CHAPTER IV

METHODOLOGY
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MATERIALS AND METHOD

With increase in population in the Delhi city, waste materials quantity also increase every day (CPCB, 1995). Out of three-selected landfills, two (Okhala and Bhalswa) are working and one (Indraprastha landfill, now Millennium Park) is closed. All of them are located near the bank of the Yamuna River. The sampling has been carried out in pre-monsoon (May), post-monsoon (Sept.) and in winter (Jan.) in each year, during period from 2003 to 2005 in and around these landfill-sites. In total eighty-three samples of ground water were collected in every season around these landfills. The sampling locations has been selected in order to get maximum representation of the probable variations in groundwater quality and land use pattern with due consideration to its hydro-geological setup of study area.

4.1 FIELD METHOD

Groundwater samples were collected in 500 ml pre-cleaned plastic bottles and rinsed with samples before collection and are completely filled with groundwater sample and capped airtight. The parameter (pH, ORP, DO, Conductivity and TDS) was analyzed in the field at the time of sampling by using water-analyzer kit using standard procedure as explained in APHA (1995). For cations 100 ml samples were filtered by using 0.45 μm filter paper and preserved insitu with ultra pure nitric acid (HNO₃). While boric acid (HBO₃) were used as preservative for nitrate analysis and stored at 4°C temperature to avoid any major chemical alteration for various physiochemical analysis (APHA, 1995). The samples were analyzed in laboratory of School of Environmental Sciences, Jawaharlal Nehru University as by following standard procedure as follows.
4.1.1 pH
The pH was measured by using Basic pH Orion (210 A+) Thermo electrode. The electrode was conditioned (1 M KCl as filling solution) and calibrated with buffer solutions of pH 4, 7 and 9.2. The temperature knob was set in accordance with the temperature of the water samples. The samples were stirred continuously in order to maintain homogeneity before noting down the pH (APHA, 1995).

4.1.2 Electrical Conductivity (EC)
The conductivity was measured in μS/cm using conductivity meter. The instrument was calibrated and set for 0.01 m KCl solution (1413μs/cm at 25°C) (Todd 1980) in water analyzer kit, and crossed checked by EC (Orion 116) Thermo electrode.

4.1.3 Dissolved Oxygen
The dissolved oxygen was measured in milligram per liter (mg/l) by using Basic DO Orion (805 A+) Thermo electrode at the moment of sampling because the dissolve oxygen concentration decreases with time as consumed in other chemical reaction or by other micro-organism (Subba Rao, 2002).

4.1.4 Oxidation Reduction Potential (ORP)
The oxidation-reduction potential (ORP) is one of the most important parameter for study of water chemistry because, it gives an idea about the surrounding condition of groundwater whether it is oxidizing or reducing. The oxidation-reduction potential (ORP) value was measured by using ORP Quickcheck model 108 electrodes in mV in field during sampling of groundwater around landfill.

4.2 LABORATORY ANALYSIS

4.2.1 Bicarbonates
The bicarbonate content was determined by the potentiometer titration method as explained in APHA (1995). The bicarbonate standards ranging from 100-1000 mg/l were prepared from sodium bicarbonate salt.
The groundwater samples (50 ml) were titrated against standard 0.02 N HCl solutions, standardized by standard NaOH solution. The end point was noted at pH 4.5 because used indicator showed colour change in acidic condition. A graph was plotted between bicarbonate standards and volume of acid consumed. The readings for samples were noted down from this graph. (APHA, 1995)

4.2.2 Chloride
The chloride has been estimated by Argentometric titration method in which mixed K$_2$CrO$_4$ indicator was used (APHA, 1995). The mixed indicator was prepared by dissolving 5g K$_2$CrO$_4$ in distilled water and subsequent adding of AgNO$_3$ solution until complete precipitation of silver chromate takes place. Mixed indicator solution was left for 12 hrs, filtered and make up to 100 ml.

While 0.0141 N silver nitrate (AgNO$_3$) solutions were prepared by dissolving 1.1975 gm of AgNO$_3$ in 500 ml distilled water and standardized by standard solutions. The silver nitrate solution was stored in brown bottle to protect reduction of silver ion to silver metal (silver mirror) by light. The groundwater samples (20 ml) mixed with mixed indicator were titrated by standard silver nitrate solution (AgNO$_3$), at the end point consumed volume of silver nitrate were noted (APHA, 1995). The concentration of chloride ion was calculated by simple formulae of

$$N_1*V_1 = N_2*V_2.$$  

4.2.3 Fluoride
The recent study has been reported fluoride problem in Delhi in current past (Sujatha et.al, 2002). Hence fluoride is one of the most important anion for Delhi groundwater study. The fluoride ion concentration was determined by Spectrophotometer by using SPADNS reagent at 570 nm (APHA, 1995). During analysis, residual chlorine free samples were used because free chlorine act as interfering radicals at time of analysis by spectrophotometer. Samples were made chlorine free by using AsO$_3$. (APHA 1995)
Samples (50 ml) +5 ml Zirconyl Acid+ 5 ml SPADNS reagent solution

The absorbance was measured at 570 nm by spectrophotometer.

4.2.4 Sulphate

The sulphate ion concentration was determined by turbiditeric method by using spectrophotometer (APHA, 1995). The method is based on the principle that sulphate ion is precipitated in acidic medium with barium chloride, so as to form barium sulphate crystal of uniform size. Light absorbance of barium sulfate suspension is measured by spectrophotometer at 420 nm and the concentration is determined by comparison of the reading with standard curve.

The 20 ml of buffer solution (prepared by dissolving 30g of MgCl$_2$.6 H$_2$O, 5 g of CH$_3$COOH.3H$_2$O, 1g of KNO$_3$ and 0.111 g of Na$_2$SO$_4$ and 20 ml of acetic acid (99 %) in 500 ml distilled water and volume made up to 1000 ml. Groundwater sample was added mixed buffer solution, while starting and a full spoon BaCl$_2$ crystal was added. This was stirred for 60 seconds with constant speed. After the stirring period, solution was poured into the absorbance cell of the spectrophotometer and absorbance reading has been taken after 5 minutes.

Sulphate ion concentration was determined by comparing reading with calibration curve prepared by carrying sulphate standard through the entire procedure. (APHA, 1995)

4.2.5 Nitrate, Nitrogen Estimation

NO$_3^-$ N was estimated by Brucine method by using Cecil Spectrophotometer (model no. 594). Brucine reagent was prepared by dissolving 0.25 g of Brucine in 10 ml of CHCl$_3$, then final sample was prepared by mixing 10 ml of groundwater sample with 0.2 ml brucine reagent and 20 ml H$_2$SO$_4$ and total volume made up to 50 ml. The yellow colour solution was developed and absorbance was measured at 410 nm (APHA, 1995).
4.2.6 Phosphate

Phosphate was determined by the Ascorbic acid method by using spectrophotometer (APHA, 1995). Phosphate standards ranging from 0.01 - 0.5 mg/l was prepared by KH₂PO₄ salt.

About 40 ml of groundwater sample/standard solution was pipette out in 50 ml volumetric flask and 5 ml of Molybdate antimony solution (prepared by dissolving 4.8 g of Ammonium Molybdate and 0.1g Potassium Antimony Tartrate in 400 ml 4N H₂SO₄ and making the total volume to 500 ml with the same acid) and 2 ml of ascorbic acid solution (2.0% w/v) was added and mixed well. The mixture was diluted to 50 ml and optical density was measured at 880 nm using Cecil Spectrophotometer (model no. 594). Graph was plotted between standard concentrations and optical density, sample concentration was calculated directly from this graph.

4.2.7 Dissolved Silica

The dissolved silica content was determined by the Molybdo Silicate method (APHA, 1995). Silica standard was prepared, ranging from 5 mg/l to 20 mg/l from Sodium metasilicate nanohydrate.

About 20 ml of groundwater sample/standard was pipette out in 50 ml volumetric flask and 10 ml of Ammonium Molybdate solution (prepared by dissolving 2g Ammonium Molybdate in 10 ml of distilled water; 6 ml of concentrated HCl was added and final volume was raised to 100 ml by distilled water) and 15 ml of reducing reagent (prepared by mixing 100 ml Metol Sulphite solution, 60 ml 10% Oxalic acid and 120 ml 25% Sulphuric acid, and making the total volume 300 ml by adding distilled water) was added and mixed well. Metol Sulphite solution was prepared by dissolving 5g Metol in 210 ml distilled water and 3 gm Sodium Sulphite was added and the volume was made up to 250 ml by adding distilled water. The groundwater samples was stirred properly and kept for 3 hours to complete the reaction. The optical density was measured at 650 nm using Cecil Spectrophotometer-594. Graph between standard
concentration and optical density was drawn and concentration of samples were recorded from it.

4.3 MAJOR CATIONS

4.3.1 Sodium and Potassium

The preserved groundwater samples were filtered by 0.45 µm filter paper before using as in flame photometer. Since, the Delhi groundwater shows very high value of sodium and potassium concentration, the groundwater samples were diluted 10 to 40 times before using in flame photometer.

Sodium and Potassium were analyzed by using AIMIL Flame Photometer (PE I). The standard solution provided MERCK was used for calibration of instrument. Graph between standard solution and concentration was drawn and concentration of samples were recorded from it.

4.3.2 Calcium and Magnesium

The preserved and filtered groundwater samples with 0.45 µm filter paper, was used for analysis of Calcium and Magnesium. The analysis of Calcium and Magnesium were carried out on Shimadzu-AA-6800, Atomic Absorption Spectrophotometer. Calcium and Magnesium were analyzed in absorption mode at the wavelength of 422.7 nm and 285.2 nm respectively.

The instrument was calibrated with standard chemical solution provided by MERCK and methodology was used as mentioned in APHA (1995).

4.3.3 HEAVY METALS (Fe, Mn, Cu, Zn, Pb and Ni)

The analysis of heavy metals is very important because of its toxic character at very low concentration also. Six heavy metals were analyzed out of so many based on availability and its toxic effect.
The preserved groundwater samples were filtered by 0.45µm filter paper before analysis. Using Shimadzu-AA-6800, Atomic Absorption Spectrophotometer attached with GF, has carried out the heavy metal analysis. Instrument was calibrated by using respective standard provided by MERCK for respective metals as required. Standard curve were drawn between absorbance and concentration from this graph concentration of water sample were calculated. Flame used for metal analysis was Air-Acetylene and Cathode lamp of respective metals were used at following wavelength.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength</th>
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<tbody>
<tr>
<td>Iron</td>
<td>248.3 nm</td>
</tr>
<tr>
<td>Manganese</td>
<td>279.5 nm</td>
</tr>
<tr>
<td>Nickel</td>
<td>232.0 nm</td>
</tr>
<tr>
<td>Lead</td>
<td>283.3 nm</td>
</tr>
<tr>
<td>Zinc</td>
<td>213.9 nm</td>
</tr>
<tr>
<td>Copper</td>
<td>324.7 nm</td>
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</tbody>
</table>

The heavy metal in solid waste (landfill leachate) is analyzed by using solution B method. For, this 0.5 g of finely powdered solid waste sample were transferred to the Teflon crucible and 4 ml of Aqua-regia (HNO₃ and HCl in ratio 1:3), 1ml Boric acid and 2 ml HF were added to each crucible, these were then sealed in metallic cases for 2 hrs. at 100 °C and allowed to cool down to room temperature. The solution content transferred to volumetric flask to make 100-ml volume. The solution was transferred to polypropylene bottles for storage. The samples were left undisturbed overnight to allow the formation and settling of Borosilicate from solution. This gelatinous precipitate is separated by centrifugation. The solution thus obtained is used for analysis of major and minor elements by GBC-902 double beam Atomic Absorption Spectrophotometer.

4.4 SECONDARY DATA
Secondary data is mainly required for simulation of solute transport in groundwater in vicinity of Okhal and Indraprastha landfill. In this study landfill is assumed as point
source for study, while Aravali ridge is used as natural boundary and the river Yamuna is used as constant head boundary. Details about modeling are discussed in chapter VII.

All the required secondary data is collected from authorized Government Organization, Department and Institution to maintain accuracy of data. Some data like water table, chemical analysis data etc. are calculated in field and interpreted in School of Environmental Sciences, Jawaharlal Nehru University based on literature. Other required secondary data like rainfall, evaporation humidity, temperature from 1990 to 2004 was collected from Indian Metrological Department (IMD), New Delhi. Aquifer status, Groundwater level fluctuation map from 1960 - 2004 were collected from Central Ground Water Board (CGWB), New Delhi. Other requirements like metal concentration in Delhi were collected from Central Pollution Control Board (CPCB), New Delhi. Along with this continuous two-year sampling and analysis has been done for validation of model.

For study area map, toposheet - 53H was used provided by the Survey of India (SOI), New Delhi. The recharge, Hydraulic Gradient, evapotranspiration and flow rate were calculated by respective formulae used by Central Ground Water Board and as given in other literature.

4.5 SOFTWARE USED

The software used in this study is mainly for simplify the environmental problem in more accurately. It also helps to understand water chemistry under subsurface more easily and efficiently. The software used in this study mainly on their requirement, out of those few is given as. SURFUR, SPSS, WATCHEM, WATCLAST, MAPSCAN, PMWIN, SURFUR, PHREEQC and ARCVIEW etc.

The Visual MODFLOW / MT3D, a software provided by Waterloo Hydrological Inc., mainly used for simulation of solute transport in vicinity of Okhala landfill. The landfill is assumed as point source for contamination of groundwater for simulation. The details about simulation have been given in chapter VII.