CHAPTER 5 SURVEY RESULTS OF THE PILOT PROJECT

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5.1 Surface Soil Survey

5.1.1 General

The surface soil survey was conducted in the P/P Area aiming at understanding of the situation of heavy metal concentration, understanding the mechanism of advection/diffusion of the heavy metals and assessing heavy metal concentrations of the P/P area for preparation of establishing the provisional environmental standards. The concept of the soil survey methods for attaining these purposes are explained below.

(1) Grid survey

Reason: The whole survey area can be considered equally.

(2) Narrow down method

Reason: The boundary of lower and higher concentration areas can be efficiently specified by the narrow down method. Experiencing the process of the narrow down method is a good opportunity for capacity development (CD) to identify the target area.

(3) Survey methods considering geological aspects and land use of the area

Reason: Since there is a history of tailings spilled mainly along a river because of the collapse of the tailings dam, it is probable that lowland and irrigation areas along the river have higher concentration of heavy metals and that highland areas consisting of hills and plateau have lower concentration of heavy metals. Consequently, application of the grid system in the process of narrow down methods should be different in lowland and highland areas.

In the lowland area, grid systems are narrowed down from 400m to 200m and 50m, accordingly. Considering the land use of the area and width of river plain of the lowland area, being mostly 50 to 100m scale, the minimum grid of 50m was decided. In highland areas, the grid system is narrowed down from 400m to 100m. Because of gentle topographic nature, a minimum grid system of 100m is considered to be enough for the highland area.

The sampling of soil was carried out by the 5 points mixing method and channel sampling from surface to 30cm deep at each sampling point. The detail of sampling methods is given in the DATA 1. The content analysis of soil was conducted for all the samples and elution analysis was conducted for 10% of all the samples except 400m grid samples, for which elution analysis was done for 10% of total samples and additional 73 samples for further consideration of distribution of elution values in the P/P area. The number of soil samples for chemical analysis was given in Table 5.1. Chemical analyses of 10 elements, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn and Mn were conducted for both of content and elution analyses.

Table 5.1 Samples Number of Content and Elution Analyses

Grid	Content Analysis	Elution Analysis
400m	679 samples	141 samples
200m	580 samples	58 samples
100m	288 samples	29 samples
50m	800 samples	80 samples
Total	2,347 samples	308 samples

5.1.2 Analytical Methods

Details of the methods of chemical analyses are given in DATA 3 and analytical methods are only briefly given here.

(1) Analytical Method of Content Analysis

Soil samples for the content analysis were digested with HF and $HClO_4$ according to ISO 14869-1 after drying, crushing and milling (ISO 11464), and they were determined by ICP (Inductively Coupled Plasma) method based on ISO 11885-1 for As, Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn. For Hg, after drying, crushing and milling (ISO 11464), soil samples were digested with HCl and HNO_3 (ISO 16772) and determined by CVAAS (Cold-Vapour Atomic Absorption Spectrometric) method based on ISO 16772. The chemical analysis including sample preparation was conducted at the Faculty of Mining and Geology, St. Cyril and Methodius University.

(2) Analytical Method of Elution Analysis

The extraction of Cd, Pb, Zn, Mn, Cr, Cu, Co, Ni, As and Hg were carried out following the methods of the Japanese Standard, Ministry of Environment's 18th announcement, dated on March 6, 2003. The sample and solvent (prepared by pure water and HCl adjusted within the range of pH 5.8 to 6.3) were mixed at 10% of weight-volume ratio, and the liquid mixture was adjusted to more than 500mL. The elution process was conducted at room temperature and atmospheric pressure by shaker, being set at a shaking frequency of 200 times/min and shaking amplitude of between 4 to 5cm in horizontal or vertical direction, for 6 continuous hours. After standing still for 10 to 30 minutes, the samples were placed in a centrifugal separator for 20 minutes at a speed of 3,000rpm, then the supernatant was filtered with a membrane filter of 0.45μm pore size.

The analytical methods for elution analysis are same as content analysis of soil samples, using ICP method based on ISO 11885 for As, Cd, Co, Total-Cr, Cu, Ni, Pb, Zn and Mn. For Hg, CVAAS (Cold-Vapour Atomic Absorption Spectrometric) method was used based on ISO 16772. The chemical analysis including elution procedure was conducted at the Faculty of Mining and Geology, St. Cyril and Methodius University.

5.1.3 Surface Soil Survey (Content Analysis)

For understanding the outline of heavy metal concentration, advection/diffusion of the heavy metals and chemical nature of the soil in the whole P/P area, 400m grid soil survey was conducted. The 200m, 100m and 50m grids survey, subsequently conducted after considering the results of precedent grid survey, do not show a general characteristic of the P/P area, since they only cover certain particular area of the P/P area. Therefore, detailed results of 400m grid survey and compiled result of whole grid survey are given in the report. Details of each of 200m, 100m and 50m grids survey results are shown in the Progress Report and Interim Report.

(1) Results of 400m Grid Soil Survey

For understanding the outline of heavy metal concentration of the whole P/P area, a total of 679 grids of 400m x 400m were set covering the whole area of the P/P area and soil samples were collected by the 5 samples mixing method for each grid. One sample was collected at the centre of the grid and the other four samples were collected at four points each of which is approximately 100m apart, respectively, to north, south, east and west from the centre point. The grid system of 400m grid is shown in Figure 5.1.

a. Nature of Soil of the 400m Grid Survey

The soil samples are most typically brown soil, silt to clay, with exception of sandy materials, which typically occur on the hill or on the riverbed. The sampling depth is mostly 30cm deep but, occasionally, especially in the hill area, C-horizon and bedrock were encountered before reaching 30cm deep. In that case, samples were collected to the depth of the appearance of C-horizon or bedrock.

As shown in the Figure 5.2, the soil samples show a wide range of pH, from 5.38 to 8.38, however, most of them (85 % of the total samples) show similar values, falling within a range of 6.90 to 7.50. The samples with lower pH occur in the hills area of northwest part of the P/P area, along the Zletovska River and near the tailings dam. While, no clear tendency of the distribution of high pH samples was observed.

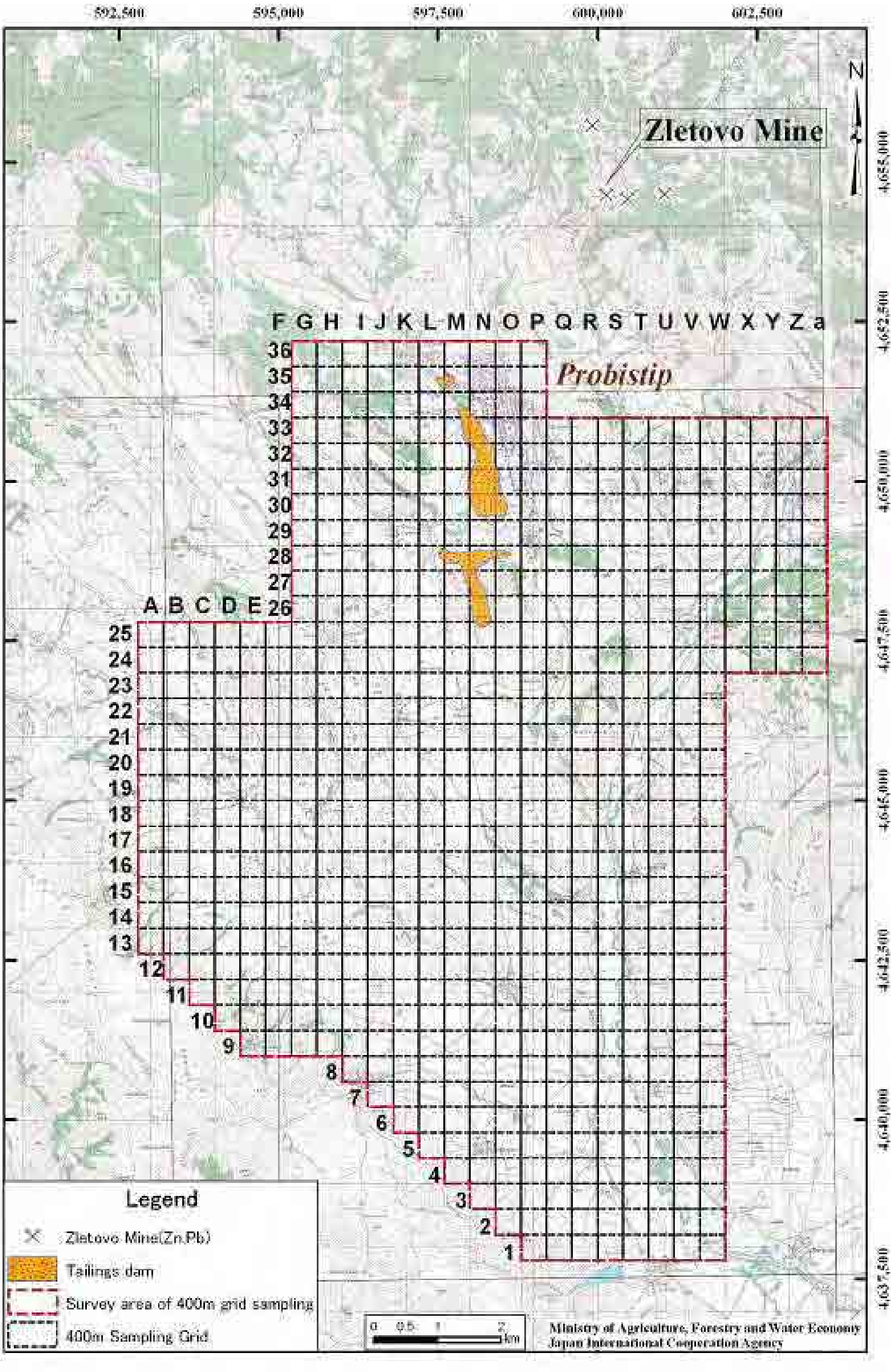


Figure 5.1 Grid System of 400m Grid Soil Survey

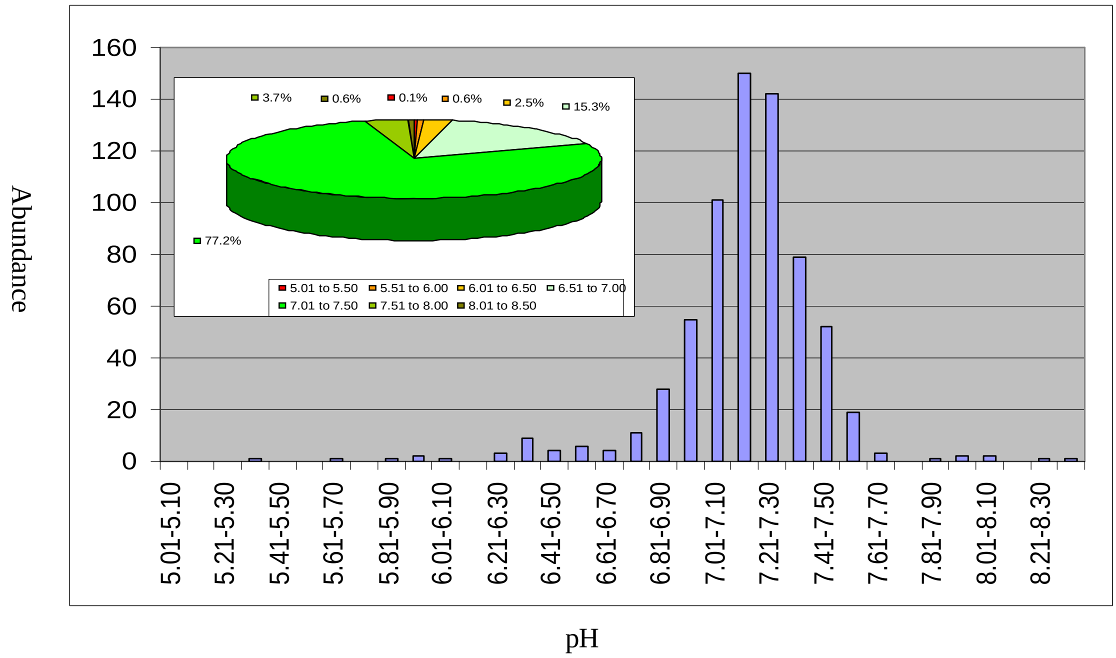


Figure 5.2 pH Measurement Results (400m Grid)

b. Results of the Content Analysis of 400m Grid Samples

The content analysis of 10 heavy metals, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn and Mn, was conducted for soil samples collected from 679 grids. The analytical results are given in Data 4 and, histograms and cumulative frequency curves of each element are given in Appendix 2.

1) Single Element Analysis

The analytical results of 400m grid soil samples were processed by computer for statistical treatment using logarithm values. In Table 5.2, the statistical values, including maximum value, minimum value, mean value and standard deviation, are shown together with the values, such as median value, upper whisker and upper fence, calculated by EDA (Exploration Data Analysis by Kurzl, 1988) method. The EDA is a method conveniently used for geochemical exploration for single element analysis. It has advantages for convenient interpretation and finding the threshold values even from the data set with small populations deviated from the main body of the data. For the threshold value, the value of defining anomaly, upper fence value of EDA was taken except Cd and Co. By the EDA method, upper fence is given as blow.

Upper fence=upper hinge + (1.5 × hinge spread)

For Cd, since many samples show concentration below detection limit and upper fence value exceeds the maximum value, the threshold value was determined from the histogram and cumulative frequency curve. Considering parental population and distribution of Co concentration with a histogram of normal distribution pattern, background + 2σ (S.D. : Standard Deviation) was taken for the threshold value of Co.

Table 5.3 shows comparison of background values (mean value) of 400m grid soil samples of the P/P area with some of the reference compositions. Comparison of the background value of the P/P area with the average soil of Bowen (1979) shows that As, Co, Pb, Zn and Mn are higher in the P/P area and Cr and Ni are lower than the average soil (Figure 5.3). While the background values of Cd and Cu of the P/P area show similar values to the average soil.

Table 5.2 Statistical Values of 400m Grid Samples

679 samples

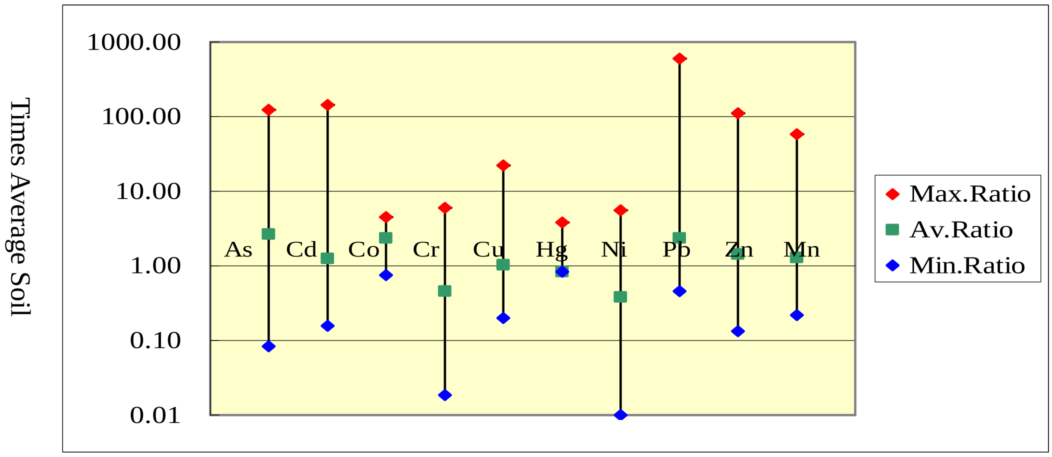
	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Below detection limit (%)	0.9	45.5	-	-	-	99.7	0.1	-	-	-
Maximum Value	740	46	36	420	670	0.23	280	21,000	10,000	58,000
Minimum Value	<1	<0.1	6.0	1.3	6.0	<0.1	<1	16	12	220
Mean Value (b)*1	16	0.22	19	32	31	0.05	19	82	130	1,300
Standard Deviation (log)	0.507	0.707	0.095	0.303	0.277	-	0.375	0.468	0.376	0.281
b + 2 S.D.*2	162	5.78	29.4	131	110	-	108	704	721	4,690
Median (EDA*3)	14	0.2	19.1	30.7	27	-	16.1	56.7	95.2	1,130
Upper Whisker (EDA)	36.9	1.0	23.1	57	48	-	38.5	120	158	1,490
Upper Fence (EDA)	209	51.2	35.3	166	112	-	128	286	276	2,290
Threshold Value	209	14.8	29	166	112	-	128	286	276	2,290
Above Threshold Value *4	18	7	7	6	33	-	21	79	88	60

*1: geometric mean, *2: background value + 2×standard deviation, *3: EDA Exploration Data Analysis (Kurzl, 1988)
*4: Number of samples above threshold value

Table 5.3 Background Values (400m Grid)

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Mean value of 400m grid survey	16	0.22	19	32	31	-	19	81	130	1,300
Average soil*1	6	0.35	8	70	30	0.06	50	35	90	1,000
B.G Con.of Holland *2	29	0.8	9	100	36	0.3	35	85	140	-

*1: After Bowen (1979): Environmental Chemistry of the Elements
*2: National background concentration of Holland



Max. Ratio: Maximum value of 400m grid survey/Average Soil
Av. Ratio: Average value of 400m grid survey/Average Soil
Min. Ratio: Minimum value of 400m grid survey/Average Soil
Average Soil: After Bowen (1979)

Figure 5.3 Comparison of 400m Grid Soil with the Average Soil

For the subdivision of concentration values for each heavy metal to produce the distribution maps of heavy metal concentration, the following three values were chosen to classify the P/P area into four areas of different concentration of heavy metals.

1. the values of the average soil of Bowen (1979)
2. Mean + 1 σ (S.D.)
3. Upper Fence or Mean + 2 σ (S.D.) (threshold value)

The values of the average soil of Bowen (1979) were chosen as the background values of the soil, because they were considered to be the general typical background values of the world.

Distribution maps of heavy metal concentration are shown in Appendix 3 and the characteristic features of each heavy metal are given below.

- **Arsenic (As):** The content concentration of As ranges from <1 to 740mg/kg with background value (mean values) of 16mg/kg which are higher than Bowen's average soil of 6mg/kg and lower than background value of Holland. The histogram shows nearly normal distribution with a small deviated population of higher concentration and the threshold value (Upper Fence) is 209mg/kg. The grids of high As concentration more than thresholds values occur in the tailings dam area and west side of the upper stream area of the Zletovska River, but they are not found in the lower stream area of the Zletovska river where Pb and Zn high concentration grids occur. The high concentration grids, also, occur surrounded by the grids of relatively higher concentrations in the area southeast of Probistip. The relatively high As grids are also observed along the Koritnica River which flows from the Zletovo Mine site and the upper stream of the Zletovska River after the Koritnica river flows in. In the lower stream area of the Zletovska River after the Kiselica River flows in, only relatively high As grids are sporadically observed. The grids with low concentration of As, lower than Bowen's average soil, are mainly found in centre to the south of the P/P area.

- **Cadmium (Cd):** The content concentration of Cd is low, ranging from <0.1 to 46mg/kg and 45.5% of the total samples show concentration below the detection limit. The background value is 0.22mg/kg, and it is similar to the Bowen's average soil. The grids with high Cd concentration occur overlapping the area of Pb and Zn high grids in the tailings dam area, along the Kiselica River and the lower stream area of the Zletovska River. Along the Koritnica River and in the area east of the Zletovo Village, Cd high grids are sporadically distributed. Other than these, the P/P area is mostly covered by low Cd concentration grid.

- **Cobalt (Co):** The content concentration of Co shows a relatively narrow range of 6 to 36mg/kg, and 80% of the samples fall in a narrow range of 15 to 25mg/kg. The Co histogram shows nearly normal distribution pattern with the centre at mean value of 19mg/kg, which is twice greater than average soil of Bowen (1979). A narrow range of the Co concentration and a normal distribution pattern of concentration histogram suggest that the Co values of the P/P area show the original chemical nature of the soil of the area, reflecting the chemical nature of the bedrock without any clear evidence of the secondary enrichment. Co high concentration grids, Co values more than 29mg/kg, occur in the northwest, northeast and east parts of the area surrounded by relatively high Co grids. The relatively high Co grids of Co concentration more than 24mg/kg are clearly observed in the southwest part of the area where high Ni concentration grids occur and they occur along the lower stream of the Zletovska River after the Kiselica River flows in. The rest of the areas are mostly covered by the grids of Co concentration more than 8mg/kg, average soil of Bowen (1979). Volcanic rocks and volcano-sedimentary sequences overlie the P/P area. Since volcanic rocks have relatively high Co concentration, the reason for relatively high background value of Co in the P/P area is attributed to geological nature of the area.

- **Chromium (Cr):** The content concentration of Cr is relatively low, ranging from 1.3 to 418mg/kg with a background value of 32mg/kg, which is less than a half of the average soil of Bowen (1979), 70 mg/kg. The histogram of Cr shows nearly normal distribution pattern with slight deviation to higher concentration side and the threshold value is 166mg/kg. The grids of high Cr concentration in the area occur northeast and central south of the area surrounded by the grids of relatively high Cr concentration. The characteristic feature of the Cr concentration in the area is a distribution of relatively high Cr concentration zone trending in NW-SE direction in the northwest of the area, which occurs overlapping the Ni high concentration grids. Other than these, the area is mostly covered by Cr low concentration grids of less than 70mg/kg.

- **Copper (Cu):** Compared to Zn and Pb, the content concentration of Cu is low, ranging from 6 to 674mg/kg with background value of 31mg/kg, which is similar value to the average soil of Bowen(1979) and background concentration of Holland. The histogram of Cu shows a pattern with clear deviation to higher concentration side, and threshold value is 112mg/kg. Similar to Zn and Pb, high Cu concentration grids are distributed in the tailings dam area, along the Kiselica River and the lower stream area of the Zletovska River after the Kiselica River flows in. Other than these areas of along the main stream of Zletovska and Kiselica, the area is covered by low Cu concentration grids of less than 30mg/kg.

- **Mercury (Hg):** Since only two grids show Hg concentration higher than lower detection limit of 0.1 mg/kg, Hg was excluded from statistical treatment. The two grids with Hg concentration, respectively, 0.23 and 0.11mg/kg, occur in the mountain east of Ratovica and other than these, the P/P Area is totally covered by low Hg concentration grids less than 0.06mg/kg.

- **Nickel (Ni):** The concentration of Ni in the area is relatively low, ranging from <1 to 280mg/kg with background value of 19mg/kg, which is less than half of the average soil of Bowen(1979) and background concentration of Holland. Histogram of Ni shows nearly normal distribution with a deviated population of higher concentration with threshold value of 128mg/kg. The distributions of high Ni grids with Ni values greater than 128mg/kg are observed surrounded by relatively high concentration grids in the area isolated from the areas of high Cu, Pb, Zn and Mn. They are small areas in northwest and northeast of the P/P area and a large area covering wheat field in southwest of the P/P area. Ni contents of the grids with high concentrations of Cu-Zn-As-Pb are commonly low, mostly less than 30mg/kg. The distribution pattern of Ni concentration seems to be different from those of mining activities related metals of the P/P area, such as Cu, Zn, As, Pb. It rather seems to be controlled by natural causes, being reflected by geological nature of the bedrock. The Ni high grids of the southwest area occur overlapping the distribution of Eocene sedimentary rock (E3 Unit). Other than above-mentioned areas, the P/P area is mostly covered by low Ni concentration grids of Ni less than 50mg/kg. .

- **Lead (Pb):** The concentration of Pb is relatively high, ranging from 16 to 21,000mg/kg with background value of 82mg/kg, which is more than twice as much as the average soil of Bowen (1979) and similar value to the background concentration of Holland. The highest value of 21,000mg/kg was obtained in the abandoned tailings dam near the floatation plant of the Zletovo Mine. Histogram of Pb shows the peak of abundance at lower concentration side of 30 to 50mg/kg and a population of higher concentration exists toward the higher concentration side with decreasing abundance. In addition to the main population, a population deviated to the higher concentration is clearly observed, suggesting occurrence of anomaly at the threshold value of 286mg/kg. Similar to Zn and Mn, high Pb grids with Pb values greater than 286 mg/kg occur in the residential area of Probistip including the Zletovo Mine property, the tailings dam area, and along the Kiselica River and to lower stream of the Zletovska river where spillage of tailings by the accidents in 1976 is expected. Other than these, Pb high grids occur along the Koritnica River, flowing from the Zletovo Mine Site, the upper stream of the Zletovska River after inflow of the Koritnica River and mountainous area of northeast part of the area. Other than these Zn high areas, the P/P area is mostly covered by the grids with Zn concentration more than 35mg/kg of average soil.

- **Zinc (Zn):** The concentration of Zn is similar to that of Pb, ranging from 12 to 10,000mg/kg with background value of 130mg/kg, which is slightly higher than average soil of Bowen (1979). Same as Pb, the highest value of 10,000mg/kg was obtained in the abandoned tailings dam near the floatation plant of the Zletovo Mine. Histogram of Zn shows a clear peak of abundance at concentrations between 63 to 111mg/kg in which 60% of the samples fall. From this peak, the abundances decrease abruptly but continue to as much as 10,000mg/kg, suggesting occurrence of anomaly at the threshold value of 276mg/kg. Similar to Pb and Mn, high Zn grids with Zn values greater than 276mg/kg occur in the residential area of Probistip including Zletovo Mine property and the tailings dam area, and along the Kiselica River and lower stream of the Zletovska river where spillage of tailings by the accidents in 1976 is expected. Other than these, Zn high grids occur along the Koritnica River, flowing from the Zletovo Mine Site and in the mountainous area near the Zletovo Village. Relatively high Zn grids are observed along the upper stream of the Zletovsca River after the Koritnica River flows in. Other than these Zn high concentration grids, most of the western half of the P/P area is occupied by Zn concentration grids of less than 90mg/kg and most of the eastern half of the P/P area is occupied by the grids greater than 90mg/kg.

- **Manganese (Mn):** The content concentration of Mn is relatively high, ranging from 220 to 58,000mg/kg with background of 1,300mg/kg, which is similar to the average soil of Bowen (1979). The samples with very high concentration of more than 30,000mg/kg occur in the tailings dam area. Histogram of Mn shows a normal distribution pattern with conspicuous peak form 870 to 1,400mg/kg, in which 60% of samples fall. Other than the main population, a population deviated to higher concentration is clearly observed with threshold value of 2,290mg/kg. Similar to Cu, Pb and Zn, high Mn grids with Mn values greater than 4,680mg/kg occur in the residential area of Probistip including Zletovo Mine property and the tailings dam area, and along the Kiselica River and lower stream of the Zletovska River. Other than these, grids of slightly high Mn sporadically occur in the area between Probistip and the Zletovska River. The grids with Mn concentration greater than 1,000mg/kg mostly occupy the P/P area.

2) Multivariate Analysis

Calculation of correlation coefficients, cluster analysis and factor analysis were conducted using the results of the chemical analysis of the 400m grid soil samples.

- **Correlation Coefficient**

As shown by the high correlation coefficients (Table 5.4) and similar distributions of high concentration grids, the heavy metals such as Cd, Cu, Pb, Zn and Mn have close relations with high correlation coefficient of greater than 0.600. Since the Zletovo Mine is Zn-Pb mine, these heavy metals are considered to represent the mining activities of the P/P area. Furthermore, high concentration grids of these occur in the tailings dam area, along the Kiselica River and in lower stream area of the Zletovska River, where tailings materials spilled over by the collapse of the tailings dam.

Ni, on the other hand, shows very good correlation with Cr (0.823), and Cr-Co and Ni-Co show relatively good correlations (grater than 0.400). Ni, Cr and Co do not show clear relations with the above heavy metals (Cd, Cu, Pb, Zn, Mn) with low correlation coefficients and they show independent distributions of high concentration grids from the above five heavy metals.

Table 5.4 Correlation Coefficient of Content Value of the Heavy Metals

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Mn
As	1.000								
Cd	0.224	1.000							
Co	-0.057	-0.033	1.000						
Cr	-0.081	-0.030	0.444	1.000					
Cu	0.338	0.624	-0.042	-0.132	1.000				
Ni	-0.101	-0.125	0.439	0.823	-0.138	1.000			
Pb	0.371	0.787	-0.126	-0.108	0.754	-0.233	1.000		
Zn	0.293	0.828	-0.046	-0.099	0.728	-0.216	0.897	1.000	
Mn	0.262	0.748	0.066	-0.046	0.716	-0.140	0.804	0.855	1.000

very good correlation, good correlation

- **Cluster Analysis**

The cluster analysis was conducted using the programme made by mrc (Mitsubishi Materials Natural Resources Corp.) for the analytical results of 400m grid samples. The dendrogram of the cluster analysis by the Ward method is shown in Figure 5.4. The Ward method is normally used for the cluster analysis, taking the correlation coefficient as distance separating each component. From the figure, similar to the results of correlation coefficient, the heavy metals are clearly classified into two groups of close relationships as shown below.

Group 1. Pb-Zn-Mn-Cd-Cu-As

Group 2. Cr-Ni-Co

The heavy metals of each groups show similar distribution patterns of high concentration grids on the distribution map. As mentioned earlier, the distributions of high concentration grids suggest that heavy metals of Group 1 (Pb-Zn-Mn-Cd-Cu-As) reflect the mining activities of the P/P area. Among the heavy metals of Group 1, the relationships of As to other heavy metals are the least expected from the correlation coefficient. The Group 2 heavy metals (Cr-Ni-Co), on the other hand, has different distribution pattern of high concentration grids from the Group 1 heavy metals, being distributed most clearly in the southwest part of the area.

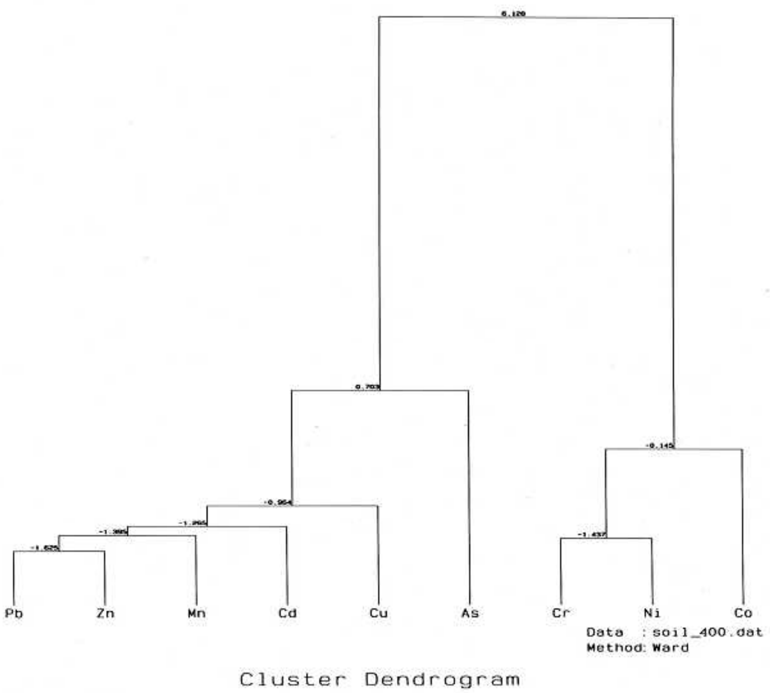


Figure 5.4 Results of Cluster Analysis (400m Grid)

- **Factor Analysis**

The Factor analysis by Varimax rotation was conducted using the programme made by mrc (Mitsubishi Materials Natural Resources Corp.) for 400m grid soil samples. The Varimax rotation is the most popular rotation method for the factor analysis. By Varimax rotation, all the variables can be more clearly represented on the orthogonal axes for understanding factors. As shown in Table 5.5, six factors were extracted from the factor analysis. Among these factors, Factor 5 and Factor 6 do not show clear relations with heavy metals and factor contributions of them are low.

Each factor of 1 to 4 is given below together with related heavy metals.

Factor 1 :	Cd-Cu-Pb-Zn-Mn	(positive)
Factor 2:	(Co)-Cr-Ni	(negative)
Factor 3:	As	(positive)
Factor 4:	Co	(negative)

As shown by factor loadings, Factors 1 and 3 have reverse relation with Factors 2 and 4, and factor contributions of Factor 3 and 4 are low compared to Factor 1 and 2.

Table 5.5 Results of Factor Analysis (400m Grid)

Elements	Factor Loading (Varimax Rotation)						Commu-nality
	Factor1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	
As	0.215	0.051	0.567	0.023	-0.018	0.000	0.371
Cd	0.876	0.007	0.062	0.054	0.085	0.218	0.829
Co	0.002	-0.428	-0.043	-0.508	0.000	-0.003	0.444
Cr	-0.016	-0.902	-0.046	-0.105	0.099	-0.034	0.837
Cu	0.732	0.071	0.303	0.004	-0.353	-0.021	0.757
Ni	-0.130	-0.892	-0.048	-0.113	-0.084	0.041	0.836
Pb	0.886	0.084	0.302	0.151	-0.001	-0.070	0.910
Zn	0.935	0.090	0.158	0.011	0.031	-0.034	0.910
Mn	0.888	0.046	0.124	-0.179	-0.070	-0.100	0.853
F.C. (%)	57.0	27.1	8.3	5.1	2.3	1.0	-

F.C.: Factor Contribution

The distributions of the grids with high factor score (more than 1.000 of absolute value) are shown in the Figure 5.5. Based on the factor analysis, together with the distribution patterns of high heavy metal concentration grid, the chemical nature of the 400m grid soil samples is summarized as below.

Factor 1 (Cd-Cu-Pb-Zn-Mn): The grids of the high factor score occur in the residential area of the Probistip, in and around the property of the Zletovo Mine, tailings dam area, down along the Kiselica River and in the lower stream area of the Zletovska River where spillage of tailings by the collapse of the tailings dam occurred. In addition to them, grids of high factor score occur, along the Koritnica River, flowing from the Zletovo Mine Site, the upper stream of the Zletovska River after inflow of the Koritnica River. The grids of high factor score are also found in mountain area near the Zletovo Village.

Factor 2 (Co)-Cr-Ni: The grids with high Factor 2 score are widely distributed over the wheat field of southwest part of the area. Other than this, the grids of high Factor 2 score occur in the northwest and northeast of the area.

Factor 3 As: The grids of high Factor 3 score occur in the residential area of Probistip to the tailings dam area, overlapping the grids of high Factor 1 score. In addition to them, the grids of high Factor 3 score independently occur in the south of the Probistip, and upper stream area of the Zletovska River before the Kiselica River flows in, but they do not occur in the lower stream area of the Zletovska River area after the Kiselica River flows in.

Factor 4 Co: The grids of high Factor 4 score occur most clearly in the area of high Factor 2 score, and other than this, they sporadically occur in the area without showing clear tendency of the their distribution.

The spillage of the tailings are clearly traced by the distribution of high Factor 1 grids, occurring along the Kiselica River and lower stream area of the Zletovska River after the Kiselica River flows in. The main sources of heavy metals causing distribution of high Factor 1 grids along the Koritnica River, a tributary flowing from the Zletovo Mine site, and Zletovska River before the Kiselica River flows in, are most probably attributed to the mining activity of the Zletovo mine site.

Considering that the Zletovo Mine is a Zn-Pb mine, Factor 1 is related to mining activities of the P/P area. Since north part of the area is close to the Zletovo Mine, similar geological units to the area of Zletovo Mine, volcanic rocks such as dacite, andesite and pyloclastic rocks, are exposed in the northeast corner of the sampling area. The distribution of high Factor 1 grids near the Zletovo Village were most probably natural causes affected by the bedrock of the area similar to the Zleotvo Mine, the bedrock enriched by heavy metals such as Pb, Zn, Cu and As.

A wide distribution of high Factor 2 grids with high concentration of Ni in southwest of the area corresponds well with a distribution of the Eocene sedimentary rock, and the cause of the Ni, Cr, (Co) enrichment in soil of the area is attributed to geological nature. Some of the high Factor 2 score grids distributed in northwest and northeast of the area were, also, most probably caused by geological nature.

The high Factor 3 grids characterised by high As occur overlapping and close to the high Factor 1 grids in the tailings dam area and some others are found isolated in the area south of the Probistip, northwest and northeast of the P/P area. The former is clearly related to the mining activities of the area and the latter are most probably related to the natural causes.

Factor 4 represents high Co concentration. Considering the narrow range of the concentration of Co of the soil in the area and no characteristic distribution of the Co concentration is observed except Co high grids in the Ni high area of the northwest part of the area, the Co concentration in the area seem to show the original chemical nature of the area without any significant secondary enrichment.

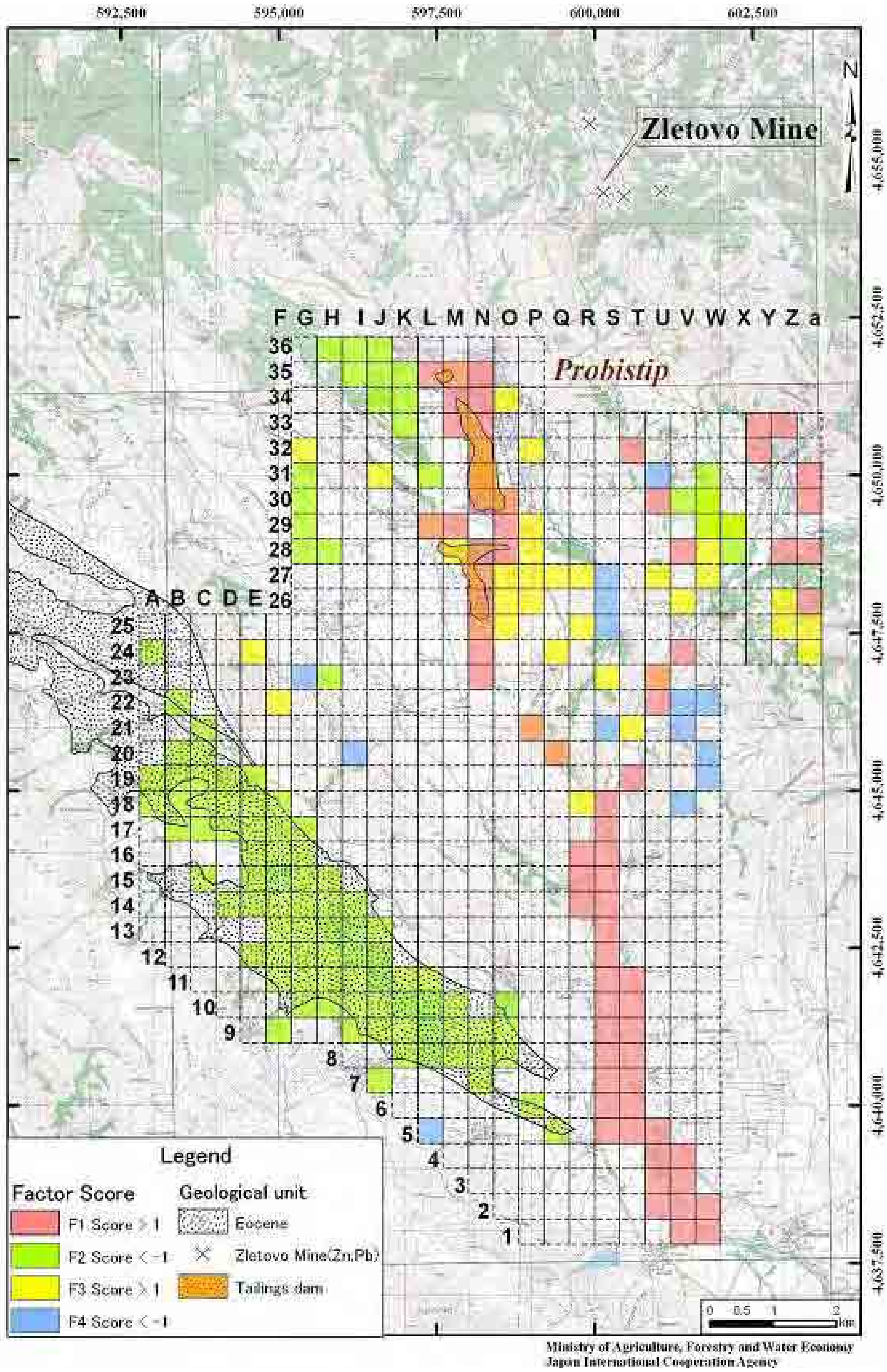


Figure 5.5 Distribution of High Factor Scores

c. Summary of the 400m Grid Survey.

The enrichment of the heavy metals in the area are most characteristically reflected by the Factor 1, particularly Pb, Zn and Mn. The high concentration areas of these elements, together with Cd and Cu, are observed in the residential area of the Probistip, the tailings dam area, along the Kiselica River and lower stream area of the Zletovska River after the Kiselica River flows in. Along these, the spillage of the tailings can be clearly traced. The areas with high concentrations of these heavy metals are, also, observed along the Koritnica River and upper stream of the Zletovska River before the Kiselica River flows in. The cause of these is attributed to the mining activities of the Zletovo Mine site. The heavy metal high areas probably by the natural causes are observed in the area. There are high Pb, Zn and As areas in the northeast of the P/P area near the Zletovo Village. As concentrations are high in the area south to southeast from Probistip. Ni concentrations are high in the northwest and southwest of the P/P area.

(2) Results of 200m, 100m and 50m Grids Survey

Based on the results of 400m grid soil survey, the soil surveys of 200m, 100m and 50m grids were subsequently conducted as shown in Figures 5.6, 5.7 and 5.8. The results of the 200m, 100m and 50m grids surveys are shown compiled together with results of 400m grids survey in the map of the distribution of heavy metals. The results of representative heavy metals are shown in Figures 5.9 and 5.10, and all of them are given in Appendix 4. Because 200m, 100m and 50m grids surveys were conducted only in certain areas, mostly in the areas of higher heavy metal concentration of 400m grid survey, the statistical values of the these grid survey do not show statistical values characterizing the whole area of the P/P area. Further, these grid surveys were conducted to narrow down the high heavy metal concentration zone defined by the 400m grid survey. For these reasons, the compiled distribution maps of heavy metal concentration were produced using the divisions of concentrations same as 400m grid survey. The values of the average soil of Bowen (1979) were chosen as the background value. The results of the each grid survey are summarized below.

a. Results of 200m Grid Survey

Based on the results of the 400m grid survey, 200m grid soil survey was conducted to narrow down the areas with high heavy metal concentration. The sampling method is same as 400m grid sampling. Grids of 200m were set over the area along the Kiselica River and Zletovska River where the high Factor 1 grids and high concentration of Pb, Zn, As and Cu grids occur, and where soil contamination related to mining is expected, to narrow down the area of high heavy metal concentration revealed by the 400m grid soil survey. In addition to them, 200m grid survey was conducted over the high As grids distributed in the area between the Kiselica and Zletovska Rivers, south of Probistip Town.

The high Pb, Zn, As and Cu concentration zones over the area along the Kiselica and Zletovska Rivers were narrowed down by the 200m grid survey. Since 200m grid sampling was conducted mainly in the area of high Pb-Zn-As concentration grids of 400m survey, compared to the factor analysis of 400m grid sampling, the factor analysis of 200m grid shows more emphasized results for Pb-Zn-As. As mentioned in the section of the 400m grid survey, the heavy metals of Factor 1 (Cd-Cu-Pb-Zn-Mn) represent the mining activities of the P/P area such as, activities of mine site, floatation plant and tailings dam. In addition, natural causes of the enrichment of these heavy metals to soil must be considered if the rocks enriched by these heavy metals are exposed. Since, in the northern part of the grid sampling area, the geological units similar to the Zletovo Mine Area, which are host rock of the ore deposits of the Zletovo Mine, are exposed, natural causes of the enrichment of heavy metals to soil in the area is most probable. The distribution of high Factor 1 score grids, with high concentration of Cd, Cu, Pb, Zn and Mn in the area along the Kiselica River and more clearly in the lower stream area of the Zletovska River after the Kiselica River flows in, is considered to be representing the spillage of the tailing material. The intermittent distribution of grids with high concentration of As, Cu, Pb, Zn and Mn and high Factor 1 score along the Koritnica River and upper stream of the Zletovsca River can be attributed to the mining activities of the Zletovo Mine site.

The concentrations of Co, Cr and Ni are generally low in the area of the 200m grid survey. Although both of As and Cd are high in the tailings materials, the factor related to high As and poor Cd was extracted by factor analysis. The grids characterising this factor mainly occur in the area between the Kiselica and Zletovska Rivers, south of Probistip, and they are considered to be by natural causes, reflecting the geological nature of the area.

b. Results of 100m Grid Survey

Based on the results of the 400m and 200m grids soil survey, 100m grid soil survey was conducted. The main purposes of the 100m grid soil survey consist of the following objectives.

- to narrow-down heavy metal high concentration zone.
- to define the boundary between high and low heavy metal concentration zone.
- to clarify the difference between natural causes and human causes of high heavy metal concentration in soil.

The sampling locations of the 100m grid soil sampling were decided based on the following criteria.

- Highland area (hilly land) : 40 grids
  Understanding the heavy metal enrichment mechanism and distribution pattern of heavy metal concentration.
- Arable area (agricultural land) : 40 grids
  Understanding the relationship between agricultural land and heavy metal concentration

and distribution pattern of heavy metal concentration.

- Alluvial area (River site): 208 grids

  Defining the boundary of heavy metal high concentration zone of the Kiselica and Zletovska Rivers and understanding distribution pattern of heavy metal concentration.

The area of Cd-Cu-Pb-Zn-Mn high grids, outlined by 400m and 200m grid survey, in the lower stream area of the Zletovska River, was further narrow-downed by the 100m grids survey, and it is considered to be representing the spillage of the tailing material. The Cd-Cu-Pb-Zn-Mn high grids in the northeast part of the P/P area is natural causes and enrichment of these heavy metals to the soil is attributed to exposure of the rocks with high concentration of these heavy metals.

The area of Ni-Cr high grids in the southwest part of the P/P area and small areas of northeast and northwest of the P/P area were reconfirmed by the 100m grid survey and they are considered to be by natural causes.

The area of As high grids distributed in the area between the Kiselica and Zletovska Rivers, south of Probistip Town, is considered to be by natural cause, reflecting the geological nature of the area.

c. Results of 50m grid Survey

Considering the results of preceding 400m, 200m and 100m grids soil survey, 50m grid soil survey was conducted. The main purposes of the 50m grid soil survey consist of the following objectives.

- to narrow-down heavy metal high concentration zone.
- to define the boundary between high and low heavy metal concentration zone.
- to clarify the difference between natural causes and human causes of high heavy metal concentration in soil.

The sampling locations of the 50m grid soil sampling were decided based on the following criteria.

- Alluvial area (River side): 600 grids,

  Defining the boundary of heavy metal high concentration zone along the Kiselica and Zletovica Rivers and understanding the distribution pattern of heavy metal concentration
- Arable area (agricultural land) : 200 grids.

  Understanding the relationship between agricultural land and heavy metal concentration and distribution pattern of heavy metal concentration.

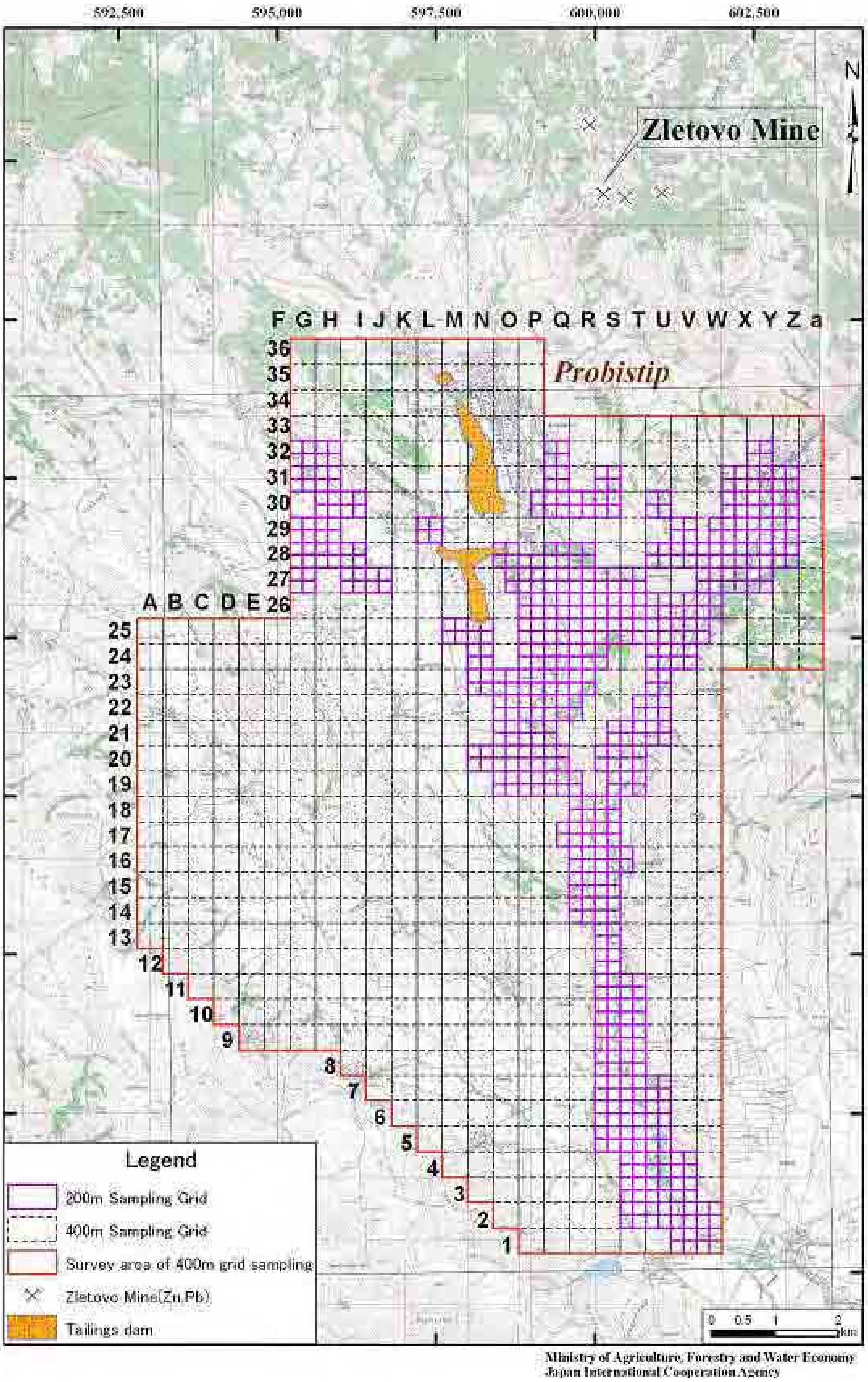


Figure 5.6 Grid System of 200m Grid Soil Sampling

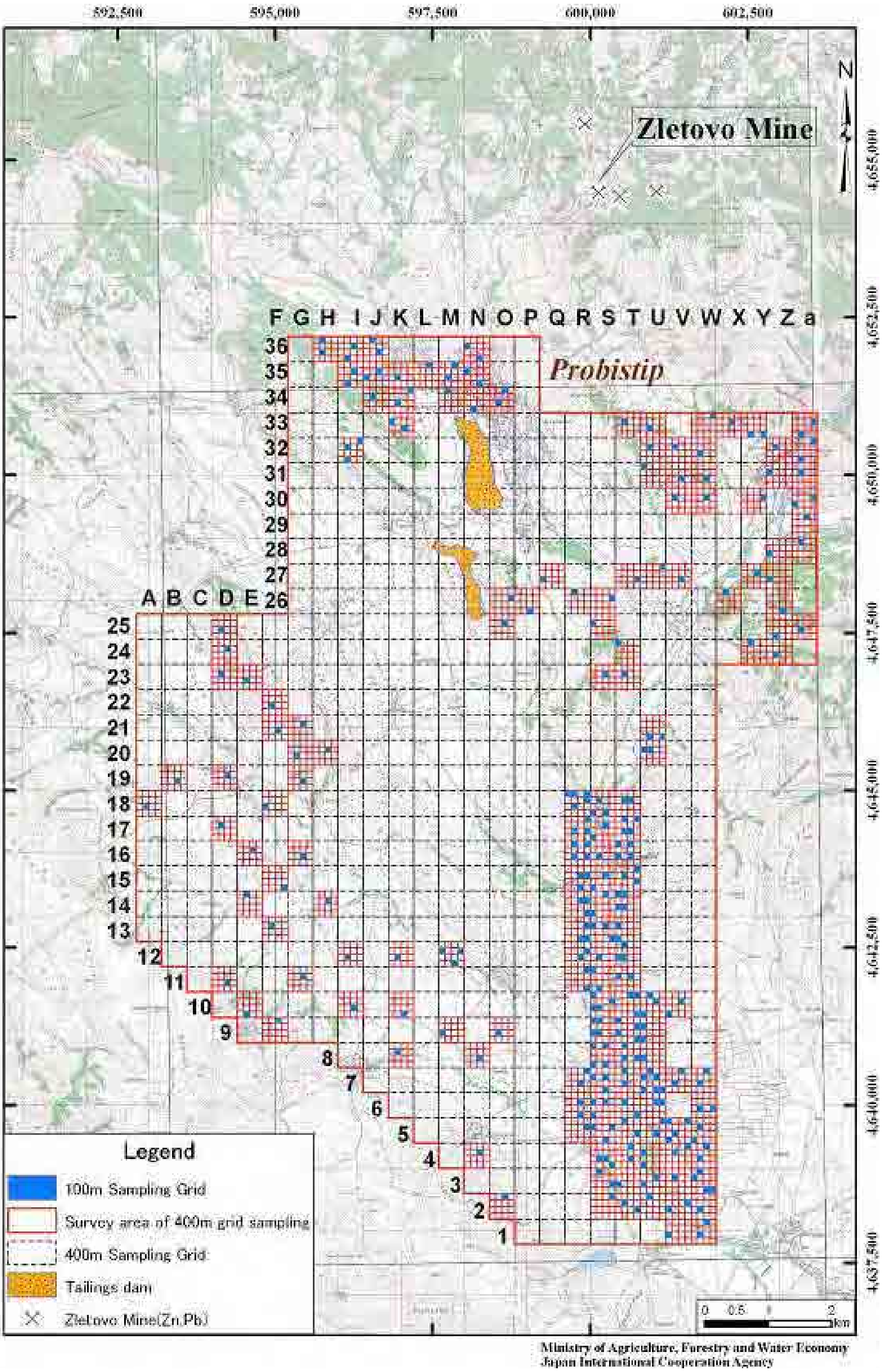


Figure 5.7 Grid System of 100m Grid Soil Survey

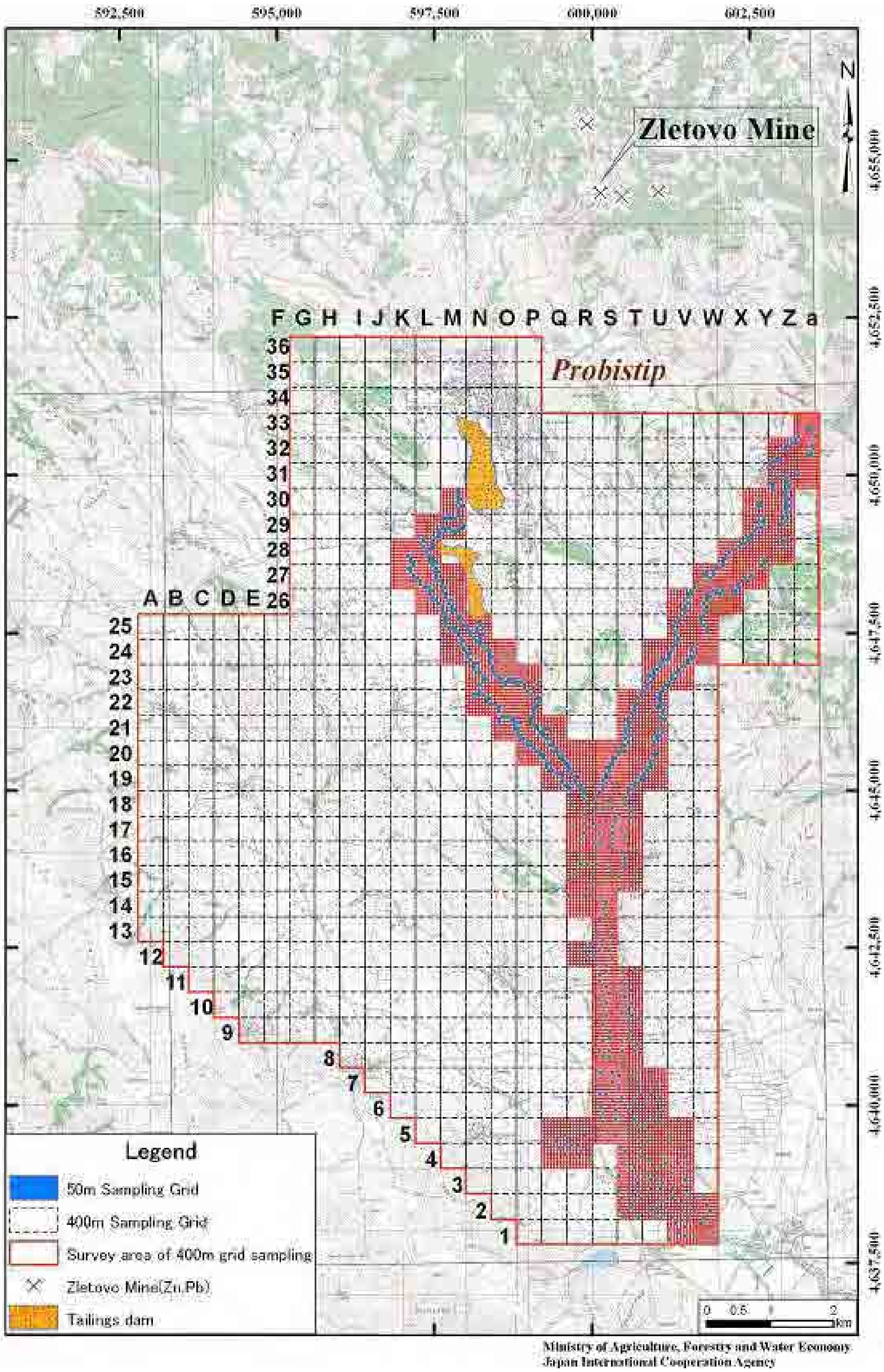
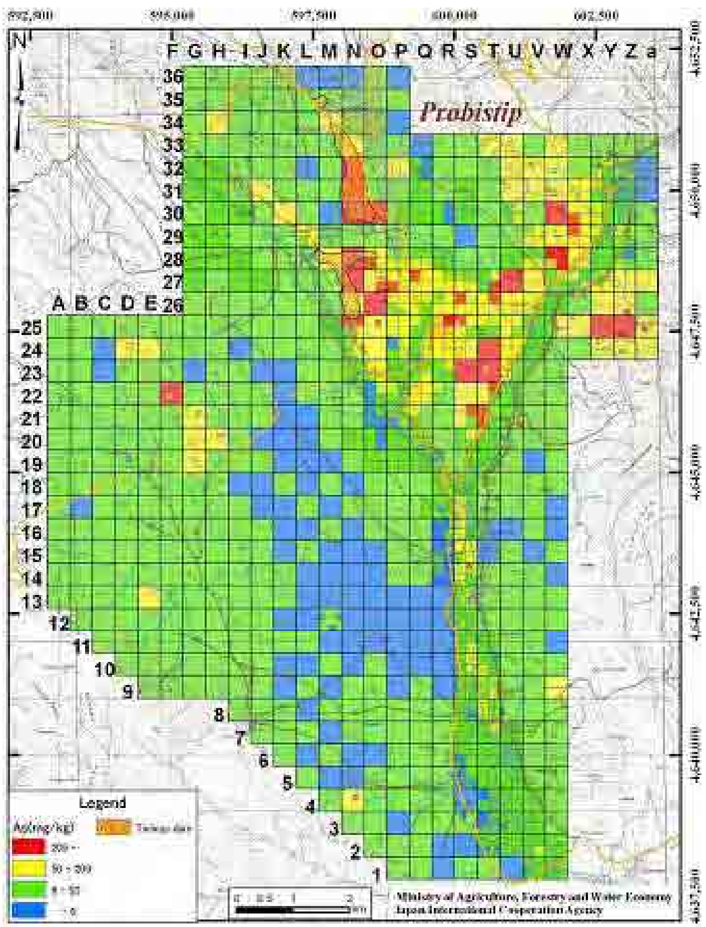
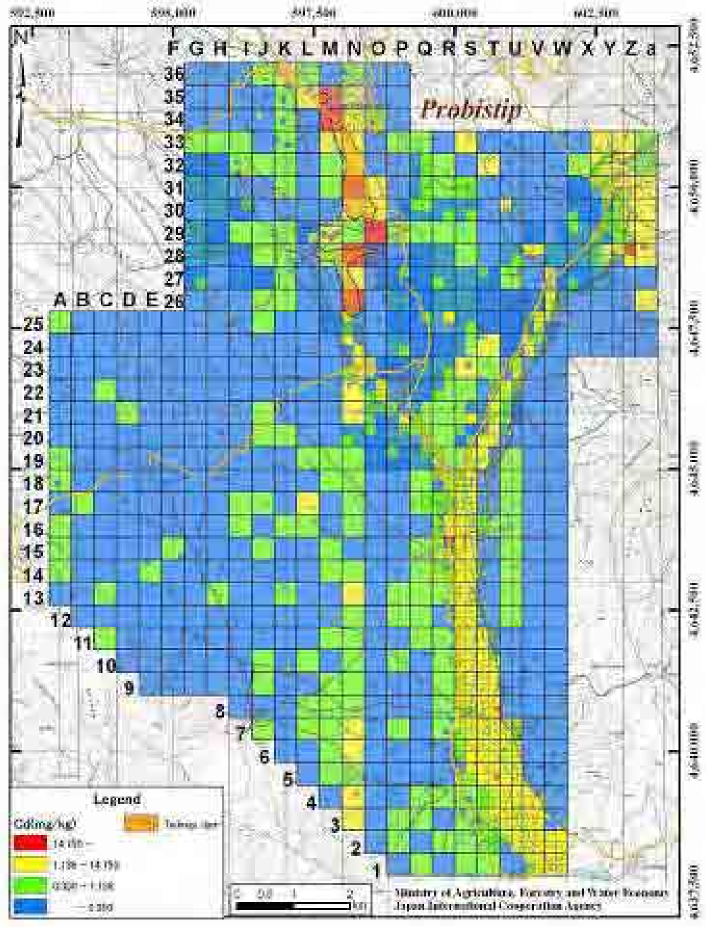


Figure 5.8 Grid System of 50m Grid Soil Survey

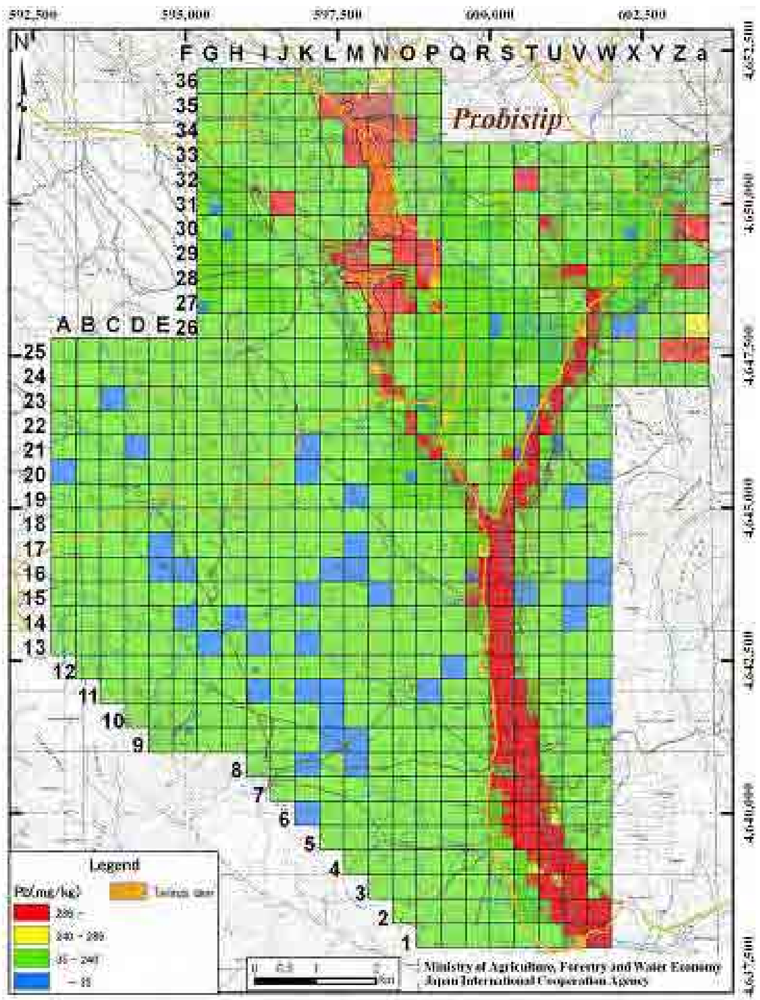


Arsenic (As)

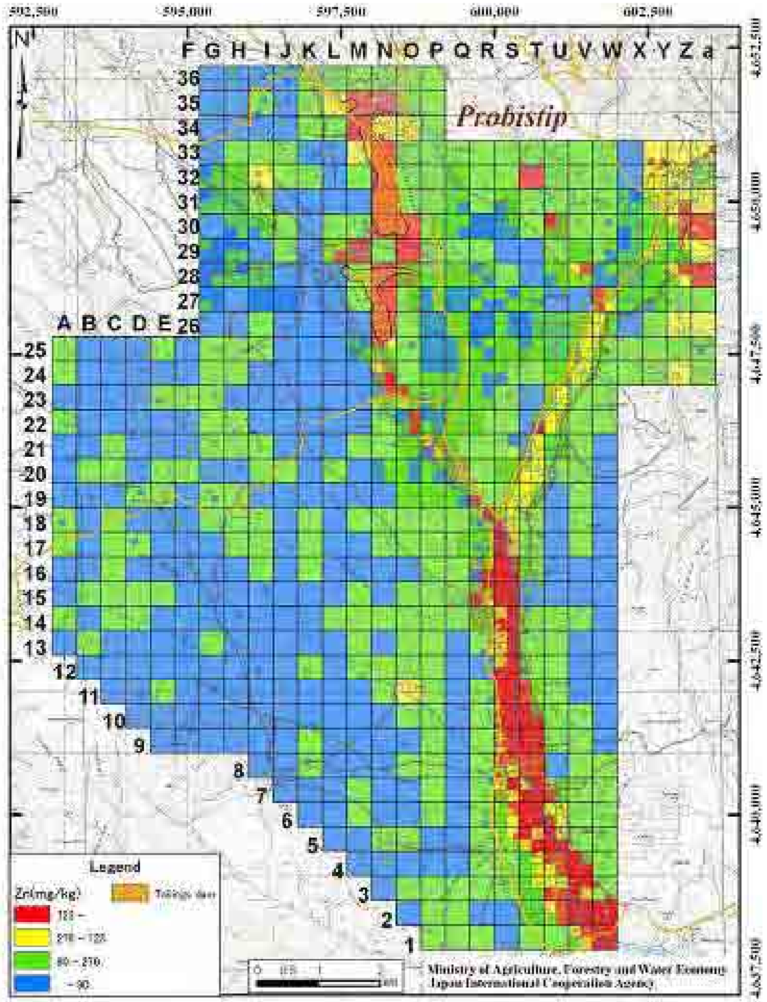


Cadmium (Cd)

Figure 5.9 Distribution of Arsenic (As) and Cadmium (Cd) Concentrations of 400m to 50m Grid Surveys



Lead (Pb)



Zinc (Zn)

Figure 5.10 Distribution of Lead (Pb) and Zinc (Zn) Concentrations of 400m to 50m Grid Surveys

The area of Cd-Cu-Pb-Zn-Mn high grids continuously distributed from Kiselica River to the lower stream area of the Zletovska River was further narrow-downed by the 50m grids survey, and it is considered to be representing the spillage of the tailing material. The Cd-Cu-Pb-Zn-Mn high grids in the northeast part of the P/P area are by natural causes and enrichment of these heavy metals is attributed to exposure of the rocks with high concentration of these heavy metals.

The small area of Ni-Cr high grids in northeast part of the P/P area is considered to be by natural causes.

d. Summary of Surface Soil Survey (Content analysis)

The results of 400m, 200m, 100m and 50m grids soil survey conducted in the P/P area are summarized as below.

1) The grid soil surveys at the grid sizes of 400m, 200m, 100m and 50m successively conducted in the P/P area resulted in identifying heavy metal high concentration zones of the various elements. These areas of higher heavy metal concentrations were narrowed down through successive soil surveys of different grid sizes and boundaries between lower and higher concentration areas were defined.
2) Among the 10 heavy metals analysed in the soil survey, As, Co, Pb, Zn and Mn are relatively high compared with average soil of Bowen (1979) and Cr, Hg and Ni are, on the other hand, relatively low. While, Cd and Cu show similar values compared with the average soil of Bowen.
3) By the multivariate analysis, the groups of heavy metals with close relationships were identified and human causes (by mining activities) and natural causes of enrichment of these heavy metals to the soil were clarified as shown on the Table 5.6 and Figure 5.11.

Table 5.6 The Areas of High Heavy Metal Concentration

Heavy Metals	Locations	Causes
Cd-Cu-Pb-Zn-Mn	Tailings Dam-Kiselica River-lower stream of the Zletovska River	Spillage of tailings materials
	The Koritnica River –upper stream of the Zletovska River	Mining activities of the Zletovo Mine Site
	Northeast corner of the P/P area	Natural causes (Geological nature)
Co-Cr-Ni	Southwest part of the P/P area	Natural causes (Geological nature)
	South of the Zletovo Village	Natural causes (Geological nature)
As	The area between the Kiselica and Zletovska Rivers	Natural causes (Geological nature)

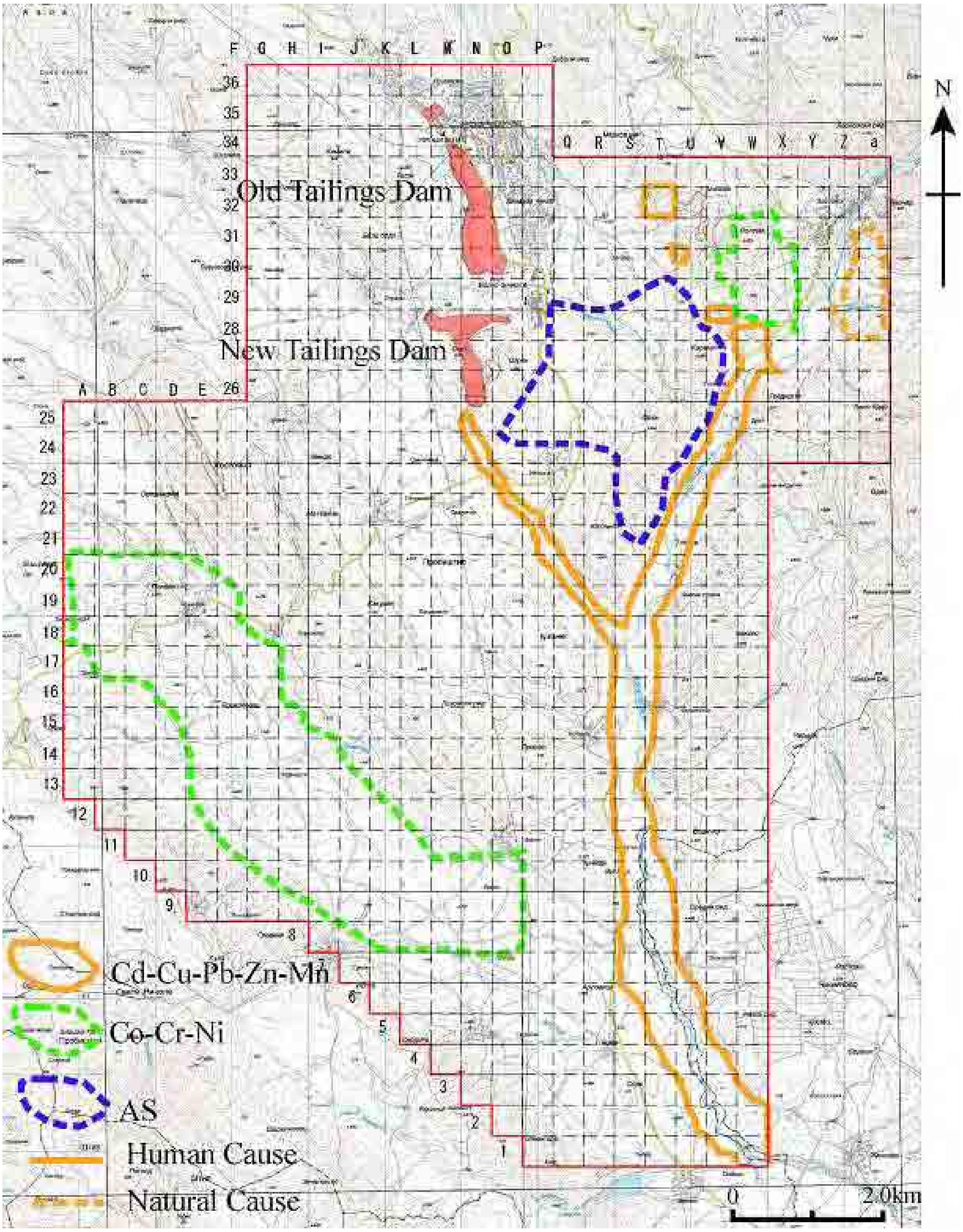


Figure 5.11 Heavy Metal High Concentration Area

5.1.4 Surface Soil Survey (Elution Analysis)

The elution analysis was conducted for 10% of surface soil samples, 68, 58, 29 and 80 samples, respectively for 400m, 200m, 100m 50m grids surveys. Later, for further investigating the relation of the results of soil elution analysis and crop analysis, 73 samples of 400m grid soil were selected for additional elution analysis, and the elution analysis was conducted for a total of 308 samples of soil survey including 141 samples of 400m grid soil samples.

(1) Analytical Results

The analytical results of elution analysis are given in Data 4. The statistical values of the elution results of 400m grid soil samples and all samples including 400m, 200m, 100m and 50m grids soil samples are respectively, shown in Tables 5.7 and 5.8. The maps of distributions of elution concentrations were drawn combining the whole samples of 400m, 200m, 100m and 50m grids samples together and they are shown in Appendix 5. The samples of 400m grids soils were colleted from the whole P/P area, while the samples of 200m, 100m and 50m grids were collected from the restricted area, mostly along the Zletovska and Kiselica Rivers. For this reason, samples of 200m, 100m and 50m grids soil do not give the general characteristics of elution analysis of the whole P/P area. Therefore, for concentration values for subdivision of the distribution map of the heavy metals concentration, the statistical values obtained from the 400m grids samples were used. The following are the values used for subdivision of the elution concentration of the heavy metals.

1. Mean Values (Background Value) (400m grid soil)
2. Mean Value + σ (Standard Deviation) (400m grid soil)
3. Mean Value +2 σ (Standard Deviation) (400m grid soil)

For assessing the results of the elution analysis, the values of Environmental Standard for Water of Macedonia Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004) were used as reference values.

The characteristic features of the results of elution analysis are given below.

a. Arsenic (As): The elution concentration of As ranges from <0.003 to 0.49mg/L with mean value (background value) of 0.0049mg/L. Similar to the content analysis results of As, the As high grids of elution analysis more than 0.032 mg/L, nearly same value as Reference Value of 0.03mg/L, occur mainly in the area between the Zletovska and Kiselica Rivers, south of the Probistip. Other than this, relatively high concentration grids sporadically occur in the south and northeast. In the area of the lower stream of the Zletovska River where high content concentration grids of Pb and Zn occur, the elution content of As is low, less than 0.011mg/L.

Table 5.7 Statistical Values of the Elution Analysis of 400m Grid Soil Samples

141 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Below detection limit (%)	41.8	73.1	91.5	27.0	1.4	71.6	26.2	7.1	2.8	0.7	-
Maximum Value	0.49	1.8	0.016	0.085	0.14	0.0004	0.11	0.51	5.7	45	8.23
Minimum Value	<0.003	<0.001	<0.005	<0.005	<0.005	<0.0001	<0.005	<0.001	<0.005	<0.005	5.61
Mean Value (b)*1	0.0037	0.0008	0.0027	0.0089	0.020	0.00007	0.008	0.007	0.04	0.13	7.15
Standard Deviation (log)*2	0.470	0.45	0.120	0.455	0.371	0.20200	0.394	0.622	0.60	0.66	0.019
b + S.D.*3	0.011	0.00	0.004	0.025	0.047	0.00010	0.020	0.030	0.17	0.58	-
b + 2 S.D.	0.032	0.01	0.005	0.073	0.110	0.00017	0.048	0.124	0.69	2.62	-
Reference Value	0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05	-
NGERV	7	5	0	9	0	5	3	54	35	27	-

Reference Value: Taken from Environmental Standard for Water of Macedonia (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn) and guideline value of WHO (Cu)

NGERV: Number of grids exceeding the referrence value

*1: Geometric means (background value), , *2: Shown in logarithm *3: background+2Standard Deviation

Table 5.8 Statistical Values of the Elution Analysis of All Samples

308 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Below detection limit (%)	33.4	40.9	90.9	32.1	1.3	70.8	32.1	9.1	2.6	0.6	-
Maximum Value	0.49	1.8	0.0716	0.085	0.28	0.0004	0.11	0.51	19.74	133.2	8.23
Minimum Value	<0.003	<0.001	<0.005	<0.005	<0.005	<0.0001	<0.005	<0.001	<0.005	<0.005	5.61
Mean Value (b)*1	0.0049	0.0013	0.0028	0.0075	0.023	0.00006	0.0069	0.0088	0.062	0.21	7.15
Standard Deviation (log)*2	0.496	0.475	0.207	0.433	0.377	0.189	0.385	0.687	0.667	0.713	0.017
b + S.D.*3	0.0152	0.0037	0.0046	0.0204	0.0543	0.0001	0.0167	0.0426	0.288	1.09	-
b + 2 S.D.	0.0477	0.0111	0.0074	0.0553	0.1292	0.0002	0.0406	0.2076	1.336	5.66	-
Reference Value	0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05	-
NGERV	20	13	0	10	2	7	5	150	106	255	-

Reference Value: Taken from Environmental Standard for Water of Macedonia (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn) and guideline value of WHO (Cu)

NGERV: Number of grids exceeding the referrence value

*1: Geometric means (background value), *2: Shown in logarithm*2: background+Standard Deviation

b. Cadmium (Cd): The elution value of Cd is generally low, ranging from <0.001 to 1.4mg/L with mean value of 0.0013mg/L and 40% of the grids have concentration less than the detection limit of <0.001mg/L. The grid with the highest Cd elution value of 1.8mg/L occurs in the area between the Zletovska and Kiselica Rivers. Other than this, high Cd grids with Cd elution value greater than 0.0062mg/L, which is slightly lower than the Reference Value of 0.01mg/L, occur in the Kiselica River and along the lower stream of the Zletovska River, overlapping Cd-Pb-Zn-Mn high grids of the content analysis. The Cd high concentration grids occur in the area where the tailings materials of spillage by the incidents remain.

c. Cobalt (Co): The elution value of Co is low, ranging from <0.005 to 0.072mg/L and more than 90 grids give elution values less than the detection limit of 0.005mg/L. None of the grids exceed the Reference Value of 0.1mg/L. A scattered distribution of the grids with slightly higher Co value is observed on the both side of the Zletovska and Kiselica Rivers.

d. Chromium (Cr): The elution value of Cr ranges from <0.005 to 0.085mg/L with mean value of 0.0075mg/L. The number of grids exceeding the Reference Value of 0.05mg/L is 10 grids, and they occur scattered over the P/P area. The distribution map of Cr elution concentration does not show any systematic distribution and no correlation to the distribution map of the content concentration of Cr is observed.

e. Copper (Cu): The elution value of Cu ranges from <0.005 to 0.28mg/L with mean value of 0.023mg/L. The number of grids exceeding the Reference Value of 0.2mg/L is two grids. They occur on the Kiselica River just below the New Tailings Dam, and other high concentration grids of Cu occur to the south and east of the New Tailings Dam. Other than these, not like Cu distribution of content analysis, no clear systematic distribution pattern of the Cu elution concentration is observed except relatively high Cu concentration grids being distributed in the lower stream area of the Zletovska River where Cu high content concentration grids occur.

f. Mercury (Hg): The elution values of Hg in the P/P area are low, ranging from <0.0001 to 0.0004mg/L and 70.8% of the grids show Hg concentration less than the detection limit of 0.0001mg/L. The number of grids with Hg concentration more than the Reference Value of 0.0002mg/L is seven and they occur on the Zletovska River, slightly lower stream from the junction of Zletovska and Kiselica Rivers, where the grids of high Pb-Zn-Mn content concentration grids occur. Other than these, a scattered distribution of high and slightly higher Hg grids is observed.

g. Nickel (Ni): The elution concentration of Ni ranges from <0.005 to 0.11mg/L with the mean value of 0.0069mg/L. The number of grids with high elution concentration of Ni with elution concentration greater than the Reference Value of 0.005mg/L is five grids and they occur in the area of high Ni content concentration areas of northwest of the P/P area, northeast part of the P/P area and southwest part of the P/P area. The Ni high grids are only sporadically distributed and no clear zone of high Ni elution value is observed even in the southwest part of the P/P area, where clear zone of high Ni content value is observed.

h. Lead (Pb): Compared with Cu and Zn, elution concentration of Pb is lower, ranging from <0.001 to 0.51mg/L with mean value of 0.0088mg/L. The grids with high Pb elution concentration occur in the lower stream area of the Zletovska River, southwest part of the P/P area and on the Zletovska River slightly up stream from the junction of the Kiselica and Zletovska Rivers. However, the distribution of high Pb grids are sporadic, and not being in accordance with results of content analysis, clear zones of high Pb concentration along the Kiselica River and lower stream of the Zletovska River are not observed for elution analysis results. Half of the grids (150 grids) have Pb concentration greater than the Reference Value of 0.01mg/L and they do not show any systematic distribution, being scattered all over the P/P area. The elution concentration of Pb does not seem to be reflected by the content concentration of Pb.

i. Zinc (Zn): The elution concentration of Zn is higher than Cu and Pb, ranging from <0.005 to 20mg/L with mean value of 0.062mg/L. The highest Zn concentration grid of 20mg/L occurs adjacent to the Old Tailings Dam. Similar to the distribution of high Zn content concentration grid, the high Zn elution concentration grids with greater than 0.70mg/kg are found continuously from the area of the Tailings Dams down to the Kiselica River and lower stream area of the Zletovska

River and they do not occur other than at these locations. Comparing the Zn elution concentration to the Reference Values of 0.1mg/L, 106 grids of the P/P area exceed this value and they are distributed mainly along and close to the Zletovska and Kiselica Rivers. Other than these areas, the grids with Zn concentration exceeding the Reference Value occur in the area between the Kiselica and Zletovska Rivers. The elution concentration of Zn seems to be reflected by the Zn content concentration.

j. Manganese (Mn): The elution concentration of Mn is high, ranging from <0.005 to 133mg/L with the mean value of 0.21mg/L. Very high Mn elution concentrations are found in the grids adjacent to the Old Tailings Dam, just below the junction of the Zletovska and Kiselica Rivers and just below the New Tailings Dam, respectively showing 130, 63 and 60mg/L. Similar to the distribution of high Zn elution concentration grids, other Mn high elution concentration grids are mostly distributed along and near the Zletovska and Kiselica Rivers. Comparing to the Reference Value of 0.05mg/L, the number of grids with Mn elution concentration exceeding the Reference Value reach to 255 and they are distributed all over the area of the P/P Area. The grids with lower Mn elution concentration tend to occur in the west apart of the area, particularly southwest of the area. The elution concentration of Mn is reflected by the content concentration of Mn.

(2) Chemical Characteristics

Correlation coefficients between each heavy metal of the elution analysis, and between elution analysis and content analysis are calculated, and they are given in Tables 5.9 and 5.10, respectively.

Table 5.9 Correlation Coefficient of the Elution Analysis

308 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
As	1.000										
Cd	0.147	1.000									
Co	0.094	0.319	1.000								
Cr	0.149	-0.004	-0.067	1.000							
Cu	0.174	0.181	0.078	0.313	1.000						
Hg	-0.080	0.094	0.106	-0.042	-0.005	1.000					
Ni	0.061	0.159	0.237	0.709	0.256	0.089	1.000				
Pb	0.195	0.125	-0.06	0.378	0.429	-0.104	0.072	1.000			
Zn	0.129	0.587	0.276	0.260	0.455	0.036	0.171	0.564	1.000		
Mn	0.151	0.598	0.529	0.112	0.218	0.154	0.289	0.284	0.733	1.000	
pH	0.048	-0.401	-0.278	0.033	-0.045	-0.115	-0.064	-0.138	-0.454	-0.511	1.000

good correlation

Table 5.10 Correlation Coefficient Between Contents and Elution Analyses

308 samples

As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
0.473	0.312	-0.001	0.327	0.368	0.055	0.437	0.427	0.684	0.462

good correlation

As shown by the high correlation coefficients and similar distribution patterns of elution concentration, following groups of heavy metals with close relations are identified.

Group 1. Cd-Zn-Mn

Group 2. Cr-Ni

The heavy metals of Group 1, Cd-Zn-Mn, shows similar distribution pattern, high concentration grids being distributed from the area of the Tailings Dam down to Kiselica River and lower stream area of the Zletovska River where tailings materials of the spillage by the tailings dam incident remains. These heavy metals show fairly good correlation between the elution and content concentrations. The elution concentrations of Group 1 heavy metals reflect the results of content analysis and the mining activities of the area, particularly the tailings dam. These heavy metals have some negative relation with pH value, showing a tendency of higher elution concentration for the samples of more acidic soil. Although Pb and Zn shows relatively high correlation coefficients, the distribution pattern of high Pb elution concentration is slightly different from those of Cd, Zn, Mn. The high elution concentration grids of Pb are distributed not only along the Zletovska River but somewhere else, particularly, southwest part of the P/P area. The elution concentration of Pb seems to be controlled by some factors other than the spillage of the tailings materials. Cr and Ni show similar distribution pattern of high concentration grids, but they do not show clear systematic patterns in the P/P area.

Using the same methods as the soil content analysis, the cluster analysis was conducted for the results of the elution analysis (Figure 5.12). From the figure, similar to the results of correlation coefficient, the heavy metals are subdivided into two groups of close relationship, Cd-Zn-Mn and Cr-Ni. In the results of content analysis, Cu and Pb are included in the same group of Cd-Zn-Mn, but they belong to the separate group of heavy metals in the results of elution analysis. The distribution patterns of high elution concentration grids of the Cu and Pb are different from those of Cd , Zn and Mn. The high concentration grids of Cd, Zn and Mn occur mostly in the area along the Zletovska and Kiselica Rivers but for Cu and Pb, the high concentration grids occur not only these areas but they occur sporadically over the area of the P/P.

The factor analysis was conducted, following the same methods as the soil content analysis, for the results of the elution analysis, and as shown in the Table 5.11, four factors were extracted. Among these factors, Factor 4 does not show clear relations with heavy metals and factor contribution is low. Each factor of Factor 1 to 3 is given below together with related heavy metals.

Factor 1 Cd-Co-Mn-Zn

Factor 2 Cr-Ni

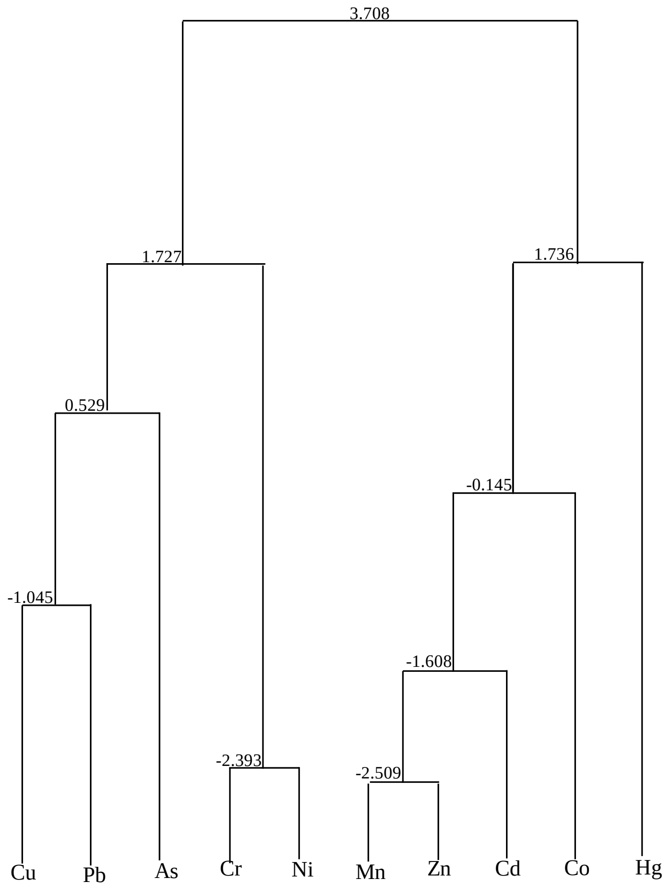
Factor 3 (Cu)-Pb-Zn

Based on the results of the factor analysis, together with distribution pattern of high elution concentration grids, the chemical nature of the elution analysis is summarized below.

a. Factor 1 (Cd-Co-Mn-Zn): Coincide with the results of content analysis, the high elution concentration of the these heavy metals sporadically occur in the area of tailings dams, along the Kiselica River to the lower stream area of the Zletovska River. By the content analysis results, these areas were confirmed to be affected by the mining activities such as tailings, characterized by high content concentrations of Cd-Cu-Pb-Zn-Mn. As shown by the correlation coefficients between content and elution analysis, the elution concentration of Zn and Mn reflect the chemical nature of the content analysis, showing fairly high correlation coefficients. In the elution analysis, Zn and Mn are most clearly affected by the mining activities of the area.

b. Factor 2 (Cr-Ni): Cr and Ni are chemically similar heavy metals, showing similar behaviour. Some of the Cr and Ni high elution concentration grids occur in the grids with high Cr and Ni content concentration enriched by natural causes. Other than these, relatively high elution concentration grids of them are sporadically distributed over the P/P area and no clear tendency of the systematic distribution pattern is observed.

c. Factor 3 (Cu)-Pb-Zn: Although three heavy metals of Cu, Pb and Zn were extracted as Factor 3 related heavy metals, the three heavy metals show different distribution patterns of high elution concentration grids. The high elution concentration grids of Zn are distributed only along the Kiselica and Zletovska Rivers, while those of Pb are distributed not only along the Zletovska and Kiselica Rivers, but some of relatively high concentration grids occur southwest and north of the area. The distribution pattern of the high elution concentration grids of Cu is much deviated toward westward. The relatively high concentration grids including high concentration grids are distributed widely in the west part of the P/P area, in addition to ones being distributed along the Kiselica and Zletovska Rivers. The three heavy metals of Factor 3 is reflecting the chemical nature of the mining activities, but in addition to it, particularly for Cu and Pb, they are controlled by some other factors to enrich elution concentration of Cu and Pb.



Cluster Dendrogram (Ward Method)

Figure 5.12 Results of Cluster Analysis (Elution Analysis)

Table 5.11 Results of Factor Analysis (Elution Analysis)

	Facrot Loading (Varimax Rotation)				Communality
Elements	Factor 1	Factor 2	Factor 3	Factor 4	
As	0.117	-0.068	0.141	-0.348	0.160
Cd	0.644	0.022	0.32	0.124	0.533
Co	0.689	-0.083	-0.145	-0.158	0.527
Cr	-0.109	-0.797	0.322	-0.095	0.760
Cu	0.104	-0.242	0.489	-0.251	0.371
Hg	0.188	-0.051	-0.062	0.246	0.102
Ni	0.231	-0.844	0.015	0.024	0.767
Pb	-0.017	-0.118	0.716	-0.258	0.593
Zn	0.525	-0.075	0.729	-0.023	0.813
Mn	0.791	-0.107	0.361	0.019	0.768
F.C (%)	35.6	27.0	30.9	6.7	-

F.C: Factor Contribution

(3) Summary

The elution analysis of 308 samples shows that Pb, Zn and Mn have high elution concentration. Respectively 150 samples, 106 samples and 255 samples exceed the Reference Value. Similar to the results of content analysis, high elution concentration grids of Zn, Mn and Pb occur from the tailings dam area, along the Kiselica River to the lower stream area of the Zletovska River. The relatively high concentration grids of these heavy metals exceeding the Reference Values are distributed not only around the Kiselica and Zletovska Rivers but also mostly all over the area including the west part of the P/P area. The elution concentrations of Co, Cr, Cu, Hg and Ni are low and less than ten samples have concentrations exceeding the Reference value. The heavy metals such as Cd, Co, Zn and Mn are related to mining activities of the area, such as tailings dam and their distribution of high concentration grids are observed along the Kiselica and Zletovska Rivers where tailings materials by the spillage incidence of the tailings still remain. Cu and Pb are slightly different from these heavy metals, the distribution of high elution concentration grids are found not only the Kiselica and Zletovska Rivers but also found in the west part of the area and they are controlled by some other factors in addition to mining activities of the area. The high elution concentration grids of the Cr, Ni and As are distributed in the area similar to the content analysis results and they are related to natural causes such as geological nature of the bedrock.

5.2 Tailings Survey

For understanding the tailings materials of the tailings dam, two boreholes, one each on the old tailings dam (TBH-1) and the new tailing dam (TBH-2), were drilled (Figure 5.13).

5.2.1 The Results of Drilling

Drilling of TBH-1 was conducted at the south end of TD-III, near the boundary between TD-III and TD-IV, of the Old Tailings Dam. At TBH-1 in the Old Tailings Dam, dark brown sandy silt occurs from the surface to 1.10m deep, and underneath this the tailings materials occur to the depth of 23.45m. The tailing materials are monotonous light to dark gray, silt to sand size material and sulphides are not visible by the naked eye. From 23.45 to 40.00 m (end of hole), bedrock consisting of andesitic tuff and mudstone occurs. The thickness of the tailings materials at this site is 22.35m.

The TBH-2 was conducted on the dyke of the New Tailings dam, approximately 80m west from the east end of the dyke. The tailings materials consisting of light brown to light gray, sandy silt occur from the surface to 27.30m deep. Although there are some variations of colour, mainly light gray and occasionally light brown or yellowish gray, the tailings materials are monotonous sandy silt material all through the drill core. The basement rock consisting of brownish red siliceous tuff appears from 27.30m and the drilling operation was terminated at 28.00m. The thickness of the tailings materials at this drilling site is 27.30m.

5.2.2 The Results of Chemical Analyses

From the drill cores a total of 28 samples, 13 samples from the Old Tailings Dam and 15 samples from the New Tailings Dam, were collected at 2m interval and they are sent for chemical analysis. Both of content and elution analyses were conducted for all of the 28 samples. The analytical methods for content and elution analyses are the same as grid soil survey, and chemical analyses were conducted at the Faculty of Mining and Geology, St. Cryil and Methodius University. The analytical results are given in Data 4.

For the calculation of the statistical values, the silt samples of the surface of TBH-1 and the bedrock samples of TBH-1 and TBH-2 were excluded for understanding the chemical nature of the tailings materials. The statistical values of the Old and New Tailings Dams are shown separately on Table 5.12 together with the mean value of the 400m grid soil survey and average soil of Bowen (1979). Combining the results of the Old and New Tailings Dams, correlation coefficients were calculated separately for content and elution analyses of the each element and in addition to them, the correlation coefficients between content and elution analyses were calculated (Table 5.13).

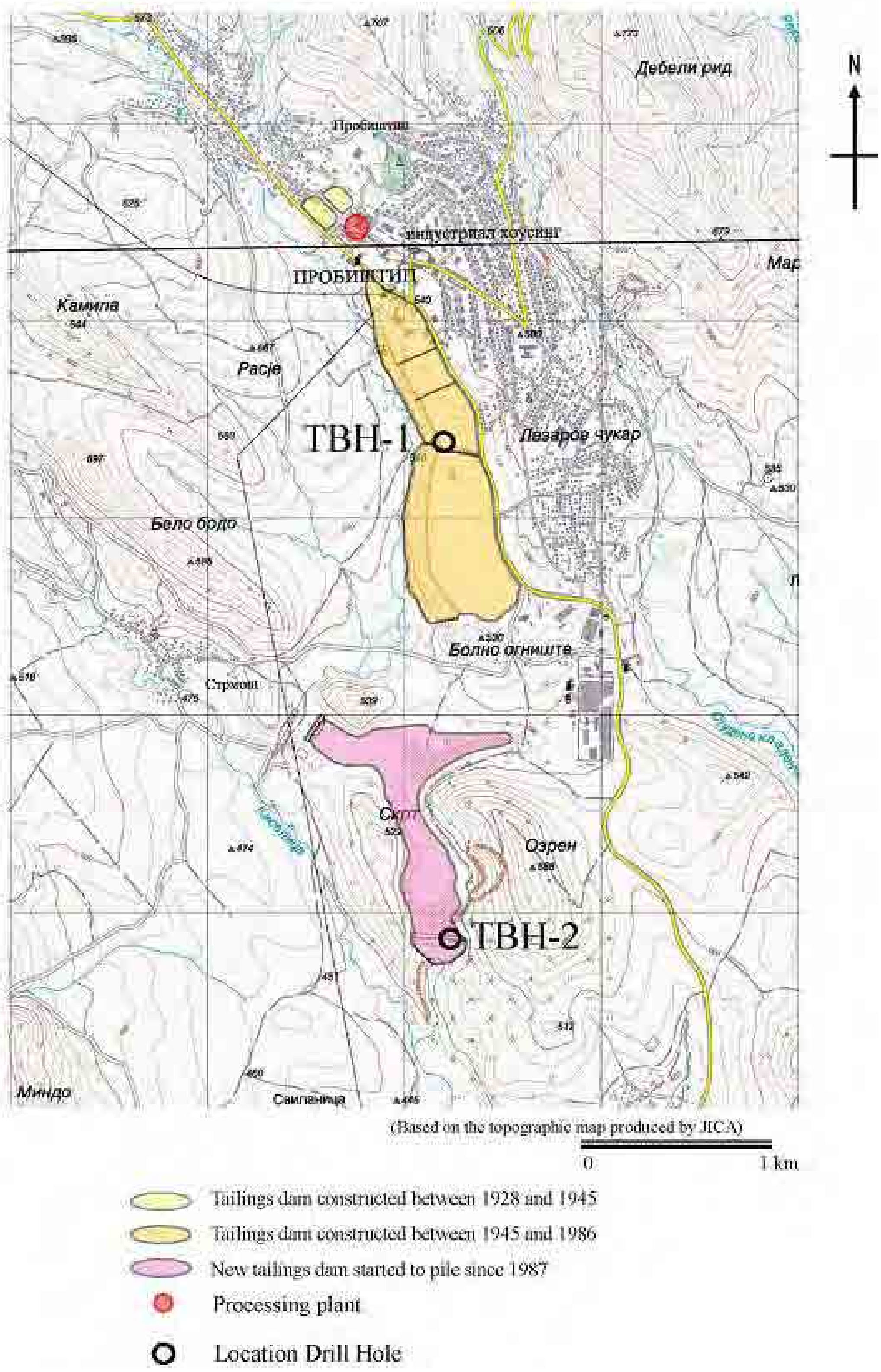


Figure 5.13 Location of Drill Holes in the Tailings Dams

Table 5.12 Statistical Values of the Analytical Results of Tailings Material

TBH-1

Old Tailings Dam-Content 11 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Maximum	400	90	24	28	450	<0.1	8.3	4,700	14,000	54,000	7.48
Minimum	160	31	10	14	290	<0.1	0.23	2,600	5,800	32,000	6.80
Mean	259	45	17	22	339	-	5.0	3,364	7,882	44,364	7.26
Standard Deviation	78	18	4	4	53	-	2.1	680	2,651	5,767	0.23
Geometric mean of 400m Grid Soil	16	0.40	19	32	31	-	19	82	130	1,300	-
Average Soil of Bowen (1979)	6	0.35	8	70	30	0.06	50	35	90	1,000	-

TBH-2

New Tailings Dam-Content 14 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Maximum	670	14	30	19	350	<0.1	13	4,600	3,200	35,000	7.40
Minimum	220	2	17	13	77	<0.1	1	360	1,300	24,000	6.94
Mean	461	8	23	16	204	-	5	2,547	2,157	31,000	7.21
Standard Deviation	116	4	4	2	74	-	3	1,101	569	3,138	0.15
Geometric mean of 400m Grid Soil	16	0.40	19	32	31	-	19	82	130	1,300	-
Average Soil of Bowen (1979)	6	0.35	8	70	30	0.06	50	35	90	1,000	-

TBH-1

Old Tailings Dam-Elution 11 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Below Detection Limit (%)	90.9	9.1	9.1	90.9	90.9	36.4	18.2	9.1	0.0	0.0	-
Maximum	0.003	0.19	0.25	0.005	0.005	0.00022	0.053	1.1	26	200	7.48
Minimum	<0.003	<0.001	<0.005	<0.005	<0.005	<0.0001	<0.005	<0.001	0.021	2	6.80
Mean	0.002	0.062	0.077	0.003	0.003	0.000	0.018	0.295	7.822	46	7.26
Standard Deviation	0.000	0.065	0.087	0.001	0.001	0.000	0.020	0.357	9.416	67	0.23
Reference value	0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05	-
NSERV	0	8	3	0	0	1	2	10	10	11	-

Reference Value: Taken from Environmental Standard for Water of Macedonia (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn) and guideline value of WHO (Cu)

NSERV: Number of samples exceeding the referrence value

TBH-2

New Tailings Dam-Eluton 14 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Below Detection Limit (%)	100.0	0.0	0.0	85.7	7.1	35.8	29.6	0.0	0.0	0.0	-
Maximum	<0,003	0.22	0.11	0.011	0.0054	0.00032	0.034	1.0	10	300	7.40
Minimum	<0,003	0.0014	0.0061	<0,005	<0,005	<0,0001	<0,005	0.001	0.098	2.2	6.94
Mean	<0,003	0.040	0.040	0.003	0.003	0.0001	0.011	0.249	2.43	57	7.21
Standard Deviation	-	0.058	0.031	0.002	0.001	0.0001	0.009	0.343	2.77	79	0.15
Reference value	0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05	-
NSERV	0	10	1	0	0	1	2	11	13	14	-

Reference Value: Taken from Environmental Standard for Water of Macedonia (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn) and guideline value of WHO (Cu)

NSERV: Number of samples exceeding the referrence value

Table 5.13 Correlation Coefficients of the Tailings Material

New and Old Tailings Dams-Content 25 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
As	1.000										
Cd	-0.538	1.000									
Co	0.743	-0.435	1.000								
Cr	-0.239	0.685	-0.181	1.000							
Cu	-0.269	0.701	-0.204	0.559	1.000						
Hg	0.000	0.000	0.000	0.000	0.000	1.000					
Ni	0.229	0.069	0.418	-0.019	0.334	0.000	1.000				
Pb	-0.110	-0.110	-0.101	0.351	0.499	0.000	0.188	1.000			
Zn	-0.530	0.985	-0.446	0.641	0.716	0.000	0.063	0.402	1.000		
Mn	-0.409	0.748	-0.382	0.799	0.676	0.000	-0.109	0.457	0.776	1.000	
pH	-0.280	0.197	-0.046	0.173	0.127	0.000	-0.050	-0.294	0.113	-0.068	1.000

New and Old Tailings Dams- Elution 25 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
As	1.000										
Cd	-0.168	1.000									
Co	-0.178	0.710	1.000								
Cr	-0.063	0.617	0.099	1.000							
Cu	-0.060	0.705	0.300	0.672	1.000						
Hg	-0.194	0.321	-0.137	0.641	0.473	1.000					
Ni	-0.158	0.739	0.980	0.208	0.374	-0.020	1.000				
Pb	-0.163	-0.163	0.610	0.573	0.561	0.163	0.677	1.000			
Zn	-0.143	0.756	0.945	0.118	0.264	-0.111	0.926	0.624	1.000		
Mn	-0.144	0.922	0.593	0.740	0.737	0.442	0.658	0.728	0.559	1.000	
pH	0.278	-0.777	-0.674	-0.360	-0.504	-0.078	-0.663	-0.613	-0.629	-0.752	1.000

Content-Elution Analyses 25 samples

As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
-0.252	0.169	-0.122	-0.082	-0.077	0.000	0.264	0.494	0.424	-0.019

very good correlation, good correlation

(1) Content Analysis

Reflecting the nature of the Zletovo Mine, the tailings material of both of the Old and New Tailings Dams are very high in As, Cd, Pb, Zn and Mn, reaching maximum values of, respectively, 670, 90, 4,700, 14,000 and 54,000mg/kg. The average values of these heavy metals are 259, 45, 3,364, 7,882 and 44,364mg/kg for the Old Tailings dam and 461, 8, 2,547, 2,157 and 31,000mg/kg for the New Tailings dam, respectively.

In addition to them, Cu is high with average value of 339mg/kg and 204mg/kg, respectively, for the Old Tailings Dam and the New Tailings Dam. The concentrations of Co of the tailings Dams are similar to the concentration of the mean values of 400m grid soil survey and average soil of Bowen (1979). Cr and Ni, on the other hand, are lower than the mean value of 400m grid soil survey and the average value of Bowen (1979). Comparing both tailings dams, Zn is much higher and Cu is slightly higher in the old tailings dam than in the new tailings dam. While As is slightly lower in the old tailings dam than in the new tailings dam. The pH values of the tailing materials are fairly constant, ranging from 6.80 to 7.48 for the Old Tailings dam and 6.94 to 7.40 for the New Tailings dam, but they tend to slightly increase tower downward.

The correlation coefficients of each elements show that Cd-Cr-Cu-Zn-Mn shows very good correlation, while Pb show good correlation only with Cu, Zn and Mn. As is slightly isolated from other heavy metals, showing very good correlation only with Co and negative correlations with Zn and Mn.

The vertical variations of content concentrations of the heavy metal in the tailings dams are shown in Appendix 6. In the old tailings dam, the heavy metal concentrations, such as Cu, Pb and Zn, are slightly lower in the shallower horizon of less than 10m and deeper horizon of deeper than 20m, and they are the highest between 15 to 20m deep. In the New Tailings Dam, a systematic chemical variation in vertical direction is not clearly observed.

(2) Elution Analysis

For assessing the results of the elution analysis, the values of Environmental Standard for Water of Macedonia Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004) were used as reference value.

Comparison with the Reference Values, elution concentrations of the tailings materials are very high in Pb, Zn and Mn, showing more than 10 times of the Reference Values for most of the samples. The maximum values of Pb, Zn and Mn reach to 1.1, 26 and 200mg/L for the Old Tailings Dam and 1.0, 10 and 300mg/L for the New Tailings Dam. Other than these, Cd is high, giving the values of few times higher than the Reference Values for the most of the samples. One sample of the Old Tailings Dam and three samples of the New Tailings Dam exceed the Reference Value of Co. Hg and Ni are generally low, but one sample of Hg and two samples of Ni of the New Tailings Dam exceed the Reference Values. The elution concentrations of As, Cr and Cu show very low values, most of them being less than detection limit and far less than the Reference Values.

The correlation coefficients show that most of the heavy metals except As and Hg show very good correlations. Most of the heavy metals are similarly high in the same samples. Clear negative relations between pH values and elution values of Cd, Co, Cu, Ni, Pb, Zn and Mn suggest higher elution values for more acidic soils.

The correlation coefficients between contents values and elution values are low for most of the heavy metals except Pb and Zn, suggesting no clear relation between content and elution values for these heavy metals. Pb and Zn show correlation coefficient of, respectively, 0.494 and 0.424, suggesting week positive correlation between content and elution values for Pb and Zn.

There are clear tendencies of elution values of Cd, Co, Ni, Pb, Zn and Mn decrease with depth. Zn and Mn of the Old Tailings Dam, for examples, are 26 and 200mg/L at the top of the Tailings Dam and they decrease to 0.021 and 2.0mg/L, respectively, at the bottom of the tailing dam.

Since the elution values of Cd, Pb, Zn and Mn of both of the tailings Dams are high, far exceed the Reference Values, if the groundwater from the tailings dams is drained to the river nearby, it causes high heavy metal concentration in the surface water.

5.3 Drilling Survey of Soil

Based on the of results of 400m and 200m grids soil surveys, groundwater monitoring and field survey, the drilling survey of soil by 5m deep (all-core) drill holes were conducted. The purposes of the survey are:

- to understand three-dimensional distribution and vertical profiles of heavy metal concentration in soil,
- to clarify the heavy metal enrichment mechanism , and
- to define the difference between natural and human causes of heavy metal enrichment in soil.

The drilling of 50 holes was conducted. The purposes and locations of the drill holes are shown in Table 5.14 and Figure 5.14.

A total of 33 holes are drilled along 6 profiles lines, three of them crossing the Kiselica River (Profiles 1, 2 and 3)) and three of them crossing the Zletovska River (Profile 4, 5 and 6). The profiles were set over the Cd-Cu-Pb-Zn-Mn high grids of surface soil survey, where high heavy metal concentrations related to mining actives are expected, for understanding the vertical profiles of heavy metal concentrations in the grids with high concentrations of heavy metals along these rivers. The other 17 holes were drilled at the locations in the grids with high concentrations of heavy metals, such as As-Pb-Zn, Ni and As, scattered over the P/P area for confirming the causes of the heavy metal high concentrations in each area.

For each drill hole, soil samples were collected at 50cm intervals from the surface to 3m and at 1m interval from 3 to 5m, and they are sent to chemical analysis.

5.3.1 The Results of Drilling

The columnar charts of the drilling are given in Data 5.

The drill cores of the drill holes along profile lines of the Kiselica and Zletovska Rivers consist of silt and clay materials including surface soil underlain by river sediments of sand and gravel (Figure 5.15). The thickness of silt and clay varies at each location. It is thicker in the upper stream area of the Kiselica River and upper stream area of the Zletovska River, exceeding more than 5m thick in some of the drill holes. Along the profiles of the Kiselica River, the silt and clay are thinner and underlain by the materials of strongly weathered rock (C-horizon of soil) in the drill holes of both sides of the profile. It gradually changes to the bedrock of tuff.

Table 5.14 List of Soil Survey Drill Holes

	Name of Borehole	X	Y	Drilling Site	Purpose
1	D18	594175	4644875	Ni high grid of southwest	Confirmation of Causes
2	E14	594600	4643325	Ni high grid of southwest	Confirmation of Causes
3	H11	595775	4641875	Ni high grid of southwest	Confirmation of Causes
4	H15	595775	4643325	Ni high grid of southwest	Confirmation of Causes
5	I36	596275	4651900	Ni high grid of north	Confirmation of Causes
6	K10	596950	4641450	Ni high grid of southwest	Confirmation of Causes
7	M10	597950	4641425	Ni high grid of southwest	Confirmation of Causes
8	M35	597625	4651620	Pb-Zn-As high grid	Tailings
9	N33	598300	4650800	Pb-Zn-As high grid	Confirmation of Causes
10	P28	600250	4646175	As high grid	Confirmation of Causes
11	Q4	599525	4639400	SAPROF Profile3-1 Pb high	Confirmation of Causes
12	R25	599820	4647600	As high grid	Confirmation of Causes
13	T3	600550	4638725	Zn high grid	Confirmation of Causes
14	U6	601475	4639200	Pb-Zn-As high grid	Confirmation of Causes
15	U30	600850	4649150	Pb-Zn-As high grid	Confirmation of Causes
16	X29	602075	4649050	As-Ni-Cr-Co high grid	Confirmation of Causes
17	a30	603100	4649475	Pb-Zn-As high grid	Confirmation of Causes
18	PF1-1	597500	4649450	Profile of the Kiselica River, immediately downstream area from the Old Tailings Dam	Confirmation of lateral and vertical spread of heavy metals
19	PF1-2	597600	4649370		
20	PF1-3	597725	4649345		
21	PF1-4	597850	4649320		
22	PF1-5	598000	4649300		
23	PF1-6	598200	4649320		
24	PF2-1	597900	4646650	Profile of the Kiselica River	Confirmation of lateral and vertical spread of heavy metals
25	PF2-2	598175	4646800		
26	PF2-3	598375	4646850		
27	PF2-4	598480	4646825		
28	PF2-5	598650	4646875		
29	PF3-1	598700	4645775	Profile of the Kiselica River Correspond to *SAPROF Profile1*	Confirmation of lateral and vertical spread of heavy metals
30	PF3-2	598825	4645825		
31	PF3-3	598950	4645950		
32	PF3-4	599050	4646025		
33	PF3-5	599170	4646100		
34	PF4-1	600300	4645785	Profile of the Zletovska River	Confirmation of lateral and vertical spread of heavy metals
35	PF4-2	600525	4645725		
36	PF4-3	600650	4645675		
37	PF4-4	600775	4645675		
38	PF4-5	600875	4645650		
39	PF4-6	600975	4645650		
40	PF5-1	599850	4643475	Profile of the Zletovska River	Confirmation of lateral and vertical spread of heavy metals
41	PF5-2	600150	4643550		
42	PF5-3	600275	4643550		
43	PF5-4	600450	4643500		
44	PF5- 5	600213	4643550		
45	PF6-1	599950	4640350	Profile of the Zletovska River	Confirmation of lateral and vertical spread of heavy metals
46	PF6-2	600113	4640375		
47	PF6-3	600375	4640475		
48	PF6-4	600575	4640525		
49	PF6-5	600700	4640600		
50	PF6-6	600850	4640650		

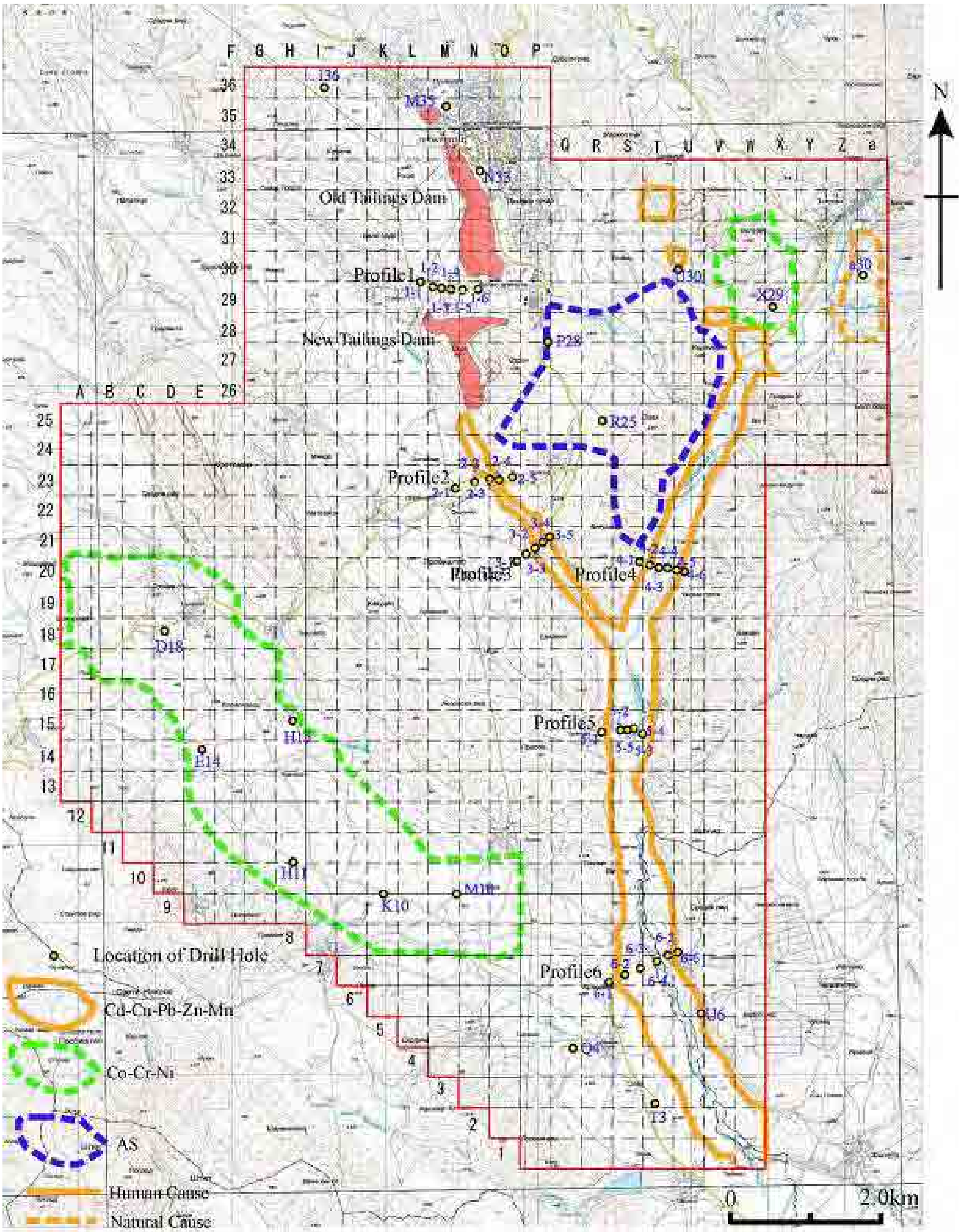


Figure 5.14 Locations of Soil Survey Drill Holes

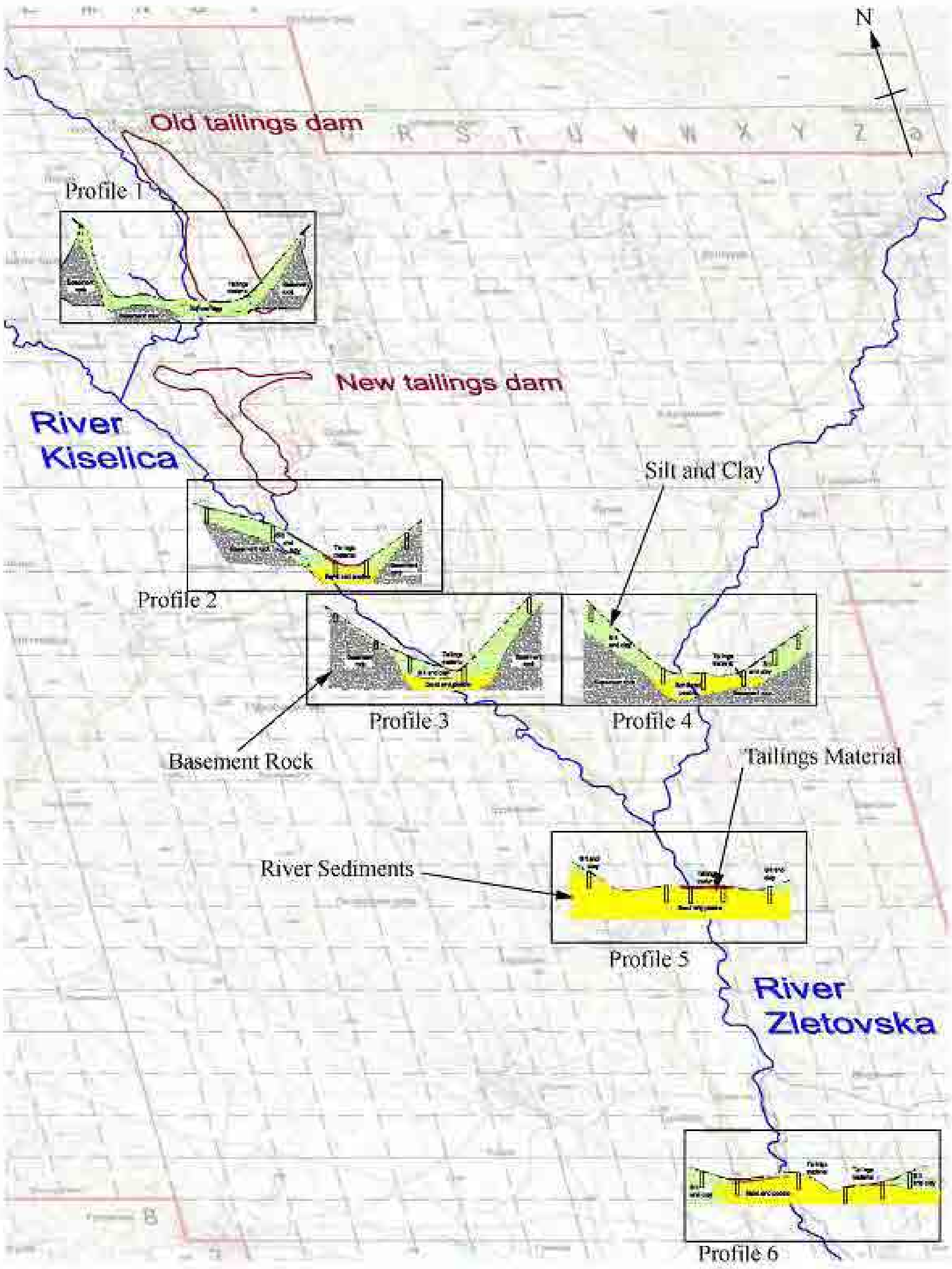


Figure 5.15 Geological Profile along the Kiselica and Zletovska Rivers

In the profiles of the Zletovska River, thick silt and clay are only found in the both side of profiles located slightly higher location from the river plain. The river deposits consisting of sand and gravel dominate the drill holes of the river plain and silt and clay are normally thin, 0.4 to 1.5m thick.

The orange brown material similar to the tailings materials occur near the surface of the most of the holes drilled at the location close to the rivers. It occasionally forms a clear layer of 40 to 60cm thick and it commonly occurs as orange brown shapeless spots in the brown soil. These spots are commonly observed at the drill holes of Profile 6. In the drill holes of the profile 5, orange brown oxidized parts are observed in the river sediments of sand and gravels.

The drill holes conducted in the Ni high concentration area of the south west of the P/P area have clay and silt layer of 0.50 to 4.20m thick on the surface and brownish gray to yellowish gray mudstone underlies it. Between the silt and clay of the surface and mudstone, C-horizon of soil occurs at the most of the holes.

Other drill holes conducted in high heavy metal concentration zone of small scale have 0.60 to 3.00m thick silt and clay layer of the surface and it is underlain by C-horizon and the bedrocks of mudstone, andesite and tuff. M-35 was conducted at the old tailing dam near the floatation plant of the Zletovo Mine. Gray, partly orange brown, tailings materials occur covered and intercalated by brown silt. T-3 hole, drilled on east side of the river plain of the Zletovska River, has 2.70m thick silt and clay with orange brown spots and it is underlain by sand and gravel.

5.3.2 Analytical Results of Core Samples

Chemical analyses of the core samples, content analysis of 439 samples and elution analysis of 45 samples, were conducted. The analytical methods for content and elution analyses are the same as grid soil survey, and chemical analyses were conducted at the Faculty of Mining and Geology, St. Cryil and Methodius University. The analytical results are given in Data 4.

(1) Content Analysis

The statistical values and correlation coefficient of the content analysis are given in Table 5.15 and 5.16, respectively.

Compared with the average soil of Bowen (1979) the results of the soil of the drilling survey show higher mean values for As, Co, Cu, Pb, Zn, Mn, lower means values for Cr Ni, and the mean values of Cd and Hg are similar to the average soil of Bowen (1979).

The high As samples occur at the R25 and some of Profile 1 and 4 holes, showing more than

300mg/kg. Cr and Ni are similarly high in same samples of drill holes such as X29, holes of the south west part of the P/P area and some of the Profile holes reaching more than 200mg/kg, but it commonly show the concentration less than 100mg/kg. Drilling M35 was conducted on the old tailings dam, and the maximum values of Cd, Cu, Pb, Zn and M, respectively, 110mg/kg, 920mg/kg, 25,000mg/kg, 19,000mg/kg and 66,000mg/kg were obtained from the samples of M35 hole. Other drill holes showing high concentrations of Cd, Cu, Pb, Zn and Mn are Profile drill hole of Profile 5 and 3, where oranges brown tailings materials are observed. pH values ranges from 5.04 to 7.71, and it tends to be lower in the Profile drill holes such as Profile 3 and 5, where orange brown tailings materials were found.

Table 5.15 Statistical Value of the Drilling Survey of Soil (Content Analysis)

5m deep Drilling-Content 439 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Below Dwtwction Limit (%)	5.2	21.8	0	0.2	0	72.7	2.7	0	0	0	-
Maximum	800	140	110	410	920	2.7	710	25,000	19,000	66,000	7.71
Minimum	<1	<0.1	5	<1	6	<0.1	<1	15	34	52	5.04
Geometric Mean	14	0.37	21	34	43	0.04	19	113	178	1,584	7.17
Standard Deviation	0.648*	0.812*	0.129*	0.387*	0.332*	0.336*	0.540*	0.608*	0.457*	0.394*	0.243
Geometric mean of 400m Grid Soil	16	0.40	19	32	31	-	19	82	130	1,300	-
Average Soil of Bowen (1979)	6	0.35	8	70	30	0.06	50	35	90	1,000	-

Table 5.16 Correlation Coefficients of the Drilling Survey of Soil (Content Analysis)

439 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
As	1										
Cd	-0.178	1									
Co	0.158	-0.02	1								
Cr	-0.229	-0.059	0.353	1							
Cu	0.375	0.538	0.129	-0.237	1						
Hg	0.09	0.201	-0.055	0.028	0.265	1					
Ni	-0.245	-0.097	0.317	0.707	-0.218	-0.007	1				
Pb	0.337	0.682	0.036	-0.215	0.774	0.326	-0.277	1			
Zn	0.215	0.763	0.044	-0.176	0.760	0.320	-0.225	0.926	1		
Mn	0.222	0.639	0.177	-0.02	0.683	0.253	-0.041	0.757	0.788	1	
pH	-0.23	-0.156	0.085	0.167	-0.291	-0.148	0.206	-0.339	-0.308	-0.262	1

very good correlation

Correlation coefficient shows two groups of heavy metals given below are closely associated each other, showing the correlation coefficients of more than 0.500.

a) Cd-Cu-Pb-Zn-Mn
b) Cr-Ni

These heavy metals of the same group are closely associated, each similarly being high in the same samples.

Following the same methods as 400m grid soil survey, the factor analysis by Varimax rotation was conducted for the samples of the drilling survey of the soil. As shown in the Table 5.17, four factors were extracted from the factor analysis. Each factor of 1 to 4 is given below together with related heavy metals.

Factor 1: Cd, Cu, Pb, Zn and Mn
Factor 2: Cr-Ni
Factor 3: As
Factor 4: Hg

Table 5.17 Results of Factor Analysis of Drilling Survey of Soil (Content Analysis)

	Factor Loading (Varimax Rotation)				Commu-nality
Elements	Factor 1	Factor 2	Factor 3	Factor 4	
As	-0.118	0.126	-0.649	-0.064	0.455
Cd	-0.836	0.046	0.336	-0.052	0.817
Co	-0.111	-0.492	-0.295	0.176	0.372
Cr	0.095	-0.821	0.17	-0.076	0.718
Cu	-0.752	0.102	-0.39	-0.125	0.743
Hg	-0.225	-0.015	-0.046	-0.522	0.326
Ni	0.129	-0.808	0.175	-0.04	0.702
Pb	-0.871	0.158	-0.251	-0.26	0.915
Zn	-0.927	0.113	-0.106	-0.215	0.929
Mn	-0.833	-0.113	-0.184	-0.091	0.749
F.C (%)	55.4	24.8	14.2	6.9	

Same as the results of grid soil survey, Factor 1 (Cd, Cu, Pb, Zn and Mn), is related to the tailings materials and chemical nature of the mineralization of this area. These heavy metals are high in the samples of Profiles 3, 5, 6 in addition to M35 hole conducted on the old tailings dam near the floatation plant. Factor 2 (Cr-Ni) is related to the chemical nature of Ni high area in the southwest of and northeast of the P/P area. Factor 3 (As) is related to the enrichment of As. The enrichment of As seems to be independent from other heavy metals. The samples of R25 hole show very high As concentration, despite relatively low concentrations of other heavy metals such as Cu, Pb, Zn and Mn. Profile 4-1 hole, drilled at the west end of the Profile 4 shows similar chemical nature with high As and relatively low concentrations of other heavy metals. Although Factor 4 (Hg) was extracted, its factor contribution is low. High Hg samples occur in the M35 holes drilled at the old tailings dam close to the floatation plant and in some of the samples of Ni high concentration area of the southwest part of the P/P area.

The vertical chemical variations of heavy metals, As, Cu, Pb, Zn and Mn, are shown together with cross sections for six profiles of the Kiselica and Zletovska Rivers in Appendix 7. In the figures, heavy metal concentrations are shown as relative values of the Average Soil of Bowen (1979) (background value).

On the Profiles 1, 2 and 3, most of the samples show heavy metal concentrations between 1 to 10 times of the background value except samples of the holes drilled near the both side of the river. Along the profiles of the Kiselica river, relatively high concentration of heavy metals reaching 10 times or more of the background values are observed for the samples of less than 2m deep at the holes close to the river.

Along the Profile 4 of the upper stream of the Zletovska River, PF 4-1 has high As concentration reaching 100 times of the background value, being affected by the As high concentration area located in the west of the drill site. On the Profiles 3, 5 and 6, the drill holes conducted near the river show high concentration of the heavy metals in the deeper part of more than 3m deep.

The concentrations of the heavy metals are shown in the Figures 5.16 to 5.19 for As, Cd, Pb and Zn using the same subdivision of the concentrations as 400m grid soil survey. In the Kiselica River high heavy metal concentration zone occurs in a narrow zone, mostly found only at the drill holes of close to the river. At the PF2-3 and PF3-4, high heavy metal concentrations occur to the deeper part. In lower stream area of the Zletovska River, high heavy metal concentration zones occur widely and much deeper. Along the Profile 6, high heavy metal concentration zone are 200m wide and it reaches to 5m deep at the centre of it.

Vertical chemical variations of 17 holes, conducted for confirming the causes of the high heavy metal concentrations to the soil, are shown in Appendix 8. The drill holes conducted in the high Ni and Cr area of the north west part of the P/P area show high Ni and Cr concentrations in the bed rock of mudstone. The enrichment of the high Ni and Cr concentrations to the soil was caused by high concentrations of the bedrock. It is same at the X29 hole, located in the north east of the P/P area, the bedrock has very high concentration of Ni and Cr. At the R25, drilled in the As high concentration area, the concentrations of As, Pb, Zn and Mn are the highest in the surface soil. Certain mechanism of the enrichment of these heavy metals in the soil must be considered for this hole. Other drilling sites show reasonably high heavy metals concentrations in the bedrock and high concentrations of the soil can be explained by natural causes.

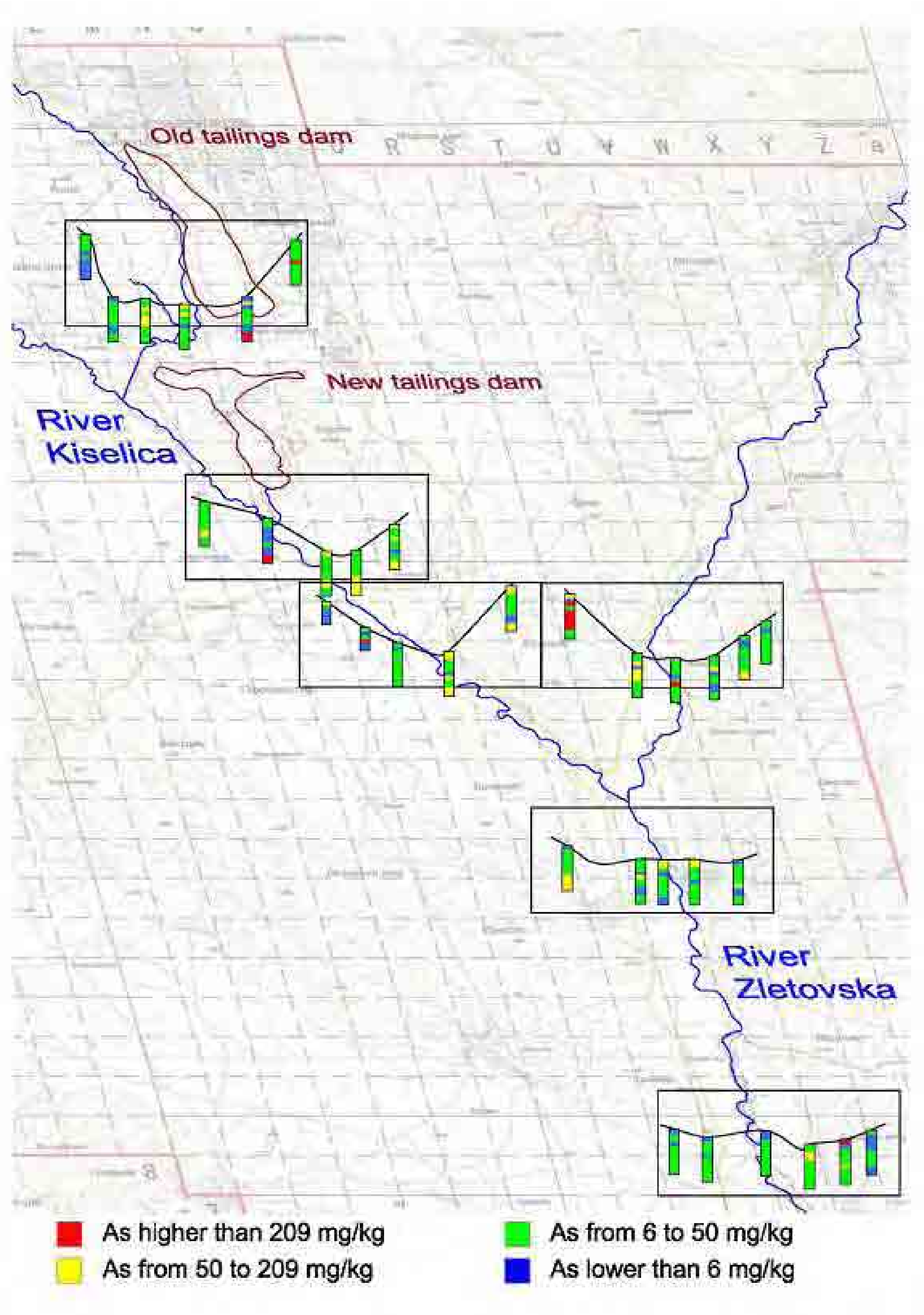


Figure 5.16 Arsenic (As) Concentration of the Profiles

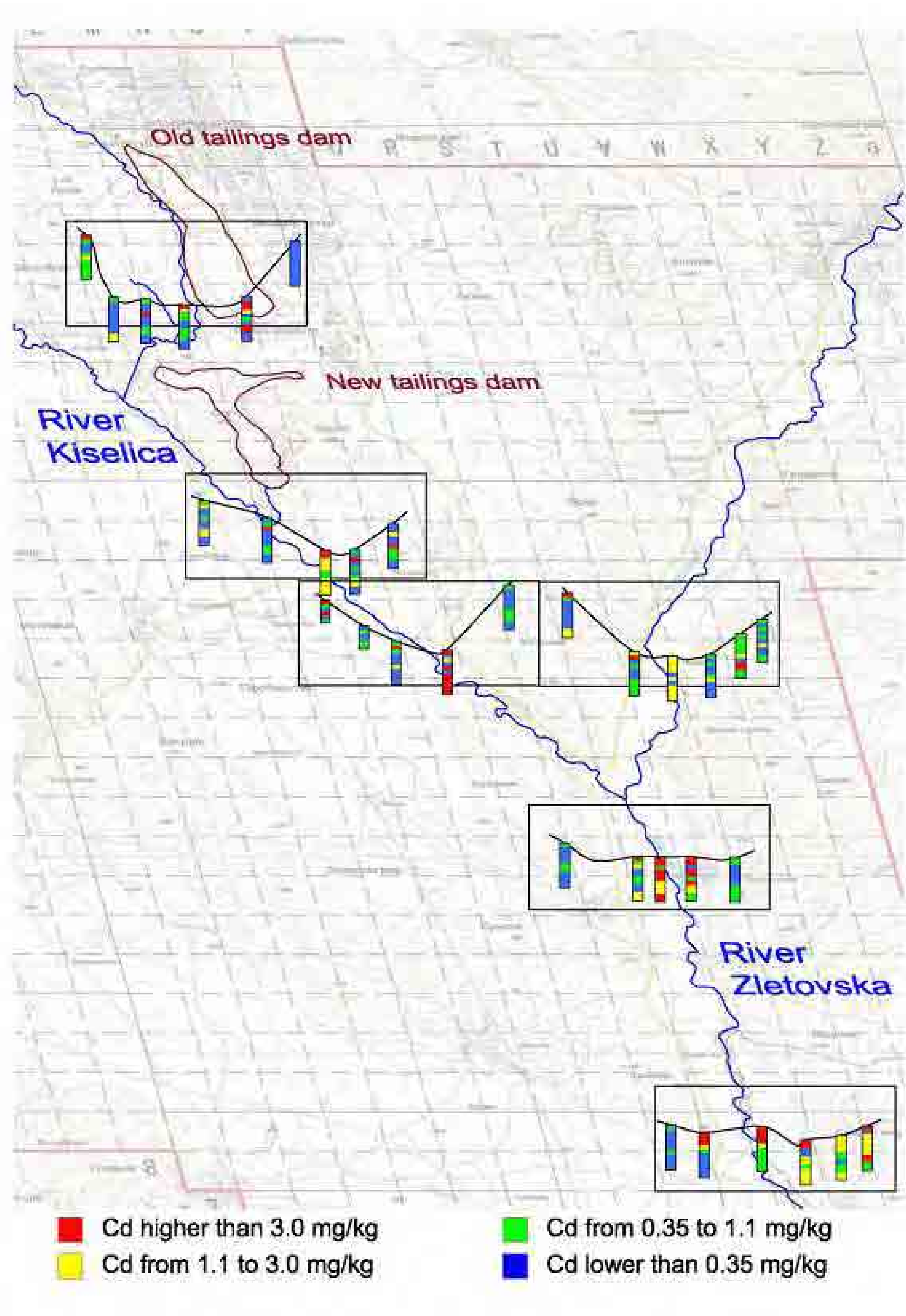


Figure 5.17 Cadmium (Cd) Concentration of the Profiles

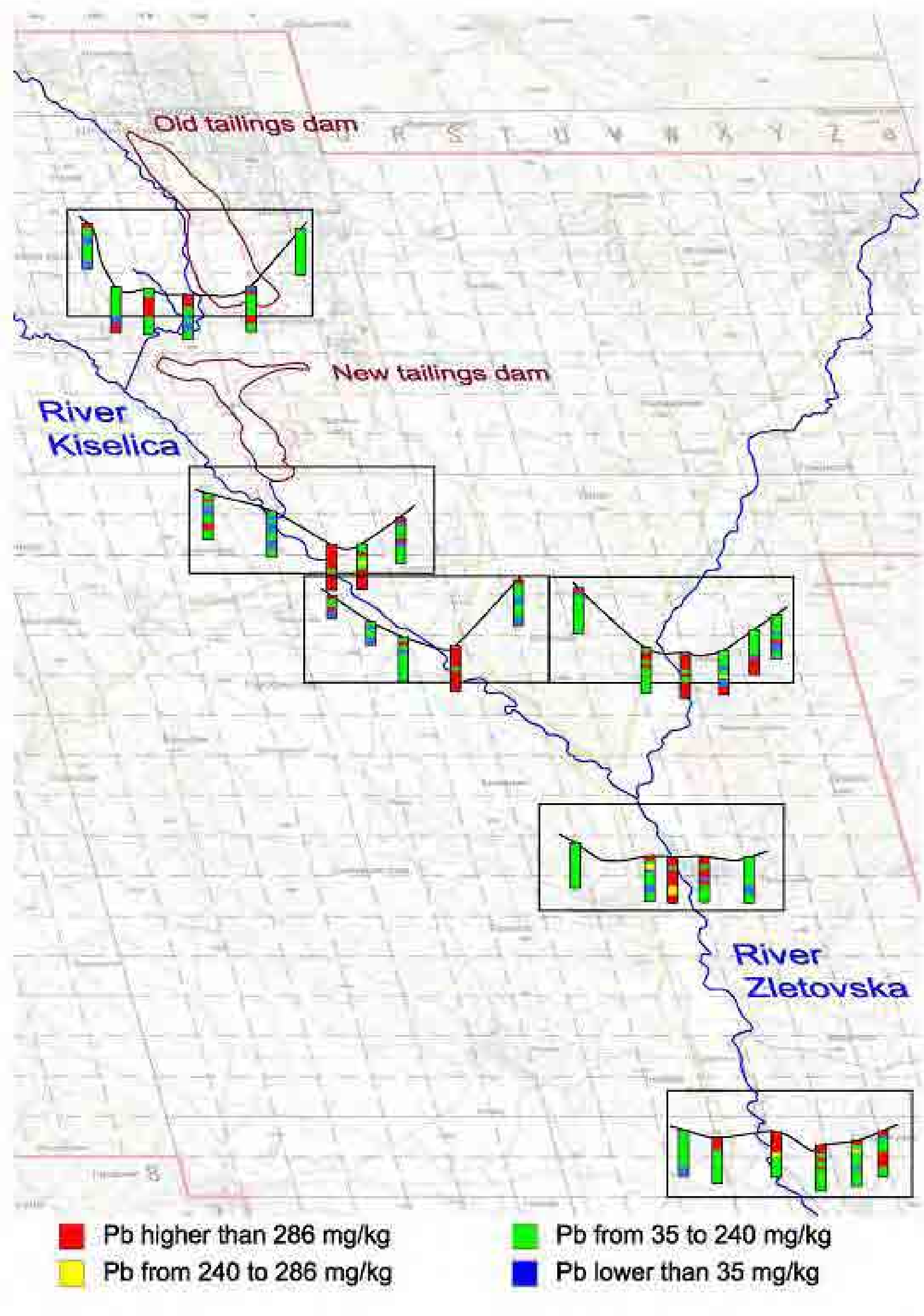


Figure 5.18 Lead (Pb) Concentration of the Profiles

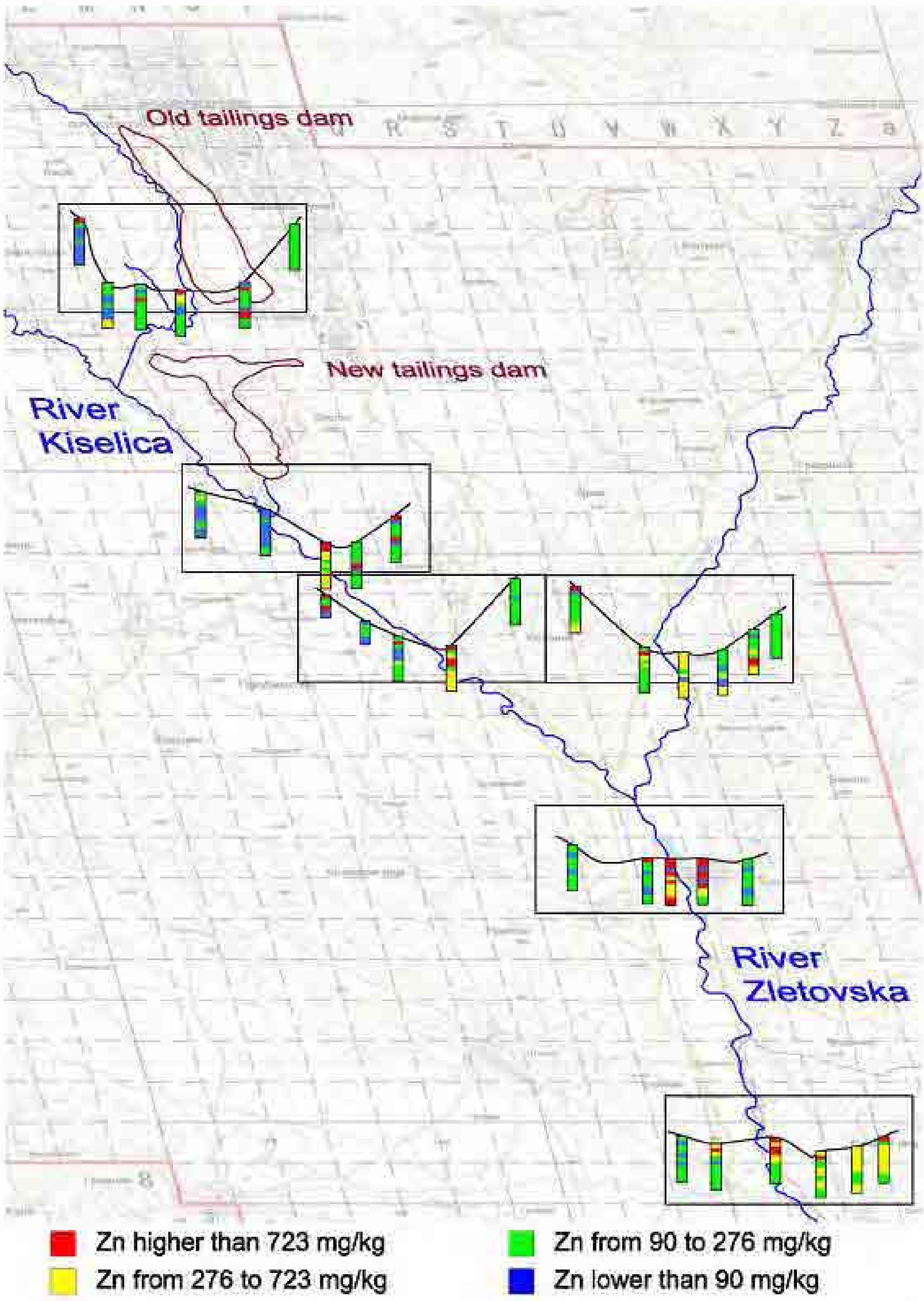


Figure 5.19 Zinc (Zn) Concentration of the Profiles

(2) Elution Analysis

Elution analysis was conducted for 45 core samples (10% of total samples) of drilling survey of soil. The samples were selected to cover the whole aspect of drilling survey as much as possible. The analytical results are given in Data 4. Statistical values and correlation coefficients are given, respectively, in Tables 5.18 and 5.19.

For assessing the results of the elution analysis, the values of Environmental Standard for Water of Macedonia Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004) were used as reference value.

Among the 10 elements, elution values of Co, Cu, Hg and Ni are low, none of the samples exceeding the reference value. While, Pb, Zn and Mn are high with the maximum values reaching to 0.11mg/L, 3.9mg/L and 29mg/L, respectively, and average values of them are 0.013mg/L, 0.20mg/L and 1.7mg/L, exceeding the References Value.

Mn is particularly high and more than half of the samples show elution values higher than the Reference Value. Almost all of the samples taken from the profile drilling crossing over the Kiselica and Zletovska Rivers have Mn elution values more than the Reference Values. Among the profiles, elution value of Mn is very high along the Profiles 3, 4 and 5, where tailings materials remain. Other than profile drill holes, Mn elution values are high at the holes drilled in the Pb-Zn-Mn high concentration areas of content analysis.

Nearly half of the samples of profile drilling have Pb and Zn elution values greater than the Reference Value. Similar to Mn, the samples with high Pb and Zn occur along the Profiles 3, 4, 5 and 6, where the tailings materials remain. Other than profile drill holes, samples with elution value greater than the Reference Value are less, three samples for Pb and one sample for Zn. They occur at the holes drilled in the Pb-Zn-Mn high concentration areas of content analysis.

The samples with Cd elution value exceeding the Reference Value are nine, and similar to Pb, Zn and Mn, all of them occur along the Profiles 3, 4, 5 where tailings materials remain. Nine samples have Cd elution value greater than the Reference Value and they occur at the holes drilled in the Cd content high area and Profiles 4 and 5.

As shown in the table of correlation coefficient, Cd, Mn and Zn have close relation and pH has negative relations with these heavy metals. Since these heavy metals are high at the profile drill holes such as Profiles 3, 4 and 5 where tailings materials of the spill incidents remain, high elution values of these heavy metals and lower pH value represent the elution nature of the tailings materials. These heavy metals seem to be still resolving to groundwater and surface water. Other than these, heavy metals such as As-Cu, Cr-Cu and Cu-Pb show good relations.

Table 5.18 Statistical Value of the Drilling Survey of Soil (Elution Analysis)

45 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Below Detection Limit (%)	28.9	28.9	68.9	40.0	8.9	66.7	40.0	24.4	6.7	6.7	-
Maximum	0.11	0.041	0.091	0.054	0.081	0.00015	0.029	0.11	3.9	29	7.43
Minimum	<0.003	<0.001	<0.005	<0.005	<0.005	<0.0001	<0.005	<0.001	<0.005	<0.005	6.48
Mean	0.01705	0.00666	0.00548	0.0098	0.020	0.00007	0.0069	0.013	0.20	1.7	7.187
Standard Deviation	0.025	0.009	0.013	0.010	0.018	0.00003	0.006	0.021	0.603	5.181	0.160
Reference value	0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05	-
NSERV	9	9	0	1	0	0	0	16	13	34	-

Reference Value: Taken from Environmental Standard for Water of Macedonia (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn) and guideline value of WHO (Cu)
NSERV: Number of samples exceeding the referrence value

Table 5.19 Correlation Coefficients of the Drilling Survey of Soil (Elution Analysis)

45 samples

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH
As	1.000										
Cd	0.077	1.000									
Co	0.445	0.073	1.000								
Cr	0.527	-0.064	0.182	1.000							
Cu	0.446	-0.029	0.266	0.529	1.000						
Hg	-0.035	0.030	-0.078	0.323	0.200	1.000					
Ni	0.082	-0.097	0.087	0.364	0.211	0.082	1.000				
Pb	0.171	-0.087	0.201	0.244	0.718	0.015	-0.023	1.000			
Zn	-0.104	0.603	0.023	-0.101	-0.085	0.110	-0.155	-0.043	1.000		
Mn	-0.179	0.507	0.006	-0.204	-0.194	0.142	-0.186	-0.140	0.895	1.000	
pH	0.068	-0.532	0.189	0.120	-0.037	-0.060	0.080	0.095	-0.718	-0.606	1.000

5.4 River Bottom Sediments Survey

Bottom sediments of river were collected at the centre and both sides of stream. A total of 6 samples, three samples in the Zletovska River and three samples in the Kiselica River were collected (Figure 5.20). In addition to the river bottom sediments, surface water samples were collected at the same sites.

The bottom sediments samples were digested with HF and $HClO_4$ according to ISO 14869-1 after drying, crushing and milling (ISO 11464), and they were determined by ICP (Inductively Coupled Plasma) method based on ISO 11885-1 for As, Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn. For Hg, after drying, crushing and milling (ISO 11464), soil samples were digested with HCl and HNO_3 (ISO 16772) and chemical analysis was conducted by CVAAS (Cold-Vapour Atomic Absorption Spectrometric) method (ISO 16772). The chemical analysis including sample preparation was conducted at the Faculty of Mining and Geology, St. Cyril and Methodius University.

The analytical results of the river sediments are given in Data 4. Although the chemical nature of river sediments and soil are different, analytical results of the river bottom sediments are shown together with the average soil of Bowen (1979) as reference value.

Three samples (BS-01, BS02, BS-03) of the Zletovska River show similar values of Pb (380 to 510mg/kg) and Zn (800 to 1,000mg/kg) concentrations, both of them being high. Although BS-03 was collected in the upper stream area before the Kiselica River flows in, where enrichment of heavy metals caused by the tailings dam and the battery factory is not expected, it shows similar values to the 2 samples (BS-01 and BS-02) collected in the lower stream area after the Kiselica River flows in. Further, among these three, As is highest in BS-03. The mining activities of the Zletovo Mine site are a possible reason for the high concentrations of Pb, Zn and As in BS-03.

The three samples of Kiselica River were, respectively, collected in areas near the mouth to the Zletovska River (BS04), down stream area from the new tailings dam (BS05) and upper stream area of the tailings dams (BS06). The three samples have high concentrations of As, Cu, Pb and Zn. Among these three, heavy metal concentrations are lowest in BS-05, which was collected in the down stream area from the new tailings dam. A possible reason for this is that the tailings materials spilled by the collapse of the Tailings Dam in 1976 have been mostly washed away in that area and current accumulation of tailing material from the tailing dam is not significant. BS04, on the other hand, has high concentrations of Pb, Zn, Mn, respectively, 1,500, 3,000 and 14,000mg/kg and some tailings materials of the incident may still remained in that site. Although BS-06 was collected in the upper stream area from the tailings dam and battery factory, the concentration of As, Cu and Pb are highest. The source of the high heavy metal concentrations in the river bottom sediments at this site is attributed to the old mining activities from ancient ages in the upper stream area of the Kiselica River in the north of Probistip.

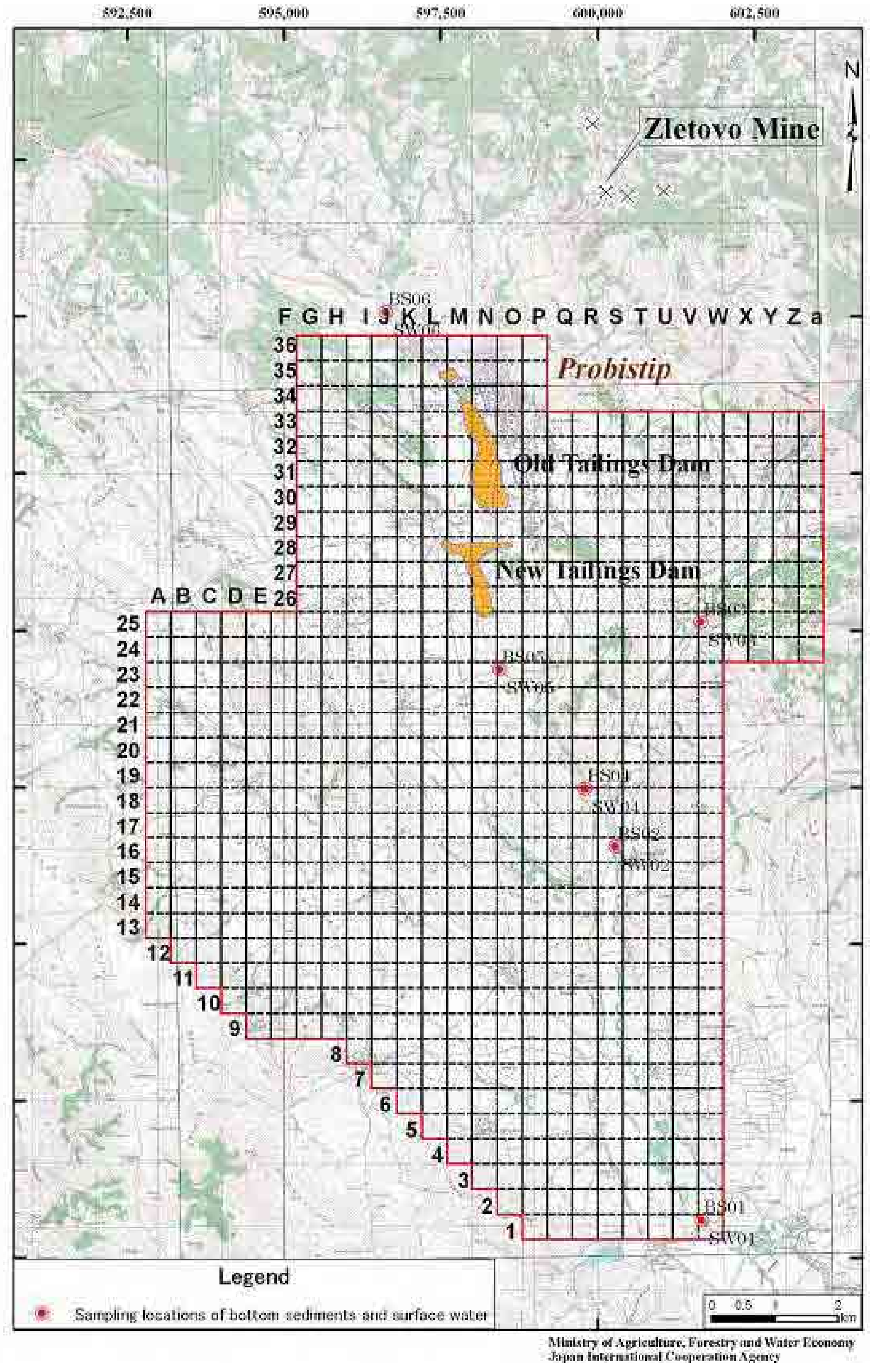


Figure 5.20 Sampling Locations of River Bottom Sediments and Surface Water

5.5 Surface Water Survey

Surface water samples were collected at the centre or at the fastest point of the flow in the river. A total of six samples, three samples in the Zletovska River and three samples in the Kiselica River, were collected at the same sampling sites of the river bottom sediments (Figure 5.20).

The analytical methods for surface water analysis is same as content analysis of soil samples, using ICP method based on ISO 11885 for As, Cd, Co, Total-Cr, Cu, Ni, Pb, Zn and Mn. For Hg, CVAAS (Cold-Vapour Atomic Absorption Spectrometric) method was used based on ISO 16772. The chemical analysis was conducted at the Faculty of Mining and Geology, St. Cyril and Methodius University.

The analytical results are shown in Data 4 together with the results of pH and EC (electric conductivity) measurements and the histograms of heavy metals concentration relative to the standard are shown in Figure 5.21. The standard values were taken from the Environmental Standard for Water of Macedonia Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004).

The analytical results of three water samples (SW-01, SW-02 and SW-03) from the Zletovska River give relatively low concentrations of heavy metals, showing values below the standard value except Mn. The concentrations of Mn are high, 0.20 and 0.13mg/L, for the two samples (SW-01 and SW-02) collected in the lower stream area after the Kiselica River flows in. For the sample collected in the upper stream of the Zletovska River, before the Kiselica River flows in, none of the heavy metal concentrations exceeds the standard value.

All of the three samples of the Kiselica River show much higher concentration of Zn and Mn, exceeding the standard values, compared to the samples of the Zletovska River. Mn concentration of SW-05, collected in the lower stream area from the tailings dam, shows the highest value, reaching to 9.21 mg/L.

For the samples collected in the lower stream area from the tailings dam, SW-04 and SW-05, only Zn and Mn concentrations exceed the standard value. Although the sample SW-06 was collected in the upper stream area from the tailings dams and the battery factory, concentration of Pb, in addition to Zn and Mn, exceeds the standard values and Cu, Pb and Zn are the highest among the six samples. Same as the river bottom sediments results, the source of the high Pb, Zn and Mn concentrations of the surface water at this site is attributed to the old mining activities from ancient ages in the upper stream area of the north of Probistip.

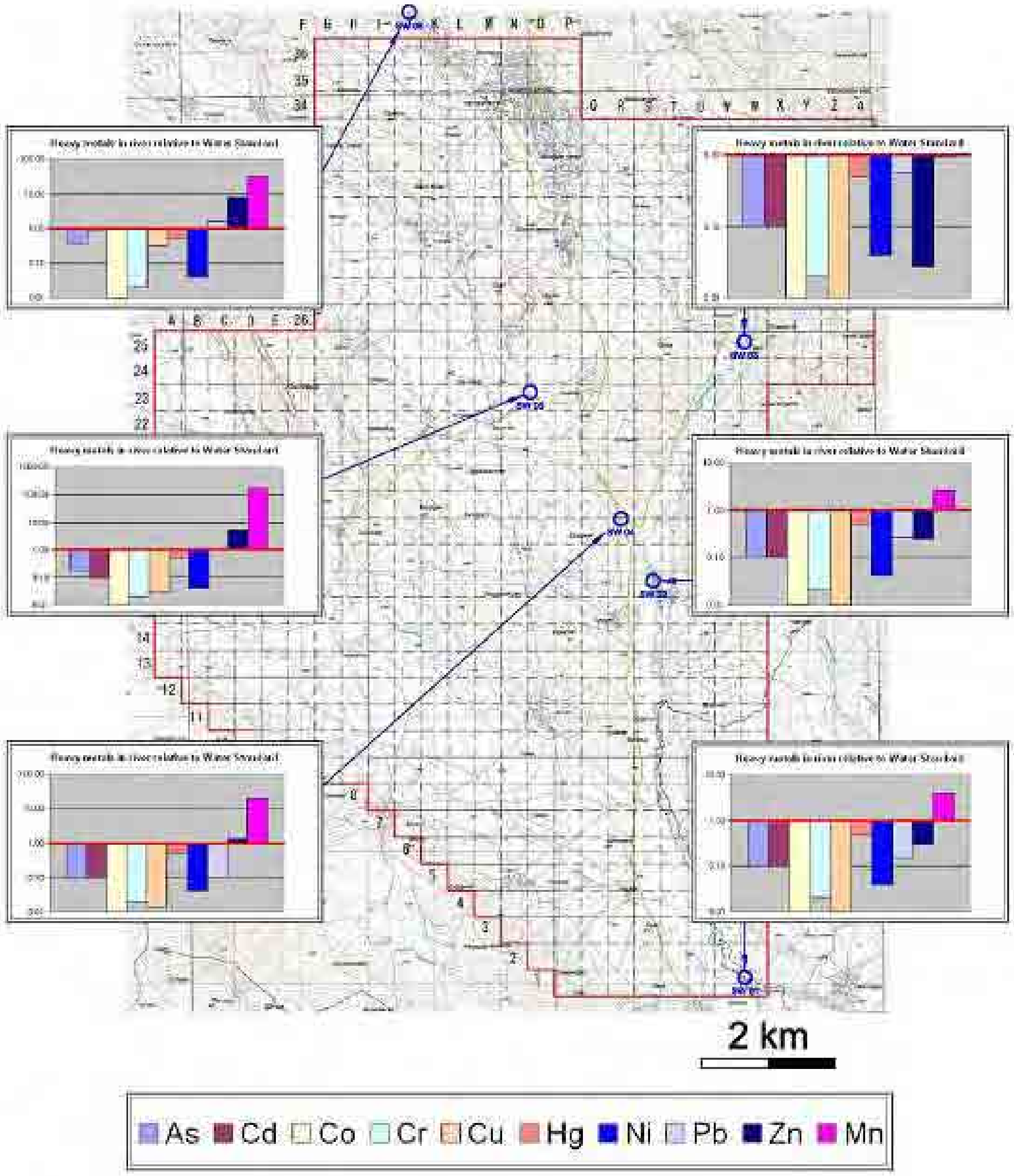


Figure 5.21 Heavy Metal Concentrations of Surface Water Relative to the Standard Value

The samples of the Kiselica River give consistently lower pH values and higher EC values compared to the samples of the Zletovska River.

In the Kiselica River, the water quality seems to be being affected by the mining activities, such as tailings and mining waste, resulted in enrichment of Cu, Pb, Zn and Mn in surface water. In the Zletovska River, on the other hand, only Mn exceeds standard value only for the samples collected in the lower stream area of the Zletovska River after the Kiselica River flows in. The affect of mining activities elevating the concentrations of heavy metal to surface water is clear only in the Kiselica River.

5.6 Groundwater Survey of the Monitoring Wells

The monitoring wells were drilled at the locations most suitable to study groundwater contamination caused by soil contamination. As shown in the location map (Figure 5.22), a total of 12 wells, six in the Zletovska River and six in the Kiselica River, were drilled. In the Zletovska River, a total of five wells, three on the river plain along the river and one each on both sides of the plains higher than the river plain were drilled in the lower stream area after the Kiselica River flows in. Another one well was drilled on the rive plain in the upper stream area before the Kiselica River flows in. In the Kiselica River, a total of five wells, three on the river plain along the river and one each on both sides of the plains higher than the river plain were drilled in the lower stream area from the tailings dam. Another one well was drilled on the river plain in the upper stream area from the tailings dam.

5.6.1 Description of Drilling Core

The schematic columnar diagrams of the monitoring well are shown in Figures 5.23 and 5.24. In the Zletovska River area, four wells drilled on the river plain (MBH-01, 02, 03 and 06) have soil (silt and clay) layer of 0.75 to 2.60m thick and they are underlain by sand layer and alluvial deposits. At the wells of MBH-02 and 03, the bedrock appears at relatively shallow depth of 2.60m and 4.30m, respectively. The two wells (MBH-04 and MBH-05) drilled on the plain higher than the river plain have soil layer of approximately 5m thick and it is underlain by alluvial deposits before reaching to the bedrocks. In the Kiselica River area, soil layer is thin with the maximum thickness of 3.20m at MBH-07, and beneath the soil layer, sand layer and alluvial deposits occur before reaching to the bedrocks. The depth of the bedrocks, consisting of tuff and mudstone, in the Kiselica River is shallow, from 1.00 to 4.55m.

At MBH-02, 03, 05 and 06 in the Zletovska River and MBH-08 and 12 in the Kiselica River, orange brown, sand to silt size, oxidized sediments with a similar appearance to the tailings materials occur. They are 25 to 70cm thick and they occur being intercalated in the brown soil or on the surface. Some tailings materials, still, remain on the river plain after 30 years from the collapse of the tailings dam.

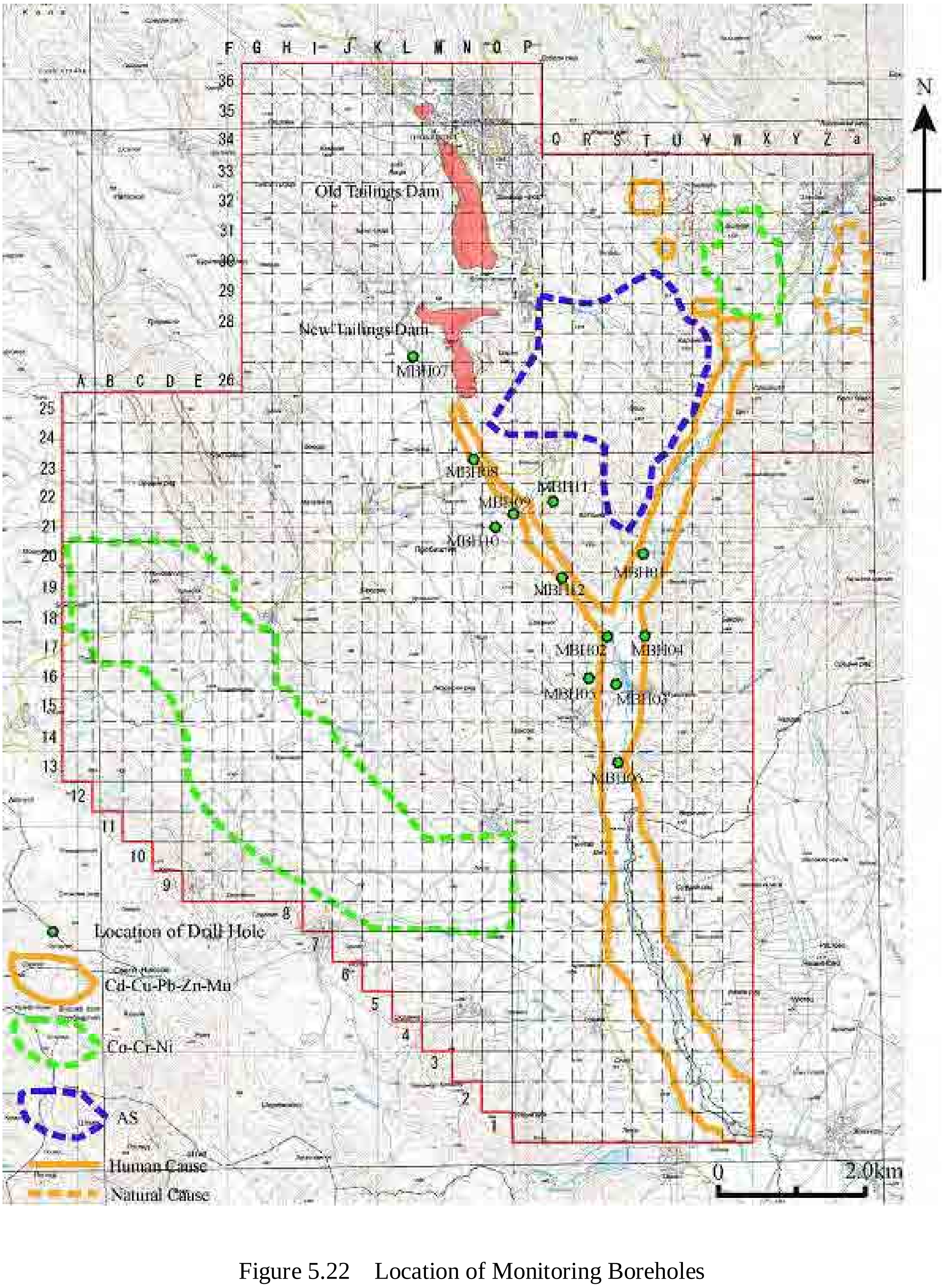


Figure 5.22 Location of Monitoring Boreholes

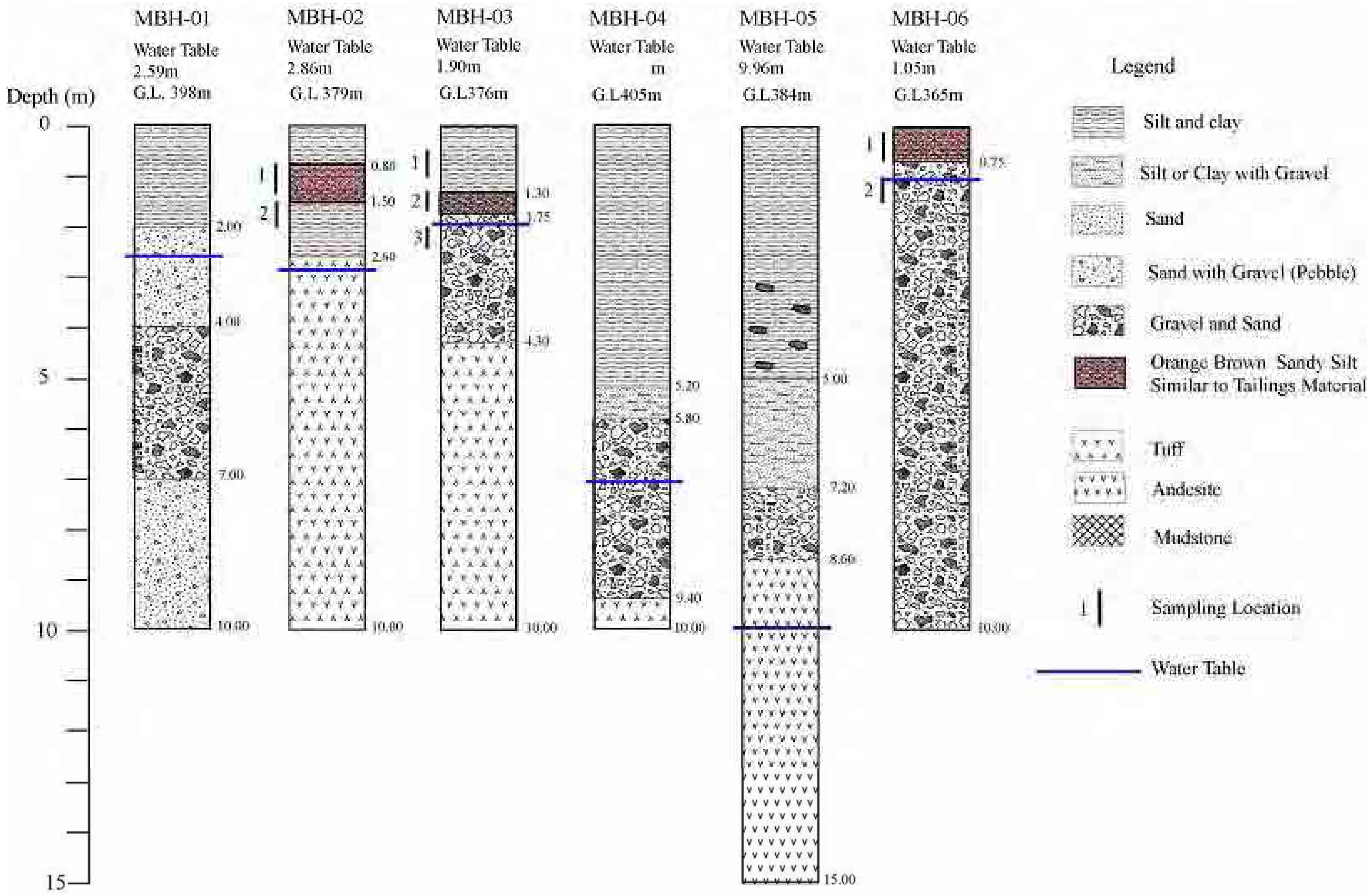


Figure 5.23 Schematic Columnar Diagrams of Monitoring Boreholes (1)

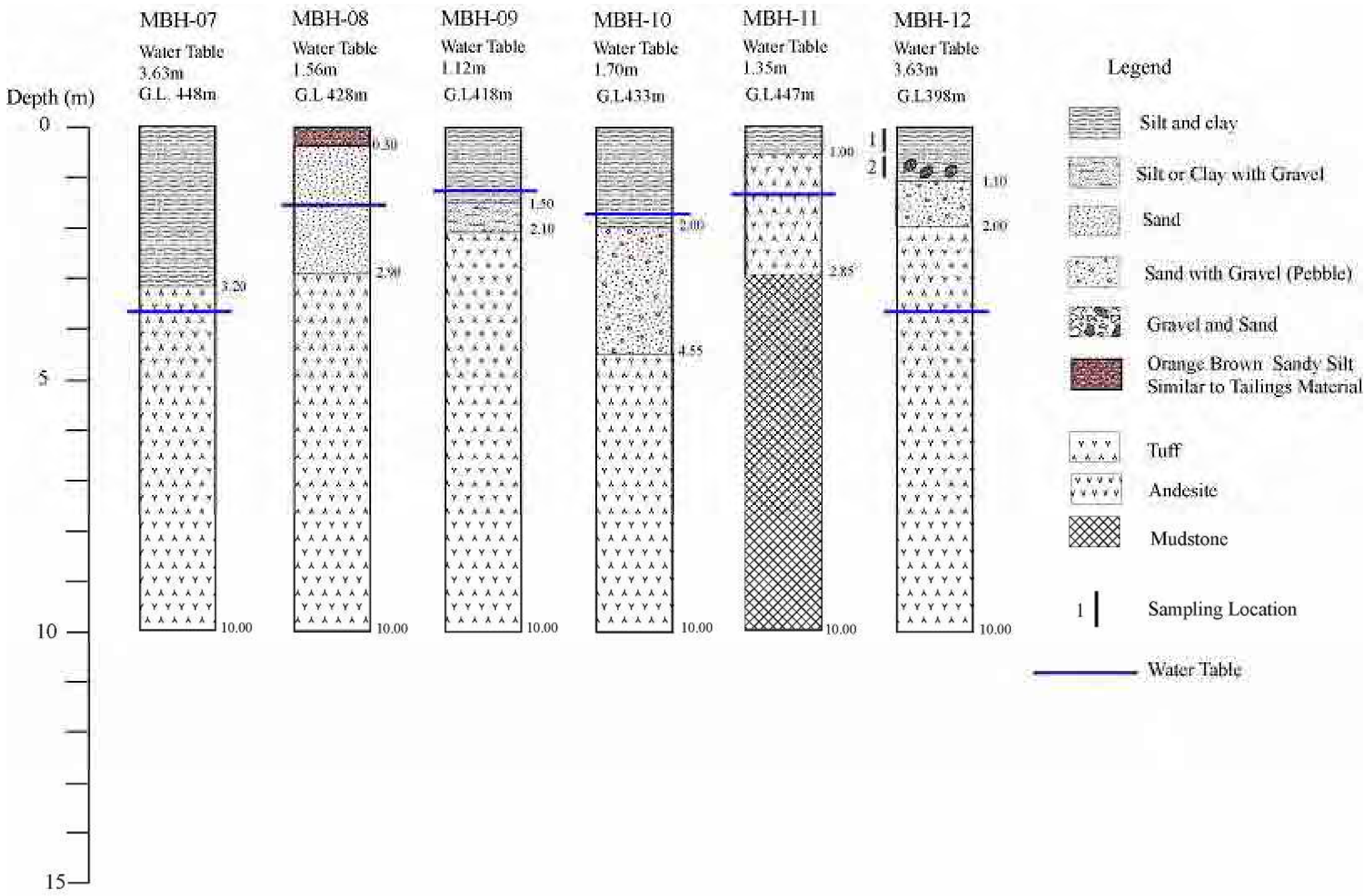


Figure 5.24 Schematic Columnar Diagrams of Monitoring Boreholes (2)

5.6.2 Chemical Analysis of the Core Samples

The orange brown sediments similar to the tailings material were collected together with brown soil occurring close to the orange brown sediments. The content and elution analyses of the nine samples were conducted and the results were given in Data 4. The analytical methods of content and elution analysis are same as the surface soil survey. The chemical analysis was conducted at the Faculty of Mining and Geology, St. Cyril and Methodius University.

The sediments similar to the tailings material have high content concentrations of As, Cu, Pb, Zn and Mn. Among these heavy metals, Pb and Zn are very high, most of them show greater than 1,000mg/kg. As shown in the previous section, the chemical compositions of orange brown sediments are very similar to the chemical composition of tailings material collected by the drillings on the tailings dam. This suggests that a part of the tailings spilled over by the collapse of the tailings dam still remains on the river plain. The sediments being distributed below and above the orange brown sediments are also high in As, Cu, Pb, Zn and Mn.

For assessing the results of the elution analysis, the values of theWaste Quality Standard of Macedonia Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn and Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004) were used as reference values.

The results of elution analysis, also, show high concentrations of Pb, Zn and Mn, respectively, reaching to 0.44, 11 and 69mg/L at maximum., and most of them show the concentration 10 to 100 times more than the reference value. In addition to them, Cd and Hg tend to be high, most of them exceeding the reference value. The heavy metals such as As, Co, Cr, Cu and Ni are low, far less than the reference value. The orange brown soil similar to the tailing materials obtained from the monitoring borehole show chemical characteristics similar to the tailing material obtained from the drilling on the tailings dam.

pH values are consistently less in the orange brown soil similar to the tailings material compared with the soil of immediate above and below, ranging from 5.79 to 7.22.

5.6.3 Monitoring of Boreholes

(1) Meteorology

Before the discussion of the groundwater, meteorological aspects of the P/P area, particularly the ones related to groundwater, are briefly given below.

The monthly precipitation at Zletovo Village in the upper stream area of the Zletovska River is shown on Table 5.20. There are variations of annual precipitations during the years from 1990 to 2003, ranging from 273.9 to 743.7mm at the average of 563.7mm. The variations of monthly precipitations are not so large and the precipitations of each month of the 12 years average change from 25.8 to 72.8mm. There are some variations in each year, however, precipitations of April, May, October, November and December are higher than other month. The lowest months of precipitations are February and March, and during the summer time of June to September the precipitations are lower than other months.

Table 5.20 Monthly Precipitations at Zletovo

Monthly Precipitation at Zletovo Precipitation Unit: mm

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
1990	0.1	17.5	7.6	83.6	30.6	25.9	23.9	23.7	6.3	30.8	15.9	162.4	428.3
1991	18.1	65.6	33.5	108.3	108.0	26.8	36.2	68.8	22.1	75.8	88.0	13.7	664.9
1992	0.1	1.4	24.3	92.3	23.8	65.0	23.7	0.0	35.3	35.7	65.5	37.0	404.1
1993	12.1	32.3	62.3	12.9	38.6	2.3	9.0	4.5	28.5	33.2	77.9	66.6	367.3
1994	46.1	15.3	5.9	129.9	32.2	37.8	76.3	22.5	19.0	25.3	17.6	75.6	503.5
1995	71.5	15.8	72.8	31.9	71.3	50.0	129.0	114.9	73.4	1.0	37.0	0.0	668.6
1997	-	-	-	-	-	-	-	-	-	137.2	46.6	90.5	-
1998	39.7	55.8	12.5	33.2	94.0	26.8	47.2	52.2	64.8	113.7	80.6	56.1	676.6
1999	31.7	27.1	36.8	69.9	48.3	87.4	62.4	6.9	37.0	59.6	70.5	61.9	599.5
2000	19.5	36.9	44.0	27.5	38.5	18.9	11.3	11.0	15.9	18.4	23.7	8.3	273.9
2001	62.3	15.4	7.7	142.7	47.8	26.0	9.1	34.4	25.4	4.5	35.2	75.9	486.4
2002	33.6	4.6	63.3	60.7	69.5	39.4	60.7	66.4	122.9	97.2	26.1	99.3	743.7
2003	110.8	22.0	0.5	31.3	84.3	51.1	34.9	54.9	6.5	134.1	17.7	53.9	602.0
Ave.	37.1	25.8	30.9	73.8	57.2	38.1	43.6	38.4	38.1	59.0	46.3	61.6	563.7

The water level reaches higher in the Zletovska River during springtime from April because of abundant precipitation together with snow melting in the upper stream area. The water level becomes lower during August, September and October.

(2) Heavy Metal Concentrations in Groundwater

The groundwater of the monitoring borehole was collected once in a month starting from August 2006 to January 2007. At the collection of water, measurements of water head depth, pH and EC (Electric Conductivity) were carried out. The analytical results of six months together with pH and EC are given in Data 4. Tables 5.21 shows average values of 6 months of heavy metal concentrations, pH and EC values for each monitoring borehole. The standard values were taken from the Water Quality Standard of Macedonia, Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn and Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004).

The analytical methods for groundwater analysis is same as content analysis of soil samples, using ICP method based on ISO 11885 for As, Cd, Co, Total-Cr, Cu, Ni, Pb, Zn and Mn. For Hg, CVAAS (Cold-Vapour Atomic Absorption Spectrometric) method was used based on ISO 16772.

The chemical analysis was conducted at the Faculty of Mining and Geology, St. Cyril and Methodius University.

Table 5.21 Average Value of the Heavy Metal Concentrations in Groundwater

	River		As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn	pH	EC
			mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l		mS/m
MBH01	Zletovska	Average	0.003	0.0031	0.035	0.002	0.121	0.00005	0.012	0.13	0.31	1.5	6.91	33
		Relative to STD	0.10	0.31	0.35	0.032	0.60	0.25	0.24	13	3.1	30		
MBH02	Zletovska	Average	0.002	0.0029	0.031	0.009	0.108	0.00005	0.012	0.34	0.34	3.0	7.30	89
		Relative to STD	0.08	0.29	0.31	0.187	0.54	0.25	0.24	34	3.4	60		
MBH03	Zletovska	Average	0.004	0.1181	0.077	0.030	0.213	0.00007	0.043	0.51	17	65	6.43	95
		Relative to STD	0.15	12	0.77	0.598	1.07	0.35	0.86	51	167	1297		
MBH04	Zletovska	Average	0.002	0.0006	0.021	0.002	0.042	0.00007	0.056	0.013	0.10	6.4	7.32	49
		Relative to STD	0.06	0.06	0.21	0.047	0.21	0.33	1.11	1.3	0.98	129		
MBH05	Zletovska	Average	0.002	0.0010	0.005	0.001	0.086	0.00005	0.003	0.15	0.20	0.24	7.61	44
		Relative to STD	0.05	0.10	0.05	0.017	0.43	0.25	0.06	15	2.0	4.7		
MBH06	Zletovska	Average	0.002	0.0015	0.011	0.002	0.107	0.00005	0.004	0.087	0.48	0.54	6.39	78
		Relative to STD	0.05	0.15	0.11	0.049	0.53	0.25	0.07	8.7	4.8	11		
MBH07	Kiselica	Average	0.002	0.0010	0.023	0.009	0.133	0.00007	0.049	0.077	0.35	15	7.12	255
		Relative to STD	0.06	0.10	0.23	0.175	0.66	0.37	0.99	7.7	3.5	306		
MBH08	Kiselica	Average	0.007	0.0029	0.009	0.003	0.184	0.00005	0.007	0.13	0.22	2.0	7.34	107
		Relative to STD	0.24	0.29	0.09	0.052	0.92	0.25	0.14	13	2.2	41		
MBH09	Kiselica	Average	0.002	0.0018	0.015	0.007	0.107	0.00007	0.019	0.21	0.18	7.4	7.18	117
		Relative to STD	0.08	0.18	0.15	0.145	0.54	0.33	0.38	21	1.8	148		
MBH10	Kiselica	Average	0.005	0.0007	0.008	0.002	0.107	0.00005	0.017	0.11	0.14	2.8	7.29	92
		Relative to STD	0.17	0.07	0.08	0.045	0.53	0.25	0.35	11	1.4	57		
MBH11	Kiselica	Average	0.014	0.0005	0.006	0.001	0.036	0.00005	0.007	0.014	0.086	0.42	7.32	86
		Relative to STD	0.48	0.05	0.06	0.024	0.18	0.25	0.15	1.4	0.86	8.4		
MBH12	Kiselica	Average	0.006	0.0005	0.007	0.001	0.083	0.00005	0.007	0.18	0.14	0.70	7.44	74
		Relative to STD	0.18	0.05	0.07	0.026	0.42	0.25	0.15	18	1.4	14		
STD (Standard Value)			0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05		

Standard Value: Taken from the Water Quality Standard of Macedonia (As, Cd, Co, Cr, Hg, Ni, Pb, Zn, Mn) and guideline value of WHO (Cu)
Average: Avalage value of six months
: Exceeding the Standard Value
Relative to STD=Average Value devided by the Standard Value

The variation of groundwater level together with monthly precipitations, pH and EC values for six months are shown in Appendix 9. Although there are some tendencies of slightly continuous increasing and decreasing of the water levels depending on the boreholes, but the groundwater levels for each wells generally do not show significant changes through six months.

There are general tendency of pH values of the groundwater continuously decrease from August 2006 to December 2006 and slightly increase in January 2007. The pH value are low at boreholes MBH01, MBH03 and MBH06 of the Zletovska River, showing average values of, respectively, 6.91, 6.43 and 6.39. The average pH values of other boreholes are similar showing values ranging from 7.12 to 7.61.

EC values tend to increase slightly from August 2006 to January 2007. The EC value is high in the Kiselica River showing average value of more than 100mS/m at the boreholes MBH07, 08 09. Among them, the borehole MBH07, located in upper stream of the New Tailings Dam has the highest average values of 255mS/m. In the Zletovska River, EC value is relatively high at boreholes MBH02 and 03, located immediate down stream from the junction of Kiselica River, having EC average values of 89 and 95 mS/m, respectively. The two boreholes of the both sides of the Zletovska Rivers, MBH04 and 05, show relatively low average EC values of, respectively, 49 and 44mS/m. MBH01, located in upper stream area from the junction of the Kiselica River, has the lowest EC of 33mS/m. From these, the groundwater of the Kiselica River has higher EC values and the water with higher EC is diluted, showing lower EC values after it flows in to the Zletovska River Area.

The heavy metal concentrations of each borehole are shown on monthly basis in Appendix 9 and characteristic feature of the heavy metal concentrations are given below.

a. Arsenic (As): As concentrations are generally low, showing mostly concentrations lower than detection limit of 0.003mg/L. Among them, only August sample of MBH08 and January samples of MBH11 exceed the Standard Value of 0.03mg/L. The borehole MBH11, located immediate southeast of the As high concentration area of soil content survey, has the highest As average concentration of 0.014mg/L.

b. Cadmium (Cd): Cd concentrations are generally low, showing mostly concentrations of less than the Standard Value of 0.01mg/L except the groundwater of MBH03 in the Zletovska River, slightly below the junction of the Zletovska and Kiselica River, where tailings materials of spillage incident remain. The concentrations of Cd at MBH03 range from 0.055 to 0.20mg/L at the average of 0.12mg/L, always exceed the Standard Value of 0.01mg/L.

c. Cobalt (Co): The concentrations of Co are always low, far less than the Standard Value of 0.1mg/L. except January samples. At the all locations, Co concentrations become higher in January compared with other months, ranging from 0.021 to 0.40mg/L and the concentrations of three holes of MBH01, 02 and 03, located along the Zletovska River exceed the Standard Value of 0.1mg/L. The enrichment of Co to the groundwater of January samples may be attributed to the mining activities recently started in the Zletovo Mine.

d. Chromium （Cr）: Cr concentrations are generally low, far less than the Standard Value of 0.05mg/L, except September and October samples of MBH03, which show Cr concentrations of 0.52mg/L, slightly higher than the Standard Value.

e. Copper (Cu): Cu concentrations of the groundwater range from <0.002 to 0.46mg/L and the concentrations slightly higher than the Standard Value were obtained at MBH03, 08, 09 and 10. For the values of six months average, only MBH03 with 0.21mg/L exceeds the Standard Value.

f. Mercury (Hg): The concentrations of Hg in groundwater are low, most of them showing concentration of less than detection limit of 0.0001mg/L and none of the sample exceeds the Standard Value.

g. Nickel (Ni): Ni concentrations of the groundwater range from <0.002 to 0.12mg/L and only four samples collected from the MBH03, 04 and 07 exceed the Standard Value of 0.05mg/L. The September and October samples of MBH04, located at the foot of hill on east side of the Zletovska River show the highest value of 0.12mg/L, and six months average value of MBH04 exceeds the Standard Value.

h. Lead (Pb): The Pb concentrations are high ranging from <0.001 to 1.31mg/L, many samples exceeding the Standard Value of 0.01mg/L. There is a weak tendency of Pb enrichment during September to October 2006 and in January 2007, and the lowest in November with a half of samples showing concentrations less than the Standard Value. All the boreholes show the six months average concentrations more than the Standard Value. Among them MBH02 and 03 located in the Zletovska River, below the junction of the Kiselica River, show the highest six month average value of 0.34 and 0.51mg/L.

i. Zinc (Zn): The Zn concentrations are high ranging from 0.01 to 22mg/L with most of the samples exceed the Standard Value of 0.1mg/L. The concentrations of Zn differ significantly depending on month and tend to be high in August 2006 and January 2007, while in November they are low with more than a half of the samples show concentrations less than the Standard Value. Similar to Pb and Mn, the six months average value exceeds the Standard Value for all the boreholes with exception of MBH04 and MBH11. Among them Zn concentrations at the MBH03 is exceptionally high all through six months, ranging from 13 to 22mg/L at the average of 17mg/L. Other than BMS03, all the samples except August sample of MBH06 show Zn concentrations less than 1mg/L. Other than MBH04 and MBH11, the six months average Zn concentrations are not so much different, ranging from 0.14 to 0.48mg/L. Relatively high values of Zn, reaching more than 0.5mg/l, are obtained from August 2006 and January 2007 samples of MBH01, 02 and 06.

j. Manganese (Mn): Mn concentrations of the monitoring borehole are very high, ranging from 0.031 to 68mg/L. With the exception of two samples, November samples at MBH05 and MBH11, all the samples exceed the Standard Value. There are some tendencies of monthly changes. The Mn concentrations tend to be high in August 2006 and January 2007, and the lowest in November 2006. The BMH03 show exceptionally high Mn concentration all through the months, ranging from 53 to 68mg/L at the average of 65mg/L. The six month averages of all the boreholes show Mn concentrations greater than the Standard Value of 0.05mg/L. Other than MBH03, MBH01, 02, 04 07, 09 and 10 show high Mn concentrations with the six months average value of greater than 1mg/L.

k. Summary: Compared with the Standard Values (The Water Quality Standard of Macedonia Class 1), Pb, Zn and Mn show significantly high concentrations in the groundwater, and the six months average values of these elements exceed the Standard Values at most of the 12 monitoring wells. Among these 12 monitoring wells, MBH03, located in the Zletovska River area, slightly down stream from the junction of the Kiselica River, has the highest Pb, Zn and Mn concentrations. The high concentrations of these elements at MBH03 are attributed to the secondary accumulation of the tailings materials in the location.

(3) Influence of Meteorological Aspects to Groundwater

As mentioned previously, the precipitation is higher in April, May, October, November and December, and lower in June to September. Although there are some exceptions but this is reflected in groundwater level. The groundwater level tends to be slightly lower from August to October, and at the some of the monitoring wells water level slightly increase from November to January responding to increases of precipitation from October. It seems that changing of the groundwater level responding to the precipitation occur approximately one to two months later..

Some of the heavy metals such as Cr, Cu, Hg, Ni, Pb and Zn show high concentration in September and October. This may be attributed to low precipitation during June to September in the P/P area. High concentrations of As, Ni and Zn in August and Co, Cr, Pb and Zn in January cannot simply be correlated to meteorological aspects, and human activities such as mining may responsible for these.

(4) Hydrology and Concentrations of Heavy Metals in Groundwater

The cross sections of groundwater profiles and contour maps with Pb, Zn and Mn concentrations in groundwater are shown in Appendix 10 and Figures 5.25 to 5.27, respectively.

The groundwater observed at all the sites are free groundwater and confined groundwater was not observed. As mentioned previously, the water table does not change significantly through 6 months of monitoring, showing the changes of 20 to 50cm from August 2006 to January 2007. In the Zletovska River, the water table exists at 1.00 to 3.00m below the surface for the monitoring holes drilled on the river plain. At the monitoring holes drilled on the both sides of river, MBH04 and MBH05, water table is deeper, respectively, 7.12m and 9.72m. At two monitoring holes drilled near the Zletovska River, the elevation of the water table is similar to surface water level. At the most of the holes water tables exists within permeable layers of alluvial deposits. At MBH05 drilled on the west side of river, water table occurs in the bedrock consisting of andesite.

In the Kiselica River, MBH07 drilled at the most upper stream site and MBH12 drilled at the most lower stream site have water table at 3.50m deep from the surface. At other four monitoring holes, the water table is shallower, 0.98 to 1.71m deep from the surface. At MBH08, the water table exists in the permeable sand layer, while at MBH09 and MBH10, drilled close to the river, the water table is observed in silt and sand layers because of the water table being raised to the same level of the surface water. At three monitoring wells of MBH07, MBH11 and MBH12, the water table is observed in the bedrock of tuff.

Along the Zletovska River, the water table becomes lower from 396m at the MBH01 to 367m at MBH06 in accordance with the topographic feature. At the MBH05 and MBH04, the water table is, respectively, 10m and 15m higher than at MBH03 drilled near the river and a flow of the groundwater toward the river from both sides of the hill is expected.

Along the Kiselica River, the water table becomes lower downward from 452m at MBH07 to 398m at MBH12 in accordance with topographic feature. The levels of the groundwater table at NBH10 drilled on west side of the river and at MBH11 drilled on the east side of the river are, respectively, 17m and 31m higher than the level of the groundwater at MBH09 drilled near the river.

Pb, Zn and Mn show significantly high concentrations in the groundwater of the Zletovska and Kiselica Rivers areas. The distributions of these heavy metals in groundwater are summarized below.

a. Lead (Pb): Pb concentrations along the Zletovska River increase toward downstream. It becomes the highest at MBH03, particularly after the Kiselica River flows in, then it becomes lower at the most down stream site of MBH06. On the E-W cross section, the Pb concentration of MBH05 located on the west side is higher compared with MBH04 of the east side with Pb concentrations close to the Standard Value. Along the Kiselica River, MBH07 located in the most upper stream area shows the lowest Pb concentrations and it abruptly increases concentrations at MBH08 and 09, then it becomes slightly lower at MBH12. This is attributed to a possible inflow of the groundwater with high Pb from a small river flowing from the New Tailings Dam. On the E-W section、MBH10 on the west side show a relatively high Pb concentration, while Pb concentration of MBH11, located on the east side, is low.

b. Zinc (Zn): Along the Zletovska River, Zn concentrations are exceptionally high at MBH03, and other holes located in the upper and the lower stream areas from this show Zn concentrations higher than the Standard Value. The reason for high concentration of Zn at MBH03 is attributed to the accumulation of tailings materials in that location. On the E-W sections, the boreholes of MBH04 and MBH05, drilled on the east and west sides of the river, show lower values of close to the Standard Value. No clear variation of the Zn concentrations of the groundwater was observed along the Kiselica River. All of the boreholes show Zn concentrations of few times higher than the Standard Value, except MBH11, which has Zn concentration less than the Standard Value.

c. Manganese (Mn): On the Zletovska River profile, the Mn concentrations of the groundwater increase toward lower stream and reach to exceptionally high value of 65ml/L at MBH03, then abruptly decrease at MBH06. The high Mn concentration at MBH03 is attributed to the accumulation of the tailings materials in the area. On E-W section, MBH04 located on the east side of the river shows very high Mn concentration compared with MBH05 on the west side of the river. Along the Kiselica River profile, Mn concentration of the groundwater is the highest at MBH07 of the upper stream. It decreases toward lower stream to MBH08, but it becomes higher at MBH09, then, again becomes lower at MBH12. On the E-W profile, Mn concentration of the groundwater is higher at MBH10 located on the west side of the river and lower at MBH-11 on the east side of the river.

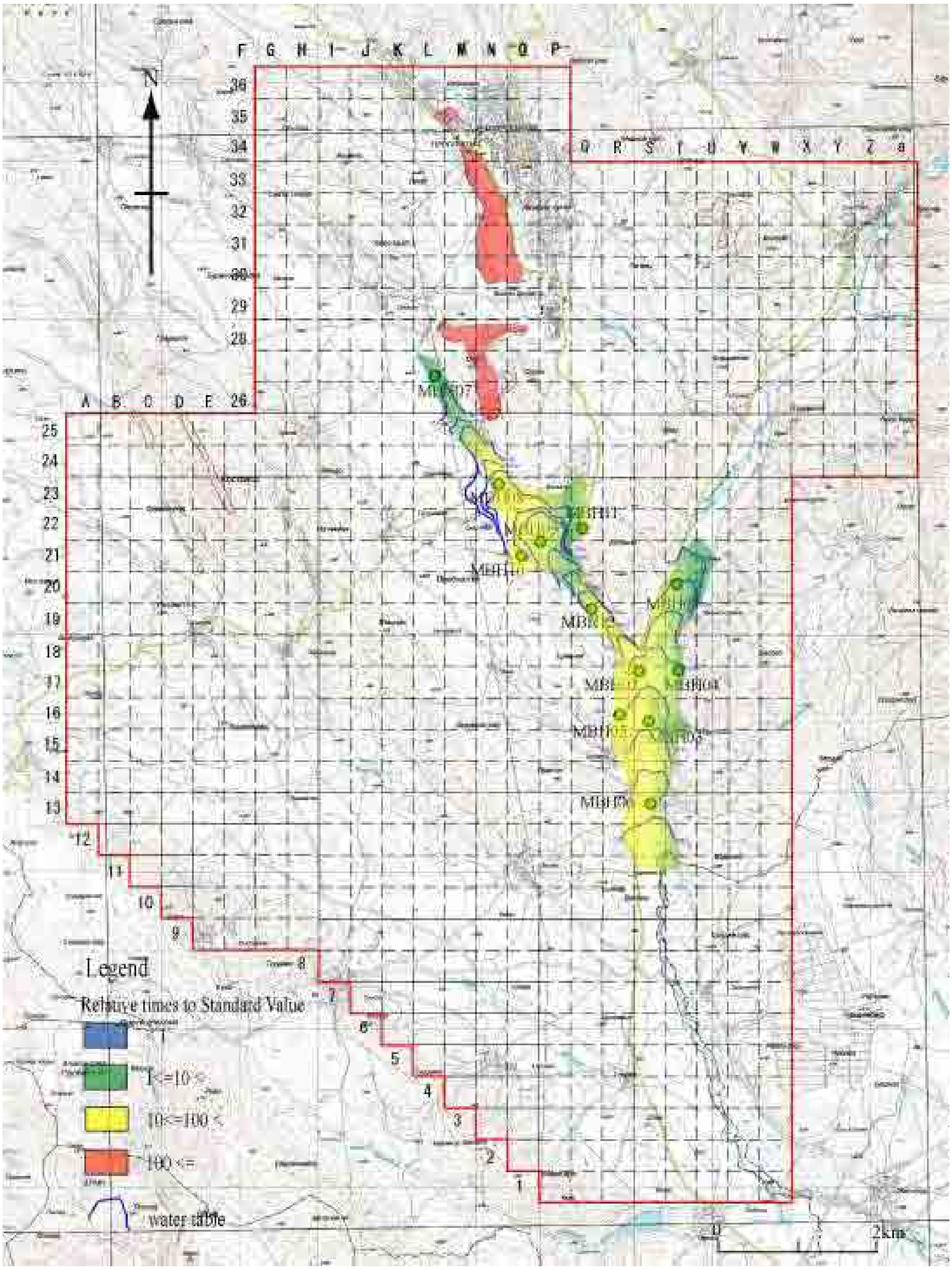


Figure 5.25 Distribution of Lead (Pb) Concentrations in Groundwater

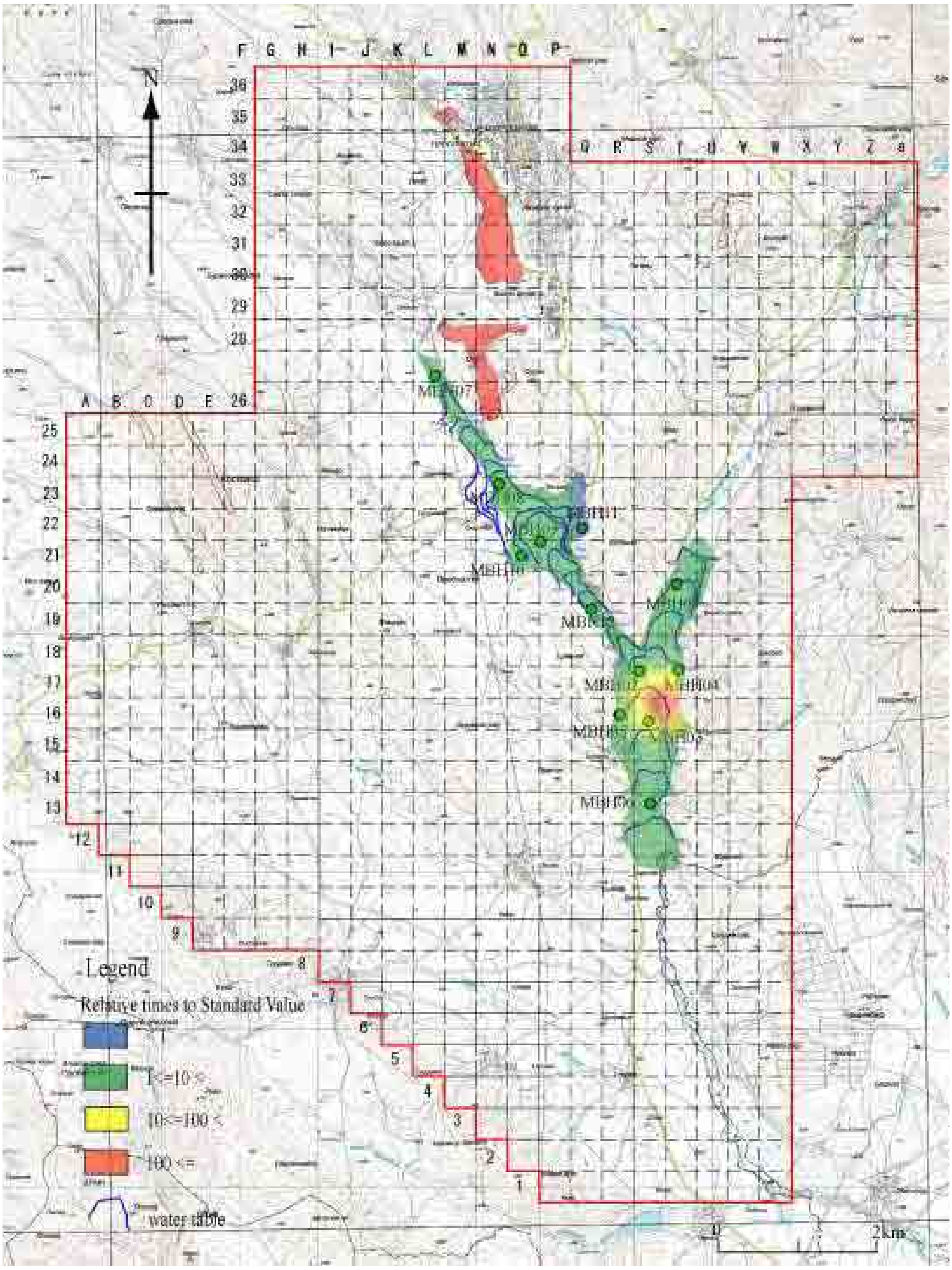


Figure 5.26 Distribution of Zinc (Zn) Concentrations in Groundwater

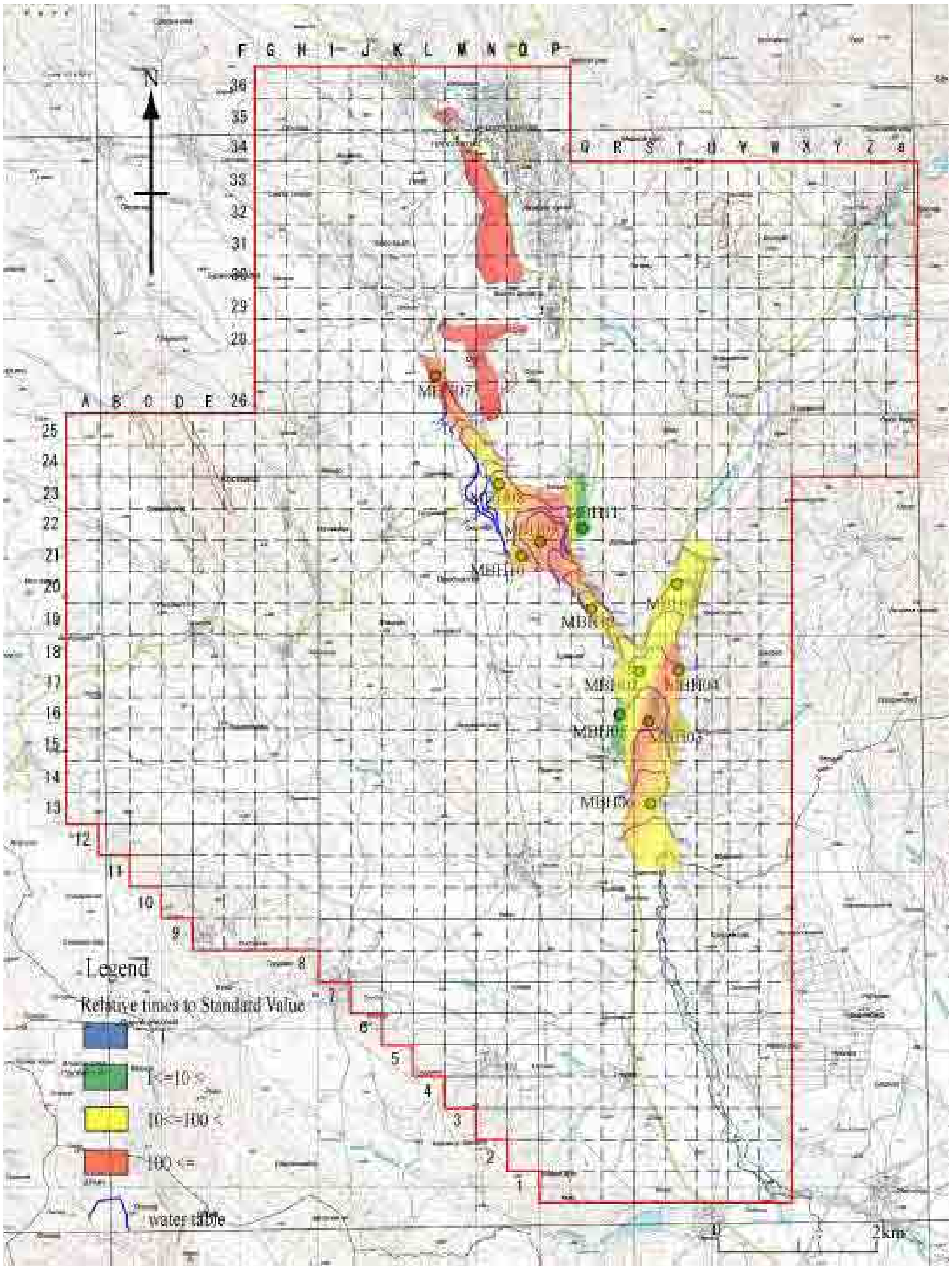


Figure 5.27 Distribution Manganese (Mn) Concentrations in Groundwater

5.7 Additional Groundwater and Surface Water Survey

5.7.1 General

The groundwater monitoring of the wells conducted during the Phase 2 survey for the 12 monitoring wells along the Kiselica and Zletovska Rivers showed that the groundwater of the wells had high concentrations of heavy metals, such as Pb, Zn and Mn, exceeding the Standard Value. For further understanding of the heavy metal concentrations of groundwater and surface water in the area of the P/P, including the groundwater of wells and springs used by local residents, additional survey of the groundwater and surface water covering the whole area of the P/P was conducted in the Phase 3 Survey.

Sampling of 126 water samples, consisting of 95 well/spring water samples collected from 29 villages/communities and 31 surface water samples, was conducted in the P/P area during June 2007. For well and spring samples, two to four samples were collected at the each village/community and information concerning well/spring, including use of water, was collected from local residents as much as possible. pH, electric conductivity (EC) and water temperature were measured simultaneously with sampling at each site. All water samples were analyzed for 10 components of heavy metals, namely As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn and Mn.

5.7.2 Analytical Method

Ten elements were analyzed for 126 water samples by Atomic Absorption Spectroscopy (AAS). Depending on the concentrations of the element, either graphite furnace or flame technique was employed. For determination of Pb, Cd, Ni, Zn, Co, Cr, Cu and Mn in groundwater, graphite furnace method was used. After filtration, the sample was injected in the graphite tube using auto-sampler. The calibration curve was obtained by standard solutions with similar concentrations with the samples. For As determination, Pd was employed as matrix modifier for stabilization. Hg was analyzed using Cold Vapor Atomic Absorption Spectroscopy (CVAAS). For the river samples with higher concentrations of Mn and Ni, the chemical analysis was conducted using flame technique. After filtration, the samples are simply sprayed into the flame and the measurements obtained were calibrated using the water standard solution. The chemical analysis was conducted at the Institute of Agriculture, St. Cyril and Methodius University.

5.7.3 Results

(1) General Information of Water

The sample locations and sample list including the results of pH, EC (Electric Conductivity) and water temperature measurements are shown in Figure 5.28 and Appendix 11, respectively.

According to the information of the local residents, among the wells and springs from which water samples were collected, more than half of them (52 sites out of 96 sites) seem to be currently used for daily life of the local residents and the rest of them are only used for livestock and irrigation (Figure 5.29).

The pH of the well and spring samples shows a relatively narrow range from 6.69 to 7.76 and the similar values were obtained from the wells and springs located in the same village. EC values, on the other hand, show a wide range from 45.6 to 381.7mS/m, and their values are not consistent among each of the well and spring within a village. pH-EC relations are shown in Figure 5.30. High EC values of more than 250mS/s were obtained from the villages of Strmos, Drenok, D. Stubol, Garjanci and Jiganci, while lower EC values of less than 50mS/m were obtained mainly from the villages located in the north part of the P/P area, such as G. Stubol, Kundino, Marcino, Dobrvo and Lesnovo.

A wide range of pH values, from 3.38 to 8.46, was obtained from the river samples. The low pH water of less than 6.00 were found in the north of Probistip, north west of Strmos and near Zarapinci. The EC values of river water, ranging from 11.5 to 182.3mS/m, were generally lower than those of well and spring water. pH and EC measurements were conducted at the temperature of 12.1 to 18.5 degree for well and spring water and 13.7 to 28.4 degree for river water.

(2) Chemical Analysis

The results of chemical analysis of groundwater and surface water are given on Data 4. The values used for assessing the water quality were listed on Table 5.22 together with average, maximum and minimum values of the analytical results. For assessing environmental quality of water, the standard values were taken from the Water Quality Standard of Macedonia Class 1 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn and Mn: Official Gazette of the Republic of Macedonia, No.18-99) and guideline value of WHO (Cu: WHO, 2004). In addition to it, for assessing well/spring water in villages, standard values were taken from the Standard of Drinking Water of Macedonia (Official Gazette of the Republic of Macedonia, 57/04).

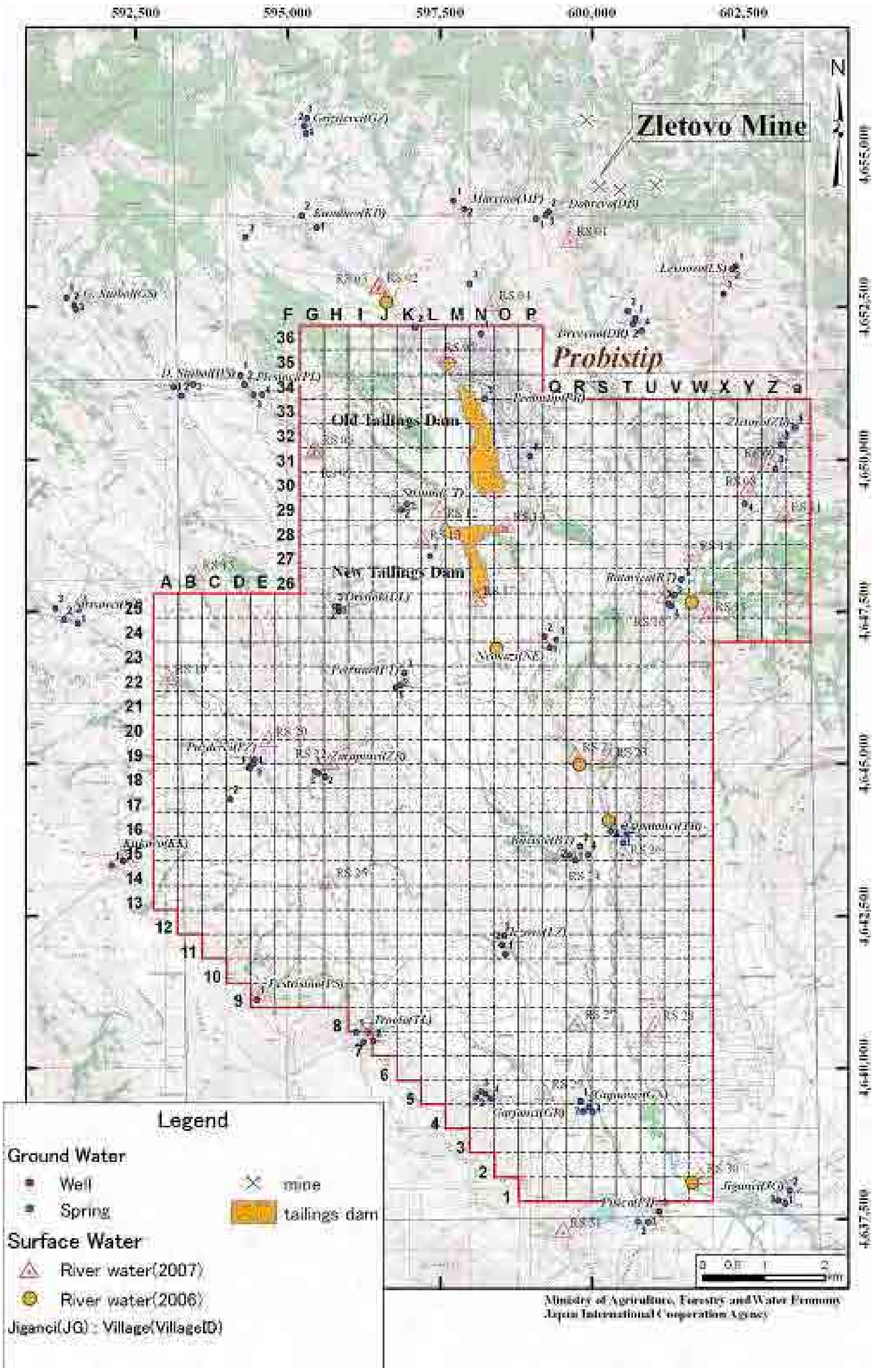
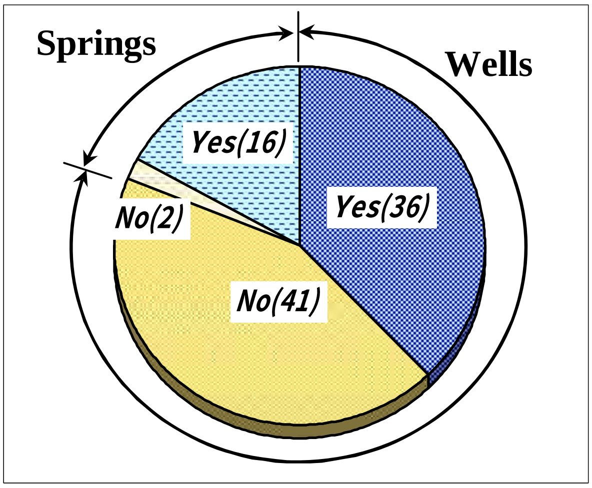


Figure 5.28 Sample Location of Groundwater and Surface Water (Additional Survey)



Yes: Used for Drinking
No: Not used for Drinking

Figure 5.29 Water-use in the P/P Area

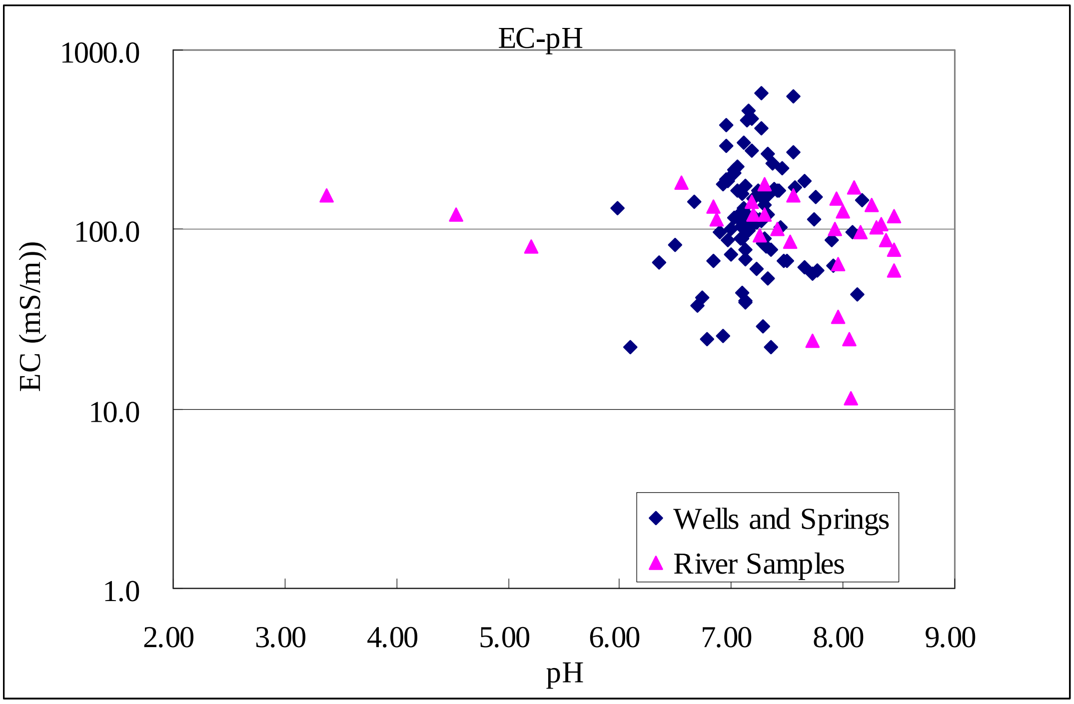


Figure 5.30 pH-EC Relations of Groundwater and River Water (Additional Survey)

Table 5.22 Reference Values of Water for the Pilot Project

(Well and spring water: 95 samples from 29 villages, surface water samples: 31 samples)

		As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Well and Spring	Maximum	0.015	0.0013	0.40	0.034	0.028	0.00018	0.068	0.028	0.29	0.019
	Minimum	0.008	0.0001	0.028	<0.005	0.006	<0.0001	0.017	0.006	<0.01	0.004
	Average	0.011	0.0003	0.067	0.010	0.010	-	0.035	0.015	0.015	0.009
	NSE W.Q.*	0	0	6	0	0	0	4	77	3	0
	NSE D.W.**	63	0	57	0	0	0	95	77	0	0
	NVE D.W.***	22	0	17	0	0	0	29	26	0	0
Surface Water	Maximum	0.039	0.0017	1.06	0.022	0.18	<0.0001	0.79	0.058	5.8	33
	Minimum	0.008	0.00004	0.008	<0.005	0.005	<0.0001	0.44	0.007	<0.01	0.006
	Average	0.013	0.0004	0.11	0.010	0.019	-	0.58	0.016	0.44	4.0
	NSE W.Q.*	1	0	9	0	0	0	31	24	6	21
W. Q.****		0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05
D. W. *****		0.01	0.003	0.05	0.05	2	0.001	0.02	0.01	3	0.05

NSE W.Q.*: Number of samples exceeding the Water Quality Standard of Macedonia

NSE D.W.**.: Number of samples exceeding Standard of Drinking Water

NVE D.W.***: Number of village exceeding Standard of Drinking Water

W.Q. ****: Standard Value taken from the Water Quality Standard of Macedonia (Class I of Regulation for Classification of Water, Macedonia) except Cu which was taken from the guideline value of WHO.

D.W. *****: Standard of Drinking Water, Macedonia (Official Gazette 57/04)

For well and spring samples, since the concentrations of heavy metals at each well and spring do not change significantly within each village, average value of the heavy metal concentrations was calculated as the value representing each village (Table 5.23).

Among 10 heavy metals, Cd, Cr, Cu and Hg do not show any significantly high concentrations, each of them, respectively, ranging from 0.00004 to 0.0017mg/L, <0.005 to 0.034mg/L, 0.005 to 0.18mg/L and <0.0001 to 0.00018mg/L, and none of the samples exceed the Water Quality Standard and the Standard of Drinking Water. While, other six heavy metals, As, Co, Ni, Pb, Zn and Mn, are high. The concentrations of these heavy metals in groundwater and surface water in the P/P area are described below and shown on Appendix 12 (all of the six heavy metals) and Figures 5.31 (As) and 5.32 (Pb).

a. Arsenic (As): All the samples, including well/spring and river, show similar As concentrations, all of them falling in a narrow range of 0.008 to 0.015mg/L, except 2 samples of RS01 (0.020mg/L) and RS06 (0.039mg/L). RS01 was collected in the Koritnica River, immediately lower stream of the mine workings of the Zletovo Mine and RS06 was collected at northwest of Stromos (Figure 5.31). Among all the samples only RS06 has As concentration exceeding the Water Quality Standard, but As concentrations of the well/spring water and river water are generally high with average values of 0.011 and 0.013mg/L, respectively. None of the well and spring water has As concentrations exceeding the Water Quality Standard, however, most of the samples (67%) show As values exceeding the Standard of Drinking Water of

Macedonia. In 22 villages out of 29, the average values of As exceed the Standard of Drinking Water. The villages with the average values of As less than the Standard of Drinking Water are distributed in the north (Marcino and Dobrevo) and in the south (Puzderci, Kukovo, Prestrisino, Garjanci and Gujnovci).

b. Cobalt (Co): Co concentrations of P/P area are high, and river water, ranging from 0.008 to 1.06mg/L at an average of 0.11mg/L, shows higher concentrations than well/spring water, from 0.028 to 0.40mg/L at an average of 0.067mg/L. Among 95 samples of spring/water, 6 and 57 samples, respectively, exceed the Standard of Drinking Water and the Water Quality Standard. The village averages exceed the Standard of Drinking Water for 17 villages, which are scattered over the P/P area. The villages with average Co values exceeding the Water Quality Standard are Strmos, Dreveno and Gstubol, and they are located in the northern part of the P/P area (Appendix 12). For the river water samples, 9 samples exceed the Water Quality Standard of 0.1mg/L. Among them, RS06, collected on the Kiselica River between Strmos and Plesinci has the highest value of 1.06mg/L. Other samples with Co values greater than the References Value are found in the Kiselica River area, mainly below tailings dams, such as RS05, RS12, RS13 and RS21, and RS14 at the mouth of Koritnica River. From these, there is some influence of mining activities to elevate Co concentrations to the river water.

c. Nickel (Ni): Ni concentrations of the P/P area are high, and it is more than 10 times higher in river water, ranging 0.44 to 0.79mg/L at an average of 0.58mg/L, than well/spring water, ranging from 0.017 to 0.068mg/L at an average of 0.035mg/L. Ni is known to be easily absorbed by soil grains during flowing underground. Low flow rate of river because of dry season and filtration of Ni by soil grains in underground are possible reasons for lower concentrations of Ni in well/spring water. Only two samples of well/spring have Ni concentrations less than the Standard of Drinking Water and all of the average village values of Ni exceed the Standard of Drinking Water (Appendix 12). Ni concentrations of river water, all of them being greater than the Water Quality Standard, are consistently high and show a narrow range.

d. Lead (Pb): Pb concentrations of well/spring and river waters are similarly high, showing values of, respectively, 0.006 to 0.028mg/L at an average of 0.015mg/L and 0.007 to 0.058mg/L at an average of 0.016mg/L. For Pb values, the Water Quality Standard and the Standard of Drinking Water are same, being set at 0.01mg/L. Most of the samples of well/spring, 77 samples out of 95 samples, exceed the Water Quality Standard and the Standard of Drinking Water. Only three villages located out of the influences of mining activities, Pisica, Troolo and Zletovo, have the village average value of Pb less than 0.01mg/L and the rest of the villages show Pb concentrations more than 0.01mg/L (Figure 5.32). Most of the river water samples, 24 samples out of 31 samples, show Pb concentrations greater than the Water Quality Standard. Among these, the ones below the tailings dams, RS06, RS10, RS12 and RS17 show higher Pb concentrations. RS02 with high concentration of 0.033mg/L is collected from a tributary of the Kiselica River, upper stream of which ancient to present time mine working exists.

Table 5.23 Village Average Heavy Metal Concentration

		As mg/L	Cd mg/L	Co mg/L	Cr mg/L	Cu mg/L	Hg mg/L	Ni mg/L	Pb mg/L	Zn mg/L	Mn mg/L
1	Buciste	0.011	0.0002	0.084	0.012	0.010	0.00005	0.0333	0.018	0.01	0.007
2	Strmos	0.012	0.0002	0.219	0.020	0.012	0.00005	0.03	0.023	0.01	0.008
3	Dobrevo	0.009	0.0006	0.036	0.006	0.006	0.00005	0.0323	0.011	0.01	0.007
4	Drenok	0.010	0.0003	0.087	0.006	0.010	0.00005	0.0393	0.014	0.01	0.006
5	Dreveno	0.012	0.0002	0.101	0.021	0.012	0.00005	0.0478	0.015	0.02	0.008
6	D. Stubol	0.012	0.0003	0.096	0.009	0.015	0.00005	0.0347	0.023	0.01	0.007
7	Gujnovci	0.010	0.0002	0.072	0.007	0.010	0.00005	0.0338	0.013	0.01	0.008
8	Garjanci	0.010	0.0002	0.078	0.012	0.010	0.00005	0.0358	0.021	0.01	0.010
9	G. Stubol	0.011	0.0007	0.124	0.021	0.008	0.00005	0.0493	0.025	0.11	0.012
10	Grizilevci	0.013	0.0003	0.070	0.003	0.010	0.00005	0.031	0.019	0.01	0.009
11	Jiganci	0.010	0.0002	0.078	0.012	0.011	0.00005	0.0387	0.022	0.01	0.010
12	Kundino	0.011	0.0003	0.061	0.010	0.010	0.00005	0.0303	0.015	0.01	0.010
13	Kukovo	0.009	0.0003	0.067	0.010	0.009	0.00005	0.028	0.014	0.01	0.009
14	Lesnovo	0.012	0.0002	0.045	0.006	0.011	0.00005	0.033	0.013	0.01	0.006
15	lezovo	0.011	0.0002	0.066	0.014	0.011	0.00005	0.0283	0.011	0.01	0.010
16	Marcino	0.010	0.0002	0.050	0.012	0.010	0.00005	0.0397	0.011	0.01	0.012
17	Neokazi	0.011	0.0002	0.043	0.004	0.010	0.00005	0.0487	0.013	0.01	0.012
18	Pisica	0.010	0.0002	0.044	0.009	0.011	0.00005	0.04	0.009	0.01	0.011
19	Plesinci	0.013	0.0002	0.060	0.014	0.011	0.00005	0.0433	0.016	0.01	0.011
20	Probistip	0.011	0.0002	0.048	0.005	0.010	0.00005	0.03	0.012	0.01	0.010
21	Pestrisino	0.009	0.0002	0.040	0.011	0.008	0.00005	0.026	0.011	0.01	0.009
22	Petrsino	0.013	0.0004	0.066	0.021	0.015	0.00005	0.045	0.017	0.05	0.013
23	Puzderci	0.010	0.0002	0.036	0.003	0.008	0.00005	0.0245	0.014	0.01	0.009
24	Ratavica	0.011	0.0003	0.051	0.015	0.013	0.00005	0.035	0.014	0.04	0.012
25	Strisovci	0.012	0.0002	0.047	0.016	0.013	0.00005	0.0325	0.017	0.02	0.010
26	Troolo	0.010	0.0002	0.038	0.005	0.009	0.00005	0.033	0.010	0.01	0.009
27	Tripatanci	0.010	0.0002	0.045	0.006	0.009	0.00005	0.0328	0.013	0.01	0.009
28	Zletovo	0.010	0.0002	0.048	0.004	0.009	0.00005	0.0328	0.008	0.01	0.010
29	Zarapinci	0.011	0.0001	0.038	0.003	0.006	0.0001133	0.0337	0.010	0.01	0.009
	Maximum	0.013	0.0007	0.219	0.021	0.015	0.0001133	0.0493	0.025	0.11	0.013
	Minimum	0.009	0.0001	0.036	0.003	0.006	0.00005	0.0245	0.008	0.01	0.006
	Average	0.011	0.0003	0.067	0.010	0.010	0.00005	0.0353	0.015	0.01	0.009
	NVE W.Q	0	0	4	0	0	0	0	28	2	0
	NVE D.W.	22	0	17	0	0	0	29	26	0	0
	W.Q.	0.03	0.01	0.1	0.05	0.2	0.0002	0.05	0.01	0.1	0.05
	D.W.	0.01	0.003	0.05	0.05	2	0.001	0.02	0.01	3	0.05

NVE W.Q: Number of village exceeding the Water Quality Standard of Macedonia

NVE D.W.: Number of village exceeding Standard of Drinking Water

W.Q. :Standard Value taken from the Water Quality Standard of Macedonia (Class I of Regulation for Classification of Water, Macedonia) except Cu which was taken from the guideline value of WHO.

D.W. :Standard of Drinking Water, Macedonia (Official Gazette 57/04)

: Value exceeding the Standard of Drinking Water
: Value Exceeding the Water Quality Standard and the Standard for Drinking Water
: Value exceeding Water Quality Standard

e. Zinc (Zn): Many of the water samples of P/P area, 86 samples out of 126 samples, have Zn concentrations less than the detection limit of 0.01mg/L, however, some of the samples show high concentrations, reaching to 0.29mg/L for well/spring samples and 5.8mg/L for river water samples. The concentrations of Zn are higher in river samples, ranging from <0.01 to 5.8mg/L at an average of 0.44mg/L, than well/spring samples, ranging from <0.01 to 0.29mg/L at an average of 0.02mg/L. Three samples, one each in the villages of Ptresino, Ratovica, and G. Stubol, exceed the Water Quality Standard of 0.1mg/L, and none of the samples shows concentrations higher than the Standard of Drinking Water (Appendix 12). For river samples, Zn concentrations higher than the Water Quality Standard of 0.1mg/L were obtained from 6 samples of RS01, RS02, RS05, RS06, RS14 and RS17, located along the Kiselica River where old mine workings and tailings dams exist and Koritnica River where water flows from the working of the Zletovo Mine. The concentrations of Zn in river water are elevated by influence of mining activities but well/spring water do not show clear tendency of the affect of mining activities.

f. Manganese (Mn): Well/spring samples show relatively low concentrations, ranging from 0.004 to 0.019mg/L at an average of 0.009mg/L, while river water shows more than 10 times higher concentrations than well/spring water, ranging from 0.006 to 33mg/L at an average of 4.0mg/L. None of the well/spring water exceeds the Water Quality Standard and the Standard of Drinking Water, while more than half of river samples exceed the Water Quality Standard. The river samples with high Mn concentrations occur along the Kiselica and Koritnica Rivers where the mining activities of the past and present exist (Appendix 12). The concentrations of Mn in river water are clearly elevated by mining activities. Other than these, samples with higher concentrations of Mn occur in the eastern tributaries of the Zletovska River and in south part of the area.

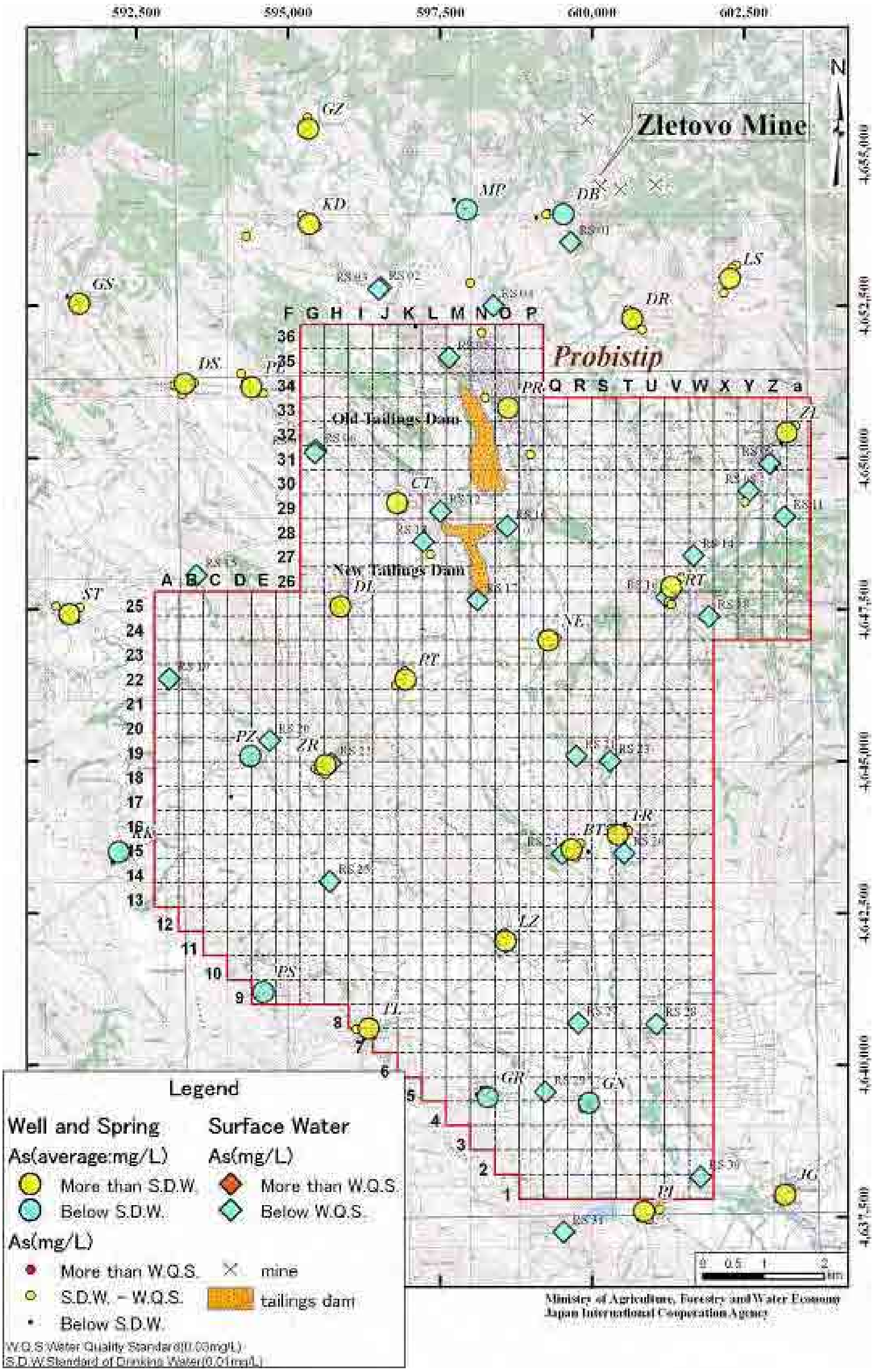


Figure 5.31 Arsenic (As) Concentrations of Groundwater and River Water

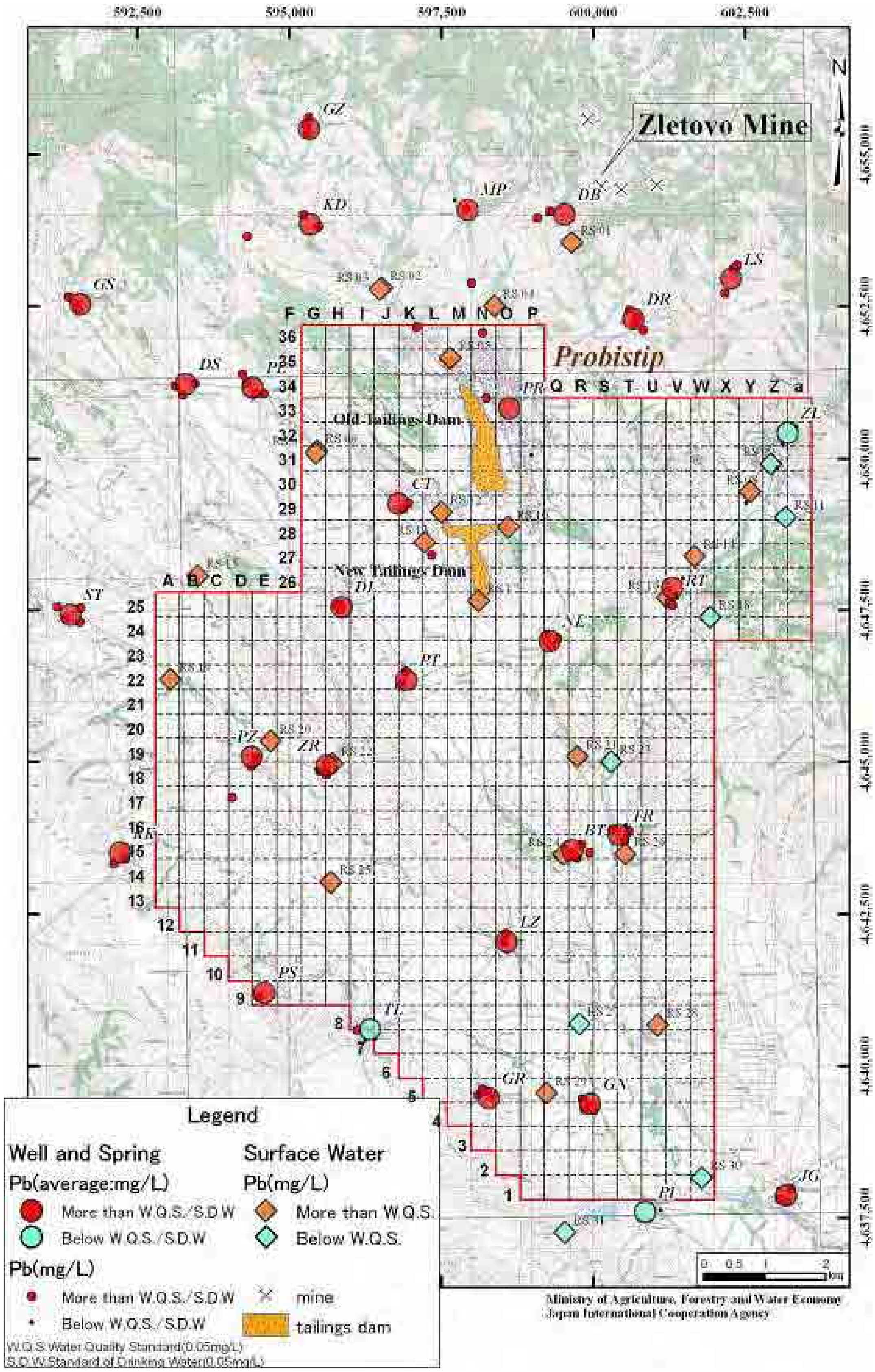


Figure 5.32 Lead (Pb) Concentrations of Groundwater and River Water

(3) Discussion

The analytical results based on the chemical analysis by AAS show that well/spring and river water in the P/P area show high concentrations of As, Co, Ni, Pb, Zn and Mn. Comparison of well/spring and river waters, river water show higher concentrations in Co, Ni, Zn and Mn than well/spring water and both of them show similar concentrations in As and Ni. The water quality of well/spring water is poor, As, Co, Ni and Pb concentrations being higher than the Standard of Drinking Water in most of the wells and springs. It is a serious helth problem that more than half of the wells/springs in the P/P area are still used as a source of drinking water by the local residents in spite of the fact that the most of them are not appropriate for drinking. The situation of river water is similar, showing Ni, Pb and Mn concentrations exceeding the Water Quality Standard at the most of the locations.

Among the heavy metals showing high concentrations (As, Co, Ni, Pb, Zn and Mn), the influences of the mining activities, including the past and the present, elevating concentrations of heavy metals, are clearly observed for Co, Mn and Zn. The concentrations of these heavy metals are clearly high in water samples along the Kiselica and Koritnica Rivers where mine workings and tailings dams of the past and the present area located. Most of the well/spring samplers show As and Ni concentrations exceeding the Standard of Drinking Water, and all of river water samples have Ni concentration greater than the Water Quality Standard. Further, all water samples including well/spring and river show similar values of As and Ni. These suggest that the high concentrations of As and Ni in water of the P/P area were caused by natural feature of the area, probably geological nature. Similar to As and Ni, most of the water samples show high Pb concentrations exceeding the Standard of Drinking Water and the Water Quality Standard, and concentrations of Pb tend to be higher in the Kiselica and Koritnica River areas. In addition to the natural causes, Pb concentrations have been elevated by the mining activities of the area.

The surface water survey of 2006 showed high concentrations of Pb, Zn and Mn for the sample collected at the Kiselica River, in the upper stream area from tailings dams and the battery factory, north of Probistip. The field survey conducted to seek a possible source of the high heavy metal concentrations in the water of the upper stream of the Kiselica River resulted in finding the old mine workings consisting of waste dumps and probable adits (Photograph 5.1 and 5.2). Among the waste dumps, there is one waste dump showing that the mining activities had continued until quite recent time. Many pyrite grains of 3 to 10mm across, without oxidation, are found in the waste dump consisting mainly of rubble of strongly altered rock. The water of creek running beside the waste dump shows pale brown color and brown oxides are precipitated on bottom of creek. At the junction of Kiselica River, north of Probistip, two water samples were collected, one each on the east (RS02) and west (RS03) tributaries. The mine workings are located in the upper stream of the sampling location RS02. Comparing the heavy metals concentrations of these two water samples, Cd, Cu, Pb, Zn and Mn are clearly high in RS02 than in RS03 because of the mining activities and geological units surrounding the mining activity areas. Not only the Zletovo Mine related mine workings and tailings dams, but also the old mine workings and geological units surrounding the mine workings located in north of the P/P area have controlled the heavy metal concentrations of P/P area. Further, diffusion of heavy metals such as Pb by dust from the tailings dams must be considered as one of the factor controlling the heavy metal concentrations in water.

Photograph 5.1 Old Mine Workings in Upper Stream of the Kiselica River

Photograph 5.2 Waste Dump of Recent Time

5.8 Crops Surveys

For environmental risk assessment of soil contamination related to mining, crop samples were collected for chemical analysis. The crops survey was conducted in Phase 2 (2006) and the additional crops survey was conducted in Phase 3 (2007).

5.8.1 Sample Locations of the Crops Surcey

In Phase 2 survey, a total of 104 crop samples, consisting of 84 wheat, 16 corn and 4 rice samples, was collected as shown in the sample location map (Figure 5.33).

Wheat is mainly cultivated in the flat area and gentle hill area to the east of the Zletovska River and locally along the Zletovska River as shown in Figure 5.34, and 84 samples of wheat for chemical analysis were randomly collected covering the whole these areas at the beginning of July 2006. Corn is locally cultivated in scattered small areas distributed mainly in the southern part of the P/P area and the areas along the Zletovska River. The corn samples for chemical analysis, 16 samples, were collected at the beginning of September 2006. Rice in the P/P area is cultivated only in the restricted area of the southeast corner, along the Zletovska River. At the beginning of October 2006, 4 samples of rice for chemical analysis were collected.

5.8.2 Chemical Analysis

Grain samples of 0.5 to 1kg were taken from an area of approximately 1m x 2m at the centre of grid for each sample and samples with mass of at least 200g are prepared for chemical analysis. A portion not appropriate for eating is discarded from the sample. Additionally gross surface contamination like soil, rotten parts of plants or leaves are removed. Sufficiently homogeneous samples are prepared in a way as usual for the preparation of foodstuffs in the normal household.

The chemical analyses of crop samples were conducted based on the method of EN 14084 and 13806 “Foodstuffs”, and nitric acid and hydrogen peroxide were selected for the digestion of crop samples following the method of EN 14084. For the determination of content value of heavy metals, the graphite furnace atomic absorption spectrometric (AAS) was used for Cd, Pb, Total-Cr, Cu, Co, Ni, Mn, and As were analysed by the graphite furnace atomic absorption spectrometric (AAS) method. Zn was analysed by flame AAS and Hg was analyzed by the cold-vapour atomic absorption spectrometer (CVAAS). The chemical analysis was conducted at the Institute of Agriculture, St. Cyril and Methodius University.

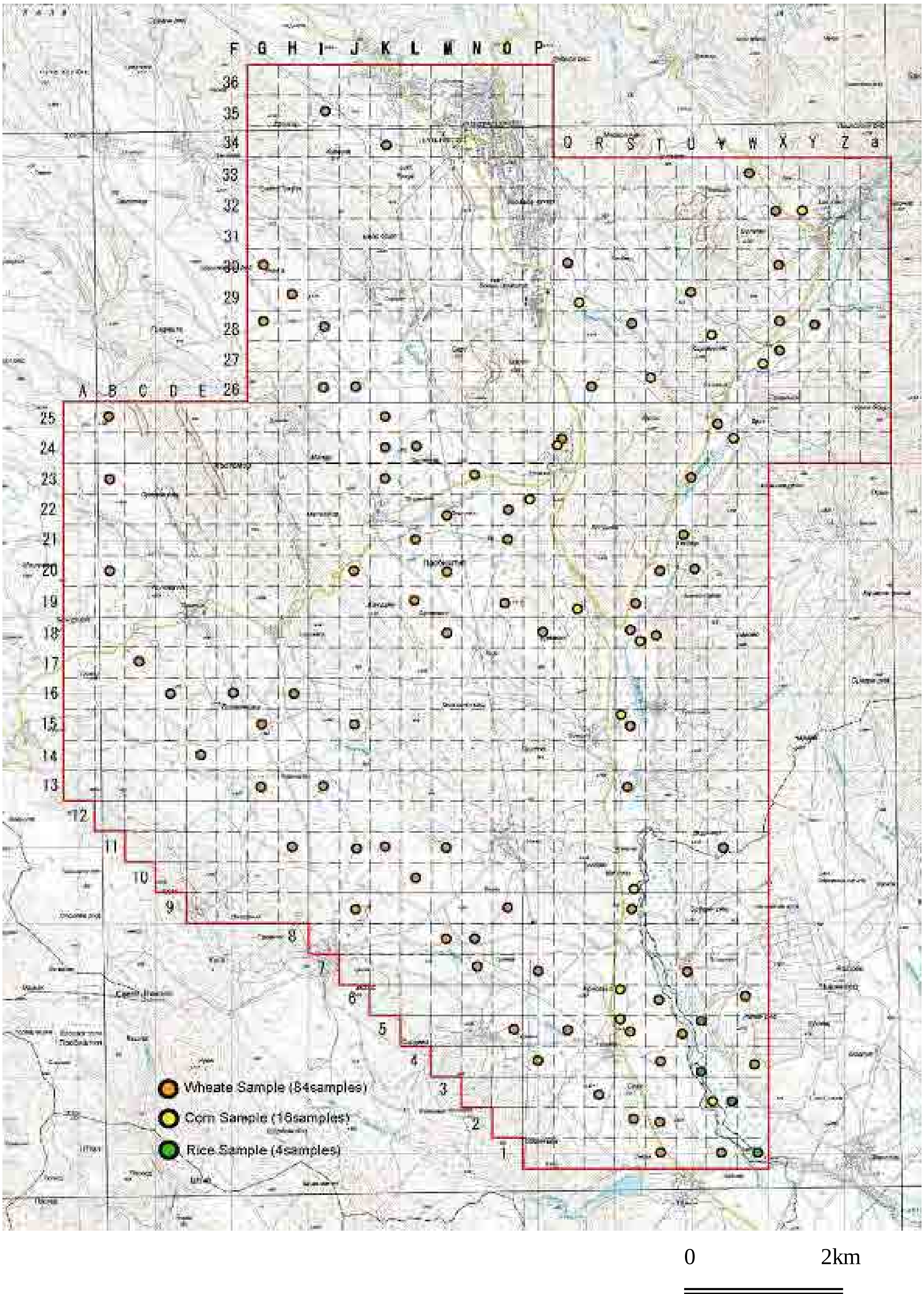


Figure 5.33　Locations of Crop Samples

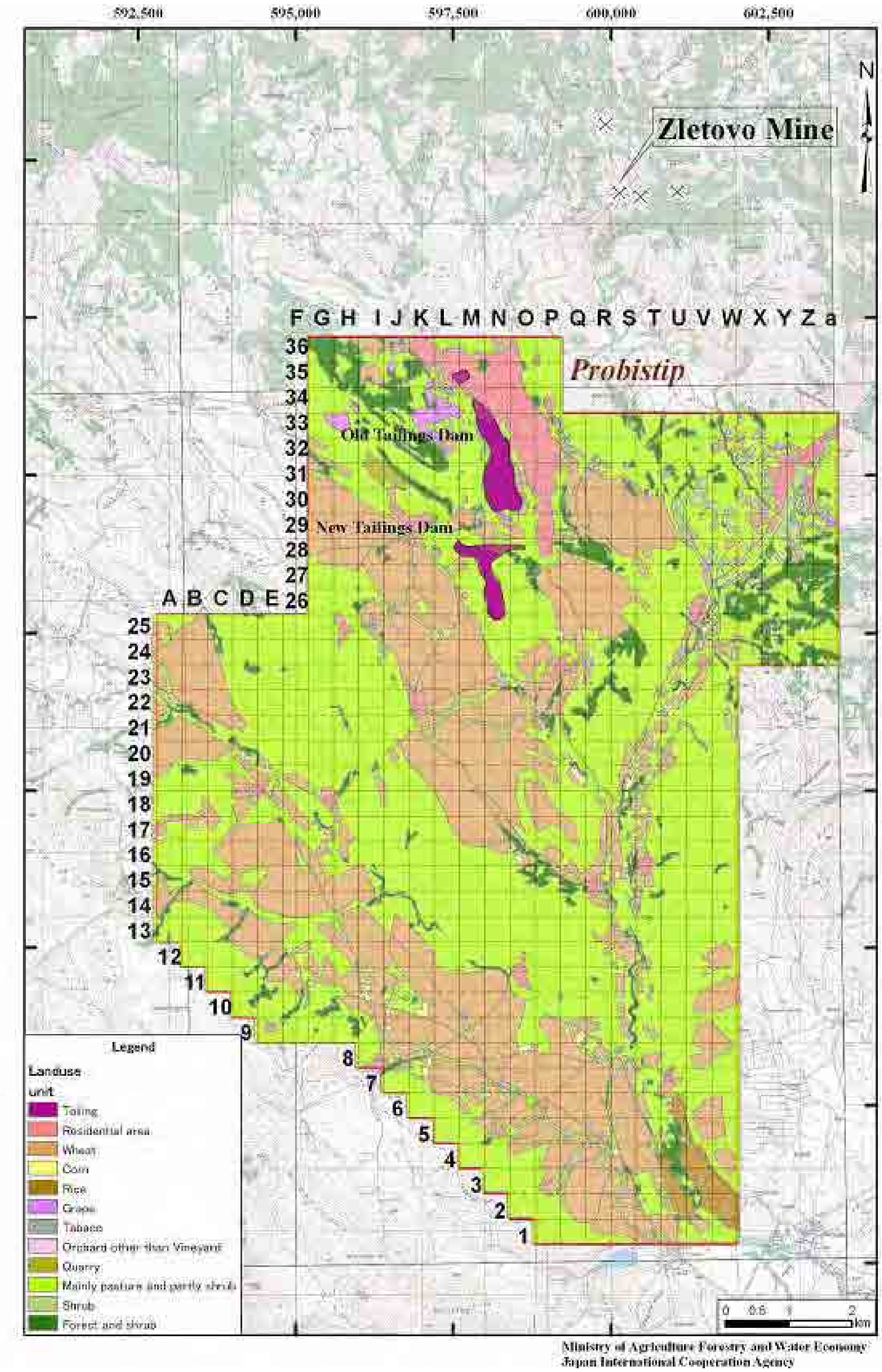


Figure 5.34 Land Use Map and Distribution of Crops (Wheat, Corn and Rice)

5.8.3 Results of Chemical Analysis of Crops

The results of chemical analysis of wheat, corn and rice are given in Data 4. Basic statistics of the analytical results and distribution of heavy metal concentrations of crops are shown in Table 5.24 and Appendix 13, respectively. The characteristic features of heavy metal concentrations in crops are given below.

(1) Arsenic (As): As content values of wheat range from <0.25 to 0.92mg/kg at the average of 0.26mg/kg, showing relatively narrow range (Standard Deviation (SD): 0.19). All samples of corn show As content values less than the lower limit of determination (<0.25mg/kg). Although only 4 samples of rice were analyzed, As content values of rice are higher than the mean value of wheat, ranging from 0.33 to 0.42mg/kg at the average of 0.33mg/kg.The value of Mean+2σ, sometimes used as threshold value, was obtained as 0.64mg/kg for wheat. Relatively high As (more than 0.6mg/kg) in wheat are found only at 6 locations, namely G28, J9, J11, J20, T18 and X32, which are located in the western and north-eastern parts and along Zletovska River in the P/P area.

(2) Cadmium (Cd): Cd content values of wheat range from <0.005 to 0.039mg/kg at the average of 0.005mg/kg, showing very narrow range (SD: 0.006). All the samples of corn show Cd content values less than the lower limit of determination (<0.005mg/kg). Cd content values of rice, on the other hand, show relatively higher concentration than those of wheat, ranging from 0.11 to 0.16mg/kg at the average of 0.13mg/kg. The value of Mean+2σ is 0.017mg/kg for wheat. Relatively high Cd (more than 0.02mg/kg) in wheat occur only at 4 locations, namely T20, U7, U23 and Y28, which are mostly located along Zletovska River in the P/P area.

(3) Cobalt (Co): Co content values of wheat range from <0.05 to 0.85mg/kg at the average of 0.15mg/kg, showing relatively narrow range (SD: 0.16). Co content values of corn range from <0.05 to 0.26mg/kg at the average of 0.09mg/kg, showing relatively narrow range (SD: 0.09). Co content values of rice range from 0.51 to 0.72mg/kg at the average of 0.60mg/kg. The content values of corn are relatively lower than the mean value of wheat, and the content values of rice are relatively higher than the mean values of wheat and corn. The values of Mean+2σ are 0.47mg/kg for wheat and 0.28mg/kg for corn. Relatively high Co (more than 0.4mg/kg) in wheat and rice occur at only 8 locations, namely J26, Q5, U23, W6 for wheat and U4, U5, V3, W1 for rice, which are located in the western part and along Zletovska River in the P/P area.

Table 5.24 Statistics of Content Analytical Results of Crops

Wheat (84 samples)

Items	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	μg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Maximum	0.94	0.039	0.85	1.7	4.3	23	47	1.9	91	44
Minimum	<0.25	<0.005	<0.05	<0.05	1.3	<0.4	<0.25	<0.05	31	32
Mean	0.26	0.005	0.15	0.38	2.3	1.4	2.9	0.27	47	39
SD (σ) *1	0.19	0.006	0.16	0.29	0.64	3.2	9.2	0.40	12	2.3
Mean+1σ	0.45	0.011	0.31	0.67	2.9	4.6	12	0.67	59	41
Mean+2σ	0.64	0.017	0.47	0.96	3.5	7.8	21	1.1	71	43
Mean+3σ	0.83	0.022	0.64	1.2	4.3	11.0	30	1.5	82	45

*1 SD (σ): Standard deviation.

Corn (16 samples)

Items	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	μg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Maximum	<0.25	<0.005	0.26	0.28	4.2	4.9	1.1	0.37	25	40
Minimum	<0.25	<0.005	<0.05	<0.05	2.2	<0.4	<0.25	<0.05	18	19
Mean	<0.25	<0.005	0.09	0.19	2.9	0.49	0.63	0.17	23	23
SD (σ) *1	0.00	0.000	0.09	0.05	0.48	1.2	0.31	0.13	2.1	6.7
Mean+1σ	-	-	0.18	0.24	3.4	1.7	0.94	0.30	25	30
Mean+2σ	-	-	0.28	0.29	3.8	2.8	1.2	0.43	27	36
Mean+3σ	-	-	0.37	0.34	4.3	4.0	1.6	0.56	29	43

*1 SD (σ): Standard deviation

Rice (4 samples)

Items	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	Mn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	μg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Maximum	0.42	0.16	0.72	0.25	6.3	<0.4	0.91	0.32	37	26
Minimum	0.33	0.11	0.51	0.16	3.6	<0.4	0.72	0.18	23	22
Mean	0.37	0.13	0.60	0.20	4.8	<0.4	0.82	0.25	29	24

(4) Chromium (Cr) : Cr content values of wheat range from <0.05 to 1.7mg/kg at the average of 0.38mg/kg, showing relatively wide range (SD: 0.29). Cr content values of corn range from <0.05 to 0.28mg/kg at the average of 0.19mg/kg, showing relatively narrow range (SD: 0.05). Cr content values of rice range from 0.16 to 0.25mg/kg at the average of 0.16mg/kg. The content values of corn are relatively lower than the mean value of wheat and are almost same to the mean value of rice. The values of Mean+2σ are 0.96mg/kg for wheat, 0.29mg/kg for corn. Relatively high Cr (more than 1.0mg/kg) in wheat occurs at only 1 location of U23, which are located in eastern part, along Zletovska River in the P/P area.

(5) Copper (Cu): Cu content values of wheat range from 1.3 to 4.3mg/kg at the average of 2.3mg/kg, showing relatively wide range (SD: 0.64). Cu content values of corn range from 3.6 to 6.3mg/kg at the average of 4.8mg/kg, showing relatively wide range (SD: 0.48). Cu content values of rice range from 3.6 to 6.3mg/kg at the average of 4.8mg/kg. The content values of rice is relatively higher than the mean values of wheat and corn. The values of Mean+2σ are 3.5mg/kg for wheat, 3.8mg/kg for corn. The wheat samples with relatively high Cu (more than 3.0mg/kg) values occur at 19 locations, which are distributed widely scattered in the whale area of P/P. However, high Cu values in corn and rice seem to occur only along the Zletovska River in the P/P area.

(6) Mercury (Hg): Hg content values of wheat range from <0.4 to 23μg/kg at the average of 1.4μg/kg, showing very wide range (SD: 3.21). Hg content values of corn range from <0.4 to 4.9μg/kg at the average of 0.49μg/kg, showing relatively wide range (SD: 0.48). All of the rice samples show Hg content value less than the lower limit of determination (<0.4μg/kg). The content values of wheat are relatively higher than the mean values of corn and rice. The values of Mean+2σ are 7.8μg/kg for wheat and 2.8μg/kg for corn. The wheat samples with relatively high Hg (more than 8.0μg/kg) occur at only 2 locations, namely F16 and K11, which are located in the south-western part of the P/P area.

(7) Nickel (Ni): Ni content values of wheat range from <0.25 to 47mg/kg at the average of 2.9mg/kg, showing very wide range (SD: 9.16). Ni content values of corn range from <0.25 to 1.1mg/kg at the average of 0.63mg/kg, showing relatively wide range (SD: 0.31). Ni content values of rice range from 0.72 to 0.91mg/kg at the average of 0.82mg/kg. The content values of wheat show much higher than the mean values of corn and rice. The values of Mean+2σ are 21mg/kg for wheat and 1.2mg/kg for corn. The wheat samples with relatively high Ni (more than 20mg/kg) occur at 4 locations, namely J20, J26, R3 and W6, which are located in the western and southern parts of the P/P area.

(8) Lead (Pb): Pb content values of wheat range from <0.05 to 1.9mg/kg at the average of 0.27mg/kg, showing relatively wide range (SD: 0.40). Pb content values of corn range from 0.18 to 0.32mg/kg at the average of 0.25mg/kg, showing relatively narrow range (SD: 0.13). Pb content values of rice range from 0.72 to 0.91mg/kg at the average of 0.82mg/kg. The content values of wheat are relatively higher than the mean values of corn and rice. The values of Mean+2σ are 1.1mg/kg for wheat and 0.43mg/kg for corn. The wheat samples with relatively high Pb (more than 1.0mg/kg) occur at 6 locations, namely J26, K23, K24, M11, W4 and X32, which are scattered in the western, northern and southern parts of the P/P area and W4 located on the terrace in the south-eastern corner of the P/P area.

(9) Zinc (Zn): Zn content values of wheat range from 31 to 91mg/kg at the average of 31mg/kg, showing very wide range (SD: 11.7). Zn content values of corn range from 18 to 25mg/kg at the average of 18mg/kg, showing relatively wide range (SD: 2.1). Zn content values of rice range from 23 to 37mg/kg at the average of 29mg/kg. The content values of wheat show much higher than the mean values of corn and rice. The values of Mean+2σ are 71mg/kg for wheat and 27mg/kg for corn. The wheat samples with relatively high Zn (more than 60mg/kg) occur at 10 locations, namely J20, J26, Q5, R3, R26, S5, S9, T18, T20 and V25, which are located in the western part, along Zletovska River in the P/P area.

(10) Manganese (Mn): Mn content values of wheat range from 32 to 44mg/kg at the average of 32mg/kg, showing relatively wide range (SD: 2.3). Mn content values of corn range from 19 to 40mg/kg at the average of 23mg/kg, showing relatively wide range (SD: 6.7). Mn content values of rice range from 22 to 26mg/kg at the average of 24mg/kg. The content values of wheat show much higher than the mean values of corn and rice. The values of Mean+2σ are 43mg/kg for wheat and 36mg/kg for corn. The wheat samples with relatively high Mn (more than 40mg/kg) occur at 9 locations, namely H11, K34, M20, M22, N8, N23, O22, S9 and T18, which are located in the northern, central and southern parts of the P/P area.

5.8.4 Characteristics of Heavy Metals Concentrations in Crops

Mean values of heavy metals concentration in crops are shown in Table 5.25.

Table 5.25 Mean Values of Heavy Metals Concentrations in Crops

Items	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**Mn**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	μg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Wheat	0.26	0.005	0.15	0.38	2.3	1.4	2.9	0.27	47	39
Corn	<0.25	<0.005	0.09	0.19	2.9	0.49	0.63	0.17	23	23
Rice	0.37	0.13	0.60	0.20	4.8	<0.4	0.82	0.25	29	24

The highest value of each element among three crops.

Comparing each crop based on the mean values, wheat is characterised by higher concentrations of Cr, Hg, Ni, Zn and Mn than those of corn and rice. Particularly, the mean concentration values of Hg and Ni are three times higher than those of corn and rice. Although the mean concentration values of Zn and Mn are higher than those of corn and rice, they are not significantly high.

On the other hand, rice is characterised by higher concentrations of As, Cd, Co and Cu than these of wheat and corn. Corn seems to have intermediate heavy metal concentrations between wheat and rice. Particularly, rice shows the mean concentration values of Cd and Co more than four times higher than those of wheat and corn. The mean concentration values of As and Cu do not show large difference.

Although corn has slightly low concentrations of Pb compared to other crops, the three crops show similar Pb concentrations.

Each of the crops of the P/P area has characteristic heavy metal concentrations, slightly different from each other.

5.8.5 Comparison of the Results with the Standard and Reference Values

The analytical results of crop analysis were compared with some of the key values. There are mainly two key values for crops currently used in Macedonia, as shown in Tables 5.26 and 5.27.

a. Standard Value: Maximum Levels of Heavy Metals in Foodstuffs (Macedonia, 2005)
b. Reference Value: Maximum Allowed Concentration in Foodstuffs (Former Yugoslavia, 1992).

For assessing the results of the crops analysis, Cd (0.2mg/kg) and Pb (0.2mg/kg) values of the Maximum Levels of Heavy Metals in Foodstuffs of Macedonia were taken as the standard value, and Hg (50μg/kg) and As (1mg/kg) values of the Maximum Allowed Concentration in Foodstuffs of the Former Yugoslavia (CFPJ, 1992) were taken as the reference value.

None of wheat, corn and rice samples exceeds the key values of As (1mg/kg), Cd (0.2mg/kg) and Hg (50μg/kg), however, 30 samples (36%) of wheat, 8 samples of corn and 3 samples of rice exceed the Pb Standard Values.

The wheat samples exceeding the standard values of Pb are mainly distributed in the areas of west of the Kiselica River and west of the Belosica River, to the south west of the tailings dams (Figure 5.35). Since concentrations of Pb in content and elution analyses of soil are not particularly high in these areas, an effect of heavy metal high dust may be attributed to high concentrations of Pb in wheat of the areas. Most of the corn and rice samples were collected in the area along the Kiselica and Zletovska Rivers, and high concentrations of Pb in corn and rice samples were caused by soil and water with high concentrations of heavy metals.

Table 5.26 Maximum Levels of Heavy Metals in Foodstuffs
(Macedonia, 2005) *1

Heavy Metal / Crops	**Pb**
	mg/kg
Vegetables	0.1
Cereals, leafy vegetables and mushrooms	0.2
Fruits	0.1
Strawberries and other small fruits	0.2

Heavy Metal / Crops	**Cd**
	mg/kg
Crops except wheat and rice	0.1
Wheat and rice	0.2
Soy grains	0.2
Vegetables and fruits	0.05
Leafy vegetables, fresh plants, celery, root vegetables and potato	0.2
Vegetables, root vegetables and potato except celery	0.1

*1: Agricultural Standards for Products", CRP 251, 2005

Table 5.27 Maximum Allowed Concentration in Foodstuffs
(Former Yugoslavia, 1992) *2

Heavy Metals / Crops	**Pb**	**Cd**	**Hg**	**As**
	mg/kg	mg/kg	mg/kg	mg/kg
Wheat/Corn	0.4	0.1	0.05	1
Rice	0.4	0.3	0.05	1

*2: Official Gazette CFPJ, 5, 1992

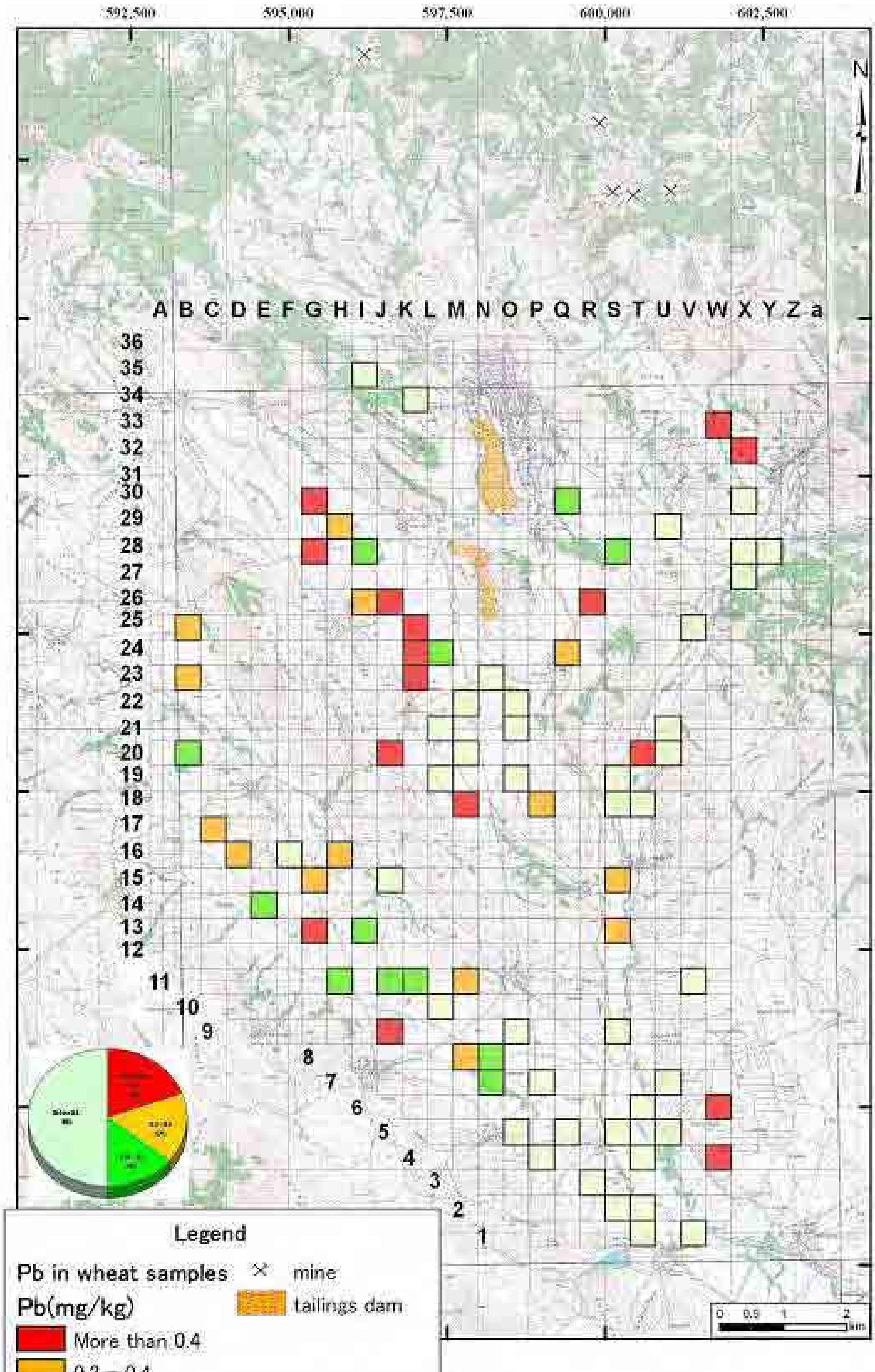


Figure 5.35 Lead (Pb) Concentrations in Wheat (Results of 2006)

5.8.6 Additional Crops Survey in Phase 3

The chemical analysis of 84 wheat samples conducted in Phase 2 (2006) survey showed 30 wheat samples with Pb concentrations greater than the Standard Values of 0.2 mg/kg. In Phase 3 (2007), sampling and chemical analysis of 32 pairs of wheat samples and soil samples were conducted to examine yearly variation of Pb in wheat and the relation of Pb concentrations between wheat and soil.

The sampling was conducted using 400m grid system of the soil survey of the P/P area. The locations of the sampling were decided based on the results of the 2006 survey and both of wheat and soil samples were collected at the centre of the each grid. The chemical analyses of wheat and soil were conducted for three elements of Pb, Cd, As. Both content and elution analyses were carried out for soil samples. The analytical methods are the same as previous soil content, soil elution and crops analyses. The chemical analyses were conducted at the Institute of Agriculture, St. Cyril and Methodius University. The analytical results of wheat and soil samples are given in Data 4, and Table 5.28 shows comparison of the results of 2006 and 2007.

Pb concentrations of wheat samples of the Phase 3 are high, ranging from <0.05 to 0.36mg/kg at an average of 0.12mg/kg, but they are lower than the results of the Phase 2 (2006) survey with an average value of 0.27mg/kg. The samples with Pb concentrations exceeding the Standard Value are seven (22%), which is less than the Phase 2 survey with 36 % of the samples being exceeding the Standard Value. Cd and As are low, most of the samples showing concentrations less than the detection limits of, respectively, <0.005 and <0.25mg/kg, and none of the sample reaches to the Standard Value of Cd (0.2mg/kg) and the Reference Values of As (1.0mg/kg).

The soil samples show low content and elution concentrations except elution concentrations of Pb, seven samples of which exceed the Reference Value of elution concentrations (0.01mg/kg).

The relations of Pb concentrations between wheat and soil samples are shown in Figures 5.36 and 5.37. As shown in the figures and correlation coefficients, being 0.233 for wheat-soil content and -0.120 for wheat-soil elution, no clear relation between wheat and soil is observed.

Comparison of Pb concentrations between 2006 and 2007 samples collected from the same grid shows that Pb concentrations of 2007 samples are consistently lower than those of 2006 samples (Figures 5.38 and 5.39).

The distribution map of Pb concentrations of wheat shows that distributions of Pb high wheat samples with concentrations greater than Standard Value are clearly less in 2007 samples compared with 2006 samples and that, in both of the cases, Pb high wheat is distributed in the same area, south west of the tailings dams (Figure 5.40).

Table 5.28 Comparison of Heavy Metal Concentrations in Wheat Samples of 2006 and 2007

	No of Samples	Pb, mg/kg	Cd, mg/kg	As, mg/kg
Maximum(2007)	32	0.36	0.007	0.30
Minimum (2007)	32	<0.05	<0.005	<0.25
Average (2007)	32	0.12	0.003	0.15
NSE RV (2007)	32	7	0	0
Maximum(2006)	84	1.9	0.03	0.94
Minimum (2006)	84	<0.05	<0.005	<0.25
Average (2006)	84	0.27	0.005	0.26
NSE RV (2006)	84	30	0	0

NSE RV: Number of Samples Exceeding Reference and Standard Values

The chemical analyses of 32 wheat and soil samples do not show any clear chemical relation of Pb between wheat and soil samples. The consistently lower concentrations of Pb in 2007 wheat samples than those of 2006 samples probably suggest a yearly variation of Pb concentrations in wheat.

It seems that yearly variations of Pb concentration in wheat caused by weather conditions and etc. exist, suggesting that long term continuous monitoring is necessary to understand the Pb concentration of wheat in the area. Pb concentration of soil, including content and elution, does not play a key role to determine Pb concentration of wheat. A combination of factors such as soil, groundwater, dust, etc. must be considered for understanding the mechanism of Pb concentration of wheat. Based on the results of 2006 and 2007, the samples with high concentration of Pb seem to be distributed in the similar area.. These areas are not recommended for cultivation of wheat as long as this environmental situation continues.

Correlation wheat- Content Soil	
Pb	0.233

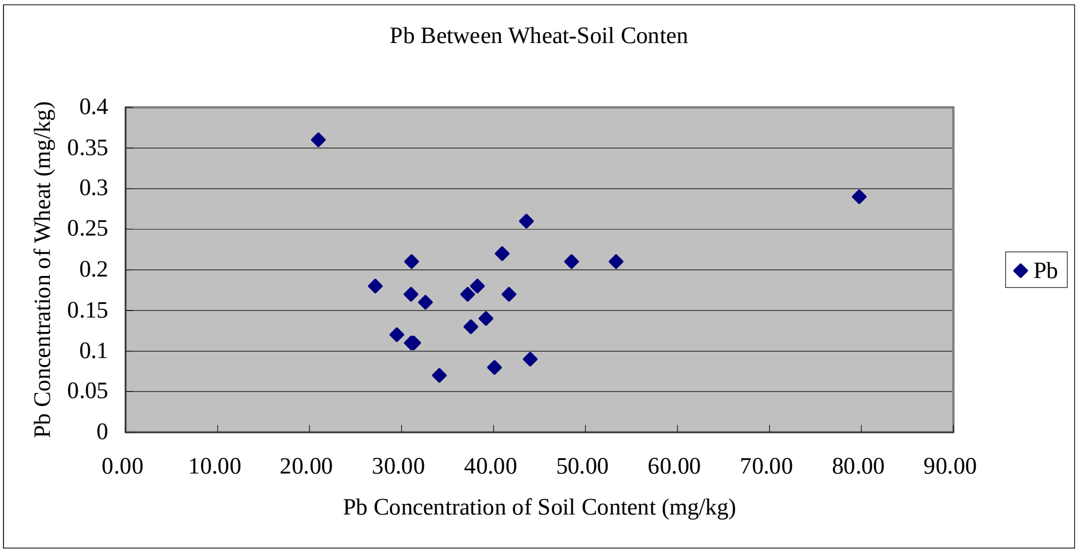


Figure 5.36 Lead (Pb) Concentrations of Wheat and Soil Content Values

Correlation wheat- Elution Soil	
Pb	-0.120

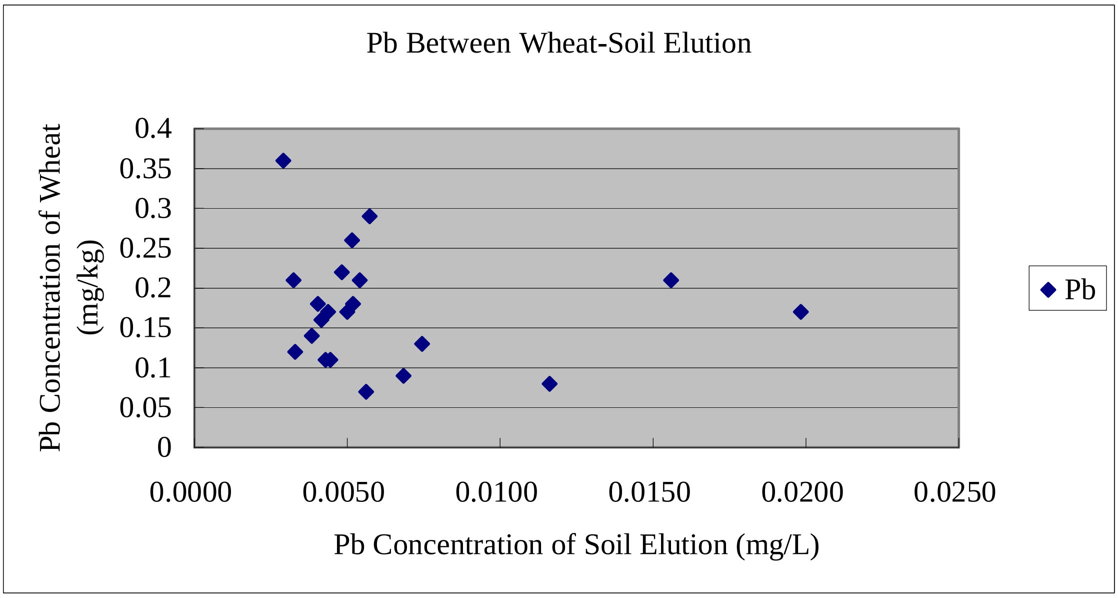


Figure 5.37 Lead (Pb) Concentrations of Wheat and Soil Elution Values

Correlation : 0.675

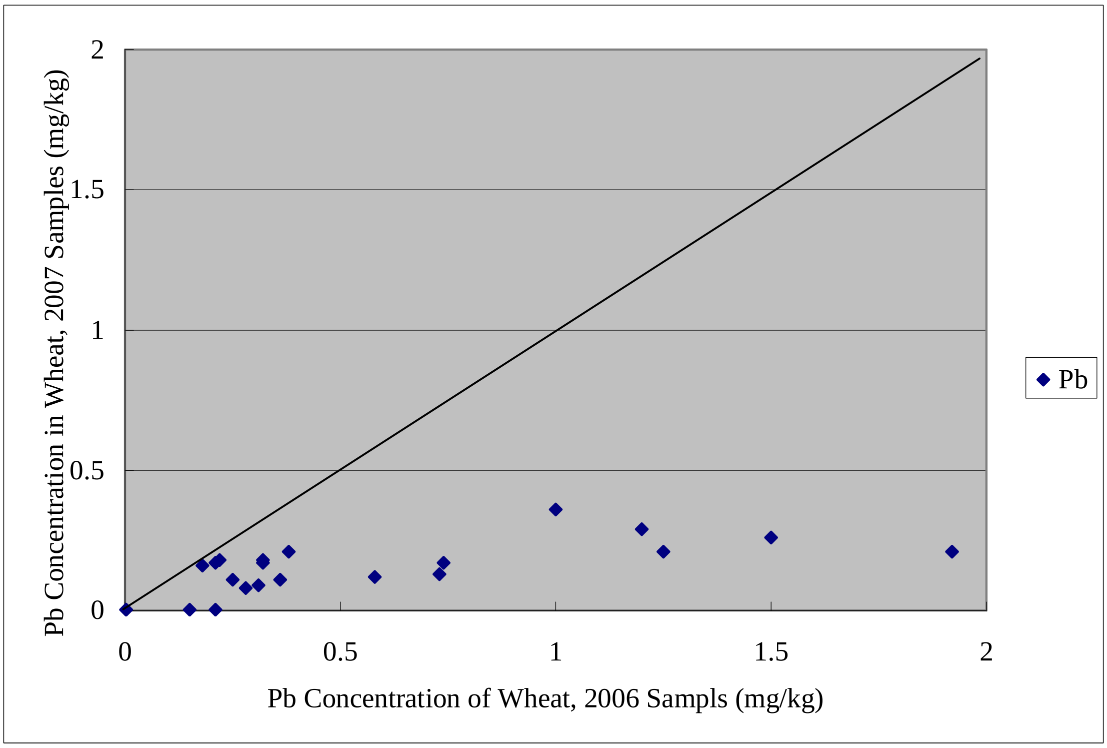
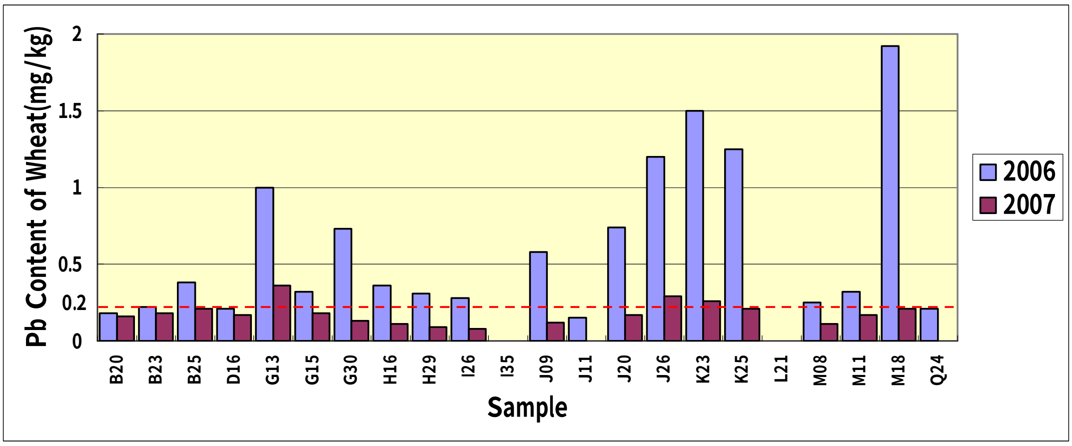
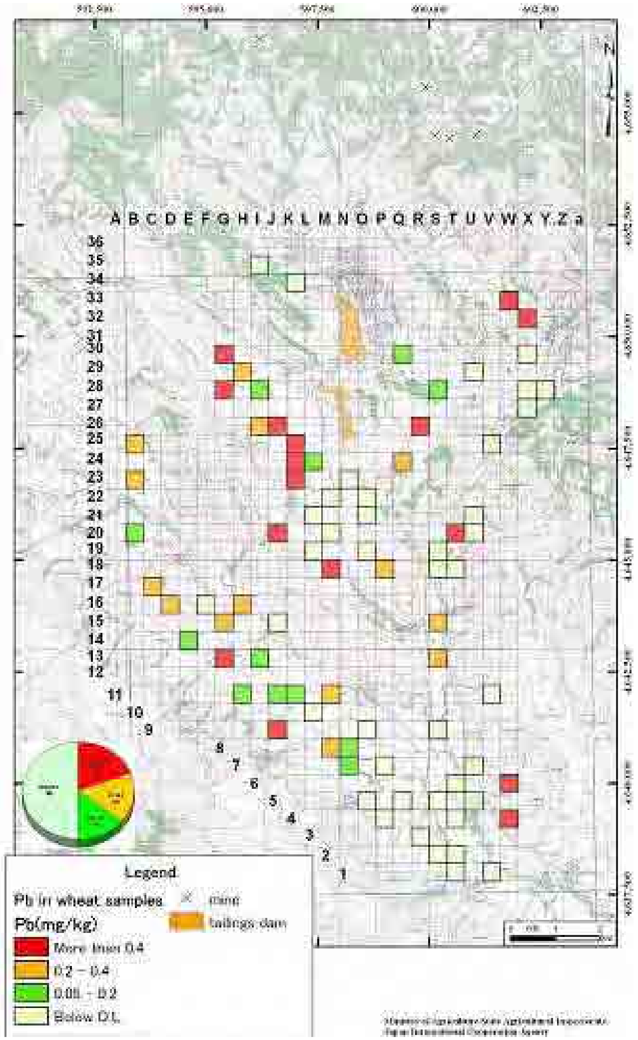


Figure 5.38 Lead (Pb) Concentrations of Wheat between 2006 and 2007 Samples

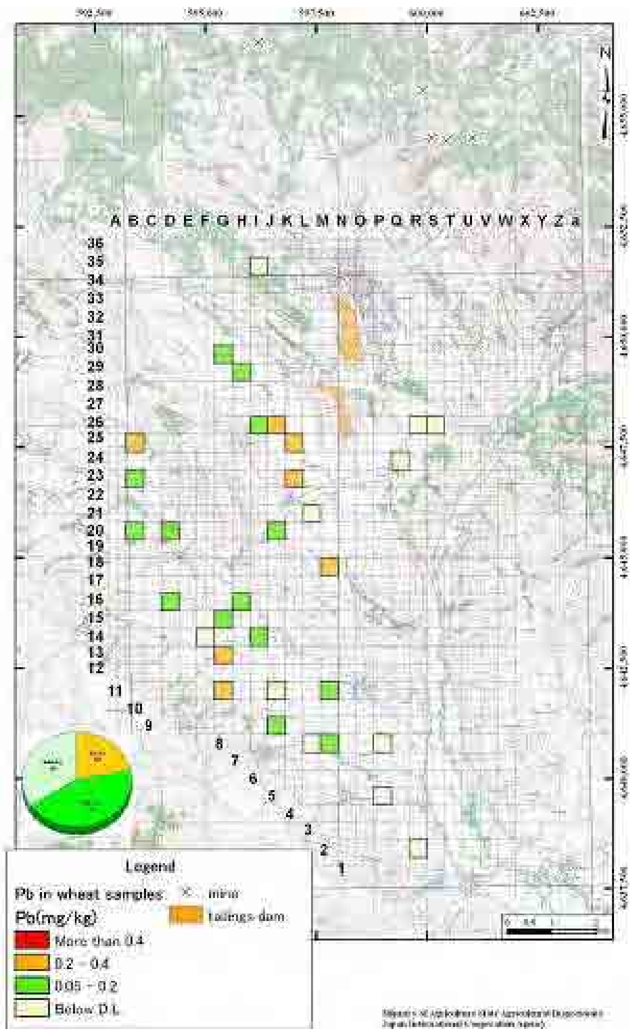


Pb Standard Value of Wheat 0.2mg/kg

Figure 5.39 Comparison of Lead (Pb) Concentrations of Wheat between 2006 and 2007 Samples



Results of 2006 Survey



Results of 2007 Survey

Figure 5.40 Distribution of Lead (Pb) Concentrations of Wheat