CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Total Concentration of Cadmium and Zinc

Ninety nine soil samples collected from the Mae Ku floodplain were digested following the EPA standard method 3051.Concentrations of cadmium (Cd) and zinc (Zn) in the digested solutions were analyzed by an ICP-OES. The results of total concentrations of cadmium and zinc in soil samples from study area were mostly shown in Appendix-A.

These results show that the cadmium level in soil from the Mae Ku floodplain ranges between 0.42 and 101.69 mg/kg with a mean value of 4.93 mg/kg. The zinc level in soil samples from the Mae Ku floodplain ranges from between 29.34 and 2,347.74 mg /kg with a mean value of 209.94 mg /kg. The standard deviation of cadmium and zinc concentration = 12.89 and 115.66, respectively. These values calculated from the deviation among the result of all samples. The ranges and means of total concentrations cadmium and zinc in soil samples are given in Table 4.1.

Table 4.1 The Statistics Values of Total Cd and Zn Concentrations in Soil Samples of Mae Ku Floodplain. (n = 99)

Parameter	**Total concentration** (mg/kg)	
	Cd	**Zn**
Mean	4.93	209.94
Standard Error	1.29	33.96
Median	1.93	115.66
Standard Deviation	12.89	337.92
Minimum	0.42	29.34
Maximum	101.69	2,347.74

Cadmium: for the most part, the cadmium concentrations in soils from the Mae Ku floodplain were higher than the "Thai background" soil cadmium concentration which is in the range of < 0.01-0.141 mg/kg (Pongsakul and Attajarusit, 1999). Kabata - Pendias and Pendias (1984) introduced that the background level of cadmium in soil general should not exceed 0.5 mg/kg. However, from the study of NRC-EHWM (2005), it was noted that the background concentration of Cd in this area is at around 3 mg/kg. However, this background level was arbitrary since at this level is majority of the total Cd distributed in the Mae Tao area.

From the comparison between the background value of this area and the study result, it was found that most of the soil samples (75.76%), their cadmium concentrations do not exceed the background level (3 mg/kg). (see Table 4.2) According to the Notification of the National Environment Board of National Environmental Quality No. 25 Act. B.E. 2547 (2004) announced the "Soil quality standards for habitat and agriculture" which allow total cadmium concentration in this soil type not exceed 37 mg/kg. As compared with this standard, it was found that 97.98 % of soil samples were not exceeded the standard.

Zinc: zinc concentrations in the soil samples (more than 75 %) mostly do not exceed the "Thai background" soil zinc concentrations reported by Pongsakul and Attajarusit, 1999) at the range of < 0.01-237 mg/kg (see Table 4.3). Somboon (1999) studied the concentration of zinc in top soil in the adjacent area which has not directly received the flow form zinc mine activities in the Mae Tao area (n = 9). He found that the zinc concentration in that area was in the range of 26.60- 62.40 mg/kg. However, in Somboon study used nitric acid and perchloric acid as extractants, aluminium heating block was used for soil digestion. When comparing to this study with that of Somboon (1999), it was found that more than 75 % of these samples under this study showed higher the zinc values than those in the study of Somboon.

Table 4.2 Cumulative Samples of the Total Cd Concentrations in Soil Samples.

Concentration (mg/kg)	Number of samples	% of the total samples
0.42-1	13	13.13
1-2	47	47.47
2-3	15	15.15
3-4	6	6.0
4-5	3	3.03
5-10	6	6.06
10-15	4	4.04
15-20	2	2.02
20-30	1	1.01
30-40	0	-
40-60	0	-
60-80	0	-
More	2	2.02
Total	**99**	**100.00**

However, in this study there were two soil samples found remarkable high both Cd and Zn concentrations. The sampling stations for these two sample soil are at the gridline numbers C11 and G10 which is located in paddy soil in the eastern part of the study area. These two data were recognized as site anomalies.

Table 4.3 Cumulative Samples of Total Zn Concentration in Soil Samples.

Concentration (mg/kg)	**Number of samples**	**% of the total samples**
29.34-50	11	11.11
50-100	32	32.32
100-150	22	22.23
150-200	8	8.08
200-250	5	5.05
250-300	6	6.06
300-350	3	3.03
350-400	2	2.02
400-450	2	3.03
450-500	0	-
500-550	1	1.01
> 550	7	7.07
Total	**99**	**100**

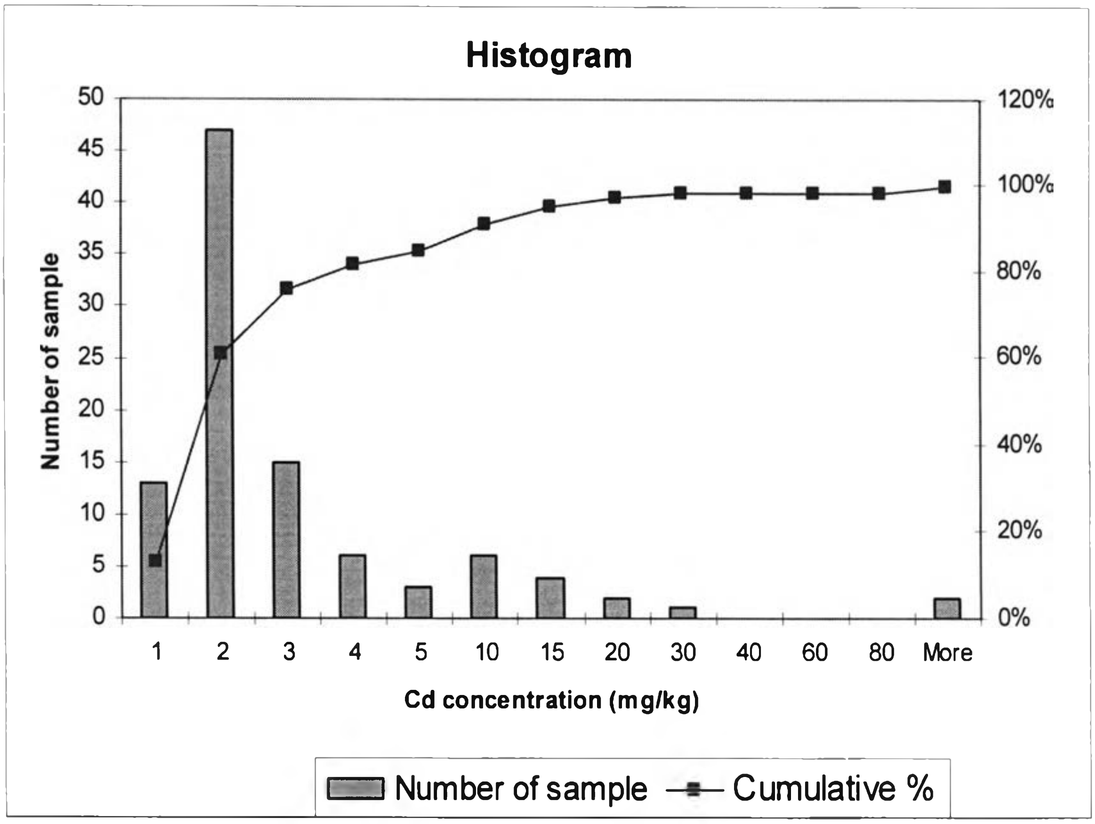

Figure 4.1 Histogram of the Total Cd Concentration in the Soil Samples.

From the Cd concentrations of soil samples in Mae Ku, to determine the distribution and assign the background level of Cd deposited in the study area, histogram was used to analyze the experimental data as shown in Figure 4.1. From Figure 4.1, the slope changing point of the histogram was found at 3 mg/kg. It means that the total cadmium concentrations in soil under this point can be classified as the background level of the soil samples in the study area and the total cadmium concentrations in soil which higher than this point were the anomalies value of cadmium concentration in the soil samples. Figures 4.2 and 4.3 show the concentration of each point of samples for total Cd and total zinc concentration respectively.

The anomaly values of cadmium concentration in the soil samples can be divided into two levels:

1. Low anomaly level: this anomaly value, total cadmium concentrations ranged between > 3 to 15 mg/kg.

2. High anomaly level: this anomaly value, total cadmium concentrations were more than 15 mg/kg.

Nonetheless, for the environmental concerns, the level of total cadmium concentrations in the soil should be divided into three levels as follows.

1. Low contaminated level: at this level, total cadmium concentrations in soil should not be higher than 3 mg/kg which is the most samples found in this level. (75.76%)

2. Medium contaminated level: total cadmium concentrations in soil at this level should be in the ranges of 3 - 37 mg/kg. There were twenty two samples at this level (22.22 %).

3. High contaminated level: at this level, total cadmium concentrations in soil should be higher than 37 mg/kg. If total cadmium concentrations in the soil samples are more than this value, it indicates that the total cadmium concentration in the soil exceeded "The soil quality standard for habitat and agriculture" of Thailand. From this study there are only 2 samples were at this level and they are remarkable high level as mention earlier.

According to the three cadmium contaminated levels, the characteristics of the cadmium and zinc distributions in the soil are shown in Figures 4.3 and 4.4, respectively. These two figures illustrate a similar distribution pattern of both Cd and Zn which indicate high concentration levels of Cd and Zn the eastern direction as compared to those in the western directions. It may be a sign that with the concentration of both heavy metals correlate to the stream flow direction which come from Doi Pha Daeng where the zinc mines are located.

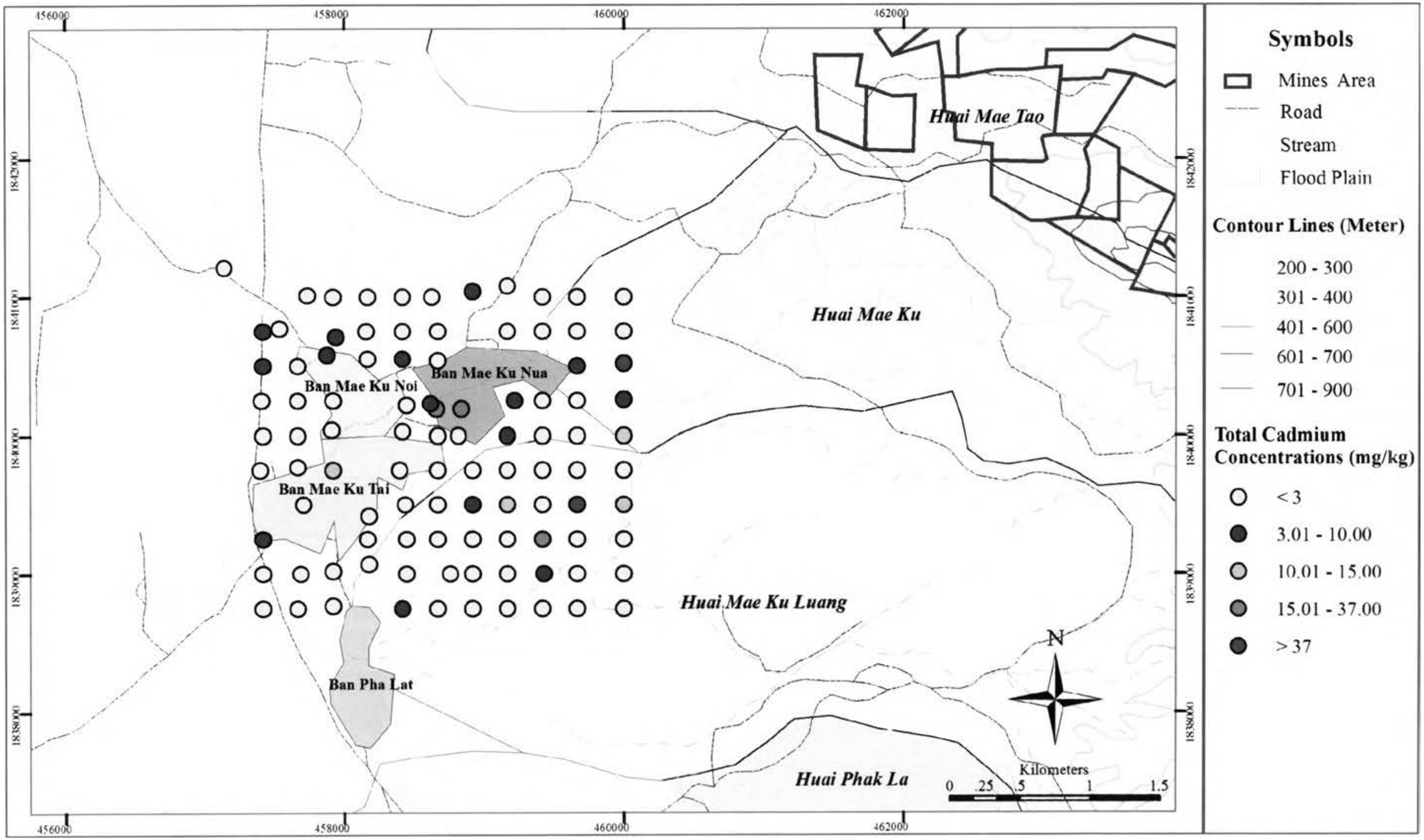

Figure 4.2 Total Cadmium Concentrations in Study Soil

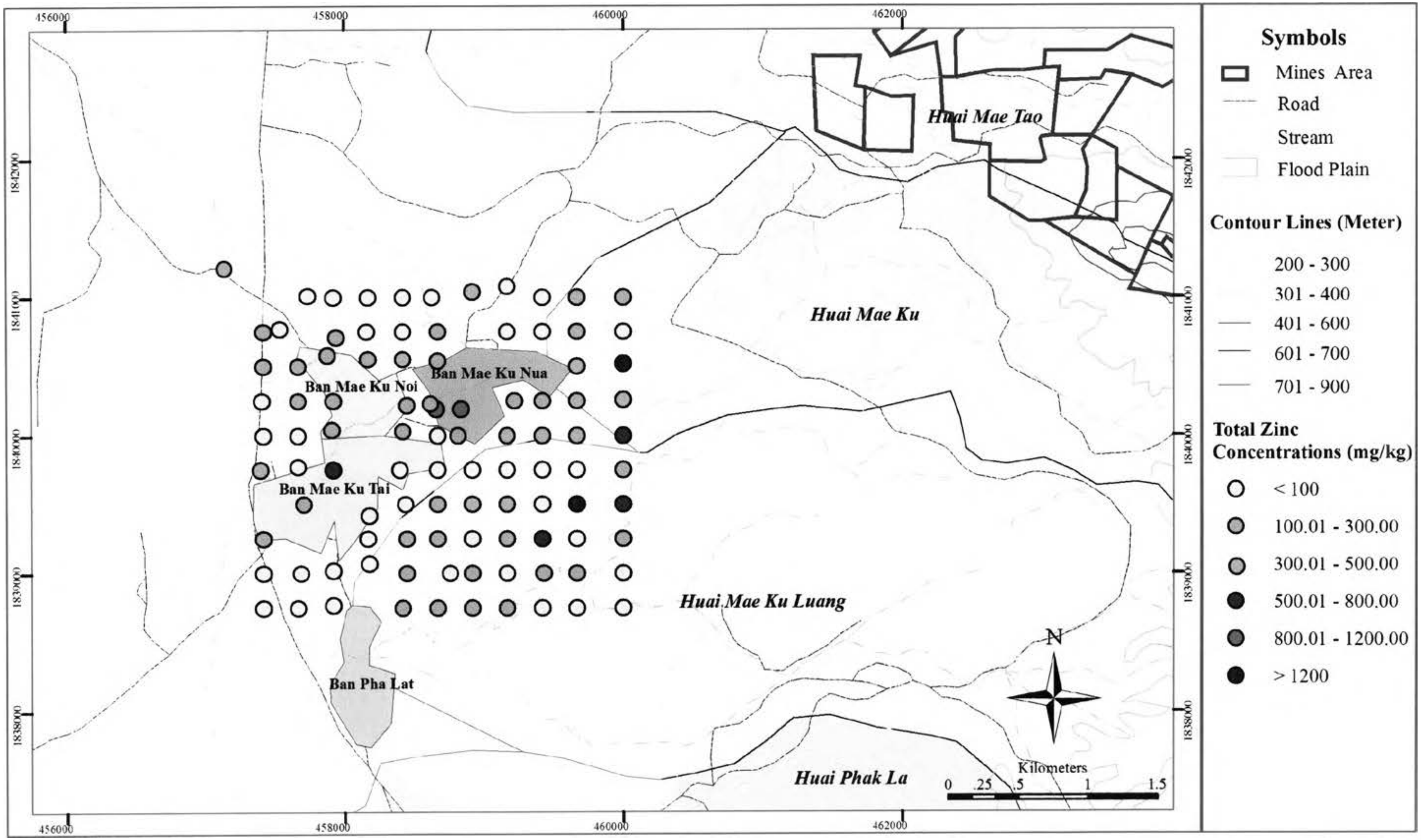

Figure 4.3 Total Zinc Concentrations in Study Soil

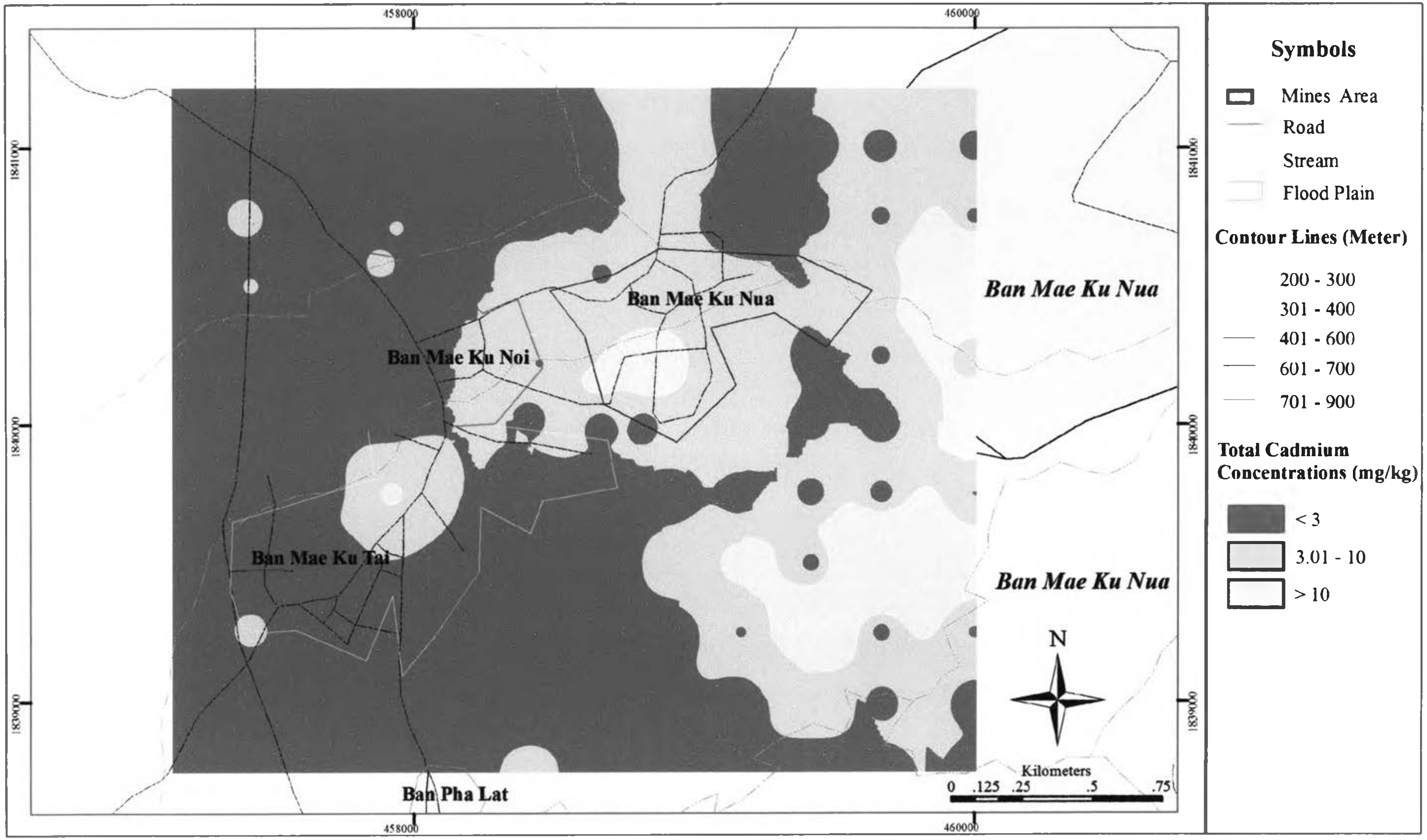

Figure 4.4 Total Cadmium Distribution at Different Concentrations in the Study Area

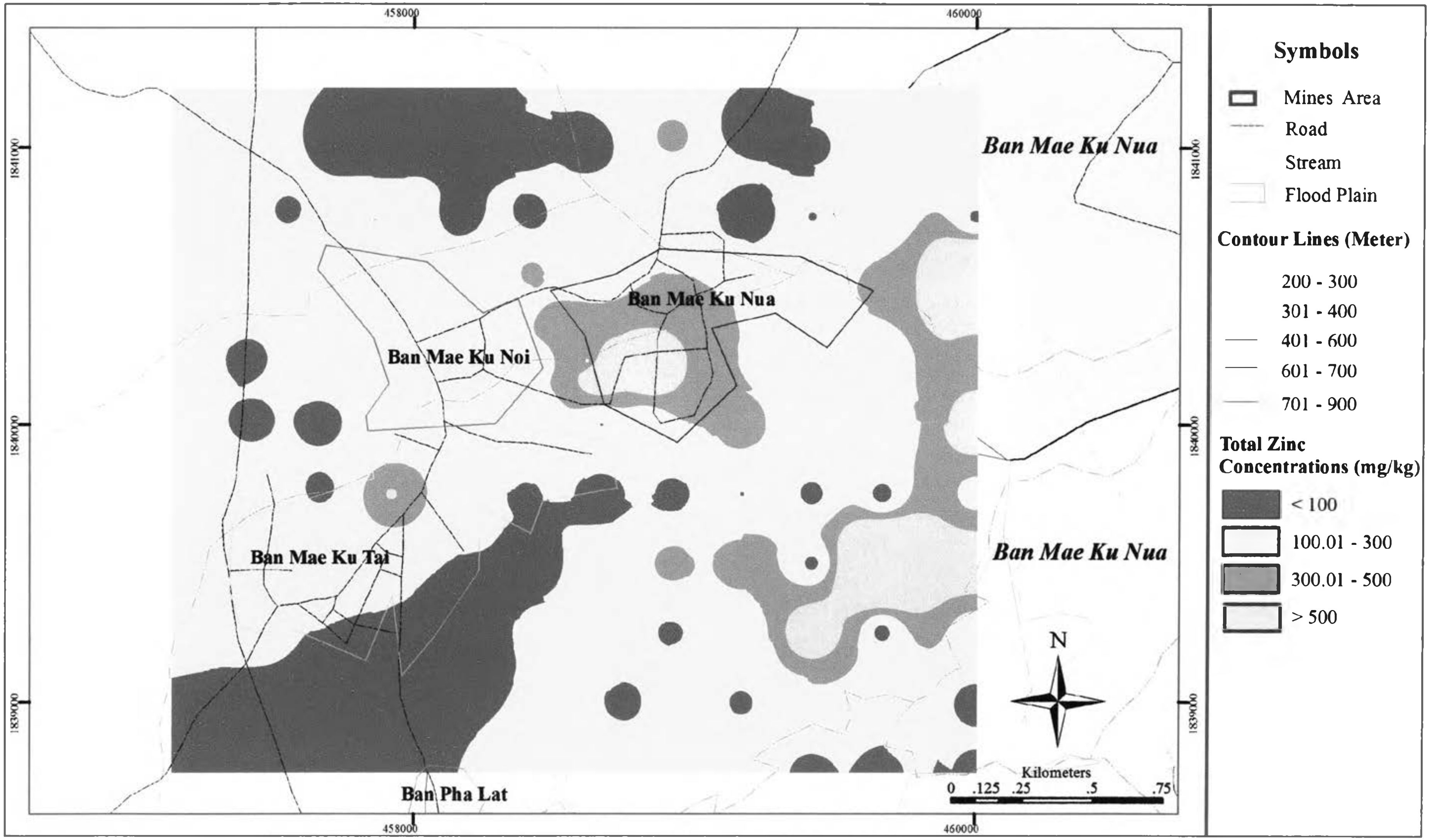

Figure 4.5 Total Zinc Distribution at Different Concentrations in the Study Area

4.2 Bioavailability Fraction (BCR1) of Cd and Zn

The BCR sequential extraction was selected for this study. However, only the BCR step1 (BCR1) “exchangeable form” was conducted in order to determine the concentrations of the most likely bioavailability fraction of Cd and Zn in soils. BCR 1 can extract heavy metal in the form that has the potential to be up taken by plants and the organisms in soil. The results of the bioavailability fractions of Cd and Zn of the 99 soil samples are shown in Figures 4.6 and 4.7, respectively. The result values of BCR1 fraction of Cd and Zn are shown in appendix A. The ranges and means of concentrations of the bioavailability fractions of the Cd and Zn values of the soil samples in Mae Ku floodplain are given in Table 4.4. (The standard deviation of cadmium and zinc concentration = 9.09 and 136.18, respectively. These values calculated from the deviation among the result of all samples)

Table 4.4 The Statistics values of the Bioavailability of Cd and Zn Concentrations in Soil Samples of the Mae Ku Floodplain. (n = 99)

Parameter	**Bioavailability concentration** (mg/kg)	
	Cd	**Zn**
Mean	2.48	55.46
Standard Error	0.92	13.83
Median	0.35	17.37
Standard Deviation	9.09	136.18
Minimum	0.03	2.04
Maximum	63.78	1,033.92

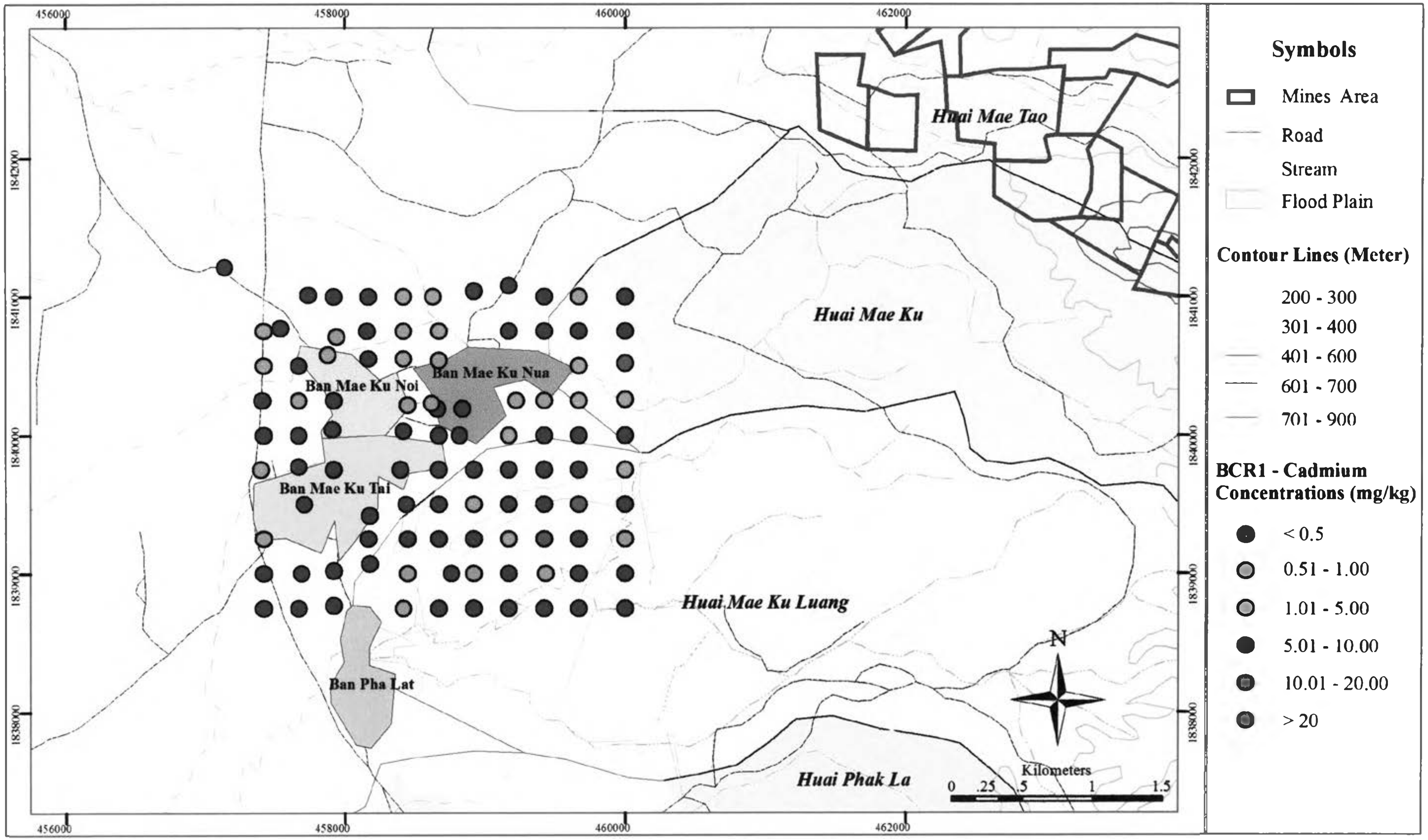

Figure 4.6 BCR 1 Cadmium Concentrations in Study Soil

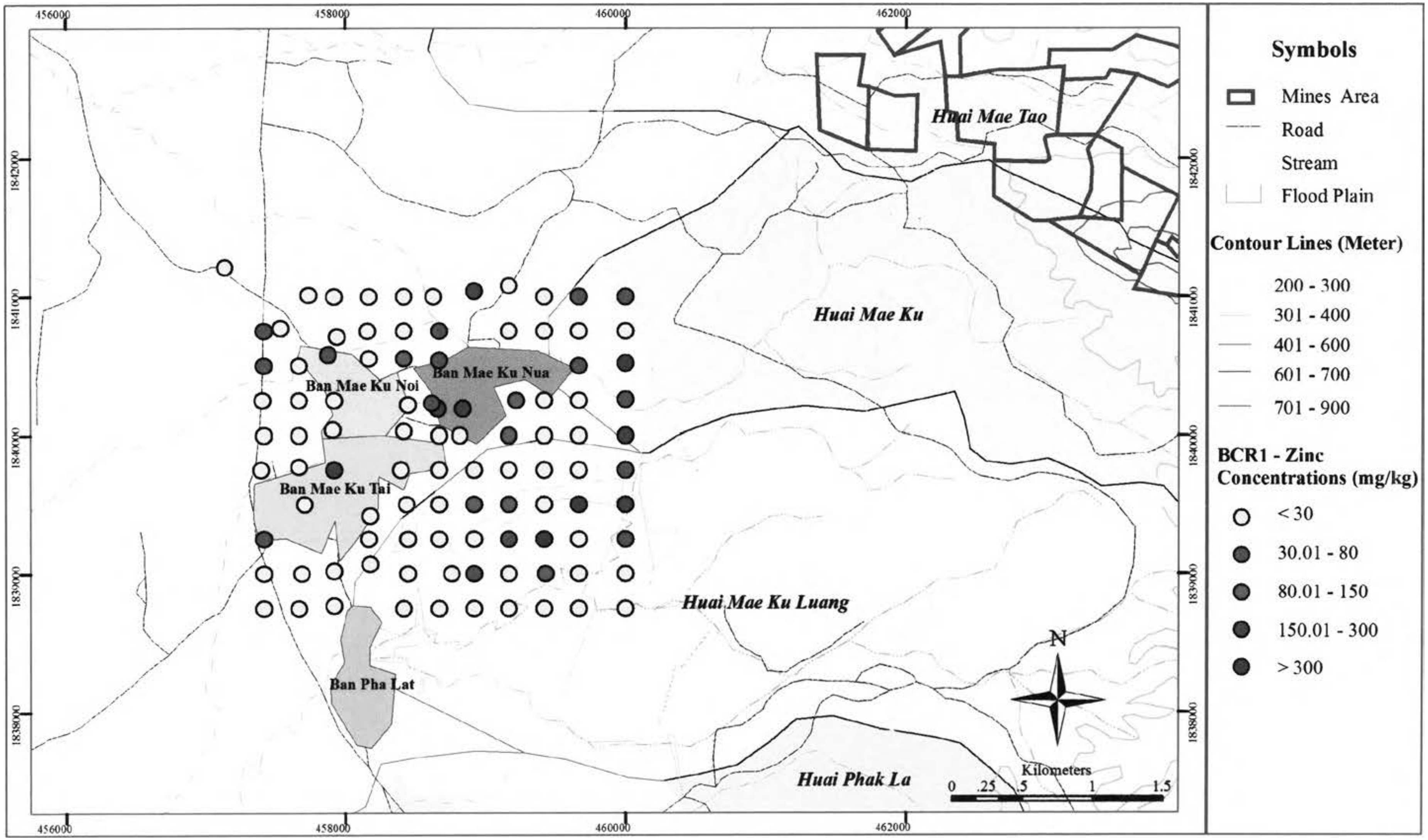

Figure 4.7 BCR 1 Zinc Concentrations in Study Soil

4.3 Relationship between the BCR1 Fraction and Total Concentration.

To determine the relationship between the bioavailability fraction and total concentration of these metals in soils, both the BCR1 fraction and total the concentrations were plotted in Figures 4.8 and 4.9, respectively. A linear relationship was found between the BCR1 fraction and the total concentration of Cd plots. The equation of this graph is y = 0.6262x - 0.7543 with the values of R^2 = 0.9955 which shows a significantly correlation of the total concentration and bioavailability of Cd in soils. It can be assumed that the bioavailability fraction is about 36 % of the total Cd concentration in soils.

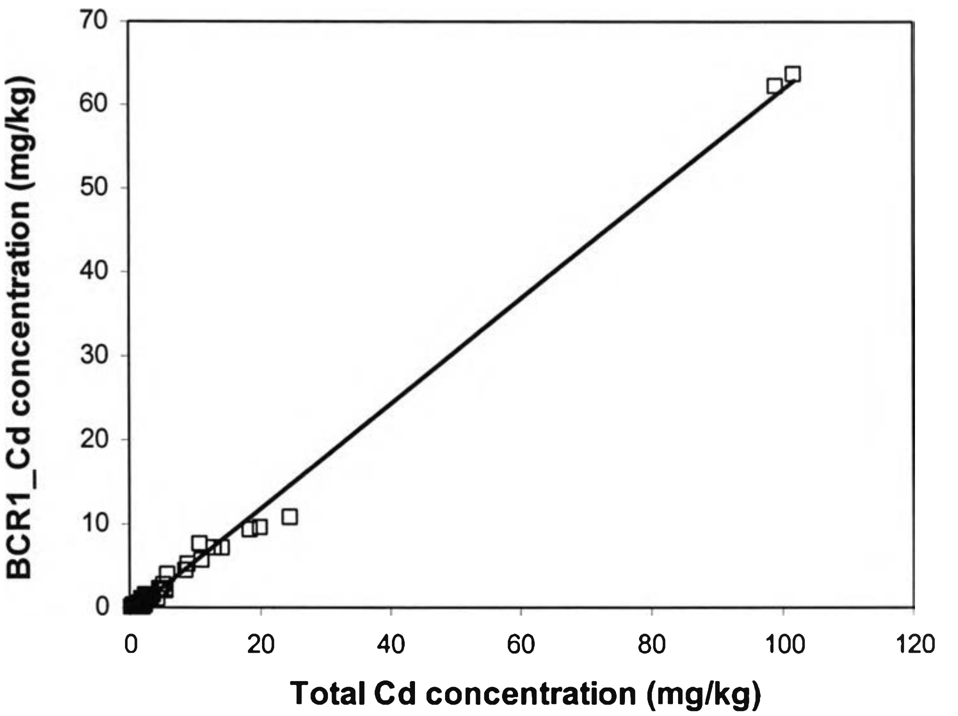

Figure 4.8 Correlation between the Bioavailability Fraction and the Total Concentration of Cd in Soils.

A similar significant linear relationship was also found between BCR1 and total concentration of Zn in the soil samples. The values of R^2 = 0.9509, which a show significantly correlation of the total concentration and bioavailability of Zn in soils. It can be assumed that the bioavailability fraction is 0.014 time of the total Zn concentration in the soils. When the ratios of bioavailability in soil between Cd and Zn were compared, it had been found that cadmium was more mobile than zinc.

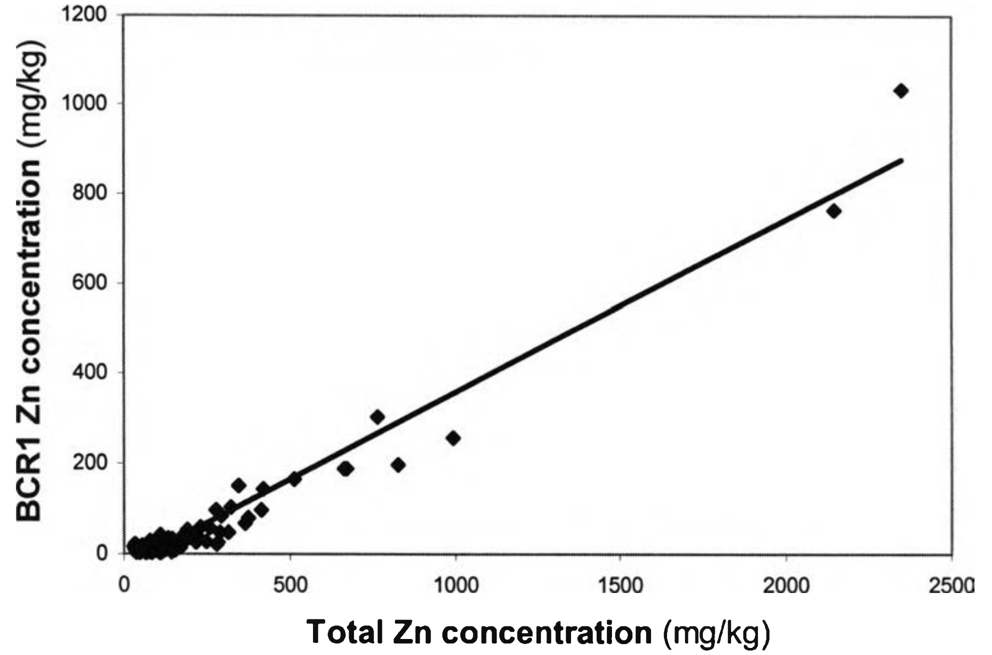

Figure 4.9 Correlations between the Bioavailability Fraction and the Total Concentrations of Zn in Soil Samples.

When comparing the bioavailability concentration of Cd in soil samples with the total concentration of Cd in soil, it was found that the ratio of the available fraction was around 36 % of the total concentrations in the soil. From the study of Kabata–Pendias and Pendias (2001), they found that in the natural condition, speciation of heavy metal in soil can be present in 6 forms: water soluble, exchangeable, organically bound, occluded bound, definite compounds and structurally bound in silicates. These six speciation can be categorized into two fractions, the immobile fraction which is the major part, and the mobile fraction (available fraction), which is the minor part. If heavy metals in soil come from the anthropogenic activities, these metals will be more mobile and more available than both weathering by nature (Lithogenic and Pedogenic).

From the results in this study, it was found that the bioavailability fraction of Cd in the study soils was increased up to 36 % of total concentrations. This may be assumed that Mae Ku area has been contaminated with Cd, particularly in the eastern part of the study area.

4.4 Comparison with Previous Study

The correlation between total Zn and total Cd concentrations of the soil samples from this present study was compared with those of the soil samples from Mae Tao studied by NRC-EHWM (2005) as shown in Figure 4.10. It was found that the correlation of total zinc and cadmium concentration in soils of the Mae Tao and Mae Ku areas show a significant linear relationship between the total concentrations of Cd (x) and Zn (y) in the soils .The equation of this plot is $y = 31.882x + 45.714$ with $R^2 = 0.9274$ for the Mae Tao area, and $y = 22.839\ x + 97.174$ with $R^2 = 0.9183$ for the Mae Ku area.

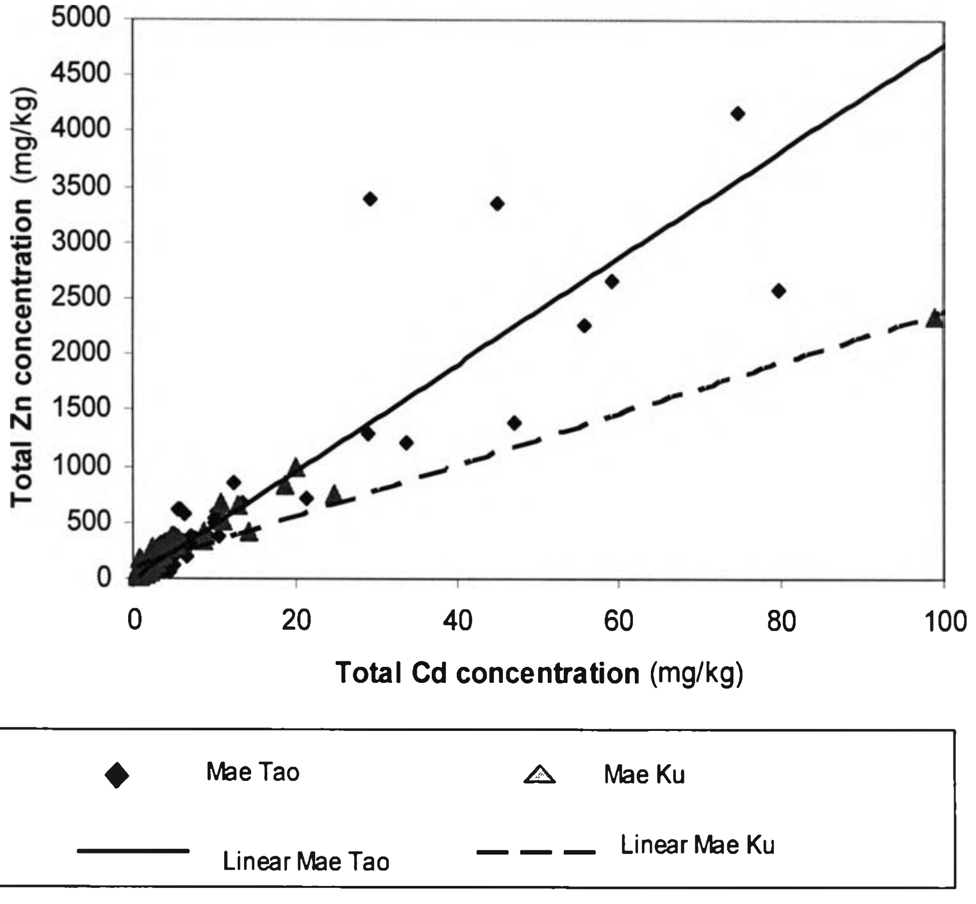

Figure 4.10 The Correlation between Total Concentrations of Cd and Zn in Soil Samples in Mae Ku and Mae Tao Areas.

Two correlation plots between Cd and Zn of two sub-catchments indicate the different ration of Cd/Zn in those two studied area. As compared between these two areas, topography is needed to be considered. From Figure 1.1 that show the 7 sub-catchments in Mae Moei River Basin. Tributaries in the sub-catchments which are the main pathway to convey sediment from upland to low land show that Mae Toa sub-catchment is the area directly receives sediment from mining activities as mentioned earlier. While Mae Ku area which is located in zinc ore deposit, however, the area is not a directly sediment receiver from mining activities. Occasionally overflow from major flooding may be the reason to convey sediment containing zinc and cadmium from the highland.

As compared the slope of the plot in Figure 4.10, the ratio of Zn to Cd in soil was found to be higher in the area of Mae Ku. The soil samples collected from both Mae Tao and Mae Ku was soil from paddy field which is located in the lowland. It is expected that the sediment deposited in the area was transported from the upland during rainy seasons. Thus it more or less comes from the same parent material and should have the similar ration of Zn and Cd. However, the plot in Figure 4.10 shows that in the Mae Toa area, Zn to Cd ratio is higher that the one in Mae Ku area. Zn is known as an element that has limitation to be up taken by rice while Cd is no limit to be up taken if it is in bioavailable form. In addition, the soil samples in Mae Ku area may have been evolved from sediment in younger age as compared to the soil in Mae Tao area; consequently, the ratio of Zn to Cd of soil in Mae Toa is higher than those in Mae Ku area.

Besides from the comparison of Zn and Cd ratio between the two sub-catchments, the ratio of the availability fraction (BCR1) and total concentration of cadmium in soils were also plotted as shown in Figure 4.11. It was found that the data of the Mae Tao area is more scatter as compared to the one from Mae Ku. . This can be confirmed by R^2 of the two linear regressions as well. The R^2 are equal 0.905 and 0.9895 for Mae Tao and Mea Ku, respectively. This event can be explained by the reason that the Mae Tao area is located in the Mae Tao sub-catchment where the zinc mines are located and has been directly receiving the run-off from highland since 30 years ago until present. Therefore, this area accumulated both aging and fresh sediments. The evolution of sediment in this area has more variation steps. This leads to the high variations of data.

To make the clear picture, the ratio of BCR1 to total Cd of the sediment samples studied by NRC-EHWM, 2005 was also plotted in Figure 4.11. It is obviously that the ratio is very low compared to the soil samples from Mae Tao and Mae Ku. This is not surprising since sediments can be considered as a secondary material (see Figure 2.3 in Chapter 2), which is in the intermediate of the development process to be soil. Thus, the most fractions present in the sediment have not been completely developed, especially, for the BCR1 fraction which needs "processes" and "time".

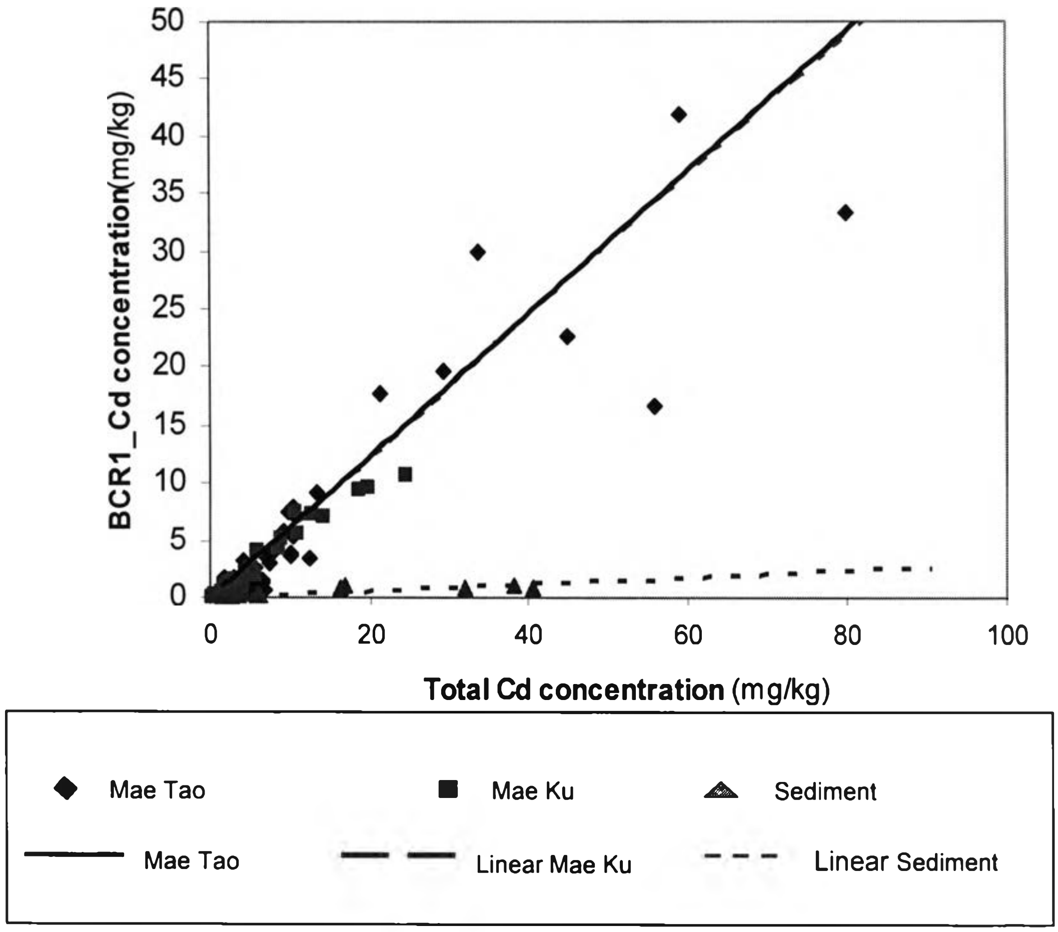

Figure 4.11 The plots of the Ratio of the Availability Fraction (BCR1) and Total Cd Concentration of the Soils from Mae Ku, Mae Tao and from Sediments.

4.5 Source of Cadmium and Zinc

The study of NRC-EHWM (2005) indicated the major source of cadmium contamination in the Mae Tao area are from zinc ore deposits of this area which was eroded by long-term natural processes as well as zinc mining activities that have been stimulated the soil and generated sediment to be convey to lowland area for more than 30 years.

The Mae Ku area also is located in the same zinc deposit area of the Mae Tao area. Therefore, it may consider these two areas are zinc and cadmium prone area and has high potential to be contaminated from overflow and heavy flooding. As mentioned earlier that Mae Tao sub-catchment directly received the sediment from upland area where zinc mines are located. As a consequence, an adverse impact on cadmium contamination from zinc ore deposit and also mine activities can be occurred directly to this area. However, for Mae Ku floodplain area, the contamination of cadmium and zinc may be occurred from flooding and overflow. Therefore the level of cadmium contamination of soil samples were found much lower than in the Mae Ku area as compared to those in Mae Tao area.

It also should be noted here that for the two anomalies at the sampling stations C11 and G10 that found cadmium concentration is very high up to 100 mg/kg. From the field observation, the two stations did not appear to have high potential of contamination e.g. closed to creeks, or located in lower elevation from surrounding area. So, this may cause from soil excavation from zinc mine in the past that may be dumped in this area. However, this reason cannot be confirmed.

From this study, it may be concluded that anthropogenic activities are the main cause of cadmium contaminated in both areas particularly, the activities that open-cut and disturb top soil including zinc mining, agriculture etc. However, as compared other activities with mining activities which generate a huge of sediment, it may not be refuse that zinc mines is the major source of cadmium contamination in these area if there is inappropriate management.