CHAPTER 1

INTRODUCTION

1.1 Cadmium and the environmental concerns

Cadmium belongs to group IIB of the Periodic Table and is a relatively rare metal, being 67th in order of element abundance. Unlike Pb, Cu and Hg which have been utilized for centuries, Cd has only been widely used in this century. It is obtained as a by-product of the smelting of Zn and other metals, such as Cu and Pb. Its principle uses are : (1) as a protective plating on steel (2) as a constituent in various alloys (3)as a constituent in pigments for plastics, enamels and glazes (4) as a stabilizer for plastics, particularly PVC. (5) as a constituent in Ni-Cd dry cell bateries (Alloway, 1990).

Despite its usefulness in industrial aspect, Cd has no essential biological function, and is highly toxic to plants and animals. However, the concentrations of Cd normally found in the environment do not cause acute toxicity. The major hazard to human health of Cd is its chronic accumulation in the kidneys where it can cause dysfunction if the concentration in the kidney cortex exceeds 200 mg/kg fresh weight. Although tobacco smoking and occupational exposures to CdO fume are important sources of this metal, the main route by which Cd enters the body is via food. The only clearly established case of soil and water pollution causing Cd poisoning in people was among rice farmers in the Jinsu Valley, in the Toyama Prefecture of Japan. A Pb-Zn mine had been causing extensive pollution of the river water and paddy soils in the flood plain of the Jinsu Vally for many years. During and after the Second World War, more than 200 elderly women, who have several children, developed skeletal deformations and kidney damage and 65 of them died. This condition ('itai-itai' disease) was primarily caused by Cd toxicity, exacerbated by dietary deficiencies of Ca, vitamin D and protein, plus the effect of pregnancies and aging. Both the locally grown rice and the drinking water had been markedly contaminated with Cd. Average Cd contents in rice were 10 times higher than local controls (0.7 mg/kg and 0.07 mg/kg fresh weight, respectively), with a maximum of 3.4 mg/kg Cd (Alloway, 1990).

Like other heavy metals, the risk of Cd contamination in the environment is mainly from anthropogenic sources (Furgusson, 1990). Non-ferrous metal mine can be a significant source of local Cd contamination, particularly those which exploit Zn and Pb ores. Zn ores invariably contain the most Cd but the actual content varies widely between different ore bodies. This factor together with mining practices, local topography and drainage all influence the intensity of contamination. Airborne contamination can arise from the wind blown dispersal of metal-rich spoil heaps, while water-borne transport of cadmium-rich material may result in contamination of agricultural land some distance downstream of the mine. Cd is extracted as a by-product during the refining of Zn ores. The two basic processes of Zn production, thermal smelting and electrolytic refining, produce different kinds of Cd-rich discharge. Thermal smelters are responsible for much larger atmospheric emission of Cd and also produce liquid wastes rich in Cd which require safe disposal. In contrast, the only major wastes associated with electrolytic plants are solid leach residues (Hutchinson and Meema, 1987).

In Thailand, the major Zn production is in Tak province. Zn smelter started operation in 1984, and seven years later Cd was produced with capacity of 850 tons/year. The metals were refined from Zinc silicate and Zinc carbonate, which contained 23% Zn and 0.23-0.38% Cd (Theerapunsatien, 1995). Wherever ZnS, $ZnCO_3$ or other sulfide ores are mined or smelted, there exists the possibility of Cd pollution (Alloway, 1990). Zinc production by electrolytic process in the same province has released large volume of Cd-contaminating wastewater. In addition, dust from smelter and wastes or tailings may contaminate the nearby area (Theerapunsatien, 1995).

Disposal of sewage sludge, which contains human excretion, domestic products and industrial effluents, is a problem facing municipalities around the world. Quantities of this biosolid continue to increase with increases in population density in cities. One alternative to disposal is recycling by agricultural utilization (Mortvedt, 1996). However, application of sewage sludge may contribute to Cd and other heavy metals contamination in agricultural land (Alloway, 1990; Jing and Logan, 1992; Lamy, Bourgeois and Bermond, 1993). The metal concentrations in these sludges are highly variable, owing to continual changes in the

composition and volume of effluent discharged into sewers. Concentrations ranging from < 1 to 3,650 mg Cd/kg in the dry matter have been reported for sewage sludges in western Europe and North America (Alloway, 1990). Sludges low in Cd and other contaminants have lower risk of food chain contamination than more contaminated ones at the same application rate (Jing and Logan, 1992). Therefore, several countries have introduced controls on the metal concentrations. The commission of the EC issued a directive specifying mandatory and recommended limits of 40 and 20 mg Cd/kg dry weight, respectively, for sewage sludges applied to agricultural soils, whereas the maximum annual load of Cd in the USA. is 1.9 kg/ha/year (Mortvedt, 1996).

In addition, phosphate fertilizers have been concerned as the entry of Cd into the human food chain via the application in the agricultural lands because phosphorites which are raw materials for the manufacture of fertilizers contain relatively high contents of Cd (Alloway, 1990; Fergusson, 1990; Sanchez-Martin and Sanchez-Camazano, 1993). Phosphate fertilizers have been estimated to account for 54-58 % Cd input into soils of western countries (Alloway, 1990). However, Mortvedt (1996) showed that plant uptake of Cd contaminants in the fertilizers was negligible and it would take 1,300 years of phosphate applications at a rate of 20 kg P/ha to reach the tolerable Cd limit (4.5 kg/ha) assuming an average Cd concentration of 0.5 mg/kg. This calculation ignored other possible Cd inputs to agricultural soils, such as sewage sludges and atmospheric deposition. In spite of that, many countries have set their regulations on Cd concentration in phosphate fertilizers.

Moreover, the relatively high volatility of Cd when heated above 400^{0} C accounts for the significance of atmospheric emissions from the non-ferrous metal production, fossil fuel combustion, refuse incineration and iron and steel production. Cd concentrations in air depend on the distance from emitting sources (Alloway, 1990). Then Cd may deposit to the land by both dry and wet deposition. Cd concentration in excess of 1,700 ppm was measured in soils near Zn smelters. At distances of 16 and 21 km from the emission sources the concentration of Cd reached the background levels of 5 and 7 ppm, respectively (Haghiri, 1974).

When reaching soil, the fate of Cd is controlled by many relating factors including its chemical forms (Lamy, Bourgeois and Bermond,1993; Chlopecka, 1996), soil pH, CEC, Clay mineral (Sanchez-Martin and Sanchez-Camazano, 1993) and other metal ions (Alloway, 1990). The metal can be found in soil in a number of forms, such as dissolved in the soil solution, electrostatically adsorbed in the colloid fraction (associated with clay minerals, oxides, and organic matter), sulphate or carbonate precipitates, and soluble or insoluble organic matter chelates (Sanchez-Martin and Sanchez-Camazano, 1993). Chlopecka et al. (1996) identified forms of Cd in contaminated soils from southwest Poland. It was found that the samples with Cd above background level to maximum tolerable level (> 0.5 - ≤ 3.0 mg/kg) and in excess of maximum tolerable level (> 3.0 mg/kg) was exchangeable form, the more phytoavailable form, with 48.7% and 32.5% , respectively, while residual fraction probably resided in primary minerals (58.7%) predominated in samples with background level of Cd (< 0.5 mg/kg). Soil pH also influences the chemical form of Cd. That is, for acid soil samples (pH < 5.6) a mean value of 44% of the fractional sum of Cd is associated with the exchangeable form, as opposed to 29% for the slightly acid to circumneutral soil samples (pH >5.6). Cadmium added to soil as carbonate is relatively mobile in acidic conditions and within a few years or less may pass to the exchangeable form (Chlopecka et al., 1996). Soil with high pH values favors the exchange of Cd by other cations – particularly divalent cations, thereby decreasing the Cd mobility. Moreover, the cation exchange capacity (CEC) as well as the soil properties relating to it, such as clay content, has strong influence on the Cd fate in soils. In soils with high CEC, Cd adsorption by the soil components prevails over its mobility, especially if the exchange complex of the soil concerned is saturated with divalent cations, and soils with high clay content favors retention by the constituent minerals (Sanchez-Martin and Sanchez-Camazano, 1993). As for the effect of organic matter, organic matter from sludge disposal reduced Cd retention by the soil across the pH range from 5 to 7 (Lamy et al., 1993). However, Sanchez-Martin and Sanchez-Camazano (1993) showed that Cd mobility is more closely related to the nature of the organic matter than it is to its content. While highly humified organic matter (C/N $\leq$ 15) favors retention over mobility, less humified organic matter (C/N > 15) contains abundant soluble fractions that favor formation of soluble complexes with Cd, thereby increasing its mobility. Christensen (1996) found that Cd solubility in calcareous soils (carbonate-rich soils) is not likely to be controlled by precipitation of $CdCO_3$

because dissolved organic carbon acts as a precipitation inhibitor and is the reason for the apparent lack of $CdCO_3$ precipitation in Cd-amended soils. Another factor controlling the fate of Cd is the effect of other metal ions. Alloway (1990) reported that competition with other metal ions, such as Zn, Ca, Co, Cr, Cu, Ni and Pb can inhibit the adsorption of Cd. Among these ions, Zn had the greatest inhibitory effect.

It is evident that metals including Cd from anthropogenic sources are potentially more mobile than those that are ultimately inherited from the geological parent material (Chlopecka et al, 1996) Furthermore, Cd is generally recognized to be the most mobile trace metal in soils. Consequently, it may cause many problems because the mobile form is phytoavailable and may pollute the waterways. Problems derived from Cd contamination in the long run are likely from discharge of wastewater or dumping of hazardous waste to waste or even arable land without appropriate treatment and management, particularly during economic crisis when economics, not environmental protection, comes first. Reduction of production cost is necessary for the survival of business. It is no doubt that treatment cost or any other budgets in environmental concerns is reduced or absolutely cut. This situation accompanying with weak regulations and penalties may cause serious environmental problems in the future.

Since Cd is much more toxic for humans than for plants, level of 0.5 mgCd/kg , which are not yet toxic for plants, must be considered as critical when the plants are used as nutriment or fodder (Sauerbeck, 1985 cited in Sticher, 1993). Furthermore, it is not possible to rely on the onset of visible symptoms of Cd toxicity to act as a warning when food crops have accumulated excessive amount of metals which could be hazardous to health. Relative large concentrations of Cd can accumulate in edible portions without the plant showing symptoms of stress (Chaney et al., 1977 cited in Alloway, 1990). Once entering the food web, the organisms take up the heavy metals from soil, water or sediment, and the metal concentration is magnified. This process is known as biomagnification. Organisms in higher trophic level may accumulate and concentrate the metals to the extent that they may cause adverse health effects. Theerapunsatien (1995), for example, found that mussel in the Ping river near sewers of the Zn refining factory contained 3.60-5.56 μg/g FW which exceeded the permissible limit.

In Thailand a number of researches involving heavy metals and plants have been focused on the uptake of metals by edible plants and the removal of metal ions in wastewater by aquatic plants. Few studies are emphasized on the physiological responses of plants exposed to toxic metals or the so called ' phytoremidiation' which is the use of plants as an alternative method for removing metals in polluted soil. In this study two cultivated vegetables, Kangkong (*Ipomoea aquatica* Forsk.) and Chinese Kale (*Brassica oleracea* L. cv group Chinese Kale) and two weeds, False daisy (*Eclipta prostrata* L.) and Swollen finger grass (*Chloris barbata* Sw.) were used as plant materials. Weeds were chosen to study the feasibility of using them for phytoremediation purpose, whilst cultivated vegetables were studied their uptake of metal. To achieve these goals, knowledge on physiological responses of plants under stress is necessary.

1.2 Objective

To study some physiological responses i.e. proline accumulation, chlorophyll content and plant growth of four selected species when exposed to Cd.

1.3 Scope of study

This study were conducted on four plant species grown by hydroponic technique in controlled environments. Cd concentrations of 5 and 20 ppm were tested but differed in the duration of study. The Cd treatment was performed when the plants had vigorous growth, approximately one month after growing in nutrient solution, and the experiment lasted for fourteen days after the plants being removed to Cd-free solution.

1.4 Anticipated benefits

1. It may provide a basis for further study in order to understand the physiological responses of plants when exposed to Cd.

2. It may partly be used as a guidance for selecting metal tolerant plants which may be used for cleaning contaminated soil.