Faculty of Resource Science and Technology

DETERMINATION OF CADMIUM IN SOIL OF KOTA SAMARAHAN

Ho Chiw Peng (36241)

Bachelor of Science with Honours
(Resource Chemistry)
2015

UNIVERSITI MALAYSIA SARAWAK

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Final Year Project Report ☑

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Determination of Cadmium in Soil of Kota Samarahan

Ho Chiw Peng (36241)

A dissertation submitted in partial fulfillment of the requirement for the degree of Bachelor of Science (Hons.)

RESOURCE CHEMISTRY

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Declaration

I hereby declare that the work in this thesis is my original research work, unless otherwise indicated or acknowledged as referenced work. It was carried out in accordance with the regulations of Universiti Malaysia Sarawak. This thesis has not been submitted at this or any other university or academic institution for any other degree or qualification.

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List of Abbreviation

ATSDR………………………….. Agency for Toxic Substances and Disease Registry

Cd……………………………….. Cadmium

Cr………………………………... Chromium

Cu……………………………….. Copper

DIR……………………………… Department of Industrial Relations

Fe………………………………... Ferrum

GPS……………………………... Global Positioning System

H_2O_2…………………………..... Hydrogen Peroxide

HCl……………………………… Hydrochloric acid

HNO_3…………………………..... Nitric acid

IARC…………………………..... International Agency for Research on Cancer

ICP-OES……………………....... Inductively coupled plasma optical emission spectrometry

I_{geo}……………………………..... Geoaccumulation index

Lab Soil Environ Sci Plant Nutr... Lab of Soil Environmental Science and Plant Nutrition

MAL…………………………….. Maximum Allowable Limit

Pb……………………………...... Lead

SOM…………………………….. Soil organic matter

SPSS…………………………….. Statistical Package for the Social Sciences

UNIMAS………………………... Universiti Malaysia Sarawak

USEPA………………………….. United State Environmental Protection Agency

Zn……………………………….. Zinc

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Determination of cadmium in soil of Kota Samarahan

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Abstract

Contamination of soil by heavy metals is a major environmental problem worldwide that need to be concerned. Among trace of elements that exist on the earth, cadmium (Cd) is said to be mostly originated from anthropogenic activities which can bring harmful effects to environment and human health. In this study, the samples were collected in 20 sampling sites at Kota Samarahan, Kuching, Malaysia. The samples were subjected to acid digestion and analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The Cd concentrations were ranged from 0.028-0.664 mg/kg where the mean Cd concentration for soils in UNIMAS and Muara Tuang area are 0.286 mg/kg and 0.188 mg/kg respectively. Both the mean Cd values from UNIMAS (P=0.018) and Muara Tuang (P=0.014) areas showed significant difference with the upper continental crust value. However, independent *t*-test analysis showed that the mean Cd concentration in UNIMAS area is not significantly different from that of Muara Tuang area (P=0.180). Soil contamination assessment was derived via geoaccumulation index (I_{geo}) and certain location was found to be moderately to strongly contaminated with the maximum I_{geo} values of 2.12. Besides, results obtained from Pearson's correlation indicated that there is no significant difference between soil parameters (pH, SOM and clay content) and Cd concentration. The soil in Kota Samarahan is categorised as moderately contaminated to strongly contaminated soil with overall mean Cd concentration of 0.237±0.160 mg/kg based on analysis and assessment conducted on UNIMAS and Muara Tuang area.

Keywords: Cadmium, soil, acid digestion, ICP-OES, I_{geo}

Abstrak

Pencemaran tanah oleh logam berat adalah masalah alam sekitar utama di seluruh dunia yang perlu diambil berat. Antara kesan unsur-unsur yang wujud di bumi, kadmium (Cd) dikatakan kebanyakannya berasal daripada aktiviti antropogenik yang boleh membawa kesan buruk kepada alam sekitar dan kesihatan manusia. Dalam kajian ini, sampel telah dikumpulkan dalam 20 tapak persampelan di Kota Samarahan, Kuching, Malaysia. Sampel tertakluk kepada pencernaan asid dan dianalisis oleh ICP-OES. Kepekatan Cd adalah antara 0.028-0.664 mg/kg dimana kepekatan Cd min bagi tanah di kawasan UNIMAS dan Muara Tuang masing-masing adalah 0.286 mg/kg dan 0.188 mg/kg. Kedua-dua nilai Cd min dari UNIMAS (P=0.018) dan Muara Tuang (P=0.014) menunjukkan perbezaan yang signifikan dengan nilai kerak benua atas. Walau bagaimanapun, analisis independent t-test menunjukkan bahawa kepekatan Cd min di kawasan UNIMAS tidak ketara berbeza daripada kawasan Muara Tuang (P=0.180). Penilaian pencemaran tanah telah diperolehi melalui indeks geoaccumulation (I_{geo}) *dan lokasi tertentu didapati sederhana sehingga kuat tercemar dengan maksimum* I_{geo} *2.12. Selain itu, keputusan yang diperolehi daripada korelasi Pearson yang menunjukkan bahawa tidak terdapat perbezaan yang signifikan antara parameter tanah (pH, SOM dan kandungan tanah liat) dan kepekatan Cd. Tanah di Kota Samarahan dikategorikan sebagai sederhana tercemar sehingga kuat tercemar tanah dengan kepekatan Cd min keseluruhan 0.237±0.160 mg/kg berdasarkan analisis dan penilaian yang dijalankan di kawasan UNIMAS dan Muara Tuang.*

Kata kunci: Kadmium, tanah, pencernaan asid, ICP- OES, I_{geo}

1.0 Introduction

Soil is said to serve as environmental contaminant reservoir due to human activities (Al-Khashman & Shawabkeh, 2006; Akan *et al*., 2013; Banat *et al.*, 2005; Chen *et al.*, 2005; Hu *et al.*, 2013; Najib *et al.*, 2012; Shi *et al.*, 2008; Wuana & Okieimen, 2011). Contamination of soil by heavy metals is a major environmental problem worldwide that need to be addressed (Alloway, 1995). There are some heavy metals which are good for the soil but in most of the cases, accumulations of heavy metal in soil lead to formation of porous and unstable soil composition that causes threat to human health (Jashiratulain, 2010). According to Hu *et al.* (2013), the accumulation of heavy metals in surface soils is affected by various environmental variables, including parent material, soil properties, and human activities (industrial production, traffic, farming, and irrigation).

Among trace of elements that exist on the earth, cadmium (Cd) is said to be originated from anthropogenic activities which is significantly dangerous for people and animals (Deska *et al.*, 2011). As reported by Chang *et al.* (2004), since the accumulation of Cd can entering into human food chain and causing adverse health effects, there is a need to concern on it. Furthermore, Cd is completely absorbed in the lungs through inhalation and it will lead to arterial hypertension and affect the kidneys (Bernard, 1995; Brodie & Matousek, 1974; Helmers & Fresenius', 1994). Several researches showed that Cd exposure may be a major factor that contributed to the development of chronic kidney disease (Järup, 2003; Johri, 2010). International Agency for Research on Cancer (IARC, 1993) had classified Cd as a class 1 human carcinogen. Therefore, it is important to determine the Cd contents in soil in order to assess the Cd contamination level in soil and reduce the potential risk of adverse health that will bring to human being.

Over the years Kota Samarahan is once a rural area, however there have been various developing project that transformed a small village to a huge and urbanised location. Frederick Bayoi, chairman of the Samarahan District Council said that the transformation of this district with enormous annual property growth is the highest experienced in Sarawak (Chin, 2011). The soils qualities of this area need to be concerned and studied as there are a lot of anthropogenic activities involved for the dramatic development. Hence, this study is important to generate some useful data as a basis for the future research that might be carried on at the same area. Furthermore, there is no similar research that has been done before at Kota Samarahan area. The level of soil contamination by Cd is an unknown and should be studied and assessed. As stated by Najib *et al.* (2012), there is no any standard guideline regarding heavy metal content in soil in Malaysia.

In this study, the Cd content in soils of Kota Samarahan from both area around University Malaysia Sarawak (UNIMAS) and Muara Tuang were determined. The aim of this study was to determine the concentration of Cd in soil of Kota Samarahan and to compare the difference of Cd content in soil between area around UNIMAS and Muara Tuang. The level of Cd contamination in soils was assessed by calculating the Geoaccumulation Index (I_{geo}) and comparing with the upper continental crust value from Wedepohl (1995) studies.

2.0 Literature review

2.1 Heavy metals in soil

Heavy metals are known to be one of the most common soil contaminants (Damodaran *et al.*, 2014). A large series of elements with relative atomic mass greater than 40 and specific density greater than 5 g cm^{-3} are characteristic that made up heavy metals (Aslam *et al.*, 2013). Out of the ninety naturally occurring elements that existed, fifty-three of them are heavy metals (Weast, 1984). Anthropogenic activities including mining, iron and steel industry, chemical industry, smelting works, agriculture, traffic as well as domestic activities are the main sources of heavy metals in the environment (Akan *et al.*, 2013; Chopin *et al.*, 2007; Ene *et al.*, 2010; Najib *et al.*, 2012; Stihi *et al.*, 2006; Suciu *et al.*, 2008). Heavy metals such as Cd, Fe, Pb, Cu, Cr and Zn have been reported in many literatures as the potential hazards and found in polluted soils (Akoto *et al.*, 2008; Yekeen & Onifade, 2012). Heavy metal pollution and their resulting long-term cumulative health effects have become a main global health concerns (Jashiratulain, 2010).

2.2 Background of cadmium in soil

Cd is a metal that usually associated with Zn, Pb, and Cu ores and found in the earth's crust (ATSDR, 2012; Jashiratulain, 2010). Pure Cd exists as a soft and silver-white metal. Solubility of Cd compounds in water is ranged from quite soluble to practically insoluble. Cd is the chemical symbol for cadmium and it has atomic weight of 112.41 g/mol (USEPA, 2013). Cd does not corrode easily and can be used in batteries, pigments, metal coatings, and plastics (ATSDR, 2012). Applications of Cd compounds are in rechargeable nickel–cadmium batteries, in pigments for glass, and as a stabilizer in polyvinyl chloride (Akan *et al.*, 2013; Järup, 2003; Nabulo *et al.*, 2006; Wuana & Okieimen, 2011).

Cadmium generally occurs in the lithosphere, sedimentary rocks and soil at concentrations of 0.20 mg/kg, 0.30 mg/kg and 0.53 mg/kg respectively. However Cd enriches in soil via natural or anthropogenic sources, or both, has become a major environmental concern (Liu *et al.*, 2013). Cd is reported as insidious and widespread health hazards trace elements (USEPA, 2013). Cd can be found in oil lubricants, car components, gasoline, incinerator emissions and industrial therefore it is one of the good indicators of contamination in soils (Li *et al.*, 2001). In many literatures showed that the concentration of Cd decreased with increasing of distance from the road where the soil were collected (Chen *et al.*, 2010; Nabulo *et al.*, 2006). However, Deska *et al.* (2011) reported that the Cd content ranged from 0.016 to 0.909 mg/kg, and it did not significantly dependent on the distance from the road. Research done by Naser *et al.* (2012) also found that the Cd content did not affected by the distance from road.

The determination of Cd content in soil which done by Najib *et al.* (2012) in Kangar, Perlis, Malaysia ranged from 0.03 to 0.90 mg/kg which was still below Maximum Allowable Limit (MAL) in soil (3.00 mg/kg). Hence, this study clearly indicates that Cd content was still under safe level and not much affected by anthropogenic activities. Another assessment conducted by Ezekiel *et al.* (2013) shows that the soil around sawmill area is moderately polluted by Cd with a concentration ranged from 0.07 - 0.47 mg/kg.

An assessment on heavy metal contaminations in urban soils is conducted by Wei and Yang (2010). They found that the Cd content is ranged from 0.15 mg/kg to 8.59 mg/kg. The mean concentration of Cd of the urban soils from all the cities of China which is 1.58 mg/kg are said to be exceed the background values of 0.097 mg/kg.

In the studies of Ripin *et al.* (2014), soils around Perlis had been analyzed and the pollution assessment was assessed. The maximum concentration of Cd was at high level of 0.63 mg/kg which has exceeded the background value of 0.12 mg/kg. However, majority state in Perlis is still considered safe with the mean concentration of Cd (0.06 mg/kg) which is still below the background value.

Table 1 Summary of Cd concentration compared with the background values of various countries.

City/Country	Mean Cd concentration (mg/kg)	Background value (mg/kg)	Soil condition	Reference
Perlis, Malaysia	0.06	0.12	safe	Ripin *et al.* (2014)
Jiang Xi, China	0.24	0.17	unfavorable	Wu *et al.* (2014)
Hong Kong	0.36	0.80	safe	Lee *et al.* (2006)
Kangar, Perlis, Malaysia	0.52	3.00	safe	Najib *et al.* (2012)
China	1.58	0.097	unfavorable	Wei & Yang (2010)
Jordan	11.61	0.30	unfavorable	Odat (2013)

2.3 Sources of cadmium contamination

Cd is naturally possessed in soil mainly through geological weathering (Liu *et al.*, 2013). However in many researches, anthropogenic influences are reported as the main contribution of heavy metals, specifically Cd, into the environment (Ezekiel *et al.*, 2013; Najib *et al.*, 2012; Ripin *et al.*, 2014; Wei & Yang, 2010). In the 20th century, Cd emissions have increased dramatically due to failure of recycling cadmium-containing products, but usually dumped together with household waste (Järup, 2003). Based on research done by Jashiratulain, (2010), in duration of a year about 12,500 tons of Cd is flowing into rivers via rocks weathering. Besides, Cd is released into air through volcanoes and forest fires. Cd is also released through anthropogenic activities. Cd is known to come from industrial, tyre abrasion, incinerator emission and lubricants (Odat, 2013; Yan *et al.*, 2012). Cd is present in fuel as anti-knock agent and released to the environment during heavy traffic as well (Ezekiel *et al.*, 2013). Furthermore, heating in metal refining process released Cd that usually associated with copper into the atmosphere (Akan *et al.*, 2013). Su *et al.* (2014) reported that Cd is an important heavy metal contaminant in the soil as well. The major contributions of Cd into soils are from application of phosphoric fertilizers. The Cd content in soils rises gradually with the utilization of a bulky quantity of compound fertilizers and phosphate fertilizers, thus Cd uptake by plants increases proportionally. Moreover, in the past few years, the mulch has been widely promoted and implemented in large expanses. The heat stabilizers containing Cd and Pb are utilized in the process of mulch production hence causes white pollution of soils which further polluted the soils.

2.4 Health effects of cadmium contamination

Cigarette smoking is one of the main sources of Cd exposure. Cd goes into the lungs through tobacco. After that, blood will bring it through other part of the body and the situation getting worse due to potentiating Cd that come from cadmium-rich food (Järup, 2003; Jashiratulain, 2010). In non-smokers, contributions of Cd into human body are mainly through cadmium-rich food (ATSDR, 1997; Järup, 2003; Jashiratulain, 2010). Recent data showed that even at a lower level of Cd exposure, in the most cases, harmful health effects such as kidney damage or even bone effects and fractures may occur. For examples, Itai-Itai disease is a disease that makes people suffers from severe pain, bone fractures, severe osteomalacia and proteinuria due to long term exposure to toxic Cd (Akan *et al.*, 2013). Cd is recognized by Agency for Toxic Substances Management Committee that has listed Cd as the sixth most toxic substance that damages human health (Su *et al.*, 2014). Furthermore, Cd was regarded as class 1 human carcinogens that have carcinogenic effects (IARC, 1993). Similarly, high concentrations of Cd in vegetables and fruits were potentially contributed to upper gastrointestinal cancer (Turkdogan *et al.*, 2003).

Cd causes damage to the lungs or even life threatening when people inhale it. Cd reach liver first via transportation of blood. Inside the bloodstream, it form complexes when bond to proteins which then transport to the kidneys. Accumulation of Cd in kidneys subsequently damages kidney filtering mechanisms. Further kidney damage occurs when the essential proteins and sugars are stimulated to be excreted from the body. Excretion of accumulated Cd in kidneys from a human body required a very long time (Jashiratulain, 2010).

2.5 Physical characteristics of soils

Degree of mobility of metals and their compounds are different in the soil fractions. Basically their bioavailability is closely dependent on several soil properties including pH values, soil organic matter (SOM) contents and clay content (Fijałkowski *et al.*, 2012; Oliveira *et al.*, 2013).

2.5.1 Soil pH

Soil pH is known to be significantly influences the dissolution metals in soil, their mobility and availability to plants (Fijałkowski *et al.*, 2012; Isen, *et al.*, 2013). Soil pH is measure of the acidity or alkalinity of the soil. Soil pH is known as negative logarithm of the hydrogen concentration. A soil is known to be acidic as the concentration of hydrogen ion increase. The pH scale is ranged from 0 to 14 where pH 7 is the neutral point. From pH scale of 0 to 7, the acidity is decreasing and from pH scale of 7 to 14, the alkalinity is increasing (Akan *et al.*, 2013). Low soil pH values are usually considerably affected by anthropogenic factors such as acid rain and agrotechnical treatments. Likewise, anthropogenic activities such as liming may lead to the opposite phenomenon which increasing the soil pH. The mobilisation intensity of heavy metals varies with increasing of hydrogen ions concentration. Generally, the mobility of metallic elements is much higher in highly acidic soils compare to neutral and alkaline condition (Fijałkowski *et al.*, 2012). In other words, heavy metals are said to be more likely retain or remain immobilised in the soil with higher pH (Gawlik & Bidoglio, 2006).

2.5.2 Soil organic matter content

Soil organic matter (SOM) is said to have a great sorption capacity with metals compare to others reactive soil constituents. The solubility, mobility and bioavailability of metals and also SOM turnover are highly affected by metal–SOM interaction (Quenea *et al.*, 2009). The organic matter solubility behaviour in soil which metal is complexed with organic matter may cause big consequences on the metals solubility (Ashworth & Alloway, 2008). Organic matter can either immobilize the heavy metals or result in their release, is all dependent on the solubility of the associated organic matter (Fijałkowski *et al.*, 2012). According to Fijałkowski *et al.* (2012), high quantity of organic matter existed in soil will reduce absorption of heavy metals by plants. Availability of metallic elements in soil is higher for land that consists of abundant organic matter. For a soil with low content of organic fraction leading to a soil that have low buffering, low cation exchange capacity, low water capacity and susceptible to erosion consequently reduces activity of microbes. Cd is one of the metals that have high binding tendency towards soil with high organic matter content. Therefore, one of the important roles of the organic matter in soil is for determination of bioavailability of heavy metals (Ezekiel *et al*., 2013).

2.5.3 Particle size distribution

The soil texture is made up from three separate size classes in different combination of sand, silt, and clay. The size range of sand, silt and clay is 2.000 mm-0.050 mm, 0.050 mm-0.002 mm and less than 0.002 mm respectively (Adeyi *et al.*, 2014). In most cases, clay fraction that mainly composed by clay minerals is used to be the important part due to its high binding ability to heavy metals (Fijałkowski *et al.*, 2012). Helios-Rybicka, E., & Kyziol J. (1991) also stated that clay minerals are an important metals carrier in soils. Clay, silt and dust fraction possess granulometric composition characteristic that lead to high sorption capacity and strong binding ability to metallic elements inclusive those with a high content of organic matter. The increase of metal cations valence, atomic weight and ionic potential increase its binding ability. The descending orders of metal cations affinity towards clay minerals are $Cu^{2+} > Cd^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$ (Fijałkowski *et al.*, 2012).

2.6 Heavy metal contamination assessment

2.6.1 Geoaccumulation index

Index of geoaccumulation (I_{geo}), is a common contamination assessment methods which was proposed by Müller in 1969. The I_{geo} is used in evaluating the soil quality by assessing the contamination levels of heavy metal in the studied soils. I_{geo} can be computed by the equation below:

$$I_{geo} = \log_2(\frac{\mathrm{Cn}}{1.5\mathrm{Bn}}) ,$$

where Cn is the measured concentration of element in soil, Bn is the geochemical background concentration in shale, the 1.5 is the factor compensating the background content caused by lithogenic effects (Banat *et al.*, 2005; Elbagermi *et al.*, 2013; Loska & Wiechula, 2003; Odat, 2013; Wei *et al.*, 2011). The I_{geo} is classified into seven grades (0 to 6) where the highest class of 6 reflects 150 folds of metal concentration corresponding to the background value (Wei *et al.*, 2011).

Table 2 The I_{geo} classes corresponding to its computed values (Wei *et al.* 2011).

I_{geo} value	I_{geo} class	Soils contamination level
0	0	Practically uncontaminated
0-1	1	Uncontaminated to moderately contaminated
1-2	2	Moderately contaminated
2-3	3	Moderately to strongly contaminated
3-4	4	Strongly contaminated
4-5	5	Strongly to extremely contaminated
5-10	6	Extremely contaminated

3.0 Materials and Methods

3.1 Study area

A total of 20 samples soil were collected from housing area and suburban area in Kota Samarahan, Sarawak, Malaysia. 10 samples were collected around UNIMAS and 10 samples around Muara Tuang respectively. Samplings of soils were conducted randomly and Global Positioning System (GPS) was used to record the sampling locations. The coordination of each sampling locations are showed in Table 3. A map that indicated the distributions of sampling sites in Kota Samarahan was drawn (Figure 1).

Table 3 GPS coordination of each sampling locations.

No.	Sampling locations	GPS coordination	
		Latitude	Longitude
1	UNIMAS 1	N01 °27' 54.3"	E110 °24' 59.9"
2	UNIMAS 2	N01 °27' 56.2"	E110 °25' 19.6"
3	UNIMAS 3	N01 °27' 45.7"	E110 °25' 46.5"
4	UNIMAS 4	N01 °28' 10.5"	E110 °25' 55.2"
5	UNIMAS 5	N01 °28' 12.1"	E110 °25' 31.5"
6	UNIMAS 6	N01 °27' 57.6"	E110 °24' 51.7"
7	UNIMAS 7	N01 °27' 45.1"	E110 °24' 40.6"
8	UNIMAS 8	N01 °27' 48.7"	E110 °24' 33.9"
9	UNIMAS 9	N01 °27' 53.5"	E110 °24' 25.1"
10	UNIMAS 10	N01 °27' 55.6"	E110 °24' 14.3"
11	Muara Tuang 1	N01 °28' 04.0"	E110 °28' 45.2"
12	Muara Tuang 2	N01 °27' 41.1"	E110 °28' 50.0"
13	Muara Tuang 3	N01 °27' 51.6"	E110 °29' 27.9"
14	Muara Tuang 4	N01 °27' 55.7"	E110 °29' 16.5"
15	Muara Tuang 5	N01 °28' 06.5"	E110 °29' 05.8"
16	Muara Tuang 6	N01 °28' 14.8"	E110 °29' 35.3"
17	Muara Tuang 7	N01 °28' 20.4"	E110 °28' 56.3"
18	Muara Tuang 8	N01 °29' 00.7"	E110 °29' 06.0"
19	Muara Tuang 9	N01 °28' 24.7"	E110 °28' 30.8"
20	Muara Tuang 10	N01 °27' 57.7"	E110 °28' 21.0"

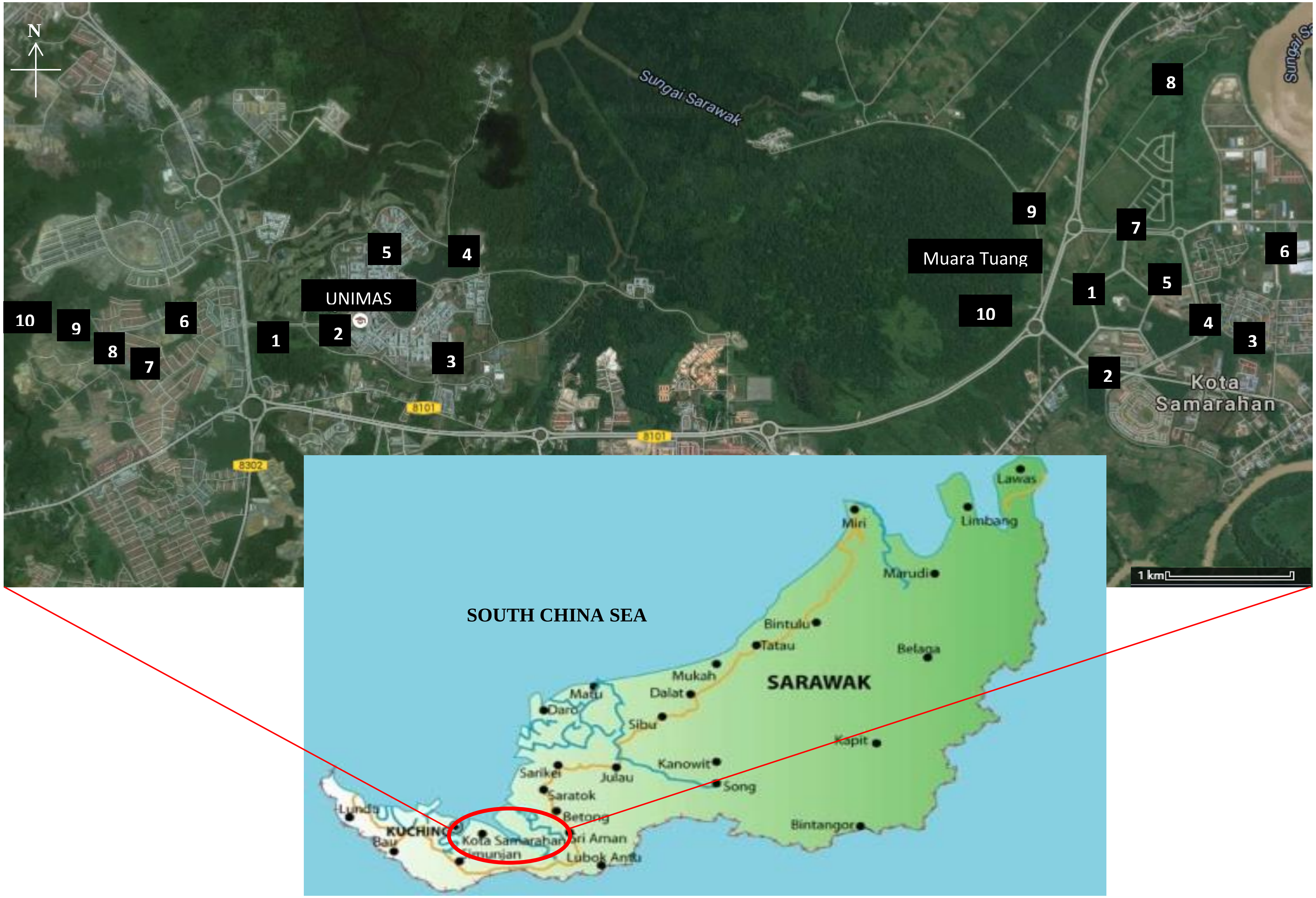

Figure 1 Distribution of sampling sites in Kota Samarahan.