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A comparative study of the subsoil in four different places
in Maktab Polis Diraja Malaysia by using Atomic
Absorption Spectroscopy

Dissertation submitted in partial fulfillment for the
Degree of Bachelor of Science (Health) in Forensic Sciences

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2007

CERTIFICATE


This is to certify that the dissertation entitled

**“A comparative study of subsoil profile in four different places
in Maktab Polis Diraja Malaysia by using Atomic Absorption
Spectroscopy”**

is the bona fide record of research work done by

MISS JULIA HASLINI BINTI MAT JUSOH

during the period December 2006 to April 2007...
under my supervision

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ABSTRACT

Atomic absorption spectrometry (AAS) is being used for determining the metal ion concentration in soil sample. It is a common analytical method for trace or ultra trace (ppm or ppb level) determination. For this study AAS was used for analyzing the presence of metal ions in soil. This comparative study was done to show the difference in metal ion concentrations in soil samples collected in different points from an uphill at forensic laboratory, maktab PDRM in Cheras. The samples were collected in four different points and in four different depths, namely topsoil, soil from ½ foot depth, soil from 1 foot depth, and soil from 1 1/2 feet depth. In total sixteen samples were collected for AAS analysis.

The purpose of this study is to compare the metal ion concentration in soil samples collected in different points and in different depths. The presence of metal ions in subsoil profile were compared and recorded. Eight metals have been chosen for comparison and their concentrations were compared. The chosen metals are K, Pb, Zn, Fe, Mg, Ca, Mn and Cu.

Before using AAS examination preliminary examination of soil viz color, pH, particles size and presence any foreign material etc have been conducted. Then examination was done using AAS to obtain the metal ion concentrations present in the soil samples collected from different points and depths. The metal ions were extracted by using EDTA solution since it form complex as with metal ion present in soil samples resulting chelate formation. Then the solution was filtered and purified for AAS analysis. I found that all the metal ions concentration different and have this technique can be used for forensic soil analysis. It shows that no two samples from two different origins have the same metal ion concentrations.

INTRODUCTION

Soil is frequently used as valuable physical evidence in forensic investigation. The soil, as a transfer evidence can link a person with a crime scene or his involvement in a crime scene (Munroe, 2001).

Soil may be defined as a complex mixture with a variety of mineralogical, chemical, biological and physical properties. It is consisting of components such as, clay, silt, sand and humus. There are different types of soil are known. The evidential value of soil stands on large variation in its characteristics. Soil has extreme complexity not only in components such as minerals, oxides, organic matter, microorganisms and their materials but also physical nature such as particle size and density. Soil has been recognized according to difference of color, mineralogy, texture and other characteristic. Murray and Georg Popp are the first scientists who examined soil evidence and solved a murder case in 1904.

Many instruments are used in forensic soil analysis such as emission spectroscopy, atomic absorption spectroscopy, neutron activation analysis, X-ray fluorescence, X-ray diffraction, differential thermal gravimetric, thermoluminescence, Fourier transform infrared spectroscopy, pyrolysis gas chromatography and laser raman spectroscopy (Pye et al., 2005).

Microscopic observation and low-power stereomicroscopic observation are important at the initial step of forensic soil examination. In general, soil is dried and then observed under a stereomicroscope (Righi, 1996). Trace elemental analysis of soil samples provides a powerful basis for forensic soil comparison (Pye et al., 2005). The soil examinations in this study include color comparison, particles size distribution, pH measurement and determination of metal ion concentration (Murray, 1975).

The metal ion concentration can be determined by using Flame Atomic Absorption Spectrometry. Atomic absorption spectrometry is a fairly universal analytical method for determination of metallic elements when present in both trace and major concentrations. In flame AAS, a sample is aspirated into a flame using nebulizer. The flame is lined up in a beam of light of the appropriate wavelength. The flame causes the atom to undergo a transition from the ground state to the first excited state. When the atoms make their transition, they absorb some of the light from the beam. The more the concentration the solution, more light energy absorbed. The light beam is generated by lamp that is specific for a target metal (Kenkel, 1994).

The lamp must be perfectly aligned so that the beam crosses the hottest part of the flame. The light passes through the flame is received by the monochromator, which is set to accept and transmit radiation at the specified wavelength and travels into the detector. The detector measures the intensity of the beam of light. When some of the light is absorbed by metal, the beam's intensity is reduced. The detector records that reduction as absorption. Then the absorption is shown on output device by the data system. The following figure 1 describes how atomic absorption process occurred.

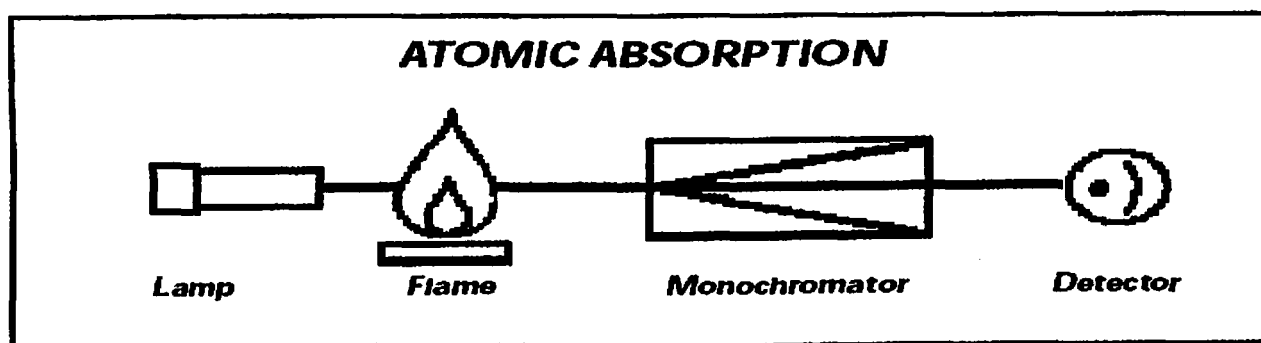


Figure 1: A schematic of the basic instrumental components of AAS

Atomic absorption spectrometry requires careful calibration. If the samples concentration is too high to permit accurate analysis in linearity response range, there are three alternatives that may help bring the absorbance into the optimum working range: **1)** sample dilution, **2)** using an alternative wavelength having a lower absorptivity, **3)** reducing the path length by rotating the burner hand. This figure (2) describes on idealized or deviation response curve obtained during running samples in AAS. Meanwhile figure (3) shows what kind of elements can be detectable by AAS

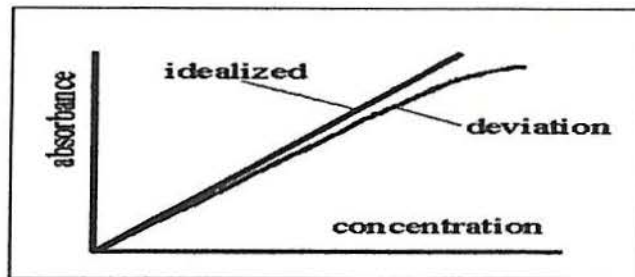


Figure 2: Idealized/deviation response curve

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mb	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Figure 3: Elements detectable by atomic absorption are highlighted in pink in this periodic table

Soil is a heterogeneous mixture of organic matter, rock fragments, mineral grains, clay, and oxides. This unique nature is useful to characterize soil as evidence. Diversity of soil is the results from soil formation process. The diverse kind of parent materials that are strongly depends on topography, climate, time, botanical and microbiological functions, conditions of watering and even human activities (Murray, 1975).

The parent materials are known as the material from which the soil is formed. Parent material could be bedrock, organic material, and an old soil surface, a deposit from water, wind, glaciers, volcanoes, or material moving down in a slope. Meanwhile climate such as heat, rain, ice, snow, wind, sunshine and other environmental forces break down the parent material and affect the soil formation process. Organisms consist of plants, animals living in or on the soil including micro-organisms. The amount of water and nutrients, the plants can affects the soil formation process. Animals living in the soil affect decomposition of waste materials and how soil materials will be moved around in the soil profile. The dead remains of plants and animals are compared with organic matter which enriches the soil. The way in which has human use soil also affect the soil formation (Murray, 1975).

The climatic process can also affect the location of soil on a landscape. Soils at the bottom of a hill will get more water than soils on the slopes, since soils on the slopes that directly face the sun will be drier than soils on slopes that do not. All of the above factors assert themselves over time, often hundreds or thousands of years. The way the five soil-forming factors interact is always different from one place to another, so soil differs greatly from each other. Each section of soil on a landscape has its own unique characteristics (Murray, 1975).

The face of a soil is also called soil profile, like the profile of a person's face. Every soil profile is made up of layers called soil horizons. Soil horizons can be as thin as a few millimeters or thicker than a meter. In fact, soil samples taken at the surface may have entirely different characteristics and appearances from soil dug deeper in the soil profile. The reason why soil horizons are different is due to the mixing of organic material in the upper horizons and weathering and leaching in the lower horizons. Erosion, deposition, and other forms of disturbance might also affect the way a soil profile present at a particular location.

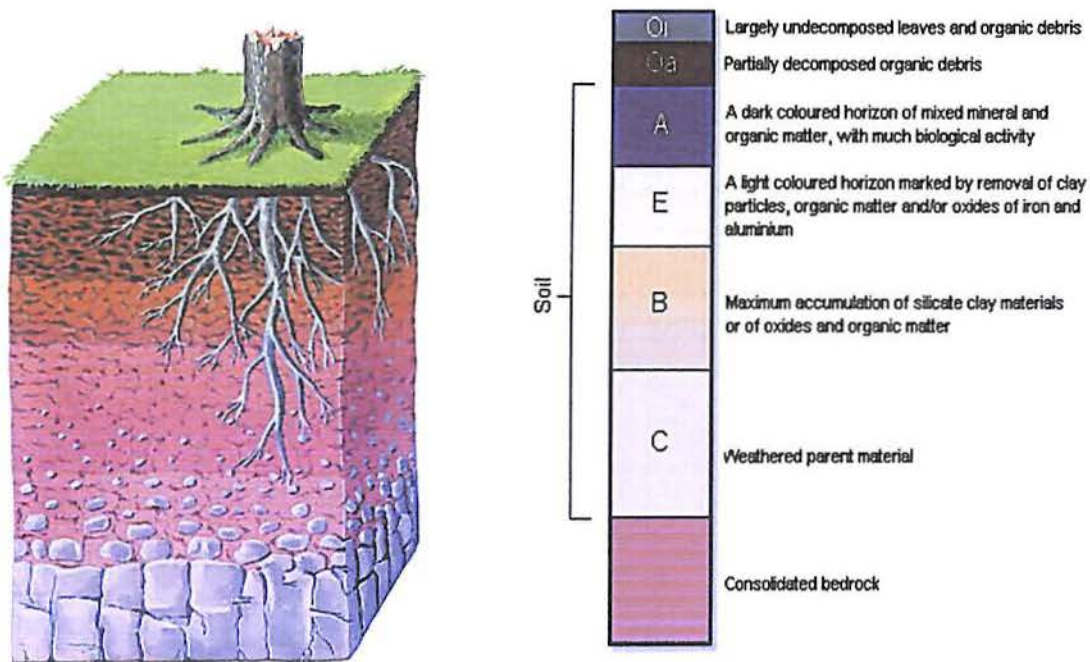


Figure 4: Layers of soil profile

The soil undergoes various changes over time. The soil undergoes pedogenesis and develops horizons. The intensity of the process varies with location because of the five soil forming factors. The integrity of five forming factors is called as the soil profile. They are consisting of several layers of soil such as O-horizon, A-horizon, E-horizon, B-horizon and C-horizon. The A horizon is a mineral horizon that is dark in color due to the incorporation of decomposed organic matter, which coats the mineral soil particles with colloidal size organic

matter. In general, the darker the mineral soil is the greater the organic matter. The E horizon develops when materials are eluviated out of a zone in the soil. The effect of this is to remove the organic matter and iron out of this zone, which causes it to be lighter in color than the horizons above or below it. E horizons are found mainly in forested soils. Below the E horizon or A horizons, there are zones of illuviation or accumulations. These are called B horizons. The B horizon is below the E and has accumulated clay and developed very strong structural peds. However, the soil undergoes significant transformations and develops different color and structure from the C horizon or parent material. C-horizons are outside the zone of soil development. C horizons are little altered by the soil forming processes. C horizons are referred to as the parent material of the soil (Wild, 1996).

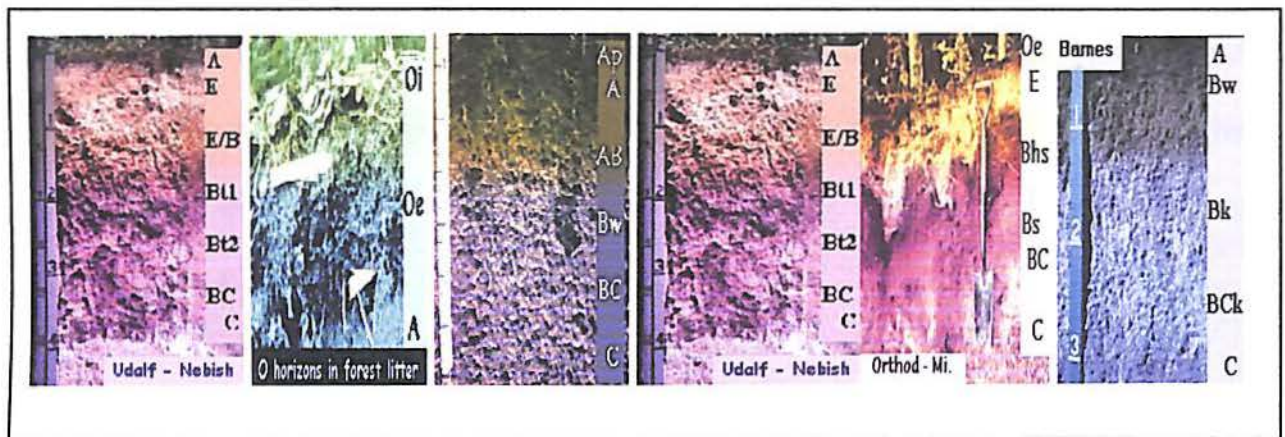


Figure 5: The different of colors of soil

Soil color is the most obvious property that gives an immediate indication of the condition of the soil system such as shown in figure 5. However, in general, soil color is controlled by soil formation processes. Soil color often indicates soil moisture status and is used for determining hydric soils. Often soil colors described by using general terms, such as

dark brown, yellowish brown, etc., soil colors are also described more technically by using Munsell soil color charts as shown in figure 7. The hue value which indicate red, yellow, blue, and lightness or darkness. The chroma describes the intensity of a color. There are about 1100 types of soil colors are known. Soil color is one of the most important features of the soil and organic matter is known to be one of the primary pigments in soil (Skye Willis, 2007).

The mineral component of a soil is made up of clay, silt and sand, often referred to as fine, medium and coarse size particles respectively. Sand grains are larger in diameter compared to silt and clay particles. There are several sizes of soil particles. The coarse sand diameter ranges from about 2.00 to 0.50 mm, medium sand ranges from 0.50 to 0.25 mm, fine sand ranges from 0.25 to 0.062 mm, silt particles size ranging from 0.062 to 0.004 mm and clay particles size vary from 0.004 to 0.0002 mm diameter. Sand is the largest particles and feels gritty to touch. Silt particles are medium sized and they feel soft, smooth and silky. The clay particles are the smallest sized and feels smooth when dry, and become sticky when wet and hard to squeeze.



Figure 6: Different particles sizes

Minerals are naturally occurring chemical compounds. They make up rocks, meteorites and, with organic matter, soils. Earth's crust is formed from the combination of many naturally occurring elements, of which eight elements are found predominant namely

oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), Sodium (Na), potassium (K), and magnesium (Mg). In this research, eight metal ions in soil samples such as, K, Mg, Fe, Pb, Zn, Cu, Ca and Cd have been chosen for soil analysis. The samples are extracted by EDTA solution and then running through AAS to get the metal ion concentration.



Figure 7: The Munsell Color System

As soil evidence has very close relation with dust and other materials such as diatoms, pollen and botanical materials for forensic science investigation. Forensic interest in soil evidence is to establish the link between two objects including a suspect, a victim, a crime scene, and often a tool or a vehicle. Therefore, what criminal investigation requires to forensic pollen analysis is to establish presence or absence of localized pollen species in soil evidence. For this purpose, generally insect pollinated species can provide useful information. Cengiz and Sakul (2001) reported application of anion analysis for forensic soil discrimination. Capillary electrophoresis was applied to soil extract obtained by shaking 10 g of soil sample with 10 mL of distilled water. Chlorite, nitrate, sulfate and phosphate contents were compared among soils.

REVIEW OF LITERATURE

Several literatures have been referred and received by the previous researchers for their elemental analysis of soil using Atomic absorption spectroscopy.

In this publication, Junger et al (1996) described about Color comparison and determination of particle size distribution for soil samples that can be carried out quite easily, and the combined data can be quite useful for soil discrimination.

Sugita and Marumo (1996) studied multiple color observation on soil samples. This method composed of color observation on air-dried soil, moistened soil, and the soil after decomposition of organic matter using hydrogen peroxide, the soil after removal of iron oxides using sodium dithionite, and the soil ignited at 850 °C in an electric furnace. Color comparison on air-dried soil alone is insufficient for discrimination of samples.

Pye et al (2005) analyzed soil samples using AAS, X-ray fluorescence (XRF), atomic absorption spectrophotometry (AAS), Inductively coupled spectrometry (ICP), spark-source mass spectrometry (SS-MS), neutron activation analysis (NAA) and energy or wavelength dispersive X-ray microanalysis (EDS and WDS).

McAlister and Smith (1995) have discussed about the rapid preparation technique for X- ray diffraction analysis of clay minerals in weathered rock minerals. They published paper in a journal entitled A Rapid Preparation Technique for X-Ray Diffraction Analysis of Clay Minerals in Weathered Rock Materials. Microchemical Journal proposed a rapid preparation technique for XRD analysis of clay minerals. As crystals of most clay minerals have platy structure, basal spacing has to be recorded by XRD.

Sugita and Marumo (2001) examined the validity of the determination of particle size distribution for forensic soil discrimination. In this study in order to obtain better

reproducibility and to achieve high discriminating power, the particle size classes were reduced to <0.05, 0.05-0.2, and 0.2-2 mm. Discriminating power examination using 73 soil samples collected systematically on the basis of a geologic map and a topography map and revealed that, 88% could be discriminated by this sieving method.

Davis et al (1984) in the paper titled 'Processing and Use of Sewage Sludge, the author analyzed traces metals such as Pb, Zn, Cu, Ni, Cd and Fe in sewage sludge produced at a sewage treatment plant in Bahrain (Tubli) and soils. From the analysis result the indicated that the soils, both untreated and treated with the sludge can be used for agricultural purposes in Bahrain.

Another paper was published in the Soil Science Society of America Journal by Willis et al (2007) that soil color can be as accurate as the lab for carbon content. Soil color can be used as a simple, inexpensive method to predict measurements of soil organic content. He said that soil color is one of the most obvious features of soil and organic matter has long been known as one of the primary pigmenting agents in soil.

The monumental work was published the textbook entitled "Forensic Geology: Earth Science and Criminal Investigation" by Murray and Tedrow (1975). It is now revised as .Forensic Geology by Murray et al (1992) along with the change of quality of examination. The author stated soil has extreme complexity not only in components such as minerals, oxides, organic matter, microorganisms and their materials but also physical nature such as particle sizes and densities. Differences soil structure and soil profile in each point of soil samples cause to the change of quality of examination and a variety of in bedrock composition can therefore cause local variations in the metal contents of the soil.

The metals in soil samples can be extracted with ammonium acetate (EDTA) and the extracts were analyzed by flame atomic absorption spectroscopy (AAS). EDTA is used to extract metals in soil and metal ion concentrations were determined using AAS. This paper regarding to environment assessment by Nowack et al. (2001) was published in "Journal of Environment Quality".

The research paper titled "Major and trace metal extraction from soil by EDTA" by Manouchehri et al. (2005) in "Journal of Analytica Chimica Akta 559" that author stated that EDTA (ethylenediaminetetraacetic acid), is a powerful chelating agent, can be used in soil sciences to determine the contents of trace and major metal in soil. These authors worked out the reactivity of trace and major elements (such as Pb, Cu, Cd, Al, Fe, Ca and Mg) with different concentration of EDTA in soil samples.

Microscopically, soil is a heterogeneous mixture consists of organic matter, rock fragments, mineral grains, clay, oxides etc. Therefore a unique particle is of important to characterize soil evidence. A small crumb is much more important, and bulk analysis frequently gives poor results for forensic soil examinations were published in "Central Forensic Laboratory of polish Police, Poland" by Mazurek et al (2001). Some particular fractions of soil can be useful for forensic soil discrimination rather than the bulk analysis.

Forensic interest in soil evidence is to establish the link between two objects including a suspect, a victim, a crime scene, and often a tool or a vehicle. Soil can be also used as transfer evidence in criminal investigation. A paper was published by Erying et al (1996) titled "Soil Pollen Analysis from a Forensic Point of View Microscope". Forensic pollen analysis is also used to establish presence or absence of localized pollen species in soil evidence.

OBJECTIVES OF THE STUDY

- 1. To compare the metal ion concentration in soil samples collected from different points and depths.**
- 2. To gain a profile of a metal content for soil collected from an uphill at Forensic Laboratory, Maktab PDRM in Cheras. Metal ion concentrations in soil samples will be determined by using AAS.**
- 3. To observe the differences in features of soil samples collected from four different point and four different depth, viz topsoil, 1/2 foot depth, 1 foot depth and 1 ½ foot depth at uphill near forensic laboratory in maktab PDRM.**
- 4. To compare the soil collected from a suspect with the soil samples collected from simulated crime scene.**

MATERIALS AND METHODS

MATERIALS REQUIRED:

i) For sample collection:

Ruler, envelopes, paper, shovel and others digging instruments as shown in Figure 8.

ii) For preliminary Observation:

Stereomicroscope, ocular microscope, glass slide, white paper and ruler

iii) For sample preparation:

Beaker, volumetric flask, funnel, filter paper, buchner funnel and vacuum pump, rod spatula, cylinder parafilm

iv) Chemical for extraction:

Ethylenediaminetetraacetic acid disodium salt (EDTA) and different standard solution

v) Equipment for analysis:

AAS (Perkin-Elmer), Dessicator, pH meter, Magnetic Stirrer and Oven



Figure 8: Implements used for soil sample collection



(a)



(b)

Figure 9: (a) and (b) shows the Atomic Absorption Spectroscopy (AAS)



(c)



(d)

Figure 10: (c) Different Standard solution (d) glass ware used for extraction



(e)



(f)

Figure 11: (e) Jet pump (f) Hot plate and Magnetic stirrer

METHODOLOGY

Sample Collection

Collected by: Julia Haslini Bt Mat Jusoh, accompanied by Wan Nursyazwani, Rosadli and Lee loong Chuen.

Date: 13 November 2006

Time: 08.00 – 15.00 hrs

Climate: Sunny and covered with cloud

Location: On uphill at forensic laboratory, maktab PDRM in Cheras

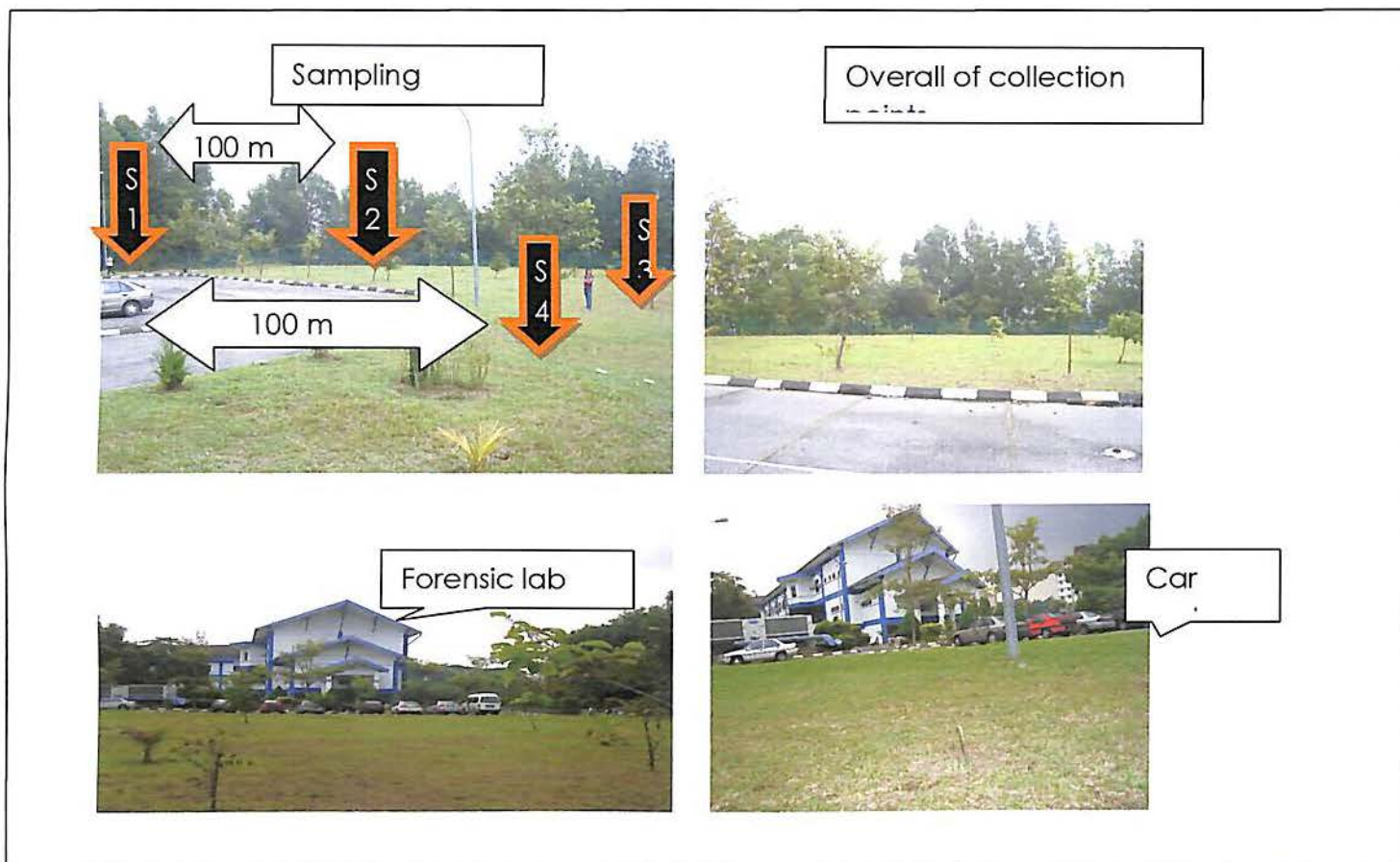


Figure 12: location of sample collection area