CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Overview

The study area of the research is Mae Tao river basin, located in Phatat Pha Daeng sub-district, Mae Sot district, Tak province, northern Thailand. The study area is located close to 2 zinc-mining companies, Tak Mining Company and Pha Daeng Company, which are considered as major source of cadmium contamination in the agriculture area within Mae Tao river basin. The cadmium concentrations in the study area vary from 0 to more than 100 mg/kg. The frequency distribution of cadmium concentration in the study area is shown in Figure 2.1. The highest frequency distribution of cadmium concentration is from 0 to 10 mg/kg. It was found that at around a half of this range of cadmium concentration, the pH value is from 6.0 to 6.5 as shown in Figure 2.2. Therefore, the studied soil for this research contained cadmium in the range of 0 to 10 mg/kg and pH value in the range of 6.0 to 6.5.

Many studies have shown that redox potential, pH, and the ratio of concentration levels of cadmium to others metals, particularly iron, manganese, and zinc, have significantly effects on cadmium uptake in rice plants, especially in the rhizosphere (Simmons et al., 2003, Kashem et al., 2001a). Rice plant root is the most accumulation of cadmium because it can absorb nutrients, water and other elements, including metals via the roots. A great proportion of Cd taken by rice plants will be retained in roots. Cadmium concentrations fall rapidly between the roots and above ground parts of rice plants and only very small proportion of cadmium taken by the roots will be transferred to rice grains.

The rhizosphere is the zone surrounding roots of plants in which complex relations exist among the plant, soil microorganisms and the soil itself. The plant roots and the biofilm associated with them can profoundly influence the chemistry of the soil including pH and the transformation of other elements.

Therefore, to adjust redox and pH in the soil solution in rhizosphere zone by different method during rice plantation practice would be expected to influence redox and pH and then to the uptake of the cadmium to rice plant.

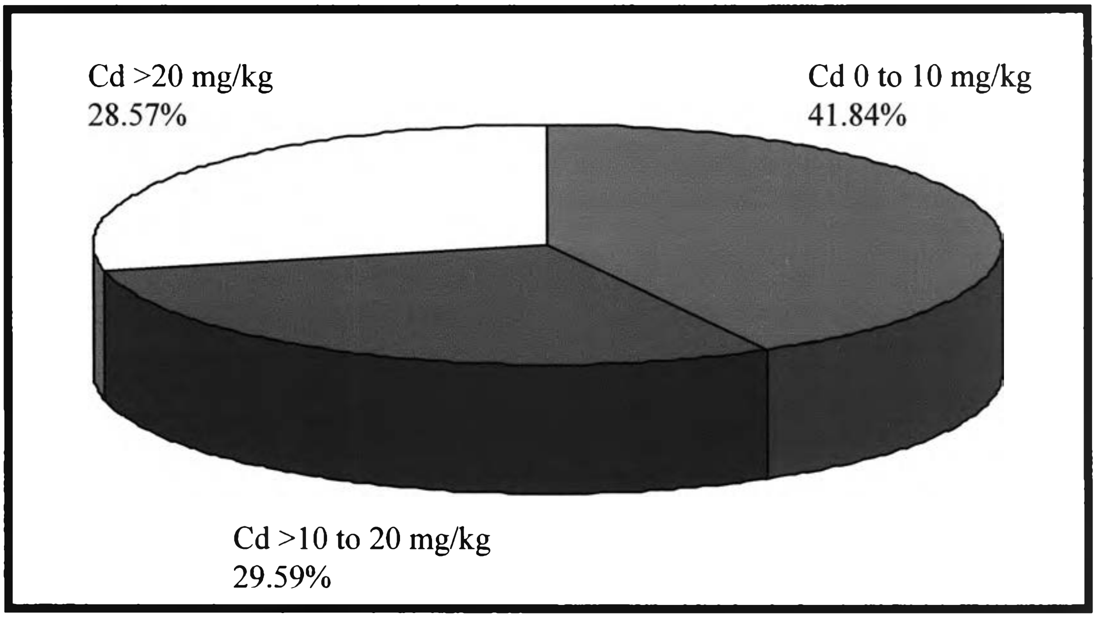


Figure 2.1 Frequency distribution of total soil Cd in Phatat Pha Daeng and Mae Tao Mai sub-districts, Mae Sot, Tak Province, Thailand.

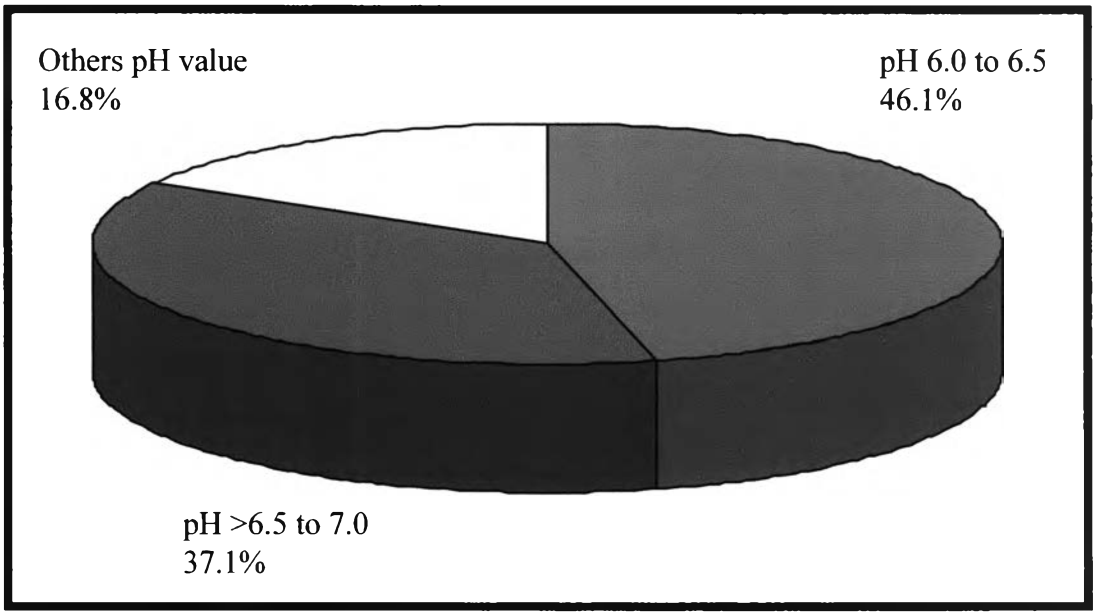


Figure 2.2 Frequency distribution of pH of 0 to 10 mg/kg soils in Phatat Pha Daeng and Mae Tao Mai sub-districts, Mae Sot, Tak Province, Thailand.

2.2 Theoretical Background

2.2.1 Source of heavy metals

Mining is one of the human activities which is a cause of heavy metals contamination in soil due to an open space from mining process and the disturbance to the stability of subsurface or natural background. Cadmium which is an element found associated with zinc is the major concern for contamination due to its released from the zinc mining activity. Cadmium is similar in many respects to zinc. Cadmium and its compounds are highly toxic. It is rare that preparation of cadmium in the laboratory should be required because of environmental concerns about cadmium. The isolation of cadmium is associated with zinc recovery as cadmium is an impurity in zinc ores as mentioned earlier.

Most zinc production is based upon sulfide ores. These are roasted in industrial plants to form zinc oxide, ZnO (http://www.du.edu/~jcalvert/phys/zinc.htm#Intr). This may be reduced with carbon to form zinc metal, but in practice ingenious technology is required to ensure that the resulting zinc does not contain oxide impurities. After this process, zinc may be refined by distillation under vacuum and this process also allows the separation of any cadmium present in the crude zinc. Before electrolysis is applied to produce zinc, cadmium impurities are removed as a precipitate (cadmium sulphate) by an addition of zinc dust. It has been known that to purify zinc mineral is too difficult and complicate, so some path of zinc mineral will be released together with cadmium and other minerals. Zinc and cadmium which were released from the zinc-mine are almost in metal sediments, zinc as zinc sulfide and cadmium as cadmium sulfide (http://www.du.edu/~jcalvert/phys/zinc.htm#Intr). This waste stream with metal sediment was contaminating the agriculture area in the study area, which make the cadmium concentration in the contaminated area to be extremely high.

2.2.2 Redox potential

Redox potential is the main characteristic of the soil which plays an important role in the uptake of cadmium in rice plants. In planted soil, an increase redox potential caused by drainage while a decrease of redox potential can be occurred in flooding condition or reducing condition. In the condition of drainage where redox potential is increased, the activity of the oxidized components also increases. As a consequence, cadmium in non-soluble form will be reduced to cadmium ions, which is a soluble form, and leads to an extremely increase cadmium phyto-availability (Simmons et al., 2003). In the opposite way, during flooding the redox potential is decreased and the activity of the reducing component also increases. Consequently, cadmium ions or cadmium in soluble form will be oxidized to cadmium in non-soluble form and results to decrease its phyto-availability for rice plants uptake. So, drainage at the grain fill stage is believed to be an important cause for high amounts of cadmium to be absorbed in rice plants due to high levels of cadmium phyto-availability.

2.2.3 pH

In general, pH of soil and soil solution refer to the concentration of proton or hydrogen ions in the solution present in soil pores and in soil solution respectively. It is in dynamic equilibrium with the predominantly negatively charged surfaces of soil particles. Thus soil pH can be affected by changes in redox potential which occur in soils that become waterlogged periodically. Reducing conditions generally cause an increase in pH, while an oxidation brings about a decrease of pH (Simmons et al., 2003). Most of heavy metal cations have higher mobility under acid conditions (low pH) and lower mobility under basic conditions (high pH). Soils generally have pH values within the range 4-8.5, owing to the buffering by Aluminium at the lower end and by $CaCO_3$ at the upper end of the range (Alloway, 1990).

2.2.4 Organic matter

Many studies show that organic matter can decrease cadmium phyto-availability (Pinto et al., 2004, Kashem et at., 2001b). Organic matter creates cadmium organic ligands complexation which less soluble, immobilize and decrease phyto-availability of the metals in soil solution. Organic matter addition in paddy soil will transform soluble cadmium and other forms of cadmium to metal-organic complex, which cannot or less uptake to plants (Kashem et al., 2001b). Organic matter which commonly used in agriculture works is animal manure, which can inhibit cadmium uptake by plants and also be a nutrients source for plants.

2.2.5 Human health effects of cadmium

Many studies show that cadmium intake and accumulation in human body is increasing the probability of renal dysfunction. Itai-Itai disease in Japan is one of the most important case studies of human health affected by long-term consumption of cadmium contaminated food. Cadmium is known to accumulate in kidneys, and it has a very long half-life in the human body, range from 10 to 33 years (Kawada and Suzuki, 1998). Cadmium pathway to human are soil → plants → human and soil → plants → animals → human. Cadmium-rich soil generally results in cadmium-rich food and higher cadmium intake and accumulation in human body (kidney). Cadmium intake to human mostly comes from food, beverages, and cigarettes, which originate in soils. Rice is the most common food in Thailand, cadmium contamination in rice cause extremely harm to human health who consume rice as their main food. So, rice cadmium contamination is one of the most concerned health problems in Thailand.

2.2.6 Rice plant growing process

There are 2 rice plant cultivars in Thailand. The major difference between 2 cultivars is life time of rice plants, 120 days and 150 days. The rice plants genotype used in the experiment is Thai Jasmine Rice 105 or in official name Thai Hom Mali

105, which is the 120 days life time. Rice plant consists of 4 major parts, which are tiller, leaf blade and leaf sheath, stem, and panicle.

The rice growing process consists of 3 main periods from the total of 9 stages, which are vegetative growth period, reproductive growth period, and maturity period as shown in Figure 2.3 (Datta and Surait, 1981). The vegetative growth period is approximately 55 days, reproductive period is approximately 35 days, and maturity period is approximately 30 days. Farmers in the study area usually drain the water out of their crops during the reproductive growth period (grain fill stage, vary from 55 to 90 days after transplanting) to gain maximum yield, and rewet up their crops 1 week after drainage. The second drainage is in harvest period after rice plants produce the maturity grain. The rice growing stage is shown in Figure 2.4 (Datta and Surait, 1981). The 9 stage of rice growing process are described as followed;

Stage1 *seedling stage*: includes the period from emergence until just before the appearance of the first tiller.

Stage2: *tillering stage*: follows the seedling stage, and starts with the appearance of the first tiller from the axillary bud in one of the lowermost nodes.

Stage 3: *stem elongation stage*: begins before panicle initiation in long growth-duration varieties and it usually occurs during the later part of the tillering stage. In short-growth-duration varieties, stem elongation and panicle development occur simultaneously

Stage 4: *panicle initiation:* begins when the primordium of the panicle has differentiated and becomes visible

Stage 5: *panicle development:* the spikelets become distinguishable and the panicle extends upward inside the flag leaf sheath

Stage 6: *flowering (anthesis)*: begins with protrusions of the first dehiscing anthers in the terminal spikelets

Stage 7: *milk grain stage*: the contents of the caryopsis (the starch portion of the grain) are first watery but later turn milky in consistency

Stage 8: *dough grain stage*: the milky portion of the grain turns first into a soft, and later hard dough

Stage 9: *mature grain stage*: grain color in the panicles begins to change from green to yellow

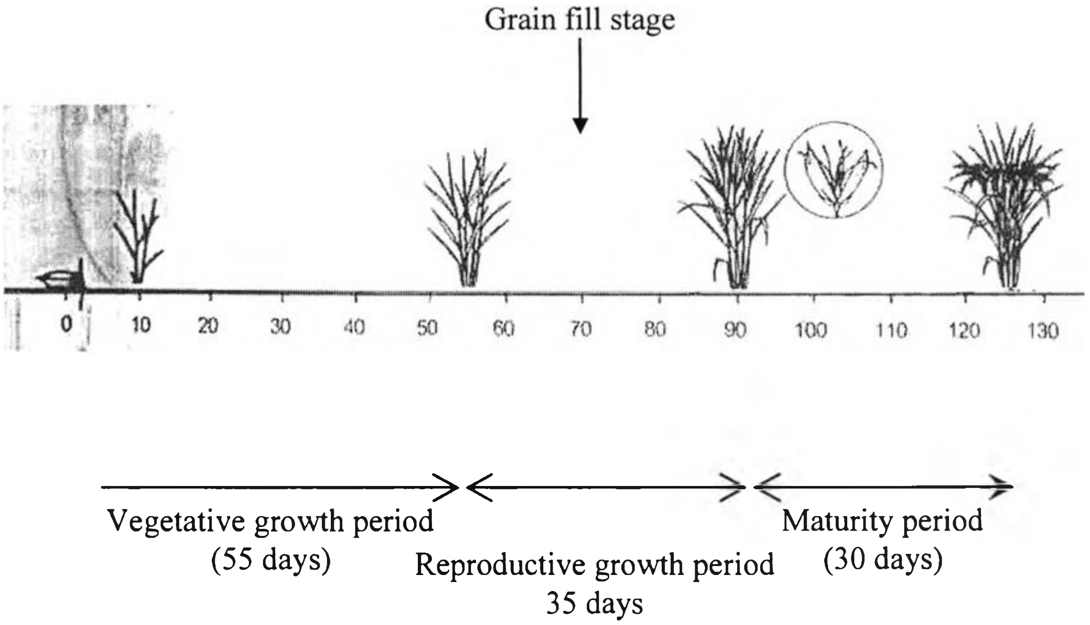
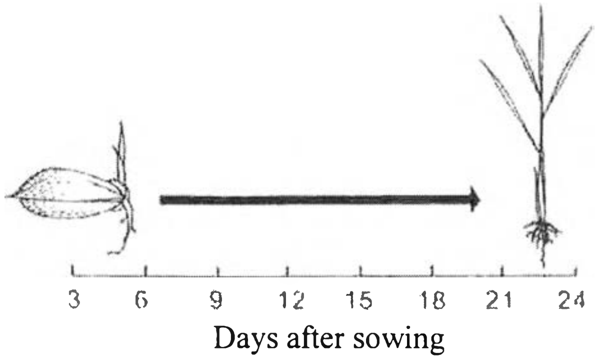


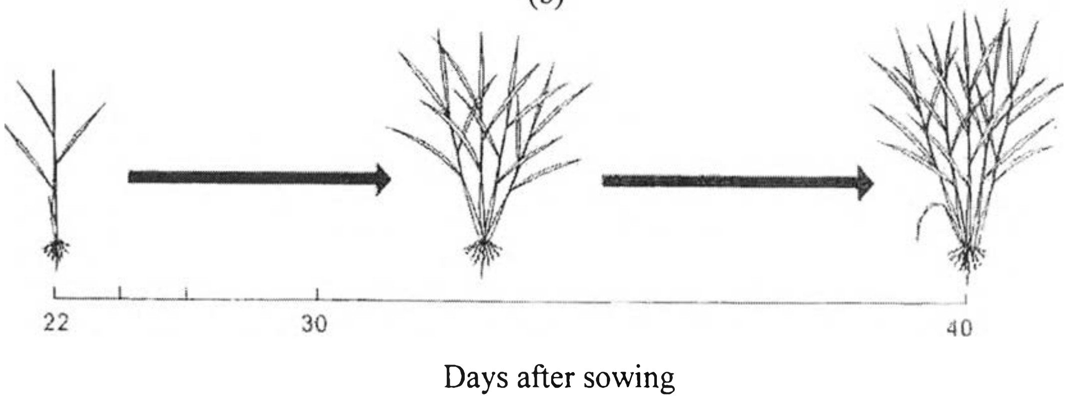
Figure 2.3: **Rice plant growing process**

(Adapt from Datta and Surait, 1981)

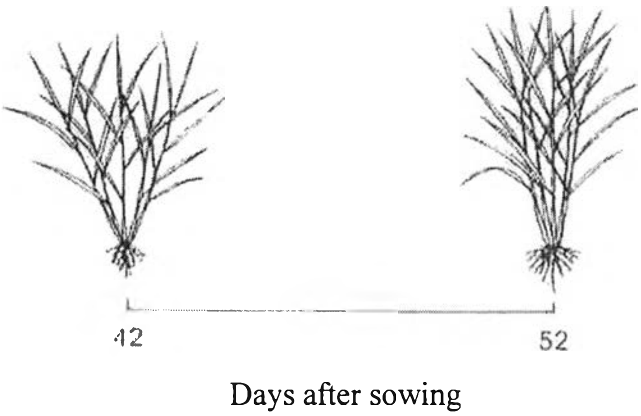
(a)


3
6
9
12
15
18
21
24
Days after sowing

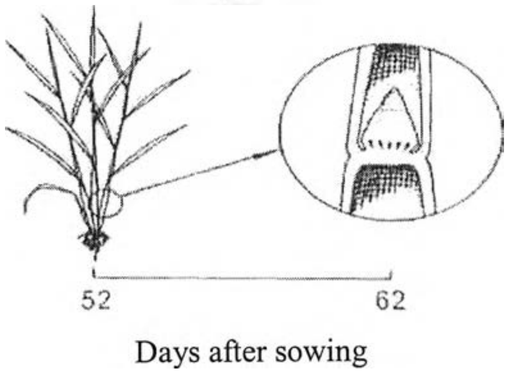
(b)


22
30
40
Days after sowing

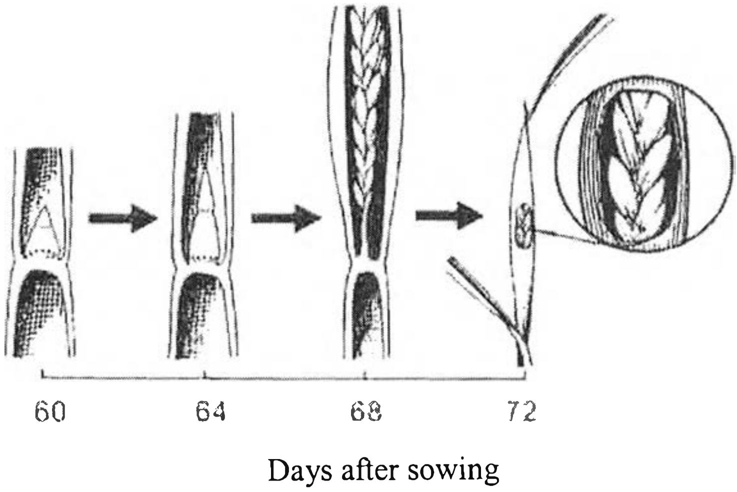
(c)


42
52
Days after sowing

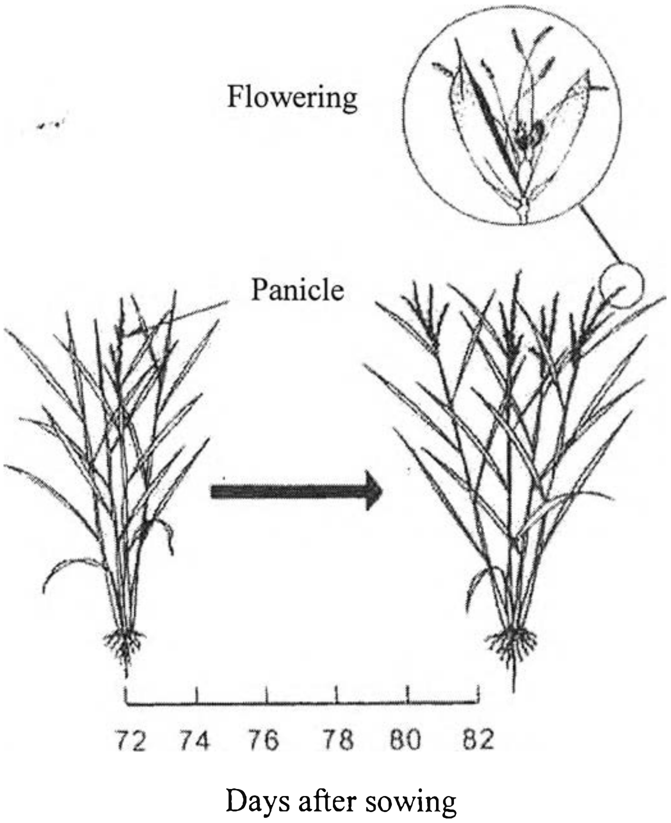
(d)



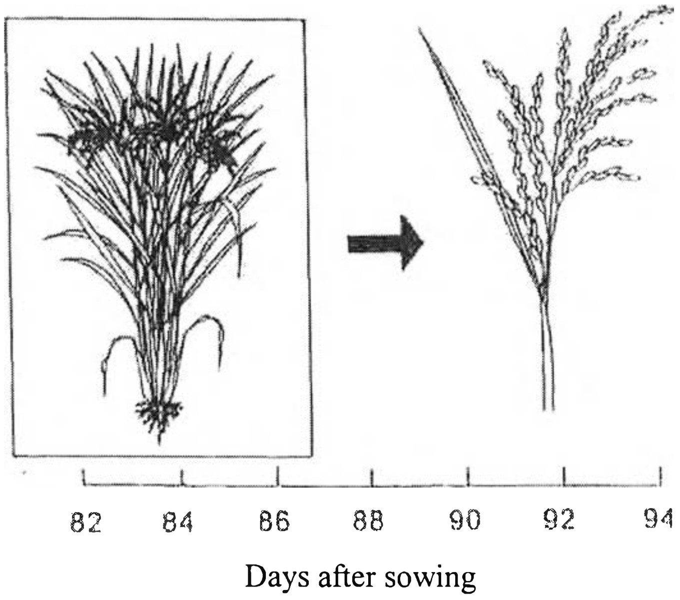
(e)



(f)


Flowering
Panicle
72
74
76
78
80
82
Days after sowing

(g)


82
84
86
88
90
92
94
Days after sowing

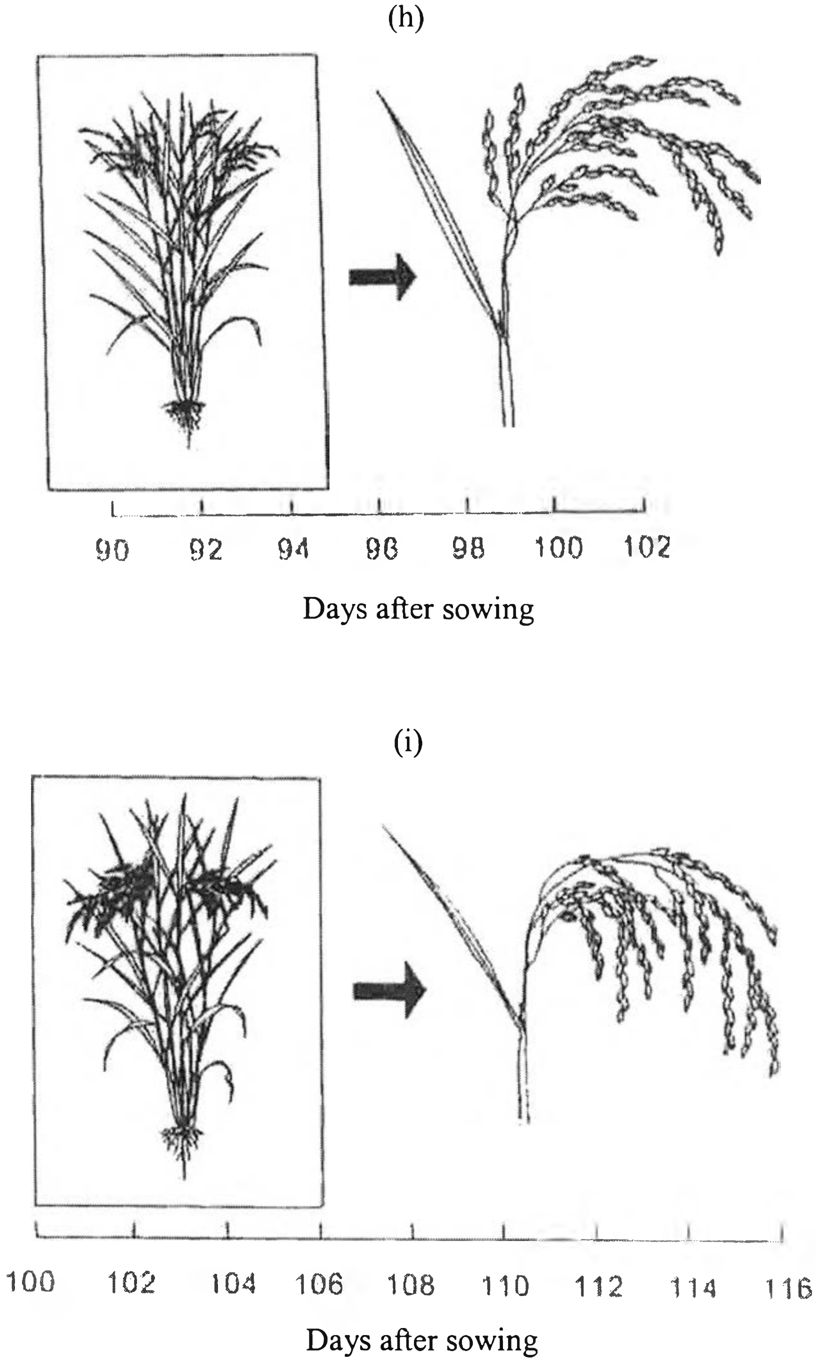


Figure 2.4: **Rice plant growing stages**;

(a) seedling stage
(b) tillering stage
(c) stem elongation stage
(d) panicle initiation stage
(e) panicle development stage
(f) flowering (anthesis) stage
(g) milk grain stage
(h) dough grain stage
(i) mature grain stage

(Adapted from Datta and Surait, 1981)

2.3 Related Previous Studies

The human health and environmental impacts of cadmium contaminations are of high concern. Cadmium is a heavy metal which can accumulate in humans, soil and plants. Cadmium in the food chain is one of the most dangerous elements. The interactions affecting the mobility of cadmium, zinc, and ferrous in paddy soils and their uptake by rice plants are not yet fully understood. Previous research has found that amounts of dietary of zinc, ferrous, and to a lesser extent calcium is known to influence the absorption of cadmium and its distribution in organs and tissues (Berglund et al., 1994; Brzóska and Moniuszko-Jakoniuk, 1997; Chaney et al., 2001). Cadmium-caused health risks associated with the long-term consumption of cadmium contaminated rice grains are made worse by rice grain ferrous, zinc and calcium contents which are insufficient for human needs (Hallberg et al., 1977; Pederson and Eggum, 1983).

Several studies reveal that there is a relationship between soil pH and reducing conditions that influence the bioavailability of cadmium uptake to plants. Maintaining flood conditions (reducing conditions) in cadmium contaminated soil during the critical grain fill stage has been shown to significantly decrease the uptake and accumulation of cadmium in rice grain. Under submerged conditions cadmium and zinc are effectively immobilized by their precipitation as cadmium and zinc sulfide minerals (Iimura et al., 1981). In addition, submerged conditions raise soil pH in acid soils, which further decreases cadmium and zinc phyto-availability (Chaney et al., 1996). Drainage of paddy soil at the grain fill stage is a common practice used by farmers to optimize rice grain yield and to facilitate harvesting. Drainage causes the oxidation of soils and results in the rapid mobilization of phyto-available cadmium, caused by the rapid transformation of cadmium and zinc sulfide to cadmium and zinc ion (Iimura et al., 1981; Chaney et al., 1996). The increased acidity also leads to the desorption of cadmium from soil organic matter (Zachara et al., 1992). Further more, drainage decreases soil pH which then further increases cadmium phyto-availability to rice plants at this critical stage (Chaney et al., 1996).

In addition, under Fe-deficiency stress, rice root will excrete solution called Phytosiderophores (PS), which can change cadmium in rhizosphere soil to a soluble form, which cause effective uptake and transport of cadmium by rice plants. Some techniques used to prevent the decreasing of soil pH, which causes increased cadmium phyto-availability. For example, liming agent has been added to contaminated soils to maintain pH as neutral and reduces cadmium via the precipitation of cadmium carbonate.

Redox potential is one of the soil characteristics, which highly effect cadmium phyto-availability. Some studies show that high redox potential and low pH cause extremely high cadmium concentrations in rice grains even though cadmium concentration in contaminated soil is quite low (Iimura et al., 1981). Some studies also show that manganese is one of the variables which affect cadmium uptake by rice plants. Organic matter addition in paddy soils to inhibit cadmium uptake to plants had been studied from many researchers. Organic matter create metal-organic complex with cadmium which immobilize and less phyto-availability to plants (Pinto et al., 2004).

Lin et al. (2003) studied the "Chemical behavior of Cd in rice rhizosphere". Their research investigated Cd concentration in soils at the root surface (rhizosphere) and in other soil regions around root surface. Soil samples were collected from the rhizosphere and other regions at varying distance from the root surfaces. NH_4OAc was used as an extracting solution for soil samples. Thier results found that extractable Cd in rhizosphere was lower than that in bulk soil. That maybe caused by the exudates of rice plant roots, which changed Cd in extractable form to complex form. Howevr, the extractable Cd in rhizosphere was a little higher than in soil located 0-10 mm from rhizosphere. They conclude that the difference in extractable Cd was greatly influenced by the combined effects of mass flow, activation and fixation.

Welch et al. (1999) studied the "Effect of nutrient solution zinc activity on net uptake, translocation, and root export of cadmium and zinc by separated sections of intact durum wheat (Triticum turgidum L. var durum) seedling roots". This research studied the effects of Zn addition on Cd uptake and translocation by durum wheat. Each plant was grown using the "split–root" technique, where each plant is grown in 2 separated pots. One pot had no Cd addition and the other pot had an addition of 0.2 μM Cd. Zn was also added to each pot at different concentration ranging from 1 - 19μM. A mixture of HNO_3 and $HClO_4$ in a ratio of 1:1 was used as acid for samples digestion. Their result shows that the highest Cd concentrations were found in the plants with the addition by low levels of Zn concentration. The Cd translocation between root sections was also highest in the plants with which both root sections were Zn deficient. Their finding out was explained by the fact that there is a competition between Zn and Cd transport at the plasma membrane of root cells and Zn could inhibit Cd uptake in rice plants. This research also found that increasing the activity of Zn^{2+} in phloem source cells can reduce the amount of Cd transferred from phloem source to phloem sink (grain).

Simmons et al. (2003) studied "The relative exclusion of zinc and iron from rice grain in relation to rice grain cadmium as compared to soybean: Implication for human health". This research investigated the mechanism affects Cd uptake by rice plants. In November 2000, rice plants were collected from 43 Cd/Zn co-contaminated fields, 20-30 rice plants were collected randomly in each field. In May 2002, 10-20 soil samples from each field were collected from 30 Cd/Zn co-contaminated fields as soil cores at 0-20 cm depth. Soil samples were digested in aqua-regia (3:1 HCl: HNO_3) using an open tube digestion method (McGrath and Cunliffe, 1985). Plant samples were digested in HNO_3-$HClO_4$ (2:1), using an open tube digestion technique. This research found that flooding soils raises soil pH in acid soils, which further reduces Cd and Zn phyto-availability. Drainage and oxidation in paddy soils prior to the grain fill stage to maximize rice grain yield and facilitate harvesting results in the rapid transformation of CdS and ZnS to Cd^{2+}, Zn^{2+}, and SO_4^{2-}. Cadmium sulfide transforms more readily than ZnS and providing Cd^{2+} to be available for uptake. So, the drainage technique employed to get maximum yields causes extremely high Cd uptake by rice plants. In addition, they found that soil pH is a major factor which controls the mobility of Cd in soils. Liming agents are a variable option to reduce the phyto-availability of Cd, where octavite ($CdCO_3$) precipitation is the major factor controlling Cd solubility.

Liu et al. (2003) studied the "Interaction of Cd and five mineral nutrients for uptake and accumulation in different rice cultivars and genotypes". This research studied the effect of Fe, Zn, Mn, Cu, and Mg on Cd uptake in different rice cultivars and genotypes. The research was conducted in the greenhouse of Yangzhou University, where 20 rice cultivars of different genotypes were planted. The plant samples were digested following the HNO_3-$HClO_4$ (4:1) procedure and then analyzed with an Optical Absorption Spectrophotometer (Perkin Elmer 2100, Germany). This research found that the ability of roots to absorb Cd may depend on both the activity of roots and the interaction between roots and soils. The proportion of bioavailable Cd was significantly affected by the redox potential in paddy soil, corresponding to the reduction of sulfates to sulfides, binding to organisms, binding with iron and manganese oxide, and absorption by soil granules. The root exudates, phytosiderophores (PS), which roots excrete under Fe-deficiency stress, can chelate Cd to form soluble PS-Cd chelate complexes, and mobilize effectively insoluble CdS in rhizosphere soil, that increases Cd uptake and transportation by plants.