Chapter 5

RESULTS

5.1 QUALITY CONTROL ANALYSIS

The analytical methods applied for analysis of Pb and Zn in soil and plants were controlled by carrying out precision and accuracy tests.

The precision test

The result of the analyses in duplication of 15 soil sample and 5 plant samples are shown in Table 5.1 together with calculated coefficient of variation of analysis.

The raw data are listed in tables A1 and A2 of appendices.

Table 5.1. Evaluation of precision for analytical methods

Element	SOIL (15 duplicated samples)		PLANT (5 duplicated samples)	
	Range (ppm)	Mean CV (%)	Range (ppm)	Mean CV(%)
Pb	48.3 - 537	5.8	1.5 - 9.4	9.8
Zn	39.8 - 862	6.2	23.5 - 40.8	7.6

The accuracy test by reference materials

Three reference samples were analyzed and results are listed in Table 5.2. The raw data are listed in Tables A3 and A4 of appendices.

Table 5.2. Results of analysis of reference materials

Reference material	Pb (ppm)		Zn (ppm)	
	Recommended by IAEA	Obtained result by the author	Recommended by IAEA	Obtained result by the author
Soil - 5	103 - 155	136	360 - 376	362
Soil - 7	55 - 71	66	101 - 113	105
Rye grass	2.3 - 2.5	2.5	30.1 - 32.9	30.5

5.2 LEVEL OF Pb AND Zn IN SOIL

The concentration of Pb and Zn at each sampling site is calculated as an average value of the concentration of these heavy metal at different depths at the same site. Tables 5.3 and 5.4 summarize the level of Pb and Zn in soil of study area. The top soil is the depth from 0 - 10 cm; middle is from 20 - 30 cm; the bottom is 50 - 60 cm.

Table 5.3 Concentration of Pb (ppm) at the different depths of sampling sites.

Sampling site	Concentration of Pb (ppm) at			**Mean of the site**	SD of Pb of depths	CV (%) of depths
	Top depth	Middle depth	Bottom depth			
1	6,630	4,660	2,560	**4,620**	2,030	44.0
2	1,440	7,260	7,090	**5,270**	3,310	62.9
3	1,360	4,000	4,620	**3,330**	1,730	52.1
4	750	878	892	**840**	79.0	9.3
5	184	234	189	**202**	28.0	13.6
6	284	440	234	**319**	108.0	33.8
7	420	365	418	**401**	32.0	7.9
8	101	220	191	**171**	62.0	36.5
9	38.5	641	79.1	**60.6**	20.5	33.9
10	26.1	78.5	44.8	**49.8**	26.6	53.3
11	33.3	38.7	42.6	**38.2**	4.7	12.2
12	51.6	62.3	54.4	**56.1**	5.5	9.9
13	46.5	51.8	47.2	**48.5**	2.9	5.9
14	40.2	46.8	45.3	**44.1**	3.5	7.8
15	38.2	40.5	51.6	**43.4**	7.2	16.5
16	30.7	41.1	51.5	**41.4**	10.4	25.3
17	44.1	64.5	59.2	**55.9**	10.6	18.9
18	30.7	32.2	43.8	**35.6**	7.2	20.2
19	2,710	5,640	2,360	**3,570**	1,800	50.5
20	1,210	1,090	1,080	**1,130**	70.0	6.2
21	2,520	2,260	2,580	**2,460**	170	6.9

Table 5.3 Concentration of Pb (ppm) at different depths of sampling sites (continued)

Sampling site	Concentration of Pb (ppm) at			**Mean of the site**	SD of Pb of depths	CV (%) of depths
	Top depth	Middle depth	Bottom depth			
22	83.9	343	722	**634**	259	40.8
23	343	306	466	**370**	85	22.8
24	55.5	64.5	89.3	**69.8**	17.5	25.0
25	34.3	43.2	61.4	**46.3**	13.8	29.8
26	397	344	449	**397**	53.0	13.3
27	41.7	54.5	47.1	**47.8**	6.4	13.5
28	33.6	35.4	51.7	**40.2**	10.0	24.8
29	59.6	69.5	78.6	**69.2**	9.5	13.7
30	247	48.4	159	**151**	99.3	65.6
31	28.1	20.6	45.1	**31.3**	12.6	40.1
32	45.6	58.1	68.2	**57.3**	11.3	19.8
33	336	549	288	**391**	139	35.6
34	30.5	33.2	55.1	**39.6**	13.5	34.1
35	43.3	66.6	88.6	**66.2**	22.7	34.2
36	64.2	105	88.7	**86.6**	20.6	23.9
37	349	248	423	**339**	8.8	25.9
38	385	407	473	**421**	46	10.9

Table 5.4 Concentration of Zn (ppm) at different depths of sampling sites.

Sampling site	Concentration of Zn (ppm) at			**Mean of the site**	SD of Zn of depths	CV (%) of depths
	Top depth	Middle depth	Bottom depth			
1	3,730	4,710	3,540	**3,990**	630	15.8
2	3,180	3,750	4,410	**3,780**	610	16.3
3	4,430	6,130	5,760	**5,440**	900	16.5
4	626	520	624	**590**	60.0	10.2
5	170	247	184	**200**	41.0	20.3
6	469	347	371	**395**	65.0	16.3
7	169	176	162	**169**	7.0	4.3
8	97.2	49.4	66.7	**71.1**	24.2	34.0
9	70.6	82.3	64.7	**72.5**	8.5	11.4
10	70.4	82.6	64.5	**72.5**	9.2	12.7
11	43.5	54.1	66.7	**54.8**	11.6	21.2
12	81.4	79.3	98.3	**86.3**	10.4	12.1
13	51.7	78.1	81.2	**70.3**	16.2	23.0
14	73.5	76.1	89.5	**70.7**	8.6	10.8
15	107	112	133	**118**	14 .0	11.8
16	45.1	49.2	63.4	**52.6**	9.6	18.3
17	61.9	53.1	71.7	**62.2**	9.3	15.0
18	49.5	55.4	73.6	**59.5**	12.6	21.1
19	2,070	2,130	1,980	**2,060**	770	3.7
20	450	497	465	**471**	24.0	5.1
21	2,360	2,510	1,980	**2,290**	2,700	11.8

Table 5.4 Concentration of Zn (ppm) at different depths of sampling sites (continued)

Sampling site	Concentration of Zn (ppm) at			**Mean of the site**	SD of Zn of depths	CV (%) of depths
	Top depth	Middle depth	Bottom depth			
22	381	330	358	**356**	25	7.1
23	391	325	450	**389**	63	16.1
24	69.3	57.1	13.3	**86.3**	40.5	46.9
25	62.9	75.5	96.4	**78.3**	16.9	21.6
26	112	198	188	**166**	4.7	28.6
27	57.3	68.5	86.4	**70.7**	14.7	20.8
28	68.4	74.3	93.1	**78.6**	12.9	16.4
29	46.3	80.2	73.1	**66.5**	17.9	26.9
30	541	529	538	**536**	65.0	1.2
31	54.2	67.1	139	**86.7**	45.6	52.6
32	149	229	150	**176**	46.0	26.2
33	472	498	472	**481**	148	3.1
34	61.6	72.7	80.2	**71.5**	9.4	13.1
35	65.2	43.6	48.0	**52.3**	11.4	21.8
36	63.8	105	97.2	**88.7**	21.9	24.7
37	455	542	564	**521**	58	11.1
38	324	361	397	**361**	37	10.1

5.3 CONCENTRATION OF Pb AND Zn AT CONTROL SITE

The soil sample from Doi Pui (Doi Suthep - Pui National Park) was taken and analyzed by the same procedure in order to compare the mean Pb and Zn level in soil with soil from the study site. The result is listed in Table 5.5.

Table 5.5 The level of Pb and Zn in soil of Doi Pui

Pb (ppm)	Zn (ppm)
28.1	86.2

5.4 THE CHANGE OF Pb AND Zn WITH DISTANCE FROM THE SOURCE OF CONTAMINATION

The data of Pb and Zn in 8 squares of three transects (also called lines) of this special study are listed in Table 5.6.

5.5 SOIL pH AND SOIL ORGANIC MATTER

Soil pH was determined for surface depth of 38 sampling sites. Soil organic matter was determined for 38 representative samples of three depths at each sampling site. The results are listed in Table 5.7. In order to have an overview of pH value in the study site, the pH values are classified to three group pH less than 6; pH from 6 to 7 and more than 7. These classified pH values are mapped in Figure 5.3 with color coding as in the case of Pb and Zn distribution.

5.6 THE CORRELATION BETWEEN Pb AND Zn, SOIL ORGANIC MATTER AND pH

In order to investigate whether there is any correlation between these 4 parameters, the correlation analysis was carried out for the confidence level more than 95 % ($P < 0.05$). The correlation coefficient for each pair of parameters is shown in Table 5.8.

Table 5.6 Pb and Zn concentration in each square of three designed transects

Square	Concentration of Pb (ppm)			Concentration of Zn (ppm)		
	Line 1	Line 2	Line 3	Line 1	Line 2	Line 3
1	912	319	41.1	4,270	1,690	102
2	1,130	427	71.8	5,580	2,370	126
3	844	131	81.2	997	817	90.1
4	921	52.5	55.7	2,830	1,500	98.6
5	1,020	359	75.4	2,030	1,250	141
6	891	436	62.8	4,360	1,790	115
7	111	633	171	5,230	1,680	125
8	725	338	241	3,930	8,870	70.1
Mean	**943 a***	**418 b***	**100 c***	**3,650 a***	**1,500 b***	**109 c***
SD	136	11.3	69.5	1,580	508	22.7
CV (%)	14.4	27.0	69.3	43.3	34.0	20.9

** There is a statistically significant difference ($P<0.05$) between any two values (for the same element) if they have different letters affixed.*

Table 5.7 pH and organic matter (OM) of sampling sites

Site	Soil pH	OM (%)	Site	Soil pH	OM (%)
1	6.9	6.2	**20**	6.9	8.2
2	6.6	6.2	**21**	5.9	7.8
3	6.8	5.9	**22**	7.3	8.5
4	5.9	7.2	**23**	6.8	8.0
5	7.0	7.0	**24**	6.6	7.8
6	6.3	8.1	**25**	7.4	9.2
7	6.5	8.1	**26**	7.5	7.6
8	5.8	9.6	**27**	6.9	7.2
9	5.8	8.5	**28**	5.6	8.6
10	6.3	8.7	**29**	6.6	8.2
11	5.8	7.9	**30**	7.2	8.6
12	5.8	9.0	**31**	6.3	7.8
13	6.0	7.6	**32**	7.5	8.2
14	6.1	8.1	**33**	6.4	7.2
15	6.3	6.8	**34**	6.4	8.2
16	6.3	8.5	**35**	6.8	8.6
17	6.3	8.2	**36**	7.4	8.9
18	6.3	6.8	**37**	7.6	9.2
19	6.6	8.2	**38**	7.1	8.5

Table 5.8. Correlation coefficient for Pb and Zn, organic matter and pH

	Pb	Zn	OM	pH
Pb	1	0.88	- 0.56	0.13
Zn		1	- 0.62	0.09
OM			1	0.03
pH				1

5.7 GIS AS A TOOL FOR RISK ASSESSMENT

Based on the content of Pb and Zn found in soil samples, the total samples were divided into 5 categories as shown in Table 5.9. The risk value of each category was used as a value datum for mapping of Pb and Zn distribution in soil.

Table 5.9. Risk value for sampling sites based on content of Pb and Zn in soil.

Concentration in soil (ppm)	Category	Risk value
< 100	background level	1: no risk
100 to 250	slightly high level	2: slight risk
250 to 500	medium high level	3: medium risk
500 to 1,000	very high level	4: very high risk
> 1,000	extremely high level	5: extremely high risk

None of the values was assigned to the low level because, in comparison with the normal distribution of Pb and Zn in soil and the earth crust, they all have higher values. Each sampling site has one risk value for Pb and one for Zn, which enables

creation of a map of distribution in soil. Figures 5.1 and 5.2 show the Pb and Zn distribution in the study area.

Two risk values, one for the risk of Pb contamination, one for that of Zn, were given for each sampling site. The risk value is dependent on the contents of those elements at each sampling site. The classification for risk values is presented in Table 5.9. Sites with the highest Pb and Zn contents are expressed by the red color similar to that of the map of Pb and Zn distribution at the study site. With decreasing content of those metals in soil samples the color is changed from red to brown, purple, blue and green. Green color in the risk assessment map represents sites with background level or, in other words, sites with no risk from Pb or Zn content in soil.

The final risk value reported on Figure 5.4 is the higher of the two values for Pb and Zn. The details of risk values for sampling sites of the study area are presented in Table 5.10.

Due to the fact that there is not enough detailed information about the comparison of the effect of Pb and Zn on ecology, plants, animals and human health, the final risk assessment map can not be drawn by overlaying of these two elements' distribution maps. The effects that accumulated by both Pb and Zn were not yet able to reported in risk assessment map. A deeper research on this must be carried out in order to solve the problem.

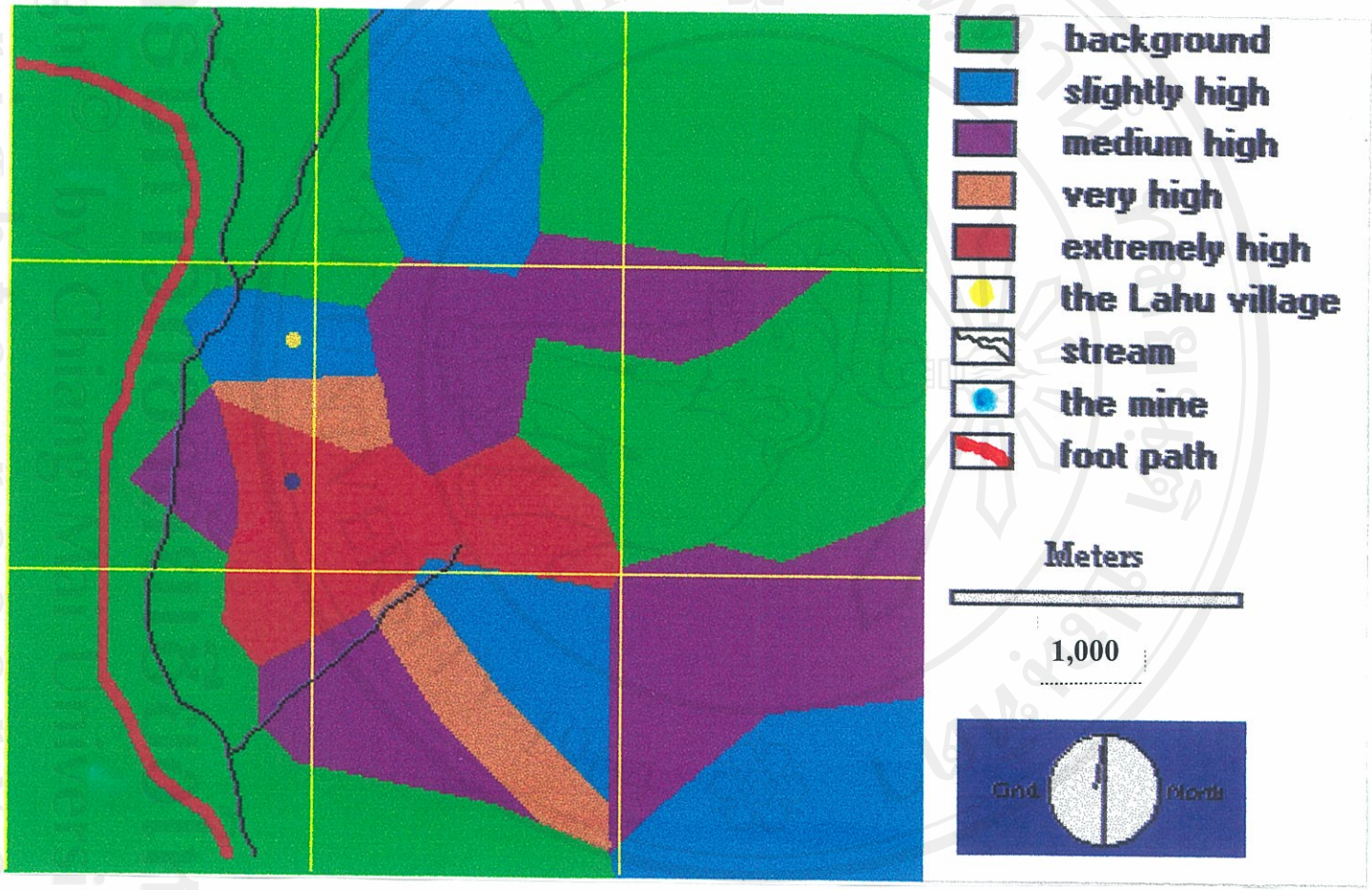

Figure 5.1 Map of Lead Distribution in the Study Area

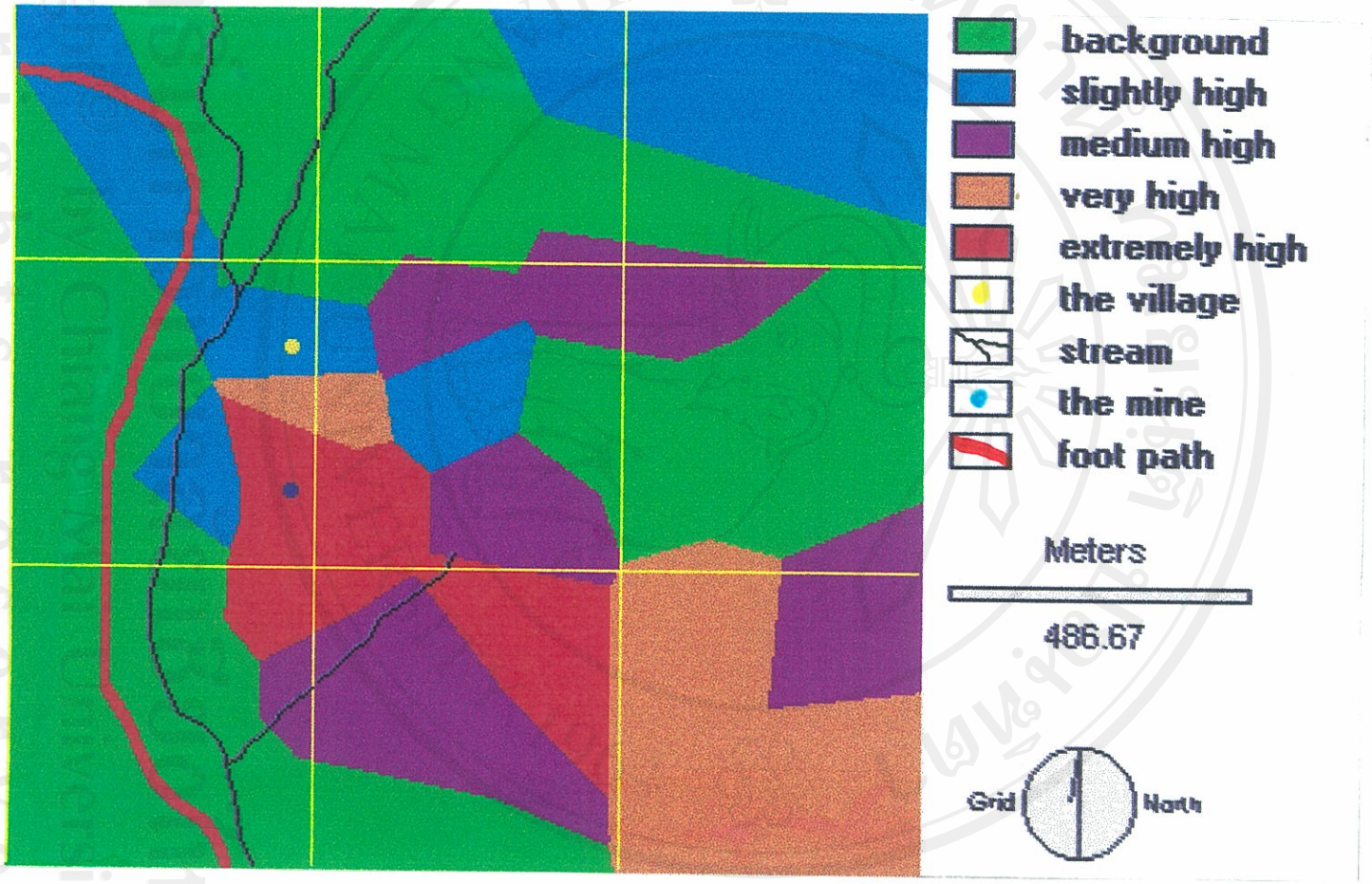

Figure 5.2 Map of Zinc Distribution in the Study Area

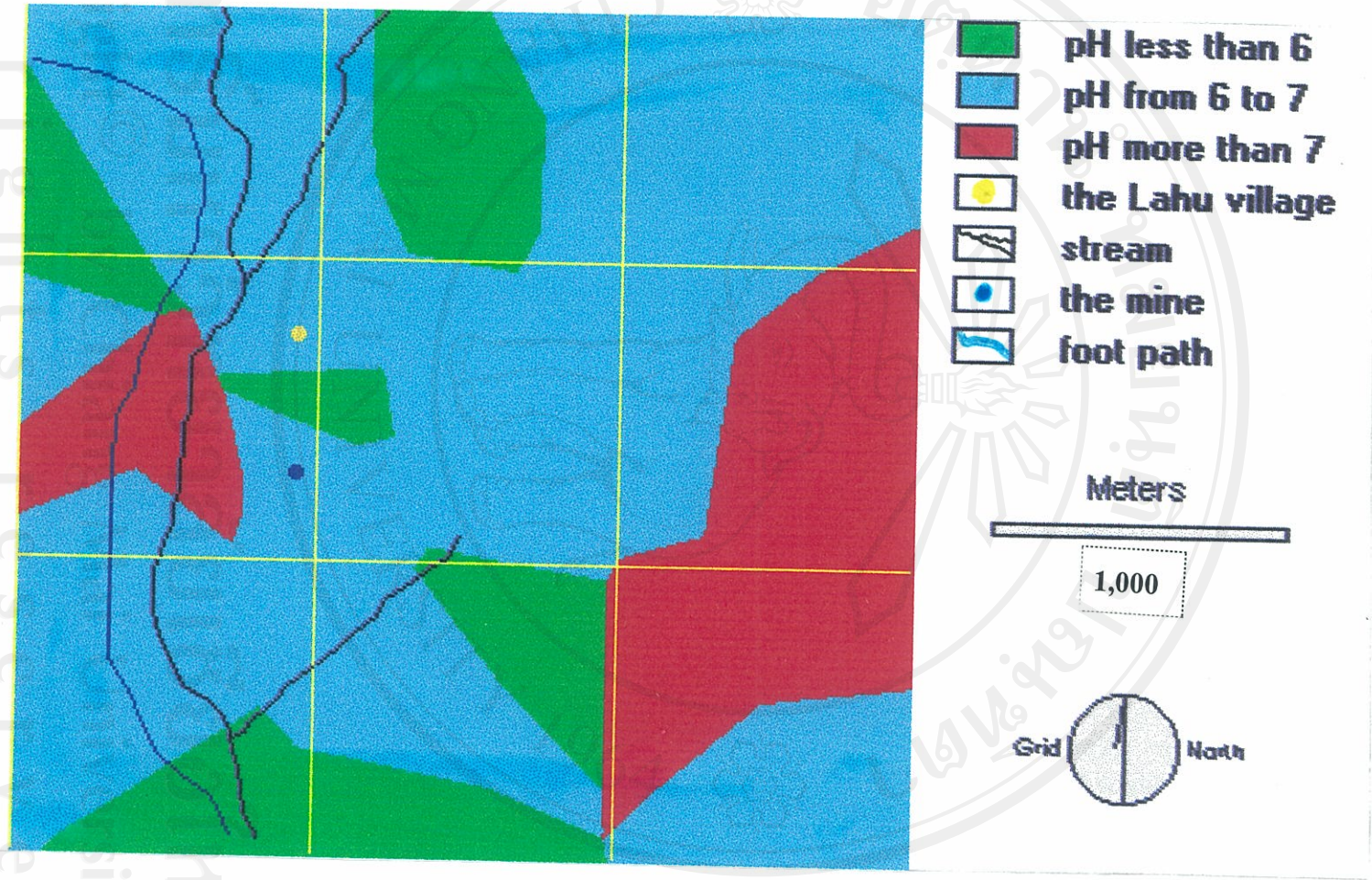

Figure 5.3 Map Soil pH Value in the Study Area

Table 5.10 Final risk value assigned for risk assessment map

Sampling site	Risk value			Sampling site	Risk value		
	Pb	Zn	Final		Pb	Zn	Final
1	5	5	5	20	5	3	5
2	5	5	5	21	5	5	5
3	5	5	5	22	2	3	3
4	4	4	4	23	4	3	4
5	2	2	2	24	3	1	3
6	3	3	3	25	1	1	1
7	3	2	3	26	1	2	2
8	2	1	2	27	3	1	3
9	1	1	1	28	1	1	1
10	1	1	1	29	1	1	1
11	1	1	1	30	2	4	4
12	1	1	1	31	1	1	1
13	1	1	1	32	1	2	2
14	1	1	1	33	3	3	3
15	1	2	2	34	1	1	1
16	1	1	1	35	1	1	1
17	1	1	1	36	1	1	1
18	1	1	1	37	3	4	4
19	5	5	5	38	3	3	3

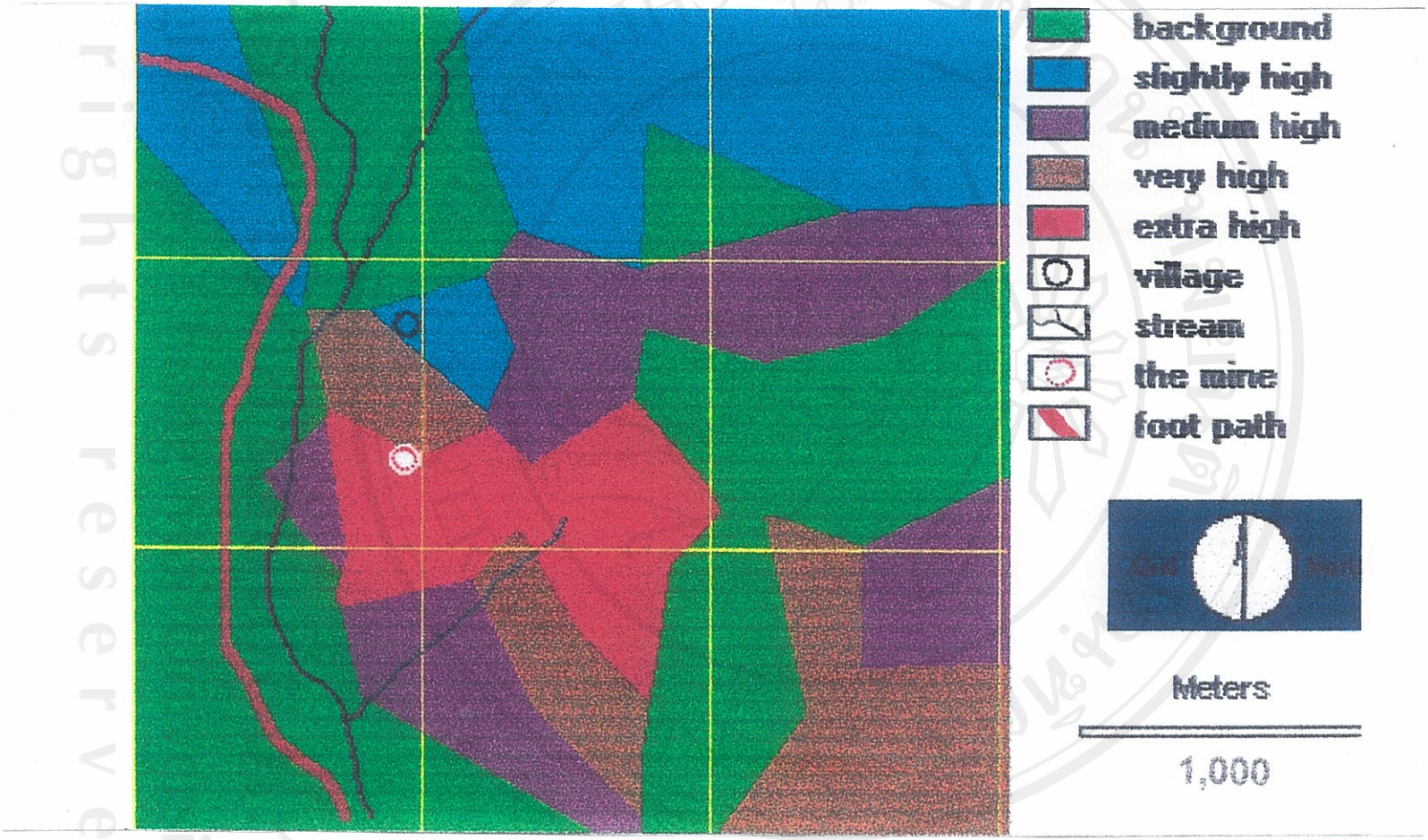

Figure 5.4 Map for Risk Assessment Based on Pb and Zn Distribution

metal content in samples of the study area also can be a cause of errors because samples need repeated dilution.

Considering the wide range and high values of heavy metal levels in samples, the CV is acceptable for an analytical method involving incomplete destruction of sample material and the results are precise and reproducible.

In order to test further the degree to which the analytical method is free of systematic error, 2 reference materials i.e. Soil 5, Soil 7 from the International Atomic Energy Agency (IAEA) were analyzed in parallel with samples by the same procedures. Compared to the verified values of these reference materials, the results of thesis work are within the confidence interval with confidence level $\geq$ 95 % as expressed in Table 5.2. Thus, the applied analytical methods are considered accurate and reliable.

Pb and Zn concentration in plants

The method used for plant digestion is a wet digestion. In the case where heavy metal levels in plant tissue are low, it is necessary to apply a separation and preconcentration technique. During the study, all of the Pb and Zn levels in plant tissues were high enough to be measured by direct aspiration. The CV obtained from precision tests reached the values of 9.8 and 7.6 for Pb and Zn, respectively. The analytical results of the rye grass reference sample from the Commission of the European Communities were also satisfactory, falling within the confidence level $\geq$ 95 %. The wet digestion method can be applied for study because it yields reproducible and reliable results.

6.2 MEAN LEVEL OF Pb AND Zn IN STUDY AREA

As can be seen in Tables 5.3 and 5.4, the mean concentration of Pb in the whole study area, ranges considerably from 31.3 ppm to 5,270 ppm and for Zn, the concentration ranges from 52.3 ppm to 5,440 ppm.

The area, where the samples were taken, covers more than 9 km^2 consisting of an area affected by mining activities as well as an area which has no evidence of human activities at all. Samples were collected from different directions and distances from the mine as well as from different land use patterns.

The sites with lowest Pb values are site numbers 11, 18, 31 and 34 where Pb values in these sites are less than 40 ppm. The sites numbered 1, 2, 3, 4 and 19, which are located nearest to the mine, have exceptionally high values of Pb. These values reach the highest values found in the surrounding area of the mine.

Zn is considered as an essential element in soil while Pb is considered as a trace element. Normally, the Zn level is higher than the Pb level in soil media. In this research, the Zn level also has a tendency to be higher than Pb when the Pb level is found to be very high. Sites 1, 2, 3, 4, and 19, which show the highest Pb levels, similarly have highest levels of Zn. The lowest values of Zn are found at sites 11, 16, 18 and 35. Two of these sites, sites number 11 and 18, also show lowest Pb level which indicates that there is a high correlation between the two elements. The statistical test revealed that the correlation coefficient between Pb and Zn in the study area is 0.88 (Table 5. 8).

5.8 THE SOIL-PLANT RELATIONSHIP OF HEAVY METALS

5.8.1 Lead and zinc uptake by ground flora in non-contaminated soil

Samples of five abundant ground flora species were taken together with soils where they were growing and analyzed for Pb and Zn content to investigate the soil-plant relationship between them. Data obtained are listed in Table 5.11. The transfer coefficient, K, is the metal concentration in plant tissue above ground divided by the metal concentration in soil.

Table 5.11 Concentration of Pb and Zn in 5 plant species and their K values.

Organs	**Mean Pb concentration (ppm)**				
	Apluda	*Selaginella*	*Microstegium*	*Ligodium*	*Anisocampium*
Root	14.4	10.1	75.7	18.2	20.7
Plant tissue	4.1	6.9	40.2	4.4	9.8
Soil	45.6	44.5	45.3	45.4	53.8
K	**0.090**	**0.155**	**0.888**	**0.097**	**0.182**
	Mean Zn concentration (ppm)				
Root	43.1	42.6	49.3	52.1	51.4
Plant tissue	17.3	19.4	31.8	29.2	17.4
Soil	41.7	56.2	40.8	57.5	67.4
K	**0.415**	**0.345**	**0.780**	**0.508**	**0.258**

5.8.2 Lead and zinc uptake by ground flora in contaminated soil

The plant samples were taken from different places with known Pb and Zn concentration in soil in order to investigate soil-plant relationship of Pb and Zn. Because species *Selaginella, Ligodium* and *Anisocampium* were not available during the whole period of sampling, the study was confined to focus only on the remaining two species, i.e. *Apluda*, *Microstegium*. The calculated soil-plant transfer coefficients (K) of Pb and Zn for these two species are shown in the Table 5.12. These two herb species are able to grow in soil extremely highly contaminated by Pb and Zn. Results for soil with low contamination soil are also included likewise in Table 5.12 to facilitate the comparison.

Table 5.12 K values for *Apluda* and *Microstegium*.

Pb (ppm) in soil	Pb(ppm) in *Apluda*	K	Pb (ppm) in soil	Pb (ppm) in *Microstegium*	K
45.1	4.1	**0.091**	45.3	40.2	**0.888**
51.1	4.3	**0.078**	12.2	42.2	**0.347**
61.2	4.1	**0.067**	339	46.1	**0.136**
155	15.1	**0.097**	2,080	60.7	**0.029**
611	42.8	**0.070**	5,120	76.4	**0.015**
2,060	84.6	**0.041**	9,870	79.4	**0.008**
2,320	92.7	**0.040**	17,700	142	**0.007**
5,130	112	**0.022**	19,700	170	**0.008**
26,300	127	**0.005**	21,700	226	**0.010**
Zn (ppm) in soil	Zn (ppm) in *Apluda*	K	Zn (ppm) in soil	Zn (ppm) in *Microstegium*	K
41.7	17.3	**0.415**	52.6	31.8	**0.604**
47.2	23.1	**0.489**	111	34.7	**0.313**
51.0	36.7	**0.720**	525	39.4	**0.075**
121	62.4	**0.514**	206	39.2	**0.019**
523	67.5	**0.129**	7,880	39.4	**0.005**
1,460	71.4	**0.049**	10,800	43.3	**0.004**
2,270	74.8	**0.033**	17,200	51.6	**0.003**
4,780	76.5	**0.016**	20,600	82.4	**0.004**
21,700	87.1	**0.004**	22,500	89.1	**0.004**