# CHAPTER II

# BACKGROUND AND PREVIOUS STUDIES



## 2.1 Study Area

### 2.1.1 Location and Geography

Mae Sot district in Tak province in the northern of Thailand is located along the Thai-Myanmar border (Figure 2.1) 500 kilometers from Bangkok, it is easily accessible either by airplane or car. For transportation by car from Bangkok to Mae Sot, it can follow highway No. 1 (Phahonyothin) and Highway No. 32 to Nakhon Sawan via Ayutthaya, Ang Thong, Sing Buri, Chai Nat.

Mae Sot district is located in the Mae Moei River Basin, which it can be divided into two features. The eastern part is the higher inter-mountainous basin. Zinc deposits have been located in some parts of this area. The western part consists of lowlands of terrace and alluvial plains of several waterways. The direction of tributaries in this area flow from east to west and extend to the Mae Moei River. From an aerial photo of Mae Sot, the Mae Moei River Basin can be divided into 7 sub-catchments, namely the (1) Huai Luang catchment, (2) Huai Pong catchment, (3) Huai Mae Toa catchment, (4) Huai Mae Ku catchment, (5) Huai Mae Ku Luang catchment, (6) Huai Phak La catchment, and (7) Huai Mai Paen catchment (Tongcumpou et, al. 2004).

The Mae Ku floodplain in the Mae Ku sub-district of Mae Sot district is located in the lowland area of the Mae Meoi River Basin. Mae Ku creek is the main source of irrigation for paddy field in this area. It comes from the highlands in the eastern part of the Mae Ku area that the zinc mine boundary is located as mentioned in Chapter 1.

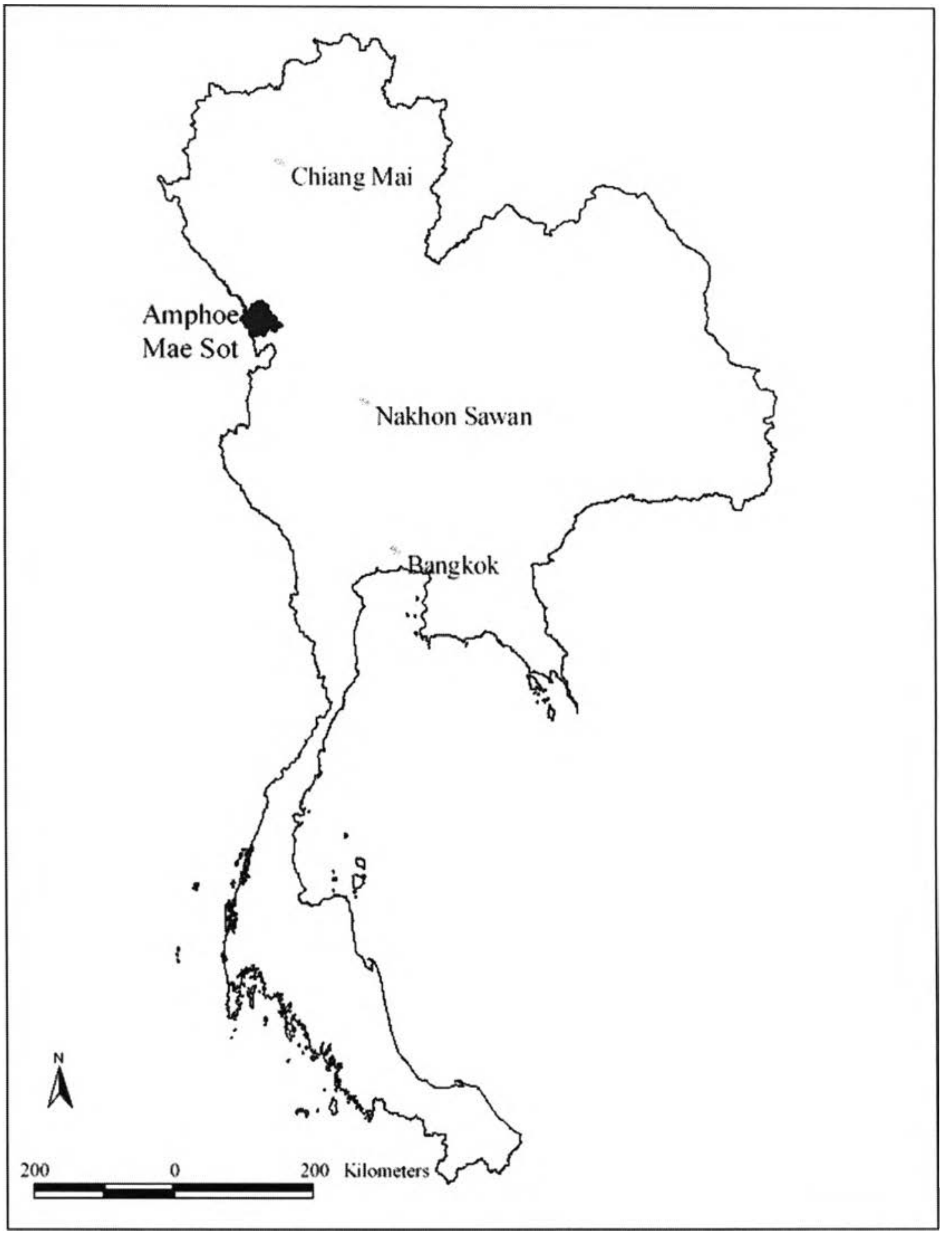


**Figure 2.1 Location of Mae Sot District in Tak Province.**

### 2.1.2 Land Use

From the field survey, Mae Ku floodplain area can be divided as follows (Figure 2.2 and Table 2.1):

- Paddy fields: most of the study area is used for rice cultivation. Irrigation water used for crop planting comes from the Mae Ku Creek. Paddy fields in this area are harvested only one crop per year. After the post harvest period of rice, corn or soy beans are grown in this area.
- Crop farm: this area is least part of Mae Ku floodplain. Corn and soy beans are the kinds of plants which is planted in this area.
- Residential area: this area is located in the centre of floodplain area.

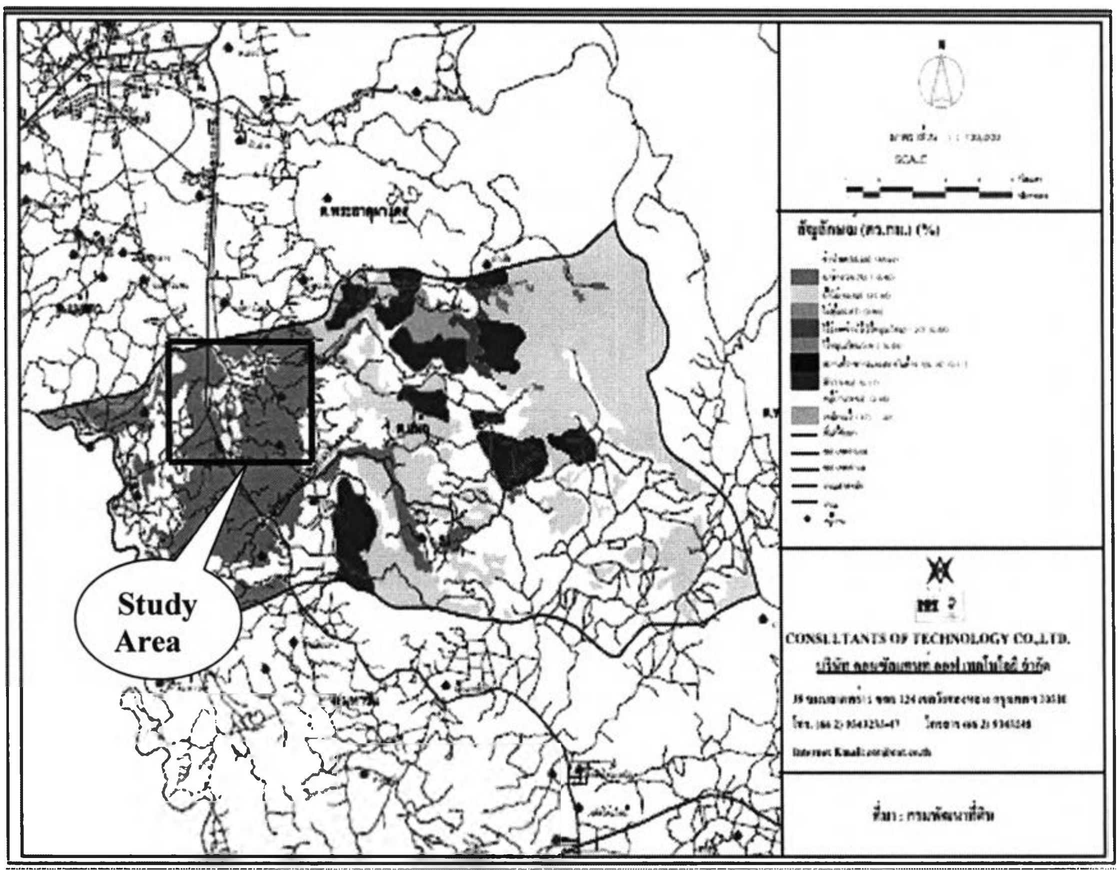


**Figure 2.2 Land Use of Mae Ku Sub-district, Mae Sot District in Tak Province.**

Source: Consultants of Technology Co, Ltd., 2006 (Adapted from Land Development Department)

**Table 2.1 Land Use of Mae Ku Sub-district, Mae Sot District in Tak Province.**

| Land Use | Area ($km^2$) | (%) |
|---|---|---|
| Corn Farm | 55.98 | 38.92 |
| Paddy Field | 26.75 | 18.60 |
| Forest | 39.39 | 27.38 |
| Shrub | 0.87 | 0.60 |
| Mobile Plantation | 2.08 | 1.44 |
| Government Institution | 0.16 | 0.11 |
| Teak Tree | 13.60 | 9.44 |
| Village | 3.54 | 2.45 |
| Mine | 1.47 | 1.02 |

Source: Consultants of Technology Co, Ltd., 2006 (Adapted from Land Development Department)

### 2.1.3 Zinc Deposit

There is a zinc ore deposit at Doi Phadaeng, in the Phratat Phadaeng sub-district of Mae Sot. There have been several zinc mines in this area over the past 30 years. At present, there are only 2 mining companies, namely Phadaeng Industry Public Co, Ltd. and Tak mining still in operation. Both zinc mines are located in the Mae Toa sub-catchment. However, some parts of the Phadaeng mine is located in the highlands of the eastern part of the Mae Ku sub-catchment, where the mine waste dumping site is located. Moreover, it is expected that there are several smaller zinc ore deposits in this area. The open pit is the method of mining in both of Phadaeng Industry Public Co, Ltd. and Tak mining. Soil and overburden were excavated in order to carry out zinc ore. Therefore, soil and overburden are wastes which contain concerned heavy metals, particularly cadmium because of cadmium and zinc associated in geological setting. A run-off collection in this area follows the dendritic pattern. When it rains in this area the sediment will be eroded from the highlands in the east and also from the zinc mine area. A run-off carrying sediment laden material flows to the lowland area in the west along the channel. These events lead to gradually increased sediment deposits along the alluvial plain and foothills.

## 2.2 Theoretical Background

### 2.2.1 Cadmium

Cadmium is a natural element which comes from the surface of the earth's crust via processes of erosion or volcanic activity. Cadmium is classified as a metallic element (symbol Cd, atomic number = 48). It is white, lustrous and tarnishable. Its atomic weight is 112.41 with a melting point at 321 °C and boiling point at 767 °C. It has low solubility in neutral condition. Cadmium typically occurs in association with zinc (Zn) in natural geologic settings. Both cadmium and zinc are elements in the group IIb of the Periodic Table and therefore these elements have similar chemical properties. In the environment, crystal structure of zinc mineral is replaced with 3-5 % of cadmium. This form is very stable. Cadmium however, has a stronger affinity with sulfur than zinc does. Cadmium also has higher mobility than zinc does in acidic conditions.

### 2.2.2 Cadmium in Soil:

Cadmium is present in the environment at the low levels, such as in atmosphere (0.1 to 5 ng/$m^3$) and in the earth's crust (0.1 to 0.5 ug/g). Cadmium concentration levels in soils are different in each of their parent soil materials. Alloway (1990) reviewed cadmium concentration in soils that were derived from igneous rocks, metamorphic rocks, and sedimentary rocks and found these to be 0.1-0.3, 0.1-1.0 and 0.3- 1.1 mg/kg, respectively. Kabata–Pendias and Pendias (1992) found that cadmium concentrations in non contaminated soil ranged from 0.06 to 1.1 ppm. It is believed that the elevated concentrations of cadmium in the environment come from anthropogenic activities. Important sources of cadmium contamination are as the follows: (1) air emissions such as from metalliferous mining and smelting, metal-using industries, phosphatic fertilizer plants, solid waste incinerators, coal combustion and road dust; (2) applications of cadmium containing materials, such as sewage sludge, phosphatic fertilizers, phosphogypsum and by-products, composted municipal waste and ash from combustion; and (3) accidental/fugitive sources such as industrial contaminated land, mine waste dumps and corroding galvanized metal structures (McLaughlin and Singh, 1999). Kabata–Pendias and Pendias (2001) reviewed that several studies indicated that under similar soil conditions the element from anthropogenic activities can more mobile and bioavailability than element in natural.

The species of trace elements in soil can be divided as follows: (1) water soluble, (2) exchangeable, (3) organically bound, (4) complexes with Fe and Mn oxides, (5) form complex with carbonates, phosphates, sulfides etc. and (6) structurally bound in silicates (residual fraction). The mobile species of trace element are water soluble and exchangeable fraction. The other species are less or immobile fraction. These forms are unavailable for plants and animals.

Normally, trace elements including cadmium in soil can be divided into two phases: (1) the solid phase, during which there is a large amount of metals in soil and (2) the solution phase, during which there is a small amount of metals that play an important role in the plant's uptake of metal. The cycle of metal in soil is a dynamic cycle. There are many processes which are concerned with the partition of metals between the solid and solution phases of soil. Metal in the solution phase will be added from metal in the solid phase. While metal in solution phase can be transformed to be metal in solid phase. Trace elements are in the primary and secondary minerals changes in environment condition. To complete the process, this fraction takes a long time to release metal in to the solution fraction (Figure 2.3).

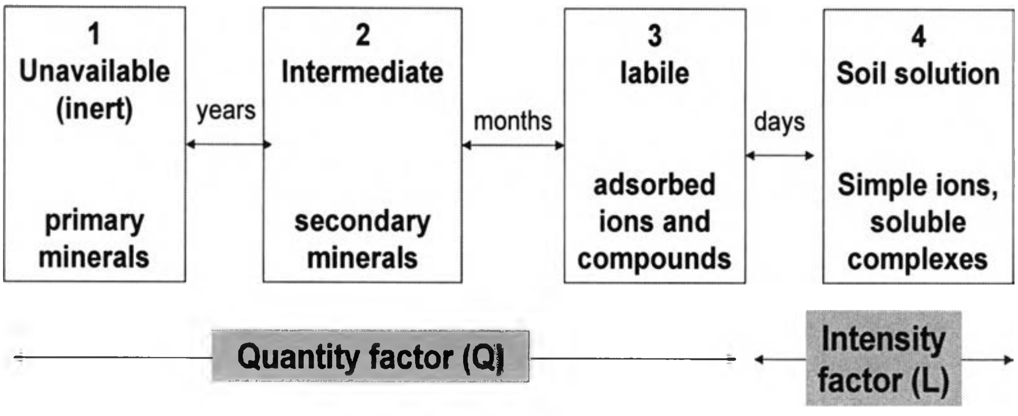


**Figure 2.3 Development of Soil from Sediment.**

Source: NRC-EHWM (2005)

### 2.2.3 Toxicity

Humans can intake Cd by ingestion and inhalation. Cadmium can absorb into the human body at about 2-6% and 30-60% through ingestion and inhalation, respectively (http://www.cadmium.org/). The toxicity of cadmium can be divided into 2 levels. Firstly, acute toxicity is the adverse effects from exposure to a high dose of cadmium at one period of time. Exposure to high levels in air may result in delayed (4-10hours) pneumonitis, and/or pulmonary edema. Secondly, chronic toxicity is the health effects that result from the accumulation of cadmium in the body over a long period of time. The two main organs affected are the bones and the kidneys. The bones get soft (osteomalacia), lose bone mass and become weaker (Osteoporosis). This causes the pain in the joints and the back, and also increases the risk of fractures. The second target organ is the kidney, which loses its ability to function and this leads to proximal renal tubular dysfunction. Acute toxicity has been rarely found in humans. Chronic cadmium intake has a high incident rate. The most common route of cadmium exposure to humans in general is the consumption of cadmium contaminated food. Average daily cadmium intakes from food in non-contaminated areas ranges from about 10-12 ug. But for the smoker, intakes are double the amount than for the non-smoker (www.Cadmium.org/exp.html). The most famous case of cadmium contamination was in Japan, where the people of the Jinzu River Basin in Toyama Prefecture suffered from "Itai - Itai" disease. The cause of the disease was the long-term consumption of food and water that was contaminated with cadmium. The cause of this contamination came from the release of mining waste into the river. The World Health Organization (WHO) has noticed a provision tolerable weekly intake of cadmium at 7 ug/kg of body weight. However, inhalation is the main route of cadmium exposure for workers who work in cadmium-related industries such as in phosphorus fertilizer plants and zinc mining and/or smelters. Cadmium is listed as reasonably anticipated to be carcinogenic in experimental animals by The National Toxicology Program (NTP). However, the International Agency for Research on Cancer (IARC) found that cadmium is carcinogenic to both animals and humans (http://www.inco.com).

### 2.2.4 Mitigation Measurements

There are many mitigation measurements in order to solve the problem of cadmium contaminated soil (Alloway, 1990) as the followings; (1) Taking out the contaminated soil or layering soil with a thick stratum of non contaminated matter .To make sure that plant roots can not get to the contaminated soil and capillarity and/or evaporation can not bring soluble cadmium in to the zone of root. This method is costly and inappropriate for a large area. (2) Decreasing the cadmium concentration in soil by leaching with acid or chelates. (3) Adding lime in soil in order to control soil pH at 7 which decrease bioavailability of cadmium in soil. This method is the most broadly used to resolve this problem. (4) Adding organic matter in to soil for increasing the adsorption capacity. (5) Flooding to make the reducing condition. This method is suitable for rice growing zone only (6) Using plant to adsorb cadmium in soil. This method usually chose non- food crops and in case of not heavily contaminated, using plant species that have low ability to accumulate cadmium.

### 2.2.5 Sequential Extraction and Bioavailability of Heavy Metal in Soil

Total heavy metals concentrations in soil generally mean the total of those metals that exist in soil. Total concentration is useful in assessment the metal loading in soil. However, to define the total concentration of heavy metal for environmental concern may not be an absolute value of that heavy metal since siliceous form of metal is not included. Most of heavy metals such as chromium, lead, also cadmium are really concerned due to their toxicity if they are exist or contaminated in the environment.. Because of these metals can cause of adverse effect to human health via food chain. Filgueiras, et al. (2002) reviewed that the accumulation of trace elements in plant and biota in soil are influenced by their concentrations in bioavailability fraction. However, to determine the bioavailability fraction from the total concentration has been studies for a few decades, however, it is often found that there are insignificant correlated of the bioavailability fraction to the metal concentration found is plats that grow in those area.

Therefore, the studying of the metal forms in soil is still interesting. The sequential extraction procedures are introduced to apply for determination of heavy metal in each fraction. The basic of this method is using of appropriate reagents which are applied in a given order to the sample. Typically, the purpose of this procedure are as follows: (1) pollution source characteristic,(2) measurement of the mobility and bioavailability of metal, and (3) identification of binding sites of metals for assessing metal accumulation, pollution and transport mechanisms. There are many kinds of sequential extraction procedures also the Standard, Measurement and Testing, (SM &T formerly BCR) sequential extraction procedure of the European Union (Filgueiras, et al., 2002). The SM&T program (also referred to as BCR throughout the report) proposed a three – step extractions provide four fractions as the follows: (1) exchangeable fractions, water and acid soluble, (2) reducing conditions, (3) oxidizing conditions, and (4) Residue fraction (this fraction is the element in the lattice of primary and secondary minerals). The definition of fractions and extraction conditions related to the SM&T sequential extraction procedures for chemical fraction of soil samples is shown in Table 2.1.

There are many factors that influence these processes in both soils and plants in soil, such as organic matter, pH, metal content, the sorption capacity of soil, redox conditions and effects of other elements. The important soil factor which influences this change is pH and redox potential of the soil. In the acidic condition, heavy metal in soil is more mobile and availability than it dose in the neutral condition. Plant factors that influence the uptake of cadmium in soil are plant species, distribution of cadmium in plants.

**Table 2.1 Definitions of Fractions and Extraction Conditions Related to the SM&T Sequential Extraction Procedures for Chemical Fraction of Soil Samples.**

| Nominal target phase | Reagent and conditions | Description |
|---|---|---|
| Exchangeable and acid and water soluble | Shaking for 16 hr. with 0.11 mol /L acetic acid | Weakly – bounded metals retained on soil surface by relatively weak electrostatic interactions, which can be released by changes in ionic composition, modifications of metals on sediment constituents or affected by production or consumption of protons. Often considered representative of available amounts. |
| Reducible | Shaking for 16 hr. with 0.5 mol /L hydroxylamine ammonium chloride, pH = 1.5 | Trace elements contained on iron and manganese (hydr)oxide are released, because of their thermodynamic instability under anoxic conditions and dissolution of metal-oxide phases under controlled Eh and pH conditions. |
| Oxidizable | Digestion with hydrogen peroxide at room temperature, evaporation, re-digestion and evaporation, then shaking for 16 hr. with 1.0 mol/L ammonium acetate | Trace elements bounded to various forms of organic matter as biotic detritus, organic particles or living organisms. The degradation of organic matter under oxidizing conditions is responsible for releasing trace elements. |
| Residual | Digestion with Aqua Regia (ISO 11466 protocol) | Trace elements in the lattice of primary and secondary minerals. In this case possible changes in environment condition the release of metals from this fraction on a time-scale of several years. |

Source: Pe'rez, G., and Valiente, M. (2004)

## 2.3 Literature Review

There had been several studies concerned cadmium contamination in many aspects such as bioavailability, cause of contamination, uptake of cadmium to plants etc. The previous researches related to this study are as follows:

**Rieuwerts, et al.** (1998) reviewed the factors influencing metal bioavailability in soils. They found that total metal concentrations could not reflect metal levels in soil solution which directly affected plants and micro biota in soil. Key soil processes involved in the solid-solution partition of Cd, Cu, Pb, and Zn were as follows; cation exchange, specific adsorption, precipitation, and complexation. These processes decreased the metal concentration in solution phase. Factors affecting the solid-solution partition of these metals were as follows: pH, redox potential, soil texture, clay content, organic matter content, iron and manganese oxides, presence of cations and anions in soil solution, and miscellaneous factors such as the metal's physico – chemical form and particle size and temperature. pH is an important factor that has the most influence on metal bioavailability in soil. In acid conditions, metals in soil have high solubility, but in alkaline conditions, their solubility is decreased.

**Liu et al.** (2004) studied metal contamination of soil and plants affected by the collapse of a tailings dam of a lead/zinc mine in China, in 1985. The adjacent area on both sides of the river was covered with sludge or wastewater from the mine tailings. Only some areas were cleaned up. Several decades later, plants and soils were sampled and the concentration of heavy metals in these samples was determined. The results showed that the concentrations of heavy metals were in the following order: of control area < cleaned up area < mining waste covered area. Soil in the contaminated area was still heavily polluted with As, Cd, Zn, Pb and Cu that highly exceeded the maximum allowable concentration levels for Chinese agricultural soils, predominantly for As and Cd. In plants, the edible parts contained the highest heavy metal concentrations.

**Jung** (2001) studied heavy metal contamination of soil and water in and around the Imcheon Au-Ag mine, Korea. Soils and waters were sampled and analyzed using AAS for Cd, Cu, Pb, and Zn. $HCO_3^-$, $F^-$, $NO_3^-$ and $SO_4^{2-}$ in water samples were analyzed by ion chromatography. Elevated concentrations of trace elements were found in tailings. Maximum concentrations in the tailings were 9.4, 229, 6160 and 1640 mg/kg extracted by the Aqua Regia method and 1.35, 26.4, 70.3 and 410 mg/kg extracted by 0.1 N HCl solution for Cd, Cu, Pb and Zn, respectively. These metals are continuously dispersed downstream and down slope from the tailings by wind and water. Because of the existence of sulfides in the tailings, a water sample taken on the tailings site was very acidic with a pH of 2.2, with high total dissolved solids (TDS) of 1845 mg/l and electric conductivity (EC) of 3820 μS/cm. This sample also contained up to 0.27, 1.90, 2.80, 53.4 and 4,700 mg/l of Cd, Cu, Pb, Zn and $SO_4^{2-}$, respectively. TDS, EC and concentrations of metal in waters decreased with distance from the tailings.

**Jung** and **Thornton** (1999) reported the contamination of trace elements from mining activities in the surface environment and its implications for soils and plants. Soils were sampled in and around a Pb/Zn mine in Korea from sites that also included the mine dump, nearby household gardens and uncultivated areas. Plant samples were collected from household gardens and from a nearby control area. Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry was conducted to determine concentrations of Cd, Cu, Pb and Zn. Concentrations in soils decreased with distance from the mine source. Metal concentrations in plant species sampled generally decreased in this order: tobacco leaves > spring onions > soybean leaves > red pepper ≈ corn grain. The ratios of metal concentrations in plants to those in soils decreased in the order Zn > Cd > Cu > Pb. The important factors influencing the bioavailability of heavy metals in soils and their uptake into food crops were pH and concentration of heavy metals in soil.

**Somboon** (1999) studied the contamination of cadmium and zinc in soil resulting from zinc mining activities in Mae Sot district, Tak province. Soil samples were collected from both upstream and downstream areas in the same watershed of the mine and from adjacent areas outside the watershed boundary. This study found that cadmium concentrations of soil samples from downstream areas were higher than samples from both upstream and adjacent areas. The average cadmium and zinc content in soil samples from downstream areas were 50.84 and 1,908.81 ppm, respectively.

**Zarcinas et al.** (2003) conducted an assessment of heavy metal pollution in cultivated soils and plants of Thailand. The elements of interest in this study were arsenic, cadmium, cobalt, chromium, copper, mercury, nickel, lead and zinc. The results of this study showed that concentrations of these elements varied wildly among the different zones of the country. They concluded that elevated concentrations of As, Co, Cr, Cu, Hg, Ni and Pb in environments might be a result of changing of soil mineralogy, but that elevated concentrations of Cd and Zn might be a result of agricultural fertilizer application and soil amendment. The authors advised that 95 percentile trace elements concentration can be used as "Investigation Levels" for metal in uncontaminated soils of Thailand. The concentration ranges for Thailand topsoil's sampled were As (0.08-29.0), Cd (0.01-0.17), Co (0.10-21.1), Cr (0.14-79.4), Cu (0.16-43.6), Hg (0.01-0.10), Ni (0.10-43.9), Pb (0.10-54.6), and Zn (0.10-71.0) mg/kg.

**Simmons et al.** (2003) studied the contamination of cadmium and zinc in a cultivated area in Thailand which was also affected by Zn and Cd co–contamination. This study collected rice and soybean samples and concurrent soil samples from the cultivated area. For soil samples, Zn and Cd concentrations ranged from 2.91-248 and 254-8036 mg/kg respectively. While for rice and soybean samples, Cd concentrations ranged from 0.02-5.00 and 1.08-1.71 mg/kg, respectively. In addition, they studied the heavy metal accumulation in any parts of the rice and soybean plants. Results indicated that Cd and Zn accumulate more in rice plants than in soybeans.

**Tongcumpou et al.** (2004) studied the distribution of cadmium from a zinc mine to cultivated areas in Mae Sot district, Thailand. Sediment, soil and water in the Mae Toa flood plain and adjacent areas were sampled in order to determine total concentrations of cadmium and zinc and the available concentrations of these elements. Most soil samples were collected from the flood plain area which had received irrigation water directly from the Mae Toa creek. The results were high concentrations both of cadmium and zinc. The results from water samples from creeks and ponds were below the standard at 0.01 ppm. This study presumed that the area of zinc deposits was the potential source of contamination. The determination of bioavailability of cadmium using the BCR method showed that there were high cadmium concentrations in soil, but that the bioavailability of cadmium was not relatively high.

**NRC-EHWM** (2005) studied cadmium distribution and bioavailability in cultivated soil and crops in the vicinity of zinc mine in Mae Sot. It was found that cadmium contamination of lowland paddy soil came from the accumulation of sediment. It was discharged from the high land where zinc ore deposits are located in that area. NRC-EHWM recommended the high background values in this area, because of the potential of zinc ore deposit in this area. The loosening fragments from the long – term natural processes and anthropogenic activities are source of contamination, particularly mining activities. It was found that relationship between available and total concentration of fresh sediment showed the low ratio. However, in the soil, this relationship showed ratio which much higher than the sediment result. This may indicate that the sediment from upland area has been deposited in this floodplain. It was assumed that more than 50 % of the study area was the cadmium contaminated soil.