RESULTS AND DISCUSSION
River Yamuna and Union Territory of Delhi

Delhi, India's capital, ranks third in population (8 million) among Indian cities and thirteenth among cities of the world (Chaudhuri, 1984). River Yamuna is not only the main source of raw water supply to Delhi, but also serves as a convenient means of disposing of industrial wastes and sewage.

The river flows through the union territory of Delhi from Palla village in north to Jaitpur village in east (Dakshini et al., 1979). During its course of 48 km stretch through the (Figure 4) capital city, 17 major and minor drains discharge waste water directly into the river through its western bank (CBPCWP, 1979). The extent to which the river gets polluted by each drain needs accurate assessment for planning its pollution control programmes.

A detailed account of the river Yamuna in Delhi and the sources of its contamination have been given elsewhere (Mathur, 1965; Rai, 1974; CBPCWP, 1979; Dakshini et al., 1979). However, no thorough investigations have been undertaken so far, to assess quantitatively the impact of each drain on the water quality of the receiving river. Obviously, such investigations have become important as data along these lines shall be invaluable for improving the quality of the river.
Fig. 4

River map of Yamuna in Delhi
Source: CBPCWP, 1979
During the period of investigations, the quantity of water released in the river from ITO Yamuna barrage is presented in Figure 5. Maximum amount discharged during rainy season resulting in a marked increase in flow rate and suspended silt. During the other periods, the discharge was low but varied monthly.

The water requirements of the Indraprastha Thermal Power Station (IPS) are at present met from the river at ITO Yamuna barrage. Nearly 600 m$^3$/s of water have been earmarked for supply to the IP station for cooling, sluicing and other purposes by the Haryana Irrigation Authorities (personal communication to the concerned). The IPS, however, has now a consumptive requirement of only 285-380 m$^3$/s (Appendix 1).

The Delhi climate, in general, is characterised by a dry and hot summer (March to May), a warm monsoon period (June to September,) a calm post-monsoon period (October to November) and a dry and cold winter (December to February). During the period of investigations, the mean annual temperature was approximately 25°C and the mean maximum temperature (42.4°C) was in the month of May, 1984 (Appendix 2). The total rainfall was 572.8 mm for the study period from March 1984 to February 1985 (Appendix 3). The average relative humidity varied from 40 to 80% (Appendix 3). During summer months, due to high temperature and low relative humidity, evaporation from the free water surface in this region has been estimated to range between 6 to 12 mm/day.(Appendix 4).
FIGURE 5: DISCHARGE DATA OF THE RIVER YAMUNA AT ITO YAMUNA BARRAGE DURING THE STUDY PERIOD.

SOURCE: YAMUNA BARRAGE OFFICE, NEW DELHI, 1985
The Indraprastha Thermal Power Station, a 282.5 MW coalfired electric-power-generating complex consisting of 5 units (1 x 36, 3 x 62.5, and 1 x 60), is located on the western bank of river Yamuna in Delhi. It was started in early 1963 and additions were made in 1968, and 1971. This station utilizes pulverised (mesh: 80), low sulphur (~0.50%) and high ash content (av. 33%) bituminous coal obtained mostly from Bihar coal fields. When operating at full capacity, this station consumes approximately 3500 t/d of coal for power generation and thereby produces 1000 t/d of coal residues - fly and bottom ashes. Nearly 80% of the total ash produced at this station is fly ash.

Prior to 1979, fly ash produced by plant operations was removed with mechanical dust collectors that had a maximum efficiency of about 75%. Electrostatic precipitators were installed on each of the 3 stacks during late 1979 and early 1982 and are estimated to be more than 99% efficient at removing fly ash from stack emissions. At present, the fly ash is collected by mechanical collectors and electrostatic precipitators installed in series, with an overall efficiency of 98% and the bottom ash is collected in hoppers located at the bottom of the furnace.

At the time of this study, the plant disposed a major portion of the precipitated fly ash and bottom ash by creating a slurry (upto 15%) with raw river waters which was then pumped from the
plant to a large settling basin excavated 3 km south of the station and adjacent to the bed of river Yamuna on its western side. The slurry subsequently got diluted in the basin by the flushing water used to maintain the pipeline free from scale. After the particles settle out in the basin, the effluent was directly discharged into the river Yamuna. No chemicals were used at the plant to adjust the pH of pond effluents before it was let out into the stream. Also the sluice water was not recycled or reused.

When the ash basin in use (A) had completely filled up with ash by August 1984, a new basin system was constructed adjacent to the original one. The ash slurry started coming into the new basin (B) from September 1984 onwards. Since then the basin 'A' acted merely as a conduit to transport the ash to basin 'B'. The total ash disposal areas including basins A and B is approximately 61100 m$^2$.

A considerable portion of ash slurry is also discharged into a sewage drain which flows adjoining the power plant and ultimately joins the river within a half km distance. The discharge from this drain into the river is extremely turbid and grey in colour. A detailed study of this drainage system was reported by Fulekar (1983).

The mode of ash handling and disposal at IPS is schematically
FIGURE 6: SCHEMATIC DIAGRAM OF ASH HANDLING AND DISPOSAL AT INDRAPRASTHA POWER STATION, NEW DELHI.
given in the Figure 6.

**Sampling Locations**

Eight sampling stations on the river Yamuna in Delhi were established between Yamuna barrage and Okhla weirage for this study to ensure a complete evaluation of the impact of ash effluents on the receiving river (Figure 7). The river portion between the power station's effluents outfall area and Yamuna barrage is termed 'upstream' or 'background'. The outfalling drains ($D_1, D_2$ and $D_3$) in the downstream of the river with respect to the power station were taken as 'control'. In this way, the direct effects of power station's ash effluents on water quality of the river could be separated from the effects of different effluents entering the river through the drains.

Stations 1 and 2 in the river were not exposed to the power station effluent discharges and therefore selected as reference sites. Station 3 was thermally influenced as a result of the warm water discharge from the power station condensers. The power station discharges ash slurry via sewage drain ($D_2+A_9$) between Stations 4 and 3 and ash leachates from ash basins (A and B) between Stations 6 and 5 respectively. The Station 5 was influenced by a sewage drain ($D_3$).

The effluents from ash basin A was sampled from March to
FIG. 7 STUDY AREA AND SAMPLING SITES
(Not to scale)
August 1984. After cessation of ash effluent flow from the settling basin 'A' in September 1984, additional stations were established at the outfall of the new basin (B) and below the confluence of ash effluents in the river. However, the sampling at the new stations began only in the month of November 1984 as there was no effluent flow from the new basin earlier.

The Stations 6 and 7 were established in the river at a distance of 5200 and 7200 m respectively from the Yamuna barrage.

The characteristics of the Drains outfalling into the study area of the river Yamuna and the sampling locations are presented in Table 7.

Sample Collection

The sampling covered a 12-month period from 27 March 1984 to 14 February 1985. The sampling frequency was once a month. This frequency was chosen to get information on seasonal variations. On each occasion, the sampling was started around 8.30 AM at Yamuna barrage and ended at Okhla nearly at 1 PM. For all sampling, the boat facilities were provided by the Flood Control Office, Delhi Administration, Delhi.

Polyethylene, 1000 ml-screw cap bottles were used as containers for the water samples. Prior to use, the bottles were cleaned sequentially in the laboratory with a detergent wash, tap water
TABLE 7
Details of the out falling drains and sampling locations between ITO Yamuna Barrage & Okhla

<table>
<thead>
<tr>
<th>Code No.</th>
<th>Name of the drain</th>
<th>Sampling locations</th>
<th>Distance in metre</th>
<th>Flow in KLD</th>
<th>Basin area in sq. km</th>
<th>Characteristics</th>
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<td>450</td>
<td>5000</td>
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<td>D2 + As</td>
<td>Sen Nursing drain</td>
<td>D2 + D2 + As</td>
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<td>Drain No. 14</td>
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<td>A &amp; B</td>
<td>Ash basin effluents</td>
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<td>6a</td>
<td>1600</td>
<td>NA</td>
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<td>old basin and new basin</td>
<td>B</td>
<td>6b</td>
<td>2100</td>
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YAMUNA BARRAGE

DRAINS

1
2

OKHLA

- - - - - - - - - -

Warm water from power plant condensers.

Mostly sewage and power plant's washings and ash slurry.

Domestic effluents.

Coal ash effluents.
rinse, 24 hr soak in 1% HNO₃ and several distilled water rinses (Subramanian et al., 1979). This cleaning process removes trace metals from the container walls and thus prevents or minimises contamination of the collected samples. The container was also rinsed in each case with a portion of the sample water before being filled with the sample.

Water samples, 30 cm below the water surface, were collected manually into sample storage bottles from slow-moving non-metallic boat. While doing so, all possible precautions were taken to minimize contamination and contact with surface films. Each bottle was filled with sample to the brim to avoid any air space (Kratochvil et al., 1982).

Three water samples were collected from each station in the river, one at the middle, and one on either side close to the river bank to test the cross-sectional variation in quality parameters and concentration of trace metals at each sampling station. From drains, the samples were collected before these discharged their contents into the river; and from the river, the samples were taken immediately downstream of the effluent outfall and at a point where mixing was complete.

To provide background water quality data for effluent waters, the influent waters to the power station were collected at the water intake (w₁) near Yamuna barrage during each sampling period.
To study the performance of ash settling basins, ash effluent was sampled before its entry into the basin (slurry) and also at the outfall into the river (leachates) on the same day when the sampling in the river was carried out.

In addition to the above, samples of ash effluent before its entry into the sewage drain \( (D_2) \) and river \( (D_2+A_s) \); and effluents of drains \( D_1 \) and \( D_3 \) at their outfalls into the river were taken during the same period.

All the above samples were taken in duplicate and brought to the laboratory within a short time after collection.

**Field Measurements**

River downstream discharge data and water supply to the power station on the sampling day were noted from the display board at Yamuna barrage.

Temperature \( (\text{to } 0.5^\circ C) \), pH (using portable Philips pH meter model PP 9040) and conductivity (using Biochem conductivity meter) of the water samples were measured *in situ*.

**Analytical Procedures**

Various physico-chemical parameters of water were determined according to the standard methods prescribed by U.S. EPA (1983), EC (1979) and APHA (1976).
Total alkalinity and turbidity of the samples were measured immediately on arrival in the laboratory by electrometric titration and turbidimetric methods respectively. Chloride was determined by AgNO₃ titration with K₂CrO₄ as indicator. Sulphate was measured by standard calorimetric techniques using "Spectronic 21" spectrophotometer. Total hardness and calcium concentrations were estimated in filtered water samples by EDTA titrations using Erichrome Balck-T as indicator. Magnesium concentration was calculated by using the following equation.

\[
\text{Mg (ppm)} = 12.16 \left[ \text{T. Hardness (epm)} - \text{Ca (epm)} \right]
\]

**Filtration**

The water samples were filtered in the laboratory immediately on arrival from the sampling locations to avoid changes in equilibrium conditions between the dissolved and suspended fraction of materials in them (Environment Canada, 1979). The filtration was carried out by passing a portion of a water sample through a 0.45 um membrane filter of cellulose nitrate (Whatmann, 47 mm dia.) placed in an all pyrex glass millipore vacuum filtering system. This portion was chosen so as to minimize clogging problems. The membrane filters were washed with 1% HNO₃ followed by rinsing in double-distilled water prior to filtration. At the end of filtration, the filters were rinsed with distilled water to remove adhering salts. (De Mora et al., 1983). The
filters were weighed before and after filtration to obtain suspended particles mass per litre of water.

Each sample so filtered was divided into two equal parts. One of these was utilized for estimation of dissolved solids by gravimetry and the other portion was preserved for metal analysis. In some samples, the total and suspended solids concentrations were determined gravimetrically and the dissolved concentration was determined by subtraction of the suspended concentration from the total concentration.

Sample preservation and storage

The filters with residue were stored in dessicators until they were used for digestion for metal analysis in the suspended fractions.

A portion of the filtered water sample was preserved by adding 3 ml of 1:1 HNO₃ per litre of sample to prevent loss of trace elements due to adsorption on the container walls and the growth of algae during storage (Batley et al., 1977). The samples were then stored in pre-washed polyethylene bottles at 5°C to prevent change in volume due to evaporation until analysis for dissolved metals could be carried out.

Sample preparation for metal analysis

The dissolved fractions were prepared for metal analysis by volume reduction, acid digestion and reflux according to the
standard methods (APHA, 1976).

For the determination of suspended metals (EPA, 1983), each membrane filter with its contents was transferred into a 250 ml Griffin beaker containing 3 ml of conc. HNO₃. The beaker was then covered with a watch glass and heated gently. When the membrane had dissolved completely, the temperature of the hot plate was increased and evaporated to dryness. The contents were then cooled, another 3 ml of conc. HNO₃ was added to it and heating was continued until digestion was complete. 5 ml of 1:1 HCl was added to the evaporated dry residue and it was heated gently to dissolve any soluble materials. The solution was filtered to remove silicates and other insoluble materials that might clog the atomiser of the atomic absorption spectrophotometer (AAS). The samples were then brought to a particular volume based on the expected concentration of metals present and metal concentrations were determined as follows:

\[
\text{ppm of sample material} = \frac{\text{Final volume of the extract} \times \text{ppm of metal in solution}}{\text{Volume of sample originally used for processing}}
\]

Metal analysis

Metals were analysed using flame atomic absorption spectrophotometer (Pye Unicam, SP 9) employing suitable standards.

Appropriate standard solutions of metals were prepared in
1% HNO₃ immediately before analysis by serial dilution of the 1000 mg/l stock solutions in polyethylene bottles. The stock solutions were prepared using high purity salts, Analar grade HNO₃ and double distilled water.

In AAS, the emission mode was used for Na and K determinations while absorption mode was used for all the other elements.

No elements were determined in the blank filter. A blank and a repeat run for every ten samples were injected to check for contamination or variation in sensitivity and repeatability.

**Fly ash sample**

Since bottom ash is the material that drops to the bottom of the wet-boiler, it is very difficult to obtain samples of bottom ash that have not been in contact with sluicing water. Hence, only grab samples of fly ash were collected in this study from the hoppers of electrostatic precipitators and mechanical dust collectors, of five different units of the power station. They were proportionately composited in the laboratory and sealed in plastic containers until use to prevent any interaction with air and moisture. Since fly ash constitutes the bulk of total ash produced at the power station (nearly 80%) and the bottom ash is relatively inert (Murtha et al., 1983) only fly ash was used for leaching and solubility studies.
Ash analysis

A known quantity of ash sample (0.2 gm) was digested completely on a hot plate after the addition of 3 ml aqua-regia and 5 ml HF. The residue remaining after digestion was brought into solution by heating it with 2 ml of HNO₃ before making upto 50 ml in a volumetric flask (Kopsick et al 1980). Atomic absorption spectroscope was used to determine the concentrations of all elements.

Particle size distribution

The particle size distribution of fly ash samples were determined by using "Granulometer" (715 E 456 CILAS). The samples were analysed for particle sizes ranging from 1 to 192 μm in diameter.

Mineralogy

To identify the crystalline compounds in composite fly ash samples, they were subjected to X-ray diffraction with Cu-Kα radiation. The samples were scanned from 3 - 70⁰ (2θ) with a Philips-Norelco goniometer. The Joint Committee on Powder Diffraction Standards data base was used for identification of crystalline compounds in the fly ash samples.

Morphology

To survey the general distribution of particle sizes and...
shapes, as well as to study particle surface morphologies, samples of fly ash particles were examined by means of Scanning Electron Microscope (SEM). Samples for SEM were prepared by slurrying small quantities of the ash with water. A small drop of this slurry was transferred to a piece of membrane filter (0.45 \( \mu \text{m} \) dia and 0.8 X 0.5 cm size) and allowed to dry in a dessicator for 24 hrs. The filter was mounted on the SEM sample stub (brass) with conducting paint (silver). It was then sputter coated with gold of about 200\(^{\circ} \text{A}\) thickness (current : 21.5 Amp, pressure : 0.05 m bar, gas : argon, cathode specimen distance : 30 mm, time : 1 min) to prevent charge build up since the ash particles are not electrically conducting. Blazers SCDO\(_{20}\) sputter device was used for this purpose. Stubs were scanned in Philips Model 501 B Scanning Electron Microscope.

**Solubility and Leaching Studies :-**

Inorganic materials, including the metals, present in coal ash leach into water during ash sluicing and settling. Many trace elements apparently are located on the surface of ash particles (Natusch et al, 1980) and thus cause water quality problems at ash disposal sites. In order to understand the chemistry of discharged ash basin waters at IPS, laboratory studies were undertaken to characterise the coal fly ash leachates and the floating solids by approximating the actual leaching conditions occurring in the ash disposal system and controlling some of the
important factors that influence leachates composition.

For this purpose, the actual water used for sluicing was collected from the river Yamuna at the power station's water intake.

Ash Leachates

The ash slurry emanating from the power station and falling into the ash basin was quantitatively monitored for a period of 12 months. Its concentration was found to be approximately 10% w/v (figure 8). Since the amount of ash produced and sluicing water taken in per day (Appendix 1) at this power station are fairly constant, the ash slurry would be quite consistent in concentration. Therefore, for leaching studies, 50 gm of the composite fly ash sample was mixed with 500 ml of freshly collected and filtered river water in a number of large and open polyethylene containers. The fly ash was kept in suspension by mechanical stirring for 1, 6, 12, 18 and 24 hrs as an approximation of ash sluicing water contact time elapsing in the basin during the various stages of ash filling. The leachates were then vacuum filtered through a 0.45 um pore size membrane filter. This pore size was chosen as the maximum size which appears to trap all ash particles on which metals might adsorb (De Mora et al: 1983) A portion of leachates was analysed for pH, EC, TDS, SO₄ and Cl and the rest was preserved by adding 3 ml of conc. HNO₃ per litre of sample in acid-washed polyethylene containers and refrigerated.
FIGURE 8: Monthly variations in concentrations of ash slurry discharged into the disposal areas.

Mean ash slurry concentration:
- $A_s \rightarrow B : 9.87\%$
- $A_s \rightarrow D_2 : 0.93\%$

TOTAL SOLIDS (mg/l)

SAMPLING PERIOD: 1984-1985
until their analysis for metals by AAS. The filtered raw river water used for leaching was analysed to provide background data for ash leachates. All analyses were done in accordance with the U.S.EPA Manual (1983). Duplicate determinations were carried out for each extraction period.

Floating solids

To determine the amount of floating solids in the leachates, 50 gm of the sample was dispersed in 500 ml of river water and mechanically stirred for 15 minutes. After allowing them to settle for 1, 6, 12, 18 and 24 hrs respectively, the floating cenospheres were removed by decantation followed by filtration. The results were expressed as percentage weight of dry ash. The ash sample was also allowed to stand for 36, 48, and 60 hrs in river water to see whether there was any change in the amount of the floating fraction with time.

The cenospheres were digested using aqua-regia and HF and analysed for their elemental composition.

To study the morphology of the floating solids, a small portion of them was transferred separately to a piece of membrane filter and allowed to dry. The filter was mounted on the SEM sample stub with conducting paint and was then overcoated with a 200 Å thick layer of gold in a high vaccum evaporator. Particle morphologies were observed by using a Philips Model 501 B Scanning Electron Microscope.