

## ANALYSIS AND POLLUTION ASSESSMENT OF HEAVY METAL IN SOIL, PERLIS

(Analisis dan Penilaian Pencemaran Logam Berat dalam Tanah, Perlis)

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### Abstract

Concentration of 5 heavy metals (Cu, Cr, Ni, Cd, Pb) were studied in the soils around Perlis, to assess heavy metals contamination distribution due to industrialization, urbanization and agricultural activities. Soil samples were collected at depth of 0-15cm in eighteen station around Perlis. The soil samples (2mm) were obtained duplicates and subjected to hotblock digestion and the concentration of total metal was determined via ICP-MS. Overall concentrations of Cu, Cr, Ni, Cd and Pb in the soil samples ranged from 0.38-240.59, 0.642-3.921, 0.689-2.398, 0-0.63 and 0.39-27.47 mg/kg respectively. The concentration of heavy metals in the soil display the following decreasing trend: Cu>Pb>Cr>Ni>Cd. From this result, found that level of heavy metal in soil near centralized Chuping industrial areas give maximum value compared with other location in Perlis. The Pollution index revealed that only 11% of Cu and 6% of Cd were classes as heavily contaminated. Meanwhile, Cu and Pb showed 6% from all samples result a moderately contaminated and the others element give low contamination. Results of combined heavy metal concentration and heavy metal assessment indicate that industrial activities and traffic emission represent most important sources for Cu, Cd and Pb whereas Cr, Ni mainly from natural sources. Increasing anthropogenic influences on the environment, especially pollution loadings, have caused negative changes in natural ecosystems and decreased biodiversity.

**Keywords:** Contamination, Heavy metals, Distribution, ICP-MS, Pollution index

### Abstrak

Kepekatan 5 logam berat (Cu, Cr, Ni, Cd, Pb) telah dikaji dalam tanah di sekitar Perlis, untuk menilai taburan pencemaran logam berat akibat perindustrian, bandarbandaran dan aktiviti pertanian. Sampel tanah telah dikumpulkan pada kedalaman 0-15cm dalam lapan belas stesen sekitar Perlis. Sampel tanah (2mm) telah diperolehi dua salinan dan melalui kaedah penghadaman hotblock dan kepekatan jumlah logam ditentukan melalui ICP-MS. Kepekatan keseluruhan Cu, Cr, Ni, Cd dan Pb dalam sampel tanah masing-masing antara 0.38-240.59, 0.642-3.921, 0.689-2.398, 0-0.63 dan 0.39-27.47 mg/kg. Kepekatan logam berat dalam tanah mengikut urutan menurun adalah: Cu > Pb > Cr > Ni > Cd. Daripada keputusan ini, didapati bahawa tahap logam berat dalam tanah berhampiran kawasan perindustrian Chuping berpusat memberi nilai maksimum berbanding lokasi lain di Perlis. Indeks Pencemaran mendedahkan bahawa hanya 11% Cu dan 6% daripada Cd berada dalam kelas sebagai banyak tercemar. Sementara itu, Cu dan Pb menunjukkan 6% daripada semua sampel dalam kelas sederhana tercemar dan logam berat lain menunjukkan pencemaran yang rendah. Gabungan keputusan antara logam berat dan penilaian logam berat menunjukkan bahawa aktiviti perindustrian dan pelepasan trafik mewakili sumber yang paling penting bagi Cu, Cd dan Pb manakala Cr dan Ni terhasil daripada sumber semula jadi. Peningkatan pengaruh antropogenik kepada alam sekitar, telah menyebabkan perubahan negatif dalam ekosistem semula jadi dan menurunkan biodiversiti Malaysia.

**Kata kunci:** Pencemaran, Logam berat, Taburan, ICP-MS, Indeks pencemaran

### Introduction

Heavy metals contamination of soils becomes a severe issue around the world as a result of anthropogenic activities that been emitted into atmosphere as aerosols and distributed in soil [1, 2, 3, 4]. They are distributed by atmosphere

within a distance and transported up to several kilometers away from their sources and transferred to the soil through wet or dry deposition [1, 5].

Heavy metals in soils have been considered as powerful tracers for monitoring impact of anthropogenic activity such as industrial emission (cement plant, fossil fuel and coal combustion chemical plants), vehicular emission, and atmospheric deposited. These lead to emission of heavy metals into the air and their subsequent deposition into soils [6, 7, 1]. Heavy metal is the most dangerous pollutant of anthropogenic environmental pollutants due to their toxicity and persistence in the environment [6, 8].

Past studies have revealed that human exposure to high concentrations of heavy metals will lead to their accumulation in the human body [9]. Heavy metal exposure to human occurs through three primary routes namely inhalation, ingestion and skin absorption. The threat that heavy metals pose to human and animal health is aggravated by their low environmental mobility, even under high precipitations, and their long term persistence in the environment [10]. Rising metal concentration in soil is serious and current concern for governmental and regulatory bodies for environmental and human risk assessment [11]. Therefore, the use of simple and accurate methods for monitoring heavy metals has a great importance among the environmental studies [12]. The assessment of heavy metal contamination can be conducted using various methods such as total heavy metal concentration [4]. The present study assessed heavy metal pollution in soils employing Pollution index (PI).

In this study, determination of total concentrations of heavy metal in soil was carried out around Perlis. Based on the result, heavy metal assessment index (Pollution Index) was calculated. The result can then be used as a basis for improving the situation and guide environmental planners and government in reducing pollution in Malaysia.

## Materials and Methods

### Study Area

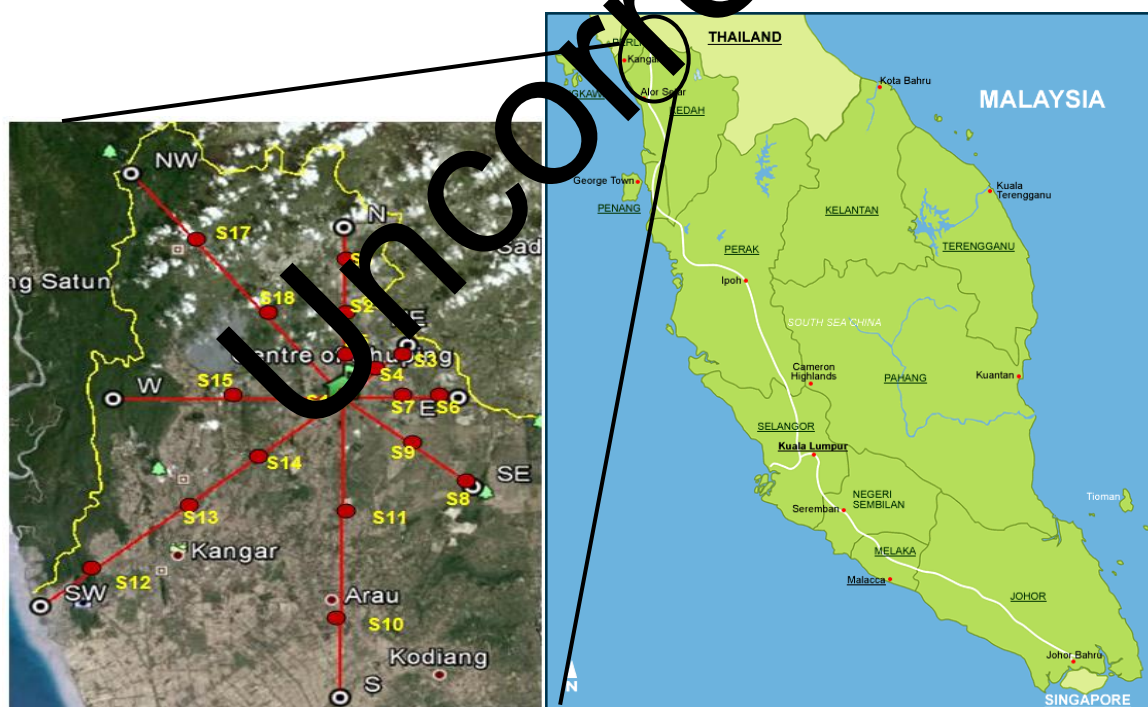


Figure 1: Location sampling site of soil

The study of heavy metal concentration has been performed in the whole Perlis state with 8 directions and Chuping as a centre according to GPS coordination as shown in Table 1. This area undergo various anthropogenic activities such as cement, chemical, quarry, power plant, transportation and agriculture activities that might contribute to heavy metal contamination. Figure 1 show a map of sampling points in the study area.

Table 1: Coordination of Sampling Site

Station Code	Location	Coordinates
S1	12KM N	N 6°38' 50.5" E 100°17' 37.8"
S2	6KM N	N 6°35' 57.3" E 100°17' 34.3"
S3	10KM NE	N 6°36' 42.3" E 100°17' 35"
S4	5.4KM NE	N 6°34' 39.6" E 100°16' 31.2"
S5	2KM N	N 6°33' 27.9" E 100°17' 15.5"
S6	7KM E	N 6°32' 27.8" E 100°21' 11"
S7	4KM E	N 6°32' 40.7" E 100°19' 37.5"
S8	10KM SE	N 6°29' 45.5" E 100°19' 32.3"
S9	5KM SE	N 6°29' 51.5" E 100°19' 35.7"
S10	20KM S	N 6°27' 33.1" E 100°17' 18.5"
S11	10KM S	N 6°27' 10.4" E 100°16' 31.4"
S12	25KM SW	N 6°21' 33.4" E 100°8' 52"
S13	20KM SW	N 6°23' 57.2" E 100°10' 49.7"
S14	10KM SW	N 6°28' 12.2" E 100°14' 44.8"
S15	7KM W	N 6°32' 47.4" E 100°13' 41.5"
S16	CENTER CHUPING	N 6°32' 40.9" E 100°17' 45"
S17	20KM NW	N 6°40' 59.5" E 100°11' 17.5"
S18	10KM NW	N 6°37' 00.5" E 100°14' 13.2"

#### Soil sampling and chemical analysis

A total 18 samples were collected at depth of 0-15cm using hand auger, stored in polyethylene bags and were oven dried at 60°C for 2days, followed by grinding with mortar and pestle and sieved using a 2 mm sieve. The soil samples were digested with the mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> using EPA method 3050B [13]. The solution obtained was filtered through a 0.45µm cellulose membrane filter and diluted to 10mL with miliQ water then stored at 4° before analysis. Concentration of in the digestion solution was determined by inductively couple plasma mass spectroscopy (ICP-MS). Analysis of the samples including soils digests and blanks was set up in duplicates.

#### Heavy metal pollution assessment

To assess contamination level of heavy metals, a pollution index (PI) of each metal was attributed to each metal using Equation 1 [14] below:

$$PI = C_n / B_n \quad (1)$$

where C<sub>n</sub> (mg/kg) is the measured concentration of each heavy metal and B<sub>n</sub> is background value for each metal. The PI of each metal was classified as either low (P ≤ 1), moderate (1 < PI ≤ 3) or high contamination (PI > 3).

## Results and Discussion

### Heavy metal in soil

The concentration of heavy metals in the soil of Perlis is listed in Table 2. All data in Table 2 were compared with allowable limit from Netherlands and China (Table 3) proposed by (Wang et al 2012, ECDGE 2010) since there are no information available in Malaysia on soil background values for heavy metal concentration [15, 16, 17]. The maximum concentration of Cu (240.59 mg/kg) and Cd (0.63mg/kg) level were higher compared with limit from Netherlands and China. Thus, attention has to be taken in order to control the level because it may results a dangerous effect for future. Meanwhile, Pb, Cr and Ni relatively below limit from other country (Table 3). Thus, we can summarized that, most of the Perlis state is still in save level, except on certain location that contribute high value of Cu and Cd which exceed allowable limit.

The result showed that all 5 elements (Cu, Pb, Cr, Ni, Cd) were highly distributed on centralized of sampling location which is on Station 2,4,5,7 and 16. This centralized area was located near the Chuping industrial area and near major road that loads a heavy traffic. Cu generally has the highest value while Cd generally has the least and the order observed for this study is Cu>Pb>Cr>Ni>Cd. The high concentration of copper was obtained at Station 2, 7 and 16 with 240.59, 110.25 and 33.46 mg/kg respectively. Cr was high at Station 4 and 5 with 3.92 and 2.69 mg/kg respectively. Meanwhile, Ni abandon at Station 5 (2.40 mg/kg) and 2 (2.08 mg/kg). Pb and Cd high at Station 16 with 27.47 mg/kg and 0.63 mg/kg respectively. According to previous report found that, heavy metal emit from cement industry which undergo process and production require energy from burning fossil fuel [5,18, 19] and vehicle emission [5, 6, 20]. This activity considered as major emission sources in atmosphere and soil [6, 18].

Table 2: Heavy metal concentration in soil (mg/kg)

Sample No.	Heavy metal concentration (mg/kg)				
	Cu	Pb	Cd	Cr	Ni
S1	3.58	0.68	0.02	1.05	1.98
S2	240.59	0.82	0.02	1.05	2.08
S3	1.16	0.88	0.02	2.01	1.62
S4	0.38	0.66	0.05	3.92	1.09
S5	1.82	1.74	0.08	2.69	2.40
S6	0.71	0.72	0.02	0.74	0.69
S7	110.25	0.37	0.02	1.32	1.59
S8	0.66	0.49	0.02	1.28	1.29
S9	0.52	0.44	ND	0.95	1.03
S10	1.18	1.10	0.02	1.58	1.72
S11	0.53	0.7	0.01	0.83	2.09
S12	1.82	1.75	0.06	1.63	2.22
S13	0.89	1.22	0.03	1.36	1.75
S14	2.91	0.80	0.03	0.91	1.37
S15	0.98	0.76	0.02	1.35	0.82
S16	33.46	27.47	0.63	1.38	1.54
S17	1.16	1.00	0.02	0.64	1.33
S18	0.86	2.90	0.06	0.93	1.72
Max	240.59	27.47	0.63	3.92	2.40
Min	0.38	0.39	0.01	0.64	0.69
SD	60.46	6.25	0.14	0.85	0.48

ND – no data (heavy metal not detected)

Besides that, some element elevated on opposite side of centralized stations such as Ni at station 11 (2.09 mg/kg) and station 12 (2.22 mg/kg). Station 12 located near power plants at Kuala Perlis that having high traffic density from that plant. In addition, ferry transportation at station 12 also gives contribution in elevated of Ni. As reported by A. Mandal et al., [5] heavy vehicular give large contribution through traffic emission. But Ni are mainly originated from natural sources, thus the concentration not greatly vary from each station [7]. Thus from the overall result, we can state that contamination level in Perlis is still in control level, just on certain location that located near industrial areas and major road that produce high level of heavy metal. For further view on contamination level in this study area, heavy metal assessment index will be carried out and explain further detail below.

Table 3: Allowable limits of heavy metal concentrations in soil (mg/kg).

Heavy metal	Netherlands <sup>b</sup>	Environmental Quality Std of Soils GB15618-1995 <sup>a</sup>	This study
Cu	0.5	0.6	0.63
Pb	40	100	240.59
Cd	40	350	27.47
Cr	15	60	2.40
Ni	30	250	3.92

<sup>a</sup>Wang et al. 2012, <sup>b</sup>ECDGE 2010

#### Heavy metal assessment

The concentration of heavy metal in soil in each station influence by various sources such as anthropogenic and naturally. Thus, a pollution index (PI) was applied to the data set to discover possible sources that might influence different distribution of elements over study area around Perlis state. The Pollution index calculated relative to the background values of heavy metals in the soils and the result as shown in Table 4.

High PI values (higher than 3) were observed in 11% of the samples for Cu, 6% for Cd (Fig 2). These indicate that Cu and Cd pollution relatively serious in Perlis soil when compare with other elements. The PI values higher generally in centralized station which is at station 2,4,5,7 and 16 where there are heavy traffic and many industrial activities than in other districts, indicating the presence of serious heavy metal pollution [21,22]. Therefore, highly contaminated samples clearly been polluted by anthropogenic emission [7]. The PI value of Cu, Pb, Cd, Cr, and Ni ranged from 0.01 to 9.01, 0.02 to 1.4, 0.06 to 5.25, 0.01 to 0.08 and 0.03 to 0.09 respectively. For Pb about 6% are classified as moderately or heavily contaminated (Fig 2) indicating there is potential the area been polluted by Pb if no remediation effort been implement. Besides that, Cr and Ni are 100% at low contamination level (Fig 2) indicating no obvious pollution for Cr and Ni. From figure 2, generally majority of study area is still in secure state where more than 70% of study area for each elements give  $PI \leq 1$  indicate low contamination. Meanwhile, less than 15% of Cu, Pb and Cd give moderately and high contamination level.

Table 4: Heavy metal concentrations (mg/kg) Pollution index (PI) of soil

Heavy metal	No. of samples	Background values <sup>a</sup>	Concentration			Pollution index values		
			Min	Max	Mean	Min	Max	Mean
Cu	18	26.7	0.38	240.59	22.42	0.01	9.01	0.84
Pb	18	19.4	0.39	27.47	2.58	0.02	1.40	0.13
Cd	18	0.12	ND	0.63	0.06	ND	5.25	0.52
Cr	18	49.3	0.64	3.92	1.43	0.01	0.08	0.03
Ni	18	26.6	0.69	2.40	1.57	0.03	0.09	0.06

ND – not detected, <sup>a</sup>CNEMC,1990[23]

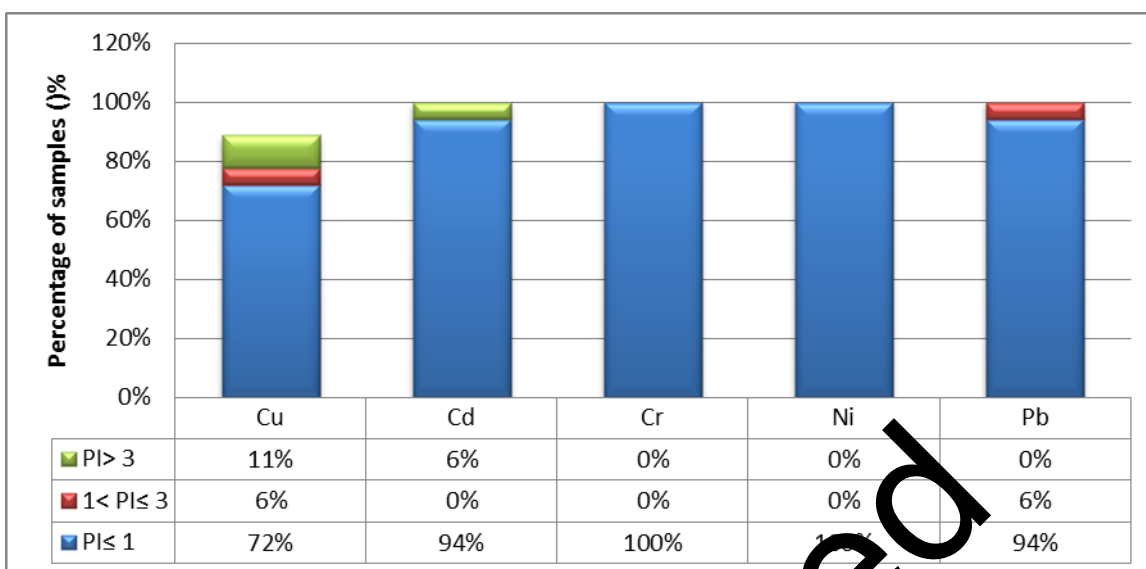


Figure 2: Heavy metal percentage based on Pollution Index.

### Conclusion

Eighteen soil samples collected from whole Perlis state were analyzed for Cu, Cr, Ni, Cd and Pb. Cr, Ni and Pb concentrations in soil were lower than allowable limits whereas Cu and Cd concentration exceeded their corresponding values. Heavy metal concentrations were assessed using pollution index (PI). In respect of Pollution index only Cu (11%) and Cd (6%) were classes as heavily contaminated. Meanwhile, Cu and Pb showed 6% from all station result a moderately contaminated and the others element give low contamination. From this result, found that level of heavy metal in soil near centralized mining industrial areas give maximum value compared with other location in Perlis. Results of combined heavy metal concentration and heavy metal assessment indicate that industrial activities and traffic emission represent most important sources for Cu, Cd and Pb whereas Cr, Ni mainly from natural sources. Increasing anthropogenic influences on the environment, especially pollution loadings, have caused negative changes in natural ecosystems, decreased biodiversity, simplified structure and lowered productivity. Consequently, it is imperative to continually assess and monitor the levels of heavy metals in the environment due to anthropogenic activities for evaluation of human exposure and for sustainable environment.

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