APPENDIX
APPENDIX- I

METHODS USED FOR ANALYSIS OF SOLID WASTE AND WASTEWATER SAMPLES

pH
The pH of solid waste sample was analysed by Jackson (1973) method with the help of Rachho pH meter. The pH was measured taking 1:10 ratio of sample (solid wastes) and deionised water.

The pH of wastewater samples were measured using standard methods given in American Public Health Association (1995). The instrument was calibrated by the standard buffer solutions of pH 4.0, 7.0 and 9.2. The repeated readings (least three times) were taken for precision and accuracy and concordant mean values were recorded.

Electrical Conductivity (E.C.)
Electrical conductivity is governed by the total ionic content of the sample. Although E.C., is non-specific property and varies with the proportion of species present. It expresses the resistance of a 1cm cube of water to the passage of a current, usually at 25°C. The electrical conductivity was measured by Systronics, Conductivity meter using 1:10 ratio of solid wastes samples & deionised water (Jackson, 1973) and wastewater by standard methods given in American Public Health Association (1995).

Kjeldhal's Nitrogen
The nitrogen was estimated by Kjeldahl’s method by acid digestion technique. Where oxidation of the samples was done by H₂SO₄, H₂O₂, K₂SO₄ (raise the boiling point of the mixture) and selenium metal was used as catalyst.
**Phosphorus**

Olsen and Bray method was used for detecting phosphorus in the solid waste samples (Okalebo and Gathu, 1993).

**Carbon and Sulphur (Organic, Inorganic and Total)**

The analysis of carbon and sulphur is based on measuring the infra red (IR) response of the CO$_2$ and SO$_2$ gases emitted upon combustion of a sample. A known amount of sample is placed in a ceramic boat (free of Carbon) and pushed into the silicon carbide furnance set at 1250°C. The combustion occurs in the presence of oxygen gas, which also acts as a carrier gas. The carbon and sulphur presents in the sample are oxidised into CO$_2$ and SO$_2$ respectively. These gases are then carried into the IR absorption cell by the oxygen gas. Moisture traps in the system ensure that only the dry gas mixture reaches the IR cell. The cell signals are selective and respond to CO$_2$ and SO$_2$ concentration in the gas mixture reaches the IR cell. The cell signals are selective and respond to CO$_2$ and SO$_2$ concentrations in the gas mixture and percentage of carbon and sulphur are read on the digital display.

Samples for total carbon and sulphur analysis were treated with deionised distilled water until they were free from halogens. This was confirmed by the absence of a white precipitate on treatment of the supernatant with a few drops of AgNO$_3$ solution. The residue was dried and 50-100 mg of the sample was accurately weighed and analysed for the total carbon and sulphur (against suitable salt standard) using the LS-1000, Eltra, auto carbon-sulphur analyser.

A portion of the halogen free dried sample was treated with H$_2$O$_2$ solution (50%) to oxidise the organic matter in the samples. Latter, these samples were used for the analysis of the inorganic carbon and sulphur fractions as described above. The organic carbon and sulphur contents were computed as the difference between the total and inorganic fractions.
Ion Chromatograph

The Metrohm, Ion Chromatography was used to identify the quantity of anions (F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) and cations (Ca, Mg, K and Na) in the wastewater samples.

Anion Analysis

Phthalic acid was used as eluent for the anion analysis. The eluent was prepared by adding 5 ml of NaOH in 950 ml of high purity water and 8.31 g phthalic acid was dissolved with warming up. Then 10 ml of acetic acid was added and the solution was left to cool down. The pH was set to 4.3 using NaOH (conductivity 400 μS/cm). Then the solution was filled with one liters of high purity water. During whole experiment the eluent flow was maintained as 0.8 mL/min and 100μS/cm sample was injected for analysis.

Cation Analysis

The cations were analysed by the eluent of 4mmol/L tartaric acid, 1mmol/L dipicolinic acid with conductivity approximately 700 S/cm. The eluent was prepared by mixing 167 mg dipicolinic acid, 0.6 g tartaric acid in 100 ml high purity water with warming up and then solution was made upto 1L with high purity water. The eluent flow was maintained as 1μL/min and the sample was injected of 10 μL.

Mercury Analysis

Mercury in selected solid waste was estimated according to the procedure described by Allen et al. (1989). One gram of sample was digested slowly in 1ml of concentrated H₂SO₄ and 10-15 ml Concentrated HNO₃. When most of the organic matter had been destroyed, the digested mixture was filtered and app. 0.5 g of KMnO₄ was added until a permanent precipitate of KMnO₄ remained. The mixture was cooled and diluted. The mixture was neutralised using 1M NaOH and bromophenol blue as indicator. The neutralised solution was diluted to 100 ml with deionised distilled water.
mercury was determined using the Cooled Vapour Technique (GBC Hydride Generator modal, HG 900). Appropriate mercury standard solution prepared by stepwise dilution of 1000 mg/L Hg, earlier prepared for analytical grade HgCl₂ salt.

20 ml of sample or standard solution was incorporated in the reaction vessel and closed tightly with the septum, to avoid leakage of gas. Then one ml of stannous chloride solution injected in the reaction vessel through the rubber septum and the solution was stirred for 90 seconds. To carry the mercury vapours generated in above reaction to detector the nitrogen gas was used, as soon the supply of nitrogen gas was turned to high position, the read button was pressed to display the readings. The reaction chamber was flushed with distilled water before next detection. The absorbance (253.7 nm) was read on the display of GBC AAS, Model-902. Blank and Certified Reference materials were treated in the same way as the sample were analysed for mercury.

**Bulk Analysis of Metals**

The samples were digested by the method given by Loring and Rantala (1992). The 0.1 g of finely grounded samples were weighed and transferred to Teflon Bombs, then mixed with 3 ml of Aqua-Regia (3HCl:1HNO₃) and 6 ml of HF was added slowly to avoid excessive frothing. Bombs were closed tightly and kept in an oven for 1 and 1/2 hours at 100°C. The bombs were removed from oven, allowed to cool and opened. The bombs were rinsed several times with de-ionised water and the digested sample was transferred to a 100 ml polypropylene flask. 5.6 g of Boric acid was weighed and transferred into a 100 ml flask and mixed thoroughly with 20 ml of de-ionised distilled water. The solution was made upto 100 ml. The samples were kept for a fortnight to precipitate out gelatinous borosilicates, the solution was filtered and analysed for heavy metals by GBC 902, AAS.
The rock standards MAG-1, SCO-2, SDC-1 and Canadian soil standards SO-1, SO-2, SO-3 and SO-4 were digested in same manner and used for calibration.

**Fractionation of Metals from Solid Waste**

The fractionation of heavy metals was done using Tessier et al. (1979) and Ma and Rao (1997). The six species were fractionated using different methods. One gram of solid waste is weighed into a 40 ml polycarbonate centrifuge tube and each fraction obtained so were analysed for different heavy metals using GBC 902, AAS.

1. **Water-soluble**

Soil sample extracted with 15 ml of de-ionised water for 2 hours.

2. **Exchangeable**

The residue from water-soluble fraction is extracted with 8 ml of 1 Molar NaOAc (adjusted to pH 5 with HOAc) for 5 hours.

3. **Carbonate-Bound**

The residue from carbonate fraction is extracted with 8 ml of 1 molar NaOAc (adjusted to pH 5 with HOAc) for 5 hours.

4. **Fe-Mn Oxides- Bound**

The residue from carbonate fraction is extracted with 0.04 Molar NH$_2$OH.HCl in 25% v/v HOAc at 96°C with occasional agitation for 6 hours.

5. **Organic Fraction**

The residue from Fe-Mn oxide fraction is extracted with 3 ml of 0.02 M nitric acid and 5 ml of 30% hydrogen peroxide (adjusted to pH 2 with HNO$_3$). The mixture is heated to 85°C for two
hours, with occasional agitation. A second 3ml aliquot of 30% hydrogenperoxide (adjusted to pH 2 with nitric acid) is added and the mixture heated to 85°C for three hours with intermittent agitation. After cooling, 5 ml of 3.2 molar NH₄OAc in 20% (v/v) HNO₃ is added and the samples diluted to 20ml and agitated continuously for 30 min.

5. Residual Fraction

The residue from organic fraction are digested using a HF-HCl/HNO₃ dissolution procedure in a Teflon bombs. A standard reference material digested in same manner was used for calibration.

After each successive extraction, centrifuging at 14Krpm for 30 minutes was used for separation. The supernatant were removed and residue was washed with 8ml of de-ionised water followed by vigorous hand shaking, and then followed by 30 minutes of centrifugation before the next extraction.