
**UNIVERSITI PUTRA MALAYSIA**

# *APPLICATION OF CHEMOMETRIC TECHNIQUES ON SPATIAL AND TEMPORAL DISTRIBUTION OF SELECTED HEAVY METALS OF LANGAT RIVER BASIN, MALAYSIA*

***FARADIAH BINTI MD. DALI***

**FPAS 2014 13**

# Application of Chemometric Techniques on Spatial and Temporal Distribution of Selected Heavy Metals of Langat River Basin, Malaysia

**Faradiah binti Md. Dali**

**Master of Science**
**Universiti Putra Malaysia**
**2014**

# APPLICATION OF CHEMOMETRIC TECHNIQUES ON SPATIAL AND TEMPORAL DISTRIBUTION OF SELECTED HEAVY METALS OF LANGAT RIVER BASIN, MALAYSIA

By

**FARADIAH BINTI MD. DALI**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science**

**November 2014**

Abstract of thesis presented to the University Putra Malaysia in fulfillment of requirement for the degree of Master Science

**APPLICATION OF CHEMOMETRIC TECHNIQUES ON SPATIAL AND TEMPORAL DISTRIBUTION OF SELECTED HEAVY METALS OF LANGAT RIVER BASIN, MALAYSIA**

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**November 2014**

**Chairman:** **Hafizan Juahir, PhD**

**Faculty:** **Environmental Studies**

This study investigates the spatial and temporal patterns of heavy metals concentration in Langat River based on primary data. Application of different multivariate approaches namely cluster analysis (CA), discriminant analysis (DA), and principal components analysis (PCA) were used in interpreting complex environmental data matrices of Langat River in Malaysia. This research was conducted from February 2012 to January 2013 at the Langat River Basin which is located in Selangor, Peninsular Malaysia. The concentrations of heavy metals were determined by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Nine heavy metals elements selected in this study include arsenic (As), mercury (Hg), cadmium (Cd), chromium (Cr), lead (Pb), zinc (Zn), iron (Fe), manganese (Mn), and nickel (Ni). The Hierrachical Agglomeraitve Cluster Analysis (HACA) successfully grouped the Langat River data into three spatial clusters based on monitoring stations with low concentration metals (LCM), moderate concentration metals (MCM) and high concentration metals (HCM). Similarities and dissimilarities among heavy metals from each monitoring stations were studied using Cluster Analysis (CA). Five out of the nine heavy metals namely Hg, Fe, Zn, Pb and Mn were found to be significant in influencing the water characteristic by means of stepwise forward and stepwise backward DA with classification matrix accuracy of 89.00% for spatial variations. Seven out of nine heavy metals assigning 84% include Hg, Fe, Zn, Cr, Pb, Ni and Mn as the most critical for the temporal discrimination based on three different water level conditions (Low, Normal, and High). PCA was conducted to identify the possible main sources of heavy metal of each monitoring station that may affect the river water quality especially attributed from anthropogenic activities such as industries, mining activities, sewage treatment plant, landfills and others based on the three clustered regions. Out of the nine parameters resulted in three PCs explaining approximately 81.59% of the cumulative variances for HCM. Meanwhile, four PCs obtained 65.61% of the total variance

for MCM region. Last but not least, for LCM, three PCs are obtained with 78.04% of total variance. The finding of this study showed that the applications of chemometrics techniques are valuable in assisting the Department of Environment (DOE) in reporting the status of Langat River water quality and can be utilized as a reference for future studies in monitoring heavy metals in rivers.

**Keywords:** Chemometric, Cluster Analysis, Discriminant Analysis, Principal Analysis, Heavy Metals

Abstrak tesis yang dukemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

**PENGGUNAAN TEKNIK KIMOMETRIK BAGI TABURAN RUANG DAN MASA LOGAM BERAT TERPILIH DI LEMBANGAN SUNGAI LANGAT, MALAYSIA.**

Oleh

**FARADIAH BINTI MD. DALI**

**November 2014**

**Pengerusi:** **Hafizan Juahir, PhD**

**Fakulti:** **Pengajian Alam Sekitar**

Kajian ini untuk mengenalpasti corak ruang dan masa kepekatan logan berat dalam Sungai Langat berdasarkan data primer. Dalam kajian ini, penggunaan multivariat yang berbeza iaitu analisis kelompok (CA), analisis diskriminan (DA), analisis komponen prinsipal (PCA) dalam mentafsirkan matriks kompleks Sungai Langat di Malaysia. Kajian ini telah dijalankan dari Februari 2012 hingga Januari 2013 di Sungai Langat yang terletak di Selangor, Semenanjung Malaysia. Kepekatan logam berat telah ditentukan dengan menggunakan Spektrometri Induktif Plasma Optik (ICP- OES). Terdapat sembilan logam unsur berat yang dipilih untuk kajian ini iaitu arsenik (As), merkuri (Hg), kadmium (Cd), kromium (Cr), plumbum (Pb), zink (Zn), besi (Fe), mangan (Mn), dan nikel (Ni). Analisis klaster (HACA) mengklasifikasikan kepada tiga kumpulan spatial berdasarkan stesen pemantauan dengan logam kepekatan rendah (LCM), logam kepekatan sederhana (MCM) dan logam kepekatan tinggi (HCM). Kajian ini telah mengklasifikasikan persamaan dan ketidaksamaan di antara logam berat dari setiap stesen pemantauan menggunakan analisis klaster (CA). Lima daripada sembilan logam berat iaitu Hg, Fe, Zn, Pb dan Mn dengan ketepatan matriks klasifikasi 89.00% untuk analisis diskriminasi bagi variasi ruang. Tujuh daripada sembilan logam berat dengan ketepatan matriks 84.00% iaitu Hg, Fe, Zn, Cr, Pb, Ni dan Mn sebagai yang paling kritikal bagi diskriminasi temporal berdasarkan tiga paras air yang berbeza (rendah, normal dan tinggi ). PCA telah dijalankan untuk mengenal pasti punca utama logam berat di setiap stesen pemantauan yang boleh menjejaskan kualiti air sungai terutamanya didapati daripada sumber kegiatan antropogenik seperti kilang-kilang, kegiatan perlombongan, loji rawatan air kumbahan, tapak pelupusan sampa dan lain-lain berdasarkan tiga kumpulan. Tiga PC mencatatkan 81.59 % daripada varian untuk HCM. Sementara itu, empat PC mencatatkan 65.61 % daripada jumlah varian bagi MCM. Akhir sekali, tiga PC mencatatkan 78.04 % daripada jumlah varian bagi LCM.

Daripada kajian ini, menunjukkan bahawa aplikasi kimometric dapat membantu Jabatan Alam Sekitar (JAS) dalam melaporkan status kualiti air Sungai Langat. Ia juga boleh digunakan sebagai rujukan untuk kajian masa depan dalam memantau logam berat di dalam sungai.

**Kata Kunci:** Kimometrik, Analisis Klaster, Analisis Diskriminan, Analisis Prinsip Komponen, Logam Berat

**ACKNOWLEDGEMENTS**

Alhamdulillah, I am so grateful and thankful to the Almighty Allah S.W.T. for giving me strength, courage, patience, and determination in ability to do preparation and completing this research successfully. It would not have been to write this master thesis without help and support of the kind hearted people around me.

First of all, I would like to express my deepest sincere appreciation goes to my supervisor, Dr. Hafizan bin Juahir for all I have learned from him and his continuous help and support in all stages of this thesis. I also would like to thank him for his encouraging and helping me in my interest and ideas. Then, I would like to thank my cosupervisor Dr. Faradiella Mohd Kusin and Prof. Dr. Norashikin Saim for their assistance, guidance, encouragement and providing critical comments whenever necessary throughout of completing this thesis.

I am also would like to thank all government agencies and staffs especially from Faculty of Environmental Studies (UPM) and Faculty Applied Science (UiTM) for its funded for doing my research. A special thanks to Alam Sekitar Malaysia Sdn. Bhd. (ASMA) that have been assisting with the site visits and providing me valuable information in order to strength my thesis. A special acknowledgement and respect to Mr. Zubir bin Othman whose advice and insight was invaluable to me. Thank a lot for your precious time in conducting and assisting me in doing analysis in the laboratory in Faculty Applied Science, Universiti Teknologi MARA. My deepest appreciation to the Ministry of Higher Education (MOHE), Graduate Research Fellowship (GRF) from Putra Malaysia for the financial support in order for me to complete this research.

I would like to be grateful to my parents Md. Dali bin Baba and Norhani bte Mohd Zaid for their constant support, encouragement, financial support, prayers and for being the most understanding parents during my ups and downs. Not forgotten to my family member Fauziah, Fadhiah and Muhammad Hakim for their supports and continuously encouraging me to keep on striving for excellence. My special thanks dedicated to my husband, Mohammad Roshide for always being beside me for his personal support, encouraging, motivates and great patience at all times.

I would like to thank all my fellow friends for always great support in all my struggles, advise, and lending me their hands in completing my thesis. There is no words can describe how much I thankful to all assistance that I have gained in completing my research. I believe only Allah can repay your all kindness for every single thing in order to achieve my dreams to come true. Honestly, these experiences have been nothing but the best in my life. Last but not least, thank you to all that have significantly or insignificantly contribute to the completion of this research.

Thank You.

I certify that a Thesis Examination Committee has met on April 2014 to conduct the final examination of Faradiah binti Md. Dali on her thesis entitled "Application of Chemometric Techniques on Spatial and Temporal Distribution of Selected Heavy Metals of Langat River Basin, Malaysia" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

**Puziah bt Abdul Latif, PhD**
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

**Shaharin bin Ibrahim, PhD**
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Internal examiner)

**Ahmad Makmom bin Abdullah, PhD**
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Internal examiner)

**Ekhwan Toriman, PhD**
Professor
Universiti Sultan Zainal Abidin (UniSZA)
(External examiner)

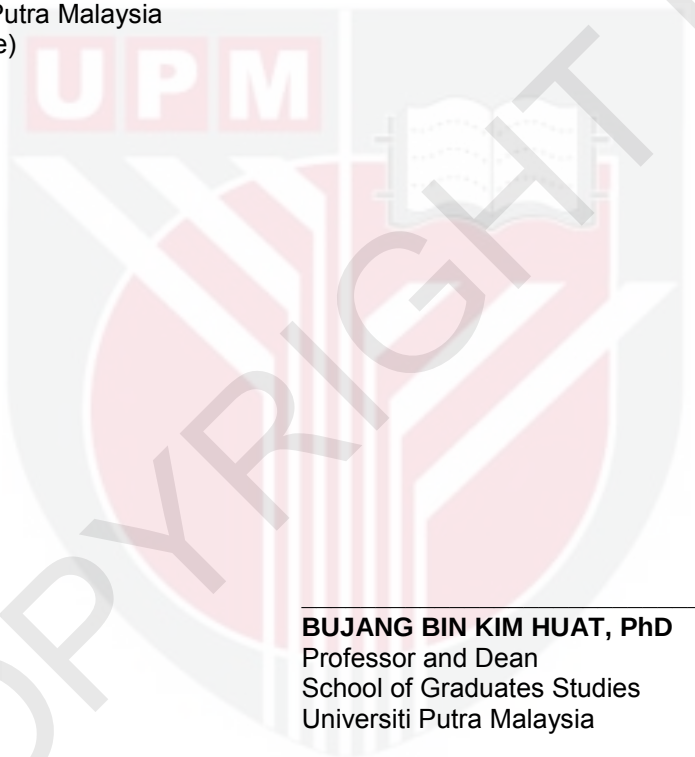
_____
**ZULKARNAIN ZAINAL, PhD**
Professor and Deputy Dean
School of Graduates Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory committee were as follows:

**Hafizan Juahir, PhD**
Senior Lecturer
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

**Faradiella Mohd Kusin, PhD**
Senior Lecturer
Faculty of Environmental Studies
Universiti Putra Malaysia
(Committee)



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| | |
|---|---|
| APHA | American Public Health Association |
| As | Arsenic |
| ASMA | Alam Sekitar Malaysia Sdn. Bhd. |
| CA | Cluster Analysis |
| COND | Conductivity |
| Cd | Cadmium |
| Cr | Chromium |
| DA | Discriminant Analysis |
| DF | Discriminant Function |
| DID | Department of Irrigation and Drainage |
| DO | Dissolved Oxygen |
| DOE | Department of Environment |
| FA | Factor Analysis |
| Fe | Iron |
| HACA | Hierarchical agglomerative cluster analysis |
| HCM | High concentration metal |
| Hg | Mercury |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectrometry |
| LCM | Low concentration metal |
| MCM | Moderate concentration metal |
| Mg/L | Milligram per liter |
| Mn | Manganese |
| Ni | Nickel |
| No. | Number |
| Obs. | Observation |
| Pb | Lead |
| PCA | Principal Component Analysis |
| PCs | Principal components |
| *R* | Coefficient of correlation |
| SAL | Salinity |
| S.D | Standard Deviation |
| TEMP | Temperature |
| TUR | Turbidity |
| UK | United Kingdom |
| UN | United Nations |
| USGS | United States Geological Survey |
| VF | Varifactor |
| WQPs | Water quality parameters |
| Zn | Zinc |

# CHAPTER I

# INTRODUCTION

## 1.1 General Background

Malaysia is encountering a persistent rapid change in area use associated with government advancement arrangements. In 2000, Selangor is the most rapidly developed and densely populated with 3.9 million occupants among the states in Malaysia (Department of Statistic Malaysia, 2000). In Malaysia, rivers are the primary wellsprings of open water supplies since river water give about 98% of the nation's water necessities. Thusly, tainting of river water quality is under obligation of the Department of Environment (DOE), Malaysia. The accessibility of good water quality is a paramount peculiarity for counteracting infections and enhancing personal satisfaction (Oluduro and Aderiye, 2007). Characteristic water holds a few sorts of debasements whose nature and sum change with wellspring of water.

Rivers in a watershed assume a significant part in acclimatizing or stealing away civil and mechanical wastewater and overflow from farming area. Rivers inflows are the principle contaminations that help most lakes in a watershed which having a tendency to affect genuine biological and clean issues (Gilbert and Wendy, 2003).

On the other hand, rivers constitute the water resources for domestic, industrial and irrigation purposes in a watershed (Yu and Shang, 2003). Subsequently, it is basic to avoid and control river contamination and to have reliable information on the quality of water for effective management. Generally, water relate ecological quality. It can get in awful condition because of incredible arrangement of waste, inordinate recovery, over-angling and continuous petroleum spills (Lin and Han, 2001; Chen *et al*., 2003).

Langat River Basin is one of the rivers which densely populated and developed zone in Selangor. Since 40 years prior, Langat River has served a large portion of the number of inhabitants in Selangor and it is a wellspring of hydropower for control surge releases (Juahir *et al*., 2010). Langat River is the significant wellspring of drinking water adjoining for different purposes in Kuala Lumpur. These situations brought the conflict between the rapid human development and the river environment which attribute to the expanding of contamination issue. In this manner, about 120 rivers basin were observed with 926 monitoring stations were established since 2004 for identifying of water contamination (DOE, 2006). For monitoring purposes, the Department of Environment has introduced a system of sampling stations along Langat River Basin to determine the water quality criteria.

## 1.2 Source of Contamination

River water quality is impacted by anthropogenic activities such as urban, industrial and agricultural activities, increasing utilization of water resources as well as natural processes like changes in precipitation, erosion and weathering. Degradation of surface water also influenced the quality of river water which can impair their utilization for drinking, industrial, recreation or for different purposes. There are two types of pollution which are from point source (PS) and non-point source (NPS). PS is discharged from manufacturing plants, treatments plants and others sources whereas NPS is diffused source of pollution such as surface runoff.

Industrialization and urbanization have brought thriving however in the meantime, it has brought about numerous environment issues especially to the river water quality. Water quality is recognized in terms of its physical, chemical and biological parameters (Sargaonkar and Deshpande, 2003). River water quality are affected by numerous elements, for example natural process such as climate change and precipitation, soil type, topography, vegetation, groundwater and flow conditions and anthropogenic activities like urban, industrial and agricultural activities.

Heavy metals are one of the sources that contribute to the deterioration of river water quality due to their persistence in the environment, bioaccumulation and high toxicity. Heavy metals have specific weights more than 5g $cm^{-3}$ (Holleman and Wiberg, 1985). Substantial metals constitute an exceptionally heterogeneous gathering of components generally changed in their substance properties and living capacities. Substantial metals are produced from a variety of naturals and anthropogenic sources which could be found all components of the environment such as from mining, smelting activities, disposal of untreated and partially treated effluents contain toxic metals (Martin, 2000; Macklin *et al.,* 2006; Nouri *et al.,* 2008; Reza and Singh, 2010) and they are discharged into a river throughout transport are disseminated between the fluid stage. Only a small portion of free metals particle is disintegrated in water and a lot of substantial metals are stored in the residue in light of the adsorption, hydrolysis and co-precipitation (Bradley and Cox, 1986; Horowitz, 1991; Macklin, 1992; Gaur *et al.,* 2005).

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic drizzle, breaking down soils and discharging heavy metals into streams, rivers, lakes and groundwater. The concentration of these heavy metals in sediments and water may be traced to the bed rock from which the sediments were derived through which the water flows. Metals after entering the water may be consumed by fauna and flora and eventually, accumulated in marine organisms that are consumed by human being (Asaolu *et al.,* 1997). In aquatic ecosystem, pollution of heavy metals is growing at an alarming rate and has become an important worldwide problem (Malik *et al.,* 2010).

The major contributor of heavy metal pollution in the environment is the manufacturing sector. This is due to the heavy metals finishing process such as

electroplating, etching, and preparation of metal components for various industries which have been identified as a major source of wastes containing high concentarations of cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni), iron (Fe), aluminium (Al), manganese (Mn), chromium (Cr) and stannum (Sn). The agricultural sector also contributes some wastes containing metals such as Cu from piggery wastes has been correlated to contamination of sediments and mollusks.

## 1.3 Effect of Heavy Metals

Heavy metals are categorized under environment pollutant because of their poisonous impacts in plant, human and nourishment. Some of the heavy metals like As, Cd, Pb, and Hg are aggregate toxic substances. These heavy metals might be bioaccumulated and biomagnified through the natural way of life through uptake at essential maker level than through utilization at customer level and not metabolized in other halfway mixes. Finally, these heavy metals were assimilated by human consumers resulting in health risks (Agah *et al.,* 2009). Metals can enter the human body either through inward breath and infusion. Heavy metals such as Cd, Ni, As, and Pb pose a number of hazards to humans and also can be potent carcinogenic and mutagenic (Mukesh *et al.,* 2008). Cu and Zn serve either as cofactor biochemical reactions and enzymatic for information of enzyme or substrate metal complex (Mildvan, 1970).

The high amassing of mercury intake can result in minamata illness whilst cadmium intake leads to itai itai disease. Meanwhile, other heavy metals cause poisoning due to drinking water contamination that from the river water (Mukesh *et al.,* 2008). Heavy metals such as Cd, Hg, Ni and Pb have the potential to cause health hazards like oxidative damage to various tissues including erythrocytes due to their toxic action on the biological system (Gupta and Shukla, 1997).

Heavy metal is one of the sources that contribute to the river water quality. Heavy metals are produced from a variety of naturals and anthropogenic sources such as from mining, smelting activities, disposal of untreated and partially treated effluents contain toxic metals (Macklin *et al.,* 2006; Martin, 2000; Nouri *et al.,* 2008; Reza and Singh, 2010) and they are discharged into a river during transport are distributed between the aqueous phase and bed sediments. Only a small portion of free metals ion is dissolved in water and large amounts of heavy metals are deposited in the sediments because of the adsorption, hydrolysis and co-precipitation (Bradley and Cox, 1986; Gaur *et al.,* 2005; Horowitz, 1991; Macklin, 1992).

## 1.4 Multivariate Analysis

Chemometric techniques are being used nowadays, which provide several avenues for exploratory assessment especially for water quality data sets and classification of water qualities (Singh *et al.,* 2005). Under this methods, the

final data that had been collected will undergoes and analysis by using multivariate statistical analysis. These techniques are powerful and advance tools that can be used in environmental collecting data.

## 1.5 Problem Statement

The Langat River consists mainly of agriculture, forests, developed area (commercial and residential) and water bodies. However, the rapid of urbanization and population increase in the Langat River Basin has resulted in changes the land use of Langat River give impact on environmental compartment recently (Lee *et. al*., 2006) where the urban expansion occurred since 1981 mainly consists of factories, shipping port, aquaculture, agriculture, sand mining which located across the river (Idrus *et. al.*, 2004). Due to a mixture of driving forces such as economic, social, infra-structural and administrative imperatives have brought economic growth and ensuing social development to the Langat Basin. Therefore, the impact of this conflict between rapid development and in population has put on the river ecosystem (Idrus *et. al.*, 2004). DOE report also stated that Langat River Basin and its tributaries were classifying as slightly polluted and polluted. This agency also has regular monitoring and water quality data which contains plentiful of data however there is still lack of data analysis which requires advance tools to extract all possible information from the river. Therefore, by using these techniques, it will provide the significant statistic data for result and it is easier to be interpreted and understanding the final findings. The application of these techniques also can be increase the level of confident in the result by statically approving based on primary data.

## 1.6 Objectives of Study

The purpose of this study is providing advance tools to help better understanding of the situation of selected heavy metals. These techniques are unbiased methods which can indicate natural associations between samples and/or variables (Tam and Wong, 2000).

The objectives of this study are:

1. To determine the concentration of selected heavy metals in surface water of Langat River Basin.
2. To identify spatial and temporal distribution of heavy metals in Langat River using chemometric techniques.
3. To obtain the optimum number of sampling station based on cluster analysis (CA).

## 1.7 Significant of Study

The application of chemometric techniques can increase the level of confident this result by statically approving based on primary and secondary data. From this research, the expected outcome for this study can added as information for other researchers that involved in this field and learn something new about chemometric. Furthermore, the Department of Environment (DOE) can use the outcome of this research for future to reduce the cost by monitoring the most significant heavy metal in the Langat River.

## 1.8 Thesis Organization

Chapter 1 is an introduction; this chapter described the general overview on background of the research, highlighting on the key point of the research such as the problem statement, objectives of the research and the significance.

Chapter 2 discussed on the literature review. This chapter reviewed on the river water quality, the existence of heavy metals in the surface water, possible sources, transport and distribution of heavy metals. This chapter also described on the sequential of chemometrics techniques.

Chapter 3 is explaining on the collection of data and how the data were organized. The sources of the data were also stated in this chapter. The process started by preparing the instruments, collecting the water samples, preserving the water samples, analyzing the heavy metals and computing the data by several statistical approaches.

Chapter 4 is highlighting on the data analysis of heavy metals by chemometrics techniques. Excel STAT was used to calculate the data. The descriptive statistics were used to describe in general the outcome for heavy metals. The box plot diagram were displays the difference in each of the heavy metals concentration for every sampling stations. Sub chapter 4.2 discussed in details on the classification of sampling station for spatial variation at study site. HACA was used to classify the concentration of heavy metals on their similarity and dissimilarity level among the sampling areas. Moreover, heavy metals were trace by using DA for spatial and temporal variations. Sub chapter 4.3 discussed the identification possible sources of heavy metals by using PCA. The findings were discussed in details at every subchapter.

Chapter 5, conclusions on the research were made.

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## BIODATA OF STUDENT

The student's name is Faradiah binti Md. Dali. She was born on 17th October 1989 in Kajang, Selangor. She is the third youngest daughter of the family. She has three siblings which is two older sisters and one younger brother. She received her primary education from Sekolah Kebangsaan Taman Bukit