CHAPTER 2

Literature Review

2.1 Mae Sot District

Mae Sot is a district in western Thailand that shares a border with Burma to the west. It is notable as a trade hub and for its substantial population of Burmese migrants and refugees. The town is part of Tak Province and is the main gateway between Thailand and Burma. Neighboring districts are (from north clockwise): Mae Ramat, Mueang Tak, and Phop Phra. The Moei River serves as a natural border between Mae Sot and the Burmese town of Myawaddy (Figure 1).

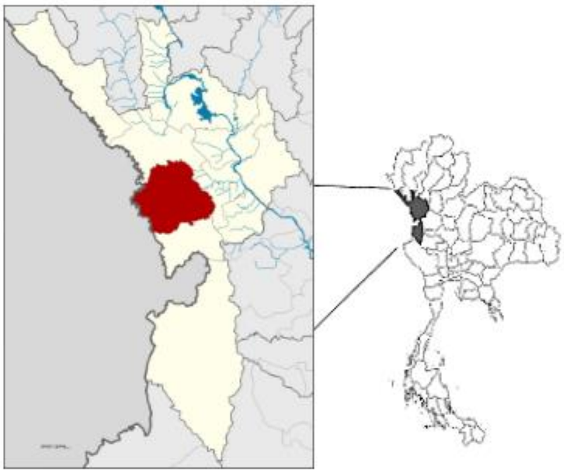

Figure 1 Mae Sot district, Tak Province, Thailand

The district (Amphoe) Mae Sot is subdivided into 10 sub-districts (Tambon), which are further subdivided into 86 villages (Muban). The city (thesaban nakhon) Mae Sot covers the whole tambon Mae Sot. Tha Sai Luat and Mae Ku are subdistrict municipalities (thesaban tambon). There are further nine tambon administrative organizations (TAO).

There are plans to create a new province, covering the five border districts of Tak Province. Additionally the town is planned to be converted into a metropolis, covering the tambon Mae Sot, Mae Pa, and Tha Sai Luat.

2.2 Zinc mining and health hisk management for cadmium contamination in Thailand

In Thailand, zinc deposit at Pha Daeng, Mae Sot is the lagest zinc deposit in Thailand. The ore are zinc carbonate and zinc silicate in the supergene enrichment in the Jurassic Kamawkala limestone near the Thai-Myanmar border (Thamjedsada and Chaiwiwatworakul, 2012). Around 1977, zinc mining activities of 3 companies were started after the Department of Mineral Reources, Ministry of Industry (International Water Management Institute, 2003) classified this area as the richest source of zinc minerals in Thailand. However, only one company has remained in the area and its gross income and profit is shown in table 1.

Table 1 Gross income and profit of the only zinc mining company in Mae Sot, Tak, 1999 - 2004 (Social Research Institute, Chiang Mai University, Thailand 2006)

Year	Gross Income in Millions Bahts (US$: 1 US$ = 40 Bahts)	Net Profit in Millions Bahts (US$: 1 US$ = 40 Bahts)
1999	4,462 (110,550,000)	145 (3,625,000)
2000	5,315 (132,875,000)	211 (5,275,000)
2001	5,222 (130,550,000)	335 (8,375,000)
2002	4,406 (110,150,000)	-29 (-725,000)
2003	4,932 (123,300,000)	284 (7,100,000)
2004	5,715 (142,875,000)	217 (5,425,000)

The Office of Environmental Policy and Planning, Ministry of Natural Resource and Environment (MNRE) is mandated to review and approve the environmental impact assessment (EIA) of 22 hazardous industries for primary prevention of industrial pollution. If once pollution is suspected, the Department of Pollution Control (DPC) is called for investigation, control activity or closed the industry.

In November 2003, Department of Agriculture (DOA), Ministry of Agriculture (MOA) sent a summary report of a 6-year study revealing serious contamination of cadmium to soil and rice grown in the vicinity of a large zinc mine to Department of Pollution Control (DPC). From the International Water Management Institute, Kasetsart University research by Simmon *et al*., in 2005 report agricultural crop from Phatat Pha Daeng and Mae Tao Mai sub-districts that irrigated by Mae Tao Creek the upper stretches of which pass through an actively mined Zn-mineralized zone. Rice grain Cd concentrations for the 1,067 fields sampled during the same period ranged from <0.01 – 7.75 mg Cd kg^{-1} with 67.5% of the fields sampled producing rice grain with Cd concentrations exceeding of 0.4 mg kg^{-1} (0.4 mg Cd kg^{-1} rice grain set by the Codex Alimentarius Commission in 2006).

Table 2 Frequency distribution (n=1067) and summary statistics of rice grain Cd in ‘high risk’ areas of Phatat Pha Daeng and Mae Tao Mai sub-districts, Mae Sot, Tak Province, Thailand (Simmon *et al*., 2005).

Rice grain Cd (mg kg^{-1})	Mean (±1 Standard Error)	Number of Fields	Frequency (%)
<0.4*	0.187 (±0.006)	347	32.52
>0.4 - 1.0	0.672 (±0.009)	324	30.37
>1.0 - 2.0	1.409 (±0.017)	241	22.59
>2.0 - 3.0	2.378 (±0.028)	100	9.37
>3.0 - 4.0	3.303 (±0.049)	31	2.97
>4.0 - 5.0	4.37 (±0.052)	15	1.41
>5.0	5.717 (±0.217)	9	0.84
Total 1067		100	

From January to April 2004, using GIS mapping based on cadmium concentration gradient in soil and rice provided by MOA/IWMI research team (Simmons *et.al*, 2005) DPC staffs collected environmental samples from Mae Tao Creek, surface water, underground water, well water, soil, rice and fish.

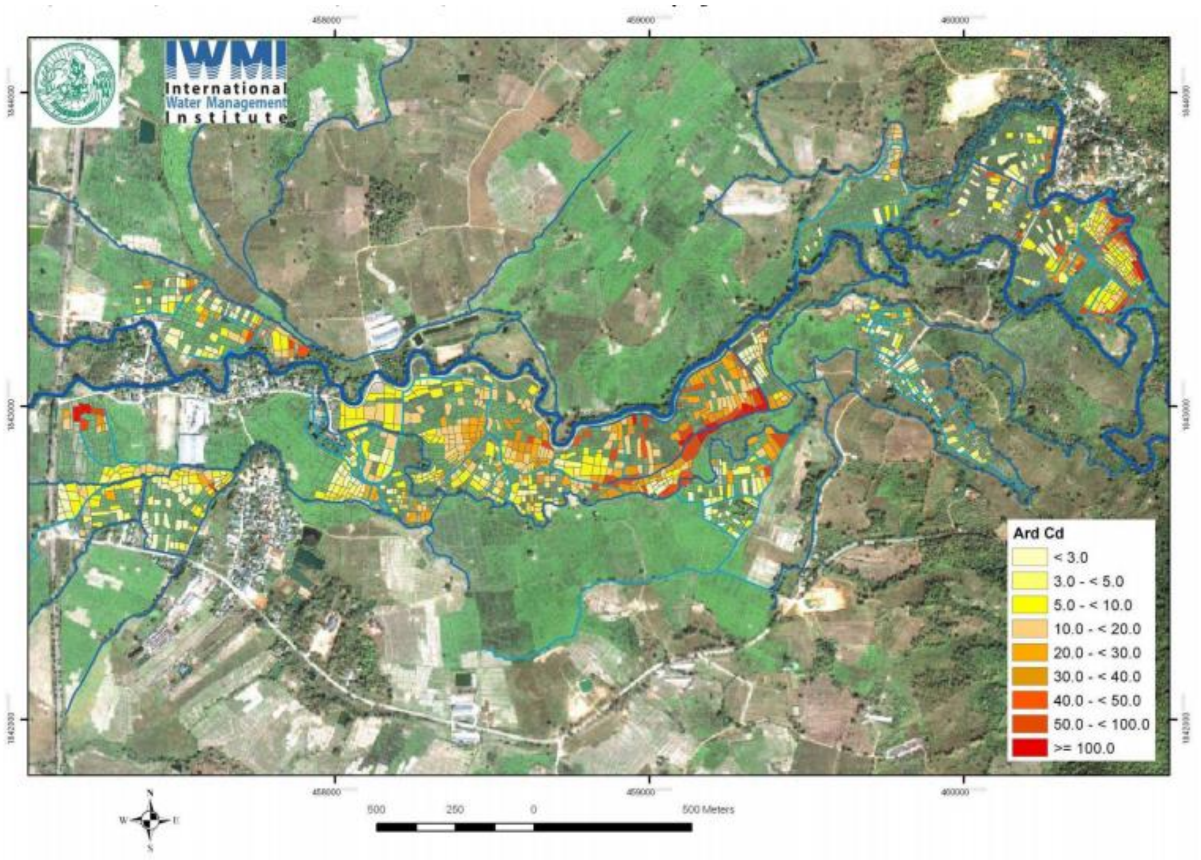

Figure 2 Total soil Cd (mg kg^{-1}) in 1,090 fields of Phatat Pha Daeng and Mae Tao Mai sub-districts, Mae Sot, Tak Province, Thailand: data derived from IWMI-DOA (2001-2003) and IWMI-LDD (2004-2005) collaborative research projects.

In 2004, after data on environmental samplings from DPC and preliminary results of population survey from Mae Sot hospital were available, an initial risk management plan was set up under auspice of special committee led by DPC. Based on the cadmium level found in soil, DPC suggested discontinuation of rice cultivation in the area. This solution was fully supported by health staffs. The local administration gave financial compensation to the residents based on the amount of rice stored from 2003 cultivation and the number of rice paddy fields owned. However, the cadmium contamination problem in Mae Sot District remains unresolved and the villagers still grow some food crops in contamination area. From the International Health Policy Program, Ministry of Public Health, Thailand report Cd exposed data include Cd and β2–microglobulin (β2-MG) in urine of the villager in contamination area. Compared to the general Thai population, Mae Sot residents gained 10–86% disability adjusted life years (DALYs) from nephrosis/nephritis, heart diseases, osteoporosis and cancer depending on their Cd exposure type and exposure level (Songprasert *et al*., 2015) .

2.3 Cadmium (Cd)

2.3.1 Basic Information

Cadmium is a chemical element with symbol Cd and atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury. Like zinc, it prefers oxidation state +2 in most of its compounds and like mercury it shows a low melting point compared to transition metals. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. The average concentration of cadmium in Earth's crust is between 0.1 and 0.5 parts per million (ppm).

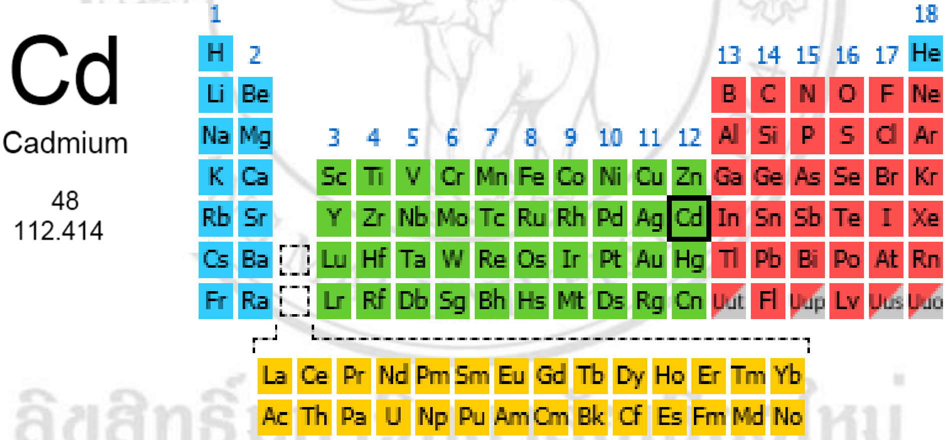

Figure 3 Cadmium in periodic table

It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany, as an impurity in zinc carbonate. Cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. It was used for a long time as a pigment and for corrosion-resistant plating on steel, whereas cadmium compounds were used to stabilize plastic. The use of cadmium is generally decreasing due to its toxicity (Morrow, 2010)

Table 3 General information of cadmium (Morrow, 2010)

Group	12	**Melting point**	321.069°C, 609.924°F, 594.219 K
Period	5	**Boiling point**	767°C, 1413°F, 1040 K
Block	d	**Density (g cm^{-3})**	8.69
Atomic number	48	**Relative atomic mass**	112.414
State at 20°C	Solid	**Key isotopes**	^{114}Cd
Electron configuration	[Kr] $4d^{10}5s^2$	**CAS number**	7440-43-9

2.3.2 Cadmium used and cadmium in natural

Applications

About three-fourths of Cd is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cd has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission (Sikry *et al.*, 2015).

Cadmium in the environment

Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cd also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides. Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. No cadmium ore is mined for the metal, because more than enough is produced as a byproduct of the smelting of zinc from its ore, sphelerite (ZnS), in which CdS is a significant impurity, making up as much as 3%. Consequently, the main mining areas are those associated with zinc. World production is around 14.000 tons per year, the main producing country is Canada, with the USA, Australia, Mexico, Japan and Peru also being the major suppliers (U.S. Geological Survey, 2015).

2.3.3 Cadmium distribution and accumulation in living organism

Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are for instance zinc production, phosphate ore implication and bio industrial manure (Llewellyn, 1992; Kuck, 1995). Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Because of regulations only little cadmium now enters the water through disposal of wastewater from households or industries. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions is dumped by production companies (U.S. Environmental Protection Agency, 1999). Cadmium can be transported over great distances when it is absorbed by sludge. This cadmium-rich sludge can pollute surface waters as well as soils. Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase (Ruangsomboon, 2004). Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants. Cows may have large amounts of cadmium in their kidneys due to this. Earthworms and other essential soil organisms are extremely susceptive to cadmium poisoning. They can die at very low concentrations and this has consequences for the soil structure. When cadmium concentrations in soils are high they can influence soil processes of microrganisms and threat the whole soil ecosystem. In aquatic ecosystems cadmium can bioaccumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms (Tarrio *et al.*, 1991). Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Animals eating or drinking cadmium sometimes get Liver disease, high blood-pressures and brain damage. The Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit (PEL) for cadmium at a time-weighted average (TWA) of 0.005 ppm. The National Institute for Occupational Safety and Health (NIOSH) has not set a recommended exposure limit (REL) and has designated it as a known human carcinogen. The IDLH (immediately dangerous to life and health) level for cadmium is 9 mg/m^3.

Table 4 Lethal dose (LD_{50}) on rat and mouse by cadmium

Lethal dose	**Organism**	**Route**	**Time**	**Reference**
LD_{50}: 225 mg/kg	rat	oral	n/a	Kotsonis and Klaasen 1977
LD_{50}: 890 mg/kg	mouse	oral	n/a	Tarasenko 1978
LC_{50}: 25 mg/m^3	rat	n/a	30 min	Yoshikawa and Homma 1974

2.3.4 Cadmium toxicity on human

The main target organ where it is concentrated mainly in cortex. Environmental exposure of cadmium occurs via food, occupational industries, terrestrial and aquatic ecosystem. At molecular level, cadmium interferes with the utilization of essential metals e.g. Ca, Zn, Se, Cr and Fe and deficiencies of these essential metals including protein and vitamins, exaggerate cadmium toxicity, due to its increased absorption through the gut and greater retention in different organs as metallothionein (Cd-Mt). Cadmium transport, across the intestinal and renal brush border membrane vesicles, is carrier mediated and it competes with zinc and calcium. It has been postulated that cadmium shares the same transport system. Cadmium inhibits protein synthesis, carbohydrate metabolism and drug metabolizing enzymes in liver of animals.

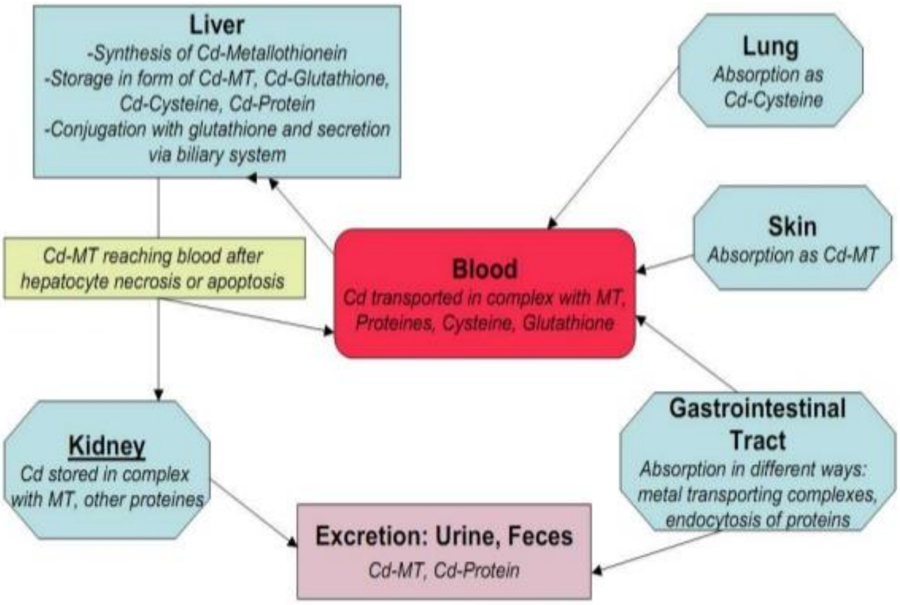

Figure 4 Metabolism, Storage and Excretion of cadmium in human body
(Journal of Occupational medicine and toxicology, 2006)

Chronic environmental exposure of cadmium produces hypertension in experimental animals. Functional changes accompanying cadmium nephropathy include low molecular weight proteinuria which is of tubular origin associated with excess excretion of proteins such as beta 2 microglobulin, metallothionein and high molecular weight proteinuria of glomerular origin (excretion of proteins such as albumin IgG, transferrin etc.). Recent data has shown that metallothionein is more nephrotoxic to animals. Cadmium is also toxic to central nervous system. It causes an alterations of cellular functions in lungs. Cadmium affects both humoral and cell mediated immune response in animals. Cadmium induces metallothionein in liver and kidney but under certain nutritional deficiencies like protein-calorie malnutrition and calcium deficiency, enhanced induction and greater accumulation of cadmium metallothionein has been observed (Nath *et al*., 1984).

2.4 Cadmium treatment processes

2.4.1 Physical and chemical treatment

Various physical – chemical treatment process effectively remove heavy metal from wastewater

1) Lime treatment removes heavy metals (Dean *et al*., 1972) as insoluble hydroxides, basic salts, or coprecipitated with calcium carbonate or ferric hydroxide. Lime precipitation does not normally permit recovery of heavy metal and is sometimes undesirable from the economic viewpoint.

2) Electrolysis is reduction of metal ions to metal (Endres, 2002) by electrons at an electrode. Electrolysis is process in which one species in solution is reduced by electrons at the cathode and another gives up electrons to the anode and is oxidized there. In hazardous waste applications electrolysis is most widely used in the recovery of cadmium, copper, gold, lead, silver and zinc.

3) Reverse osmosis (Bakalár, 2009) uses high pressures to force permeate through the membrane. It operates on a different principle in that the membrane is selectively permeable to water and excludes ionic solutes.

4) Ion exchange (Erdem *et al*., 2004) is a means of removing cations or anions from solution onto a solid resin, which can be regenerated by treatment with acids, bases and salts. The greatest use of ion exchange in hazardous waste treatment is for the removal of low levels of heavy metal ions from wastewater.

5) Activated carbon adsorption (Kadirvelu *et al*., 2001) effectively removes some metals from water at the part per million levels. Sometimes a chelating agent is sorbed to the charcoal to increase metal removal.

In the past, removal of heavy metals has been largely benefit of wastewater treatment process. Currently, however, more consideration is being given to design and operation parameters that specifically enhance heavy metals removal as part of wastewater treatment.

2.4.2 Biological Treatment

Conventional methods (such as chemical precipitation, ion exchange and membrane processes) for removal of metallic ions from industrial effluents may be ineffective or extremely expensive, especially when the metal concentrations in solution are low as in the range of 1-100 mg/L. The need exists for a cost-effective process that is efficient for removal of heavy metals from the effluents. Biosorption, a new technology for heavy metals removal offers certain distinct advantages when compared with existing technologies. These advantages are described below.

1) Metals at low concentrations can be selectively removed.

2) Biosorbents can be cheaply produced and some of them have higher uptake capacities than those of ion exchange resins and temperature.

3) Effluent concentrations meet the regulations.

4) This method is able to operate over the wide ranges of pH

5) Its capital investment and operation costs are low.

6) The cost and environmental liability of toxic sludge disposal are minimized by recovery of metals and biosorbents for reuse in industry.

Therefore, this method has been widely studied and also recognized as a promisingly alternative for removal of heavy metals in metal-bearing wastewater.

2.5 Biosorption and bioaccumulation

2.5.1 Biosorption

The first stage, usually referred to as passive uptake, is an initial rapid and reversible accumulation step. This kind of adsorption is also termed “ biosorption”. Biosorption can be considered as a collective term for a number of passive accumulation processes such as physical and chemical adsorption, ion exchange, coordination, complexation, chelation and microprecipitation. Biosorption can be demonstrateated with both dead and living biomass (Chojnacka, 2010).

2.5.2. Bioaccumulation

The second stage, usually referred to as active uptake, is a slower intracellular bioaccumulation is often irreversible and is related to the metabolic activity. This slow phase of metal uptake can be due to a number of mechanisms, including covalent bonding, surface precipitation, redox reaction, crystallization on the cell surface or, most often membrane transport of the metal ions into cell cytoplasm and binding to proteins and other intracellular sites. Sometime this slow uptake requires metabolic energy, indicating an active transport system (Świątek and Krzywonos, 2014).

2.6 Bacteria

Bacteria are single celled microbes. The cell structure is simpler than that of other organisms as there is no nucleus or membrane bound organelles. Instead their control center containing the genetic information is contained in a single loop of DNA. Some bacteria have an extra circle of genetic material called a plasmid. The plasmid often contains genes that give the bacterium some advantage over other bacteria. For example it may contain a gene that makes the bacterium resistant to a certain antibiotic. Bacteria are classified into 5 groups according to their basic shapes: spherical (cocci), rod (bacilli), spiral (spirilla), comma (vibrios) or corkscrew (spirochaetes). They can exist as single cells, in pairs, chains or clusters. The widespread use of metals has prompted many microbiologists to examine the relationship between heavy metal toxicity and bacterial resistanc. Heavy metals are defined as those which have a density of over $5 g/cm^3$, and thus include many of the transition and coinage metals. The reversion to heavy metal biocide use has been suggested as a possible solution to antibiotic resistance. On the other hand, bacteria that are resistant to certain heavy metals have been proposed to be economically useful in biomining and bioremediation. The constant race between heavy metal toxicity and bacterial resistance will likely give rise to many ingenious applications in the future, so it is important to understand the underlying mechanisms.

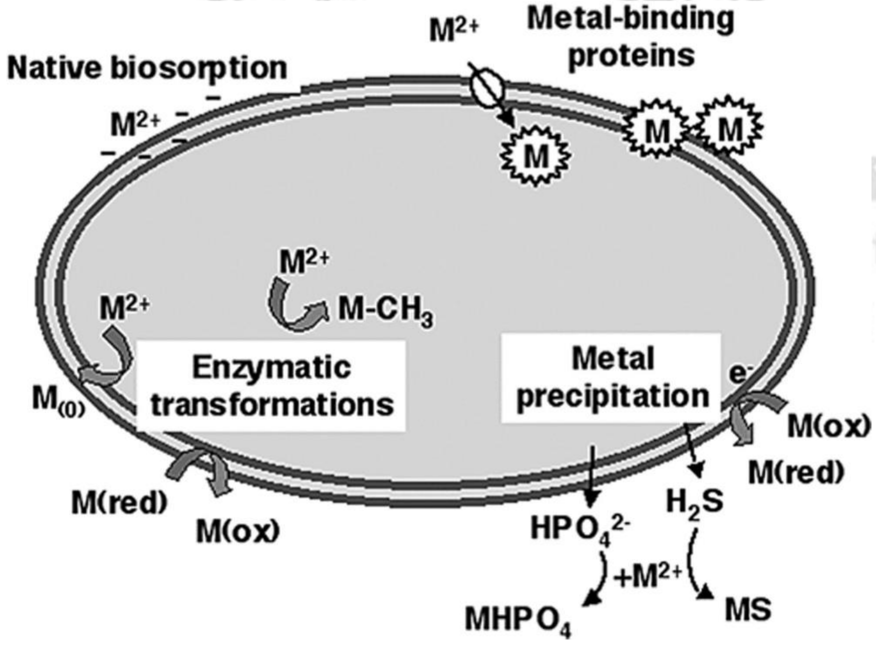

Figure 5 Mechanism of bacteria for resistance and detoxification of metals

2.7 Immobilization Bacteria

Immobilization of microbial cells has received increasing interest in the field of waste treatment (Winnicki *et al*., 1982; Westmeier and Rehm, 1987; Heitkamp *et al*., 1990; Hallas *et al*., 1992; Cohen, 2001; Ahmad *et al*., 2012). Compared with conventional suspension system, the immobilized microorganism technology offer a multitude of advantages, such as high biomass, high metabolic activity and strong resistance to toxic chemicals (Cassidy *et al*., 1996)

2.8 Relevance Researches

Simmon *et al*., (2004) reported about the problem of Cd contamination. Thai government try to solve the problem by promote the villagers to turn the plantation of food crops such as rice into energy crops as sugarcane. However, some villagers still grow rice in contaminated area.

Ruangsomboon, (2004) found that cadmium contamination does not only occur in food crops but it is present throughout the food chain. Therefore, Cd removal in contaminated area has to be developed.

Ruanchaiman (2009) studied the dispersion of the cadmium resistant bacteria. The contaminated soil was collected in Mae Sot district, Tak Province, Thailand. The highest number of bacteria was found in the lowest Cd contaminated area. On the other hand, the lowest number of bacteria was found in higher contaminant. Among 9 strains of Cd resistant bacteria, 2 best strains of strong Cd resistant bacteria were found in soil sample. Two strains were identified by to be Alcaligenes sp. and Arthrobactor sp. by 16S rDNA sequence analysis. One from these 2 Cd resistant bacterial strains can be selected for utilizing in remediation process.

Chompoothawat (2010) studied the efficiency of Cd removal by using an exopolymer producing bacterium, *Ralstonia* sp. TAK1. This bacteria exopolymer can absorb heavy metals by interaction between cation of heavy metals and functional group of polymer. In this study, the carbon source of cultivation medium that gave the highest exopolymer production was focused. The result showed that the highest exopolymer production (5.39 g/L) was found in 2% of glucose growth media at mid-stationary phase (24 hr.). The highest removal efficiency at stationary phase was 41.73% and the highest adsorption capacity was 15.02 mg Cd/ g. dry wt. *Ralstonia* sp. TAK1 was suggested to be applied for bioremediation of Cd.

In Sombatjinda works (2004), the treatment processes in immobilized cyanobacteria was developed. *Nostoc paludosum* and *Rivularia* sp. exhibited the highest cadmium removal rate and also showed high growth rate. Then, the percent of immobilized ability and Cd removal rate of these two species were compared in different cultivation processes. They suggested that, *Rivularia* sp. should be cultivated in free cell process with air bubble aeration because the highest rate of Cd removal (96.10% mg/ g dry wt.) was occurred in free cell process. The highest Cd removal rate of *N. paludosum* (95.46% mg/ g dry wt.) was occurred in immobilized cell process with rotary shaker.

Kitvatanachai *et al*., (2005) used the *Culex quinquefasciatus* mosquito for studies about the led toxicity and led uptake. Mosquito larvae were cultured in led different concentrations of 0.05, 0.1, and 0.2 mg/l. The result show the significantly reduced hatching, egg-production, and emergence rates, compared with the unexposed group ($p<0.05$). In 24 hours, The LC_{50} of lead was 0.18 mg/l. However there’s not report for Cd toxicity test by this method.