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A Comparative Study of Subsoil Profile
In Southern End of Golf Ground, Health Campus, USM, Kubang Kerian
by Atomic Absorption Spectroscopy (AAS)

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

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Certificate page

CERTIFICATE

This is to certify that the dissertation entitled

“A Comparative Study of Subsoil Profile
In Southern End of Golf Ground, Health Campus, USM
Kubang Kerian by Atomic Absorption Spectroscopy (AAS)”

is the bonafide record of research work done by

Ms. Asfarina bt Jamal Mohideen

During the period of 16th January 2006 to 16th April 2006

under my supervision.

Signature of supervisor:



Name and address of supervisor:

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ABSTRACT

Atomic absorption spectrophotometry (AAS) is being used for analyzing various metals present in soil. This comparative study of soil profile by AAS is done to show the difference in metal ion concentrations in different soil samples, which were collected from four different points such as S1, S2, S3 and S4 in southern side of golf ground, USM, Kubang Kerian. In each point, samples were also collected in four different depths, namely the topsoil, soil from ½ foot depth, soil from 1 foot depth, and soil from 1½ feet depth. These 16 soil samples have been analyzed using AAS.

In this study, the analysis of soil samples was done in two ways. Firstly preliminary examinations were made under stereomicroscope. Secondly the samples were examined under AAS to find out the different metal ion concentration present in the soil samples collected in different points and different depths. The metal ions were extracted using EDTA, because EDTA form complex with many metals to form chelate compounds. The extracted compounds were purified and run through AAS and recorded the different metal ion concentrations.

The purpose of this study is to compare the metal ion concentration in soil samples collected in different points and in different depths from the southern end of golf ground. The presence of metal ions in subsoil profile were compared and recorded. To make a fruitful study, ten metals have been chosen and their concentrations present in the above 16 soil samples were studied. The chosen metals under this study include Na, K, Pb, As, Zn, Cd, Fe, Mg, Ca and Cu. The selection of the most suitable elements for forensic discrimination purposes is depending on the nature of soil under question.

Also carried out a simulated crime scene soil analysis where in crime scene soil sample and soil collected from the suspected were analyzed under AAS. The result clearly indicated similar metal ions concentration present in both samples. Hence this is a better method for the forensic analysis of soil.

INTRODUCTION

Soil can provide important information to criminal investigations as transfer evidence because many criminal cases take place under circumstances such that soil transfers to a criminal or victim. Soil is a complex mixture with a variety of mineralogical, chemical, biological and physical properties. The variation in soils from place to place makes soil valuable evidence to prove linkage between suspect and a crime scene (Marumo, 2003). Actually, there is considerable variation among soil components even within a particular area where a pedogenically uniform soil is distributed, allowing us to differentiate soil samples (Sugita and Marumo, 1996)

There are various methods of forensic examination of soils evidence includes a) screening based on color composition and size distribution for soil discrimination, b) density gradient distribution, c) mineralogical examination by application of scanning electron microscope equipped with an energy dispersive x-ray spectrometer (SEM-EDX), X-ray diffraction (XRD), and differential thermal analysis for identification of clay minerals, d) analysis of soil organic matter using Fourier transform infrared absorption spectrometry (FTIR), application of soil microorganism and their activity, and f) inorganic contents analysis by atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectroscopy (ICP-MS) (Pye et al., 2005)

In this research, the soil examinations include color comparison, particle size distribution, studying the pH variation and finally metal ion concentrations study.

Major and trace elemental analysis of soil samples provides a powerful basis for forensic comparison of soils, sediment and rock (Pye et al., 2005). Weathering of bedrock and pedogenic processes can result in elevated heavy metal concentration in the soil. Small scale

variations in bedrock composition can cause local variation in the metal content of the soil. A study has found distinct differences between two sites on the basis of their elemental composition (Nowack, 2001).

Several techniques are available to determine elemental composition in soil sample, includes 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) (Pye et al., 2005). In this study elemental analysis of soil samples were carried out using flame atomic absorption spectrophotometer (FAAS).

In flame AAS, a liquid sample is aspirated and mixed as an aerosol with combustible gasses (acetylene and air). The mixture is ignited in a flame of temperature ranging from 2100 to 2800 degrees (depending on the fuel gas used). During combustion, atoms of the element of interest in the sample are reduced to atomic state. A light beam from a lamp whose cathode is made of the element being determined is passed through the flame into a monochromator and detector. Free, excited ground state atoms of element absorb light at characteristic wavelengths; this reduction of the light energy at the analytical wavelength is measured of the amount of the element in the sample.

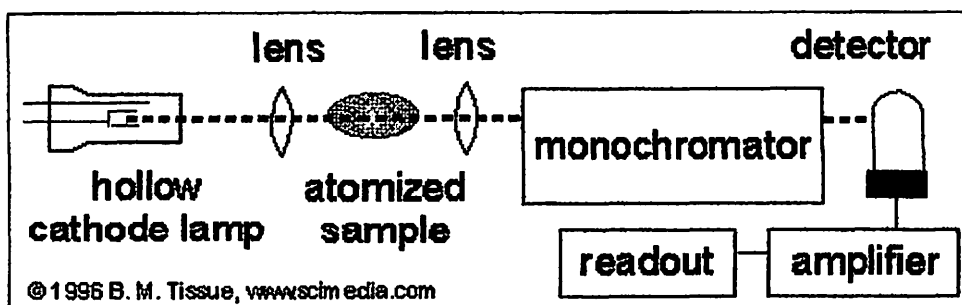


Figure 1: Schematic of an atomic-absorption experiment

Soil is naturally occurring, unconsolidated or loose material at the surface of the earth, which is capable of supporting plant and animal life. Soil consists of mineral and weathered rock fragments, organic matter, gases, water and living organism. Soils are formed through the interaction of five forming factors; parent material, climate, organisms, topography and time. The relative influence of each factor varies from place to place, but combination of all five factors normally determines the kind of soil developing in any place (Saferstein, 1987).

Parent material is the unconsolidated mineral and organic deposits in which soils are developing. It determines the mineralogical composition and contributes largely to the physical and chemical characteristic of soil. The kind of parent material also influences the rate at which soil forming process take place. The next factor is, climate in which temperature, precipitation and frost action have profound influence on the soil forming process which occur within a region. The kind of climate determines the nature of the weathering processes that will occur and the rates of these chemical and physical processes. Besides that, all living organism actively influence the soil formation. The organism includes bacteria, fungi, vegetation and animals. Human being also affects soil formation by disturbing the natural course of weathering by their daily activity. The formation of soils is a continuing process and generally takes several thousand years for significant changes to occur. Next factor is topography, which defined as the shape of the land surface. Its slope and position on the landscape, which greatly influence the kinds of soil formed. For example, soils developed on higher elevations and sloping area are generally excessively drained.

The interaction of this five soil forming factors results in development of a soil profile (figure 3). *A* horizon generally corresponds to 'topsoil', where biological activity is often greatest and plant roots most concentrated, *B* horizons generally considered as 'subsoil',

where constituents including clay may accumulate, where else *C* horizons, is material below the developed soil affected by weathering, *R* horizons is an unweathered bedrock and *O* horizons was predominantly composed of organic matter.

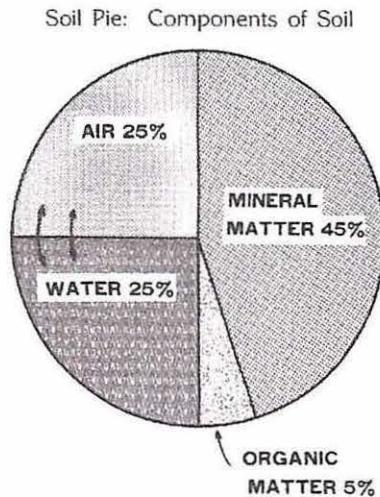


Figure 2: Component of soil

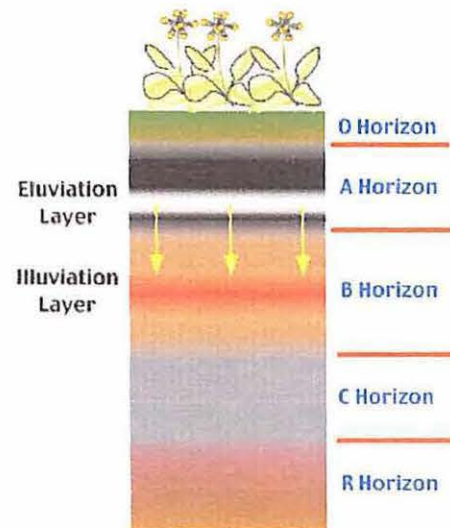


Figure 3: Soil profile

Soil is generally divided into three main classes; sand, silt and clay. Sand particles are large enough to grate against each other and they can be detected by sight and sand shows no stickiness or plasticity when wet. Sand sizes can be classified as coarse sand (2.00mm to 0.5mm), medium sand (0.5mm to 0.25mm) and fine sand (0.25mm to 0.003mm). Silt grains cannot be detected by feel, but their presence makes the soil feel smooth and soapy and only very slightly sticky. Silt particles size ranging from 0.062mm to 0.004mm. The characteristic of clay is the stickiness. If the soil sample can be rolled easily and the sample is sticky and plastic when wet, it indicates high clay content. Clay particles sizes vary from 0.004mm to 0.0002mm.

A mineral is defined as being naturally occurring elements or compound that is formed by inorganic processes and contains a crystalline structure. Minerals in soil form the basic framework of soil. Minerals originally form when once-heated Earth mineral magma (molten rock) cools and form solid igneous rock. During the cooling process of magma, ions become bonded together, due to electrical attraction. The attracted, bonded ions remain fixed in position and produce solid crystalline minerals within igneous rock. The Earth crust formed and continues to form in this manner. Earth crust contains a combination of naturally occurring elements, of which eight elements are predominant: oxygen (O), silicon (Si), aluminium (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg). Combination of these elements along with other naturally occurring elements forms Earth's crust produce wide variety of mineral.

This study includes determination of ten selected metals ion concentration in soil samples such as Na, K, Mg, Fe, Pb, Zn, Cu, As, Ca and Cd. Metals in soil samples were extracted with prepared EDTA solution. Then the extracts were directly run through atomic absorption spectroscopy (AAS) to determine the metal ions concentration in respective sample. One extraction made from a particular soil sample is enough to find out all 10 metal ions using AAS.

Color is the most distinguishable property of soil in which the pedogenic environment and history are reflected. There are as many as 1 100 soil colors are known (figure 4); hence the comparison of color offers a logical first step in a forensic soil comparison (Saferstein, 1987). The soil must be dry for the comparison, as moisture significantly alters the color. Soil color is usually registered by comparison of a standard color chart (Munsell Book of Colors) (figure 5) (Sugita and Marumo, 1996).

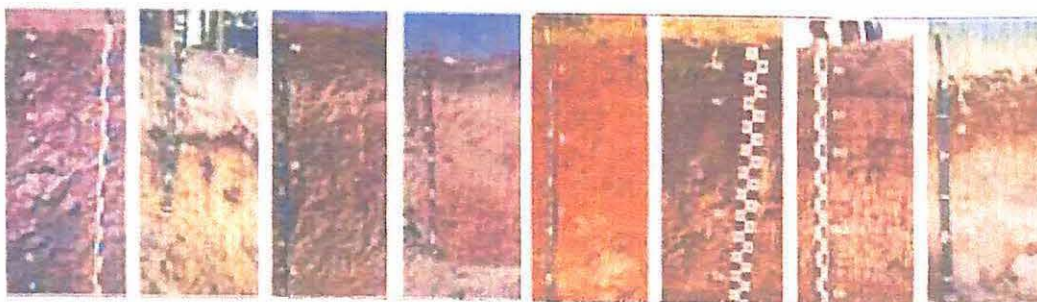


Figure 4: Varies soil color



Figure 5: The Munsell and Earth Colors color charts

REVIEW OF LITERATURE

There are only few studies are made regarding elemental analysis of soil samples by atomic absorption spectroscopy. Most of the journals related to analysis of soil for environmental purposes. Though studies are not directly link to forensic purpose, it had been applied as references to support this research work.

Pye et al. (2005) had published an article in "Journal of Forensic Science International" entitled "Elemental analysis of soil samples for forensic purposes by Inductively couple plasma (ICP) spectrometry". In this study, the author focuses in instrument measurement precisions where the author compare several techniques are available to determine metal composition in soil.

They stated that major and trace elemental composition is an important attribute of soils and sediment can be used for forensic comparisons. Techniques available to determine element, include X-ray fluorescence (XRF), atomic absorption spectrophotometry (AAS), inductively coupled plasma spectrometry (ICP), spark-source mass spectrometry (SS-MS), neutron activation analysis (NAA) and energy/wavelength dispersive X-ray microanalysis (EDS and WDS). Every technique has got its own advantages and disadvantages in terms of sample size requirements, the range of elements can be analyze, detections limits, methods of sample preparation, and accuracy of results.

Another article published in "Journal of Forensic Science International", by Sugita and Marumo (1996), is "Validity of color examination for forensic soil identification". In this paper, the author insisted the importance of soil color comparison in criminal investigation. Soil color was measured by comparison with Munsell color chart after several treatments,

such as (1) air-drying, (2) moistening, (3) organic matter decomposition, (4) iron oxide removal and (5) ashing. This method was further validated by applying it to simulated crime scene. According to above authors, about 70% of soil could be differentiated by comparing the colors of soil before and after drying. Color is the most distinguishable property of soil in which the pedogenic environment and history are reflected. Color examination of soil can be a supportive method to prove soil evidence and is a helpful guideline for forensic scientists.

Another paper published in “Journal of Forensic Science International”, by Sugita and Marumo (2001), is “Screening of soil evidence by combination of simple techniques: validity of particle size distribution”. In this article, the authors stated that test and control soil samples must be compared and interpreted considering intra and intersample variation. Determination of particle size distribution for soil sample can be carried out easily, which involve simple techniques and useful for discriminating among similar soil samples. The author also found that particle size distribution by sieving could successfully differentiate soil samples with high discriminating power, and its use in combination with color examination allowed discriminating 99.5% of 2628 sample pairs.

The fourth paper titled “Assessment of Cd, Pb and Zn contamination in roadside soils and grasses from Gipuzkoa (Spain)” was published in “Journal of Chemosphere” by Garcia and Millan (1998). Superficial soils and grasses at two distances from eight different locations near to roads were collected for analysis. Total contents of Cadmium, Copper, Iron, Manganese, Lead and Zinc in soil samples were determined by Atomic absorption spectroscopy (AAS). Chemical extractants, DTPA (diethylenetriaminepentaacetic acid) have been used to extract heavy metal content in soils. The main purpose of this study is to assess the effect of distance and the location on the metal contents in road soils and grasses and to

corroborate the source of pollution using factor analysis. As a result, author found the effect of the traffic as source of pollution.

Another article relating to environment assessment by Nowack et al. (2001), titled “Elevated lead and zinc contents in Remote Alpine soils of Swiss national Park” was published in “Journal of Environment Quality”. In this paper, above author states that weathering of bedrock and pedogenic process can result in elevated heavy metal concentration in the soil. Small-scale variations in bedrock composition can therefore cause local variations in the metal contents of the soil. Soil profiles were sampled at a different altitude, representing soils developed above different bedrock. Besides natural origin, other external source of heavy metal in soils is pollution caused by anthropogenic activities, such as metal mining, smelting and processing. The metal in soil samples can be extracted with ammonium acetate or EDTA and the extracts were analyzed by flame atomic absorption spectroscopy (AAS).

Another article been published in “Journal of Environment Pollution” by Imperato et al. (2003), titled ‘Spatial distribution of heavy metals in urban soils of Naples city (Italy). The purpose of study is to assess the urban soil pollution by measuring the concentration of Cu, Cr, Pb and Zn on surface and subsurface soil. Soil sample from different depth such as surface soil sample (0-2cm), 10, 20 and 30 cm depth were collected. EDTA been used to extract metals in soil and metals concentration in extracts was determined using AAS. Besides analyzing metal, soil mineralogical examination also carried out in this study. Soil been submitted to X-ray and electron microscope analysis to determine the mineral contents. Author found that the Naples urban area has been affected by human activity which leads to a high accumulation of heavy metals Cu, Pb and Zn.

A report entitled “Background concentration of metals in Florida soil” was published by Robert Brinkmann (1998). The objective of study is to examine the concentration of total Pb, As, Sr, Ba, Zn, Cu, Ni, Sc, V, Cr, Al, Fe, Mg, Mn, Ca, Na, K, and Ti in selected soil throughout the state. Soil suborders were selected for soil profiling. Samples were collected from each horizon and digested for element analysis using atomic absorption spectroscopy. According to author, the result shows that the metal concentration varies greatly within soil profiles and among the soil suborders. The metal content within soils of Florida varies greatly with soil suborder and within individual profiles.

One of forensic paper titled “Forensic comparison of soil samples: Assessment of small-scale spatial variability in elemental composition, carbon and nitrogen isotope ratios, color, and particle size distribution” was published in “Journal of Forensic Science International”, by Pye et al. (2005). The study was taken to assess small variability in four surface soil properties at two locations in Berkshire, UK. The soil properties analyzed were (1) major and trace elemental concentration, (2) carbon and nitrogen isotop ratios, (3) color and (4) particle size distribution. Major and trace metal composition in soil determined by inductively coupled plasma spectrometry (ICP-AES and ICP-MS). Author found distinct differences between the two sites on the basis of their elemental composition.

Another paper published in “Journal of Analytica Chimica Akta 559” by Manouchehri et al. (2005), titled “Major and trace metal extraction from soil by EDTA”. In this article, above author state that EDTA (ethylenediaminetetraacetic acid), is a powerful chelating agent, widely been 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. They selected EDTA

for soil analysis because the complexity of these reagents involved in removal of heavy metals for contaminated soils in soil cleaning procedure (Manouchehri et al., 2005).

An article was published in the “Japanese Journal of Science and Technology for Identification” by Marumo (2003), titled “Forensic examination of soil evidence”. In this study, author stress the importance of soil in criminal investigation as transfer evidence. The variation in soils from place to place makes soil valuable evidence to link suspect and crime scene. According to author, mineralogical examination is essential in forensic soil identification. Besides that, author also states the importance of observation of soil color.

In the Criminalistics book by Saferstein (1987), in the chapter “Forensic Characteristic of Soil”, describes about various methods of forensic soil analysis, including soil color examination, density gradient tube techniques, particle size distribution, mineral analysis and chemical analysis such as heavy and trace metal concentration analysis.

OBJECTIVE OF THE STUDY

1. To observe the differences in properties of soil samples collected from four different points and four different depths, namely the topsoil, soil from $\frac{1}{2}$ foot depth, 1 foot depth, and 1 1/2 feet depth in southern end of Golf ground at USM Kubang Kerian.
2. To compare the metal ion concentrations in soil samples collected from different points and depths.
3. To prepare a profile of metal content for soil collected from a selected area in golf ground at USM. Metal ion concentrations in soil samples are determined using Atomic Absorption spectroscopy (AAS).
4. To compare the soil collected from a suspect with that of sample collected in a simulated crime scene.

MATERIALS AND METHODS

MATERIALS

Sample collection:

Trowel, ruler, envelopes, papers, and plastic bags.

Preliminary observation:

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

Sample preparation:

Ceramic container, beaker 500ml, 100ml and 50ml, volumetric flask 1000ml and 50ml, funnel, filter paper, buchner funnel and vacuum pump, pipette 1ml, rod, spatula, cylinder 500ml, parafilm, and E-pure water.

Chemical:

EDTA (Ethylenediaminetetraacetic acid disodium salt) (formula weight 372.24) and metal ion standard solution (1000mg/l).

Equipment:

Atomic Absorption Spectroscopy (AAS) (Perkin-Elmer), Dessicator, pH meter, Magnetic stirrer and Oven.



Figure 6: Instruments used for soil sample collection



(a)



(b)

Figure 7: (a) and (b) shows the Atomic Absorption Spectroscopy (AAS)



(a)



(b)



(c)



(d)

Figure 8: (a) and (b) shows the apparatus used in sample preparation, (c) buchner funnel and vacuum pump and (d) standard solution used to calibrate AAS.

METHODOLOGY

Sample Collection

Collected by: Asfarina and Siti Hasmah, accompanied by the Supervisor Mr. T. Nataraja Moorthy, with technologies Mr. Sanusi and Mr. Zul.

Time: 1530-1700 hours

Date: 3rd Jan 2006

Climate: Sunny, but land is wet by previous day's rain

Location: Golf Ground at USM Kubang Kerian

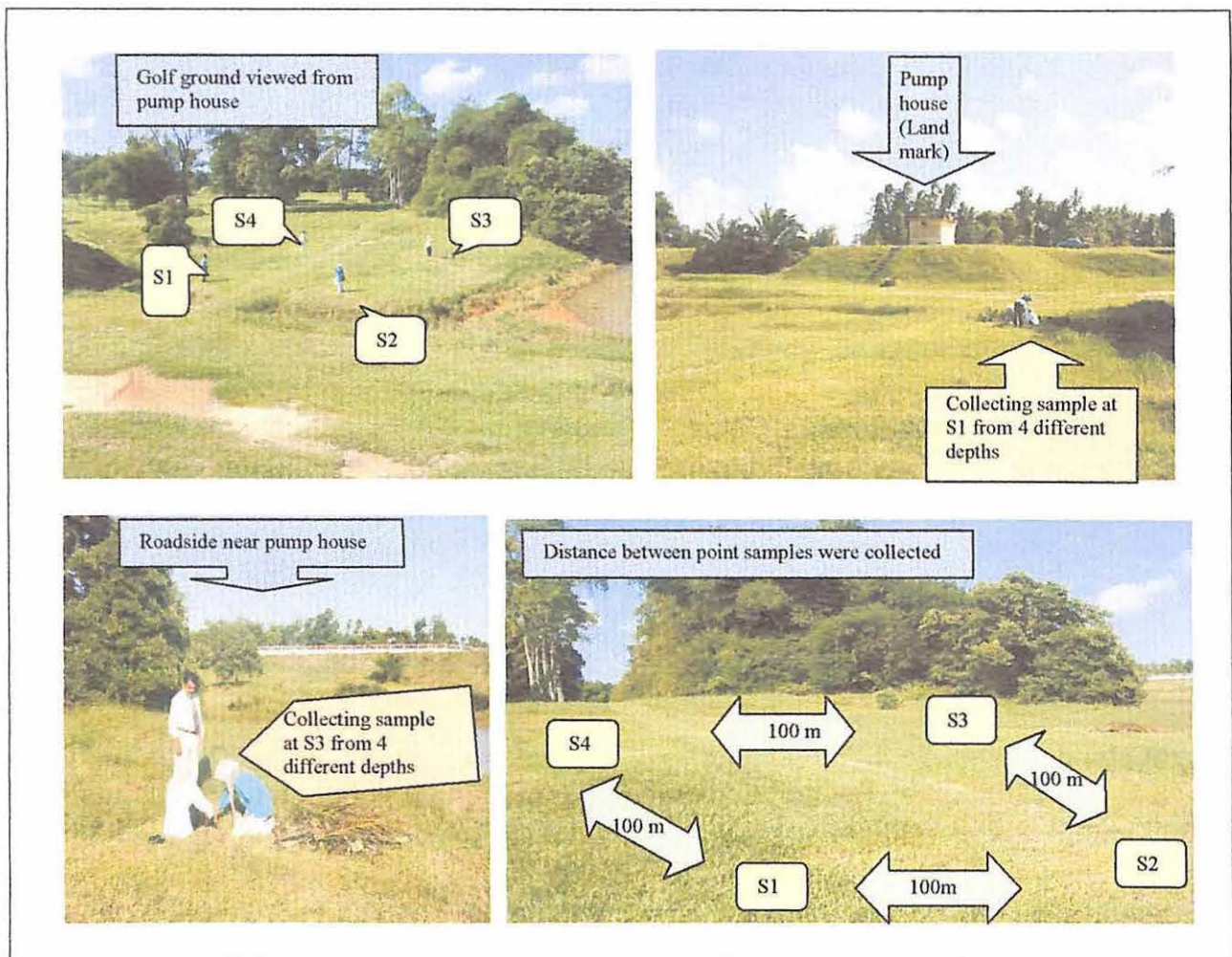


Figure 9: Sample collection area