \frac{(A-B)N \times 100}{W}$$

A = HCl solution used to titrate sample (mL)

B = HCl solution used to titrate blank (mL)

N = Concentration of HCl solution (N)

W = Weight of sample (g)

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Soil Texture

(Pipette method)

Equipments

1. Beaker (glass and plastic)
2. Cover glass
3. Measuring cylinder
4. Centrifuge
5. Centrifuge tube
6. Stirring rod
7. Policeman
8. Plunger
9. Aluminum can
10. Pipette apparatus
11. Hot plate.
12. Hood
13. Hot air oven
14. Mechanical stirrer
15. Time piece
16. Thermometer
17. Sieve shaker
18. Water bath
19. Desiccator

Chemicals and preparation

1.Preparation of calgon solution

Mix 35.7 g of $(NaPO_3)_6$ and 7.94 g of (Na_2CO_3) with 1 liter of distilled water to make a solution

2. H_2O_2 (50%)

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3. 1 N NaOAc pH 5

Add 82 g of NaOAc to 800 mL of deionized water and add 27 mL of glacial acetic acid adjust volume to 1,000 mL with deionized water and adjust solution pH to 5 by adding acetic acid

4. Sodium citrate solution 0.3 M

Add 88 g of sodium citrate and adjust volume to 1 L by adding deionized water and thoroughly mix a solution

5. Sodium bicarbonate solution 1 M

Add 84 g of sodium bicarbonate and adjust volume to 1 L by adding deionized water and thoroughly mix a solution

6. Pure sodium dithiosulphate ($Na_2S_2O_4$)

Procedures

1. Weigh 10 g of soil sample with through the sieve nest with a 2 mm sieve and place the weighted samples into 600 mL beaker and add 5-10 mL of hydrogen peroxide to each beaker. The samples were analyzed in replicates of two of each sample. Add more H_2O_2 when the reaction subsides, rinsing the sides if necessary. After that the samples were refluxed on hot plate at 50-60 °C for 1-2 hour with out boiling. If the samples have high organic contents should be add hydrogen peroxide again. Repeat steps until most organic matter has been destroyed, as determined by color of sample and rate of reaction.

2. The replicates of two soil sample from 1, bring one beaker for dry at 105°C for 24 hour until weight were constant and use for calculation **(a)**.

3. Add about 10 mL of Calgon solution in another one beaker. Stir for about 15 minutes this will disperse the aggregates in the soil.

4. Separation of the sand fractions

4.1 Wet the screen of a 53 µm sieve with water.

4.2 Slowly pour the solution in step 3 through the sieve. Collect the solution passing through the sieve in a 1,000 L beaker.

4.3 Collect the sand particles remaining on the 53 µm sieve into a dish. Using a distilled water rinse stream, pass this fraction through a stack of sieves with sizes between 53 µm and 2 mm (arranged coarsest on top, finest on the bottom). Shake

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the sieves for approximately 5 minutes. Add any solution passing through the 53 µm sieve to the 1,000 mL beaker containing the rinsing from step 2.

4.4 Label, weight, and record the mass of a aluminum drying dish for each sieve used. Transfer the soil particles retained on each sieve to the appropriate weighting dish. Rinse sieve to ensure allow particles are transferred.

4.5 Oven dry the sand fraction captured on each sieve.

4.6 Weigh and record the mass of the oven-dried sand fraction and dishes.

4.7 Calculate the mass of soil collected on each sieve **(b)**.

5. Analysis of the Clay and Silt Fraction

5.1 Label weight and record the weight of three aluminum drying cans.

5.2 Place the dispersed mixture which has been allowed to soak into a 1,000 mL graduated cylinder. Rinse beaker thoroughly with distilled water to ensure that all soil particles are in the cylinder.

5.3 Add 10 mL of dispersing agent to the cylinder.

5.4 Add sufficient distilled water to bring the volume in the solution to 1,000 mL.

5.5 Cover the cylinder with lab film and briefly mix solution by shaking the cylinder.

5.6 Allow the solution to equilibrate overnight.

5.7 Mark the point which is 5 cm below the top of the liquid surface.

5.8 Shake the cylinder for at least two minutes to ensure that the soil is dispersed throughout the solution. Record the time that shaking is stopped.

5.9 Gently insert the 20 mL pipette to the marked depth of 5 cm in the cylinder's liquid.

5.10 Using a controlled vacuum, withdraw 25 mL of solution in approximately 12 seconds.

5.11 Gradually remove the full pipette from the solution.

5.12 Discharge the liquid from the pipette into a previously weighted and numbered aluminum drying dish.

5.13 Using a small amount of distilled water, rinse the pipette into the drying dish.

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5.14 Oven-dry the samples at 105±5°C until the water evaporate.

5.15 Cool the drying dishes in a desiccator and then weigh and record weight **(c)**.

6. Calculate % sand, % silt, % clay

Weight of dry soil = a g

Weight of sand = b g

$$\% \text{ sand} = \frac{100 \times b}{a} \%$$

Pipette soil solution = 20 mL

Weight of clay = c g

$$\% \text{ clay} = \frac{1{,}000 \times c}{20a} \times 100 \%$$

$$= \frac{5{,}000 \times c}{a} \%$$

Amount of calgon must be removed from weight of clay before calculated

% silt = 100-(% sand + % clay)

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BIOGRAPHY

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