

CHAPTER 3

MATERIALS AND METHODS

3.1 Landfill Site

The municipal landfill in Sabak Bernam district, where agricultural activity involving coconut, rubber and oil palm plantations is the main profession, was chosen for the present study. Plate 3.1 and 3.2 show the general view of the landfill, which shows the typical Malaysian solid wastes such as glass, metals, paper, plastics, coconut, rubber and oil palm plantation wastes etc.. This site commenced operation as disposal site in 1993. It is 10 acres in area. It is estimated that the disposal site can be used until the year 2001 (Alam Flora Sdn. Bhd.). For the scope of the current work soil samples were acquired from 3 boreholes at various depths. The locations are designated as BH1, BH2, and BH3. BH1 site is inside the landfill area itself whereas BH2 and BH3 sites are two opposite sides around the landfill (Fig. 3.1). In this study, tests were performed to establish the heavy metal contamination and movement in and around the municipal solid waste disposal facility in Sabak Bernam. The study includes physical and chemical characterization of the soil and leachate samples from the landfill.



Plate 3.1 Sabak Bernam landfill site



Plate 3.2 Typical landfill waste at Sabak Bernam landfill

3.2 Soil Sampling

The three soil sampling sites BH1, BH2, and BH3 are shown on the map (Figure 3.1). Rotary drilling was carried out using multi-speed rotary boring machine YBM 2WS. Undisturbed samples were collected at depths of 2m, 15m, 20m, 25m, 30m, and 35m at each site. After boring to the required depth, the borehole was first cleared of disturbed material. A standard split spoon was installed and driven into the soil by 65kg automatic drop hammer falling freely from a fixed height of 75 cm along a guide rod.

Three surface soil samples were also collected from the borehole areas BH1, BH2, and BH3 respectively. The sampling depth was 20cm -25cm. At each site, replicate sediment grabs were taken using a Ponar dredge. Before any sediment samples were taken, the grab samples were each examined to see that a clean grab was accomplished, and that the bottom sediment was not excessively disturbed in the process. Once this was satisfied, a small sample of approximately 100g weight was taken in the middle of the grab just beneath the top surface using a non-metallic spatula in order to reduce metal contamination from the sampler. The samples were then placed in sealed plastic bags, which had been pre-washed with dilute nitric acid, and taken to the laboratory for analysis.

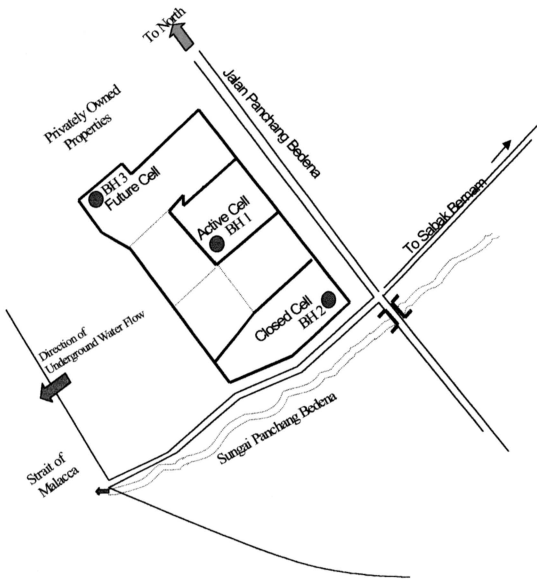


Figure 3.1 Sabak Bernam Landfill Site map with boreholes locations.
(BH=borehole)

3.3 Soil Characterization

3.3.1 pH

Fresh soil samples collected from each site were used in the determination of soil pH. Soil pH was determined on a 1:1 ratio of soil: water paste using pH meter (model no. HI8314) (Lim *et al*, 1997).

3.3.2 Specific Gravity

The specific gravity of soil can be defined as the weight in air of a given volume of soil particles to the weight in air of an equal volume of distilled water at a temperature of 40°C. It is often used in relating a weight of solid to its volume. Soil specific gravity was determined by standard density bottle method.

3.3.3 Moisture content and Organic Matter

Moisture content and organic matter of the composite soil samples were determined from the difference in the weights of samples before and after heating at 105°C for 24h and 550°C also for 24h, respectively (APHA, 1992).

3.3.4 Particle Size Analysis

Particle size analysis of the soil was done by hydrometer method (Day, 1967) using sodium hexametaphosphate (Calgon) as a dispersant. The hydrometer method determines the percentage of sand, silt and clay in the soil using the differential settling rates of soil particles from suspension in water. Large particles (i.e. sand) settle out of suspension more rapidly than do small particles (i.e. clay). The hydrometer is designed to measure the density of the suspension.

3.3.5 Heavy Metal Contents

In the laboratory the soil samples were oven dried at 80°C for 3 days. Each day during the drying period, the soil samples would be taken out and mixed thoroughly. Upon drying, approximately one-gram portion of the samples were finely ground using a porcelain mortar and pestle. After grinding each sample, the mortar and pestle were cleaned with dilute acid, rinsed with distilled water and dried. 250mg of ground sample was then measured into a 100mL Teflon beaker followed by addition of 10mL concentrated nitric acid and 10mL of concentrated hydrofluoric acid. The samples were left to digest in the fume cabinet overnight at room temperature. The next morning, 3ml of perchloric acid was added into each beaker, which was then placed on hot plates set at 120°C. Once the acid had evaporated to dryness, 2mL of concentrated nitric acid was added

and the samples were reheated to dryness. The beakers were then set aside to cool. Finally, 2mL of 10% nitric acid was pipetted into the beakers, and after a few swirls to dissolve the residue, the samples were poured into plastic scintillation vials. Each beaker was then rinsed with 18mL of double distilled water and this was added into vial. Prior to analysis of the metals, 10mL 1/50 dilutions for Al and 1/20 dilution of the other metals were prepared from the standard solutions. Concentrations of all metals were determined using Inductively Coupled Plasma (ICP) spectrometer (Baird 2000).

Strict quality control was maintained during analysis of the metals. The Teflon beakers and their covers were cleaned by soaking in concentrated nitric acid for 3 days followed by rinsing with double distilled water. After each use, the beakers were first wiped with acetone, rinsed with double distilled water before they were soaked in concentrated nitric acid. Before use, the plastic scintillation vials were first soaked in 10% nitric acid and placed on a warm hotplate for three days, following which they were rinsed with double distilled water

3.4 Leachate Sampling

Leachate was collected from the leachate collection pond. One liter samples were taken in duplicate samples in High-Density Polyethylene 1-litre bottles for metal determination. One mL of concentrated Nitric Acid

was added immediately after leachate collection to prevent the sorption of metal ions onto the sides of the container prior to metal analysis. The samples were refrigerated and filtered through a 0.45µm Millipore filter prior to analysis.

3.5 Leachate Characterization:

3.5.1 Conductivity and pH:

Electrical conductivity (EC) was determined with a conductivity meter (Model no. 8033) and a combination pH electrode was used to measure pH.

3.5.2 Total Suspended Solids

Total solid represents both suspended and dissolved solid. Total suspended solids are that portion of the total solids retained by a filter (sometimes referred to as filterable solids, since they can be filtered out). The procedure for measuring total suspended solids is a simple gravimetric analysis involving the difference in weights before and after a sample of leachate is passed through a glass fibre filter. Dissolved solids are considered to be the residue left after the evaporation of a known volume of the filtrate at 103°C.

3.5.3 Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures to determine the consumption of oxygen by the microorganisms that are present in the sample. A reaction time of 5 days is normally used for the measurements of BOD. The nutrient dilution water was prepared in a suitable bottle by adding 2.0 mL each of phosphate buffer, MgSO_4 , CaCl_2 , and FeCl_3 solutions/L. Nitrification inhibitor 2-chloro-6-trichloro methyl pyridine was also added (10mg per liter of dilution water) to prevent oxygen consumption via nitrification. The nutrient dilution water was then aerated until dissolved oxygen reached saturated level (7.9-8.2 mg/L). Leachate samples were diluted with nutrient dilution water using guideline given by Rump and Krist (1992). After dilution, sample was mixed and carefully transferred to the airtight test bottles of the specified size avoiding formation of air bubbles. For each test three BOD bottles were setup. The ground glass stoppers were then applied without generating any air bubbles. The dissolved oxygen concentration was immediately determined using one of the triplicate samples with the YSI Model 57 DO meter. The remaining bottles were then and incubated in the dark at 20°C temperature for 5 days. After 5days of incubation remaining dissolved oxygen was determined. A blank sample consisting of the inoculated dilution water was measured in parallel.

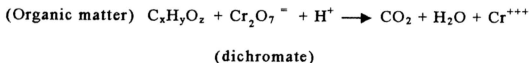
The biochemical oxygen demand was calculated using following formula:

$$\text{BOD}_5 \text{ (mg/L)} = (C-D) \times A/B + D$$

- A = total volume after dilution (mL)
- B = volume of undiluted sample (mL)
- C = oxygen consumption of diluted sample after 5 days (mL)
- D = oxygen consumption of dilution water after 5 days (mL)

3.5.4 Chemical Oxygen Demand

The chemical oxygen demand (COD) determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong oxidant. Dichromate reflux method oxidized the organic matter chemically instead of biologically. Potassium dichromate is generally used as an oxidizing agent. COD was determined by refluxing 20ml of leachate sample for 2hr. in the 0.25M potassium dichromate solution and a mixture of silver sulfate and sulfuric acid using TECATOR COD digestion unit. The reaction, in unbalanced form is-



After refluxing with an acid, the excess dichromate was measured by

titrating with a reducing agent, 0.1M ferrous ammonium sulfate (FAS). The difference between the chromate originally added and the chromate remaining is the chromate used for oxidizing the organics. The more chromate used, the more organic were in the sample, and hence the higher COD. During each set of test, one blank with distilled water and one potassium hydrogen phthalate (KHP) standard were used to evaluate the technique and quality of reagents. KHP has a theoretical COD value of 500mg/L. Final COD value in mg/L was calculated using the following relationship:

$$\text{COD} = \frac{(A - B) \times M \times 8000}{\text{mL sample}}$$

A= mL FAS used for blank

B= mL FAS used for sample

M= molarity of FAS

3.5.5 Total Organic Carbon (TOC)

TOC analyzer (Shimadzu 5000) was used to measure total organic carbon. The total combustion of a sample yields some significant information on the amount of organic carbon present in a leachate sample. TOC methods utilize heat and oxygen, ultraviolet irradiation and chemical oxidants to convert organic carbon to carbon dioxide (CO₂). The CO₂ was measured directly by an analyzer.

3.5.6 Kjeldahl Nitrogen

Kjeldahl nitrogen is the sum of ammonium and those organic nitrogen compounds, which can be converted to ammonium under Kjeldahl reaction conditions. The portion of organic nitrogen may be obtained by subtracting the ammonium content from the Kjeldahl nitrogen value.

A 100mL-water sample was placed in the Kjeldahl flask and treated with 1g of reaction mixture (5g selenium, 5g copper sulphate, and 250g-sodium sulphate mixture) and 10mL of ethanol. After shaking, 10mL of concentrated Sulphuric acid was added and the mixture heated to boiling until a light green colour was obtained and black particulars are no longer visible. Boiling was then continued for 30 minutes. This process removes nitrite and nitrate. After cooling and diluting with water to a total value of approximately 300ml, the content was transferred to the 1L flask after rinsing the Kjeldahl flask twice. A few drops of phenolphthalein solution were then added together with sufficient sodium hydroxide to change the colour of the content red.

The flask was then attached to the distillation apparatus and approximately 200mL distilled over, during which the end of the condenser was dipped into the absorber. The ammonium content was then determined titrimetrically or photometrically depending on the original nitrogen content. The photometric method was preferred for a nitrogen

content of less than 100mg/l, whereas the titrimetric method is employed at higher concentrations.

The distillate was collected in a 250ml volumetric flask containing 50ml water, 100ml of this solution was mixed with 3 drops of the mixed indicator solution and the titration carried out with 0.025 M sulphuric acid until a colour change from violet to green is observed. A blank sample of water was titrated in the same way.

Titrimetric determination:

$$\text{Kjeldahl N (mg/L)} = a \times b \times 700 \text{ mg/c} \times d \text{ mL}$$

a = consumption of 0.025 M H_2SO_4 (mL)

b = aliquot of distillate taken (mL)

c = sample volume (mL)

d = total volume of distillate (mL)

3.5.7 Heavy metal determination

The concentration of the elements was determined using the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Prior to analysis of the metals from leachate samples, 100mL 1/50 dilutions for Al and 1/20 dilution of the other metals were prepared from the standard solutions. Concentrations of all metals were determined using Inductively

Coupled Plasma (ICP) spectrometer (Baired 2000). Strict quality control was maintained during analysis of the metals.

3.5.8 Other determinations

Alkalinity, Hardness, Chloride, and Sulphite were determined using Hanna Instruments HI4817 test kit. Methods used are briefly described below.

(a) Alkalinity

Alkalinity is the quantitative capacity of a sample to neutralize an acid to a set pH. Alkalinity was measured in two steps. First step converts hydroxide ions to water and carbonate ions to bicarbonate. This is called Phenolphthalein alkalinity. Since bicarbonate ions can be converted to carbonic acid with additional hydrochloric acid, it is known as total alkalinity. First the Phenolphthalein alkalinity was determined by neutralizing the sample to a pH of 8.3 using a dilute hydrochloric acid solution and a phenolphthalein indicator. The phenolphthalein colour change was from violet to yellow. The total alkalinity of the leachate sample was determined by neutralizing the sample further by adding hydrochloric acid solution until the sample pH was 4.5 and colour change was from yellow to violet. Total alkalinity was calculated using titration volume.

(b) Hardness

An ethylene-diamine-tetraacetic acid (EDTA) titration determined hardness level as mg/l calcium carbonate of a leachate sample. An appropriate volume of sample was first adjusted to a pH of 10 using a buffer solution. Eriochrome black T was added as an indicator, which chelates with metal ions such as magnesium or calcium to form a red coloured complex. As EDTA was added, metal ions formed a complex with it. After all the free metal ions have been complexed, an excess EDTA removes the metal ions complexed with the eriochrome black T and formed a blue coloured solution. This colour changed from red to blue determined the end point of the titration. Amount of CaCO_3 was calculated from titration volume.

(c) Chloride

The chloride level was determined by a mercuric nitrate titration. The pH of the sample was lowered to approximately 3 by addition of nitric acid. Mercuric ions reacted with chloride ions to form mercuric chloride. When excess of mercuric ions were present in the solution; it formed a complex with diphenylcarbazone and changed the colour of the solution from yellow to violet. Amount of chloride was calculated from the titration volume.

(d) Sulphite

This parameter was determined by iodometric method. Iodide ions reacted with iodate ions in the presence of sulphuric acid to form iodine. The sulphite present in the leachate sample then reduced the iodine back to iodide. An excess of iodate ions generated additional iodine, which formed a blue complex with starch. The end point of this titration was determined by the change in colour from colourless to blue. From the amount of titration solution the amount of sodium sulphite was calculated.