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# Studies on Some Polycyclic Aromatic Hydrocarbons (PAHs) in Sewage

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SES:

/ K. Lenin Babu Auth

Sup: D.K. Banerjee



SCHOOL OF ENVIRONMENTAL SCIENCES  
JAWAHARLAL NEHRU UNIVERSITY INDIA  
NEW DELHI - 110067  
1989

JAWAHARLAL NEHRU UNIVERSITY  
NEW DELHI-110067

CERTIFICATE

The research work embodied in this dissertation entitled "Studies on some Polycyclic Aromatic Hydrocarbons (PAHs) in Sewage" has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma of any University.

*K. Lenin Babu*

K. LENIN BABU  
(Candidate)

*L.K. Pandey*

Dr. L.K. Pandey  
(Dean)

*D.K. Banerjee*

Dr. D.K. Banerjee  
(Supervisor)

July, 1989  
School of Environmental Sciences  
Jawaharlal Nehru University  
New Delhi.

## A C K N O W L E D G E M E N T S

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*K. Lenin Babu.*  
(K. LENIN BABU)

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## CHAPTER - I

### INTRODUCTION

Population explosion and nuclear war have gained world wide attention in the last four decades. While the former leads to qualitative decline in human life, the later threatens to bring about destruction of the human civilisation. In addition to these problems mankind faces an equally serious threat from the pollution of his environment. The pollution of human environment is multi-dimensional and has both local and global ramifications. Throughout history man tried to conquer the environment for his development. Technological progress brought about fundamentally different routes of the matter and energy transfer in the environment which have disturbed nature's delicate balance and equilibrium.

Until recently however people paid no attention to the long term consequences of their activities. Various developments in industrial and agricultural practices and the growth of numerous cities have added many pollutants in the form of gases, liquids and solid wastes to the environment, quite freely. Many substances of industrial, agricultural and domestic origin are not used by organisms and take no part in the biological cycle of the biosphere. As a result nature loses its

capacity, for self-purification and cannot cope with the alien burden which man throws onto it.

Initially, on the continents, the harmful influence of industrial and other wastes is more or less localised, although they begin to affect considerable areas such as river basins, cities, inland seas and coastal water; later these tend to produce global effects. It is hence obvious that a great proportion of industrial pollution leads to polluting of various water resources. Yet the seriousness of this problem has still not evoked a proper assessment.

"Taken for granted" would be the apt way to describe many people's feelings on the subject of water pollution. "We should be concerned about water supply" is a truism, but just how concerned should we be?

The system of water circulation is known as hydrological cycle. As in any other natural cycle there is roughly a constant amount in circulation at any given time i.e. the fresh water resources are a finite resource. (over 97% at any given time is in the seas and less than 1% only is actually available for life processes).

In earlier years when water pollution was often the cause of epidemics of typhoid and cholera, the common definition of water pollution, referred to the discharge of untreated or inadequately treated municipal sewage. Later, the cause of water pollution also included the discharge of gross amounts of industrial wastes which caused overt nuisances. Where such conditions still exist, it is relatively easy to identify such discharges as the cause of water pollution. In recent years, though municipal sewage and industrial waste treatment works have been constructed, a great variety of complex waste materials have emerged from homes and factories, which cannot be eliminated or controlled by these works. Hence it has become necessary to define more precisely what is meant by water pollution.

In a special staff report on water pollution in 1963, the U.S. Senate Public Works Committee notes that "the world pollution has different meanings for different people". The committee maintained that water pollution exists when the quality of water is reduced, its volume diminished, it becomes unsuitable for reuse and becomes instead of a benefactor a nuisance to health" The federal water pollution control act of the U.S.A.

defines pollution as discharge of matter which endangers the health or welfare of any person.

The materials which cause water pollution range from simple to highly complex substances. As society advanced in science and technology, the problem became compounded by new discoveries and by mixing of old and new pollutants. The principal source of materials which cause pollution are the sewers of cities and towns, industries, drainage from farms, forests and city lawns carrying fertilizers and chemicals used to control insects and weeds.

#### WATER POLLUTANTS:

Water pollutants fall into three general groups. Those such as sewage, that reduce dissolved oxygen in the water thereby producing conditions in which fish and other forms of aquatic life cannot survive.

The second major group consists of physiologically toxic substances for example, phenols, cyanides, arsenics or pesticides.

Third group comprises nutrients e.g. nitrates and phosphates which stimulate prolific growth of algae



and aquatic plants. The end effect of pollutants in this group resembles that of the first group i.e. depletion of dissolved oxygen by the decay of an abnormally high population of plants.

As early as 1960 U.S. Senate Subcommittee on water resources identified and divided water pollutants into eight standard categories.

1. Oxygen demanding wastes
2. Infectious agents
3. Plant nutrients
4. Organic Chemicals
5. Inorganic elements and compounds
6. Sediments
7. Radio active materials and
8. Heat

SOURCES:

The major sources of water contamination are domestic, industrial and agricultural wastes as well as solid waste, thermal pollution, oil spills and radio active waste.

Domestic waste is generated by many sources occupying large geographical area and consists primarily of sewage from homes and commercial establishments.

Generally, the impurities in domestic waste are diluted and largely organic and oxidized by bacterial decomposing which requires dissolved oxygen. A common indicator used to monitor this type of input in receiving waters is the BOD (Biological Oxygen Demand). In this decomposition is measured over a 5 day period.

Although some of the Indian population is domiciled in buildings connected to sewage treatment systems; the majority of these are inadequate or inefficient and consist mainly of primary and secondary treatments. These systems bring sewage to the central treatment plant and after minimum treatment release this material into water ways. This practice of concentrating and releasing effluents leads to high N.P. levels as well as reduced oxygen concentration in many of the receiving waters.

The majority of the Indian population resides in areas that are unsewered and either release raw sewage into water ways or rely on septic tanks for waste disposal; sewage disposed by means of septic tanks leads to serious localised problems.

Since industrial pollutions occur in large amounts in specific geographical areas, the collection and treatment of these materials should be easy to accomplish. A very small fraction of industrial units using water in their manufacturing process, adequately treat water prior to its release. Since the specific types of industrial contamination vary with geography and natural resources of a particular locality. No attempt can be made to correlate water contamination on regional basis. Merely the possible sources of contamination can be identified. Wastes from textile manufacturing process are generated from the washing out of the impurities in the fibres, as well as discarding the chemicals used in the processing of the fibres. Generally these wastes are organic compounds, having a high BOD and are extremely alkaline.

From Meat, dairy and sugar beet processing, as well as brewing, distilling and canning operations generate large amounts of organic by-products that are disposed off in waste water. When the water is discarded with these by products, it leads to high BOD and consequent oxygen depletion in the receiving waters.

The effluents released from pulp and paper processing operations is a mixture of chemicals used in the digestion of raw wood chips, cellulose fibres and dissolved lignin. This waste water also contains wood preservatives such as penta chlorophenol, sodium penta chloro phenate and methyl mercaptan, all of which are toxic to fish. This effluent is brownish in colour and lowers the photosynthetic rate of the aquatic community by hindering sunlight penetration.

Metal industries place a wide array of contaminants in their waste water. The specific contaminants and concentration depend solely on particular manufacturing process employed. Other industries release traces of metals produced or plated in their waste water. Metals commonly found in these waste waters are chormium, mercury, nickel, lead, copper and cadmium.

Agricultural wastes include the pesticides that are sprayed on crops, as well as sediments, fertilizers, plants and animal debris that are carried into water ways during periods of rain fall or as run off and during irrigation of farm land. Over fertilisation is harmful and may lead to entrophication.

Solid wastes vary in composition with the socio-economic status of the generating community. The following materials may be classified as solid wastes. (American Public Health Association 1961).

Garbage: which includes all decomposable waste from house-holds as well as from food, canning, freezing and meat processing operations that are not disposed in waste water.

Rubbish: includes also non-decomposable wastes. These materials may be either combustible or non-combustible former includes garden wastes, cloth and paper the latter include masonry, some chemicals, metals, glass etc.

Sewage sludge is generated from the settling process in primary secondary and tertiary processes which must be removed periodically.

Other miscellaneous materials which cause water pollution include industrial wastes such as chemicals, paints and explosives as well as mining wastes such as slag heaps and mine tailings.

Many electric generating companies use water in the process of cooling their generators. This heated water is then released into the system from it was drawn, causing a warming trend of the surface waters. Thermal pollution results when heated effluents are released into poorly flushed systems, in these cases, permanent temperature increases often result, which tend to decrease the solubility of oxygen. When heated water is released into large well flushed marine systems, there is little, if any, permanent temperature rise. There are, however, problems related to the operations of plants utilizing marine water in cooling processes.

Oil pollution results from the accidents involving oil tankers and from spills at off-shore oil drilling sites. A more persistent source of oil pollution results from the practice of oil tankers, after they deliver the oil, to fill empty tanks with sea water to act as ballast for the return trip. Prior to docking, sea water ballast contaminated with oil is discharged. Although, this practice is illegal it is difficult to prevent.

The major source of radio active wastes are nuclear explosives, accidents at nuclear power plants,

fuel reprocessing plants and research laboratories and hospitals that release these wastes, into the atmosphere or waste water. Presently most of the interest centres on radio active iodine and strontium, since man is at the end of the food chain that concentrates these elements.

#### CONSEQUENCES OF POLLUTION:

Various contaminants earlier discussed may be conveniently subdivided into four categories on the basis of their effects on given systems regardless of their sources.

1. Substances that lead to oxygen depletion
2. Excess of plant nutrients
3. Agents of biological dysfunction
4. Sedimentary and erosional processes

A contaminant may fall into one or more of these categories depending upon various factors such as its mode of action, the amounts of dilution it encounters, as it travels from the point of input and tolerances of organisms encountered. Therefore, each

contaminant must be evaluated in terms of particular characteristics of receiving waters. For example, the consequences of releasing a small amount of raw sewage into a shallow, artificial pond would be totally different from the release of the same amount into a deep ocean. The difference is not because of marine and fresh water but because of the volume, circulation pattern and degree of dilution.

Each contaminant should be evaluated not only in terms of particular characteristics but the effects of synergism must also be considered. Synergism is defined as combination of factors that reinforce the activity or effects on each other. For example cyanide while toxic to aquatic life is extremely lethal in the presence of cadmium and/or zinc.

#### REDUCTION IN OXYGEN LEVELS:

Factors as diverse as oil spills, heat, suspended sediment, organic waste are known to decrease the available oxygen in a given system. Although the end result in all the above cases is the same i.e. oxygen depletion, the mechanisms leading to it vary and four



types of mechanisms can be identified.

1.           Decreasing the photosynthetic rate of plants. This can be caused by increasing turbidity which occur from suspended particles that enter a given system either by erosion during rainfall or during irrigation of crops. Excessive addition of sediment will reduce dissolved oxygen by hindering sunlight penetration which is essential for photosynthesis where oxygen will be a by-product. If it continues for long it may eliminate plant life altogether which means no food for primary consumers. The subsequent decay of these organisms will further increase BOD. Light may also be physically blocked by powerful coloured effluents from textile industry and paper mill.

2.           Decreased oxygen solubility: Oxygen levels are decreased with an increase in temperature of given systems. Lakes are particularly sensitive to increase temperatures, since this reinforces the temperature density barrier and prevents efficient mixing of surface euphotic zone and hypolimnion. Thus, if temperature input is great enough to prevent or delay the normal fall overturn, severe and prolonged anaerobic conditions

will occur in hypolimnion. This will result in overkill in hypolimnion populations. Moreover, higher temperature will favour bacterial growth, the net result is increasing the decomposition rate in the regeneration zone.

3.           Decreased diffusion of oxygen : Substances which prevail at the air water interface, blanket the water surface and physically prevent the oxygen atoms entering the system, reduce the amount of available oxygen. For example, oil and leaves of deciduous hard woods. In addition they increase BOD by decomposition.

4.           Increasing oxygen demand: In general, organic contaminants, entering a system from municipal sewage treatment plant, animal waste from feed lot cleaning operations and plant and animal residues from food processing operations are the major source of organic wastes entering our water ways. All these will eventually reach regeneration zone and decrease the dissolved oxygen and further accelerate the problem.

EXCESS OF PLANT NUTRIENTS :

The addition of plant nutrients to marine

and fresh water system will have a number of deleterious effects. Eutrophication (over fertilization) is one of them. Over fertilization is harmful since it destroys the integrity of a community by rapidly altering the nutrient relationship and animal plant inter-relationship that have slowly evolved over the centuries. The end result is generally the elimination of all or many of the normal populations which are replaced by a few opportunistic forms that are more tolerant to the rapidly changing conditions. The most important source of excessive nutrients in water ways occur through the use of inorganic fertilizers on the farm lands.

#### AGENTS OF BIOLOGICAL DYSFUNCTION :

This term refers to any compound that either directly kills organisms or that interferes with their physiological activity in such a manner so as to threaten the success of a natural population in a given system. In addition any material that appears to be harmless or have a negligible effect when ingested, assimilated and so on by members of one population tend to accumulate in the tissues of these or other organisms as it passes up the food chain to ultimately effect the success of higher consumers, would also

fall into this category. This phenomenon is known as biological magnification. The major materials in this category are various persistent pesticides, heavy metals (Cd,Pb), by products of plastic industry (PVC & PCB). D.D.T. (chlorinated hydrocarbon pesticide) provides the classic examples of biological magnification.

#### SEDIMENTS AND EROSION :

Sediments have a variety of deleterious effects on water ways. They enter waterways and interfere with photosynthesis and also clog the gills of fish and also settle down and blanket normal bottom sediment and eliminate spawning areas and smother the eggs of many species. In agricultural areas, they tend to be coated with various pesticides that are applied to crops, thus increasing the burden on the water system.

#### CARCINOGENIC COMPOUNDS AND POLYCYCLIC AROMATIC HYDROCARBON

Over the past decade, we have begun to realise the enormity of problems we face with toxic persistent environmental contaminants. We have learned that they

have very harmful effects on organisms at higher levels of the food chain. We have learned that they pose a serious threat to man. Some are carcinogens and others are teratogenic and are spread far and wide on the globe. Polychlorobiphenyls (PCB's) are present in the loons of northern lakes and even in polar bears. We have discovered that some of these substances are very persistent in the environment and can accumulate over long periods of time at higher levels in the food chain. But the challenge is only beginning. There are many compounds we have only begun to learn about both in terms of their biologic effects and their pathways in environment. PAH's are one of them.

More than four million chemicals are known today. (MAUGH 1978). Over 60,000 compounds of these are in common use and about one thousand new chemicals are brought into commerce every year. It has been estimated that four out of five occurrence of cancer in man are due to environmental effects such as carcinogens in air and water (KEITH 1976). As early as 1915, YOMAGIWA and ICHIKAWA showed that coal tar could produce cancer in animals. PAH were isolated as a result of subsequent research for the responsible

agents. PAHs are chemical carcinogens found in atmosphere and water. They occur as a result of incomplete combustion involving carbon and hydrogen. These PAH's were shown to include compounds of vary carcinogenic potency. It is believed, that some of the PAH especially Benzo (a) Pyrene (B(a)p) are carcinogenic to man. (Falk et al, 1964). Experiments showed that continuous exposure at low concentration was more dangerous than a high single dose and that even the slightest exposure to carcinogenic PAH's would cause irreversible damage (WHO 1970). Skin and subcutaneous application of only few micrograms of the stronger PAH carcinogens produced fatal tumours in laboratory animals. Polycyclic Aromatic Hydrocarbons (also known as Polynuclear Aromatic Hydrocarbons) are fused compounds built on benzene rings. When a pair of carbon atoms are shared, the aromatic rings are considered to be fused. Fusion imparts chemical properties which are a combination of those of benzene, a highly aromatic compound and those of olefinic hydrocarbons. The lowest PAH is Naphthalene consisting of two fused rings, whereas the ultimate member is Graphite, an allotropic form of elementary carbon. The environmentally significant PAH range lies between naphthalene

coronene (C<sub>24</sub>, H<sub>12</sub>). Physical and chemical-properties vary approximately in regular trend with molecular weight, whereas aqueous solubility and vapour pressure decrease logarithmically with increasing molecular weight (NEFF 1979). Thus PAH differ in their environmental behaviour and interactions with biological systems. Although PAH are not actually toxic to most forms of life, several compounds are either known or suspected carcinogens. The addition of alkyl substitutes generally enhance the carcinogenic potency of PAH whereas hydrogenation and methylation cause decrease in potency. Based on their physical and chemical properties, PAH can be grouped into two classes.

1. Aromatics with low molecular weight and 2-3 rings, such as naphthalene, phenanthrenes and anthracene.
2. Aromatics with high molecular weight and 4 to 7 rings (ranging from chrysene to coronene) which are not acutely toxic but proven carcinogens.

Estimation of man's yearly PAH intake amounts to 3 to 4 mg with fruits, vegetables and bread to .1 mg

with fats and oils of vegetable origin and to 0.05 mg with smoked meat or fish and drinking water. The mean cumulative dose of PAH to a 70 year old human might be 3 mg from food (excluding vegetables) 2 mg from vegetables and 0.3 to 0.4 mg from drinking water. Although water is not primary amongst the contributors of PAH, its control is necessary as it is an indispensable and irreplaceable food stuff. Man's drinking water is obtained from different sources. Therefore, attention must be paid to the surface waters, that is the waters of rivers and lakes, ground water as well as waste water and the by products of waste water purification as sewage sludge which can be used for soil cultivation.

WEDGEHOOD and COOPER (1954) pioneered the study of carcinogens in water. They qualitatively detected Benzo (a) pyrene and other polycyclic aromatics in industrial waste water from a gas work. Studies by BRNEFF(1983) indicated that natural source and domestic sewage proved as important a source of PAH of industrial origin. As a result, there is a justifiable concern regarding PAH measurement and its ultimate control in water.



The World Health Organization (WHO) made a list of PAHs that generally occur in water environment and selected six out of them which are most common viz.

	<u>Compound</u>	<u>Carcinogenicity</u>
1.	FLUORANTHERENE	-
2.	BENZ (ghi) PERYLENE	-
3.	BENZ (k) FLUORANTHERENE	-
4.	INDENO (1,2,3-cd) PYRENE	+
5.	BENZ (b) FLUORANTHERENE	++
6.	BENZO (a) PYRENE	+++

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In the above list only three are carcinogenic. The other two have been reported to be teratogenic. For the present work, the following five compounds are chosen. Apart from the three carcinogens mentioned above, the other two have been reported to be present in sewage and waste waters.

	<u>Compound</u>	<u>Carcinogenicity</u>
1.	BENZO (a) PYRENE	+++
2.	BENZ ANTHRACENE	+
3.	BENZ (b) FLUORANTHERENE	++
4.	BENZ (ghi) PERYLENE	-
5.	CHRYSENE	++

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Out of these five only Benz (ghi) Perylene is not potent carcinogen. But the studies by P.S. KHILLARE (1987) showed that high concentrations of Benz (ghi) Perylene is found in automobile exhaust in Delhi. Hence to have better understanding about its behaviour, this compound was selected.

#### WASTE WATER TREATMENT :

With population explosion and urbanization, many communities reached a point where disposal of sewage into water ways led to wide spread pollution of that water way. Eventually this leads to the water quality of adjacent receiving water bodies declining to such a state that the sewage has to be treated in order to preserve or restore the integrity of waterways or aquifers.

Thus waste water treatment works come to play a vital role in reducing the impact of effluents in receiving water bodies. The growing demands for water will call for considerable expansion in sewage treatment for two reasons.

Firstly, due to the limitations of the hydrological cycle and the difficulties of indefinite extension of catchment areas, the water resources are limited. Hence the only means through which additional water can be procured is through processes which facilitate the purification and reuse of water. This means that, rivers which have been in the past treated largely as open drains must be increasingly treated to the point where they can provide the water to meet the demand. Discharges into such rivers will have to be cleaned up. So doubling the demand for water means doubling of the sewage that has to be treated. This implies very high standards of treatment so that effluents can be returned to rivers, from which, subsequently abstraction is practiced.

Sewage treatment works could be defined as a system that receives comparatively strong sewage and discharges very weak sewage as effluent. Its function is to accelerate the processes that occur in the self purification of rivers and its methods are largely the intensification of the same processes under artificially advantageous conditions. The effluent discharged from sewage works should meet number of conditions (HODGES et al 1973).

It should not

- a. Kill fish or their food
- b. Contain solids that settle on river bed
- c. Contain oil or grease that contaminate rivers
- d. Raise the BOD of receiving waters more than 4 ppm
- e. Interfere with the abstraction of water for reuse
- f. Prevent agricultural use
- g. Raise the temperature in the river unduly.

Any of the above conditions may govern the required standard at a particular works. The main processes in sewage treatment are intended to rendering innocuous the voluminous flow, during which solids are removed from flow as solids or sludge. Secondary activity of sewage works is treatment and disposal of these sludges.

There are two major types of flow in our sewers. The first is from domestic and commercial premises and effluents from industries. This is called as foul sewage. Second one is because the rain water does not percolate into the ground because of impermeability of roads and other structures. This also should be channelled away through sewers. This is called as

storm water and much fluctuations occur in foul sewage flow rate but more than half of daily sewage comes between noon and 20.00 hours.

Three distinct kinds of sewage treatment works can be found:

- a) Separate system in which storm water will be released at any convenient point while foul sewage will be carried for treatment separately.
- b) Combined system: Here both foul sewage and storm water will be mixed and carried in same sewers.
- c) There is partial separate system where some storm water drains, the rest connects with foul sewage. Uncontaminated storm water does not require any treatment but its contamination by foul sewage must be guarded against.

Treatment processes in sewage works involve the following steps:

- a) Preliminary treatment: As sewage arrives for treatment, it is first passed through barred grills to

remove large suspended solids while brooms or brushes at the surface level remove floating matter, grease and oil. This process is called screening.

b) Sedimentation: In the next stage of treatment an attempt is made to settle out as much as possible of the suspended organic solids. Chemicals may be rarely added to the sewage and it is stirred gently to make the solid particles stick together and settle faster to form the primary sludge. The sludge is about 90% water and is removed fairly quickly lest it begins to decompose and worsen the quality of the liquor above it.

c) Biological oxidation: The foregoing processes have been physical but the next stage of treatment exploits the purifying activities of micro organisms. Two distinct types of plants are in common use, percolating filter and aeration tanks. In this process the liquor flows through tanks in which the level of dissolved oxygen is maintained at as high a value as possible either by bubbling in of air through diffusers or by intense splashing with brushes or blades. The real work is done by a community of micro organism living in the activated sludge. The organisms are

bat eria, yeasts, molds and protozoa. Activated sludge tanks should provide about 10 hours of retention time.

d) Humus tanks: The solids remaining in the liquor after biological oxidation will settle much more readily. The settling basins used for this sedimentation are called humus tanks.

e) Sludge: The sludge from primary sedimentation has a water content of about 90% and the sludges from humus tanks are often 99% water. The object of sludge treatment is to ensure that the treated sludge is free from parasites and pathogenic organisms and that is inoffensive. The sludge is subjected to enzymatic action of anaerobic bacteria for thirty to sixty days at about 30°C temperature in closed digestion tanks. During digestion the sludge settles and liquid left floating above it is returned to mix with fresh sewage at the inlet to treatment plant. In the course of digestion, gas is produced. It consists of 60-75% methane, 15-30% CO<sub>2</sub> with some nitrogen oxygen and hydrogen-sulphide. Moist, digested sludge drains very readily and the fixed dewatering is done by spreading the sludge on drying beds. This drying may take no

longer than a week and dried sludge can be used as fertilizer.

This is the working model of conventional sewage treatment. Okhla sewage disposal works which started functioning in 1937 varies from the above model.

The Okhla sewage disposal works receives the largest volume of sewage in the capital city. It receives 70 mega gallons per day. Its catchment area consists of the following areas: I.S.B.T., Red Fort, Jama Masjid, Dariya Ganj, Connaught Place, Kotla Ferozshah, India Gate, Pragati Maidan, Safdarjung Enclave, Sarojini Nagar, Dhaula Kuan, Hauz Khas, Greater Kailash, Tughlakabad, Lajpat Nagar, Jawahar Lal Nehru University, Vasant Vihar, etc. 95% of total raw sewage is of domestic origin. The pH of raw sewage is 7.4 to 7.6, suspended particulate load is 300-400 mg/l. Biological oxygen demand is 200-250 mg/l chemical oxygen demand is 300-400 mg/l. Raw sewage after screening is directed to primary sedimentation tanks. Here it is retained for 2 hours and 40-45% of total suspended matter settles down. After this primary treatment, 40 M.G.D. of raw sewage is released for irrigation purposes only 30 MGD is



given further treatment. This 30 MGD of primary treated sewage is sent to aerobic with blades. Aeration is carried for six hours. The suspended particle load drops to 70-100 mg/l and 150-160 mg/l respectively. Then the sewage is sent to humus tanks where it is retained for 8 hours. After this stage the sewage will have BOD 20 mg/l, COD 20 mg/l, suspended particulates less than 50 mg/l and pH 7.5. Then the sewage is released to the Agra Canal from which subsequent abstraction occurs for irrigation purposes.

The sludge from primary sedimentation, approximately 0.3 MGD is pumped for anaerobic digestion. The digestion is carried for 25-30 days, 7 lakh cubic feet of gas is formed during digestion out of which 60% is methane. The uppermost layer of liquid is sent to mix with fresh raw sewage and digested cake is left for sun drying and finally disposed off as manure cake.

During monsoons or whenever, there is no need for water for irrigation, the untreated 40 MGD is directed to Agra canal. No chemicals are used at any stage of treatment.

OBJECTIVES OF STUDY:

Municipal waste-water discharges have been increasingly over the last decade as major source of polycyclic aromatic hydrocarbons in aquatic environment. The presence of PAH in waste-water is mainly because of street runoff, (which incorporates atmospheric dust, road-wear particles and automobile oils and greases). Domestic waste water is self explanatory to the presence of PAH in sewage. The carcinogenicity of some of the PAHs on the one hand and lack of their data for Delhi area, primarily prompted the undertaking of this study. The main objectives of the present study is to assess the presence of five environmentally important PAHs in the urban sewage of Delhi at various stages of its treatment, and after its treatment at Okhla sewage treatment plant.

## CHAPTER - II

### REVIEW OF LITERATURE

Polycyclic Aromatic Hydrocarbons (PAH) are homologs of benzene, in which three or more aromatic rings are joined in different configurations. They represent a class of man-made environmental pollutants which also occur naturally in the environment (AFGHAN 1984 et.al). PAH can originate from natural sources or emitted in the course of a wide range of anthropogenic activities. These include automobiles and other petroleum burning engines, refuse burning, industrial processes, domestic heating appliances and tobacco smoking. PAH compounds are produced by the incomplete combustion of fossil fuels and other organic materials. POTT a prominent English surgeon described in 1975 an occupational disease of chimney sweeps. He correctly ascribed skin cancer affecting the scrotum and thighs to the continual exposure of the tissue to soot. Systematic application of coal-tar to the skin of the ears of rabbits for a year was found to induce initially papillomas and then carcinomas that metastasized into lymph glands (YAMAGIWA AND ICHIKAWA 1918). This has been confirmed by other workers using differing animal species. Coal-tar fractions obtained at different temperatures had different carcinogenic properties. It

became established that the only tar fractions distilled at 400-600°C and above are carcinogenic, distillation at 800-850°C results in the highest yield of carcinogenic products. It was concluded that carcinogenic products have high boiling points, are stable when heated repeatedly, do not contain sulphur or arsenic neither acid nor alkali. These characteristics placed the neutral, PAHs, with a high boiling point under suspicion as carcinogenic agents. Painting the skin of mice with 0.30% solution of dibenz (ghi) anthracene resulted in almost half of the animals developing, after 6 months, firstly papillomas and then carcinomas. After persistent and painstaking work, COOK, HEWITT and HIEGER (1933) succeeded in isolating Benzo (a) pyrene from coal, which induced cancer in mice in half the time taken by dibenz (ghi) anthracene. Dimethyl benz (a) anthracene was first synthesized in 1938 and when tested, proved to be the most important of all carcinogenic PAHs. Methyl chloroanthracene (MCA) was synthesized in U.K. from desoxycholic acid and is approximately equal to Benzo (a) pyrene in its carcinogenic properties (CHADWICK et. al 1977).

Some PAHs and particularly B(a) P, can induce malignant growths in any organ or tissue to which they are applied e.g., skin, sub-cutaneous tissue, lung,

stomach etc., in mice, rats, hamsters, rabbits and other laboratory animals. Different animal species and tissues are sensitive to different degrees. Mice are extremely susceptible to skin cancer and sarcoma. Rats are refractory to skin cancer induction. Guinea pigs are least sensitive to PAHs. (SHABAD, 1977). Workers exposed to coal gas and tars show organ specific cancers particularly lung cancer (KENNETH and JEAN 1978). Carcinogenic PAH induce distant as well as local tumors, for example, lung adenomas are induced in mice by subcutaneous application. Carcinogenic PAHs can also pass through the placenta and induce tumors in the progeny, as demonstrated by experiments in vivo (BULAY and WATEN BERG, 1971) and in vitro using organ cultures (SHABAD et.al 1975). Not all PAHs are carcinogenic and those that are, differ widely in terms of potency. A great deal of effort has therefore been expended in trying to discover the scientific basis for the structure - activity relationship that exists within the hydrocarbon as a class of chemical carcinogens. The K-region of PAHs which were known to be most chemically reactive and electron dense regions of hydrocarbon molecules, initially attracted much attention (PULLMAN and PULLMAN 1955) and this has followed by a period in which the metabolism of hydrocarbons was

intensively investigated (SIMS and GROVER, 1974). It was known that aromatic double bonds present in the molecules could be metabolized by the so called drug - metabolizing enzymes that are widely distributed throughout the animal kingdom and that enables many species to transform foreign compounds into water soluble derivatives that can be excreted. Moreover, it was also found that when PAHs were metabolized by these enzymes in vitro reactive intermediates were formed. Initially these intermediates were thought to be simple epodixes. However over the last few years, it has become apparent that the reactive species are most probably diolepoxides. These are most reactive of the bay region. Metabolites of this type are currently under investigation (review by GROVER 1980), since differences in their properties and in their rates of formations and further metabolism may help to explain the very marked structure activity relationship that exists within the Polycyclic Aromatic Hydrocarbon compounds.

#### OCCURANCE OF PAH IN THE ENVIRONMENT:

We can recognise two principle sources responsible for PAH presence in the environment viz. natural

source and anthropogenic sources.

The existence of a natural background concentration of PAH has been established. It consists of PAH biosynthesized on a worldwide scale by plants and microorganisms on land, and in the water (AIZENSHTAT, 1973) and formed during open burning of forests and prairies not ignited by man (National Academy of Science 1972). Volcanic activity is an additional source (GRENIER et.al 1977). The environmental concentration of carcinogenic PAH when expressed in terms of B(a) P, is in the order of a magnitude of 10-20 mg/kg of dry organic substances and constitute between 1 and 20% of total carcinogens (ZOBELL ). The concentration in the upper layers of the Earth is in the range of 100-1000 mg/kg of carcinogenic PAH and results from the activity of soil bacteria and from decayed plants. Rainout, washout and sedimentation lead to the addition of carcinogenic hydrocarbons to the soil. Uncontaminated ground water will have a concentration in the range of 0.001-0.010 mg/l of carcinogenic PAH. This very low but still measurable concentration is probably due to the leaching of PAH from upper soil layers. In contrast fresh water lake with a normal aquatic biota,

but still untouched or slightly contaminated by human activities will have approximately ten times higher concentration of 0.010 - 0.025 mg/l. The global amount of background concentration is rather complicated to assess because of the difficulty of calculating the total weight of the plant kingdom and micro organisms on land, in the soil and in the fresh and marine water bodies. Volcanic activity represents a powerful pyrogenic process and the production of natural PAH is the likely outcome. (INITSKY; BELITSKY and SHABAD 1975) detected B(a)P in the samples of fresh volcanic ash and of plants near volcanoes.

#### ANTHROPOGENIC SOURCES:

1. Automobile Emissions: Particulate matter emitted from vehicular engines contains organic compounds, some of which are carcinogens (KOTIN et.al 1954, HOFFMAN et.al 1965, GRIEMER 1977, STUPFEL 1976, SHABAD 1977). The classes of carcinogens identified thus far, include unsubstituted PAH and amino acid substituted PAH. The presence of precursors of radical intermediates in fuel would be expected to facilitate



PAH formation. Conjugated dienes and aromatics in fuel should provide a maximal enhancement of fuel related PAH formation (BOUBEL and RIPERTON 1963, HOFFMAN and WYNDER 1963, BAGEMAN 1964, National Academy of Sciences 1972). The worldwide trend to reduce the lead content of gasoline in order to reduce lead emission into atmosphere is likely to have the effect of increased content of PAH (CAMARSA and SPENCER 1977). It should be noted that although it was found that the levels of PAH emitted by diesel engines are lower than those of gasoline, their emissions are suspected to be much more mutagenic and carcinogenic than those from gasoline; based on the results from the AMES test. (AMES et.al 1975 , BARTH and BLACKER 1978, WEI et.al 1950). It is suggested that the stronger carcinogenicity and mutagenicity of diesel engine dust comes from the formation of nitro derivatives of PAH, due to reactions between NOX and PAH. (LOFROTH et.al 1980, ROSENKRANZ et.al 1980). The major non-combustion transportation source of PAH is the degradation of automobile tyres in use. Carbon blocks used in the tyre manufacturing contain PAH and other organic compounds of high molecular weight (FAL et.al. 1960, MARCHESANI et.al 1970, National Academy of Sciences (N.A.S) 1972).

2. Industrial Emission: Petroleum industry catalytic cracking process by which organic molecules in crude oil are broken down into higher components is the major direct source of PAH (NAS 1972). Another process of relevance in the petroleum industry is the air blowing of asphalt (NAS 1972).

3. Emission in the Working Environment: There are many examples of increased risk in humans exposed to carcinogenic PAH. The oldest example is the increased risk of scrotal cancer in chimney sweeps exposed to coal tar and soot. Another branch of industry in which the observed raised incidences of cancer are thought to be attributable to PAH, is the coal gas industry (DOLL et.al. 1972). More than 100 compounds were identified in the working atmosphere of an aluminium coke plant. The majority of the compounds identified are parent PAH or their methyl, dimethyl, and/or their ethyl derivatives (BJORSETH 1979).

4. Domestic Heating Emissions: HANGEBRAUCK etc.al (1967) concluded that one of the most important sources of B(a) P is the inefficient burning of coal, oil, gas and wood in regular domestic fires.

5. Refuse Burning Emissions: The intentional combustion of solid wastes as a method of disposal can contribute significantly to overall PAH emissions (HANGEBRUCK 1967, WADLEIGH 1968).

6. Tobacco Smoking: A major source of non-industrial indoor pollution is tobacco smoking (BALUSKINOVA 1964). Cigarette smoke condensate is one of the most complex mixture of compounds in environment. Almost 1000 different PAH have been identified in cigarette smoke condensate (SMOOK 1978).

#### PAH IN SOILS:

SHABAD and DIKUN (1959) demonstrated the presence of B(a) P in a parkzone in Leningrad. YANISHEVA and KIREEVA were able to demonstrate that there was a relationship between soil B(a) P concentration and distance from industrial source. The highest total PAH concentration reported was 3,00,000 micrograms/kg for a soil near a highway in Switzerland (BLUMER et.al 1977). Rainout, washout and sedimentation lead to the addition of carcinogenic hydrocarbons to the soil. Loses of B(a) P from the soil take place mainly during spring and summer following increased deposition during

water. Leaching occurs from the upperdown to the lower layers of the soil (SHABAD 1973). Plant uptake, throughout the roots, can account for some reduction in soil PAH concentration and also by decomposition by U.V. radiation. Bacterial breakdown also occurs. The use of irrigation water from contaminated source can add B(a) P to soils and plants grown on soils with high PAH concentration absorb B(a) P through the roots and translocate to shoot.

#### PAH IN WATER:

Undoubtedly, city street runoff is one of the main source of PAH in surface waters. Road-tar-dust contains upto half a gram of carcinogenic substances. SARTOR et.al (1974) confirmed the importance of the street surface runoff for surface water adding 1.9 mt/a.

The 1973 NAS workshop estimated that approximately 6 million tons of petroleum hydrocarbons enter the ocean annually. As it has been reported that B(a) P enter the ocean each year (NAS 1975). For the future, a certain increase in world consumption of oil is certain and with intensified offshore explorations, stricter rules to protect water environment

become essential. The connection for the prevention of pollution from ships prepared by the Intergovernmental Maritime Consultative Organisation (IMCO) in 1973, will, once enforced, under normal operations reduce oil pollution by about 95%.

Combustion produced PAH transported by air are one of the most likely source of PAH in the aqueous environment (ANNELI HASE and RONALD A. HITES. 1981).

In the early 1950s some papers were published, from which it could be inferred that PAHs would be present in surface waters receiving sewage effluents (WEDGEWOOD and COOPER 1953,54) detected PAHs in industrial sewage effluents. ROBERT C BARRLOR (1982) from his work on primary sewage effluent concluded that aromatic compounds ranging from naphthalene to coronene can be detected in the particulate material of sewage effluent. PAH such as retene and perylene, derived in part from diagenetic processes, were generally in low abundance or undetected in sewage samples. Many particulate samples were dominated by phenanthrene. A major source of PAH is mostly street runoff, road wear particles and automotive oils and greases, all of which contribute PAH derived from pyrolysis and combustion processes.

Rapid sedimentation of organic wastes via incorporation into zoo planktons fecal pellets has been discussed by CARPENTER(1978). In particular he found that generally PAH were preserved during transport through the water column to sediments.

#### THE FATE OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER:

As two modes of formation, water and anthropogenic exist, there are two modes of degradation - physical oxidation and biological reduction. Of these, the most important is physical oxidation i.e. photooxidation. It occurs both in atmosphere and water environment. Other physical processes that take place in water and waste water treatment plants are oxidation with ozone, chloridioxids or other chlorine compounds. One study (BORNEFF et.al 1983) led to the conclusion that B(a) P degradation in antural waters will depend on water depth; seasonal changes (due to fluctuation in solar radiation), on ambient temperature and dissolved oxygen. Moreover degradation rate will be higher at top layers where illumination, temperature and dissolved oxygen are high, but will decrease with depth to reduce water clarity - reduced illumination,

reduced temperature and dissolved oxygen. A number of experiments showed that removal of PAH during waste water treatment by mechanical process will have a limited efficiency. The dissolved PAH are best removed by chemical processes, the most effective being ozonation with chloridioxide.

The ability of marine organisms to concentrate PAH has been demonstrated. But controversy still exists with respect to their capability to degrade PAH. Biological treatment processes have little or no efficiency in removing PAH. (G.W. MALANCY, P.A. LUTIN, L.K. HICKERSO, 1960). The NAS report stated that microorganisms capable of oxidizing petroleum constituents under favourable conditions are present virtually in all parts of marine environments, but reliable data on biological degradation is not available. It is important to stress that aquatic microorganisms will degrade PAH, but their very existence depends on surrounding environmental conditions, changes, will effect metabolism and growth rate (NAS 1975). Several investigations have indicated that various PAH are metabolised in mammalian cells with some of their end products being polycyclic quinones (BORGAN A.H.,

DARVEY.N., AGNOLI. T.T., CROCKER, 1973). Some metabolic pathways in mammalian systems are found to involve oxidases and other enzymes (NAS).

#### PHOTO OXIDATION OF PAH:

Photooxidation involves energy transfer from the triplet state of aromatic compounds yielding singlet oxygen. PAHs have strong absorption for U.V. radiation at wavelength 300-400 nm (present solar radiation at ground level) and most of them are readily photooxidised and the by products will be oxygenated compounds. The most common photooxidation reaction of PAH in solution is formation of endoperoxides. Photolysis or pyrolysis of such peroxide produces a variety of results including dialkylation and ring cleavage. Diones can also be formed when no endoperoxides can be formed. For example Benzo (a) pyrene yields a mixture of 6.12 dione and 3.6 dione (MASUDAY and M.KARUTSUNE 1966).

#### POLYCYCLIC AROMATIC HYDROCARBON BODY BURDENS IN MAN:

It is now well established that the effect of chemical carcinogens is directly related both to



the dose and duration of contact with carcinogenic agent. It is thus important to know "body load" to which man is exposed during his life time. Man is exposed to PAH from the atmosphere, from food and water. Over a 70 year life span, food intake of PAH is likely to be about 5 mg. Inhabitants of large cities, in addition, will gain 12-16 mg from inhalation. (SHABAD and DILUN 1959). Intake of PAH in water will normally be extremely low. Much of the PAH in water will be excreted, Shabad and Dilun found that the tissues of elderly town dwellers contained 1000 times as B(a) P than might have been expected from normal intake figures. LINNIK S. MIRNY and SHABAD (1971) showed that the activities of enzymes systems in the body leads to the formation of oxyderivatives which are no longer carcinogenic in activity.

There has been a considerable effort applied to the determination of maximum allowable concentration (MAC) of PAH in the atmosphere, since this represents the major exposure source to which man is subjected. B(a) P levels are often taken as indicators for establishment of MAC values and the standard can be set by reference to backgrounds levels that are continuously monitored.

ANALYTICAL METHODS:

The PAH fraction of many environmental samples is usually of a high compositional complexity; several hundred compounds spread over a wide concentration range. Over the past 40 years several methods have been developed for the analysis of PAHs . Most of the methods used, employ various forms of chromatography at some stage of the analysis. A comparison of all types of methods has been done and it is concluded that PAH analysis requires absorption spectrometric or spectrophoto fluorimetric methods.(SAWICKI 1967).

Since its birth in the early 1970s high performance liquid chromatography (HPLC) has been used extensively for the separation of PAHs. At present, HPLC does not approach the high separation efficiency of capillary column gas chromatography. However, HPLC does offer several advantages for determination of PAHs. First, HPLC does offer a variety of stationary phases capable of providing unique selectivity for separation of PAH isomers that are often difficult to separate by G.C. In HPLC, selectivity is

achieved due to interactions of the solutes with both the stationary phase and the mobile phase rather than only the stationary phase as in G.C.

Ultra-violet absorption and fluorescence spectroscopy provide extremely sensitive and selective detection of PAHs in the HPLC. Finally, the HPLC provides an extremely useful fractionation technique for the isolation of PAHs for subsequent analysis by other chromatographic and spectroscopic techniques. Due to these characteristics, HPLC has been employed extensively for the determination of PAH in air particulates, water sediments etc. (WISE 1983).

Gas chromatography has been used in the separation of PAHs since the late 1950s and early 1960s. The efficiency of the method mainly depends upon the columns packed with properly selected stationary phase. Studies with packed columns in gas liquid chromatography include the determination of PAHs in air borne particulates (LAO et.al 1973 ; JOHN and NICKLESS 1977, THOMAS et.al 1978). Mass spectrometers (MS) specially in combination with gas chromatography is the most powerful analytical tool attributed today in the identification of individual compounds present in complex mixtures. The main drawback of MS is the

difficulty in separating positional isomers (BJORN JOSEFFSON 1983).

Presently fluorescent analysis is used in many studies which determine PAHs quantitatively and qualitatively (ARGARU 1970). As PAHs strongly absorb in the UV radiation a potentially important advantage of fluorescence over U.V. visible absorption analysis, is the inherent involvement of two usual wave lengths. In the fluorescence method quenching is defined as, any process wherein the fluorescence quantum efficiency of a particular compound is decreased by interactions with other constituency of a sample. Molecular oxygen is a notorious fluorescence quencher of many organic molecules including PAHs. Procedures for quantitative fluoremetric analysis of PAH, therefore, usually include a deoxygenated step. (CATZ et.al 1978, WHERY 1983).

## MATERIALS AND METHODS

The present study was carried out to assess the presence of some polynuclear aromatic hydrocarbons in a typical urban sewage. The study comprised three steps:

### SAMPLING:

A brief resume of Okhla sewage treatment works has been given earlier. The present study eight sampling sites were selected. Each site represents different stages in the treatment (thus covering from raw sewage to completely treated sewage).

The samples were taken from:

1. Raw Sewage.
2. After Aerobic Treatment.
3. After secondary treatment.
4. The sludge going to digester.
5. Fresh digested sludge.
6. Partially treated outgoing waste water.
7. Completely treated outgoing waste water.
8. Sun-dried sludge.

### SAMPLE PREPARATION:

500 ml. of sample was collected in brown coloured bottles and these bottles were kept at 0°C till the extraction was carried out. In case of sun-dried sludge 500 g. was taken and wrapped in aluminium foil. It was also kept at 0°C until extraction was carried out.

Spectrograde cyclohexane supplied by Glaxo Chemicals was used as the solvent for extraction of PAHs. Extraction was carried out as per Borneff, 1983.

500 ml. sample was mixed with 400 ml. of cyclohexane and distributed over three 500 ml. conical flasks. Using magnetic stirrer the mixture was stirred continuously for 16 hours. This time is quite enough for complete extraction. The supernatant cyclohexane layer was separated after allowing for overnight settlement, and decantation. In case of the sludge 250 g. was taken and powdered thoroughly. It was extracted with 400 ml. cyclohexane and the same procedure was followed.

The extracted solution was concentrated using the solvent in a Buchi Rotary Evaporator. After concentration, the sample (20 ml. in volume) was transferred to graduated glass sample tube. The samples were stored at  $-7^{\circ}\text{C}$  until further analysis was performed.

#### THIN LAYER CHROMATOGRAPHY:

For proper separation of PAHs to two dimensional thin layer chromatography was used. A paste of 25 gm. of Aluminium oxide in 50 ml. distilled water was spread over five 20 x 20 cm. plates. They were air dried for half an hour and then kept vertically in an oven at  $110^{\circ}\text{C}$  for 40 minutes. The thickness of Aluminium layer is 3 mm.

60 micro litres of sample extract was spotted at one corner, one cm. from the bottom. This was developed in first direction with Hexane and Ether in 19:1 ratio. (Analytical grade reagents supplied by S.d. Fine chemical Ltd.) The development in first direction took above 60 minutes for solvent phase to cover 15 cm. distances.

The plates were taken out from glass chamber and after the dried completely, the plates were turned by 90° and placed in second chamber consisting Propanol, Acetones, distilles water of 2:1:1 ratio. Within three hours, the solvent travelled 15 cm. After two dimensional development was complete, the PAH compounds were identified by compaing the spots under uv light with the standards.

The standard mixture sample was prepared by dissolving 3 mg. of each of the PAH mentioned earlier in the cyclohexane. This sample was also subjected to the same proceedure as above.

#### SPECTROFLUOROMETRY:

Quantitative estimation of PAH was done by spectroflurometry method. For this purpose the instrument used was Farrend system-3 Scaning spectrofluourometer.

Before recording the flurosence measurement the solution to be analysed was purged with fine stream of nitrogen for 3 min. The identifying wave lengths for each standard compound were determined on the basis of maximum fluroscence intensity against particular

wave lengths (Scanning). Quantification of PAH in mixture without separation was done in accordance with the method used and recommended by Chaudet and Kaye (1961).

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Compound	Extation spectra nm.	Emission spectra nm.
Benzo (a) Pyrene	300	409
Benzo (b) Fluroanthene	302	424
Benzo (ghi) Perylene	304	419
Chrysene	311	365
Benz Anthracene	295	386

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Standard Solutions:

A series of standard solutions of each standard compound were prepared in concentration range of  $10^{-3}$  to  $10^{-9}$ M.



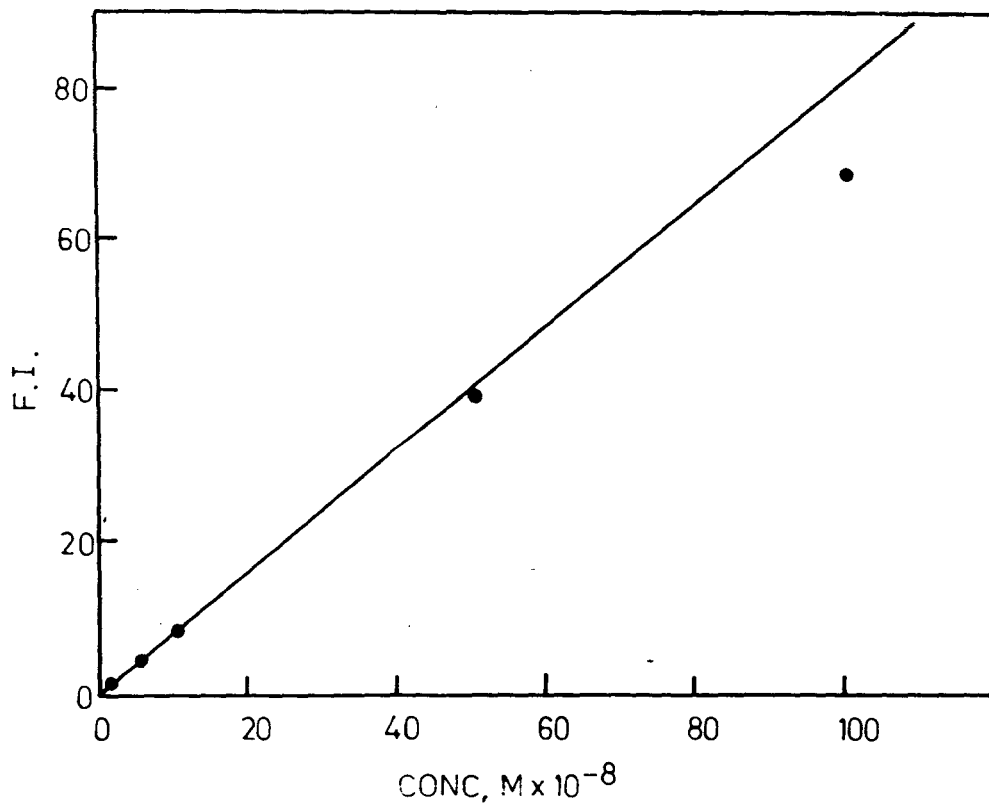


FIG. RELATION OF F.I. TO CONC. (BaP)

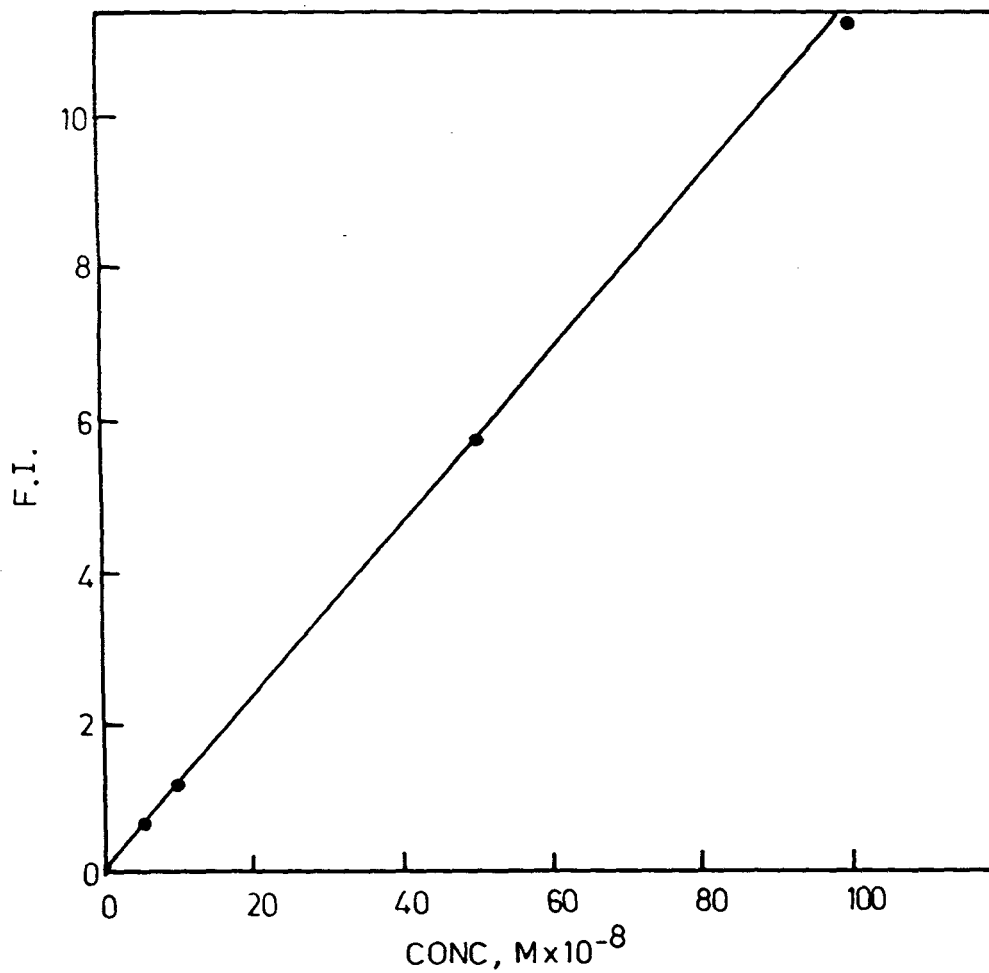


FIG RELATION OF F.I. TO CONC. ( Benzo(a) anthracene.)

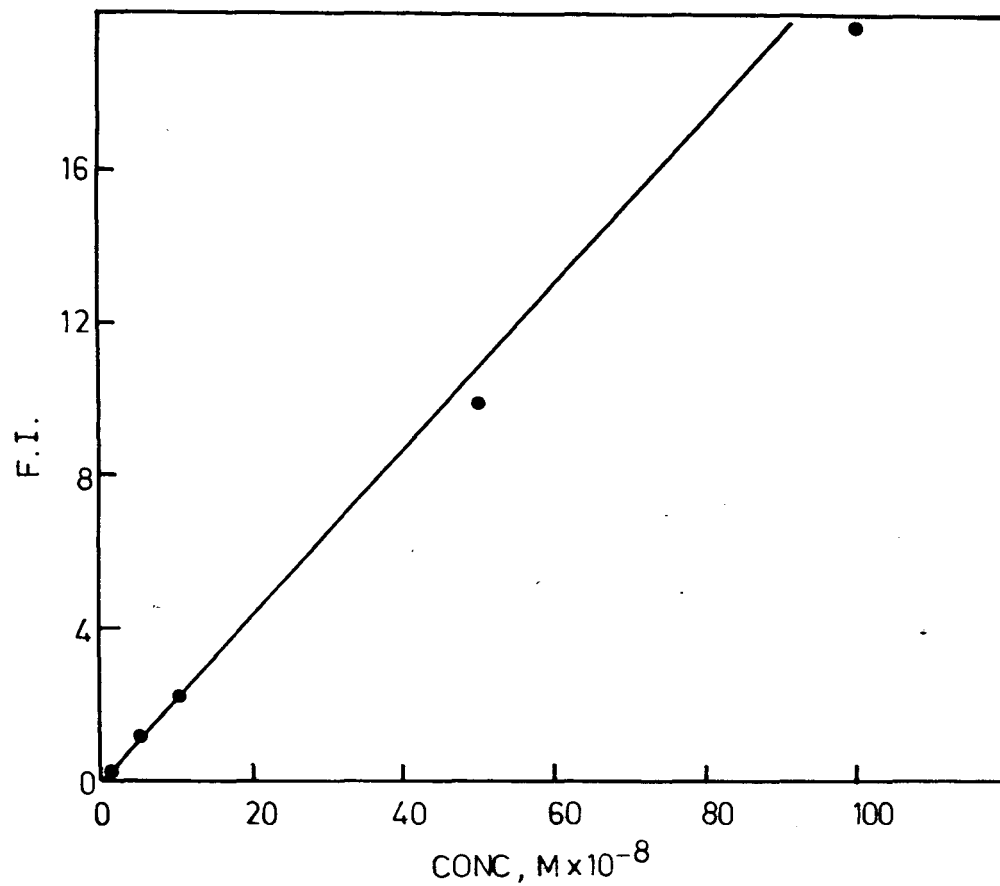
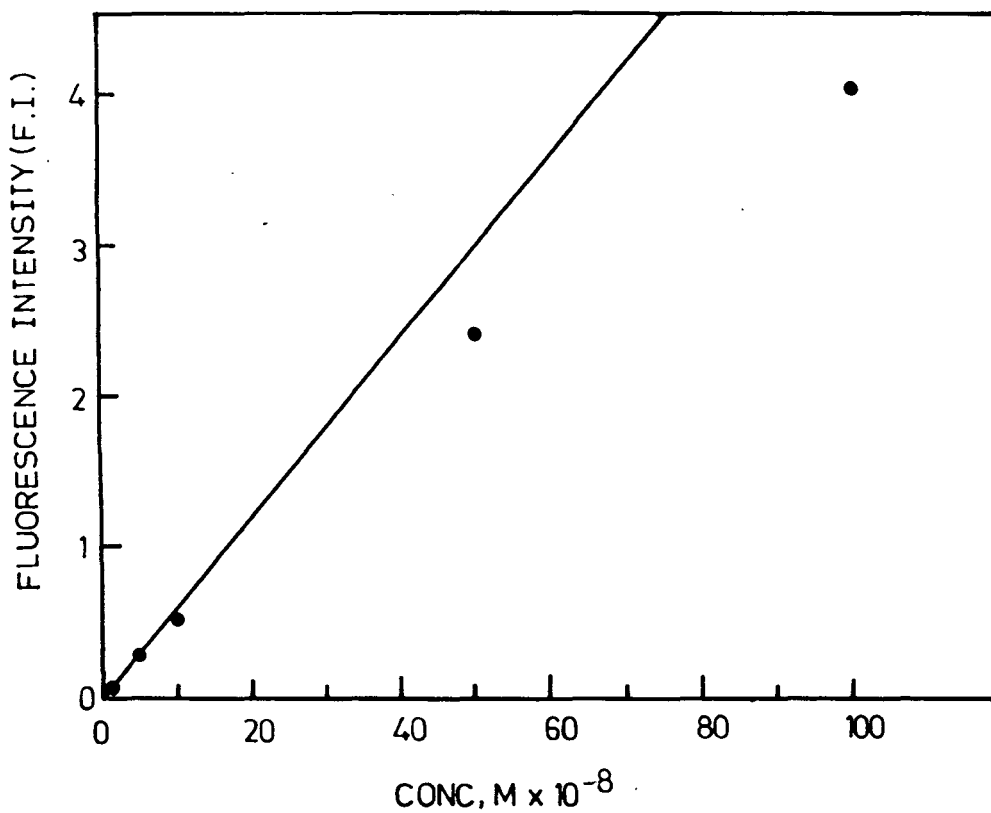


FIG. RELATION OF F.I. TO CONC. (Bghi P)



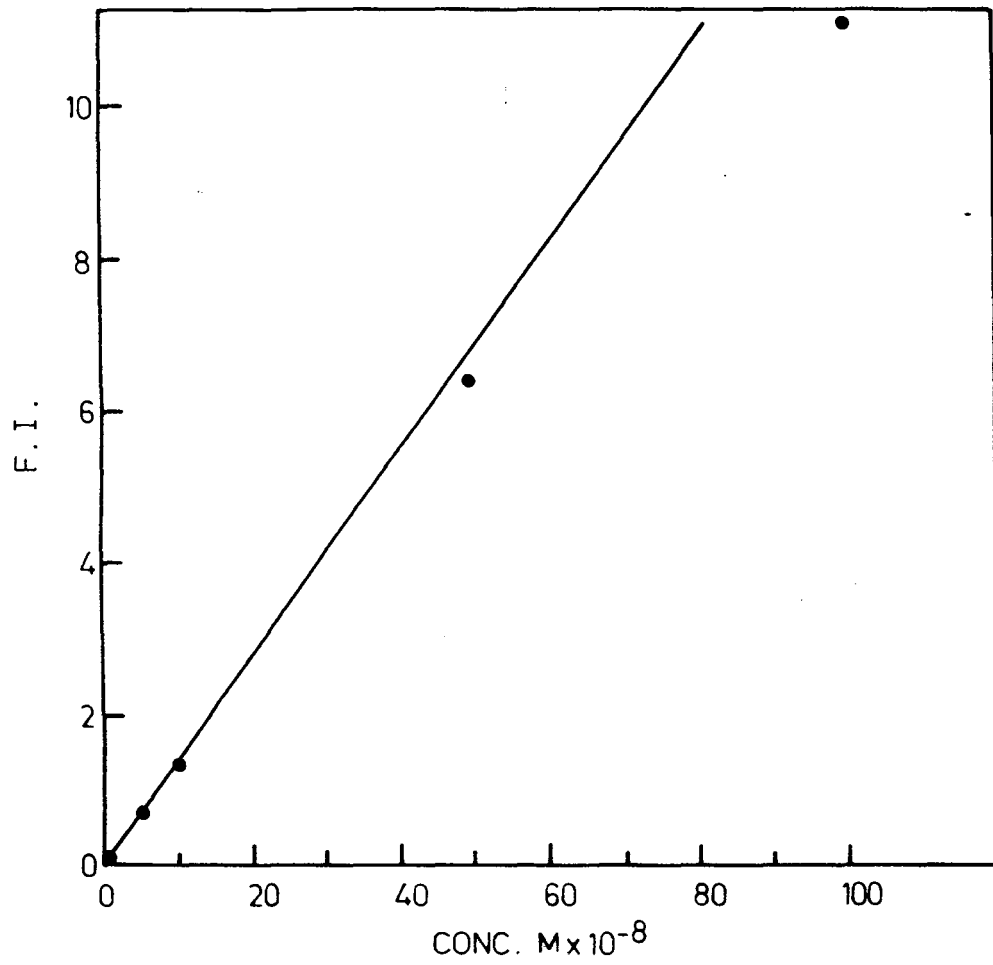


FIG. RELATION OF F.I. TO CONC. (BbF)

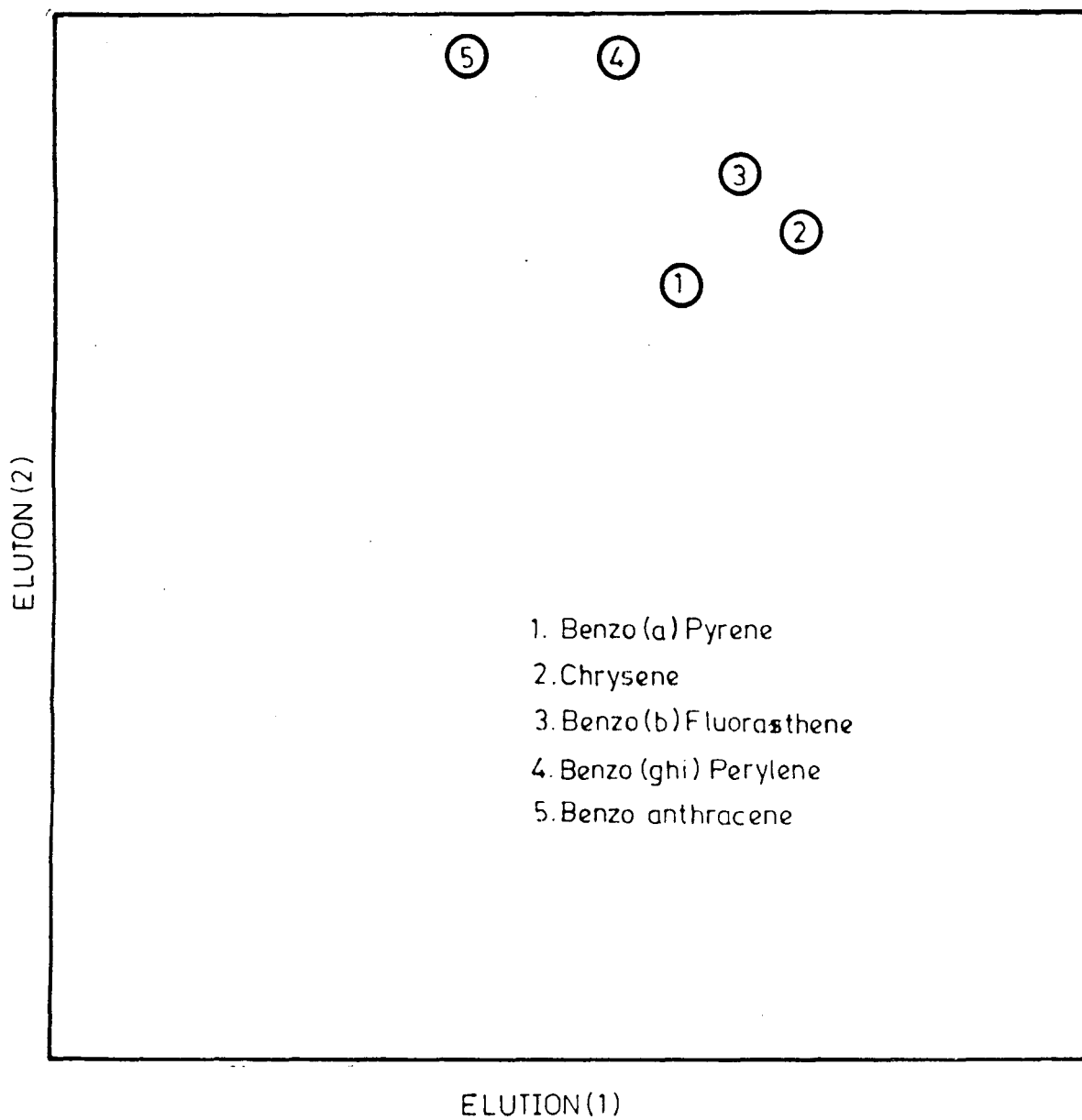
RESULTS AND DISCUSSION

## Qualitative Analysis:

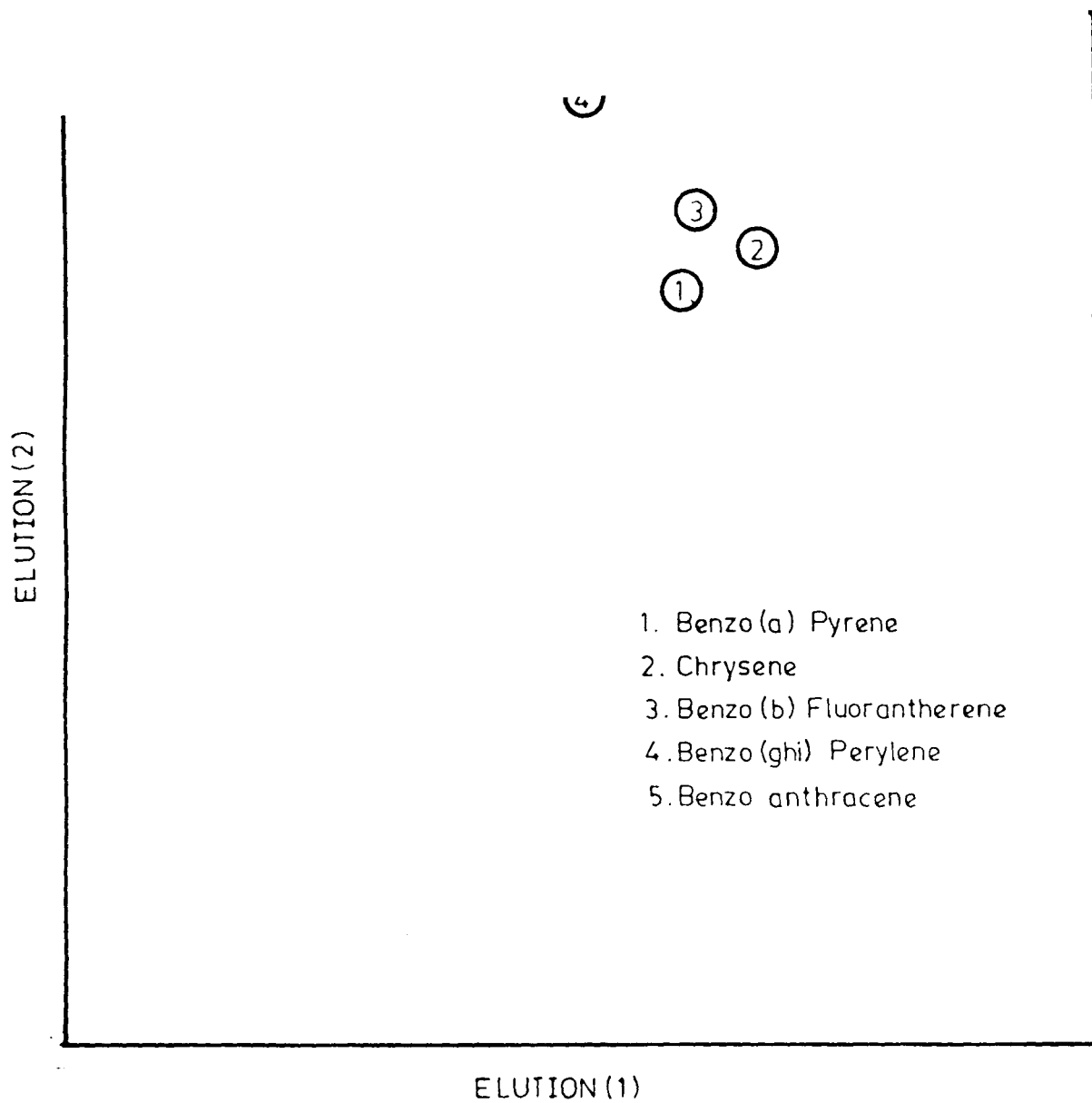
In the qualitative analysis the two dimensional thin layer chromatography method was used. At first, individual standard solutions were analysed. The distance travelled by them was noted. Then sample solutions were placed on T.L.C. plates and the two dimensional development was carried on for all samples. The fluorescence activity at various locations was marked by visual comparison and the five PAH compounds were identified. The results obtained are represented in Table I.

Polycyclic Aromatic Hydrocarbon Compounds

Sample	Benz anthracene	Benz (ghi) Perylene	Benz (b) Fluoranthene	Chrysene	B(a)P
Raw Sewage	✓	✓	✓	✓	✓
Aerobic Treatment	✓	✓	✓	✓	✓
Secondary Treatment	✓	✓	✓	✓	✓
Sludge to digester	✓	✓	✓	✓	✓
Fresh digested Sludge	✓	✓	✓	✓	✓
Outlet (partially treated)	✓	✓	✓	✓	✓
Outlet (completely treated)	✓	✓	X	X	X
Manure cake	✓	✓	✓	✓	✓

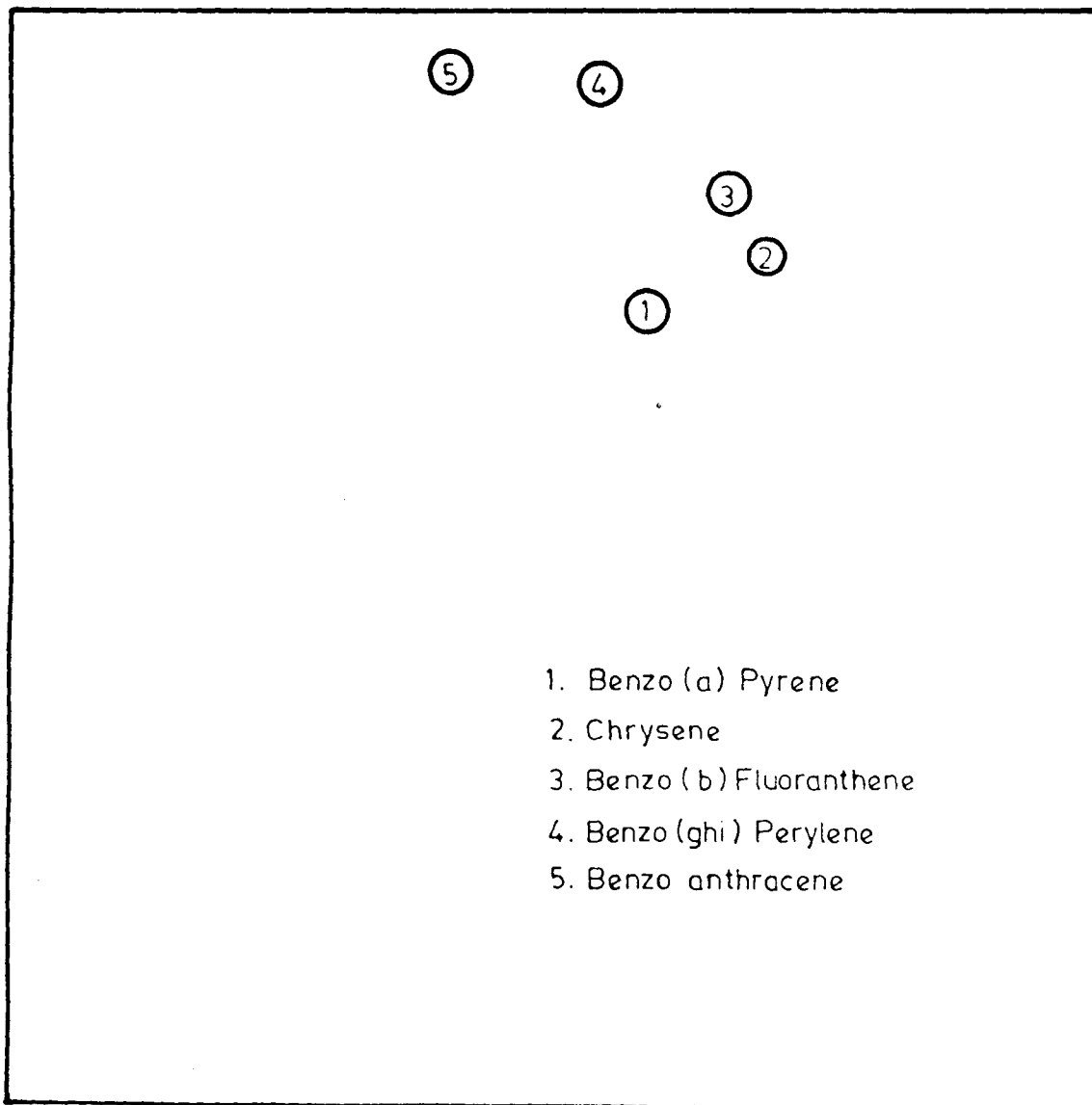


Standard Chromatogram



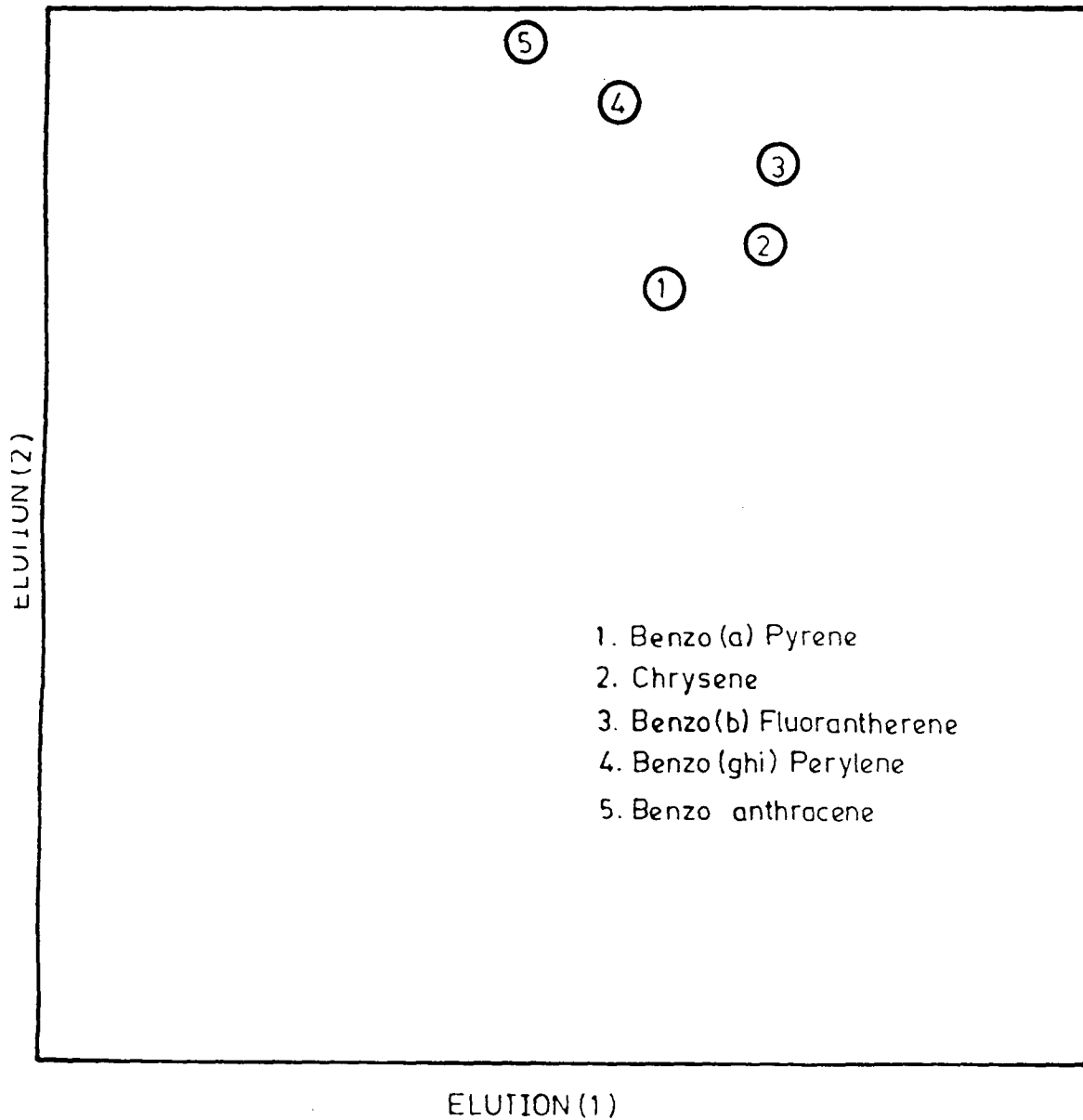
Chromatogram of Raw Sewage

ELUTION (2)



ELUTION (1)

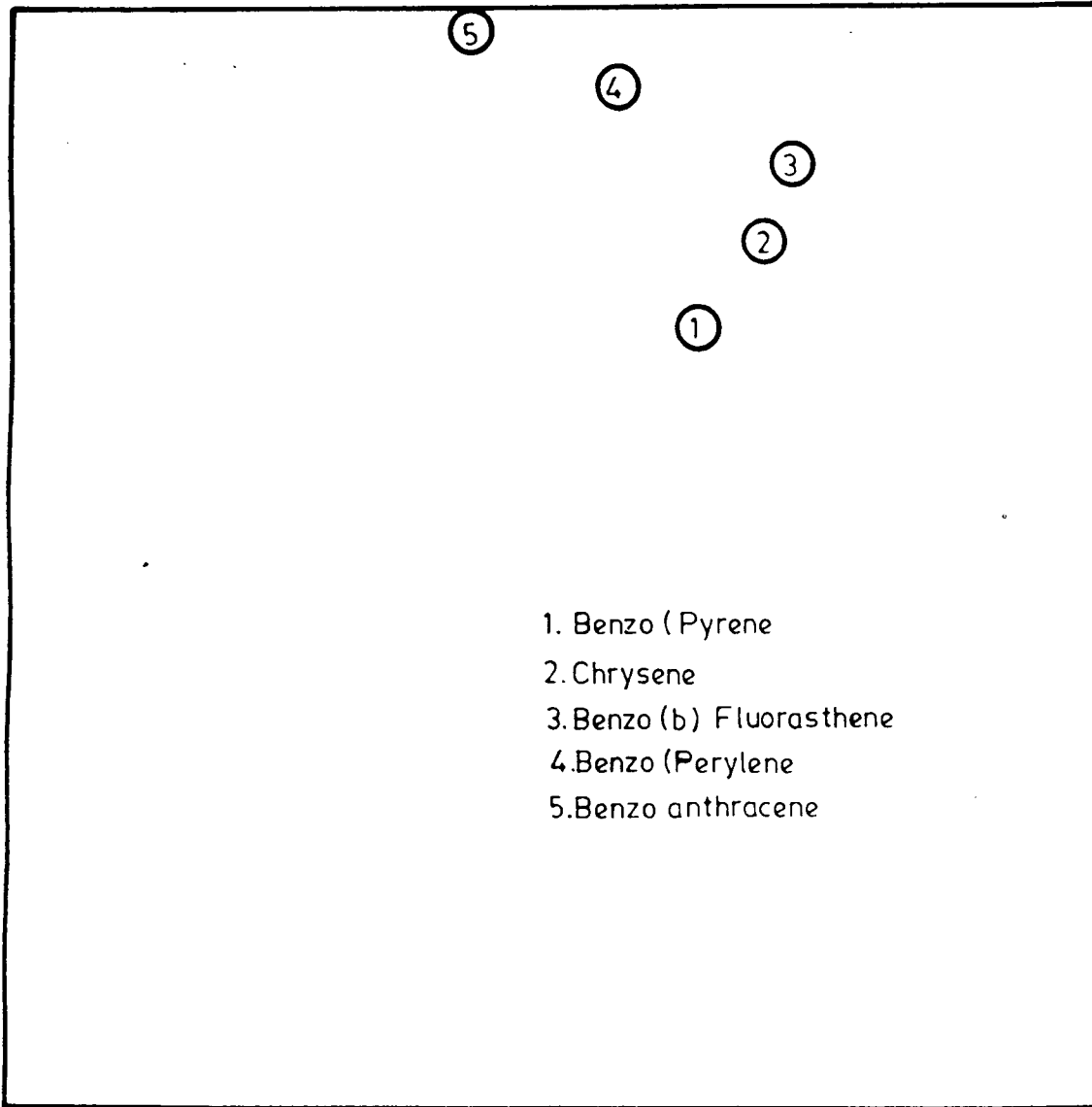
Chromatogram of Sample from Aerobic treatment



Chromatogram of Sample from Sludge going to digester

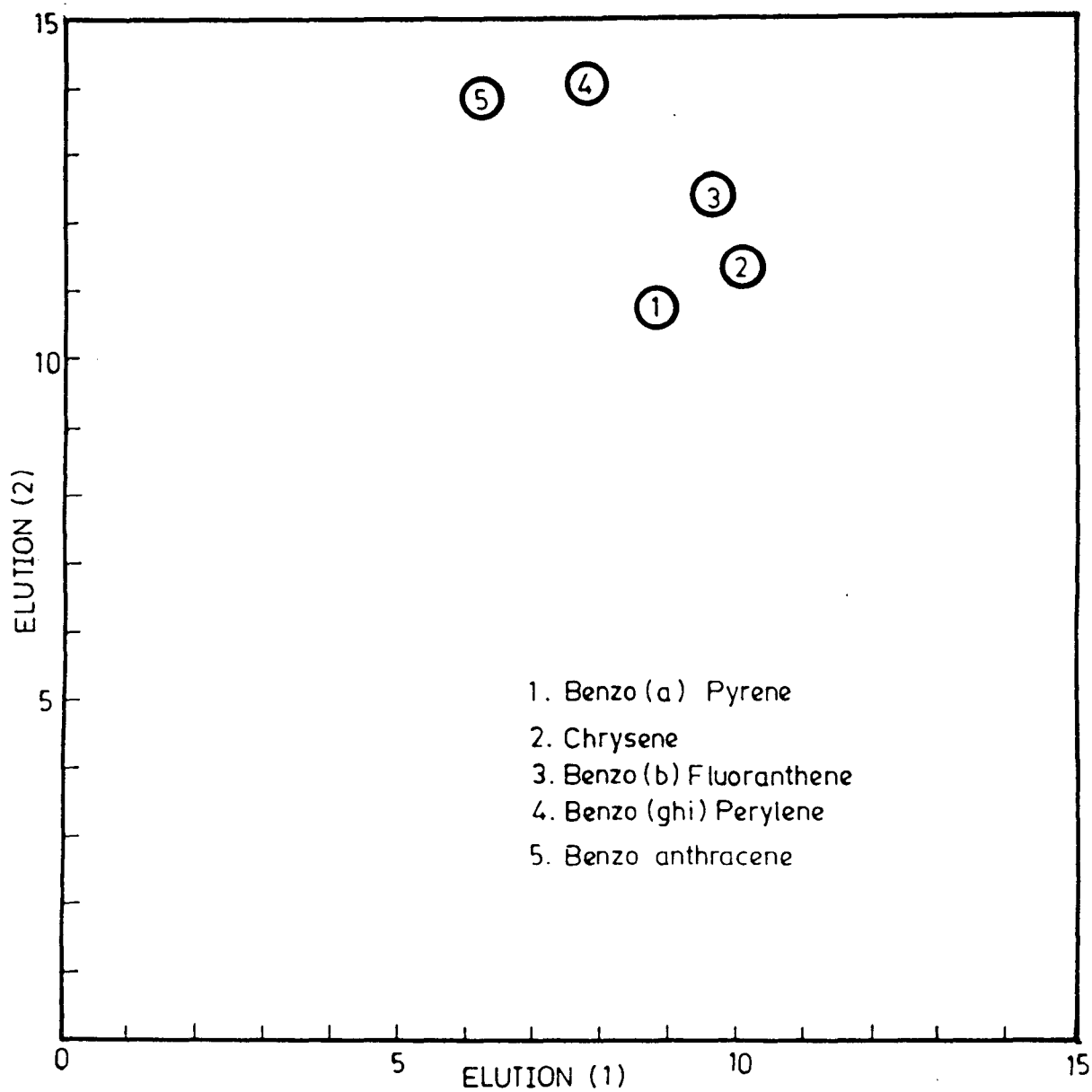


ELUTION(2)

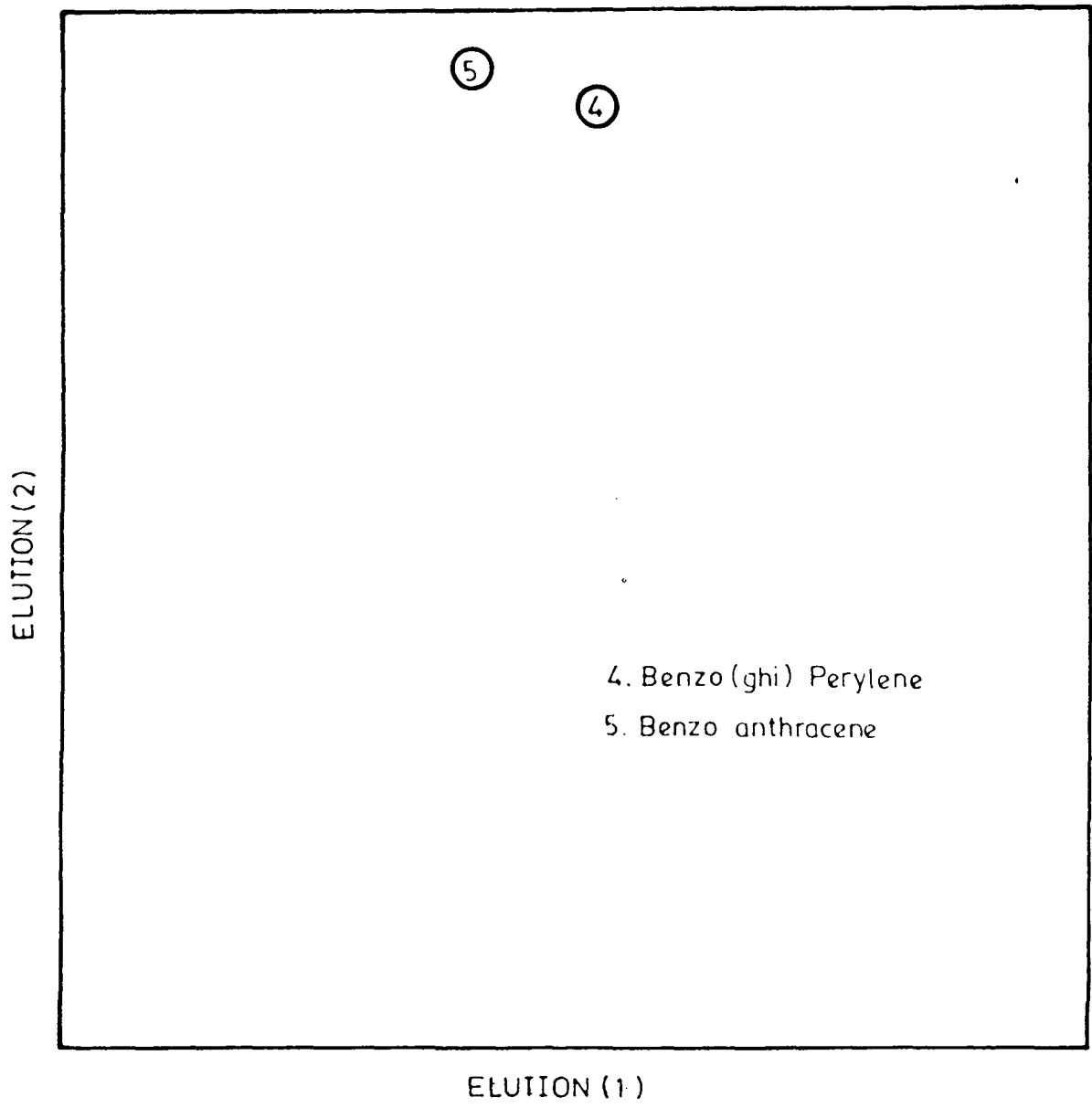


ELUTION (1)

Chromatogram of Sample from Fresh Digested Sludge

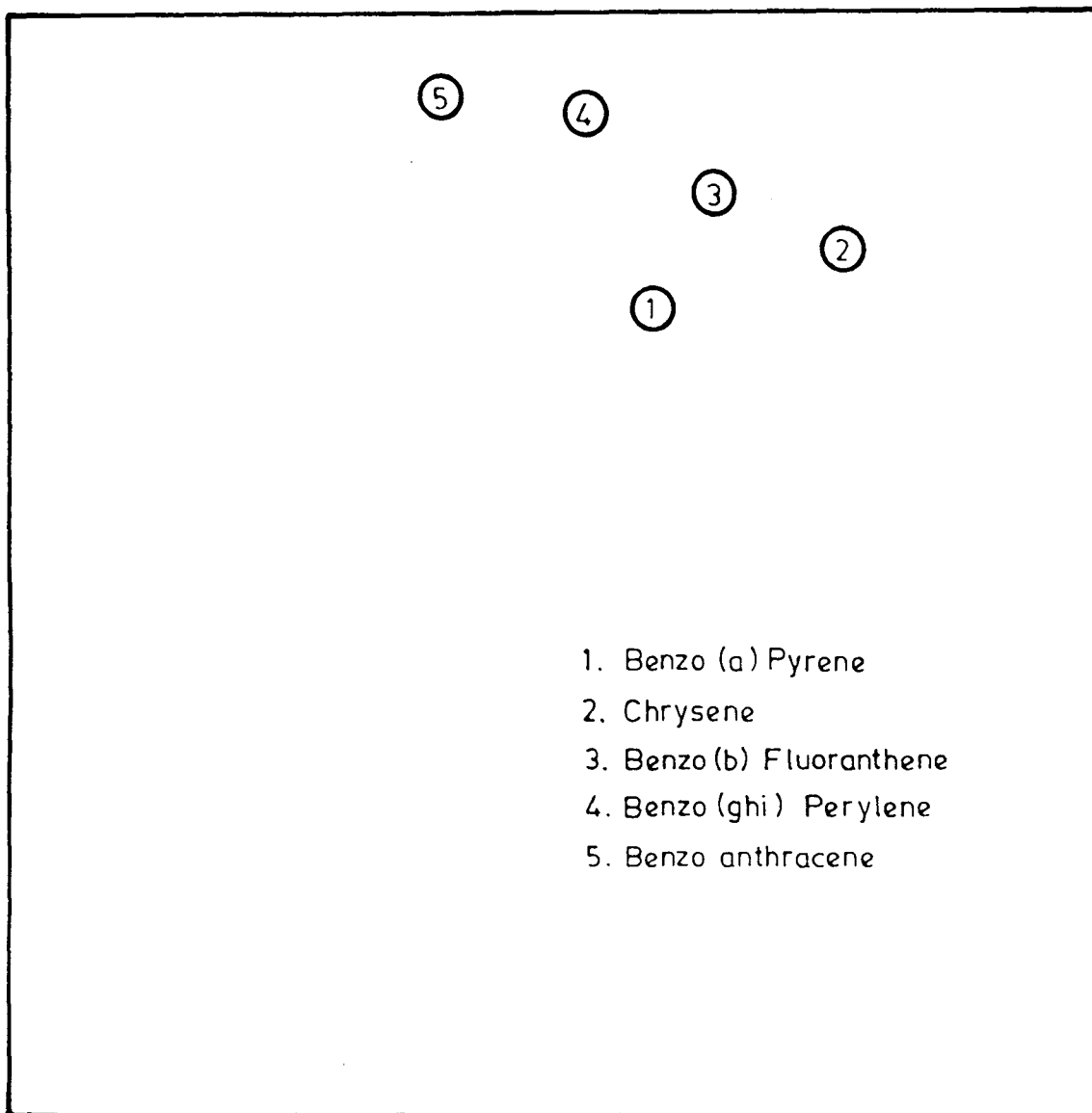


Chromatogram of Sample from outgoing water (partially treated)



Chromatogram of Sample from outgoing water (Completely treated

ELUTION (2)



ELUTION (1)

Chromatogram of Sample from Sun-dried Sludge

## Quantitative Analysis:

After the confirmation of the presence of five selected PAH compounds in most of the samples, the next stage of analysis ie. quantitative analysis was carried on. The concentration of these compounds are shown in the following tables, from II to VI.

TABLE II

Sl.No.	Sample	Benzo(a) Pyrene mg/l.
1.	Raw Sewage	32.4
2.	Sample from Aerobic treatment	13.0
3.	Sample from Secondary treatment	0.706
4.	Sludge going to digester	2.0
5.	Digested fresh sludge	2.0
6.	Outgoing water (partially treated)	0.8
7.	Outgoing water (Completely treated)	0.03
8.	Manure cake or Sun-dried Sludge	1.21 mg/kg.

TABLE III

S.No.	Sample	Chrysene mg/l.
1.	Raw Sewage	3.1
2.	Sample from Aerobic treatment	0.3979
3.	Sample from Secondary Treatment	0.1326
4.	Sludge going to digester	5.5268
5.	Digested fresh Sludge	4.827
6.	Outgoing water (Partially treated)	0.3316
7.	Outgoing water (completely treated)	0.1
8.	Sun-dried Sludge	4.0 mg/kg.

CONCENTRATIONS OF CHRYSENE IN SEWAGE AT  
VARIOUS STAGES OF TREATMENT

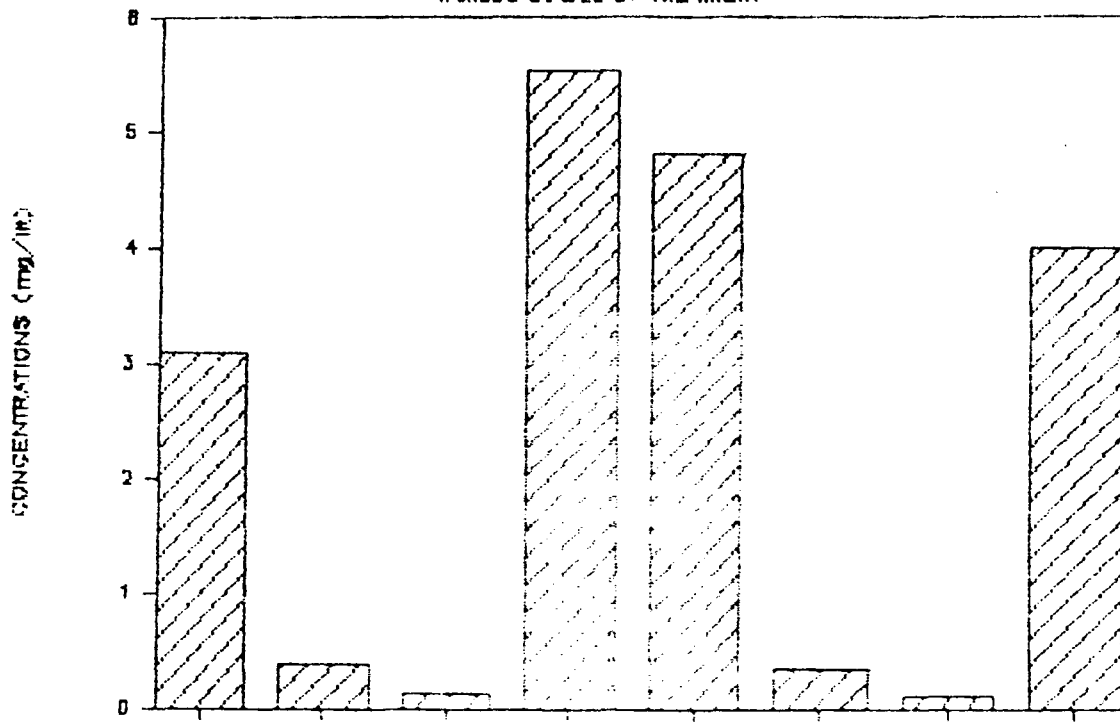
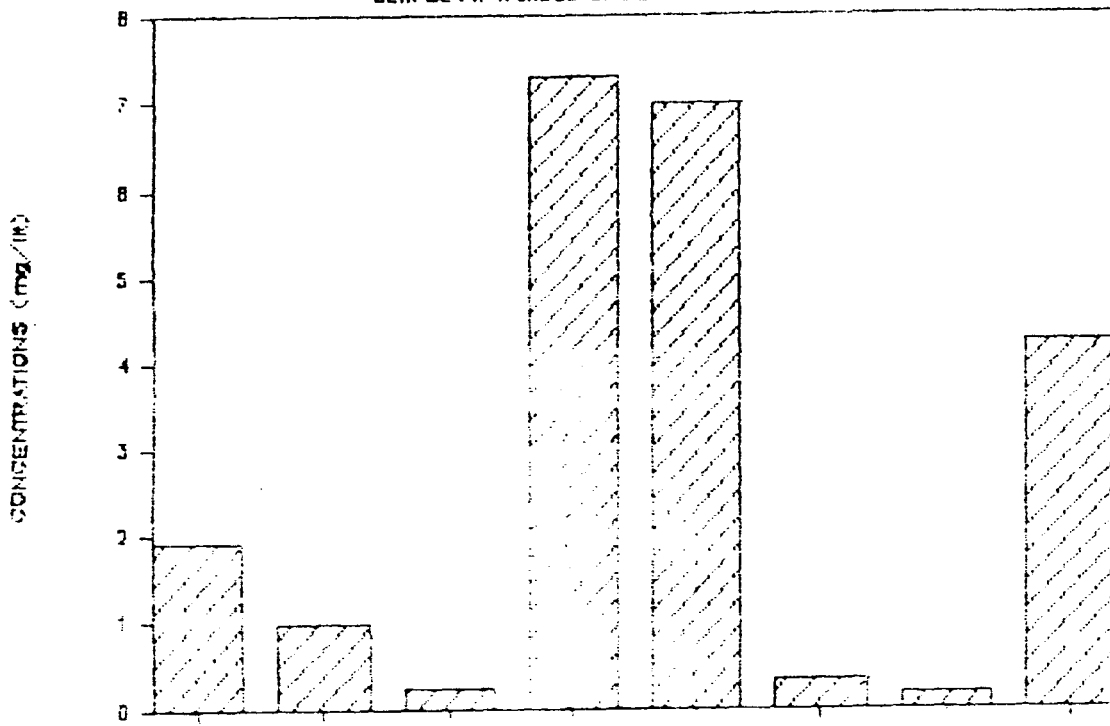


TABLE IV

S.No.	Sample	Benzo (ghi) Perylene (mg/l)
1.	Raw Sewage	6.6392
2.	Sample from Aerobic Treatment	2.74
3.	Sample from Secondary treatment	1.46
4.	Sludge to digestor	173.50
5.	Fresh digested Sludge	170.0
6.	Outgoing Water (Partially treated)	3.0
7.	Outgoing water (completely treated)	0.913
8.	Sun-dried Sludge (Manure Cake)	110.0 mg/kg.



### CONCENTRATION OF BENZ ANTHRACENE IN SEWADE AT VARIOUS STAGES OF TREATMENT



### CONCENTRATIONS OF BENZO(ghi)PERYLENE IN SEWADE AT VARIOUS STAGES OF TREATMENT

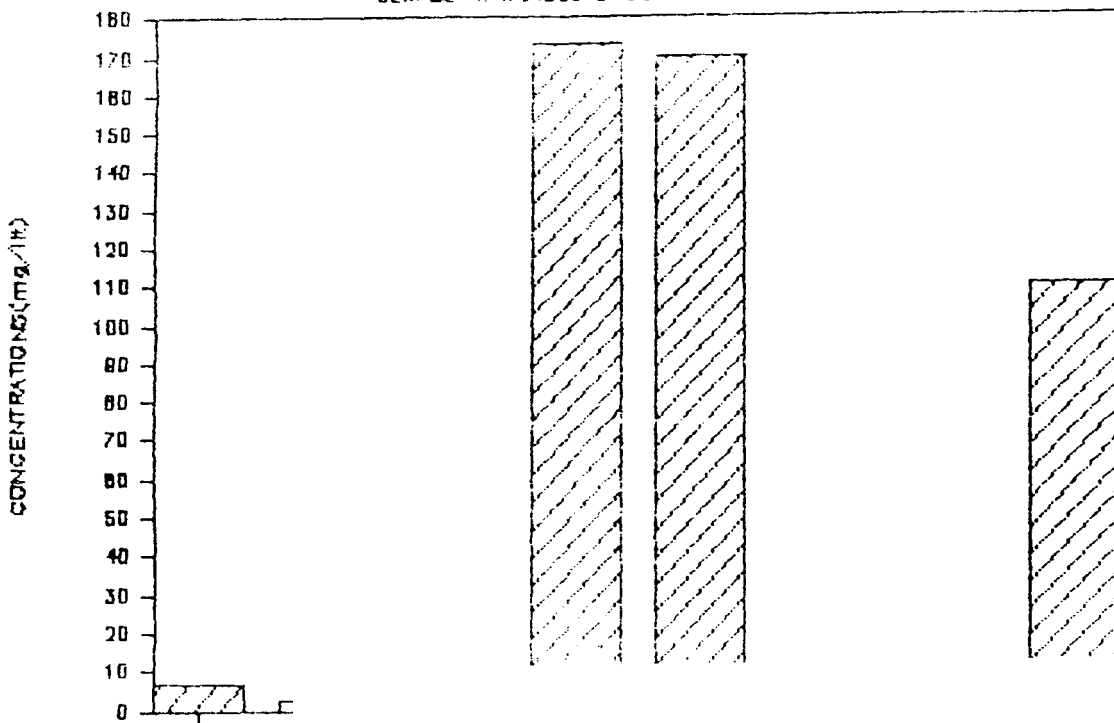


TABLE V

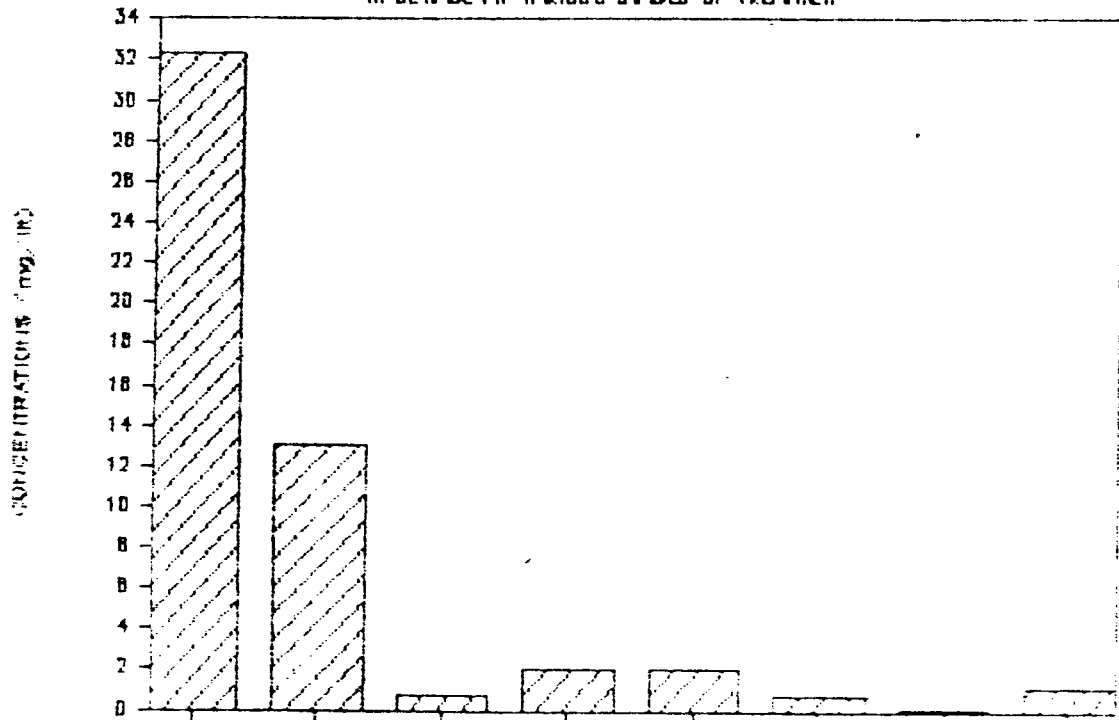
S.No.	Sample	Benz Antheracene (mg/l)
1.	Raw Sewage	1.9136
2.	Sample from Aerobic treatment	0.9874
3.	Sample from Secondary treatment	0.2374
4.	Sludge to digestor	7.305
5.	Fresh digested Cake	7.0
6.	Outgoing Water (Partially treated)	0.328
7.	Outgoing water (completely treated)	0.1584
8.	Sun-dried Sludge	4.23 mg/kg.

TABLE VI

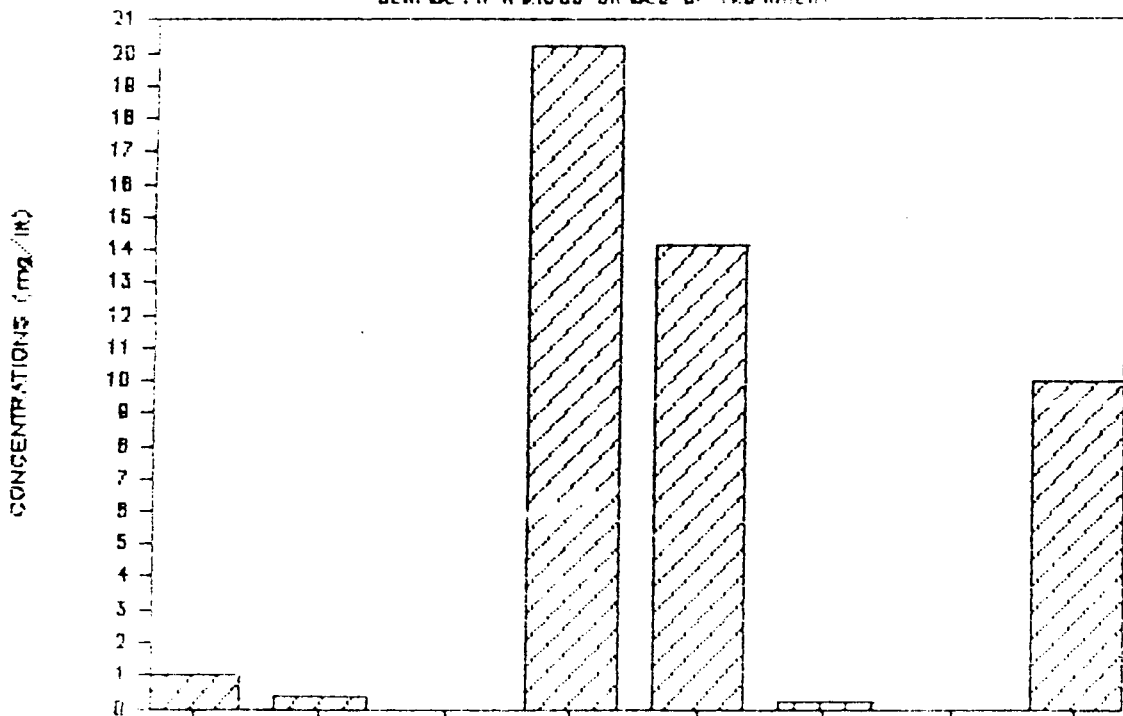
S.No.	Sample	Benz (b) Fluoranthene (mg/l)
1.	Raw Sewage	1.009
2.	Sample from Aerobic treatment	0.4037
3.	Sample from Secondary Treatment	ND
4.	Sludge going to digester	20.18
5.	Fresh digested Sludge	14.18
6.	Outgoing water (Partially treated)	0.201
7.	Outgoing water (Completely treated)	ND
8.	Sun-dried Sludge (Manure cake)	10.0 mg/kg.

N.D.= Not detectable

### BENZO (a) PYRENE CONCENTRATIONS IN SEWADE AT VARIOUS STAGES OF TREATMENT



### BENZ (B) FLUORANTHENE CONCENTRATIONS IN SEWADE AT VARIOUS STAGES OF TREATMENT



One can not determine the presence of PAH in the waste water on the basis of its containing suspended and flocculated materials, for this it is essential to know the kind of sewage input. Domestic waste water is the largest polluting source. PAHs mainly occur in particles or settled onto them. PAH's could be solubilized by detergents, but high concentrations of detergents which are necessary to solubilize PAH are not generally available in water. PAH is also absorbed by live algae and subsequently after the algae die, precipitation occurs. A certain amount of PAH is dissolved in with the liquids of planktons, for this reason unpolluted river and lake waters generally will not show high concentration of carcinogenic substances.

Physical sedimentation is an essential factor for the elimination of PAH water systems. Sedimentation is an important physical method to remove PAH, not only for sewage purification and natural cleaning of lakes but also for drinking water. It has been observed that after several hours in a sedimentation basin, about 90% of PAH was removed (BORNEFF-1977).

There are several reports available about the effectiveness of water treatment processes in the removal of PAH. In 1963 GRAFF and NOTHAFFT studied the effects of chlorination on dissolved Benzo (a) Pyrene and concluded that in practice one should not expect great success with a chlorine dose of approximately 0.3 mg/l. But Borneff ascertained 50-60% reduction in B(a) P with the chlorination of raw water at 1 mg/l chlorine. Yet in practice the degree of efficiency will never reach the 100% mark, only with very high doses of chlorine one can expect to get most effective removal of PAH. But there has been some apprehension that chlorine in drinking water has the effect of producing Co-carcinogens.

Physical purification methods can also be used. Investigations (BORNEFF 1977) showed that activated carbon in practice can reduce total PAH by 90%. We can say that sedimentation and sand filtration removes two thirds of the total PAH. More efficient removal may be attributed to the association of PAH into larger particles coagulation possess can transfer the PAH into large particles which can be filtered. With chlorination as a final step, we can

expect elimination of 90% after the coagulation process and 95% after final filtration.

There are numerous sources which contribute PAH significantly to waste water viz. atmospheric fall out, fly ash precipitation, road run off, industrial effluent and domestic sewage. Due to their low aqueous solubility and vapour pressure. PAHs are sorbed by particulate matter. The sorptive affinity of PAH is exploited in their removal in waste water treatment processes such as coagulation and flocculation, sedimentation and filtration with sand or activated carbon.

Based on laboratory studies, SOUTHWORTH (1979) showed that the volatilization rates of several PAH decreased with decrease in vapour pressure. The rate of change was inversely related to the number of aromatic rings. This implies that PAH with four or more rings will have insignificant volatilization loss under all environmental conditions.

Reactions involving singlet oxygen are unimportant in the atmosphere since its residence is limited

owing to quenching by other interactions, but photo oxidation by singlet oxygen seems to be dominant process for the break down of several PAHs. Under ozone and light, half lives of several PAHs vary between a few minutes to a few hours. Alkyl PAH appear to be more susceptible to photo oxidation than the parent PAH (ZAFARIOU, 1977) (RADDING et al 1976) PAH sorbed to particulates are more susceptible to photo oxidation than in solution. Photolysis products are either (i) endoperoxides that undergo secondary reactions to yield a variety of products or (ii) diones.

The above described processes contribute to the removal of major portion of PAH from sewage. In addition biological mechanism also affect PAH concentration. Those reactions involve the introduction of two hydroxyl groups through a dihydroxyl intermediate into the aromatic nucleus (GIBSON 1976, 1977). The hydroxyl groups could be ortho or para to each other and undergo subsequent enzymatic cleavage. Lower molecular weight PAH can be degraded completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (for example naphthalene by *Pseudomonas putida*) (JERINA et al 1971) whereas high molecular weight form various phenolic and acidic metabolites.



From the Table II - VI, it can be noted that raw sewage has fairly high concentrations of all the five compounds. But at subsequent stages, the concentration decreases i.e. the sample from the aerobic treatment stage. This decrease in concentration can be explained by the fact that polycyclic aromatic hydrocarbon compounds are absorbed on to suspended particles which are removed at the first stage. The solubility of high molecular weight aromatic compounds decreases logarithmically with increasing molecular weight and low vapour pressure, hence 90% of polycyclic aromatic hydrocarbon compounds are adsorbed onto suspended matter.

A two hour retention in the primary sedimentation tank removes about 50% of suspended particulates, thus the PAH concentration is reduced. The reduction rate of PAH more than 50% at this stage. The photosensitivity of polycyclic aromatic Hydrocarbons adsorbed on particulates is strongly dependent upon the nature of the surface upon which the compound is attached. For example Benzo (a) Pyrene is highly resistant to Photo-oxidation when adsorbed on flyash. But it photolyses efficiently in liquid solution. All the

high molecular weight polycyclic aromatic compounds are rapidly transformed in a water solution by the action of sunlight. This accounts for the higher reduction of concentration of PAHs at the aerobic treatment stage (Zeep and Schlotzhaver - 1979).

As we move from the aerobic treatment stage to the secondary treatment, sewage is intensely splashed by paddles thus increasing the dissolved oxygen and promoting the biological oxidation by various micro organisms. These micro organisms by introducing two hydroxyl groups through a dihydroxial intermediate into the aromatic nucleus and further enzymatic cleavage result in the formation of various phenolic and acid metabolites.

Since waste water is continuously and vigorously stirred, very small losses result as dissolved hydrocarbons eventually enter the atmosphere across the air-water interface through evaporation (Mc AULIFFEE - 1977).

Singlet oxygen generated by various reactions is one of the dominant factors which reduces PAH concentration. Half lives of these PAH were studied under ozone and light, varying from a duration of a few minutes to a few hours. In atmosphere the singlet

oxygen reactions with PAHs are relatively less important, but in solutions, it plays vital role. The photolysis products are either diones or peroxides.

All these reactions are not restricted to any particular treatment stage, rather they keep taking place at all stages. All these factors further reduce the concentration of PAH. As the sewage is moved from aeration tanks to the humus tank, further sedimentation occurs (after biological oxidation, the finer particles which escaped sedimentation in the primary treatment will settle faster). This explains the further decrease in the concentration at the secondary treatment stages.

Since the turbidity of sewage decreases sunlight penetration is increased and this enhances PAH decomposition. Thus the outgoing water shows minimum concentration of polycyclic aromatic hydrocarbons.

The 40 M.G.D. sewage which is released for irrigation activities shows high concentration of PAH. This is because of suspended particles to which PAHs are adsorbed and reduced photolysis. From the values given in tables II to VI we can say that further treatment of sewage after the primary treatment is very effective in the removal of PAH.

At every stage of treatment wherever the suspended particles are removed, there occurs decrease in the PAH concentration. All the settled matter is collected and is known as sludge. Since it contains high values of organic compounds this is pumped to the anaerobic treatment plant for methane production. Since the sludge going to digester is nothing but concentrated particulates upon which PAH are adsorbed, it is obvious that, sludge possesses high concentration of PAHs.

Sludge coming out from the digester shows reduced concentrations. But considering the time, spent in the digester which is 25 - 30 days, the rate of decrease is apparently very low. It means that the anaerobic treatment has a minimal influence on the degradation of PAH compounds.

About 7 days after the sludge comes out from the digester and is dried on open fields, it takes the shape of sludge cake, the concentration of PAHs was found to decrease more than during the anaerobic treatment.

From the above results it can be interpreted that in the decomposition of PAH or reduction of their concentration in sewage waters, the following factors, play an important role.

1. Suspended particulate removal
2. Photo oxidation or photolysis
3. Aerobic biological treatment.

The Anaerobic treatment has an insignificant role in the decomposition of PAH compounds.

C O N C L U S I O N

From the survey of literature and results obtained, the fate of PAHs can be described as follows:

The Okhla sewage treatment works release 40 MGD sewage out of 70 MGD for irrigation purposes immediately after primary sedimentation. This sewage contains approximately 4.75 PPM total load of the five PAHs investigated. 30 MGD is released after secondary treatment for irrigation purposes, this contains approximately 1.202 PPM. Sun dried sludge is disposed off as manure cake. A major portion of it is delivered to New Delhi Municipal Corporation as fertilizer for city lawns. This manure cake contains a total PAH load of about 100 PPM. PAH from sewage is ultimately entering the soil. Plants grown on soils with high PAH concentrations absorb B(a) P through their roots and translocate it to the shoot. Aster (*Aster nova-belgii*) and nasturtiums (*Tropacolum majus*) grown on soils highly polluted with PAH, have been shown to contain 6.3 times as much PAH, as the same species grown on control soils. Treatment with contaminated soil does result in B(a) P. accumulation in sunflower (*Helianthus annuus*) seeds. Levels in soils in excess of 100 mg/kg may give rise to significant increases in B(a) P concentration in vegetables (HENTSKY, BELITSKY and SHABAD 1975). It is not possible to

accurately interpret the PAH uptake by plants and its effects on the food chain without a further detailed study. However, it can be said into certainly that it is a cause for concern and indiscriminate use of sludge cake as a manure or fertiliser should be treated with caution.

Okhla sewage plant is expanding its infrastructure so that it can treat 120 MGD sewage upto secondary treatment level. It will become operational by 1991. Once it comes into action, the PAHs concentration in outgoing water may be further reduced. That probably would mean an enhancement in PAH concentration of manure cake, so a detailed study of PAH in manure cake and its ultimate behaviour should be made.

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