CHAPTER IV

RESULTS AND DISCUSSION

4.1 QUALITY ASSURANCE OF ANALYTICAL METHOD

4.1.1 Analytical Method

There are a number of analytical methods used for the determination of trace metals in environmental media (e.g. soil, water, air, etc.). However, there are only a few instrumental methods with sufficiently high detection power currently applied in routine analysis of many environmental samples like soil. In this study, the flame Atomic Absorption Spectroscopy (AAS) was used to determine the lead level in soil with a Detection Limit of 15 ppm. AAS determines one element at a time. Aside from being simple in operation, spectrophotometers are commercially available. Thus, this method was used.

Setting the machine at its optimum operating conditions and using the German Standard Analytical Method modified after the Method adopted by Institute of Environmental Studies, University of Toronto, Canada (Van Loon, 1980) of sample preparation described in Section 3.3. resulted in reliable soil analysis. The accuracy of this analytical method was confirmed by the use two soil Certified Reference Materials (IAEA Soil 7 and Soil 5) recommended by international organizations. Satisfactory results were obtained as discussed in detail in Section 4.1.2.

4.1.2 Quality Assurance

Accuracy problems in many trace analyses are oftentimes encountered by many scientists. Since in environmental protection, the analytical data provide the quantitative basis for the estimation of exposure; and the introduction of legal measures and their supervision, it is obvious that the elimination of these error sources and continuous protection of the quality of the data is extremely important (Stoepler, 1988). Thus, the extent of systematic errors during sample collection, sample preparation, and analytical determination was always minimized and controlled.

Furthermore, the analytical method was verified by analysis of two soil certified reference materials (CRMs) recommended by various national and supranational agencies and producers. Specifically, the two CRMs (IAEA Soil 7 and IAEA Soil 5) recommended by International Atomic Energy Agency (IAEA) based at Vienna Austria, provide the laboratories of its member states the ability to evaluate the accuracy of their analytical methods used for the determination of selected geochemical, environmental and similar materials. However, the control of some errors is still incomplete, unless an accurate application of the most powerful analytical methods as well as utmost contamination minimization in the laboratory are being employed. At any rate, results in this study revealed almost an accurate result in comparison with the certified reference materials.

As standard operating procedure, the IAEA Soil 7 and IAEA Soil 5 were simultaneously analyzed together with the unknown samples. In the standardization method, the same analytical procedure was used in sample solution preparation for Soil 7 and Soil 5 except for the initial sample preparation since the recommended IAEA Certified Reference Materials (Soil 7 and Soil 5) are already commercially available. In the same manner, at a given absorbance from the AAS Perkin Elmer, the level of lead (ppm) in both the soil samples and the CRMs (Soil 7 and Soil 5) were determined by the use of the same calibration graph as discussed in Section 4.2. Results in the evaluation revealed that the mean difference of lead level (ppm) between the result of the analytical method used in this study and the recommended value by IAEA were 5 ppm and 10 ppm for Soil 7 and Soil 5 respectively (Table 1). These differences constitute only 8.33 % and 7.72 % for Soil 7 and Soil 5 respectively, which are found to be very minimal. The minimal differences of these results imply an accurate analysis since it is approaching to a 100% level of confidence.

Furthermore, the accuracy of the results could also be supported by the level of confidence interval at significance level of 0.05 ppm recommended by IAEA. As a comparison , results showed that the mean lead level of Soil 7 and Soil 5 are at 55.08 ppm and 139.10 ppm respectively, which fall within the recommended confidence interval of IAEA at 55- 71 ppm and 103-155 ppm respectively. It is very obvious that the forgoing analytical procedure used was accurate and confident.

Table 1 *The mean difference of lead level (ppm) between the German Analytical Method and the IAEA recommended values for two IAEA Certified Reference Materials (Soil 7 and Soil 5)*

IAEA Soil Standard	Lead Conc (µg/g) - Analytical Method	Recommended Concentration by IAEA*	Confidence Interval- (Significance Level = 0.05 µg/g)	% Difference	Mean Difference (ppm)
Soil 7	55.08	60.00	55 - 71	8.33	4.92
Soil 5	139.10	129	103 -155	7.72	10.10

** IAEA - (International Atomic Energy Agency), Vienna Austria,*

4.2 Evaluation of Results by Calibration Curve

The concentration of the analyte in 42 soil samples, IAEA Soil 7 and Soil 5) was obtained through the use of the calibration curve (Figure 13) derived from the prepared calibration standard solutions containing calculated concentrations (Appendix 1). In order to obtain more accurate results in the analysis, fresh calibration standard solutions were always prepared during every set of sample analyses. Likewise, the maximum analyte concentration in calibration solutions was limited to the concentration which yields an absorbance of $\log_{10(e)}$ (0.434) in Flame AAS as recommended for the optimization of the condition of the Perkin Elmer AAS instrument. This concentration can be estimated by the reference to a sensitivity table supplied by the manufacturer of the AAS set. It was made sure that the concentration in the sample solution did not exceed that in the calibration solutions. Thus, dilution of the standard solution had been undertaken. The use of AF (Abbreviated from "Absorbance Fit") Computer Software aided to compute the lead concentration of the analytes based on the calibration curve derived from calibration solutions. This program is loaded and run by DOS from the file AF.EXE. From the absorbance readings of calibration solutions, a calibration curve was produced (Figure 13). This calibration curve was obtained from the two sets of readings of the calibration solutions read before and after the reading of sample solutions (Appendix 4). As previously stated, the analyte

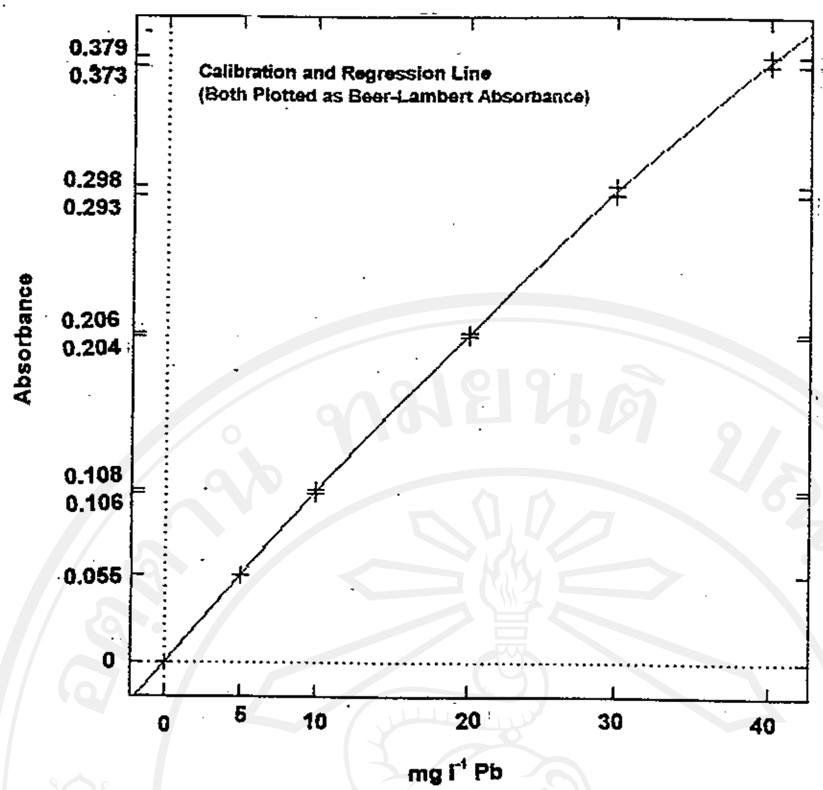


Figure 13 Calibration curve derived from Soil analysis on Sept. 16, 1996 with calibration data shown in Appendix 4

concentration corresponding to a given absorbance obtained from Perkin Elmer AAS, could be obtained from this calibration curve with the aid of the AF Program. Results of a sample output are given in Appendix 4.

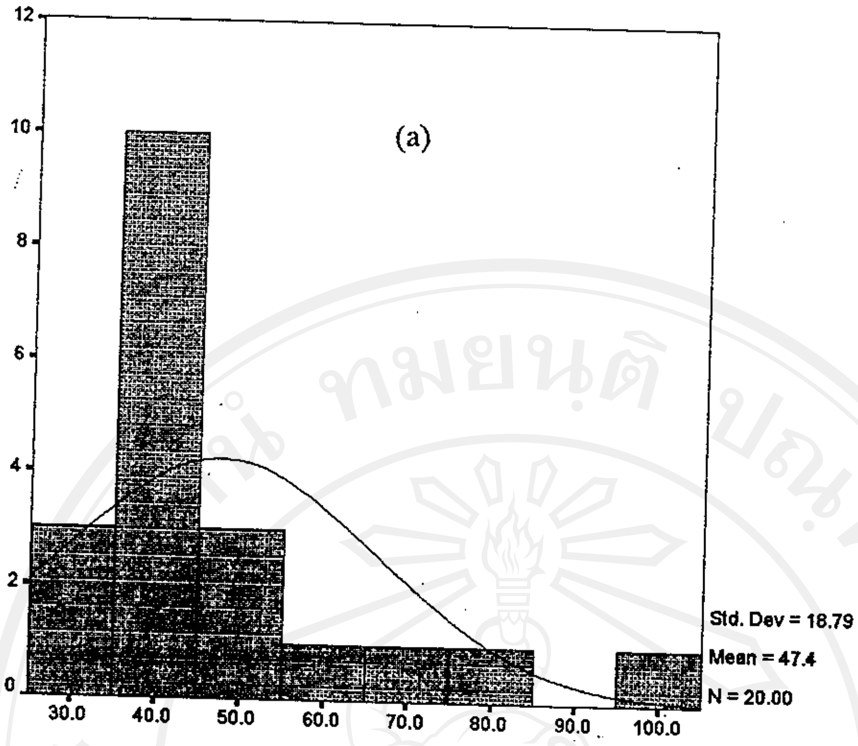
However, the amount of lead (ppm) in soil with a given weight (g) of soil sample could be computed using the example mathematical computation in Appendix 5. This process was applied to all the sets of sample analysis, done at several times. Thus, there are different analyte concentrations corresponding to a given absorbance given by different calibration curves used different sets of sample analyses .

4.3 Statistical Analysis of the Data

4.3.1 Frequency Distribution

The histogram was used as the initial tool in analyzing statistical data of this study. As a familiar method of displaying numeric information, it provided a useful starting point of discussion which could be easily understood. Results in the frequency distribution of lead (ppm), organic matter content (%) , pH and clay content (%) in soil at different grids of Chiang Mai City are shown in Figures 14 -15.

Results revealed that the mean level of lead accumulation in soil at different sites/girds of Chiang Mai City lies at 47.4 ppm (S.D. at 18.79 ppm.) where most of the values are between 30 - 55 ppm. On the other hand, the mean level distribution of other parameters such as pH and organic matter content were also subjected to histogram analysis using the same approach above. Results also showed that the mean distribution of pH was at 7.22 (S.D=0.22) while the organic matter content (%) and the clay were at 3.72 % (S.D.=0.79) and 14.9 % (S.D=2.20) respectively. However, to further analyze the results statistically, the SPSS program was used to test the significance between grids which shall be discussed in the preceding section (Section 4.3.2).



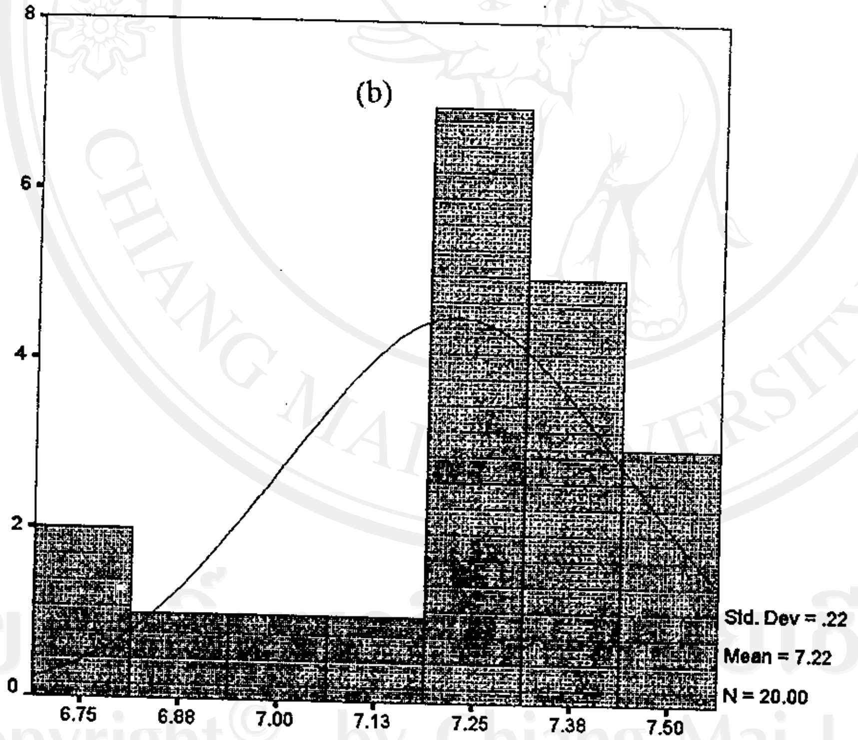
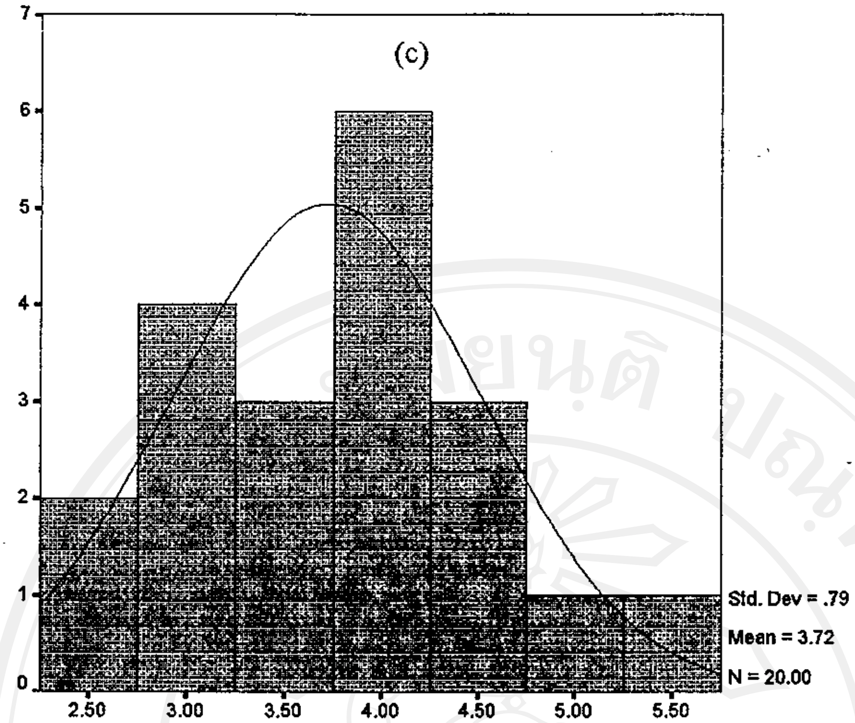


Figure 14. Histogram of Pb (a) and pH (b) distribution in soil of Chiang Mai City.



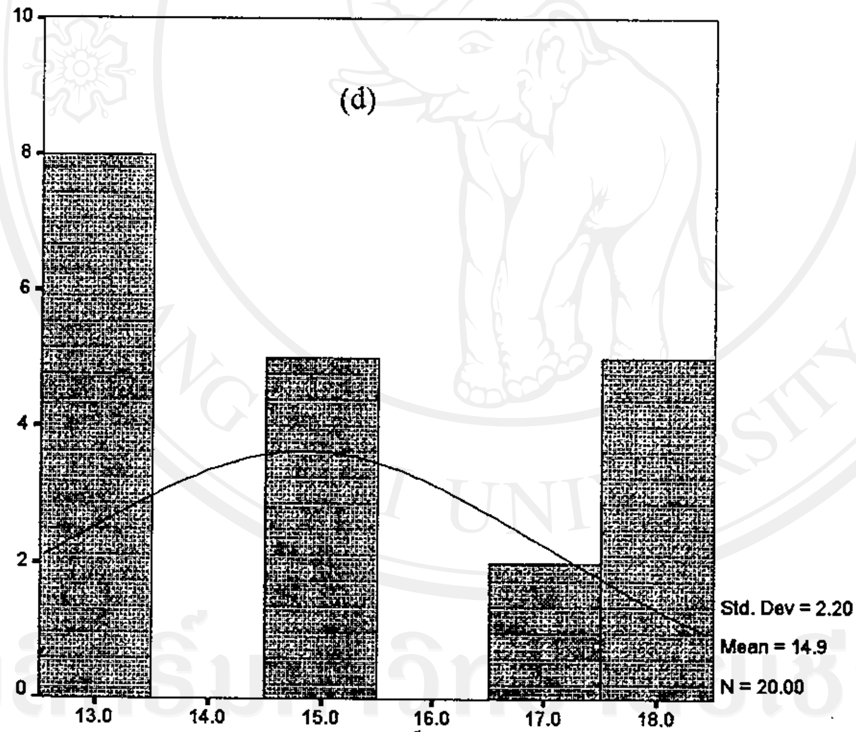


Figure 15. Histogram of organic matter content (c) and clay content (d) distribution in soil of Chiang Mai City

4.3.2 Test of Significance Between Grids

The means and dispersion of samples can be used to test the possibility that the samples might represent the same population. The use of Analysis of Variance (ANOVA) in a Completely Randomized Design (CRD) through the SPSS Software aided to further analyze statistically the different parameters collected in this study. This technique was used in order to find a valid estimate of σ^2 and to compare the means yields under several treatment (i.e. grid no.).

As previously cited in the methodology for statistical analysis, there were 20 grids that were analyzed using the SPSS Software. Results from the Analysis of Variance revealed that no significant difference between different grids of all the parameters analyzed except for the clay content (Table 2). The significant difference among sites could be manifested by the given F-Prob. values. If F- Prob. values is greater than 0.05, it does not show a significant difference between grids.

To further analyze the data whose means have significant difference, (e.g. clay content) the Least Significant Different (LSD) test was used. Results in the statistical analysis showed that some areas differ significantly as revealed by the LSD test for mean of different grids (Appendix 9).

Table 2 . ANOVA[1] table for lead (ppm), pH, organic matter and clay content of different grids using Complete Randomized Design (CRD)

Parameter	Degrees of Freedom	Sum of Squares	Mean Squares	F Ratio	F Prob.	SD	Standard Error
Pb (ppm)	19	13408.9485	705.7341	1.4271	0.2183^{ns}	24.44	3.8647
pH	19	1.8473	0.0972	1.0540	0.4528^{ns}	0.3077	0.0486
Organic Matter Content (%)	19	24.3895	1.2837	1.4571	0.2052^{ns}	1.0379	0.1641
Clay Content (%)	19	183.10	9.6368	2.8344	0.0127^{s}	2.5374	0.4012

1/ Output of the SPSS Computer Program
ns = not significant s = significant

4. 4 . Lead Level (ppm) Analysis

4.4.1 Mean Level of Pb Contamination

The lead level (ppm) in soil of Chiang Mai City varies at different grids (Figure 16). The mean value ranges from 26 19- 102.98 ppm with a mean level of distribution at 47.40 ppm (Figure 14). The variation of lead level (ppm) in soil may be influenced by the degree of contamination contributed by several sources which shall be discussed in Section 4.4.2. Lead, being a constituent of the Earth's crust, has already been in soil since before the start of human population. Based on U.S. Geological Survey (1976), the mean lead level (ppm) in an unpolluted soil ranges from 10 - 40 ppm dry weight (Ewers and

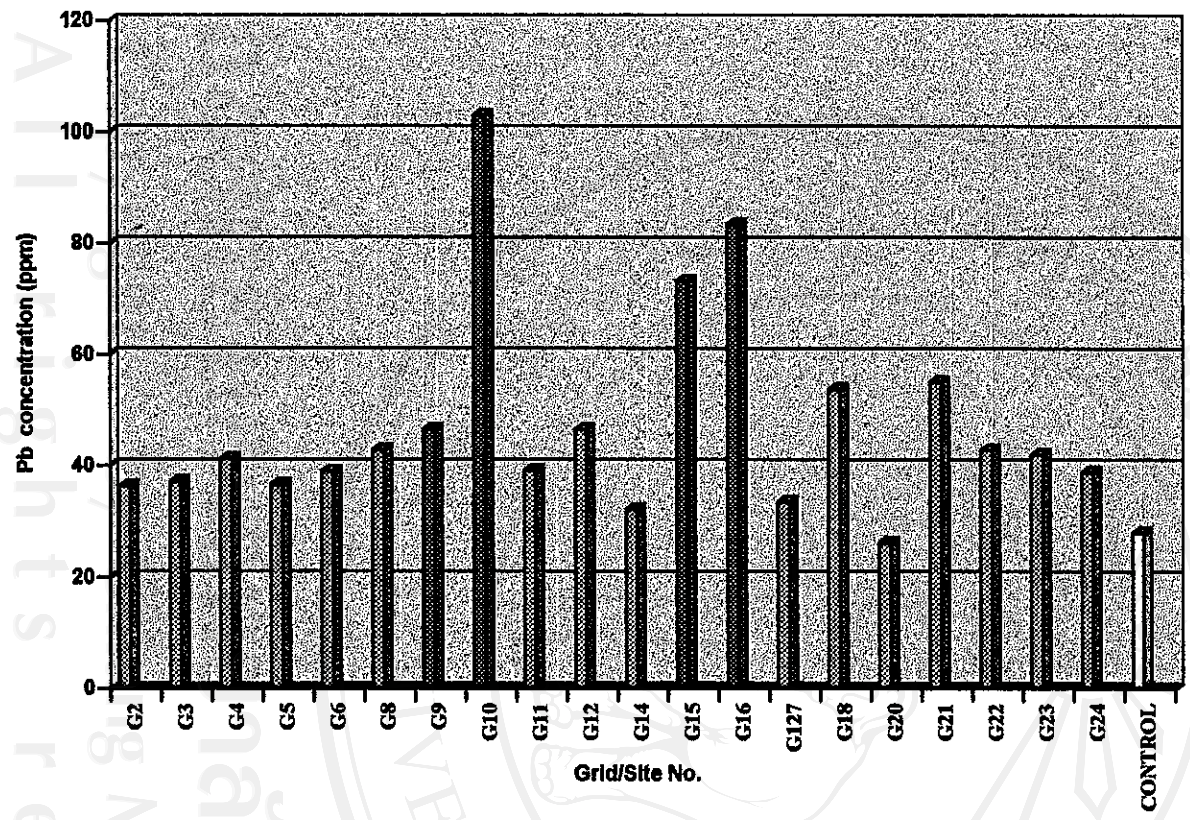


Figure 16. Mean lead level (ppm) in soil at different grids of Chiang Mai City

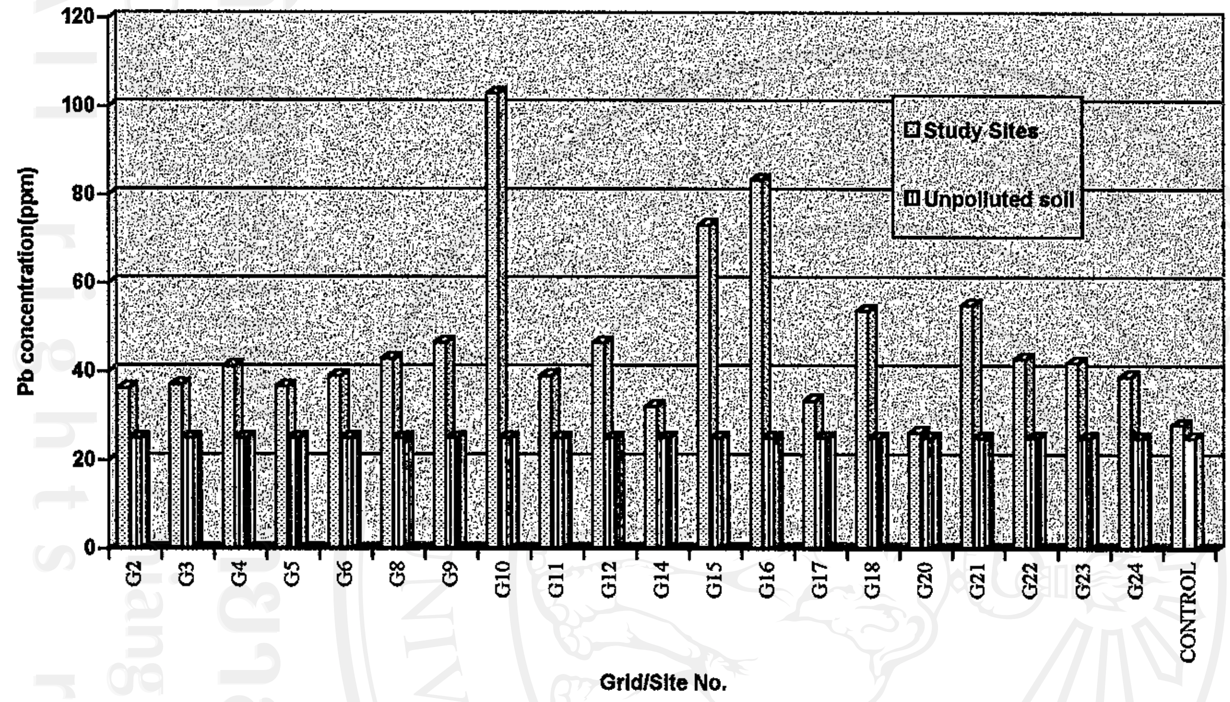


Figure 17. Difference in Pb level (ppm) in soil at different grids of Chiang Mai City compared with the worldwide level of unpolluted soil at 25 ppm

Schlipkoter, 1991). In general, soils tend to reflect the composition of their parent materials.

Although there had been so many results obtained from many countries on the normal level of lead in unpolluted soil, it is estimated that Pb level in the worldwide scale is at 25 ppm (Kabata-Pendias and Pendias, 1984). However, due to widespread lead pollution in many ecosystems, it is believed that most of these soils are likely to be enriched of this metal, especially on the top soil horizon. As reported by Ewers and Schlipkoter (1991) a significant increase in lead level in surface soil has been found particularly, in inner city areas, near busy highways and near lead works.

Like many other urban ecosystems, the soil of Chiang Mai City is believed to have been contaminated by lead as manifested by its high mean lead level of 47.40 ppm compared to the mean lead level of unpolluted soil of 25 ppm. Results revealed that all grids in Chiang Mai City under study differ comparatively with the worldwide scale level at 25 ppm as shown in Figure 17. This result showed that lead contamination in soil at Chiang Mai City had probably been influenced by human activities. However, the degree of its present level of lead contamination may or may not pose possible risk based on the threshold/limiting values set by international standards for risk assessment analysis. This assessment shall be discussed the following section (Section 4.5).

4.4.2 Sources of Lead Contamination

There are many sources by which the soil in Chiang Mai City can be contaminated with lead. Since there is no geological source of anomalous lead in the vicinity, the soil of Chiang Mai City has already been contaminated by this trace element due to on-going human activities. Although there are other possible sources of lead contamination in soil, like disposal of unwanted materials/wastes incorporating lead products (i.e. batteries) and the occasional flooding by water probably contaminated with lead, the most probable main source of lead found in this study is the airborne deposition of lead due to vehicular emission. There is some evidence which could prove that the above main source had caused much in the accumulation of lead in soil.

Lead is added to gasoline because this is the most convenient and economic method of increasing the octane ratings of all grades of gasoline (Kabata- Pendias and Pendias, 1984). Several reports indicated that automobile traffic contributes 90% of the atmospheric lead emission (Ewers and Schlipkoter, 1991). Thus, the major part of lead found in the atmosphere is the result of the combustion of leaded gasoline.

Lead is emitted into the atmosphere as organolead resulting from the production of tetramethyllead (TML and tetraethyllead (TEL) which are used as antiknock additives as previously mentioned. Usually these organolead compounds (TML and TEL) occur in urban atmospheres at levels ranging from 5 to 200 ng /m^3 (Ewers and Schlipkoter,1991). Since evaporation and automotive emissions of unburned TML and TEL are found to be the main environmental source, the highest levels are found in parking garages, gasoline stations and busy streets in central urban area where high pressures of human activities are going on. Usually, organolead makes up to 5-10% of the concentration of particulate lead in urban areas (Nielsen, 1984). Since automotive emission is found to be the main source of lead in this study, the lead may occur mainly in a form of PbBrCl (Ewers and Schlipkoter, 1991)

Chiang Mai City in particular, has an increasing demand and continuous use of motor vehicles (i.e. motorbikes, cars, etc., usually using leaded gasoline). This could have enhanced the lead accumulation in soil and other environmental media. Based on the recent registration as of 1994, (Appendix 10) there is already a total of 532219 vehicles registered in Chiang Mai City and the number is expected to increase in the coming years due to increasing development of the city. From 1991-1994, there was an average rate of increase of registered vehicles of 12.4 % where a high percentage of registrants comprises motorbikes and personal cars that are believed to be great consumers of leaded gasoline. The use of leaded gasoline is most often in motorbikes which constitute the largest number of vehicles moving in Chiang Mai City (Appendix 11). It is observed that high percentage of these motorcycles are using leaded gasoline compared to cars and buses, some of which are already using diesel fuel.

Although Thailand adopted a ban on the use of leaded gasoline in 1996, observation revealed that, up to the present, there are still gasoline stations that are offering leaded gasoline. Since soil contamination with heavy metals is usually quite permanent as reported by Davies (1980), Johnson et.al (1975), Purves (1977) and Kitagishi and Yamane (1981), the soil of Chiang Mai City has likewise permanently accumulated this trace element for the past years. The year of implementation of the ban for use of unleaded gasoline may not significantly reduce the present lead level because of the above reasons. However, the limitation of this study, is that no data are yet available as to what proportion of vehicles in Chiang Mai are using leaded and unleaded gasoline. Likewise, no information is yet available on the effectiveness of the implementation of the ban on the use of leaded gasoline. Probably in the future, the complete eradication of leaded gasoline in the market may lower the lead level compared with the present condition if no other sources (i.e. factories producing lead) will be established. Therefore, the increasing rate of demand for motor vehicles may likewise increase airborne deposition and enhance Pb accumulation, if no measures to completely eradicate leaded gasoline in the market are undertaken.

Moreover, the recent traffic survey conducted (January, 1996) by the ERA Student, Batch 1995 of Chiang Mai University, revealed that the old Chiang Mai City has already a high traffic density (cars/hr) during peak hours from 7:00 am to 8:00 am and low density from 9:00 am to 10:00 am as shown in Appendix 11. The survey of the traffic density shows that motorcycles and personal cars still constitute the largest percentage of motor vehicles moving in Chiang Mai City (Appendix 10). Since these motor vehicles are believed to be large users of leaded gasoline, accumulation of lead near areas with high traffic densities is also high. The above findings of the ERA Batch 1995 on the traffic density is another manifestation that the probable source of lead contamination in soil has motor vehicles.

The impact of pollution in Chiang Mai City due to traffic could also be manifested by the difference between the lead concentration in soil of Chiang Mai City and that of the control area in Mae Rim District about 12 km from Chiang Mai City (Figure 18). Results revealed a high difference in lead level, especially in areas with high traffic densities (old Chiang Mai City) as shown in Figure 18. This high difference could probably be attributed to high deposition of airborne lead near the city center owing to high traffic densities in an urban ecosystem like Chiang Mai City.

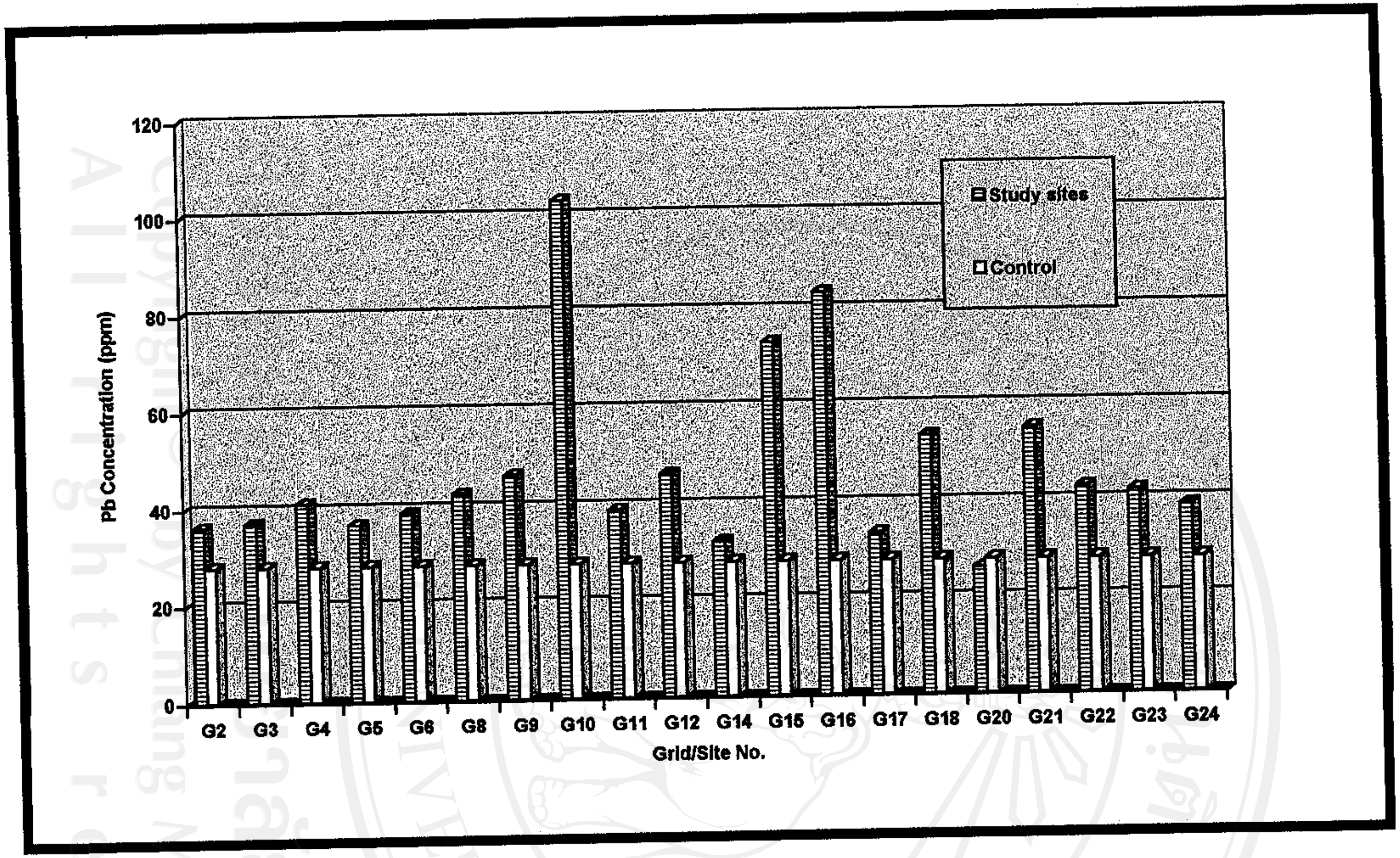


Figure 18 . Mean difference of Pb level in soil at different grids of Chiang Mai City compared with the Pb level at 28.02 ppm in control area at Mae Rim District

Results in this study also revealed that even the control area had already been contaminated with lead because of its difference in lead level compared with that of the worldwide level of 25 ppm. It shows that the contamination in the soil of control area could also have been affected by on-going human activities like traffic. Literature further revealed that lead emitted from vehicles is transported in aerosols to a certain distance depending on the particulate size and the meteorological conditions. It is a fact that there is progressive removal of lead from the atmosphere through wet and dry deposition which may likewise continuously contaminate the soil in the control area by lead. This wet and dry deposition had been widely reviewed by Schwertman and Tylor (1977), Folkeson (1979) and Thomas (1979).

Moreover, based on an American study on roadside and urban concentration, the mean air lead concentration is related to the traffic volume and the distance from the highway as cited by Hepple (1971). Thus, lead contamination in the control area could also be attributed to airborne deposition of lead due to the nearness of the sampling area to the highway which is only about 200 meters away. Likewise, the above literature could also show that there might be probable airborne deposition of lead as smaller particles transported at a certain distance especially from Chiang Mai City which is still near to the control area. At any rate, the above evidence could prove that airborne deposition of lead into the soil was the most probable source of lead. It could be portrayed that the continuous use of leaded gasoline will consequently produce a relatively high emission of lead into the atmosphere. As a consequence there will be the possibility of increasing the present lead level in the soil.

The occasional flooding that occurs in the city almost every year may be another probable source of this metal. Lead that has been accumulated in other areas could be transported through flooding. Geographically, Chiang Mai City is located in the alluvial plain of Chiang Mai Basin and lies along Mae Ping River and Mae Kha Canal. Flooding by water contaminated with lead may lead to transport of this element by leaching and transfer up to a certain distance along the alluvial plain especially along the river system.

However, no study yet had been conducted on the transportability of this metal through flooding. In fact results in this study revealed that a low level of lead occurs in areas along the river which shall be discussed in Section 4.4.3. Probably, leaching of Pb from the city could have occurred and leached Pb could have been transported to downstream areas.

4.4.3 Lead Level Distribution Analysis

Although the lead level distribution in soil of Chiang Mai City does not vary significantly, there are however areas which manifest high lead level concentration like Grid 10, 15 and 16 as shown in the Figure 19. These grids are located within the Chiang Mai moat where large population pressures and human activities are going on. As a result, high traffic densities are observed in these areas, leading to high vehicular emissions. As previously discussed, the high level of lead present on these grids could be associated with the traffic densities in these areas. The proximity of these areas to the main road systems may have contributed to the degree of the airborne deposition of lead attributed to motor vehicles. Although there are some other possible sources as previously discussed, the main source could have been by vehicular emission. as is evident through comparing the Pb level with that of other areas where there are less vehicular emissions.

To further supplement the above results, findings revealed that the lowest level of lead was found in Grid 20. This site happens to be a military area used by the Royal Thai Airforce. Based on observations, vehicular activities in this area are controlled where there is a limited entry of motor vehicles. Although private cars are allowed to enter,

motorcycles are highly restricted except for those of airforce personnel. In this case, the level of emission of airborne lead is likewise minimized and as a result a low level of Pb was found.

On the other hand, low levels of lead were also found in areas (grids) along the Mae Ping River as shown in Figure 19. This low level of Pb could have been attributed by the leaching of Pb due to flooding. It is known that the city is situated along the alluvial plain of Chiang Mai Basin and occurrence of a yearly flood is prevalent. However, the leaching and washing of lead in the soil is dependent on the stability of soil, soil type and the present of organic matter content. These factors may likewise affect the transport of this element to the lower streams. Results found out that most of the soils in Chiang Mai City are from sandy loam to loamy sand which are vulnerable to soil erosions, thus, leaching was possible.

Moreover, the above results could be further supplemented by the results of the environmental study conducted by students of ERA Batch 1995 of Chiang Mai University (Unpublished, 1996). An Environmental Quality Map (Figure 20) was produced using GIS-IDRISI Program which was the product of the overlay of traffic density , lichens and birds. The parameters like lichens and birds are used in this study since they are good bioindicators for air pollution. Results revealed that low environmental quality was

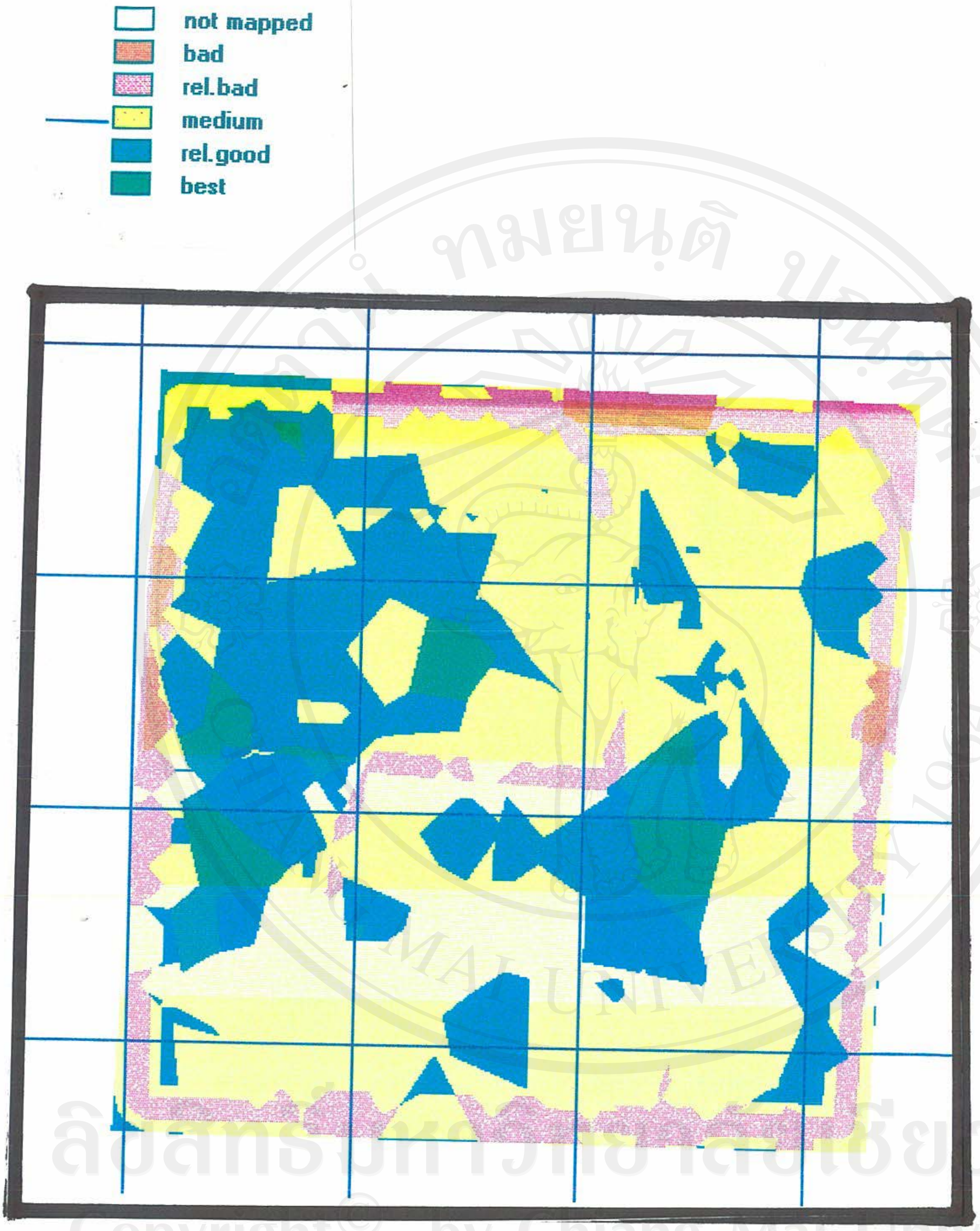


Figure 20 Environmental quality map of Chiang Mai City from the GIS Study of ERA Batch 1995 of Chiang Mai University

observed in areas along the Chiang Mai moat and nearby main road systems. Where traffic density was high, low densities of lichens and birds are found. The result of the present study coincides with the result of the study conducted by the ERA Students.

4.5 Risk Assessment of Lead Contamination

4.5.1 Risk Assessment Based on Lead Immobility Model

The assessment of risk caused by Pb accumulation in soil, was based on the bonding strength of soil towards absorbed lead as affected by factors like pH, organic matter content and clay content (Table 3). These factors usually affect the mobility of Pb in the soil. In this study, the Pb immobility model after the Sewage -Sludge Regulation of the Federal Republic of Germany (DVWK Leaflet for Water Resources 212/1988) was used. This model was applicable to risk for water resources which was applied in this study because the most probable risk that could have an impact towards lead accumulation in the soil environment of Chiang Mai City is mainly to water because the study areas are not agricultural areas for food production. Thus, the risk assessment in relation to the mobility of Pb through plant uptake was not given so much emphasis.

Table 3 *The bonding strength and conditions of several factors affecting Pb mobility in soil set after the Sewage - Sludge Regulation (DVWK Leaflet for Water Resources 212/1988)*

Factor	Rating/ Scale	Limiting values									Factor conditions
pH		2.5	3	3.5	4**	5	5.5	6	6.5	7.8	
	Bonding Strength	1	2	2	3	4	5	5	5	5	Low pH dissolves metal, high mobility, high risk High pH, greater adsorption, less mobility, low risk Low pH, metal ions increases, mobility of cations increases
Organic Matter %		0.5	1.00	1.5	2**	2-8	8-15	>15			High organic matter, more absorption, less mobility and low risk.
	Bonding Strength	1	2	3	4	5	5	5			
Clay Content (%)		0-1	1.2	3.5	8**	(17)	17-25	25-45	>45		Low clay content, adsorb less metal, high mobility, high risk.
	Bonding Strength	1	2	3	4	5	5	5	5		
Lead (ppm)		< 25	26 - 50	51 - 99	100**	150	200	300	>500		

***** Limiting values recommended internationally***

Bonding Strength Rating:* *0 = None, 1 = very weak, 2= weak , 3 = medium, 4= strong , 5 =very strong

Based on the bonding strength of soil to adsorb metal (eg. Pb), the conditions and threshold/limiting values are tabulated in Table 3. The bonding strength was rated from 1 - 5 depending its propensity to adsorb metal at a given minimum value of a certain parameter such as pH, organic matter content and clay content. No. 1 represents the lowest bonding strength while No.5 the highest. This means that as its binding strength increases, it likewise increases its capacity to adsorb metals. The minimum limits and conditions were set as tabulated in Table 4 These minimum limits served as baseline standard limit for setting risk assessment in this study.

There are several mechanisms by which lead may be immobilized in soils. As stated by Ewers and Schlipkoter (1991), the atmospheric lead deposited in soil is retained in the upper (2-5 cm) soil layers, especially in soils with at least 5 % organic matter content and a pH of 5 or above. A high organic humus fraction and high soil pH are the most important factors of lead immobility in the soil. Furthermore, there are also other factors such as adsorption of lead onto the clay minerals which is normally associated with the textural type of soil (i.e. clay loam, sandy loan, loam, etc.). The determination of the above given factors such soil pH, organic matter content and the clay content were the factors considered in risk assessment of lead accumulation in soil of Chiang Mai City. Since soil has been known to be a sink of heavy metals (e.g. lead), the consideration of the above factors affecting lead mobility from the soil to the water systems was given emphasis in this study. Kabata-Pendias and Pendias (1984) stated that lead is generally insoluble and so poorly transferred from one medium to the other. However, there are several conditions that lead is mobilized in the soil and may contaminate water system as well as plants (through plant uptake) and animals (through inhalation) and in the food chain. These conditions have certain values and limits which are usually recommended as international standards so that beyond these limits (either low or high), lead will pose a possible risk to human and animal health.

For risk assessment of lead accumulation in soil, the limits and conditions are recommended by the Sewage Sludge Regulation (DVWK, 1988) as shown in Table 3. The following are the minimum limits by which the binding strength of such factors may affect Pb accumulation and mobility: pH= 4; organic matter content = 2% ; clay content = 8 % ; and lead level = 100 ppm. Soil characteristics being below or above these limiting values will affect the accumulation of lead in soil and at certain level of lead accumulation (i.e. > 100 ppm) may pose possible risk in the food chain (plant-animals-humans). Table 3 shows that as the value of the parameter increases, the binding strength of soil to adsorb metal also increases. This simply means that at high pH, high organic matter content and high clay content soil can strongly absorb Pb. As a consequence, the risk to the water resources also decreases. However, these conditions are only true of factors like pH, organic matter content and clay content. In the case of Pb level, it is very obvious that as the Pb level in soil increases, there is also a corresponding increase of risk to the environment.

The relative mobility of some trace elements in soil (e.g. Pb) is dependent on soil pH as investigated by Fuller (1977). He stated that Pb is slowly mobile at pH from 6.7 - 8.8 . A low pH dissolves metals and mobilizes the trace elements thereby increasing the possibility for uptake by the flora and fauna and thus increasing toxicity and risk (Smith and Sticher, 1991). As a consequence, there is also an increase in risk to water resources through leaching.

Moreover, high organic matter content in soil has a complex influence on the behavior of trace elements. A recent report by Zimdahl and Skogerboe (1977), concludes that the majority of the lead immobilized in soil is associated with the organic matter content. At high organic matter content, there is also high absorption of this heavy metal (Pb), thus, decreasing the Pb mobility in the soil and likewise decreasing the risk towards water resources and to the environment. This condition had been reported by Flemming et. al. (1968) who state that the characteristic localization of the Pb was in the soil surface in most soil profiles and primarily related to the surfacial accumulation of organic matter. They stated further that greatest Pb concentration is also found in the organic top horizon of cultivated soil. In this case therefore, organic matter content could be considered as one of the most important sinks of Pb in polluted soil.

Furthermore, the clay content in soil is also one of the factors in the risk assessment of Pb accumulation. The degree to which the soil type affects the accumulation of trace elements (e.g. Pb) in soil was investigated by Norrish (1975), Riffaldi et.al. (1976), Tidball (1976) and Schnitzer and Kerdorff (1981). They stated that the Pb accumulation is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter content. To some extent, Smith and Sticher (1991) stated further that the amount of metal adsorbed is dependent on the type of soil component. Thus, a certain amount of clay in the soil which is responsible for metal adsorption, may likewise affect Pb mobility. However, the ability of clay minerals to influence lead accumulation is not as great as other factors like pH and organic matter content. As stated by Smith and Sticher (1991), the amount of metal absorbed is dependent on the type of soil component. But it appears that clay minerals adsorb smaller quantities of metals compared to other sorbents such as oxides and organic matter content. However, as one of the indicators of lead accumulation, it was still considered and determined.

4.5.2 Risk Assessment by "Multi-Criteria Evaluation" or *Modeling*

In order to meet the specific objective of assessing the risk of lead accumulation in soil of Chiang Mai City by modeling , it is frequently the case that several criteria will need to be evaluated. Such procedures are called "Multi-Criteria Evaluation" or sometimes called *modeling*. There are two most common procedures for multi-criteria evaluation developed by Voogd (1983), and Carver (1991). These procedures are composed of weighted linear combination and concordance and discordance analysis. However, in this study, the weighted linear combination recommended by Voogd (1983) was used. At a given threshold/limiting value tabulated in Table 3 (Section 4.5.1), risk indices of each parameter are established (Table 4). By the use of the Voogd Weighted Linear Combination (Equation 3), ranges of suitability values were established based on Table 4.

Table 4 Risk indices of different parameters (Pb, pH, organic matter content, clay content based on Table 3

Particulars	Value Range				
Categories	Very Low	Low	Medium	High	Very High
Risk Indices	5	4	3	2	1
Pb (ppm)	<50	50-75	75-100	100-150	>150
Organic Matter (%)	> 11.50	5 - 11.50	2 - 5.00	1.5 - 2.00	< 1.00
pH	> 5.5	5.00 - 5.5	4 - 5.00	3.5 - 4.00	< 3.00
Clay Content (%)	> 21	17 - 21	8 - 17	3.5 - 8	< 3.5

***Risk Indices** 1 = Very high risk 2 = High risk 3 = medium risk*
4 = low risk 5 = very low risk

In the weighted linear combination, each factor ***i***; (usually the risk index of the given factor) is multiplied by a weight which is subjectively given by the researcher. Weights are rated according to the degree of importance of the factor that will contribute towards the risk to the environment under study (e.g. soil of Chiang Mai City). This method was used to evaluate the fact that not all factors contribute the same degree of risk depending the importance of each factor's role towards the environment. The summation using Equation 3 will derive a final suitability value and risk indices at a given level of threshold limits based on Table 4. as shown in Table 5.

In this study, based on several criteria and literature, the weights assigned to each factor were as follows : lead level (ppm) = 40 %; organic matter content (%) = 30%; pH = 20%; and clay content = 10%. The above weights were multiplied by a given factor and summed up to come up with a suitability value shown in Table 5 and this table will serve as the standard for risk analysis in each grid/site. This suitability value is variable depending on the number of factors considered in the assessment of risk. However, in this study, only four factors were considered and always rated accordingly to a total of 100 % . From the suitability values, final risk indices were established at a given level as shown in Table 5. There were nine levels of suitability values that were derived in this model. However, only 5 levels were considered in this study. Thus, data were reclassified into

Table 5 ***Suitability values and final risk indices of recommended tolerable/limiting values based on Table 4.***

Pb	Score (i)	Wt. (Wi) 40%	Organic Matter	Score (i)	Wt. (Wi) 30%	pH	Score (i)	Wt. (Wi) 20%	Clay content	Score (i)	Wt. (Wi) 10%	Suitability Value	Suitability Range	Final Risk Index
500	1	0.40	0.00	1	0.30	2.00	1	0.20	1.00	1	0.10	1	0 -1.0	1
300	1	0.40	0.50	1	0.30	2.50	1	0.20	1.00	1	0.10	1	0 - 1.0	1
200	1	0.40	1.00	1	0.30	3.00	1	0.20	1.20	1	0.10	1	0 -1.0	1
150	2	0.80	1.50	2	0.60	3.50	2	0.40	3.50	2	0.20	2	1.1 2.0	2
100	3	1.20	2.00	3	0.90	4.0	3	0.60	8.00	3	0.30	3	2.1-3.0	3
75	3	1.20	5.00	3	0.90	5.00	3	0.60	17.00	3	0.30	3	2.1-3.0	3
50	4	1.60	11.50	4	1.20	5.50	4	0.80	21.00	4	0.40	4	3.1-4.0	4
25	5	2.00	15.00	5	1.50	6.00	5	1.00	40.00	5	0.50	5	4.1-5.0	5
15	5	2.00	15.00	5	1.50	6.50	5	1.00	45.00	5	0.50	5	4.1-5.0	5

Risk Indices:

1 = very high risk *2 = high risk* *3 = medium risk*
4 = low risk *5 = very low risk*

five different levels making the medium value at 3 as the baseline. The main point to use this model is to have the possibility of mapping the risk assessment by GIS even without the use of computer. It means that at a certain risk index derived from suitability value in Table 5, we can already point out the condition of the areas under study

In order to assess the risk of lead accumulation in soil of Chiang Mai City using the Multi-Criteria Evaluation by Voogd Weighted Linear Combination, (Voogd 1983) suitability values in each grid were computed as shown in Table 6. Comparing the resulting suitability values in each grid in Table 5, the final risk indices of each grid was assigned. From the UTM Map of Chiang Mai City, the risk index of individual grids are plotted. according to the 5 established categories using a legend. As a result, a risk assessment map of lead accumulation in Chiang Mai City was produced using the above model (Figure 21).

Result of the mapping of risk showed a very low risk situation in most of the areas as shown in the map except in Grids 15,16, and 21 as well as Grid 10 which exhibited a low to medium risk situation respectively. This result could be attributed by the high level of lead concentration in these areas and with other factors such low organic matter content and clay content, except for the pH which was found to have the same conditions

Table 6. Suitability and risk indices of different grids of Chiang Mai City using Multi-Criteria Evaluation based on Table 5.

Grid No	Pb	Score (i)	Wt. =40%	Org. Mat.	Score(i)	Wt=30%	pH	Score(i)	Wt. =20%	Clay	Score(i)	Wt. =10%	Suit. (S)	Index	Category
G2	36.21	5	2.00	3.94	3	0.90	7.35	5	1.00	12.50	3	0.30	4.20	5	very low
G3	37.03	5	2.00	2.48	3	0.90	7.49	5	1.00	12.50	3	0.30	4.20	5	very low
G4	41.16	5	2.00	3.78	3	0.90	7.08	5	1.00	17.50	4	0.40	4.30	5	very low
G5	36.58	5	2.00	4.39	3	0.90	7.20	5	1.00	17.00	4	0.40	4.30	5	very low
G6	38.92	5	2.00	5.07	4	1.20	6.95	5	1.00	12.50	3	0.30	4.50	5	very low
G8	42.79	5	2.00	4.50	3	0.90	7.40	5	1.00	15.00	3	0.30	4.20	5	very low
G9	46.46	5	2.00	3.28	3	0.90	7.42	5	1.00	17.50	4	0.40	4.30	5	very low
G10	102.98	2	0.80	3.34	3	0.90	7.29	5	1.00	15.00	3	0.30	3.00	3	medium
G11	38.97	5	2.00	3.94	3	0.90	7.32	5	1.00	17.30	4	0.40	4.30	5	very low
G12	46.46	5	2.00	3.90	3	0.90	7.22	5	1.00	17.50	4	0.40	4.30	5	very low
G14	32.17	5	2.00	3.22	3	0.90	6.89	5	1.00	15.00	3	0.30	4.20	5	very low
G15	73.21	4	1.60	4.40	3	0.90	7.38	5	1.00	12.50	3	0.30	3.80	4	low
G16	83.43	3	1.20	3.15	3	0.90	7.48	5	1.00	12.50	3	0.30	3.40	4	low
G17	33.50	5	2.00	2.74	3	0.90	7.26	5	1.00	12.50	3	0.30	4.20	5	very low
G18	53.68	5	2.00	5.45	4	1.20	6.78	5	1.00	18.00	4	0.40	4.60	5	very low
G20	26.19	5	2.00	2.80	3	0.90	6.80	5	1.00	12.50	3	0.30	4.20	5	very low
G21	55.00	4	1.60	3.79	3	0.90	7.25	5	1.00	15.00	3	0.30	3.80	4	low
G22	42.80	5	2.00	2.77	3	0.90	7.22	5	1.00	12.50	3	0.30	4.20	5	very low
G23	41.97	5	2.00	4.10	3	0.90	7.48	5	1.00	17.00	4	0.40	4.30	5	very low
G24	38.82	5	2.00	3.42	3	0.90	7.20	5	1.00	15.00	3	0.30	4.20	5	very low

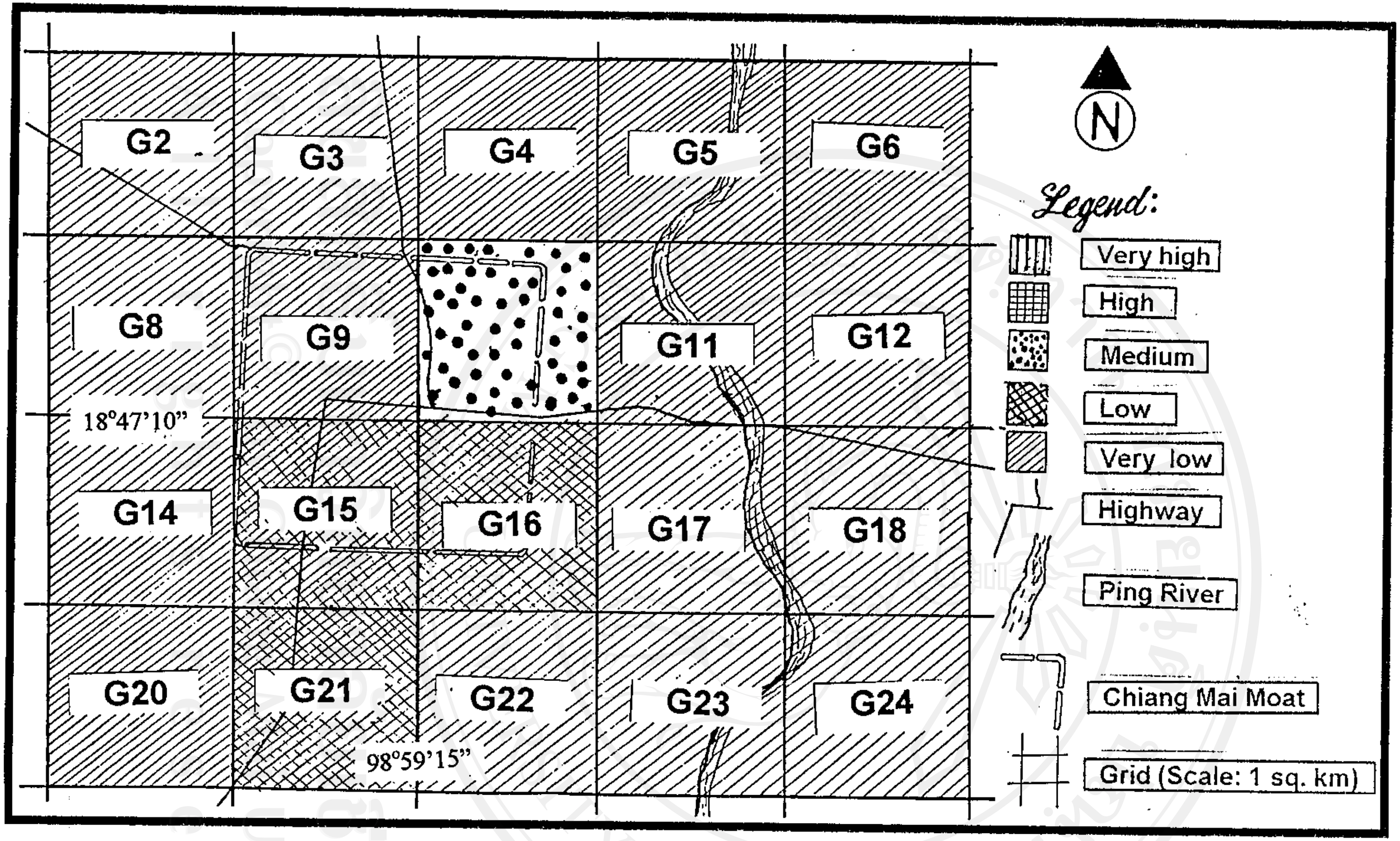


Figure 21 Risk assessment map of soil of lead accumulation in soil of Chiang Mai City using the Multi-Criteria Evaluation

in all grids (5= very low risk) based on Table 4. To further analyze the situation using other tools, a computer-based GIS-IDRISI program was used which shall be discussed in the preceding section (Section 4.5 3). Result in the manual mapping using the Multi-criteria evaluation was compared again to the computer-based using the IDRISI-Software.

4.5.3 Risk Assessment by GIS-IDRISI Software

The IDRISI is a grid-based geographic information and image processing system developed by the Graduate School of Geography at Clark University, USA. This is a raster-based microprocessor GIS and image processing system (Eastman,1992). Although there are variety of software tools available to assist the assessment of risk in the environment, this study used the IDRISI program which is available at the Department of Biology of the Faculty of Science of Chiang Mai University. This is another tool to assess the risk of lead accumulation in soil aside from the previously discussed, the "Multi-Criteria Evaluation".

In the computer-based risk assessment the scanning of the reference map using the Micrografx -Software Program (TIF) was the initial step. In this study, the UTM Map of Chiang Mai City was used with identification :"*Changwat Chiang Mai-Series L9013,* *Edition-3-RTSD"*. Only a portion of the map was scanned consisting of 20 grids at 1 sq km each which are the study areas. A cartographic model in GIS was adopted for this purpose as shown in Figure 22. The map was then imported into the database of the IDRISI-Program as an spatial database using special commands: BIPIdris, TIFIdris in order to import the resource map from TIF file of the Micrografx to IDRISI. The database in IDRISI is the central to the system. It is a collection of maps and associated information in digital form usually concerned with the earth's surface features On the other hand, the spatial database is the component part of the database that describes the geography (shape and position) of the earth's surface. Moreover, the use of COMPOSIT command in IDRISI made it possible to create the color composition by combining three bands of colors such as red, green and blue.

The use of the lead immobility model after the Sewage Sludge Regulation (DVWK 212/1988) enhanced the risk assessment analysis. As stated by Hunsaker et. al. (1993), that GIS and environmental models are not really integrated but they are just used together. Thus, the above model was used together as a part of the GIS -IDRISI analysis It is in the lead immobility model that classification of values are based. At a certain value of each parameter such as Pb (ppm), pH, organic matter content and clay content, the risk indices are formulated based on the recommendation of Sewage Sludge Regulation (DVWK,1988). The risk indices are shown in Table 4. This table was also used in the

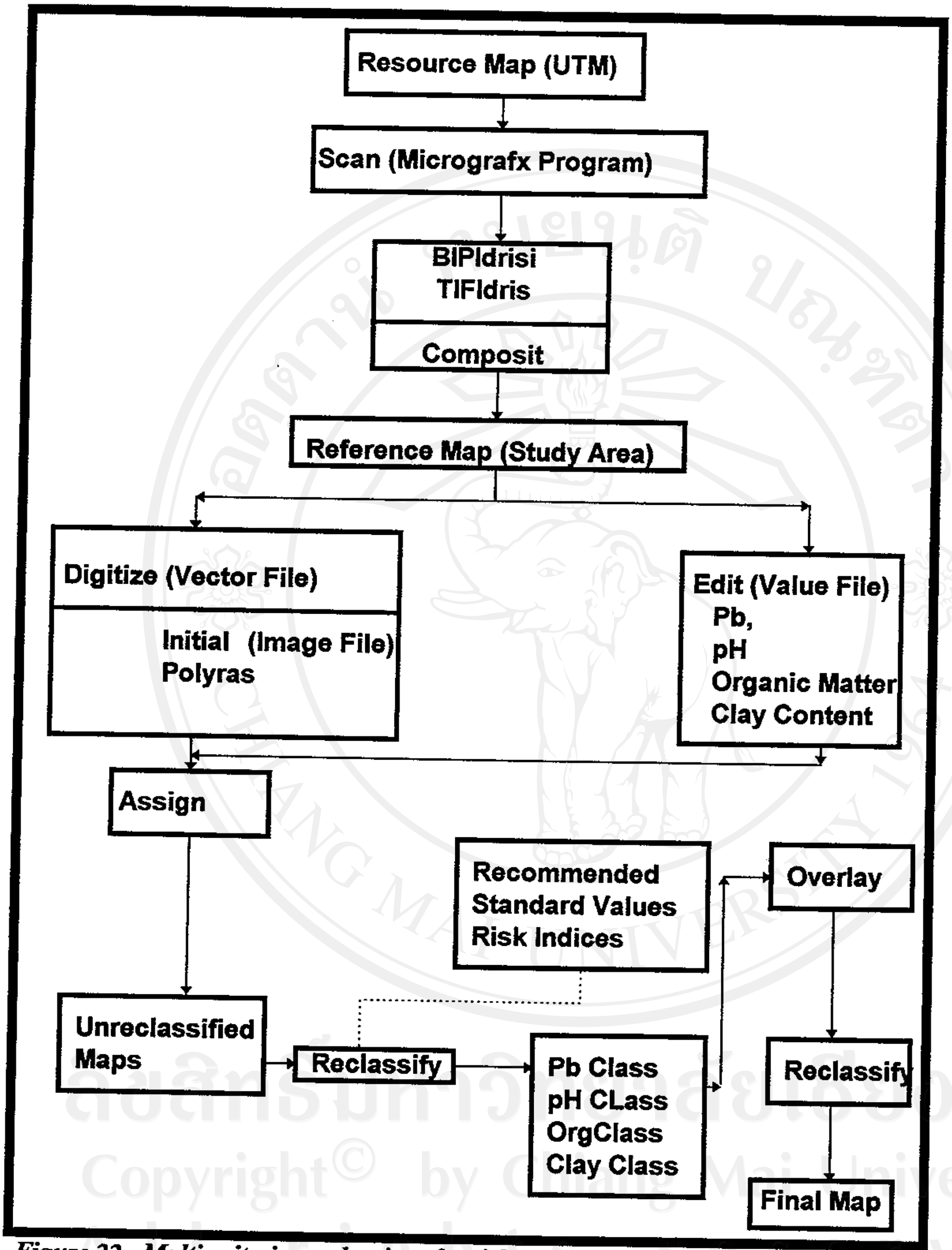


Figure 22. Multi-criteria evaluation for risk assessment in GIS-IDRISI Program

One of the component parts of the GIS is the Map Digitizing System where one can take existing paper maps and convert the map into digital form. In this study, the scanned (UTM Map, *Changwat Chiang Mai-Series L9013, Edition-3-RTSD*) was used as the reference map for digitizing. In the digitizing of map, two techniques of map data representation were used such as the vector and the raster techniques. In the vector techniques- boundaries or course of the features are defined by a series of points that were joined with straight lines to form graphic representation having the features of X and Y coordinates, latitudes and longitudes of the Universal Transverse Mecator (UTM) map of Chiang Mai City.

On the other hand, the raster technique- the graphic representation of features and the attributes they possess are merged into a unified data files. The raster system have substantially more analytical power than their vector counterpart in the analysis of continuous space and thus ideally suited to the study of data that are continuously changing over space such as lead concentration, organic matter content, pH, clay content and the like. In this study, it is the raster files that is given much emphasis. Vector files in polygon forms were converted first into raster files after digitizing using special commands INITIAL and POLYRAS. and saved as an image file having different IDs in each grid.

In the digitizing process, each grid is given an identification number (i.e ID 1...... ID20) as a qualitative attribute code. Then, these ID s were integrated into the attribute database which describes the characteristics or qualities of the feature. At a given factor value, an attribute value file was made through special command (EDIT).Thematic value was assigned in each grid with corresponding ID based on the average value of each parameter as shown in Table 6. The attribute value file of each parameter is then assigned using a special IDRISI command "ASSIGN" to the digitized resource map (image file) and resulting to an unreclassified map of a certain parameter in a cartographic display (either in computer screen or hardcopy). The map has color codings depending on the attribute values assigned and the color palette used. The same palette was used in all the parameters. The GIS cartographic analysis allows to take selected elements of the database and produced the map output as shown in Figure 23. The map (Figure 23) shows the lead level distribution of soil at different grids as an output of the assigned attribute value file assigned to the digitized reference map (image file) The output in Figure 23 is a hardcopy of a printer device (Hewlett Packard Deskjet 690C), although the output can also be seen on screen as previously mentioned. Since there are 4 parameters considered in this study, the attribute files of other parameters were also assigned to the same image file using the same approach above. As a result, different unreclassified maps were produced representing each parameter. Each map were also reclassified based on

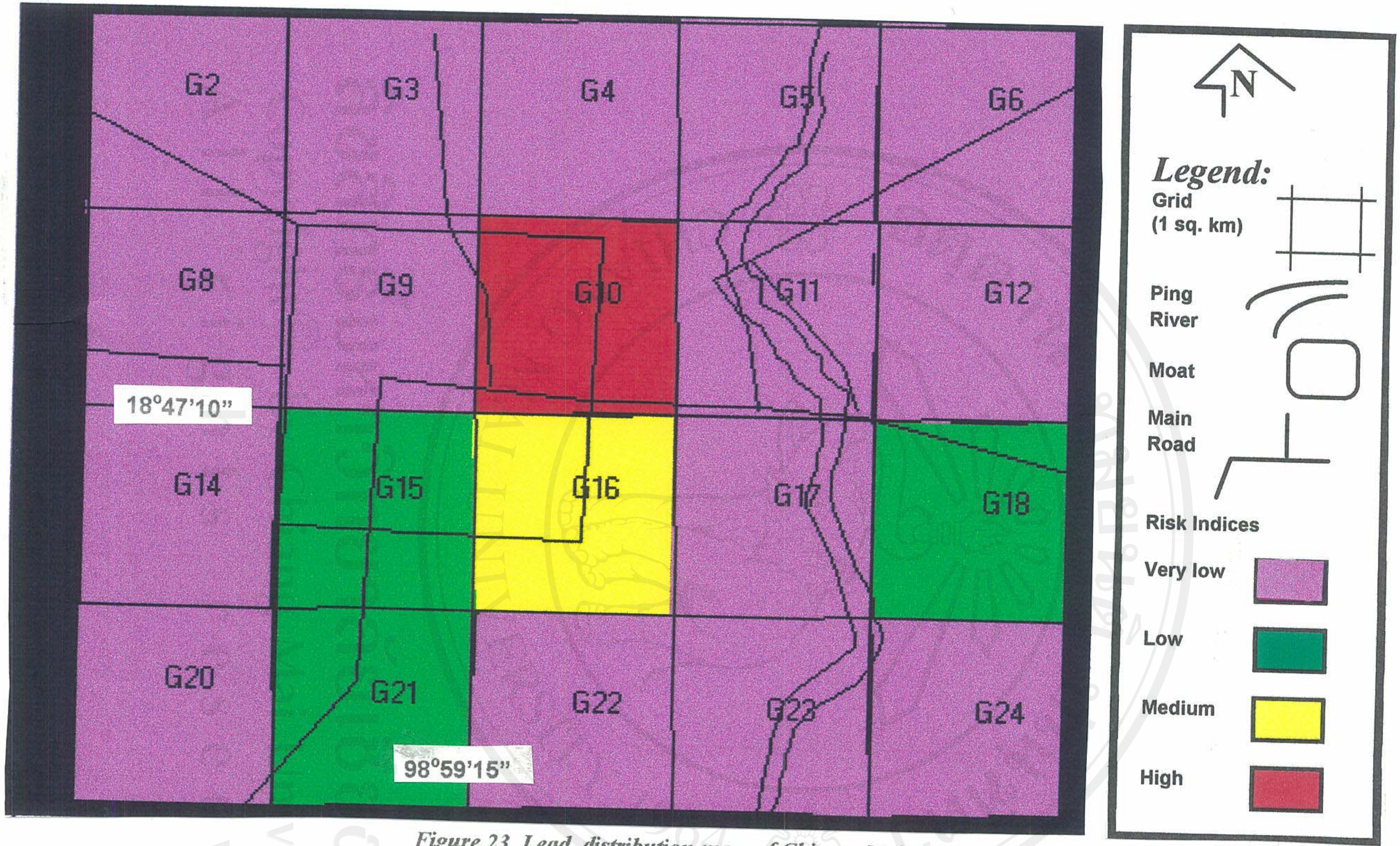


Figure.23 Lead distribution map of Chiang Mai City

Table 4 and then saved as image files. These image files were used in the map overlays for final risk assessment analysis.

The OVERLAY is the hallmark of this spatial data analysis (Fedra , 1991). Thus, in order to further assess the risk considering other factors (i.e. Pb, organic matter content, pH and clay content), the geographic analysis system of GIS with the " OVERLAY " feature. enhance the analyses. As a component part, it has the ability to digitize spatial data with assigned attribute values to the features. Likewise it has also the ability to compare different entities based on the common geographic occurrence. Thus, in the overlay of the different image files of each parameters resulted to a different map output a shown in Figure 24.

Result in the overlay maps of 4 parameters showed 11 different classes of features recognized by different color combinations shown in the legend as well as in the histogram of the overlaid map. These different colors portrayed several information depending on the degree of which the factors or the combinations of these factors had influenced on that particular area. Since, only five categories (1-5) were used in this study, the 11 classes of features were again reclassified further to only five categories (5= very low, 4 = low and 3 = medium, 2 = high and 1 = very high). As a result, a different map output was obtained as shown Figure 25 as the final risk assessment map of this study.

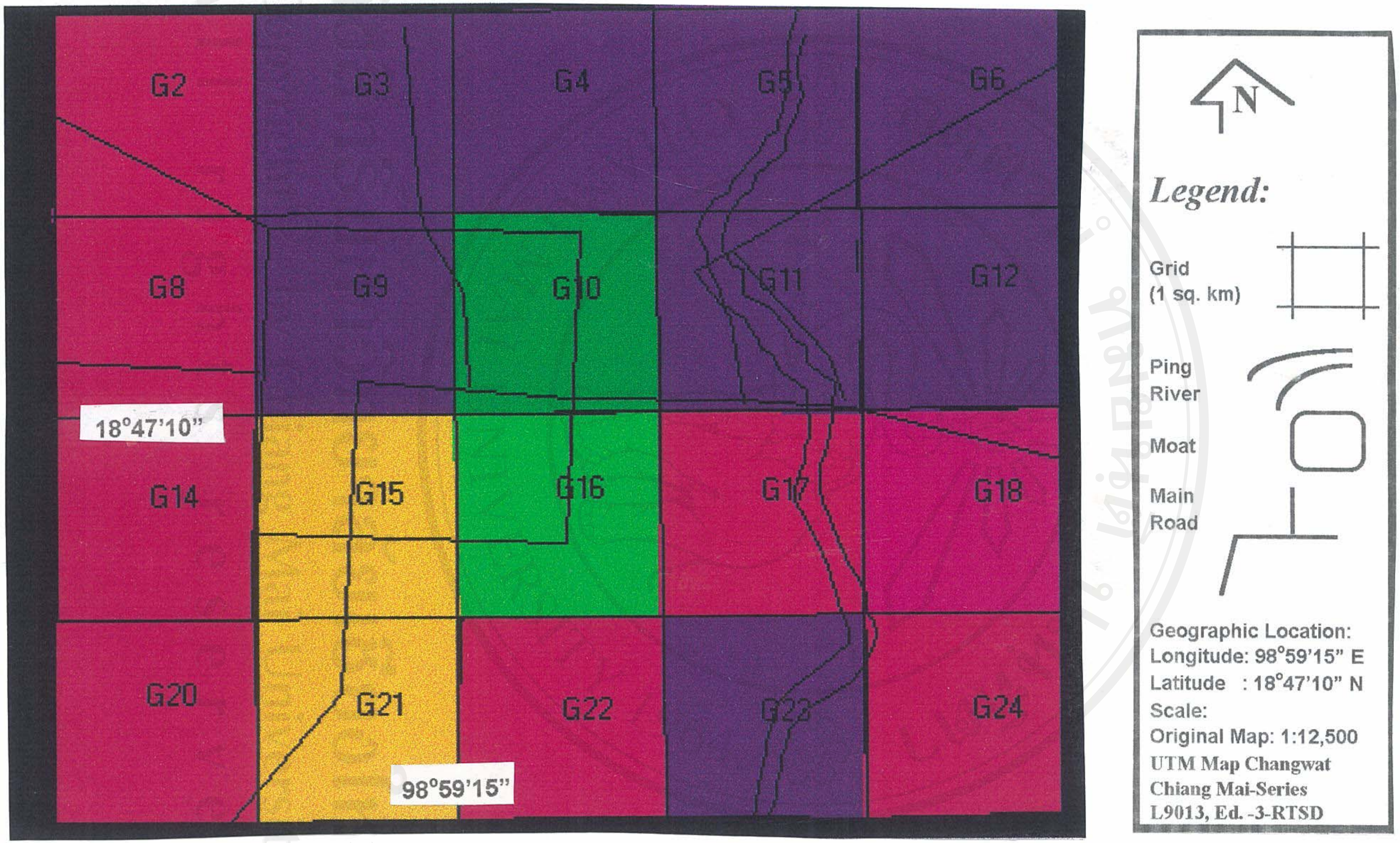


Figure 24 Overlay map (unreclassified) of 4 parameters (Pb, organic matter content, pH and clay content)

To be consistent, the same palette was used as in the individual parameters. showing the same color coding in the legend. The color code described point out the environmental condition of that particular area.

Result in the histogram revealed that only three categories were common in the reclassified map such as 5= very low, 4 = low and 3= medium. after the risk assessment analysis by GIS. As shown in the map output (Figure 25), a very low risk situation was revealed in most areas except for Grid 10 which medium and Grids 15, 16, and 21 which are low. It was found out that the same result was obtained using the computer-based GIS-IDRISI software that with the Multi-Criteria Evaluation Method. This shows that both methods can be used in the risk analysis of lead accumulation in soil of Chiang Mai City

However, in order to have more meaningful results, these methods are need to be verified through further research considering a wider range of environmental media like water, plants, dust/air and other ecosystems in order to come up with a holistic manner in assessing risk of a certain environment like the urban ecosystem. Furthermore, the use of other models to fully assess the risk of other heavy metals affecting the environment could be very beneficial in further studies. But results in this study can already be used a baseline method in formulating risk analysis of any environment especially the soil.

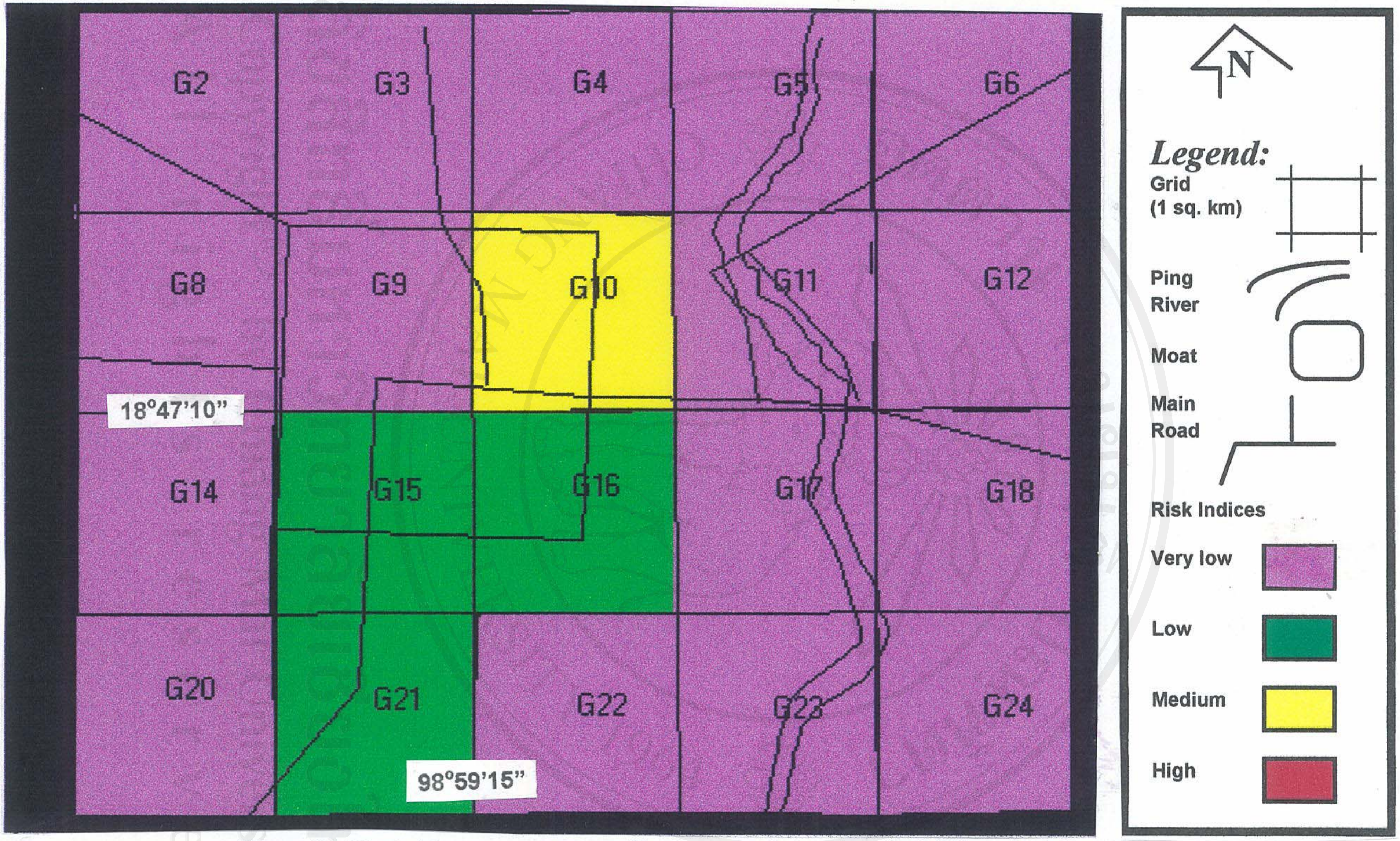


Figure 25 Final risk assessment map of lead accumulation in soil of Chiang Mai City (GIS)