ESTIMATION OF NON-DIETARY CADMIUM EXPOSURE AND RISK ASSOCIATED WITH IT IN FARM COMMUNITY LIVING IN MAESOT, TAK PROVINCE

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การประมาณค่าของแคดเมียมที่ไม่ได้ผ่านทางการบริโภคและความเสี่ยงที่เกี่ยวข้อง ในชุมชนเกษตรกรรมในพื้นที่อำเภอแม่สอด จังหวัดตาก

นางสาว วิไลลักษณ์ นิยมมณีรัตน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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วิไลลักษณ์ นิยมมณีรัตน์ : การประมาณค่าของแคดเมียมที่ไม่ได้ผ่านทางการบริโภคและความเสี่ยงที่เกี่ยวข้องในชุมชนเกษตรกรรมในพื้นที่อำเภอแม่สอดจังหวัดตาก (ESTIMATION OF NON-DIETARY CADMIUM EXPOSURE AND RISK ASSOCIATED WITH IT IN FARM COMMUNITY LIVING IN MAE SOT, TAK PROVINCE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : Nyein Nyein Aung, Ph.D., 98 หน้า.

การประมาณค่าของแคดเมียมที่ไม่ได้ผ่านทางการบริโภคและความเสี่ยงที่เกี่ยวข้องในชุมชนเกษตรกรรมในพื้นที่อำเภอแม่สอด จังหวัดตาก ทำโดยวิธีรับสารเข้าสู่ร่างกายทางหลอดทดลอง (*in vitro* bioaccessibility method) และนำมาเปรียบเทียบกับพื้นที่ควบคุม ปริมาณแคดเมียมในดินมีค่าตั้งแต่ ND (ไม่สามารถตรวจวัดได้) - 162 มก./กก. สำหรับปริมาณแคดเมียมในดินในพื้นที่ที่พักอาศัยและเกษตรกรรมมีค่าตั้งแต่ ND - 156 มก./กก. และ 1.32 – 162 มก./กก. ตามลำดับ ค่าการรับสารแคดเมียมเข้าสู่ร่างกายทางหลอดทดลอง มีค่าตั้งแต่ 8.6 – 96% ค่าเฉลี่ยในการรับแคดเมียมต่อวันผ่านทางการบริโภคดินโดยไม่ได้ตั้งใจในประชากรกลุ่มเกษตรกร, ประชาชนทั่วไป, เด็กอายุ 6 – 8 ปี และเด็กอายุ 1 – 5 ปี มีค่า 3.47, 0.95, 1.9 และ 3.8 มคก./วัน ตามลำดับ เมื่อทำการประเมินการได้รับแคดเมียมโดยปรับด้วยน้ำหนักตัวของประชากรในพื้นที่ที่ทำการศึกษา ปริมาณการได้รับแคดเมียมในเกษตรกรเพศชายและหญิงมีค่า 0.35 และ 0.42 มคก./สัปดาห์/กก. น้ำหนักตัว ปริมาณการได้รับแคดเมียมในประชากรที่ไม่ได้ทำการเกษตรเพศชายและหญิง, เด็กอายุ 6 – 8 ปี และเด็กอายุ 1 – 5 ปี มีค่า 0.10, 0.12, 0.70 และ 2.0 มคก./สัปดาห์/กก. น้ำหนักตัว ตามลำดับ ซึ่งค่าที่ได้จากการได้รับแคดเมียมต่อสัปดาห์จะนำไปทำการคำนวณและประเมินค่าที่นำไปสู่ค่าที่ยอมรับได้ (Tolerable intake, TI-s) ซึ่งถูกกำหนดโดยองค์กร US.EPA ผลการศึกษาพบว่าเด็กอายุระหว่าง 1 – 5 ปีได้รับแคดเมียมผ่านทางการบริโภคดินโดยไม่ได้ตั้งใจโดยมีค่าเปอร์เซ็นต์ที่ยอมรับได้สูงและบางครั้งสูงเกินค่าที่ยอมรับได้ ดังนั้นการได้รับแคดเมียมในเด็กอายุ 1 - 5 ปี จึงมีความจำเป็นต้องมีการเฝ้าระวัง ปริมาณแคดเมียมในดินในพื้นที่ที่ทำการศึกษา และปริมาณการได้รับแคดเมียมผ่านทางการบริโภคดินโดยไม่ได้ตั้งใจมีค่าสูงกว่าพื้นที่ควบคุม เนื่องจากค่าการรับสารเข้าสู่ร่างกายทางหลอดทดลองมีความจำเพาะ ดังนั้นจึงต้องตรวจวัดการรับสารแคดเมียมเข้าสู่ร่างกายจากธรรมชาติ ผลจากการศึกษาพบว่าการรับสารแคดเมียมเข้าสู่ร่างกายทางหลอดทดลองจากดินในพื้นที่ที่ทำการศึกษามีความสัมพันธ์อย่างมีนัยสำคัญกับ แคลเซียม แมกนีเซียม และ สังกะสี ($p < 0.01$) นิกเกิลอาจมีการแข่งขันกับแคดเมียมในการละลายในกระเพาะอาหารโดยมีความสัมพันธ์กันน้อย ($p < 0.1$) ซึ่งแสดงให้เห็นว่าความสัมพันธ์ระหว่างสารประกอบแคดเมียมอินทรีย์ในดินสามารถนำมาเชื่อมโยงกับการรับสารแคดเมียมเข้าสู่ร่างกายทางหลอดทดลอง

สาขาวิชา : การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต วิไลลักษณ์ นิยมมณีรัตน์

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5187627420: MAJOR ENVIRONMENTAL MANAGEMENT
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WILAILUK NIYOMMANEERAT: ESTIMATION OF NON-DIETARY CADMIUM EXPOSURE AND RISK ASSOCIATED WITH IT IN FARM COMMUNITY LIVING IN MAE SOT, TAK PROVINCE. THESIS ADVISOR: NYEIN NYEIN AUNG, Ph.D., 98 pp.

The non-dietary exposure of cadmium (Cd) among farm community in Mae Sot, Tak Province and its risk associated was estimated by using an *in–vitro* oral bioaccessibility method comparing with the control site. Total Cd concentrations in soil were ranged from ND - 162 mg/kg. For residential and agricultural areas, the Cd concentrations in soil were ranged from ND - 156 mg/kg and 1.32 - 162 mg/kg, respectively. Bioaccessibility of Cd was ranged from 8.6 – 96.0%. Average daily intake of soil cadmium via incidental soil ingestion among farmers, normal adults (non-farming), children aged 6-8 years and younger children aged 1-5 years were 3.47, 0.95, 1.9 and 3.8 μg/day, respectively. When the intake estimations were adjusted with body weight, the intake among men and women farmer were 0.35 and 0.42 μg/week/kg BW, respectively. The intake among normal adults men and women (non-farming), children aged 6-8 years and young children aged 1-5 years were 0.10, 0.12, 0.70 and 2.0 μg/week/kg BW, respectively, which contribute to a considerable amount of tolerable intakes (TI-s) set by US.EPA. The results indicated that Cd intake via incidental soil ingestion pathway alone in children aged 1-5 years may contribute to high percentage of TI-s and sometimes exceed the TI-s. Therefore, Cd intake among young children is needed to be surveillance. The Cd concentrations in soil and Cd intake via incidental soil ingestion in the contaminated site are significantly higher than those in the control site. Since bioaccessibility is site-specific, the nature of bioaccessible Cd was determined. The bioaccessible Cd in soil in the contaminated site behaved similar to Ca, Mg and Zn at $p < 0.01$, significantly. Ni might compete in dissolution with Cd in the gastric environment (negative correlation at $p < 0.01$, significantly). A significant positive correlation of bioaccessible Cd with bioacessible Ni ($p < 0.01$) confirmed the possibility of competing Ni with Cd Bioaccessible Cd showed a weak correlation with organic matters at $p > 0.1$ indicating that organo-Cd complexes in the site might be somewhat bioaccessible.

Field of Study : Environmental Management Student's Signature Wilailuk Niyommaneerat
Academic Year : 2009 Advisor's Signature

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CHAPTER I

INTRODUCTION

1.1. Background and Motivation.

Cadmium (Cd) is one of the most highly toxic metals and also has a potential on environmental contamination because it is ubiquitous in environment. It is known as carcinogenic and accumulates in the mammal kidney and it has long half-life about 10 – 33 years in human body (Ellis et al., 1979 and Suzuki et al., 1988). Naturally, it occurs with zinc ores from mine drainage. Cd is used largely in batteries and pigments, for example in plastic products. For the chronic exposure, the daily intake of Cd is mainly from food, beverage and smoking. In addition, human uptake of Cd through contaminated food such as rice and plants grown in Cd enriched soil. Previous researches reported that Japanese have the highest renal Cd levels in the world and followed by Thailand, Hong Kong and Taiwan because of rice- eating habit (Kawada et al., 1998).

In Thailand, there is a zinc deposit at Doi Pha Daeng, Phra Tat Pha Daeng sub district in Mae Sot District, Tak Province, Thailand. This area started zinc mining for more than 30 years by several companies. Consequently, it has faced to cadmium contamination in agricultural system. The cadmium contamination state is quite critical. This is because cadmium is not only found in lowland soil surrounding the zinc mines but it is also detected in soil, sediment, water, agricultural products(rice, garlic and soybean etc.,); 0.5-218 mg/kg cadmium in soil, which exceeds standard by 72 times (EEC: The economic Community about 3mg/kg) (Simmon et al., 2003). The elevated concentration of cadmium in cultivated soil and rice grain was investigated by International Water Management Institute (IWMI) and Land Development Department (LDD) of Thailand in 2001-2003. The concentrations of total cadmium in soil samples were much higher than those found in the Thai “background” soil zinc and cadmium concentrations which is in the range from <0.01 to 237 mg/kg and from <0.01 to 0.141 mg/kg, respectively (Pichit Pongsakul and Surasit Attajarusit, 1999).

Moreover, 20% of populations in Mae Sot have accumulated cadmium in their blood and urine exceeding the normal level (up to 6-10 ug/g creatinine for moderate high level and > 10 ug/g creatinine for high level. The WHO standard of cadmium in blood and urine are 5µg/l and 2µg/l, respectively. In addition, these people may reveal indication of irrevesible renal dys function and urinary calculus since they have consumed cadmium contaminated rice and water for long period of time (Department of Disease Control, 2004).

Significant amount of increases in soil cadmium content result in an increase in the uptake of cadmium by plants; the pathway of human exposure from agricultural crops is thus susceptible to increases in soil cadmium. In addition, soil ingestion can be a major route of human exposure to many immobile soil contaminants. This research was planned to assess upon oral exposure risk of cadmium contaminated in soil. In this study, non – dietary exposure of Cd was studied and investigated the amount of Cd that reach to human because this exposure pathway is often neglected but the most important exposure pathway to heavy metals especially among young children due to hand-to-mouth behavior. Non dietary exposure pathway is the result of direct ingestion of soil/dust participles. The following daily soil ingestion rates shows that human are ingesting soil without knowing.

Human expose to the environmental contaminants in 4 exposure pathways or routes; viz., dietary, non-dietary, inhalation and dermal. In this reserach, non – dietary exposure was studied to investigate soil Cd that reach to human without passing food. It is an exposure of soil particles that adhere to the hand and breathing soil or household dust, where coarser particles stuck in throat area, and directly reach into the stomach. This phenomenon is more pronounced among the children due to hand to mouth activity as a normal process of growth. Non-dietary exposure pathway can be a predominant exposure pathway for heavy metals due to the persistent and immobile nature of them in soil (Aung et al., 2004). Human exposure to environmental contaminants can be assessed via biomarkers such as urine and blood. However, since biomarkers track the total body burden of environmental pollutant exposure, it is unable to estimate exposure level of each pathway. An indirect method of exposure assessment is simply measuring of the contaminant in the environmental media that human encountered and the contact rate with the media. Daily exposure assessment, in this study, was carried out by simply multiplying the soil Cd concentration at the particle size that adhere to the human hands and the daily soil ingestion rates determined by other institutions. The assessments was extended to weekly exposure and compared with the Tolerable Intake (TI) levels. However, not all the contaminant that have contacted human and that entered into the human body can be reached into body system; only the bioavailable portion can be reached. In a few recent decades, bioavailability/bioaccessibility concept received attention in soil pollution. Bioavailability, which is assessed by *in-vivo* animal tests by feeding the soil associated with certain contaminants and measuring the body burden. However, animal test are costly and do not relate well with humans. Thus, *in-vitro* methods known as oral bioaccessibility methods, which simulate human digestive system, have been introduced to estimate the oral exposure risk of persistent environmental pollutants. These *in-vitro* methods were usually validated with the results obtained by *in-vivo* methods to prove that the estimations are close to the bioavailable values. (Ruby et al., 1999 and Environmental Agency, 2002)

In our study, an *in-vitro* soil oral bioaccessibility test developed by Solubility/Bioavailability Research Consortium (SBRC) of the United States, for screening the contaminated sites was applied to provide the complementary information for Cd contamination as well as for estimation of exposure risk to the farm community. The SBRC method, which simulates only the stomach condition of humans and was validated through the swine *in-vivo* tests, is currently adopted by British Geological Survey and nominated as one of the candidate methods for standardizing bioaccessibility test at the European platform on bioavailability and bioaccessibility, the BioAvailability Research Group Europe (BARGE) (Oomen et al., 2002). Moreover, this method was listed as a standard operating procedure by the United States, Environmental Protection Agency (US EPA, 2008).

1.2 Objectives

The main objective of this study is to estimate the non-dietary exposure of cadmium (Cd) and the risk associated with it in farm community living in Mae Sot district, Tak Province.

The sub-objectives are as follows:

1. To estimate the amount of non-dietary ingestion exposure in the farm community and its contribution to maximum permissible exposure level
2. To assess the risk associated with non-dietary exposure of Cd in the study area by using *in–vitro* oral bioaccessibility method and compare it with the control site
3. To study the nature of bioaccessibility through the relationships with certain soil properties, other metals and minerals since boiaccessibility is site-specific

1.3 Hypothesis

Non – dietary exposure route of soil contaminants and the risk associated with it, which is often overlooked in the exposure scenario. However, contribution of this exposure route in the farm community of interest may be high.

1.4 Scopes of the Study

1. This research focuses on Cd contamination in soils and exposure risk associated with it in farm community living in Mae Sot area in Tak province. Thus, the samples were collected mainly from farm community areas such as playgrounds, school, park and household compounds, as well as from paddy fields and other areas that grow rubber, corn and sugar-cane. Geographic references of all sampling points were checked by using Global Positioning System (GPS).
2. Total and bioavailable Cd concentration was determined at soil size of <250μm, which is known to be the cutoff size of soil particles that adhere to human hands.
3. Cd exposure via non-dietary ingestion pathway was estimated by multiplying total Cd and soil ingestion rate of each population groups (farmers, normal adults,

children and younger children). The contribution of non-dietary exposure route was determined by comparing exposure results with Tolerable Intake (TI) levels.

4. An *in-vitro* stomach condition simulation method was applied to determine bioavailable Cd in soil samples, thereby, estimate the risk associated with non-dietary exposure of Cd. This method was developed by Solubility/Bioavailability Research Consortium (SBRC), USA.

5. Risk associated with non-dietary exposure of Cd that being estimated from the study area would be compared with those from control site, a place situated in a non-zinc mineralized area, where, soil samples were collected in the same manner as done in the study area. The significance of the difference was determined using statistical tool.

6. Certain soil properties (soil pH and soil organic matter), total Cd, oral bioaccessible Cd and other metals (Zn, Ni, Pb) and mineral concentrations (Al, Ca, Fe, Mn) were determined in order to identify study of nature of bioaccessibility at the study site. Statistical analysis was done to find the correlation among total Cd, bioaccessible Cd, certain soil properties and the other minerals and metals in order to identify the nature of bioaccessible Cd in the study area since bioaccessibility has site-specific nature.

7. Chemical analysis was done by using Graphite furnace atomic absorption spectroscopy (GFAAS) or Flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma optical emission (ICPOES), (Total concentration of Ag, Pb, Zn, Ni, Ca, Al, Fe, Mn, Mg, Fe, B, Ba, Bi,Co, Cu, Cr, Ga, K, Li, In, Na, Si, Sr, TI with ICP).

8. Statistical analysis was done by SPSS 17.0 program.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1. Background

2.1.1Cadmium

Cadmium is a soft, malleable, ductile, toxic, bluish-white bivalent metal. It is similar in many respects to zinc but forms more complex compounds. Cadmium (atomic number 48, relative atomic mass 112.40 with a boiling point at 767^{o}C and melting point at 321^{o}C) occurs in the 0 and +2 oxidation states. It forms many divalent compounds, mostly inorganic. It has low solubility in neutral condition. In environment, crystal structure of zinc mineral replaced with 3-5% of cadmium. This form is very stable. Cadmium has a stronger affinity with sulfur than zinc does. Cadmium also has higher mobility than zinc does in acidic solutions (Siriluk Janpho, 2005)

In addition, Cadmium-containing ores are rare and found to occur in small quantities. However, traces do naturally occur in phosphate, and have been shown to transfer in food through fertilizer application. Greenockite (CdS), the only cadmium mineral of importance and always associated with sphalerite (ZnS). As a consequence, cadmium is produced mainly as a byproduct from mining, smelting, and refining sulfide ores of zinc. And small amounts can be found in lead and copper. Small amounts of cadmium, about 10% of consumption, are produced from secondary sources, mainly from dust generated by recycling iron and steel scrap. Production in the United States began in 1907, but it was not until after World War I that cadmium came into widely use.

Cadmium was for a long time used as pigment and for corrosion resistant plating on steel. Cadmium compounds were used to stabilize plastic. With the exception of its use in nickel-cadmium batteries, the use of cadmium is generally decreasing in all other applications. This decrease is due to the high toxicity and carcinogenicity of cadmium and the associated health and environmental concerns. (Source: Wikipedia, 2009 and EHC 214)

2.1.2 Cadmium in soil

The level of cadmium is 0.1 to 5ng/m^3 and 0.1 to 0.5µg/g in atomosphere and earth's crust respectively (ICdA, 2009). Cadmium concentrations in non contaminated soil ranged from 0.06 to 1.1 ppm (Kabata-Pendias and Pendias, 2001). Cadmium in soils is derived from both natural and anthropogenic sources. Natural sources include underlying bedrock or transported parent material such as glacial till and alluvium. Anthropogenic input of cadmium to soils occurs by aerial deposition and sewage sludge, manure and phosphate fertiliser application. Cadmium is much less mobile in soils than in air and water. The major factors governing cadmium speciation, adsorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands, and competition from other metal ions (OECD, 1994). Cadmium in soils must be distinctly classified in three separate areas with regard to their relative effects on human health and the environment; these three areas are agricultural soils, non-agricultural soils, and controlled landfills. Cadmium in controlled landfalls is virtually immobile, and is unlikely to have any effect on human health or the environment simply because it is so well contained (Eggenberger and Waber, 1998, NUS, 1987). Cadmium in non-agricultural soils will generally not affect human health as it does not enter the food chain readily or may do so only indirectly by transfer from non-agricultural soils to agricultural soils via airborne or water transport. However, the amount thus transferred is considered to be relatively low and is not expected to be a significant proportion of the cadmium in non-agricultural soils. Cadmium in agricultural soils is likewise relatively immobile under normal conditions, but could become more mobile under certain conditions such as increased soil acidity and its cadmium level may be enhanced by the usage of phosphate fertilisers, manure or sewage sludge.

In addition, the species of trace elements such as cadmium in soil can be devided as follows: (1) water soluble, (2) exchangeable, (3) organically bound, (4) complexes with Fe and Mn oxides, (5) form complexes with carbonates, phosphates, sulfides, etc. and (6) structurally bond in silicates (residual fraction). The trace element which are water soluble and exchangable fraction act as mobile species. The other species are less or immobile fraction. (Siriluk Janpho, 2005)

Organic matters in soils can strongly adsorbed cadmium. It can be extremly dangerous when cadmium is presents in soils because of increases uptaking cadmium into foodchain. Acidified soil enhances effectively cadmium uptake of plant. This is a potential danger to animals and humans that are dependent upon the plants for survival. This is may be the reason that human today are exposed to cadmium, close to the level that affects kidney function. In oeder to take effective measure to decrease cadmium levels in the environment and food stuffs, knowledge of the sources and levels of cadmium in the agricultural environment is necessary. The FAO/WHO Joint Expert Committee on Food Additives and Contaminants (JECFA) has established a provisional tolerable weekly intake of Cadmium (PTWI) that set as 7 µg/kg body weight. (Parada Maneewong, 2005). Nevertheless, the European Food Safety Agency set lower tolerable weekly intake to 2.5 µg/kg body weight resulting in more concern on human health.

In the past, cadmium contamination in areas where food has been grown. This was particularly so for rice crops in Japan in the 1950s and 1960s where cadmium concentrations from 200 to 2,000 ppb were found (Elinder, 1985). In general, soils which have been historically contaminated with cadmium from industrial operations are no longer used for agricultural purposes. In those cases where old industrial installations which are cadmium-contaminated are subsequently employed for growing crops, suitable remediation techniques do exist to immobilise the cadmium present in the soil and thus to control the risk to human health. There is, however, no doubt that old sites which are so contaminated do require proper risk management and control by cleaning up or immobilising the existing excess cadmium in the soil.

2.1.3. Risk of Cadmium

2.1.3.1 Toxicity of Cadmium

Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancer. It is highly toxic metal. Upon exposure, cd is rapidly transported by blood to different organs in the body where half-life in humans is 15-20 years. It has no essential biological function and highly toxic to plants and animals. Accidentally or Inaccidentally cadmium contaminated to environment pass through many transport processes such as soil/dust, air, water, food can be the one of the reason that impact on environment and especifically on human health. Ingestion of contaminated soil has been recognized as an important exposure pathway of cadmium (Cd) for humans, especially for children through outdoor hand-to-mouth activities.

2.1.3.2 Human Intake of Cadmium

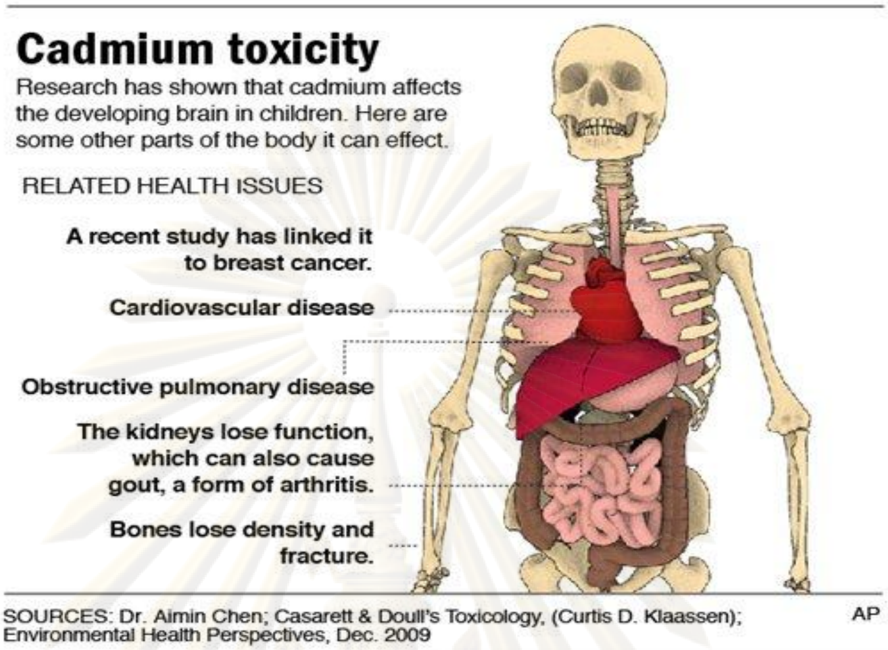
Human can intake cadmium directly or indirectly which are come from food, cigarette smoking and occupational exposure. From ingestion that is food, it comes from plants grown in soil or meat from animals which have ingested plants grown in soil. Thus, it is the cadmium present in the soil and the transfer of this cadmium to food plants together. Some have estimated that 98% of the ingested cadmium comes from terrestrial foods, while only 1% comes from aquatic foods such as fish and shellfish, and 1% arises from cadmium in drinking water (Van Assche, 1998). From cigarette smoking, smokers absorb amounts of cadmium comparable to those from food, about 1 to 3 ug of cadmium per day, from the smoking of cigarettes. It has been reported that one cigarette contains about 1 - 2 ug of cadmium and that about 10% of the cadmium content is inhaled when the cigarette is smoked (WHO, 1992). In general cigarette smoking is a habit which cans more than double the average person's daily cadmium intake. Cigarette smokers who are also occupationally exposed may increase double risk of their total cadmium intake. In order to estimate cadmium exposure in agricultural areas, occupational exposure to cadmium is mainly and evaluates by include additional intakes through food, tobacco, and poor personal hygiene practices (WHO, 1992).

2.1.3.3 Health effect for human exposure of cadmium

Cd and Cd compounds are, compared to other heavy metals, relatively water soluble, thus, also more mobile, more bioavailable and tend to bioaccumulate. Chronic Cd exposure produces a wide variety of acute and chronic effects in humans. Cd accumulates in the human body and especially in the kidneys. According to the current knowledge, kidney damage (renal tubular damage) is probably the critical health effect (Figure2.1). Other effects of Cd exposure are disturbances of calcium metabolism, hypercalciuria and formation of stones in the kidney. High exposure can lead to lung cancer and prostate cancer (Young et al., 1991).

Cd can enter to human via many pathways. Principally, it enters into human body by eating contaminated food, smoking cigarettes, and working in Cd-contaminated work places. Level of Cd exposure can be determined by measuring Cd levels in blood or urine. Blood Cd can reflect recent Cd exposure, but Cd in urine indicates accumulation or kidney burden of Cd. Urine is the main route of excretion of Cd with average daily excretion for humans being about 2 to 3 μg. Daily excretion shows only a small percentage of the total body burden, which accounts for the 17 to 30 years half-life of Cd in the body. In additions, unabsorbed Cd is removed from the gastrointestinal tract by fecal excretion. 0.01% of total body burden has been reported as daily Cd excretion. (Young et al., 1991)

From Oral exposures route and inhalation exposure , the primary target is kidney that effect as renal tubular proteinuria is the primary toxic effect of long-term Cd exposure and gastrointestinal tract by acute exposure to high levels of Cd. Cd compounds may cause irritation, vomiting, nausea, and diarrhea. In addition, other targets are the liver, bones, testes, and cardiovascular system have been shown to be affected to various degrees by Cd. (Young et al., 1991). For chronic cadmium exposure, effects occur mainly on the kidneys, lungs, and bones. A relationship has been established between cadmium exposure and proteinuria (an increase in the presence of low molecular weight proteins in the urine and an indication of kidney dysfunction) (WHO 1992, OECD, 1994).



SOURCES: Dr. Aimin Chen; Casarett & Doull's Toxicology, (Curtis D. Klaassen); Environmental Health Perspectives, Dec. 2009

Figure 2.1. Cadmium health effect on human's body

Sources: Adapted from Dr.Almin Chen; Casarett & Doull's Toxicology, (Curtis D. Klaassen); Environmental Health Perspectives, Dec 2009

2.1.4. Direct and Indirect Effect in Environment (Environmental impact)

Cadmium is an element that occurs naturally in the earth's crust and is released to the environment from point sources such as industrial discharges and from non-point sources such as agricultural runoff (Goyer, 1996). There is concern over the elevated levels of cadmium entering the environment as a result of improper mining techniques and from the fertilizer applied to agricultural fields, which may contain up to 1500 mg/kg on a dry material base (Anderson et al., 1981).

In addition, many countries confront with environmental impact of Cadmium - contaminated problems in soil, food, river to all food chain crops of human health. The first case study was observed in 1950 at Jinzu river basin, Toyama prefecture, Japan. As a result of Kamioka Zn mine released liquid wastes into the river that normally used within the community and paddy field irrigation causing Itai-itai disease and greater than hundred lives were lost. Thereafter, they found Cd in contaminated soil around the river bank at 4.85 mg/kg soil or around 14 times of unaffected soil (0.34 mg/kg soil) (ICETT, 1998). In Thailand, the biggest Zn deposit situates in Mae Sot district, Tak province and the estimated mine production capacity is 50 000 metric tons (Padaeng Industry Public Co., Ltd., 2008). Mining actions for example drilling, several explosions, material transfer, mine tailings disposal and drainage may cause the Cd distribution throughout the area, as mentioned in the research by Soil Analysis Division, Land Development Department, Thailand. The average Cd level in the sediment of cinder stacks was 228.5 mg/kg soil (Nitayaporn Tunmanee and Jurai Thongmarg, 2007).

In the case of black shale deposits in parts of the United Kingdom and USA contain elevated cadmium levels, thus leading to high soil concentrations in these areas. High soil concentrations are more commonly found in areas containing deposits of zinc, lead, and copper ores. Indeed, such areas are often characterized by both soil and aquatic contamination at the local level. The mining of these ore bodies has further increased the extent of such contamination (Lund et al., 1981).

Increased emissions of cadmium from the production, use and waste disposal of the metal, combined with its long-term persistence in the environment and its relatively rapid uptake and accumulation by food chain crops, contribute to its potential hazard. Soils may be contaminated with cadmium from the air, by the application of water, fertilizers or pesticides which contain cadmium, or by the discharge of cadmium-containing waste materials or mine drainage or mine activities (Page et al., 1986).

2.1.5. Exposure pathways

2.1.5.1 Definition of Exposure assessment

Exposure assessment is the process that focuses on the interface between the environment is containing the contaminant(s) of interest and the organism(s) being considered and define the exposures that occur, or are anticipated to occur, in human populations. Although the same general concepts apply to other organisms, the overwhelming majority of applications of exposure assessment are concerned with human health, making it an important tool in public health (IPCS, 1993 and EHC, 214). It is the process of estimating or measuring the magnitude, frequency and duration of exposure to an agent, along with the number and characteristics of the population exposed. Ideally, it describes the sources, pathways, routes, and the uncertainties in the assessment (Zartarian et. al. 2005).

In addition, Exposure assessment can use exposure analysis which is the science that describes how an individual or population comes in contact with a contaminant, including quantification of the amount of contact across space and time. 'Exposure Assessment' and 'Exposure Analysis' are often used as synonyms in many practical contexts (Lioy, 1990).

2.1.5.2 Applications of Exposure assessment

Quantitative measures of the exposure are used as (1)In Risk assessment of toxicology in order to determine risk from substances released to the environment (2)In establishing protective standards (3)In Epidemiology, to distinguish between exposed and control groups(4)To protect workers from some occupational hazards(Lioy, 1990 and EHC, 214).

In order to assess exposure in human health two approaches are normally used. The first approach is to include personal exposure monitoring (point of contact) and biological markers of exposure. The second approach include environmental sampling, combined with exposure factor information, modeling and questionnaires, which includes of the contaminant in all media encountered by the target during all activities, multiplied by the amount of time spent in each location, or the contact rate with each media. The one of the direct approaches that point of contact, the continuous measurement of the contaminant reaching the target through all routes. The examples of direct methods include air sampling using a personal portable pump, split food samples, hand rinses, breath samples or blood samples. Examples of indirect methods include environmental water, air, dust, soil or consumer product sampling coupled with information such as activity /location diaries (EPA, 2010 and EHC, 214).

2.1.5.3 Exposure routes or pathways

In general, exposure routes are defined as the different ways a substance may enter the body. The route may be dermal, ingestion or inhalation. Exposure may occur through contact of the contaminant with the skin, eyes or lungs, and then absorption of human body takes place, and finally transport to the blood (Environment Protection Agency, 2002). Contact between a contaminant, an organism and human can occur through any route. It can be classified in different exposure routes such as (1) non-dietary exposure route: soil ingestion and housedust, (2) dietary exposure route: water ingestion, food ingestion and mother milk (3) Dermal exposure route (4) inhalation exposure route as shown in Figure 2.2 (Zartarian et. al. 2005, EHC 214 and EPA, 1997).

Exposure to a contaminant can and does occur through multiple routes, simultaneously or at different times. In many cases the main route of exposure is not obvious and needs to be investigated carefully. For example, exposure to soil in contaminated site can obviously occur by eating food in that area, but also through the directly incidental ingestion of soil (Simcox 1995, Zartarian et. al. 2005 and EHC 214).

This research focuses on non-dietary exposure route, that is, soil ingestion of Cd in Mae Sot, Tak province. Soil ingestion rates from U.S. Environmental Protection Agency (EPA) was used to analyze exposure assessment; 200 mg/day as soil ingestion rate of farmer and younger children, 50 mg/day and 100 mg/day for normal adult and older children respectively for risk assessment (EPA, 1997 attachment E). Several studies have been conducted to estimate the amount of soil ingestion rate. Soil intake has been assessed by tracer studies, a methodology that measures trace elements in feces and soil. Through this study, soil ingestion rate of farmer, adults and children is well understood and the amount of these soil ingestion rates in daily basis can be estimated (EPA, 1991).

The risk assessment can defined as the process of quantifying the probability of a harmful effect to individuals or populations from certain human activities. The risk asseesment in this study was done by examining the results of the discipline of exposure assessment. As different location, lifestyles and other factors likely influence the amount of contaminant that is received. Particular care is taken to determine the exposure of the susceptible population(s).The exposure assessment was combined with other possible data to produce an estimate of risk.

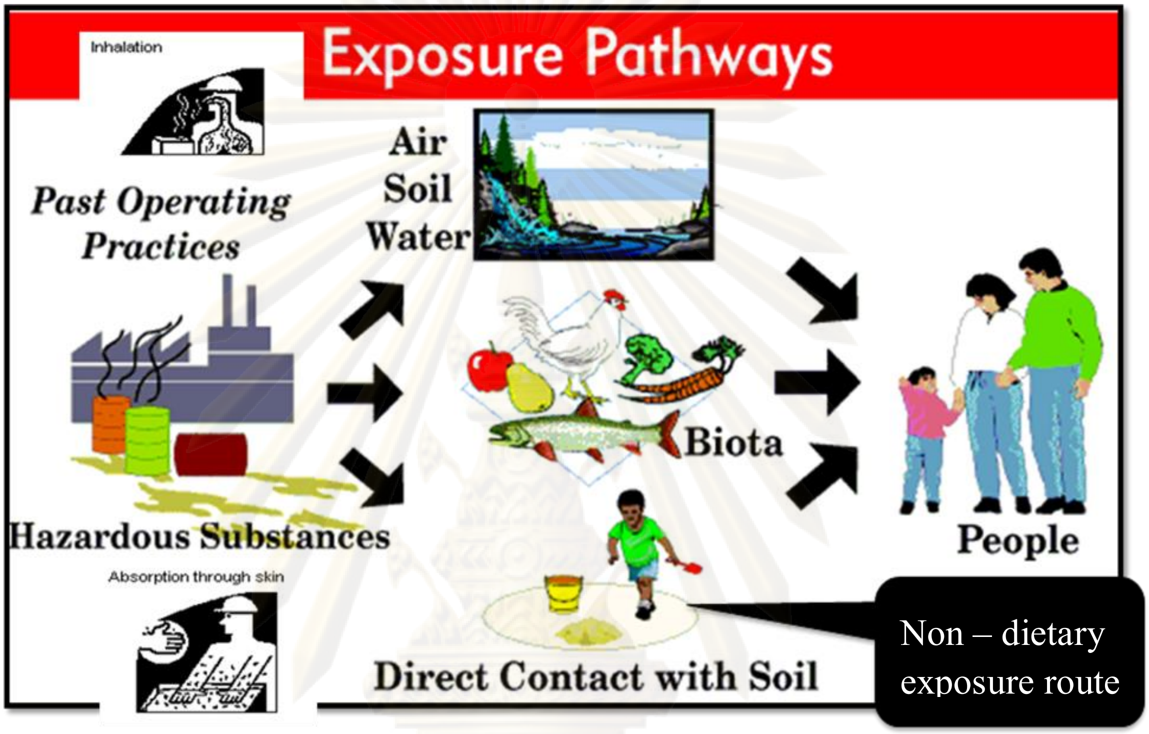


Figure 2.2. Exposure Pathways (Source: Adapted from EHC 214, EPA, 1997)

2.2. Cadmium in Mae Sot, Tak Province, Thailand

In Thailand, heavy contamination of Cd in rice field, soil and water supply was investigated especially, 3 companies started zinc mining in Mae Sot, Tak province, Thailand in 1977 and contamination of Cd in rice and soil was reported. Between 1998 and 2003, International Water Management Institute (IWMI) and the Ministry of Agriculture studied and found that 154 paddy fields in the 8 villages were contaminated with Cd up to 94 times higher than international safety standards (Padungtod et al., 2002). The results were confirmed and approved by Pollution Control Department of Thailand (PCD) that water supply in Mae Sot was contaminated. Their finding showed that residents of eight villages in Mae Sot, Tak area exposed to high Cd levels and at risk of developing all sorts of illnesses including kidney failure. There is about 0.5-218 mg/kg cadmium in soil, which exceeds standard by 72 times (EEC: The economic Community about 3mg/kg) (Simmon et al., 2003).

2.2.1. Study Area Phase I

Study site and the situation of the problem

Mae Sot district in Tak province is located on the Thai-Myanmar boarder. It is hidden in mountainous area with supply of water from Moei River and small Creeks. The local residents had depended on rice, soybean and garlic cultivations for at least 3 generations. Rice grown in this area has obtained national award-winning products for many consecutive years. Around 1977, zinc mining activities of 3 companies started after the Department of Mineral Resources; Ministry of Industry classified this area as the richest source of zinc minerals in Thailand. However, at present, only one company has remained in the area namely Pha Daeng Industrial Public Company (Yuwadee Kardkarnklai, 2007).

The researchers from International Water Management Institute (IWMI) were the first group to address the incident of Cd contamination in this area began in 1998. Dr. Robert W. Simmons, a senior researcher and his team decided to conduct a study in Mae Sot district, Tak province, Thailand. They foresaw that rice growing in the vicinity of zinc mine could lead to Cd contamination, because Cd co-exists naturally with zinc and would inevitably cause adverse health effect among the exposed population (Yuwadee Kardkarnklai, 2007 and Chantana Padungtod, 2002).

During 1998 – 2000**,** IWM phase I study was conducted and the researchers determined that the most potentially polluted area where water was naturally supplied by Mae Tao Creek. Their finding indicated that sediment was suspected of having highly contaminated with Cd. It was concluded that the evidences were not sufficient to confirm that whether Cd was from natural zinc mineralized area or contamination by zinc mining activities, flooded or eroded into natural and man-made water supplies then irrigated into rice paddy fields, and eventually transferred from soil into rice, the plant known to absorb Cd completely (Yuwadee Kardkarnklai, 2007 and Chantana Padungtod, 2002). Their results showed that Cd levels in 154 soil samples ranged from 3.4 – 284 mg Cd/kg soil which were 1.13 – 94 times European Economic Community (EEC) Maximum Permissible (MP) soil Cd concentration of 3.0 mg/kg soil and 1,893 times above Thai standard of 0.15 mgCd/kg soil. Almost 70% of fields produce rice grain with Cd above international standard. Moreover, rice samples from 90 fields were found to be contaminated with Cd ranging from 0.1 to 4.4 mg/kg rice while the mean background Thai rice Cd concentrations as reported by Pongsakul and Attajarusit (1999) was 0.043 ± 0.019 mg/kg rice. With this amount of Cd presented in rice and based on Thai daily rice consumption, it was estimated that local residents would have been exposed to Cd 14 – 30 times higher than the Joint FAO/WHO Expert Committee on Food Additives (JECFA) Provisional Tolerable Weekly Intake (PTWI) of 7 µg Cd / kg body weight (BW) per week (Yuwadee Kardkarnklai, 2007, Chantana Padungtod, 2002 and JECFA, 2003).

2.2.2. Study Area Phase II

The second phase of their study was expanded to cover the downstream part of Mae Tao Creek. Cd level in soil samples was found to be 72 times higher than European Union (EU) standard and 80 % of rice samples were contaminated with Cd higher than Food and Agriculture Organization (FAO) and Japanese standards. This concentration of Cd could lead to 2.8 – 11 times higher than the aforementioned PTWI set by JECFA. (Yuwadee Kardkarnklai, 2007, Chantana Padungtod, 2002 and JECFA, 2003).

A research team from Department of Pollution Control (DPC), Thailand collected environmental samples from Mae Tao Creek, surface water, underground water, well water and soil from January – April, 2004. Rice and fish were also sampled and results were summarized in Table 2.1. Concurrently, Ministry of Public Health (MOPH) staffs located the exposed population and biological samples were collected for Cd measurements (Yuwadee Kardkarnklai, 2007 and Chantana Padungtod, 2002).

In 2009, Cd and Zn Concentrations in soil were determined in the five study sites. The mean total concentrations of Cd in surface sediments and soils ranged from 64–1458 mg/kg while that of Zn ranged from 2,733–57,012 mg/kg. These results obviously much higher than the permissible levels for contaminated soils. The comparison was decribed in Table2. 2. (Chetsada Phaenark, 2009)

Table 2.1: Standards of Cadmium concentration used by Department of Pollution Control for environmental samplings in Mae Sot area (January – April 2004) (Yuwadee Kardkarnklai, 2007)

Type of samples	Low contamination	Medium contamination	High contamination
Underground and surface water	≤ 0.01 mg/L	0.01 - < 0.1 mg/L	≥ 0.1 mg/L
Water from Mae Tao Creek	≤ 0.05 mg/L	0.05 - < 0.5 mg/L	≥ 0.5 mg/L
Sediment in Mae Tao Creek	≤ 3.5 mg Cd /Kg soil	3.5 - < 35 mg Cd / Kg soil	≥ 35 mg Cd / Kg soil
Soil from rice paddy fields	≤ 3 mg Cd / Kg soil	3 - < 30 mg Cd / Kg soil	≥ 30 mg Cd / Kg soil
Rice grown on contaminated soil	≤ 0.2 mg Cd / Kg rice	0.2 - < 1 mg Cd / Kg rice	≥ 1 mg Cd / Kg rice

Table 2.2: Guidelines for Cd and Zn contaminated soils (Adapted from Chetsada Phaenark, 2009)

Total concentrations(mg/kg)			
Guidelines	Cd	Zn	References
Non-contaminated soil	0.02 - 2	1- 900	Alloway, 1995; Bowen, 1979
The toxic levels with respect to plant growth	3.00-8.00	70 - 400	Kabata-Pendias and Pendias,1984
The European Union maximum permissible level for sludge amendedsoils according to the soil pH (lowvalue for pH 6, high value for pH 7)	1.00-3.00	150-300	European Economic Commission, 1986
Thai background level	0.002-0.141	0.1-140	Pongsakul and Attajarusit,1999
Thai investigation level	0.15	70	Zarcinas et al., 2004

2.2.3. Health effect in the study area

Mae Sot hospital staffs, supported by health staffs from Tak Provincial Health Office and Bureau of Occupational and Environmental Disease, Department of Disease Control, classified approximately 100,000 residents in Mae Sot district into exposed and non-exposed group based on the duration of living in the area and rice consumption habit. Among the exposed, 7,697 residents aged 15 years and older were asked to donate urine samples for Cd concentration measurement. (Yuwadee Kardkarnklai, 2007)

The results showed that 45.6% of surveyed population had urinary Cd levels <2µg/g while 4.9% had Cd between 5-10µg/g creatinine and 2.3% had Cd concentration >10 µg/g creatinine. Using World Health Organization Standard (WHO) of 2 µg/g cratinine for environmental exposure, 5 µg/g creatinine for occupational exposure, >10 µg/g creatinine for possible renal damage caused by Cd. (Chantana Padungtod, 2002)

It can be concluded that selected areas of Mae Sot district (Figure 2.3) were highly contaminated with Cd and that this level of contamination has already posed excessive risk of having Cd-induced renal failure among the local residents who habitually consumed contaminated rice or incidentially or accidentially exposure or occupational exposure to contaminated soil (Yuwadee Kardkarnklai, 2007 and Simmon et al., 2005).

For proper management, the government's effort is to launch this project, that is, the consumption of contaminated food grown in the areas is the main source of excessive cadmium exposure and improvement in the soil contamination is very difficult, the production of rice and other crops for human consumption should be prohibited. These measures can prevent further accumulation of cadmium in the body of the exposed population. The production of non-food crops in these areas is strongly recommended by the government. Having suggestion from some experts, the sugar cane which can be produced to be ethanol is an option, due to high demand of oil and good price in the market at this time. The issue is whatever whether there is market product quarantine or what else of non-food crops suitable and valuable (Yuwadee Kardkarnklai, 2007)

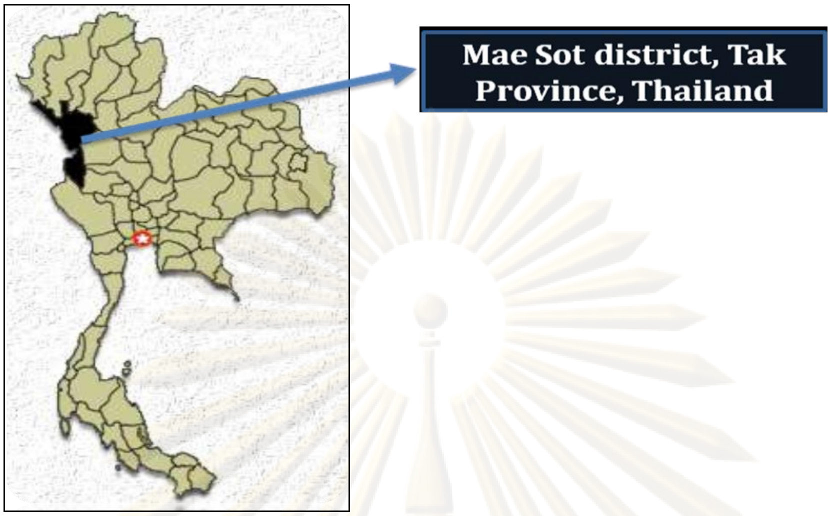


Figure 2.3 Map of Mae Sot district, Tak province, Thailand

2.3. Bioaccessibility and Bioavailability method

2.3.1 Bioaccessibility/Bioavailability

The environmental risk to humans from heavy metals by soil ingestion can be evaluated by measuring their bioaccesibility or bioavailability. Bioavailability is defined as the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract (Ruby et al., 1999, Oomen et al., 2002, EPA, 2007 and RIVM report 711701042). The bioaccessibility has been defined as the fraction of compound that is released from its matrix in the gastrointestinal tract and available for absorption (Ruby et al.,1999, Oomen et al., 2002, Marisa Intawongse, 2006 and Oomen et al., 2006). The concept of bioavailability and bioaccessibility can summarized by as follows (Figure 2.4) (Gron et al., 2003)

Inaddition, Bioavailability refers to the availability of a metal to enter and affect a biological system. The most bioavailable and therefore most toxic form of cadmium is the divalent ion (Cd^{2+}). Exposure to this form induces the synthesis of a low molecular weight protein called metallothionen, which can then bind with cadmium and decrease its toxicity. This normally takes place in the liver of fish and humans. But if the cadmium concentration is high, the metallothionen detoxification system can become overwhelmed and the excess cadmium will be available to produce toxic effects (Bradl, 2005; Landis and Yu, 2003, Wright and Welbourn, 2002).

A test for bioaccessibility of contaminants in soil should be designed to simulate a realistic worst case scenario based upon the description of the human digestion and uptake processes, that is, it should enable estimation of the highest bioaccessibility likely to occur. In last few years, studies of bioavailability (*in vivo* studies with experimental animals) and bioaccessibility (*in vitro* dissolution studies simulating the gastrointestinal tract) on the soils are investigated and compared.

The general trend in the United States of America is towards accepting bioavailability as one tool in a "weight of evidence" approach, where results obtained with several, each in their own right imperfect, tools are combined to provide sufficient basis for decisions on land use, remediation goals. In both of the Netherlands and United Kingdom, bioaccessibility data has been used for site specific risk assessment and considerable efforts are done to expand the data set and to use the data in exposure modelling. (Gron et al., 2003)

Evidence of a strong correlation between *in-vitro* bioaccessibility and in-vivo bioavailability data for different soil types is considered as key condition for acceptance of *in-vitro* bioaccessibility method in human health risk assessment (Environment Agency, 2005, Gron, 2005, US EPA, 2005, Saikat, 2006). This is needed to provide confidence in *in-vitro* method and a scientific justification for incorporation of data as alternatives of current default values into risk assessment modelling.

It has been validated of existing *in-vitro* methods in the United Kingdom. However once an *in-vitro* method is developed in conjunction with a carefully designed *in-vivo* study, this would reduce the need for any further animal studies in the long term.

The *in-vitro* test regulates pH and the transit time of a test soil-solution of simulated stomach and intestinal contents to mimic the chemistry and function of human's gastrointestinal tract (Oomen et al., 2002, Marisa Intawongse, 2006 and Enviromenatl agency, 2002). These methods are both rapid and inexpensive, and require only a day and only a small fraction of the cost of an *in-vivo* study.

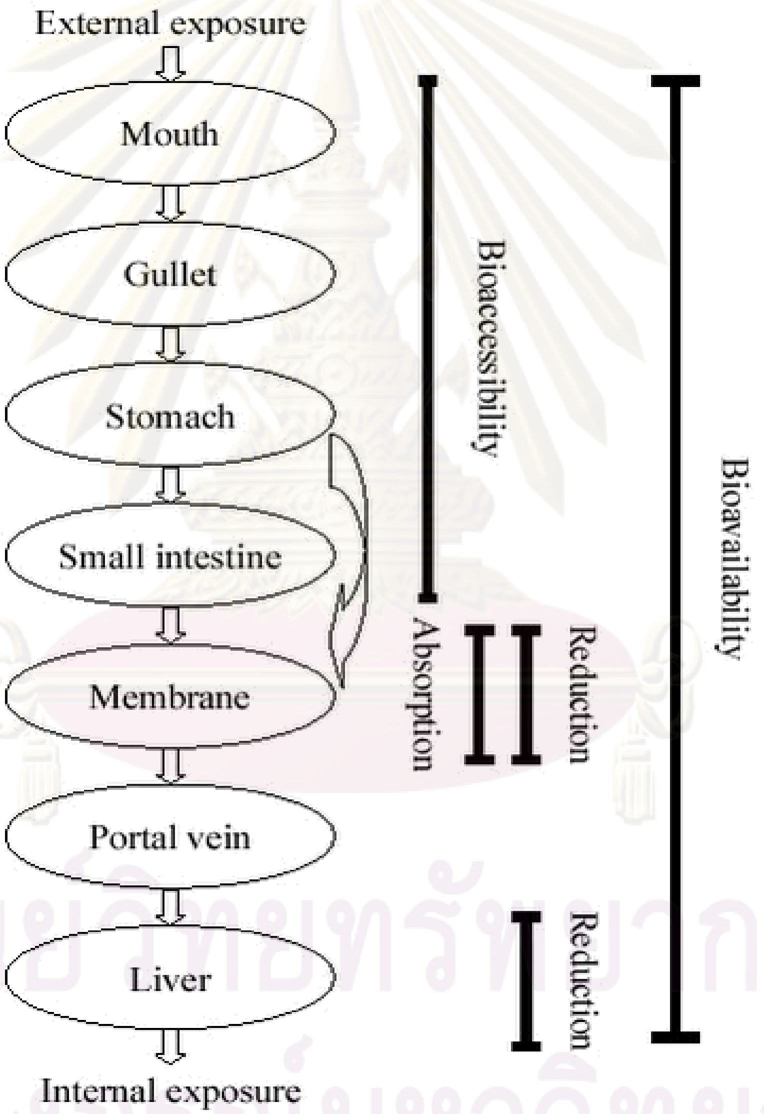


Figure 2.4. ***In – Vitro*** **Bioaccessibility method (Gron et al., 2003)**

2.4. Literature Reviews

Zarcinas et al., (2004) collected 318 soil (0–15 cm) and 122 plant samples in order to assess heavy metal pollution of agricultural soils and crops of Thailand. Their study was conducted with the aim of evaluating the normal ranges of heavy metals in agricultural soils of Thailand as well as the heavy metal concentrations in crops grown on these soils. Many heavy metals (Zn, Cd, Al, Fe and Pb) were determined in soils using *aqua regia* digestion, and in plants using nitric acid digestion .The results indicated that concentrations of heavy metals varied widely among the different regions of Thailand. For the results of soil data analysis, they found that concentrations of other heavy metals except Cd and Zn were strongly correlated with concentrations of Al and Fe, indicating that the variations were due to changes in soil mineralogy. Thus, the widespread contamination of soils by these elements through agricultural activities is not strong. On the other hand, Cd and Zn were strongly correlated with organic matter and concentrations of available and *aqua regia* extractable phosphate; this is attributed to input of contaminants in agricultural fertilizers and soil amendments (e.g. manures, composts).

Simmons et al., (2005) investigated and found the high concentration of Cd and Zn that it contaminated in rice grain and soil at Mae Sot, Tak province, Thailand. Their results indicated that the contamination was associated with irrigation supply transferred to fields. In additions, the results showed that the concentration exceeded maximum permissible level of EU standard, for soil Cd and Zn concentrations in the area ranged from 0.5 to 284 mg/kg and 100-8036 mg/kg respectively higher than the Thai Investigation Level of Cd and Zn in soils 1800 and 114 times respectively determined by Zarcinas et al., (2003). Rice grain Cd concentrations in the 524 fields sampled, ranged from 0.05 to 7.7 mg/kg. Over 90% of the rice grain samples collected that containing Cd at concentrations higher than the Codex Committee on Food Additives and Contaminants (CCFAC) draft Maximum Permissible (MP) level for rice grain of 0.2 mg/kg. The researchers also estimated Weekly Intake values ranged from 20 to 82 ug Cd per kg Body for rice consumption in term of public health perspective. This data was first demonstrated a significant public health risk to local communities. Moreover, their work suggested that an irrigation sequenced-based field classification technique in combination with strategic soil and rice grain sampling and the estimation of WI values via rice intake alone may be a useful decision support tool to rapidly evaluate potential public health risks in irrigated rice-based agricultural systems receiving Cd contaminated irrigation water.

Padungtod et al., (2002) studied health risk management for Cd contamination in Thailand via the environmental sampling, population survey, and clinical assessment. It was concluded that Cd was found highly contaminated in the areas of Mae Sot district. This contamination can cause high risk in renal failure in human that routinely uptake contaminated rice. The results showed that high Cd contamination in sediments, soil and rice. In addition, Department of pollution control (DPC) reported a significant difference Cd concentrations in sediments sampled along Mae Tao creek. They concluded that zinc mining activities might attribute Cd contamination in natural water supply. For population survey, people who ate rice grown in contaminated area had higher significant level of urine Cd concentration than people who ate rice purchased from markets or other districts. Older population had higher urinary Cd levels compared to younger populations and females had higher level of urinary Cd than males.

Intawongse and Dean (2006) reported that estimation of oral bioaccessibility using *in – vitro* gastrointestinal extraction is useful to estimate trace elements of chemicals or heavy metal risk in human. Their research aimed to investigate oral bioaccessibility from metal or metalloids in food and soil samples in different *in–vitro* models. The variable parameters that influenced bioavailability such as gastric and intestinal pH, food constituent, residence time and particle size were investigated and studied. This paper concluded that the *in-vitro* bioaccessibility tests are still in early stage of development and suggested that certified references methods (CRMs) are required for further comparisons.

Schroder et al., (2003) reviewed the capacity of an *in-vitro* gastrointestinal (IVG) method to predict relative bioavailable Cd from soil ingestion. The effect of the food-dosing vehicle (i.e., dough) in IVG method also was evaluated in this study and bioaccessible Cd determined by the IVG method was compared with relative bioavailable Cd measured from dosing trials using juvenile swine for 10 soils contaminated with Cd from 23.8 to 465 mg kg^{-1}. In addition, Bioaccessible Cd was measured in the gastric extraction and intestinal extraction steps of the IVG method. The results showed that the gastric extraction step without dough (63.0%) get the higher mean of bioaccessible Cd than gastric extraction step with dough (38.2%). It is possible that phytic acid associated with the addition of dough decreased bioaccessible Cd. Moreover, their study reported the relationships between bioaccessible Cd and *in-vivo* relative bioavailable Cd.The results showed linear regression between the gastric extraction step Cd using dough in the extraction and *in-vivo* relative bioavailable Cd was not significant (p = 0.098, r = 0.55), but a strong linear relationship was found between the gastric extraction step Cd without using dough in the extraction and the *in-vivo* relative bioavailable Cd (p < 0.01, r = 0.86).They concluded that the gastric extraction step of the IVG method without dough has the capacity to provide an estimate of the relative bioavailability of Cd, As, and Pb in contaminated soil.

Oomen et al., (2002) conducted a multi-laboratory comparison and evaluation of five *in-vitro* digestion models to compare the bioaccessibility of soil contaminants. These are the Simple Bioavailability Extraction Test (SBET) used by the British Geological Survey (BGS, United Kingdom) is a static gastric model, the German DIN model applied by the Ruhr-Universita¨t Bochum (RUB, Germany), the digestion model of RIVM (The Netherlands) are static gastrointestinal models, a static gastrointestinal approach is used for the SHIME procedure (LabMET/Vito, Belgium) and the TIM method by TNO (The Netherlands) is a dynamic gastrointestinal model. The results showed that The SBET method gives high bioaccessibility values, especially for Cd and Pb. However, researcher pointed that they could not conclude which of the five models is best, and indicated that a tool like an *in-vitro* digestion models can be useful in actual risk assessment of contaminated soils.

Aung and Yoshinaga (2004) compared the oral bioaccessibility method developed by Solubility/Bioaccessibility Research Consortium, USA (SBRC) and the compliance test for new Contamination Control Law by Ministry of Environment, Government of Japan (MoE). In the MoE-SBRC comparison, key differences included extractant composition (1M HCl vs 0.4M glycine of pH 1.5), L/S ratio (3:100 vs 1:100), duration of extraction (2 hrs vs 1 hr), and extraction temperature (room temperature vs 37^{o}C). They pointed out that since SBRC method solubilized the soil contaminants, the extraction might be not only the acidity but also the complex formation with gylcine, which might reflect the condition in human stomach, where the complexation with the substances in food or gastric juice constituents was expected.

Krissanakriangkrai et al., (2009) determined the magnitude of cadmium pollutants in water, sediment, fish and shellfish that have been found to cause adverse effects to human in region of Mae Sot district, Tak province. In their study, rainy months were found to have higher cadmium concentrations than during dry months. It may be due to agricultural and mining run off. Their study concluded and recommended that future monitoring of home grown vegetables which were consumed in this area, and other aqua biotic organisms should be continued given that mining activities are ongoing in this area; health risk assessment and risk management should be performed. They pointed out that the environmental standard of Thailand should be revised since the soil standard of cadmium is far higher than that found in other countries.

CHAPTER III

METHODOLOGY

3.1 Materials

All the reagents (HNO_3, HCl and Glycine) used in the experiments were analytical reagent grade. All solutions were prepared with deionized water with a resistance of 18.1 MΩ cm.

3.1.1Chemicals

Chemical used in this study are listed in Table 3.1

Table 3.1 Chemical list

Chemicals	Supplier/Grade
Boric acid	Carlo Erba/For analysis
Cadmium Standard Solution 1000mg/l Cd for AA in nitric acid 0.5mol/l	Scharlau/For analysis
Glycine	Merck/For analysis
Hydrofluoric acid 48%	AnalaR/For analysis
HydroChloric acid 37%	Carlo Erba/For analysis
ICP multielement standard Solution IV 1000mg/l	Merck/ Analytical Grade
Nitric acid 65%	Carlo Erba/For analysis
Silicon standard for ICP in 2% nitric acid	Fluka/Analytical Grade

3.1.2 Glassware

Plastics and glasswares were soaked with 1%HNO_3, at least, overnight and rinsed well with deionized water three times prior to use.

3.1.3 Instruments

These instruments were used in this study which are described in Table 3.2.

Table 3.2 Instruments List

Instruments	Model
Ashing Furnace: Carbolite, England	AAF 11/18/201
Balance: Satorious, USA	TE214S
Flame and Graphite Furnace Atomic Absorption Spectrophotometer (FL-AAS/GF-AAS): Analytik Jena, Germany	ZEEnit 700
ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) Varian, Australia	Vista MPX Axial
Microwave Digestion and Extraction system: Milestone, Italy	ETHOS PRO S/N 127547
pH meter: Dusseldorf,Germany	HACH LANGE
Test Tube Rotator: Biosan, Latvia	Multi RS-60

3.2 Methods

3.2.1 Field Investigation

The sampling sites were randomly selected from highly contaminated areas as described by the previous studies (Figure 3.1), along farm community living areas in Mae Sot area, Tak province (Figure 3.2). Field investigation was conducted in May and June of 2009, rainy season. On the other hand, Nakornpathom province was selected as a control site, where residential areas and agricultural areas are closely situated like in Mae Sot, but several kilometers away from zinc mineralized area.

3.2.2 Sample Collection

The soil samples were collected from the surface soil (2 - 15 cm depths after clear off 1 cm topsoil). All soil samples were collected by using a stainless steel trowel. Composite sampling method was applied (EPA, 1996), thus, a single sample was a composite of at least 3 samples taken in 1 m x 1 m distance at a sampling point. Attention was paid to ensure each sample was collected from similar depth. Cleaning and wiping the trowel after each collection were done to avoid the cross-contamination among the samples. The soil samples were kept into polyethylene bags, which were sealed and labeled. All 75 samples was collected from contaminated and control site. Sixty five samples were collected from both of residential areas (n=47) and agricultural areas (n=18) from the Mae Sot area in Tak Province. Ten samples were collected from control site; from both of residential areas (n=7) and agricultural areas (n=3) from Nakornpathom Province.

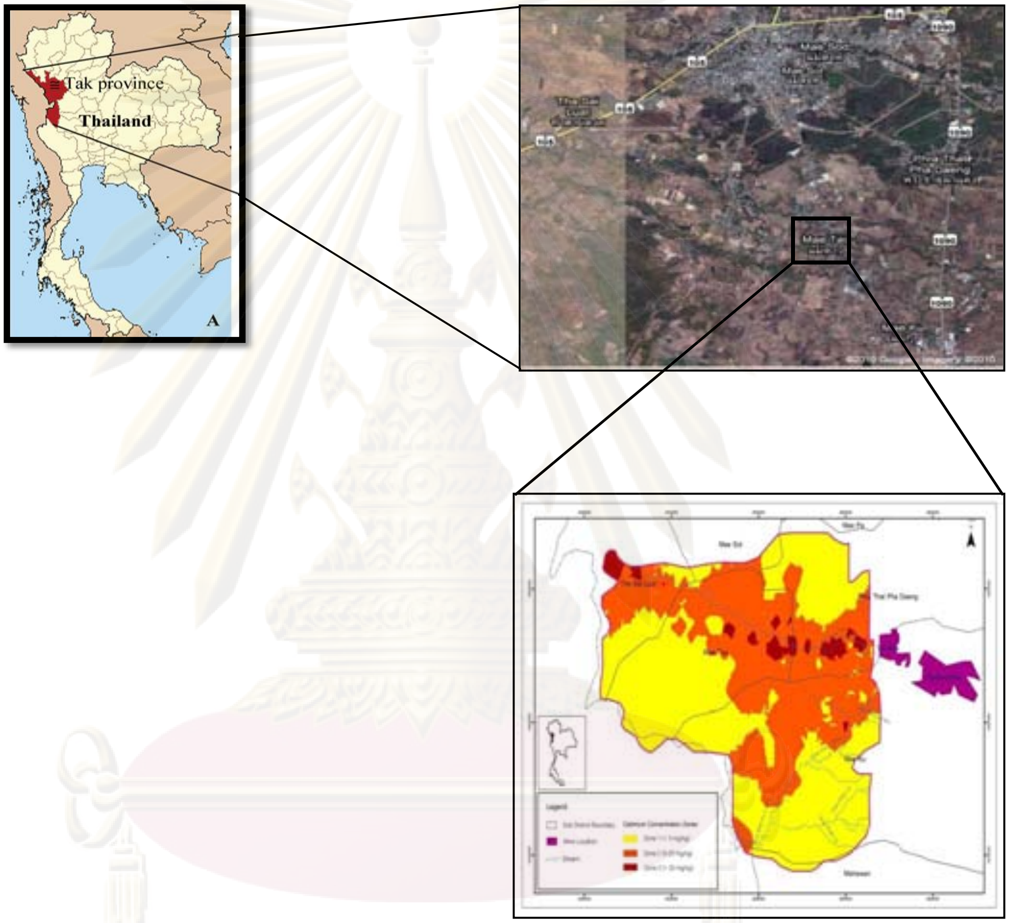


Figure 3.1 The map of Thailand showing Mae Sot district, Tak province and the sampling site

A) B)

Figure 3.2 Sample Collection site A) Househould Compound B) Paddy field

3.2.3 Sample Preparation

Soil was dried at 45^0C in electric oven for 24 hours. Dried soil samples were grinded using mortar and pestle and passed through 65 mesh sieve (< 250 µm).When considering the site fraction of soils, many previous studies have used different particle sizes for analysis such as <2mm, < 125 µm, <150 µm and 250 µm .This study concerned on accidental ingestion of soil particles, thus, the particle size of soil need to be uniformity as to the size fraction that adheres to hands. The appropriate size fraction is < 250 µm grain size, because it is considered to be the optimum size to adhere to hands (Duggan et al.1985). Cross contamination between the samples were avoided by using proper cleaning scheme.

3.3 Experiments

All the methods and procedures are categorized with each objective as shown in Figure 3.3

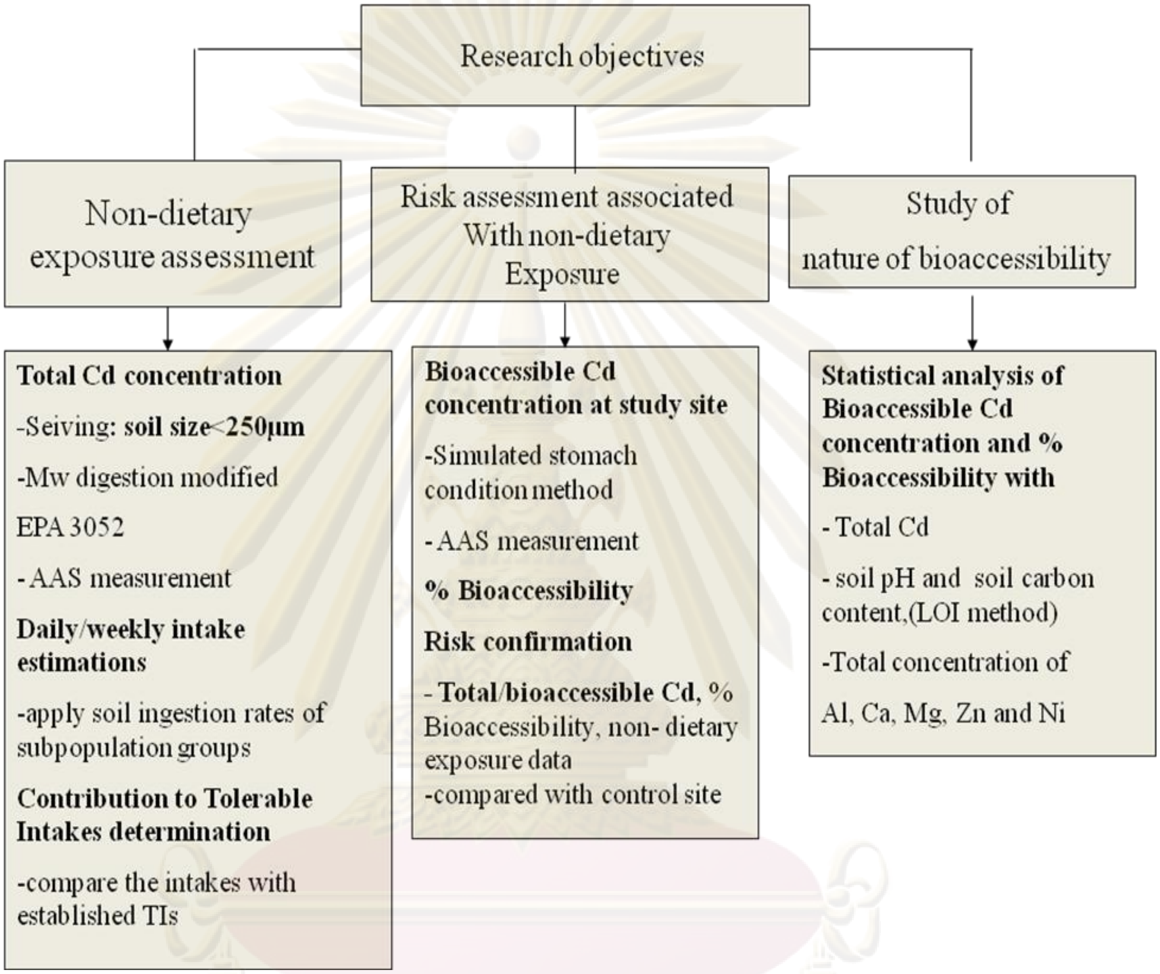


Figure 3.3 Experimental Framework

3.3.1. Soil properties

Soil pH and soil organic matter those were determined, because these properties are known to have the effects on bioaccessibility and many other important processes in the soil. Moisture content was determined to describe soil Cd concentrations in dry weight basis.

Moisture Content

In order to measure moisture content in the soil samples, some of each soil samples were weighed also include container of soil samples. Then the soil samples were dried at 105^{o}C in the electric oven. After that the container was removed and allowed cooling in room temperature (25±2°C). Reweigh the samples and calculate moisture content of soil samples were done by using the equation 1. This method is based on removing soil moisture by oven-drying a soil sample until the weight remains constant. The moisture content (%) is calculated from the sample weight before and after drying. (Adapted from soil survey standard test method AS1289 B1.1)

$$\mathbf{MC\% = (W2-W3) / (W3-W1) \times 100} \qquad (1)$$

When;

W1 = Weight of container (g)
W2 = Weight of moist soil + container (g)
W3 = Weight of dried soil + container (g)

Soil organic matter

Soil organic matter was analyzed by using Loss on ignition (LOI) method. The LOI method is an inexpensive alternative for soil analysis, and also reliable and suitable for soil carbon analysis (Schulte and Hopkins 1996; Konen et al. 2002). Analysis of organic carbon in soils using dry combustion techniques is quicker and less labor intensive than traditional acid digestion methods and soil analysis. For the LOI method, soil is oxidized at a high temperature (500 – 575 ^{o} C), and the mass loss is proportional to the organic-matter content of the soil (Wright et.al. 2008).

The clean crucibles were weighed. One tea spoonful of soil was added into the crucible and reweighed again. Next, the sample was placed into the pre-heated muffle furnace that was set at 550^{0}C for 4 hour. The sample was removed and allowed to cool at room temperature (25±2°C) in the cleaning desiccators' and then weighted. LOI was calculated as the difference between the oven-dry soil mass (dry weight) and the soil mass after combustion (ash weight), divided by the oven-dry soil mass (Schulte and Hopkins 1996) as the following equations (2)

$$\%LOI = (\text{Dry weight} - \text{Ash weight}) / \text{Dry weight} \times 100 \quad (2)$$

Soil pH analysis

Soil samples were measured by mixing deionized water with the soil in a 1:1 weight ratio by pH meter. Five grams of each soil samples and 5ml of deionized water were added and stirred for 5 seconds into a cup. The samples were let stand for 10 min. After that, the soil and water slurry were continuously stirred, the electrodes of pH meter was lowered into the soil – water slurry surface, then read the pH meter while stirring the soil water slurry. (Soil Analysis Handbook of References Methods 4th edition (1999)

3.3.2. Total of cadmium in soil

Digestion and Measurement (Modified EPA method 3052)

Digestion method was modified according to Chen and Ma (2001) in order to achieve complete extraction of Cd in soil. Total Cd concentrations in soil were determined using HCl: HNO_3 in ratio 3:1 plus HF by microwave digestion oven. 65% nitric acid, 37% hydrochloric acid and 40% hydrofluoric acid in analytical grade were used to analyze in this study (adapted from microwave digestion application note manual: USEPA method 3052). 0.5 grams of soil samples were weighed in PTFE vessel and then add 9 ml of 65% nitric acid, 3 ml of 37% hydrochloric acid and 3 ml of hydrofluoric acid. The vessels were placed into microwave system (The sample was heated at $180^{o}C$ for approximately 5 min and remained at $180^{o}C$ for another 10 min to accelerate the leaching process by microwave digestion system). Next, the sample was allowed to cool at room temperature (25±2°C). Then, adding 5ml of H_3BO_3 (5% solution was added) to neutralize excess HF. The sample was then digested in microwave system (The sample was heated at $160^{o}C$ for approximately 8 min and remained at $160^{o}C$ for another 7 min to accelerate the leaching process by microwave digestion system). Next, the sample was allowed to cool at room temperature (25±2°C) and filtered with Whatman disc filter paper No.42. After transferring into 50 ml volumetric flask, the solution was diluted with deionized water and adjusted volume to 50 ml. Finally, the solution was kept in polyethylene bottle prior to analyzed. Total Cd in the digested soil samples were measured by using graphite furnace atomic absorption spectroscopy (GFAAS) or flame atomic absorption spectroscopy (FAAS). This method was claimed to achieved 94% of soil Cd (Chen and Ma, 2001)

Quality Assurance and Quality Control

Analytical method and instrumental measurements were verified and calibrated by using Certified Reference Material, Catalog No.CRM 025-050 (RTC) (Lot No.JG025) in order to acknowledge the accuracy of total digestion procedures for determination of metals in this study. Every digestion of each 20 soil samples were included one of CRM in the digested stage. Thirty percent of soil samples were tripricated for control quality and check the precision of the results.

3.3.3. Total Bioaccessibility

An *in–vitro* stomach condition simulation test developed by Solubility/Bioavailability Research Consortium (SBRC method) was used to measure Cd in synthetic gastric juice. *In – vitro* extraction estimate oral bioaccessibility that simulates the human stomach condition is important when assessing chemical risk to humans (Marisa Intawongse and Dean, 2006). Cd exposure assessment by incidental ingestion of soil and dust were overestimated if the bioaccessibility is not taken into account.

To simulate SBRC test, 0.4M glycine solution was prepared and adjusted pH 1.5 with 37% HCl. Then, dried and seived soil samples (< 250 μm) were mixed with glycine solution in ratio 1:100 and checked pH again in order to keep at 1.5.The mixed solution was placed in the end-over-end motion rotator, for 1hr at 37^0C and adjusted speed to 30± 2rpm. After that, the solution was filtered by PTFE membrane (pore size 0.45 μm) and measured bioaccessible Cd by using graphite furnace atomic absorption spectroscopy (GFAAS) or flame atomic absorption spectroscopy (FAAS). Bioaccessible Cd is the fraction of Cd that is mobilized from soil into gastric digestive juice, which can be calculated as following equation (3).

$$\textbf{Bioaccessibility (\%)} = \frac{\textbf{Contaminant mobilized from soil during digestion (}\mu\textbf{g)}}{\textbf{Total Contaminant present in soil (}\mu\textbf{g)}} \times 100 \quad (3)$$

3.3.4. Other minerals, metals and the nature of bioaccessible Cd

To investigate role of other minerals and metals that might have influenced on Cd bioavailability in soil, Total concentration of Ag, Pb, Zn, Ni, Ca, Al, Fe, Mn, Mg, Fe, B, Ba, Bi,Co, Cu, Cr, Ga, K, Li, In, Na, Si, Sr, Ti were determined and measured by using ICPOES inductively coupled plasma optical emission. Several geochemical and environmental parameters would affect the metal bioavailability and oral bioaccessibility. The most predominant parameters may include, total metal concentration, metal complexation, influence of other metal cations, and environmental factors such as pH. (Luoma, 1983). Salomons and Forstner (1984) proposed that in polluted systems like acid-mine drainage, point sources commonly deliver metals in a soluble phase, or associated with organic matter, and the proportion of dissolved metals and their bioavailability tends to be higher. In addition, interaction among metals can result both in stimulation and antagonism, where stimulation occurs when uptake of one metal induce synthesis of binding sites that affect accumulation of both metals and antagonism can be observed in simultaneous exposures to several metals. Stimulation of Cd uptake by Pb exposure and Zn by Cd exposure have been observed in rats, while antagonism between Zn and Cd occur in phytoplankton and microalgae (Luoma, 1989). A number of sequential chemical extraction techniques and methods are applied to determine the portion of bioavailable metals and elemental behaviors of the metals. However, these extractions are all “operational”, that is they are not completely specific to metals or chemical phases and difficult to achieve mass balance of the metals (John and Leventhal, 1995).

In this study, the trend or the nature of the bioaccessible Cd was determined only through the statistical means; correlation between bioaccessible Cd and pH, organic matter, soil minerals and metals would explain the trend of Cd bioaccessibility to an extent; complete characterization is not the focus of this study.

3.3.5. Non –dietary Cadmium exposure assessment and Risk assessment

Non- dietary Exposure assessment of Cd was done by simply multiplying the total Cd concentration in the soil with the soil ingestion rates as following equation (4). Soil ingestion rates applied in this study are assessed from US EPA since it is the leading institution and intensively study the exposure of soil contaminants through soil ingestion and the size of the particles that adhere to human hands. Thus far, soil ingestion rate determination or relating studies have never been done in Thailand. U.S. Environmental Protection Agency (EPA) determine 200 mg/day as soil ingestion rate of Farmer (adult) and young children (0-6 years), 50 mg/day and 100 mg/day as soil ingestion rate of normal adults (non farming) and children (6-8 years) respectively for risk assessment (EPA, 1991 and EPA, 1997 attachment E).This value based on RME (Reasonable maximum exposure) analyses that using in HHRA (Human health risk assessment). These rates were used to evaluate Cd exposure assessment in soil via non-dietary exposure pathway to farmers, normal adult, young children and children in this study.

$$\mathbf{DI_{non\text{-}dietary} = C_{Cd} \ X \ R_{daily\ ingestion}} \qquad \mathbf{(4)}$$

Where; $DI_{non\text{-}dietary}$ = Daily intake via non-dietary pathway (µg/day)

C_{Cd} = soil Cd concentration of <250 µm (µg/kg of soil)

$R_{daily\ ingestion}$ = daily soil ingestion rate (mg/day)

(200 mg/day for farmers, 100 mg/day for normal adults, 100 mg/day for older child, 200mg/day for a child younger than 6 years)

(Note: paddy soil /corn/sugar cane/ rubber plantation soil Cd concentrations was used for estimating daily intake of the farmers and community Cd concentrations was used for estimating daily intake of the normal adults and the children.)

Two tolerable intakes were applied in this study; the Provisional Tolerable Weekly Intake (PTWI) of Cd, 7 ug/week/kg body weight set by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). PTWI is defined as estimate of the amount of the substance that can be exposed weekly over a life time without appropriate health risk. In 2009, European Food Safety Authority (EFSA) set the tolerable weekly intake as 2.5 ug/week/kg body weight. We used both tolerable intakes to access the risk of Cd exposure associated with incidental soil ingestion. This PTWI and TWI value was used to evaluated risk assessment of Cd in farmer, adult and children in this research by the calculation of estimation Weekly Intake (WI) as following equation (5)

$$\mathbf{WI_{non\text{-}dietary} = (DI_{non\text{-}dietary}\ X\ 7)\ /\ AVE.\ BW} \qquad \mathbf{(5)}$$

Where: $WI_{non\text{-}dietary}$ = Weekly intake via non-dietary pathway on body weight basis
(µg Cd/ kg/week)
AVE. BW = ave. body weight of Thai adults and children (kg)
7 = unit in days/week

In order to calculate body weight based Cd intake via soil ingestion average body weights for Thais from WHO report was used and presented in Table 2.1 and 2.2

(Note: Thai man weigh 68.9 kg average (age group of 25-60 yrs), Thai woman 57.4 kg (age group of 25-60 yrs), Thai child older than 6 years 19.07 kg(age groups of 6-8 yrs), Thai child younger than 6 years 13.14 kg (age groups of preschool children) (WHO, 1998)

Table 3.3 Average body weight of Thai male and female (WHO, 1998)

Sex	Weight(kg)	Height(cm)
Male	68.9	169.4
Female	57.4	156.9

Table 3.4 Average body weight of Thai child older than 6 years and Thai child younger than 6 years (WHO, 1998)

Age (yrs)	Body weight(kg)
1	9.2
2	11.65
3	13.55
4	15.16
5	16.24
Average	13.14

Age (yrs)	Body weight(kg)
6	16.7
7	19.2
8	21.3
Average	19.07

In oreder to define the risk associated with Cd intake via soil ingestion, the contributions to tolerable intakes were calculated with the following equation:

$\mathrm{CI}_{\text{soil ingestion}}$ = Estimated body weight based Cd intake via soil ingestion/TI (6)

Where; $\mathrm{CI}_{\text{soil ingestion}}$ = Contribution Index of Cd soil ingestion
TI = Tolerable Intake

Two tolerable intakes were applied in this study; (1) The Provisional Tolerable Weekly Intake (PTWI) of Cd, 7 ug/week/kg body weights set by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). PTWI values initially set for cadmium was 400 – 500 µg per person (WHO, 1989). These levels were based solely on a critical renal concentration of 100 – 200 µg Cd/g wet kidney cortex weight, attainable after a cadmium intake of 140 – 260 µg/day for over 50 years or 200 mg over a lifetime. Despite the narrow safety margin, the PTWI for cadmium at 7 µg/kg body weight was retained, which is translatable to 70 µg per day for a 70 kg person. A toxicokinetic model predicts, based on similar assumptions, that the renal cortical cadmium level of 50 µg/g wet weight could be attained at the cadmium intake of 1 µg/kg body weight/day over 50 years, which is the same as the current FAO/WHO guideline. The renal cortical cadmium 50 µg/g wet weight corresponds to urinary cadmium 2 µg/g creatinine, but kidney effects have been observed at urinary cadmium levels as low as 1µg/g creatinine. These finding suggest that current intake guideline (at 70 µg per day for a 70 kg person does not provide sufficient health protection. With a similar consideration of the kidney as a toxicity target, however, (2) In 2009, European Food Safety Authority (EFSA) set the tolerable weekly intake from 7 to 2.5 μg/week/kg body weight. The Cd intakes in study area were compared with the control site (Nakornpathom province).

3.3.6. Statistical and data analysis

Statistical analysis was done by SPSS17.0 program (Statistical Package for the Social Sciences) in order to find correlation among total Cd, bioaccessible Cd, certain soil properties and the other minerals and metals, the bioaccessiblity results of study area and the control site .

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Total Cadmium and Bioaccessibile Cadmium

Sixty five samples were collected from both of residential areas (n=47) and agricultural areas (n=18) from the Mae Sot area in Tak Province. Ten samples were collected from control site; from both of residential areas (n=7) and agricultural areas (n=3) from Nakornpathom Province (Table 4.1). The Cd concentrations in study site and control site of soil samples were described in Table 4.2. These samples were digested by EPA standard method 3052, though modification was made to achieve full extraction of Cd from soil. The presences of Cd in digested solution were analyzed by FLAAS or GFAAS. The result of total concentrations of Cd in soil samples from study area are shown in Table B-3, B-4 in Appendix B.

Of all the 75 samples collected from contaminated and control site, Cd was found in 63 samples collected from contaminated areas. Cd levels in two samples from contaminated areas and all of 10 samples from control sites, were under detection limit. Two samples which were lower than detection limits were collected from typical residential areas. It was noted that some houses in relatively effluent neighborhood mend the soil for better building support. It is assumed that soil of such application were probably brought from the places where Cd concentrations in soil is low. The average %RSD for measurement of CRM (Certified References Material) in five replicates were found to be 12% and those of the total and bioaccessible Cd were 6% and 3%, respectively. The inter-day and intra-day reproducibilities were calculated. The %RSD for four measurements of CRM were 12% and 6% for inter-day and intra-day, respectively.

Table 4.1 Study site samples (n = 65) and control site samples (n=10)

	No. of the sample	Sampling Places
Study Site (n=65)	7	Paddy Fields
	11	Corn, Sugarcane, Rubber and Banana Fields
	33	Household Compounds
	9	Household Compounds near Creek
	4	School
	1	Temple
	65	**Total**
Control Site (n=10)	3	Paddy fields
	3	Household compounds
	4	General community areas
	10	**Total**

Table 4.2 Mean, Median, Range of Total Cd and Bioavailable Cd in study site and control site

	Total Cd (mg/kg soil)			**Bioaccessible Cd (mg/kg soil)**		
Sample	**Mean±SD**	**Median**	**Range**	**Mean±SD**	**Median**	**Range**
Residential Area of study site (n=47)	19.1±28.7	10.8	ND-156	12.4±21.5	5.25	ND -115
Agricultural Area of study site (n=18)	17.4±37.1	7.19	1.32-162	11.3±25.9	2.96	0.37-112
Control site (n=10)	ND	ND	ND	ND	ND	ND

ND*= Non Detectable

Table 4.2 shows the analytical results of mean, median, minimum and maximum values of total and bioaccessible Cd concentrations in soil samples of the study site and control site. The values were determined for the soil size of <250 µm. These results showed that total cadmium level in soil samples along residential areas and agricultural areas ranges from ND – 162 mg Cd/kg soil with a mean value of 18.6 mg Cd/kg soil. For residential areas, the soil Cd concentration ranged from ND - 156 mg Cd/kg soil and soil Cd concentration in agricultural areas ranged from 1.32-162 mg/kg soil. Among our samples, high Cd concentrations, as high as > 100 mg Cd/kg soil were observed from those collected in a sugar cane field and a household compound. The highest value among these samples is 162 and 156 mg Cd/kg soil that found in agricultural area and residential area, respectively. However, in the report made by Padungtod et al, (2002), a joint research on quantification soil and rice Cd, made by International Water Management Institute (IWMI) and Department of Agriculture, Ministry of Agriculture found that soil Cd ranged from 3.40 -284 mg Cd/ kg soil. Among our samples, even the sample collected from sugarcane field, which is believed to be very high in soil Cd, the concentrations do not exceed 200 mg Cd/kg soil. Soil Cd in this study were lower than Padungtod's (2002) study. The possible reason is that the areas of highest contamination were not incorporated in the sampling of this study or the particle size of soil from which they determined Cd concentration may be smaller. Figure 4.1, the histogram of concentration ranges, shows that majority of the samples are < 30 mg Cd/kg soil. According to Padungtod (2002) and Kardkarnklai (2007), this range is known to be medium contamination of Cd in soil from rice and paddy fields, though the particle size of their study was unknown. European Economic Community (EEC) Maximum Permissible (MP) set soil cadmium concentration as 3.0 mg Cd/kg soil and the Thai „background" total soil Cd concentration ranges from 0.002 to 0.141 mg/kg (Pongsakul & Attajarusit 1999). In addition, Zarcinas et al (2004) studied a total of 318 soil samples throughout Thailand and reported that Cd concentration in Thai soil range from 0.01-1.3 mg/kg soil, with a mean concentration of 0.03 mg/kg soil. Much higher concentration in this study compared to their values might be due to the fact that the study area is zinc-mineralized area and association of zinc and cadmium is common. Moreover, soil sample cadmium concentrations from some sampling sites were found to be above the permissible limits of soil quality standard for agricultural use in Thailand (37 mg/kg soil) set by Pollution Control Department (PCD), Ministry of Natural Resources and Environment, Thailand. Five samples from residential areas and one sample from agricultural areas of study site exceeded the Thai standard of 37 mg/kg soil. Excluding two samples of lower than detection limit, average Cd level in soil samples was found to be 6.2 and 124 times higher than European Union (EU) Standard and Thai soil standard respectively with maximum value which was 54 and 1080 times of EU and Thai standard. The results showed that cadmium levels in 63 samples ranged from 0.560 – 162 mg Cd/kg soil which were 3.7 - 124 times higher when compared with Thai soil standard set as 0.15 mg/kg soil (Zarcinas et al, 2003). In addition, 47 samples exceeded EU standard (3.0 mg/kg soil). From the residential areas, the average cadmium was higher than agricultural areas. The highest average cadmium concentrations found in agricultural areas is in sugarcane field. The results showed higher cadmium concentration in study site when compared with control site (Nakornprathom province) as shown in Table 4.2

In this study, the comparison was made among the samples collected from the fileds and the residential areas of close proximity. Cd and Zn concentrations of a rubber plantation and the two household compounds – one of them is near Mae Tao Creek – situated nearby, were compared. Higher Cd and Zn concentrations in the near Creek samples, 15.3 and 391 mg/kg soil respectively, were observed comparing to other household compound sample and rubber plantation, 6.59 mg Cd/kg soil and 263 mg Zn/kg soil and 2.41 mg Cd/kg soil and 200 mg Zn/kg soil respectively, explained the metals were transported from the mining area situated upstream via sediment transportation. Another finding was between the sugarcane field sample and the household situated across the road. The Cd and Zn concentrations of the household sample and field samples were 3.73 mg Cd/kg soil and 260 mg Zn/kg soil, and 17.8 mg Cd/kg soil and 1290 mg Zn/kg soil respectively. The different % bioaccessibility between these samples, 40% and 96% indicated that the possibility of different soil between the sampling site of close proximity.

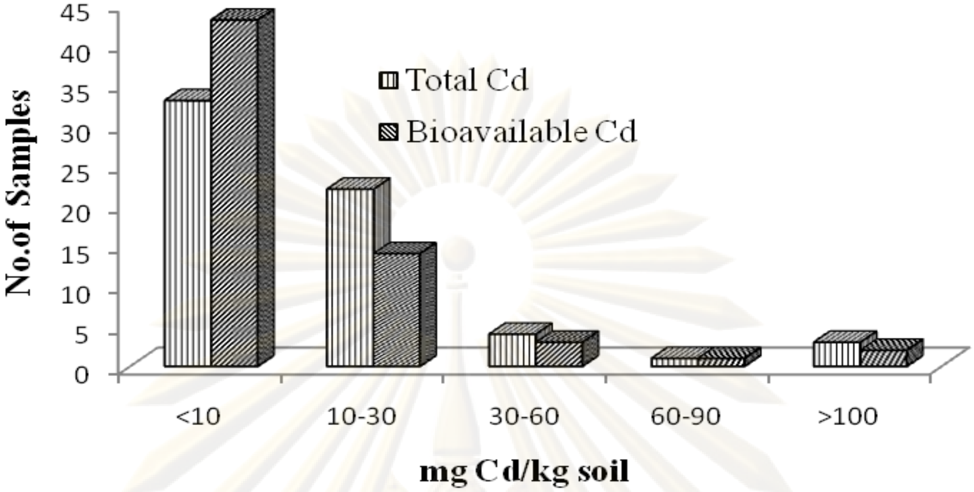


Figure 4.1 Histogram of concentration distributions among the samples collected from contaminated areas

This assumption led to the conclusion that this level of contamination might pose the high risk of having cadmium body burden among the local residents in Mae Sot, Tak areas.

4.2 Estimated Cd intakes

The intake calculations were based on soil Cd concentrations, soil ingestion rate and body weight among population groups in this study area. Daily Cd intake was calculated by simply multiplying the total Cd concentration in the soil with the soil ingestion rates as described in equation 4 of chapter 3. Calculation of Cd intake among resident living in control site was done by multiplying soil ingestion rates and instrumental detection limit as described in Table 4.3 and Table B-10, B-11 in Appendix B. Cadmium concentration in soil samples collected from residental areas were used to access daily and weekly Cd intakes of non farming adults, and children. The soils Cd concentration of the agricultural areas were used to calculate daily and weekly cadmium intake of farmers. Estimated daily intakes were described in Table 4.3. Daily intake of soil cadmium via incidental soil ingestion route is higher among the farmers because of their work nature. Also, young children ingest quite a high rate of soil particles – in fact, household dust of soil origin in indoor environment - via hand-to-mouth activity. The results showed that farmers in the study area are estimated to expose soil cadmium an average of 3.47 µg on daily basis; this intake can be as high as 32.4µg/day when the calculation is made through maximum agricultural soil Cd level (Table 4.3).

For daily intake of residential areas, the results showed that normal adults (Non-farming), children 6-8 years and younger children 1-5 years are estimated to intake Cd 0.95, 1.9, 3.8 µg/day, respectively. The maximum daily intake in normal adults (Non-farming), children 6-8 years and younger children 1-5 years are 7.81, 15.6 and 31.2 µg on daily basis. The highest estimated daily intake of Cd was found in young children because soil ingestion rate among this population groups is high. Many researchers suggested that younger individuals have high rates of renal cadmium accumulation because of a very high rate of soil cadmium ingestion (Horiguchi et al., 2004 and Kikuchi et al., 2003) and Satarug et al., (2002) revealed that renal cadmium accumulation found greater in young age groups than older age groups, indicating higher exposure risk among children compared to adults. The intake estimation was adjusted with bodyweight in order to estimate weekly intakes of population groups. The results showed that the highest weekly intake was found in young children (1-5 years), so the risk of cadmium in young children is quite alarming and more concern. The weekly intakes of Cd among the population groups were estimated by adjusting with respective bodyweight. The results are presented in Table 4.4.

Table 4.3 Mean, Median, Range of Daily Intakes in contaminated areas and control sites

Daily Intakes (µg/day) of Study site (n=63)				
	Farmer	**Normal Adults (Non-farming)**	**Children 6-8 years**	**Young Children 1-6 years**
Mean	3.5	0.95	1.9	3.8
Median	1.4	0.54	1.1	2.2
Range	0.26-32	0.03-7.8	0.06-15	0.11-31

Table 4.4 Mean, Median, Range of Weekly Intakes and Contribution to Tolerable Intake of contaminated areas (n = 63)

Weekly Exposure (µg/kg B.W.)				Average CI[c] of JECFA[a]	Average CI[c] of EFSA[b]	Maximum CI[c] of JECFA[a]	Maximum CI[c] of EFSA[b]
	Mean	**Median**	**Range**				
Farmer men	0.35	0.15	0.03-3.3	0.05	0.14	0.47	1.3
Farmer women	0.42	0.18	0.03-4.0	0.06	0.17	0.56	1.6
Adults men	0.10	0.05	0.00-0.79	0.01	0.04	0.11	0.32
Adults women	0.12	0.07	0.00-0.95	0.02	0.05	0.14	0.38
Children 6-8 years	0.70	0.40	0.02-5.7	0.10	0.28	0.82	2.3
Younger Children 1-5 years	2.0	1.2	0.06-17	0.29	0.81	2.4	6.7

a = JECFA- Joint FAO/WHO Expert Committee on Food Additives (JECFA) set Provisional Tolerable Weekly Intake (PTWI) is 7µg/week /kg bodyweight , b = EFSA - European Food Safety Authority (2009) set Tolerable Weekly Intake (TWI) is 2.5µg/week /kg bodyweight, c = Contribution Index of Cd soil ingestion calculated from equation :CI = estimated body weight based Cd intake via soil ingestion/Tolerable Intake.

In order to evaluate the risk associated Cd contamination in soil in study site, the intake estimation were extended by comparing with guidelines values. The Contribution Indices (CI-s) of Cd intake via soil ingestion were calculated in order to get the contributions of Cd intakes among the residents to the Tolerable Intakes (TIs) by dividing estimated body weight based Cd intake via soil ingestion with Tolerable Intake (TI). The contribution indices among population groups viz., farmers, non-farming adults, young and children 6-8 years are described in Table 4.4, along with CI values. The average CIs were 0.01 of Provisional Tolerable Weekly Intake (PTWI), 0.02, 0.10 and 0.29 for the adult men, women, children (6-8 years old) and younger children (1-5 years old) residing in the study area, respectively (Figure 4.2). PTWI, set by The Joint of Food and Agriculture Organization (FAO)/World Health Organization (WHO) Expert Committee on Food Additives (JECFA), is the tolerable intake via all exposure pathways for population of all ages with maximum soil Contribution Indices among residential areas, 0.11, 0.14, and 0.82 and 2.4 in adult men, adult women, children 6-8 years and young Children 1-5 years, respectively (Figure 4.4). Among the non-farming population groups, young children of 1-5 years of age were estimated to have highest average weekly intake of Cd. With the soil ingestion rate we applied in this study, the young children living in two household compounds have a potential of exceeding more than 1.5 or 2 folds of Tolerable Intake set by JECFA with Cd intake by soil ingestion pathway alone. The average CI values are 0.05 and 0.06 among farmer men and women of Provisional Tolerable Weekly Intake (PTWI) set by JECFA with maximum Contribution Indices which are 0.47 and 0.56. In comparison with European Food Safety Authority (EFSA) guidline value that set Tolerable Weekly Intake (TWI) is 2.5µg/week /kg bodyweight (EFSA, 2009). From Table 4.4, the cadmium intake among population groups contributes 0.14 and 0.17 of Tolerable Weekly Intake (TWI) for farmer men and farmer women. The CI were as high as 1.3 and 1.6 with TWI set by EFSA among the farmer men and women who work in sugarcane field where total Cd was 162 mg/kg soil. Thus, farmers who work in this field have a potential of having Cd intake higher than the tolerable intake level. Considering other exposure routes, farmers working in the fields of high soil Cd has risk in term of Cd exposure. Moreover, the contributions indices (CI-s) are 0.04, 0.05, 0.28 and 0.81 in adult men, adult women, children 6-8 years and young children 1-5 years respectively (Figure 4.3). In addition, when calculation of contribute to Tolerable Intake were estimated on maximum level of CI-s which are 0.32, 0.38, 2.3 and 6.7 in adult men, adult women, children 6-8 years and young children 1-5 years respectively (Figure 4.5). When compare with tolerable intake set by EFSA, children living in 9 households have a potential of exceeding the tolerable intake; the exceedance can be 6 folds higher. Since Cd have tendency of staying long in human body, the accumulation of Cd in children"s body throughout their lives is alarming. In addition, compared to men, women have higher tendency of Cd intake when adjusted with bodyweight. High absorption rates of Cd in women of reproductive age groups due to high prevalence of low and empty iron stores as well as variations in half-life were reported (EFSA, 2009). A few studies reported on sex differences and cadmium accumulation; Satarug et al (2002) showed that Austrian female had twice the level of cadmium in their liver and kidney than male and Uetani et al (2006) studied and reported that it had significance diffrences of cadmium accumulation betweem male and female. Schroder et al., (2003) also reported that iron deficiencies in both human and rats have been shown to increase cadmium in both human and rats, These studies suggest that women subject in the contaminated area might have higher Cd accumulation and body burden of Cd than men.

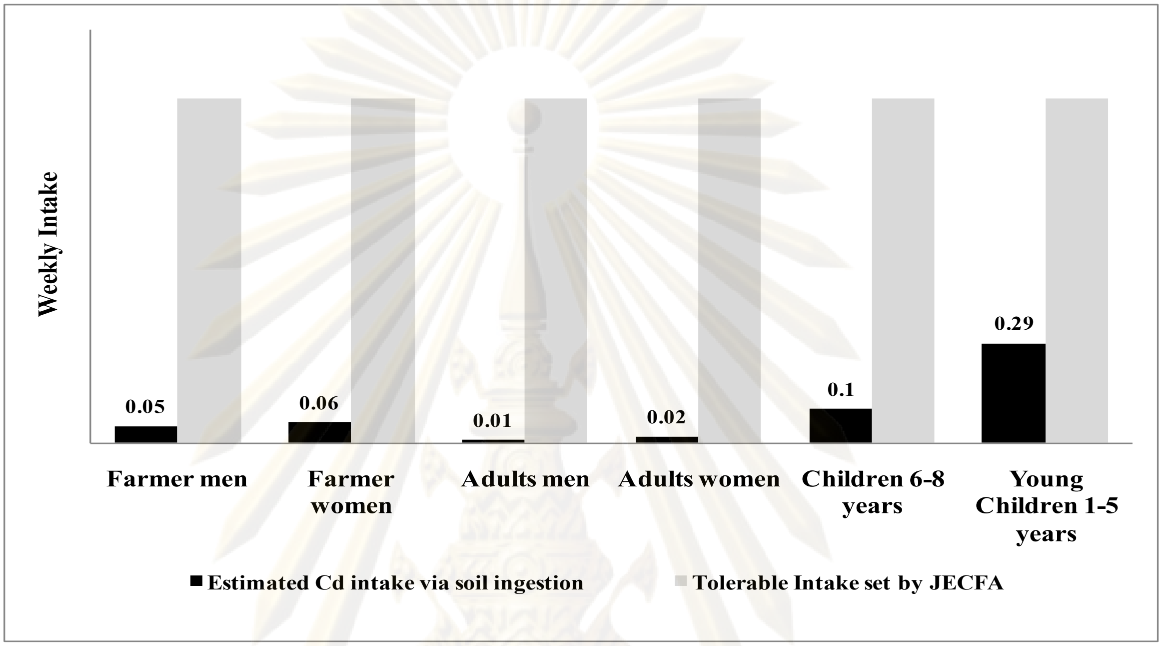


Figure 4.2 Average Cd intake among population groups in comparison with Provisional Tolerable Weekly Intake of JECFA

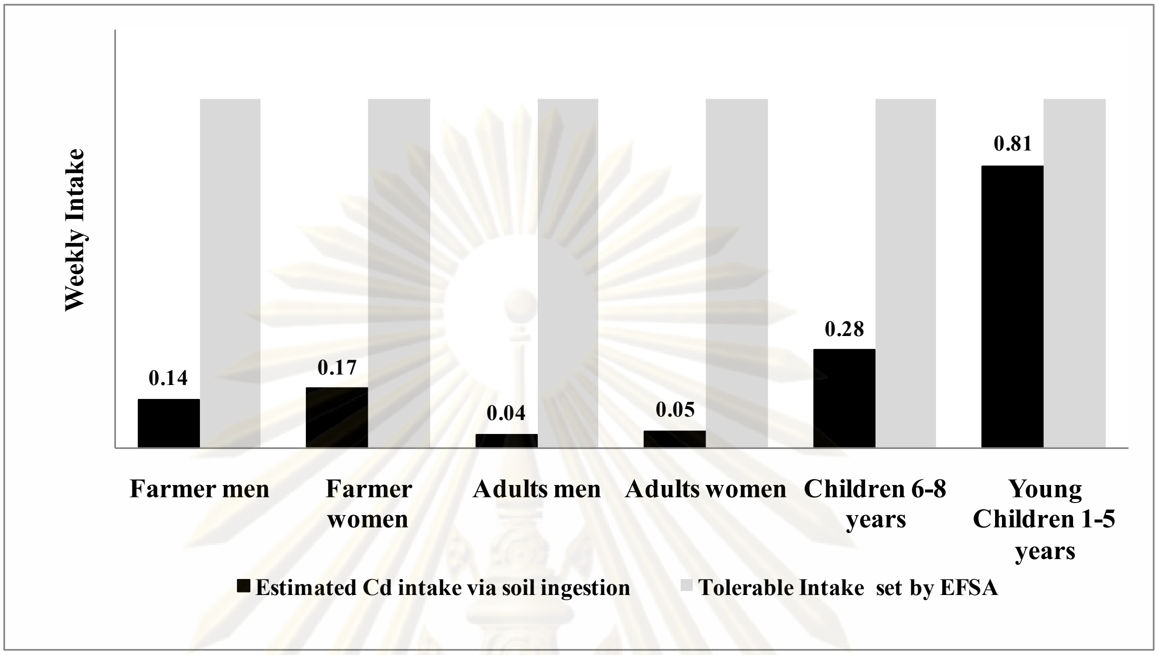


Figure 4.3 Average Cd intake among population groups in comparison with Tolerable Weekly Intake of EFSA

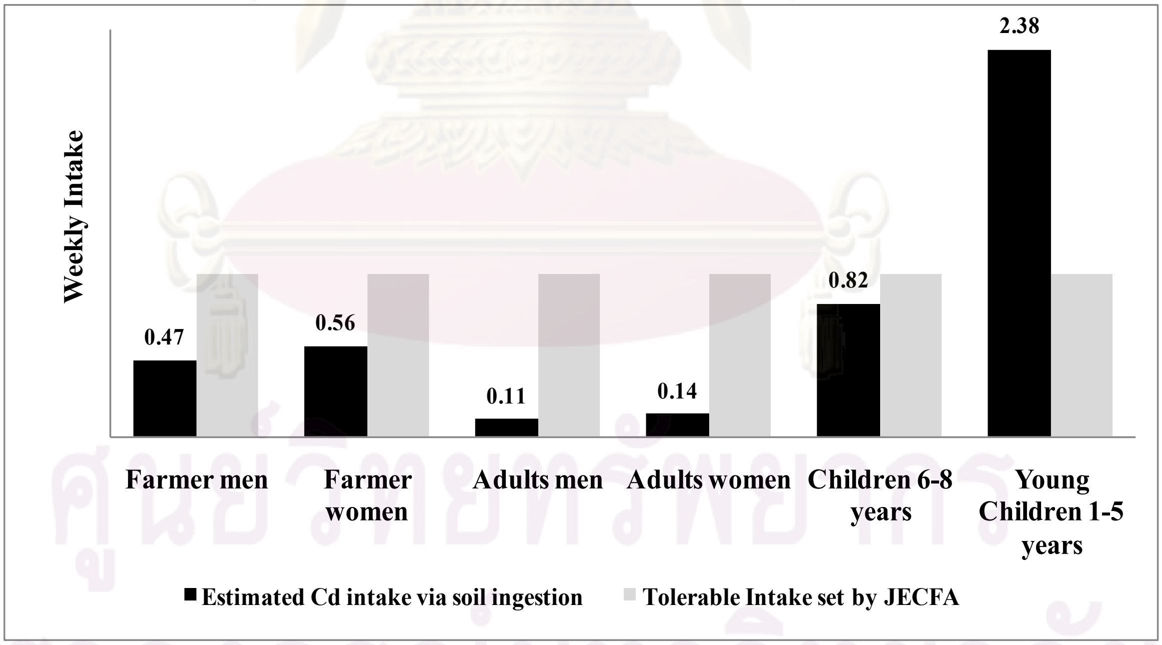


Figure 4.4 Maximum Cd intake among population groups in comparison with Provisional Tolerable Weekly Intake of JECFA

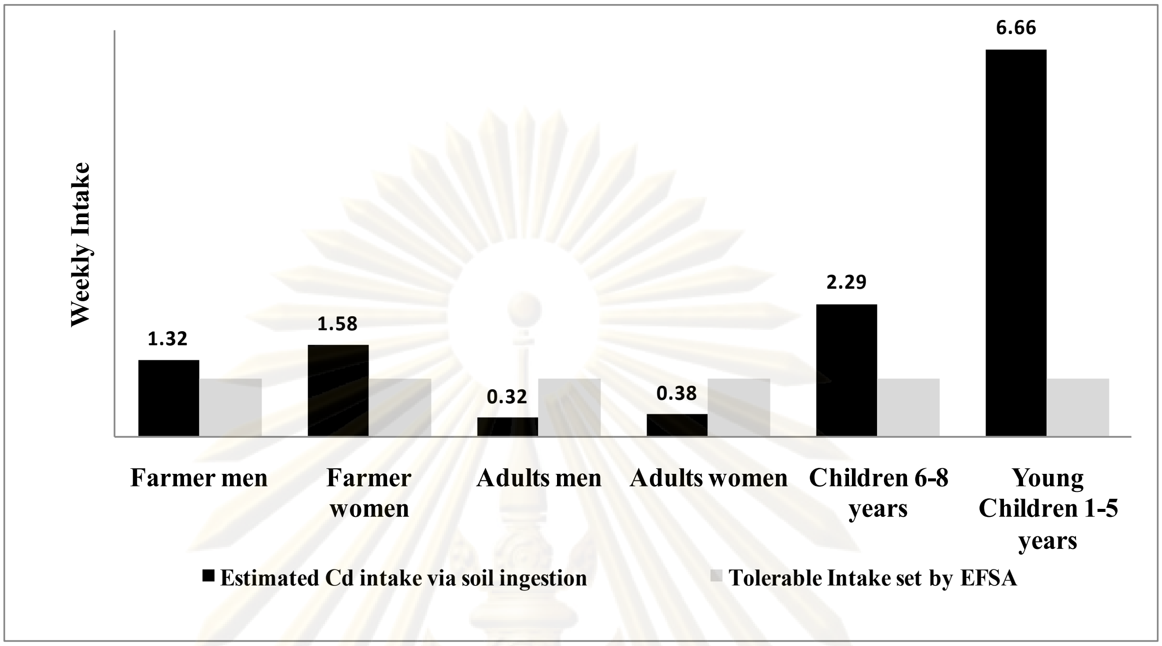


Figure 4.5 Maximum Cd intake among population groups in comparison with Tolerable Weekly Intake of EFSA

4.3 Bioaccessibilty and Cd exposure

Bioavailability is site specific; that is, different soils are known to give different bioavailability or bioaccessibility values (Freeman et al. 1992; Ruby et al. 1996; Hamel et al.1998). It would be very expensive and time-consuming to assess the oral bioavailability of each soil sample with *in vivo* studies, so an *in vitro* model is preferable. Therefor, an *in vitro* digestion model has been developed as a simple, cheap, and reproducible tool to investigate the bioaccessibility of soil contaminants (Oomen et al., 2002).The bioaccessibility was determined in *in vitro* digestion model.This study use *in-vitro* stomach condition simulation test developed by Solubility/Bioavailability Research Consortium.These *in vitro* digestion model represent a worst-case situation and more specific to children, because soil ingestion is an important route of exposure for children due to frequent hand-to-mouth behavior (Duggan and Inskip, 1985)

The average bioaccessibility results in our study showed around 55% in both of residential and agricultural areas. The results of bioaccessibilty values in this study shows large variation (8.6 – 96%) as show in Table 4.5; this must be due to the fact that soil compositions differ from place to place. Wide variation (most likely to be around 20% to 60%) of Cd bioaccessibility in urban playground soil in Uppsala, Sweden was reported by Ljung et al., 2007. The maximum values were around 90% in both areas; this adds up the risk of soil cadmium in the region.

Table 4.5 % Bioaccessibility in study site and control site

	Bioaccessibility (%)		
Sample	**Mean**	**Median**	**Range**
Residential Area of study site (n=45)	54%	57%	12-96%
Agricultural Area of study site (n=18)	55%	61%	8.6-96%
Control site (n=10)	-	-	-

Moreover, figure 4.6 showed the majority of all samples have %bioacessibility between 35-70%. Four samples out of total 18 samples of agricultural areas showed the bioaccessibility higher than 70% and 9 out of 18 fall in the range of 35-70% bioaccessibility. Ten samples out of 45 samples collected from residential areas showed the bioaccessibility higher than 70% and 26 samples fall in the range of 35-70% bioaccessibility. The bioaccessibility of Cd in residential areas are higher than that in agricultural area but it is not very significant (*p*= 0.097). The high bioaccessibility values in residential areas indicate higher risk among population groups in residential areas. Upon exposure, Cd is rapidly transported by blood to different organs in the body where half-life in humans is 15–20 years, the risk due to soil Cd accumulation among children throughout their life is quite alarming. Bioaccesibility data relevant with human health and more effect on human health than general total concentrations of contaminants because it is an as a tool for human health. The different in bioaccessibility in the residential samples and field samples is expected due to input of soil amendments and fertilizers during agricultural activities for several years might have changed the soil mineralization scenario to an extent.

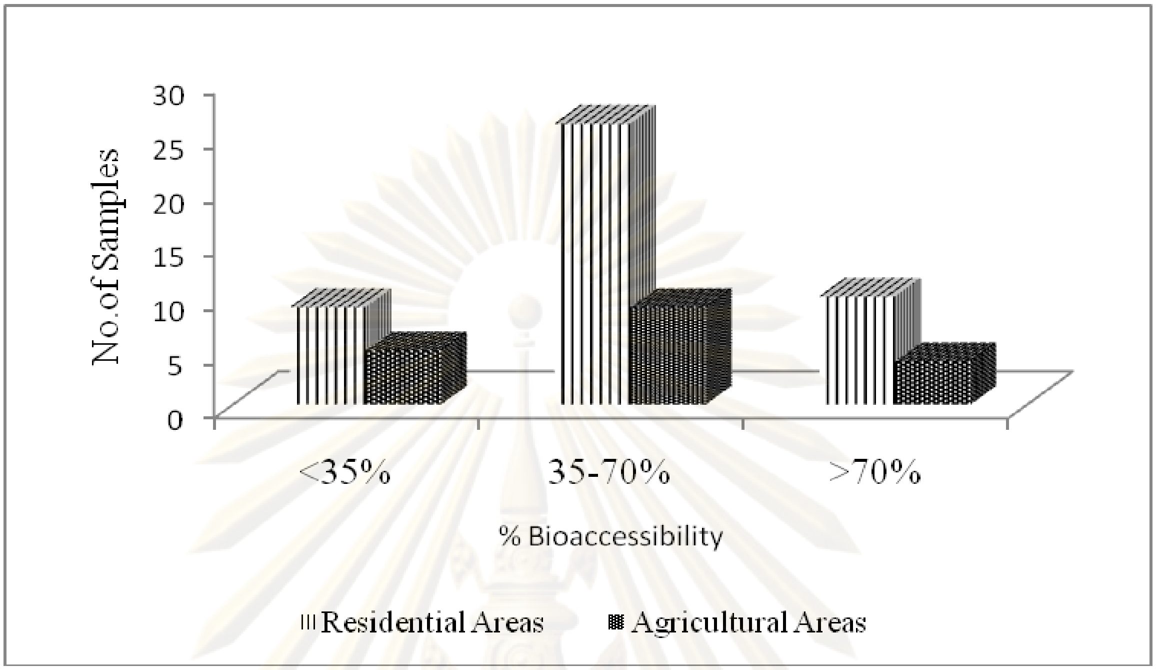


Figure 4.6 Histogram of % bioaccessibility in the study areas

A relationship between the non-dietary exposure of Cd among the residents and the amount of bioaccessibility at each sampling site was conducted. The estimated weekly intakes were classified into three groups depending on the contribution to Tolerable Intakes; if a particular CI values is less than 0.35, that is, the estimated intake contributes less than 35% of Tolerable Intake set by JECFA and EFSA, it is classified as "low", if the CI is between 0.35 to 0.70, it is in the "medium" class and if higher than 0.70, it is in "high" class. Similarly, bioaccessibily values of sampling sites are classified into three groups; if a particular % bioaccessibility is less than 35%, it is classified as "low", if the % bioaccessiblity is between 35 to 70%, it is in the "medium" class and if higher than 70%, it is in "high" class. Table 4.6 presents the number of samples that fall into each category of contributions and bioaccessibility values. In this sense, one sampling site in the agricultural area exhibits moderately high Cd exposure potential (high contribution to TI and medium bioaccessibility) for the farmers via soil ingestion assessed by both concepts, viz., contribution to Tolerable Intake and bioaccessibility. Also, six sampling sites suggest high exposure potentials via soil ingestion (high contribution to TI and high bioaccessibility) and 12 sampling sites show moderately high Cd exposure potential for young children of 1-5 years old (4 sites: medium contribution and high bioaccessibility, 8 sites: high contribution and medium bioaccessibility). Three sampling sites out of a total of six high Cd exposure potential sites for young children showed high potential for children older than 6 years too. The location of the sampling sites of high Cd exposure potential was found in residential areas for both of young children (1-5 years) and children (6-8 years). All the six sampling sites that suggest high exposure potentials via soil ingestion (high contribution to TI and high bioaccessibility) were found to be distributed along Mae Tao Creek, aligned in east to west direction. The total Cd concentrations of these sampling sites ranged from 18.6 to 156 mg Cd/kg soil.

Table 4.6 Classification of the sample according to contribution to Tolerable Intakes and Bioaccessibility

a) Contribution of Cd exposure to JECFA's PTWI among farmers vs. bioaccessibility

	No. of Sampling site		
Bioaccessibility / Contribution	Low (<35%)	Medium (35-70%)	High (>70%)
Low (<35%)	5	8	4
Medium (35-70%)	-	1	-
High (>70%)	-	-	-

b) Contribution of Cd exposure to EFSA's TWI among farmers vs. bioaccessibility

	No. of Sampling site		
Bioaccessibility / Contribution	Low (<35%)	Medium (35-70%)	High (>70%)
Low (<35%)	5	8	4
Medium (35-70%)	-	-	-
High (>70%)	-	1	-

c) Contribution of Cd exposure to JECFA's PTWI among children (6-8 years) vs. bioaccessibility

	No. of Sampling site		
Bioaccessibility / Contribution	Low (<35%)	Medium (35-70%)	High (>70%)
Low (<35%)	9	26	8
Medium (35-70%)	-	-	1
High (>70%)	-	-	1

d) Contribution of Cd exposure to EFSA's TWI among children (6-8 years) vs. bioaccessibility

	No. of Sampling site		
Bioaccessibility Contribution	Low (<35%)	Medium (35-70%)	High (>70%)
Low (<35%)	9	22	5
Medium (35-70%)	-	4	2
High (>70%)	-	-	3

e) Contribution of Cd exposure to JECFA's PTWI among young children (1-5 years) vs. bioaccessibility

	No. of Sampling site		
Bioaccessibility Contribution	Low (<35%)	Medium (35-70%)	High (>70%)
Low (<35%)	9	22	5
Medium (35-70%)	-	2	2
High (>70%)	-	2	3

f) Contribution of Cd exposure to EFSA’s TWI among young children (1-5 years) vs. bioaccessibility

	No. of Sampling site		
Bioaccessibility Contribution	Low (<35%)	Medium (35-70%)	High (>70%)
Low (<35%)	6	11	2
Medium (35-70%)	3	4	4
High (>70%)	1	8	6

4.4 Nature of Bioaccessible Cd

Fractionation using BCR sequential extraction is the way of estimating bioavailability of soil contaminants; four fractions are mainly determined by extraction of different solvents of increasing strength; fraction (1) exchangeable and acid soluble metals, which is regarded as most bioavailable fraction, fraction (2) metals bound to iron managanese oxides, fraction (3) metals bound to organic matter and sulfides and fraction (4) residue. We intend to correlate the Bioaccessibility of Cd contaminated area with some soil characteristics, metals and minerals in order to partially characterize the bioaccessibility of Cd though these correlations were not taken as a substitute for BCR method. Correlation of bioaccessible Cd with soil pH, soil organic matter, and the concentration of some soil metals and minerals such as Fe, Mn, Si, and Ca were determined and statistical correlations were determined using SPSS 17.0

4.4.1. Soil properties

The characteristics of the soil samples in this study are presented in Table 4.7. Certain soil properties such as soil pH, organic matter were determined in order to define the nature of bioaccessible Cd and estimate from which fractions of Cd are bioaccessible. The detailed measurements are described in Table B-1, B-2 in the appendix A.

Table 4.7 Soil properties of the study site (n=65) and control site (n=10)

Sampling Site	Soil Properties	Mean	Median	Range
Study Site (n=65)	**Moisture**	23%	21%	6.8-59%
	pH	7.3	7.4	4.7-8.2
	LOI %	90%	93%	38-101%
Control Site (n=10)	**Moisture**	31	24	19-59%
	pH	5.7	5.9	4.0-7.6
	LOI %	89%	89%	83-95%

The pH value of soil in study site was around neutral and slightly acidic in control site. Soil pH is an indication of the soil‟s chemistry and fertility. The pH affects the chemical activity of the elements in the soil, as well as many of the soil properties. Soils generally have pH values within range 4 – 8.5(Alloway, 1999). Brady et al., (1984) stated that the normal pH is 5-7 in soils of humid regions, and pH 7-9 in the soil of arid regions. Many nutrient cations such as zinc (Zn^{2+}), aluminium (Al^{3+}), iron (Fe^{2+}) and manganese (Mn^{2+}) are soluble and available for uptake by plants below pH 5.0, although their availability can be excessive and thus toxic in more acidic conditions. In more alkaline conditions they are less available; pH levels also affect the complex interactions among soil chemicals. Phosphorus (P), for example, requires a pH between 6.0 and 7.5 and becomes chemically immobile outside this range, forming insoluble compounds with iron (Fe) and aluminium (Al) in acid soils and with calcium (Ca) in calcareous soils. The soil orgainic matter was determined by using Loss on ignition (LOI) method in this study. In LOI method, soil is oxidized at a high temperature (500 – 575 ^{o}C), and the mass loss is proportional to the organic-matter content of the soil (Wright et al., 2008). Organic matter can form organic ligands in order to form soluble complxes with metals and prevent them from being absorbed or precipitated Moreover, within soil profile, Ag, Cd, Cu, Pb and Zn are found concentrated in the surface horizon soil as a result of cycling through vegetation, atmospheric deposition, and adsorption by the soil organic matter (Alloway, 1999).

4.4.2. Soil minerals and metals

The total and the bioaccessible soil minerals and metals determined in this study are described in the Table 4.7

Table 4.7 Total concentrations and the bioaccessible of other soil metals and minerals in study site*

Study site	Total metals and minerals (g/kg soil)			Bioaccessible metals and minerals (g/kg soil)		
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**
Ag	0.001	0.001	0.0003- 0.004	0.0006	ND	ND-0.003
Al	16.8	17.5	0.220 - 27.9	0.914	0.814	0.253-2.98
Ca	4.67	3.81	0.140- 17.9	5.97	4.82	1.44-14.3
Cu	0.04	0.04	0.020- 0.140	0.012	0.009	0.004-0.090
Fe	21.4	20.2	0.110- 48.5	1.57	1.09	0.349-4.95
K	8.23	8.01	3.63- 16.4	0.424	0.341	0.076-1.34
Mg	0.82	0.65	0.200- 4.62	1.99	0.92	0.164-17.4
Mn	0.74	0.59	0.002-3.17	0.463	0.474	0.170-0.842
Na	8.06	8.14	4.25-13.6	5.07	0.129	0.045-66.0
Ni	0.77	1.16	0.007-1.73	0.01	0.01	0.002-0.021
Pb	0.05	0.04	0.010- 0.100	0.024	0.022	0.005-0.069
Si	506	513	409 - 589	0.914	0.59	0.254-4.46
Zn	0.6	0.3	0.030- 4.75	0.238	0.126	0.020-2.18

*One-time measurement, ND= Non detectable

4.4.3 The correlations and data analysis

No significant correlation was found with bioaccessible Cd and pH; the significant negative correlation with Al ($p < 0.01$) might indicate that non-bioaccessible Cd might bound to Al oxides, and the significant negative correlation with Ni ($p < 0.01$) may imply that Ni compete with Cd in dissolution in gastric juice. A significant positive correlation of bioaccessible Cd with bioacessible Ni ($p < 0.01$) confirmed the possibility of competing Ni with Cd. A moderately significant negative correlation of bioaccessible Cd with Si ($p < 0.1$) indicated that the Cd bound to silicate structure is non-bioaccessible. Significant ($p < 0.01$) positive correlation of bioaccessible Cd with total Zn might exhibit that it might behave similarly in the gastric environment. However, no significant correlation between bioaccessible Cd and bioaccessible Zn was observed ($p > 0.1$). Significant correlation with bioaccessible Cd and total Ca ($p < 0.01$) and Mg ($p < 0.01$) might indicate that they sometimes behave in the similar ways. According to McBride (1980), calcite absorb Cd initially by a fast reaction that involves exchange of Ca^{2+} by Cd^{2+} at the surface as shown below:

$$Cd^{2+} + CaCO_3\ (s) = Ca^{2+} + CdCO_3\ (s)$$

In the reaction between the two metal carbonates, the metal cation of the least soluble carbonate, Cd^{2+} is preferentially adsorbed at the carbonate surface (Mcbride, 1994). Moderately significant ($p < 0.1$) relationship was maintained in the correlation of bioacessble Cd and bioaccessible Ca supporting the similar extraction in stomach environment, though the correlation of bioaccessible Cd and bioacessible Mg was not observed ($p > 0.1$). A negative but not significant ($p > 0.1$) correlation was found between bioaccessible Cd and soil organic matter. A meaningful explanation was not available but it is possible the form of CdS is more predominant than stable complexes of Cd and organic matter in fraction (3) of soil Cd in the samples.

However, the correlation data alone do not allow conclusive determination of the nature of Cd oral bioaccessibility at the study site because it depends on numerous geochemical and environmental factors and complete characterization of metal bioacessbility is not possible with straightforward analyses.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

(1) Daily intake of soil cadmium via incidental soil ingestion of farmer is an average of 3.47 µg on daily basis; this intake can be as high as 32.4 µg/day. The results showed that normal adults (Non-farming), children 6-8 years and younger children 1-5 years are estimated to an average intake Cd 0.95, 1.9, 3.8 µg/day, respectively. The intake estimation was adjusted with body weight in order to estimate weekly intakes of all population groups. The average weekly intake are 0.35 and 0.42 µg/kg B.W. among farmer men and women respectively. Normal adults (Non-farming) men and women, children 6-8 years and young children 1-5 years are estimated to intake Cd 0.10, 0.12, 0.70 and 2.0 µg/kg B.W., respectively. In order to evaluate the risk associated Cd contamination in soil in study site, the intake estimation were extended by comparing with guidelines values. The Contribution Indices (CI-s) of Cd intake via soil ingestion were calculated in order to get the contributions of Cd intakes among the residents to the Tolerable Intakes (TIs) by dividing estimated body weight based Cd intake via soil ingestion with Tolerable Intake (TI). Two tolerable intakes were applied in this study; the Provisional Tolerable Weekly Intake (PTWI) of Cd, 7 ug/week/kg body weight set by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). In 2009, European Food Safety Authority (EFSA) set the tolerable weekly intake as 2.5 µg/week/kg body weight. Among the farmer men and women, the average CI are 0.05 and 0.06 (with PTWI set by JECFA), 0.14 and 0.17 (with TWI set by EFSA). The average CI are 0.01, 0.02, 0.10 and 0.29 of PTWI set by JECFA for the adult men, women, children (6-8 years old) and younger children (1-5 years old) residing in residential areas, respectively. In addition, the average CI of TWI set by EFSA are 0.04, 0.05, 0.28, 0.81 in adult men, adult women, children 6-8 years and young Children 1-5 years respectively, indicating that Cd intake via incidental soil ingestion pathway alone contribute to certain percentage of Tolerable Intakes.

(2) The results of bioaccessibilty values in this study ranged from 8.6 – 96%. Four samples out of total 18 samples of agricultural areas showed the bioaccessibility higher than 70% and 9 out of 18 fall in the range of 35-70% bioaccessibility. Ten samples out of 45 samples collected from residential areas showed the bioaccessibility higher than 70% and 26 samples fall in the range of 35-70% bioaccessibility. The bioaccessibility of Cd in residential areas are higher than that in agricultural area but it is not very significant (p= 0.097).

(3) When bioaccessibility values of the sampling sites that contribute to Cd intake, one sampling site in the agricultural area exhibits moderately high Cd exposure potential (high contribution to Tolerable Intake (TI) and medium bioaccessibility) for the farmers. Also, six sampling sites suggest high exposure potentials via soil ingestion (high contribution to TI and high bioaccessibility) and 12 sampling sites show moderately high Cd exposure potential for young children of 1-6 years old (4 sites: medium contribution and high bioaccessibility, 8 sites: high contribution and medium bioaccessibility). Three sampling sites out of a total of six high Cd exposure potential sites for young children showed high potential for children older than 6 years too. All the six sampling sites that suggest high exposure potentials via soil ingestion (high contribution to TI and high bioaccessibility) were found to be distributed along Mae Tao Creek, aligned in east to west direction. The total Cd concentrations of these sampling sites ranged from 18.6 to 156 mg Cd/kg soil.

(4) The nature of bioaccessible Cd was studied. The significant correlation was found with bioaccessible Cd and total Ca ($p < 0.01$), Mg ($p < 0.01$) and Zn ($p < 0.01$) might exhibit that these three might behave similarly in the gastric environment. However, no significant correlation between bioaccessible Cd and bioaccessible Zn was observed ($p >$ 0.1). Moderately significant ($p < 0.1$) relationship was maintained in the correlation of bioacessble Cd and bioaccessible Ca supporting the similar extraction in stomach environment, though the correlation of bioaccessible Cd and bioacessible Mg was not observed ($p > 0.1$).

For correlation with organic matter, a negative but not significant ($p > 0.1$) correlation was found between bioaccessible Cd and soil organic matter. A meaningful explanation was not available but it is possible that the form of CdS is more predominant than stable complexes of Cd and organic matter in fraction 3 (metals bound to organic matter and sulfides) of soil Cd in the samples. In addition, no significant correlation was found with bioaccessible Cd and pH; the significant negative correlation with Al ($p < 0.01$) might indicate that non-bioaccessible Cd might not bound to Al oxides. The significant negative correlation with total Ni ($p < 0.01$) may imply that Ni compete with Cd in dissolution in gastric juice. A significant positive correlation of bioaccessible Cd with bioacessible Ni ($p < 0.01$) confirmed the possibility of competing Ni with Cd. A moderately significant negative correlation of bioaccessible Cd with Si ($p < 0.1$) indicated that the Cd bound to silicate structure is non-bioaccessible.

5.2 Recommendation

Human expose to Cd via soil ingestion or inhalation show significantly pathways while dermal exposure is not regarded to be significant. Van Assche, (1998) estimated that ingestion accounts for 95% of total Cd intake in a non smoker. Although the assumption for the general population is that much of Cd which enters the human body by ingestion comes from terrestrial foods, the exposure scenario among the inhabitants living in the contaminated site may be different. Management measures may reduce the transfer of Cd from contaminated or naturally high in Cd soil into the local food chain; incidental soil ingestion can be controlled by personal hygience. In such a case of direct soil ingestion, how much Cd can be dissolved in the gastric environment and made accessible for human absorption is the crucial information. The production of non-food crops in these areas is strongly supported by the government. Having suggestion from some experts, the sugar cane which can be produced to be ethanol has been an appropriate option, due to high demand of oil and good price in the market at this time. The following management measures are recommended:

(I) Remediation

(II) Public Education

(I) Remediation:

A thorough scanning of soil Cd and bioaccessiblility should be checked in the residential area depending on landuse. The sampling sites that showed high contribution to Tolerable Intake-s and confirmed by high bioaccessibily to the residents, and their surrounding areas deserve remediation. Even if full remediation is not feasible, there are alternatives to lessen the chance of exposing soil Cd among the residents. Covering with turf and shrubs in sites of high Cd concentration is recommended since it is widely report as low-cost and effective counter measure. Lange et al (1994) reported how soil covering with turf might reduce the exposure of soil, contaminated lead, thereby, blood lead level of the exposed children may reduce.

(II) Public Education:

Public education to the resident on health effects associated with Cd exposure pathways is strongly recommended. The farmers, usually the migrant workers, rural poors of the neighboring country, Myanmar, may be unaware of the Cd contamination problems in the region. Farmers rarely wear protective clothing due to heat related discomfort may raise not only raise exposure of Cd in soil but also the exposure potential of the environmental contaminants. In addition, smoking habit may increase daily Cd intake via inhalation pathway because a greater proportion of inhaled cadmium is retained by the body and high portion of inhaled cadmium is absorbed by human's system.

Regarding, the Cd exposure risk among the younger children, the education of the parents and the caregivers about good personal hygiene practice and balanced nutritional status is a must. Simple hygiene practice such as frequent hand washing and careful supervision of the caregivers may reduce the contact with dust and at risk behaviors such as sucking fingers and toys. Simple housekeeping such as mopping floor instead of using brooms or vacuuming – since most vacuum cleaners do not trap <20 μm particles and will simply re-entrain them into the air, from which they will then resettle to the surface-cleaning window frames, windowsills and household furniture rather than dusting, would reduce the Cd exposure due to non-dietary ingestion pathway and generate the safer home environment from soil contaminants, since household dust is most likely to be finer soil particles (Aung et al , 2004). Balanced diet, high in iron and calcium such as spinach and dairy products, could be recommended. Krissanakriangkrai et al, (2009) reported the high accumulation of Cd in muscle tissues of fishes and shellfishes in Mae Tao creek and pointed out health risk to the consumers. Moreover, consuming homegrown vegetables may pose a risk since the plant bioavailability of Cd in soil at the site can also be high. With sound public awareness, the Cd burden in the region would be greatly reduced.

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APPENDICES

APPENDIX A

Detailed Procedure for Sample Analysis

A-1 Sampling

(a) Composite Sample:

(1) Soil samples are prepared by throughly mixing several grab samples. In the control sites, soil samples were randomly selected .All soil samples consisted of the top 2 inches of the soil excluding debris at the top-most part. Each sample is a homogenous composite of 3 sub-samples within 1m X 1m plot. All sampling points were at least 50m away from the busy highways and roads.Special care was taken to ensure sub-samples obtained were of similar size and depth. The same procedures were also done in the study sites samples

A-2 Analytical technigues:

Total acid digestion procedures

ICP

- **Stock standard solution**: ICP – Multi Element Standard Solution at 1000 ppm
- **Working Standard Solution:** Prepared ICP – Multi Element Standard Solution of 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.40, 0.60, 0.80, 1.0, 2, 3, 4, 5, 10 ppm (Adjusted Volume with 1% (v/v) HNO_3)

FLAAS

- **Stock standard solution**: Cadmium Standard Solution 1000mg/l for AA in nitric acid 0.5mol/l
- **Working Standard Solution:** Prepared Cadmium standard solution of 0.5, 1, 2, 3, 4, 5 ppm (Adjusted Volume with 1% (v/v) HNO_3)

GFAAS

- **Stock standard solution**: Cadmium Standard Solution 1000mg/l for AA in nitric acid 0.5mol/l
- **Working Standard Solution:** Prepared Cadmium standard solution of 0, 5, 10, 15, 20, 25, 30 ppb (Adjusted Volume with 1% (v/v) HNO_3)

(c) Calculation Method

The result in mg/kg soil should be calculated as follows:

Results = A X (B/C)

Where; A= Analytical Results (mg/l)
B= Final Vol (ml)
C = Weight of soil (g)

A-3 Accuracy and Precision

*% Recovery = (Result*100)/True Value*

Sample	CRM 025-050 (mg/kg)	Analyze Result Concentration (mg/kg)	%Recovery
Cd 1	369	301.91	81.8
Cd 2	369	293.18	79.5
Cd 3	369	290.71	78.8

Certificate of Analysis				
Element	**Ref Value (mg/kg)**	**S.D.**	**Confidence Interval**	**Prediction Interval**
Cd	**369**	**46.3**	**350-388**	**271-466**

APPENDIX B

Analytical Results

Table B-1 Soil parameters of soil samples in contaminated areas

Samples	Place	pH	Moisture Content %	LOI %
J1	House Compound	6.6	21	94
J3	Corn field	7.4	25	87
J10	House Compound	7.4	30	95
J11	House Compound	7.2	18	96
J14	House Compound	6.3	14	98
J19	House Compound near creak	7.6	21	96
J21	House Compound near creak	7.5	28	91
J27	House Compound	7.3	29	92
J31	Field	6.1	26	91
J33	Mid Maetao school compound	7.8	14	95
J38	South Maetao school compound	6.9	26	89
M1	House Compound	7.2	6.7	94
M3	Field	4.7	16	86
M4	Rubber tree plantation	7.5	14	88
M5	House Compound	7.2	14	93
M8	Paddy field	7.3	38	79
M13	House Compound	7.2	27	86
M15	House Compound	7.4	41	84
M16	School playground	7.7	17	95
M17	House Compound	7.8	19	96
M22	Sugarcane field	8.1	25	94
M26	Sugarcane field	6.7	17	92
M27	Sugarcane field	7.4	18	93
M28	House Compound	6.2	26	95
M31	Paddy filed Maetao	7.6	19	91
M32	House Compound near creak	8.1	15	93
M33	House Compound	7.6	16	38
M35	House Compound	7.4	17	99
M36	House Compound near creak	8.2	30	93
M39	House Compound	6.9	20	92
M40	House Compound near creak	7.2	26	91
M45	Sugarcane field near house	7.1	10	95
M46	Thasai luet near house	7.5	12	95

Table B-1 Soil parameters in soil samples in contaminated areas

Samples	Place	pH	Moisture Content	LOI %
M2	House Compound	7.6	18	87
M6	House Compound	7.2	14	88
M7	House Compound	7.6	29	80
M9	Sugarcane field	6.8	19	84
M10	House Compound	7.1	15	91
M11	Paddy filed	7.0	21	52
M12	House Compound	7.3	22	66
M19	House Compound	7.4	15	93
M20	Banana plantation	7.4	16	92
M21	Paddy field	7.2	17	93
M23	Field	8.1	36	94
M24	House Compound	7.4	29	89
M25	House Compound	7.7	23	92
M29	Sugarcane field	7.7	24	93
M30	Near Creak sample	7.7	39	90
M34	House Compound	7.8	30	95
M37	House Compound	7.4	12	93
M38	House Compound	7.8	21	99
M41	House Compound	7.7	21	95
M42	House Compound	7.8	28	95
M47	House Compound	7.5	15	92
J2	Corn filed	7.3	30	83
J4	Temple compound	7.3	59	83
J5	Sugarcane field	7.5	26	91
J6	House Compound	7.7	21	91
J8	House Compound	7.2	26	88
J9	House Compound	6.7	30	95
J12	School	6.9	16	95
J26	House Compound near creak	7.4	48	97
J28	House Compound near creak	7.6	19	94
	Mean	7.3	23	90

Table B-2 Soil parameters in soil samples and of control sites

Sample	pH	LOI %	Moisture Content %
S1	6.6	89	21
S2	4.0	95	27
S3	5.9	83	59
S4	5.3	91	22
S5	6.2	90	41
S6	6.0	87	22
S7	5.6	87	20
S8	5.8	87	58
S9	4.5	92	19
S10	7.6	90	25
	Mean	89	31

Table B-3 Total cadmium concentrations, Bioavaialble Cd, Bioaccessibility of soil samples in residential areas

Samples	Total Cd concentration (mg/kg soil)	Total Cd concentration (mg/kg soil) dry weight basis	Bioaccessible Cd (mg/kg soil)	Bioaccessibility (%)
M2	9.47	7.77	3.23	34.2
M6	15.3	13.1	11.9	77.8
M7	63.6	45.2	51.0	80.1
M10	3.73	3.17	1.51	40.5
M12	47.6	37.1	33.0	69.4
M19	2.16	1.84	1.00	46.0
M24	26.9	19.1	20.0	74.3
M25	7.02	5.41	3.98	56.8
M30	16.9	10.3	11.0	64.9
M34	27.2	19.0	19.0	69.8
M37	6.03	5.31	5.81	96.2
M38	28.7	22.7	19.9	69.5
M41	17.1	13.5	10.2	59.5
M42	18.6	13.4	13.1	70.8
M47	17.9	15.2	12.3	68.6
J4	110	45.1	80.7	73.3
J6	12.8	10.1	9.87	77.1
J8	46.5	34.4	29.4	63.2
J9	156	109	115	73.4
J12	11.6	9.87	7.98	68.8
J26	13.7	7.10	10.6	77.7
J28	35.9	29.1	27.6	76.7
J1	17.7	14.2	6.67	37.6
J10	10.8	4.9	2.33	21.6
J11	1.92	1.58	0.300	15.6
J14	1.15	0.980	0.620	54.5
J19	6.24	4.93	2.97	47.6
J21	10.8	7.78	5.25	48.5
J27	4.57	3.24	3.00	65.7
J33	0.730	0.630	0.32	43.9
J38	2.16	1.60	0.26	11.9
M1	8.24	7.66	1.32	16.0
M5	6.59	5.66	3.22	49.0
M13	12.6	9.23	5.67	44.9
M15	2.36	1.39	1.35	57.4
M16	3.42	2.84	0.950	27.7
M17	1.01	0.820	0.400	39.3
M28	1.22	0.910	0.280	23.0

Table B-3 Total cadmium concentrations, Bioavaialble Cd, Bioaccessibility of soil samples in residential areas

Samples	Total Cd concentration (mg/kg soil)	Total Cd concentration (mg/kg soil) dry weight basis	Bioaccessible Cd (mg/kg soil)	Bioaccessibility (%)
M32	6.96	5.91	3.18	45.8
M33	10.4	8.74	2.64	25.4
M35	16.8	13.9	7.68	45.8
M36	2.24	1.57	1.57	70.0
M39	12.4	9.94	5.65	45.5
M40	21.4	15.9	5.19	24.2
M46	0.560	0.500	0.380	67.4
Mean	19.1	13.37	12.4	53.7

Table B-4 Total cadmium concentrations, Bioavaialble Cd, Bioaccessibility of soil samples in agricultural areas in agricultural areas

Samples	Total Cd concentration (mg/kg soil)	Total Cd concentration (mg/kg soil) dry weight basis	Bioaccessible Cd (mg/kg soil)	Bioaccessibility (%)
M9	17.8	14.39	17.0	95.5
M11	2.04	1.61	1.41	69.2
M20	15.3	12.8	11.9	77.9
M21	1.76	1.46	0.810	46.0
M23	18.1	11.6	12.9	71.4
M29	162	123	111	68.9
J2	7.37	5.16	4.69	63.6
J5	7.00	5.25	4.09	58.4
J3	6.55	4.91	3.56	54.4
J31	4.43	3.28	1.26	28.4
M3	1.32	1.11	0.800	60.8
M4	2.41	2.07	0.370	15.5
M8	8.81	5.46	0.750	8.60
M22	9.50	7.12	3.26	34.4
M26	1.57	1.29	1.12	71.1
M27	2.70	2.21	1.66	61.5
M31	35.2	28.5	23.5	66.8
M45	8.48	7.63	2.66	31.4
Mean	17.4	13.27	11.3	54.7

Table B-5 The total concentrations of other soil metals and minerals in study site and control site*

Metals and minerals (g/kg soil)	Study sites (n=63)			Control sites (n=10)		
	Mean	Median	Range	Mean	Median	Range
Ag	0.001	0.001	0.0003- 0.004	0.020	0.002	0.010-0.200
Al	16.8	17.5	0.220 - 27.9	19.7	19.8	17.7-21.1
Ca	4.67	3.81	0.140- 17.9	1.02	0.760	0.560-2.01
Cu	0.040	0.040	0.020- 0.140	0.180	0.080	0.060-0.560
Fe	21.4	20.2	0.110- 48.5	29.8	32.2	15.2-36.0
K	8.23	8.01	3.63- 16.4	14.3	13.8	10.7-21.0
Mg	0.820	0.650	0.200- 4.62	0.360	0.280	0.190-0.900
Mn	0.740	0.590	0.002-3.17	0.290	0.260	0.110-0.500
Na	8.06	8.14	4.25-13.6	10.5	9.80	7.60-18.2
Ni	0.770	1.16	0.007-1.73	0.040	0.040	0.030-0.050
Pb	0.050	0.040	0.010- 0.100	0.040	0.030	0.030-0.060
Si	506	513	409 - 589	457	466	415-490
Zn	0.600	0.300	0.030- 4.75	0.070	0.070	0.050-0.080

*One-time measurement

Table B-6.The Limits of Detection of metals and minerals

Name of metals and minerals	Limits of Detection (LOD) (µg/kg soil)
Ag	3
Al	34
Ca	2
Cu	11
Fe	10
K	0.1
Mg	0.25
Mn	1.4
Na	0.1
Ni	10
Pb	8
Si	40
Zn	0.3

LOD = Limits of Detection, Source: Manuscript Detection Limits of novAA, ZEEnit model of Graphite Furnace Spectro photometer

Table B-7 Daily and Weekly Intake and Contribution to tolerable intake of JECFA and EFSA in agricultural areas

Sample Code	Daily Intake (µg/d)	Weekly Intake (µg/kg)		Contribution Index to PTWI set by JECFA		Contribution Index to TWI set by EFSA	
	Farmers	Farmers		Farmers		Farmers	
		Men	Women	Men	Women	Men	Women
M9	3.55	0.36	0.43	0.05	0.06	0.14	0.17
M11	0.41	0.04	0.05	0.01	0.01	0.02	0.02
M20	3.05	0.31	0.37	0.04	0.05	0.12	0.15
M21	0.35	0.04	0.04	0.01	0.01	0.01	0.02
M23	3.62	0.37	0.44	0.05	0.06	0.15	0.18
M29	32.41	3.29	3.95	0.47	0.56	1.32	1.58
J2	1.47	0.15	0.18	0.02	0.03	0.06	0.07
J5	1.40	0.14	0.17	0.02	0.02	0.06	0.07
J3	1.31	0.13	0.16	0.02	0.02	0.05	0.06
J31	0.89	0.09	0.11	0.01	0.02	0.04	0.04
M3	0.26	0.03	0.03	0.00	0.00	0.01	0.01
M4	0.48	0.05	0.06	0.01	0.01	0.02	0.02
M8	1.76	0.18	0.21	0.03	0.03	0.07	0.09
M22	1.90	0.19	0.23	0.03	0.03	0.08	0.09
M26	0.31	0.03	0.04	0.00	0.01	0.01	0.02
M27	0.54	0.05	0.07	0.01	0.01	0.02	0.03
M31	7.03	0.71	0.86	0.10	0.12	0.29	0.34
M45	1.70	0.17	0.21	0.02	0.03	0.07	0.08
Mean	3.47	0.35	0.42	0.05	0.06	0.14	0.17
Median	1.44	0.15	0.18	0.02	0.03	0.06	0.07
Range	0.11-32.4	0.01-3.29	0.01-3.95	0.002-0.47	0.002-0.56	0.005-1.32	0.006-1.58

Table B-8 Daily and Weekly Intake in residential areas

	Daily Intake (µg/day)			Weekly Intake(µg/kg)			
Sample Codes	Normal Adults	Young Children (1-5 years)	Children 6-8 years	Normal Adults		Children	
				Men	Women	Young 1-5 years	older 6-8 years
M2	0.05	0.20	0.10	0.01	0.01	0.11	0.04
M6	0.10	0.40	0.20	0.01	0.01	0.21	0.07
M7	0.15	0.60	0.30	0.02	0.02	0.32	0.11
M10	0.20	0.80	0.40	0.02	0.02	0.43	0.15
M12	0.25	1.00	0.50	0.03	0.03	0.53	0.18
M19	0.30	1.20	0.60	0.03	0.04	0.64	0.22
M24	0.35	1.40	0.70	0.04	0.04	0.75	0.26
M25	0.40	1.60	0.80	0.04	0.05	0.85	0.29
M30	0.45	1.80	0.90	0.05	0.05	0.96	0.33
M34	0.50	2.00	1.00	0.05	0.06	1.07	0.37
M37	0.55	2.20	1.10	0.06	0.07	1.17	0.40
M38	0.60	2.40	1.20	0.06	0.07	1.28	0.44
M41	0.65	2.60	1.30	0.07	0.08	1.39	0.48
M42	0.70	2.80	1.40	0.07	0.09	1.49	0.51
M47	0.75	3.00	1.50	0.08	0.09	1.60	0.55
J4	0.80	3.20	1.60	0.08	0.10	1.70	0.59
J6	0.85	3.40	1.70	0.09	0.10	1.81	0.62
J8	0.90	3.60	1.80	0.09	0.11	1.92	0.66
J9	0.95	3.80	1.90	0.10	0.12	2.02	0.70
J12	1.00	4.00	2.00	0.10	0.12	2.13	0.73
J26	1.05	4.20	2.10	0.11	0.13	2.24	0.77

Cont'd from Table B-8

J28	1.10	4.40	2.20	0.11	0.13	2.34	0.81
J1	1.15	4.60	2.30	0.12	0.14	2.45	0.84
J10	1.20	4.80	2.40	0.12	0.15	2.56	0.88
J11	1.25	5.00	2.50	0.13	0.15	2.66	0.92
J14	1.30	5.20	2.60	0.13	0.16	2.77	0.95
J19	1.35	5.40	2.70	0.14	0.16	2.88	0.99
J21	1.40	5.60	2.80	0.14	0.17	2.98	1.03
J27	1.45	5.80	2.90	0.15	0.18	3.09	1.06
J33	1.50	6.00	3.00	0.15	0.18	3.20	1.10
J38	1.55	6.20	3.10	0.16	0.19	3.30	1.14
M1	1.60	6.40	3.20	0.16	0.20	3.41	1.17
M5	1.65	6.60	3.30	0.17	0.20	3.52	1.21
M13	1.70	6.80	3.40	0.17	0.21	3.62	1.25
M15	1.75	7.00	3.50	0.18	0.21	3.73	1.28
M16	1.80	7.20	3.60	0.18	0.22	3.84	1.32
M17	1.85	7.40	3.70	0.19	0.23	3.94	1.36
M28	1.90	7.60	3.80	0.19	0.23	4.05	1.39
M32	1.95	7.80	3.90	0.20	0.24	4.16	1.43
M33	2.00	8.00	4.00	0.20	0.24	4.26	1.47
M35	2.05	8.20	4.10	0.21	0.25	4.37	1.50
M36	2.10	8.40	4.20	0.21	0.26	4.47	1.54
M39	2.15	8.60	4.30	0.22	0.26	4.58	1.58
M40	2.20	8.80	4.40	0.22	0.27	4.69	1.62
M46	2.25	9.00	4.50	0.23	0.27	4.79	1.65
Mean	1.15	4.60	2.30	0.12	0.14	2.45	0.84
Median	1.15	4.60	2.30	0.12	0.14	2.45	0.84
Range	0.03-8.1	0.11-32.4	0.06-16.2	0.003-0.82	0.003-0.99	0.06-17.3	0.02-4.99

Table B-9 Contribution to Tolerable Intake of JECFA and EFSA in residential areas

	Contribution Intake to PTWI set by JECFA				Contribution Intake to TWI set by EFSA			
	Normal Adults		Children		Normal Adults		Children	
Samples	Men	Women	Young 1-5	older 6-8	Men	Women	Young 1-5	older 6-8
M2	0.00	0.00	0.02	0.01	0.00	0.00	0.04	0.01
M6	0.00	0.00	0.03	0.01	0.00	0.00	0.09	0.03
M7	0.00	0.00	0.05	0.02	0.01	0.01	0.13	0.04
M10	0.00	0.00	0.06	0.02	0.01	0.01	0.17	0.06
M12	0.00	0.00	0.08	0.03	0.01	0.01	0.21	0.07
M19	0.00	0.01	0.09	0.03	0.01	0.01	0.26	0.09
M24	0.01	0.01	0.11	0.04	0.01	0.02	0.30	0.10
M25	0.01	0.01	0.12	0.04	0.02	0.02	0.34	0.12
M30	0.01	0.01	0.14	0.05	0.02	0.02	0.38	0.13
M34	0.01	0.01	0.15	0.05	0.02	0.02	0.43	0.15
M37	0.01	0.01	0.17	0.06	0.02	0.03	0.47	0.16
M38	0.01	0.01	0.18	0.06	0.02	0.03	0.51	0.18
M41	0.01	0.01	0.20	0.07	0.03	0.03	0.55	0.19
M42	0.01	0.01	0.21	0.07	0.03	0.03	0.60	0.21
M47	0.01	0.01	0.23	0.08	0.03	0.04	0.64	0.22
J4	0.01	0.01	0.24	0.08	0.03	0.04	0.68	0.23
J6	0.01	0.01	0.26	0.09	0.03	0.04	0.72	0.25
J8	0.01	0.02	0.27	0.09	0.04	0.04	0.77	0.26
J9	0.01	0.02	0.29	0.10	0.04	0.05	0.81	0.28
J12	0.01	0.02	0.30	0.10	0.04	0.05	0.85	0.29
J26	0.02	0.02	0.32	0.11	0.04	0.05	0.89	0.31

Cont'd from Table B-9

J28	0.02	0.02	0.33	0.12	0.04	0.05	0.94	0.32
J1	0.02	0.02	0.35	0.12	0.05	0.06	0.98	0.34
J10	0.02	0.02	0.37	0.13	0.05	0.06	1.02	0.35
J11	0.02	0.02	0.38	0.13	0.05	0.06	1.07	0.37
J14	0.02	0.02	0.40	0.14	0.05	0.06	1.11	0.38
J19	0.02	0.02	0.41	0.14	0.05	0.07	1.15	0.40
J21	0.02	0.02	0.43	0.15	0.06	0.07	1.19	0.41
J27	0.02	0.03	0.44	0.15	0.06	0.07	1.24	0.43
J33	0.02	0.03	0.46	0.16	0.06	0.07	1.28	0.44
J38	0.02	0.03	0.47	0.16	0.06	0.08	1.32	0.46
M1	0.02	0.03	0.49	0.17	0.07	0.08	1.36	0.47
M5	0.02	0.03	0.50	0.17	0.07	0.08	1.41	0.48
M13	0.02	0.03	0.52	0.18	0.07	0.08	1.45	0.50
M15	0.03	0.03	0.53	0.18	0.07	0.09	1.49	0.51
M16	0.03	0.03	0.55	0.19	0.07	0.09	1.53	0.53
M17	0.03	0.03	0.56	0.19	0.08	0.09	1.58	0.54
M28	0.03	0.03	0.58	0.20	0.08	0.09	1.62	0.56
M32	0.03	0.03	0.59	0.20	0.08	0.10	1.66	0.57
M33	0.03	0.03	0.61	0.21	0.08	0.10	1.70	0.59
M35	0.03	0.04	0.62	0.21	0.08	0.10	1.75	0.60
M36	0.03	0.04	0.64	0.22	0.09	0.10	1.79	0.62
M39	0.03	0.04	0.65	0.23	0.09	0.10	1.83	0.63
M40	0.03	0.04	0.67	0.23	0.09	0.11	1.88	0.65
M46	0.03	0.04	0.68	0.24	0.09	0.11	1.92	0.66
Mean	0.02	0.02	0.35	0.12	0.05	0.06	0.98	0.34
Median	0.02	0.02	0.35	0.12	0.05	0.06	0.98	0.34
Range	0.0004-0.12	0.0005-0.14	0.009-2.46	0.003-0.71	0.001-0.33	0.001-0.40	0.024-6.91	0.007-2.00

Table B-10 Daily Intake of control site

Samples	Daily Intake (µg/d)			
	Farmer	Normal Adults (Non-farming)	Children 6-8 years	Younger Children 1-5 years
Control site samples (n=10)	0.02	0.0049	0.01	0.02

Table B-11 Weekly Intake of control site and Contribution to Tolerable Intake set by JECFA and EFSA

Control site samples (n=10)	Weekly Intake (µg/kg)	Contribution Index to PTWI set by JECFA	Contribution Index to TWI set by EFSA
Farmer			
Men	0.002	0.0003	0.0008
Women	0.0002	3.49E-05	9.77E-05
Normal Adults (Non-farming)			
Men	0.2	0.029	0.08
Women	0.24	0.034	0.10
Children 6-8 years	0.004	0.001	0.001
Young Children 1-5 years	0.011	0.002	0.004

BIOGRAPHY

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