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FATE OF TRACE ELEMENTS PRESENT IN INDUSTRIAL EFFLUENTS DISCHARGED INTO RIVER

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PREFACE

With the rapid increase in population and growth of industrialisation in the country, pollution of natural water by municipal and industrial wastes has increased tremendously. The pollution is objectionable and damaging for varied reasons. Of primary importance are the possible hazards to the public health. Of a lesser consequence, but still very real, is the aesthetic damage to the attributes of streams and destruction of the economic values of clean natural waters. The pollution of rivers and streams by industrial wastes and domestic sewage has increased tremendously and producing the most unsanitary conditions in the environment.

Considering these aspects in view, it has been planned by the author to compile and evaluate the present state of affairs with regard to trace element pollution in water bodies. The present investigations would be a step towards understanding the nature of pollutants and their effects on the quality of water of the river. The report also describes upstream/downstream approach for measuring the changes in the concentration and/or load to the river.

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ABSTRACT

A reconnaissance survey of the extent of metal contamination in the river Kali was conducted. The river system has been impacted heavily by the discharges of untreated municipal, agricultural and industrial effluents. In the main channel of the river downstream of the industrial complex, the metal contaminations were found to be 3-4 times background. The concentrations of iron, zinc and copper were found to be 0.41, 0.04 and 0.015 mg/L respectively in the upstream (background level) section during october survey. The same were found to be 0.56, 0.07 and 0.016 mg/L during december survey. However the concentration of lead and cadmium were found to be nil during both the surveys.

The river Kali is a typical receiving water course for untreated municipal and industrial effluents. Mass balance calculations conducted for iron, zinc and copper indicate that differences found in load along the river may be mainly due to the contribution of non-point sources of pollution due to agricultural activities. The difference may also be attributed due to some point sources of pollution which could not be identified in the course of investigations.

1.0 INTRODUCTION

It has been known for several decades that trace quantities of certain elements exerts a positive or negative influence on plant, animal and human life. However, more recently, greater interest has been taken with regard to the specific role of these elements. Generally, the term trace element is rather loosely used in current literature to designate the elements which occur in small concentration in natural biologic systems.

The growing public concern over the deteriorating quality of the environment has led to a generalized usage when referring to trace elements. Thus, for practical purposes, other terms such as trace metals, trace inorganics, heavy metals, microelements and micro nutrients are being used synonymous with the term trace elements.

Today heavy metals are of enhanced importance in industry. In the last decades pollution of the environment therefore has been studied with interest. Many rivers in densely populated areas contain large amounts of metals. Metal concentrations in rivers are able to oscillate in wide ranges . One important fact in varying the concentrations in water is the influence of metals bound to sediments. The heavy metal load of sediments often reaches such high levels that a sudden desorption would be a great danger. Therefore sorption and desorption processes influence water quality to a great extent.

Another important factor in increasing metal concentration is the existence of complexes such as humides or other organic substances. With regard to this, the influence of the complexes EDTA and NTA (both produced by humans) are of interest. Dependent from other elements and from the concentrations of complexes, they enrich metals in water. In fertilizers EDTA is able to reach concentrations of up to 100 micro gram per liter, normal values of wastewaters reach 3 mg/L.

In this report we investigated the extent of metal pollution in a stretch of river Kali in western Uttar Pradesh.

1.1 Trace Elements Essential to Human Life

It is well known that the major ions such as sodium, potassium, calcium and magnesium are essential to sustain biologic life. However, it is less known that at least some further six metals, chiefly transition metals, are essential for optimal human growth, development, achievement and reproduction. The essential elements, which the human body requires have been listed in Table 1 alongwith approximate concentration levels based on an average 70 kg body weight (Vahrenkamp, 1973).

Table 1. Essential metals and respective concentrations for human beings (expressed in mg/70 kg body weight; Vehrenkamp, 1973)

Metal	Concentration
Na	70,000
K	250,000
Ca	1,700,000
Mg	40,000
Fe	7,000
Zn	3,000
Cu	150
Mn	30
Mo	5
Co	1

It is clearly evident from Table 1 that there is marked differences in the concentration of the listed elements, currently known to be essential to human life. In accordance with these levels, a distinction can be drawn with regard to the alkali and alkaline earth metals on the one hand, and the heavier metals exceeding the atomic mass of calcium - often referred to as heavy metals - on the other.

Sodium and Potassium : Both metals are highly concentrated in bodily fluids and are widely distributed throughout the human body. Accordingly, they are not considered as trace elements, but rather as macroelements. Being the most mobile cation, it is not surprising that apart from an involvement in metabolic processes these ions participate in nerve impulse conduction via the brain (Williams, 1971).

Magnesium and Calcium : These are the next most mobile metal ions which are widely distributed throughout the human body and thus cannot be considered as being trace metals. Their unequal distribution pattern is similar to their alkali metal counterparts. Magnesium ions chiefly participate in functions within the cell; they are found complexed to nucleic acids and are necessary for nerve impulse transmissions, for muscle contractions and metabolic functions. Calcium ions having a greater affinity for oxygen containing ligands are less mobile than magnesium ions. This results in the presence of crystalline calcium salts, e.g., phosphate and oxalate, in the circulatory blood system. The insolubility of many calcium salts is reflected by the formation of bones and teeth in which calcium is deposited as hydroxyl-apatite (Vahrenkamp, 1973). This calcium is far the most abundant metal in the human body.

Trace Metals : The essential transition metals including zinc are capable of forming stable coordinate bonds to fixed positions of immobile protein molecules, where they function mainly as catalysts i.e., they induce or enhance enzymatic activity. In the highly specific metalloenzymes the metal is firmly associated with the protein and often constitute the active centre of the living cell, catalyzing only one specific reaction or type of reaction. This explains why in some cases trace concentrations have such a powerful, directive influence on the biologic function within the human body.

Manganese : It is the second most abundant metal in nature (exceeded only by iron). The chemistry of Mn^{2+} resembles that of Mg^{2+}, both ionic species preferring weaker donors such as phosphate and carboxylate groupings to form stable bonds. Due to the ready interchangeability of manganese and magnesium in biologic systems, the specific biochemical role of manganese has proved extremely elusive for many years. It was known that many enzymes are activated by manganese in vitro, a property notably shared with magnesium.

Iron : It is the most abundant transition element. This is also probably the most well-known metal in biologic system (hemoglobin in blood - the oxygen-carrying protein molecule of blood regarded as the most important iron(II) complex consisting of the globin protein with four heme units attached to it).

Cobalt : It is relatively scarce in the earth's crust, but the human body requires vitamin B12, which is a cobalt(III) complex, to form hemoglobin. In fact, cobalt is widely distributed throughout the human body, without, however, excessive concentration in any particular organ or tissue. Having the ability to occupy low symmetry sites in enzymes, cobalt(II) is an enzyme activator.

Copper : It is known that Cu(I) is found in enzymes capable of carrying oxygen as hemoglobin does, and that it is actually required in the formation of this substance.

Zinc : It is one of the most abundant of the essential elements required by the human body and approximately 100 times as abundant as copper (Vahrenkamp, 1973). Zinc appears to be present in all mammals. As with cobalt(II), zinc(II) has the ability to occupy low symmetry sites in enzymes, and can therefore function as an essential constituent of several of them.

Molybdenum : This metal is involved in electron transfer processes as in xanthine and purine oxidations of milk. Nitrogen fixation is also coupled to a molybdenum process.

1.2 Health Hazard Due to Some Trace Elements

Arsenic : In spite of its toxicity, it has been employed for its medical virtues in the form of organic arsenicals, and in partial prevention of selenosis. The stable and soluble inorganic arsenites and arsenates are readily absorbed by the digestion tract, abdominal cavity and muscle tissue. Excretion of arsenate is faster than of arsenite, mostly in urine. Arsenate has a low order of toxicity and does not inhibit any enzyme system due to its lack of affinity to hydroxo and thiolgroups.

Long term ingestion of arsenic-contaminated drinking water from wells has produced gastrointestinal, skin, liver and nerve tissue injuries. In Taiwan, widespread occurrence of Black-foot Disease resulted from high levels of arsenic in ground waters - the maximum arsenic value amounted to 2.5 mg/L (Haberer and Normann, 1971). Chronic arsenic poisoning appears to be regional, but certainly not limited to Taiwan. For example, in the Mexian village, Toreon, 60 % of the inhabitants showed varying degrees of chronic intoxication from drinking water which contained 4-6 ppm As (Zaldivar, 1974)

The importance of arsenic as a health hazard is well known, example of chronic poisoning have been reported for water with arsenic concentrations of 210 µg/L to 1000 µg/L (Aston et al., 1975).

Cadmium : It is being the middle member of the periodic sub-group consisting of Zn, Cd and Hg reveals intermediate properties. All three elements display a profound capacity of combining with - SH (and imidazole-containing ligands; the stability of such complexes increases in the order of Zn < Cd < Hg. Cd and Hg compete with and displace Zn in a number of Zn-containing metalloenzymes by irreversibly binding to active sites, thereby destroying normal metabolism. This, of course, leads to the above stability sequence which is best explained on the basis that sulfhydryl is a soft donor, cadmium and mercury are soft acceptors, whereas zinc is a borderline case.

Chromium : Chromium is one of the least toxic of the trace elements on the basis of its oversupply and essentiality. Generally, the mammalian body can tolerate 100-200 times its total body content of Cr without harmful effects. Chromium(VI) compounds are approximately 100 times more toxic than Cr(III) salts. The stomach acidity leads to reduction of Cr(VI) to Cr(III) of which gastrointestinal absorption is less than 1 %.

Copper : The presence of copper in plant and animal tissues was recognised more than 150 years ago. Long before it was recognised as an essential element in the diets of birds and mammals, it was detected as a component of blood proteins of snails. The first indication that copper deficiency occurs naturally in livestock dates back to 1931 with regard to 'salt-sick' cattle in Florida. Later it was established that copper deficiency is a casual factor in a disease of sheep and cattle occurring in parts of Holland where it was termed lechsucht. The basic biochemical defects were subsequently related to enzymatic activity of copper.

Chronic copper poisoning of sheep in Australia revealed that Cu retention was dependent on the molybdenum status of the diet, which in turn dependent upon the inorganic sulfate of the diet and the animal (Underwood, 1971). This impressive discovery was followed by further revelations that there are interactions among trace elements such as a reciprocal copper-zinc antagonism. In other words, copper toxicity or deficiency in animals is not merely dependent upon copper intake, but also upon dietary levels of Zn, Fe and Ca.

Copper is an essential metal in a number of enzymes. Excessive intake of copper results in its accumulation in the liver. Generally copper toxicity is increased by low Mo, Zn, and SO_4^- intake.

Lead : Lead resembles the divalent alkaline earth group metals in chemical behavior more than its own Group IVA metals. It differs from the Group IIA metals in the poor solubility of lead salts such as hydroxides, sulfates, halides, and phosphates. Under normal conditions more than 90% of the lead retained in the body is in the skeleton. Although lead is a nonessential element it is present in all tissues and organs of mammals.

Mercury : It is considered a nonessential but highly toxic element for living organisms. Even at low concentrations, mercury and its compounds present potential hazards due to enrichment in the food chain. Poisoning by methylmercury compounds presents a bizarre neurological picture as observed in large-scale outbreaks in Japan and Iraq. The higher toxicity of mercury than cadmium cannot be attributed to the smaller ionic radius and greater penetration of the Hg^{2+} ion (Venugopal and Luckey, 1975).

Molybdenum : It is an essential nutrient for all nitrogen-fixing organisms and occurs regularly in all plant and animal tissues. High dietary concentrations of molybdenum are harmful to several animal species; all cattle are susceptible to molybdenosis, a scouring disease known as tearts which arises from ingestion of excessive amounts of this element from the herbage of affected areas. Acute or chronic toxic effects have not been reported for humans.

Selenium : In trace amounts it is essential for growth and fertility in animals and for the prevention of various diseases. Seleniferous soils and vegetation may lead to an oversupply and result in poisoning. All degrees of selenosis exist ranging from a mild, chronic condition to an acute form resulting in the death of the animal. chronic selenosis is characterized by dullness and a lack of vitality, stiffness and lameness, due to erosion of the joints of the long bones. In acute selenium poisoning the animals suffer from blindness, abdominal pain and death may result from respiration failure.

Silver : It generally occurs in the form of salts having a low solubility and is consequently excreted in feces. Most of the soluble Ag^+ (aq) ingested remains impregnated in tissues forming a stable bond to -SH or -SR groupings. When larger quantities are assimilated by skin tissue, silver sulfide leads to permanent discoloration of both skin and eye tissue, a condition known as argyria. Silver salts are exceptionally toxic toward freshwater fish.

Zinc : It is one of the most abundant essential trace element in the human body. It is a constituent of all cells, and several enzymes depend upon it as a cofactor. Concern has arisen because of the intimate connection of zinc with cadmium in the geosphere and biosphere. In soil, the ratio of cadmium varies from approximately 1:300 to 1:2900 by mol; in seawater, the molar ratio is 1:35; in the adult human kidney, the molar abundance of cadmium can reach or exceed three-fifths that of zinc, varying widely from individual to individual and from one geographic area to another.

Moderately increased zinc concentrations in water stemming from the release of zinc from drainage pipes due to corrosion do not induce any clinical manifestations. The results of laboratory tests on animals indicate, however, that the metabolism of humans may be affected especially of children and patients already suffering from irregular metabolism.

1.3 Scope of the Study

Studies on in-stream reactions and sediment dynamics have received increased attention during recent years. There are several reasons for this. Because of substantial efforts to reduce point pollution sources the relative effect of nonpoint pollution has increased. This has increased the need to identify major sources of nutrients and trace elements deposited within the river system.

A commonly used approach to study in-stream reactions, deposition, erosion or resuspension is chemical mass balance (Yuretich and Batchelder, 1988; Katz et al., 1985; Paces, 1985; Christophersen and Wright, 1981; Plummer and Back, 1980).

Trace elements particularly heavy metals have a great ecological significance due to their toxicity and accumulative behaviour. These elements, contrary to most pollutants, are not bio-degradable and undergo a global eco-biological cycle in which natural waters are the main pathways. The determination of the concentration levels of heavy metals in these waters, as well as the elucidation of the chemical forms in which they appear, is of prime target in environmental research today. The present report presents briefly the quality of water of river Kali with particular regard to trace elements and discusses mass balance for these elements for a 25 km long river reach in the western Uttar Pradesh.

2.0 SOURCES OF METAL POLLUTION

The sources of metal pollution can be classified into following five categories:

i) Geologic Weathering
ii) Mining Effluents
iii) Industrial Effluents
iv) Domestic Effluents
v) Atmospheric Sources

2.1 Geologic Weathering

This is the source of baseline or background levels. It is to be expected that in areas characterized by metal-bearing formations, these metals will also occur at elevated levels in the water and bottom sediments of the particular area. Obviously, mineralized zones, when economically viable, are exploited to retrieve and process the ore. This in turn leads to disposal of tailings, discharge of effluents and possibly smelting operations which result in atmospheric pollution. In consequence, the general problem arises of how to distinguish between natural geologic weathering and metal enrichment attributable to human activities. Not many examples are known for which the interactions between natural weathering processes and mineralized zones are completely devoid of a human contribution. For example, there is a evidence that the high mercury content in rocks encountered in the catchment of the La Grande River, Canada, may be responsible for high mercury levels in organisms (Boyle and Jonasson, 1973).

Regional geochemical maps have been compiled for some areas and, in exceptional cases, countrywide. These maps are based on computerized data of multi-element analysis and reflect the natural composition of both soils and rocks, thus providing baseline information on the occurrence and distribution of trace elements.

Such regional geochemical maps for England and Wales have revealed that the background level of arsenic in stream sediments lies in the concentration range 0-7 ppm, whereas the higher concentrations in anomalous areas can be in excess of 150 ppm (Aston and Thornton, 1975). High concentrations are connected with sulfide mineralization, for instance in South-West England, North Wales, and the Lake District of North West England.

A study conducted by Colbourne et al. (1975) confirmed that the stream sediment patterns for arsenic and copper in the Dartmoor area of South-West England may be correlated with significant enrichment of these elements in soils derived from rocks within the metamorphic aureole around the Dartmoor granitic intrusion. Previously it had been concluded that the source of arsenic within intrusion. Arsenic is in fact an ubiquitous element and has been reported to be present in solids at an average concentration of 5 mg/kg.

Arsenic-rich hot springs arising from geothermal activity feed the Waikato River of North Island, New Zealand. Submerged aquatic plants from this river were found to contain a maximum of 650 mg/kg dry mass as compared to arsenic levels below 12 mg/kg in plants growing in natural soils (Reay, 1972).

Similarly, geothermal sources in North Island are a natural source for mercury enrichment. A comparative study (Weissberg and Zobel, 1973) between the effects of mercury-containing effluents from a pulp and paper mill into Lake Maraetai and geothermal discharges in Lake Rotorua, revealed that mercury accumulation in sediments from the industrial source did not exceed the enrichment in sediments from the geothermal source. It was thus concluded that mercury contamination of Lake Rotorua is solely due to natural enrichment, especially since sediments from both lakes contained no apparent variation with increasing depth.

Several theoretical models have also been presented for the natural cycle of mercury, which has received much attention during the past decade as a result of catastrophic mercury poisonings due to man's impact. A noteworthy contribution (Garrels et al., 1975) related to the differences between pre-man cycle cnd man-included cycles of mercury reveals that mass transfer the pre-man sedimentary cycle of Hg significantly resulted between the earth's surface and the atmosphere. This cycle has been disturbed by an increased rate of Hg input resulting from mining activities, emissions from chlor-alkali production, combustion of fossil fuels, roasting of sulfide ores and, in general, the increased utilization of Hg by man. Precipitations such as rain probably contain large amounts of Hg, which may again be easily recycled from soils to the atmosphere. Bacterial methylation of inorganic mercury certainly represents an important intermediary process for the release of mercury from soils, sediments and surface waters.

2.2 Mining Effluents

The effects of mine effluents on the water quality in rivers and lakes, as well as on the biotopes, particularly on the fish population, have been known for many years. One of the very first descriptions of this problem is the fifth report of the 1868 River Pollution Commission (Anon, 1874) in Britain, where especially grave damage was caused by the disposal of toxic metals from lead, zinc and arsenic mines in mid-Wales (Lewin et al., 1977). All these streams are turbid, whitened by the waste of the lead mines in their course, and flood water in the case of all of them bring down poisonous slimes which, spreading over the adjoining flats, either befoul or destroy the grass, and thus injure cattle and horses grazing on the dirtied herbage, or, by killing the plants whose roots have held the land together, render the shores more liable to abrasion and destruction on the next occasion of high water.

Agricultural problems arising from metal contaminations influenced by past and present mining activities were investigated by Griffith (1918), who explained the unproductiveness of certain fields in north Cardiganshire as due to toxic levels of lead and zinc in the soils.

Generally, Welsh rivers and lakes are remarkably devoid of urban and industrial metal pollutants since little or no wastes are discharged into the feeder streams. However, significant concentrations of heavy metals have caused a severe deterioration of the water quality. For example, the presence lead, copper and zinc has caused a high mortality rate amongst fish and other living organisms in some Welsh streams (Abdullah and Royle, 1972). It has thus been concluded that heavy metals are leached from the outcrops of mineralized zones and spoil heaps of diffused mines drained by such streams (Alloway and Davies, 1971; Davies, 1972, 1976, 1977; Davis and Lewin, 1974; Brown, 1977; Davies and Roberts, 1978).

In Poland Pasternak (1973) investigated waste waters from the region of Bolesaw where large deposits of lead and zinc are mined and processed. The results indicate variable concentrations of lead and zinc in flotation effluents, the maximum reported concentrations being 10.3 mg/L for Pb and 1.7 mg/L for Zn. Surprisingly, the underground water from the mine at Bolesaw, which discharges directly into the Sztola River, is considerably more enriched with Pb (maximum value 300 mg/L) and Zn (maximum value 1800 mg/L).

In the United States the increasing consciousness of the environment since the 1960s has led to the recognition that metal accumulation in mine effluents is one of the main problems of water protection (Reppert, 1964; Smith and Frey, 1971; Parsons, 1977). In Colorado alone, 450 miles of surface streams are classified as affected by mill tailing and metal drainages (Wentz, 1974). Hill (1973) reports Fe levels of over 200 mg/L in mine drainage. In groundwater of the mineral belt of the Front Range, Colorado, the limit set by U.S. Public Health Service is exceeded in 14% of the samples for Cd, 51% for Fe and 74% for Mn (Klusman and Edwards, 1977). In Idaho, it is mainly the Kellogg Smelterville Area in Silver Vally (Miller et al., 1975) and the Cataldo Mission Flats in the catchment area of the Coeur d'Alene River (Galbraith et al., 1972) as well as other areas in the Coeur d'Alene Basin (Mink et al., 1971; Rabe and Bauer, 1977), which are most affected. Pollution by mine drainage in the Cheyenne River System, Western South Dakota, and in the Upper Clark Fork River and selected tributaries is described by Mink et al. (1972). Water, sediment and fish from the North Anna River in Virginia affected by acidic mine drainage from abandoned pyrite mines were analysed by Blood and Reed (1975) and characteristic enrichment of toxic metals were found.

Mork and Wai (1989) studied the distribution and mobilization of arsenic in the creeks around the Blackbird mining district, Idaho. They have reported that the sediments in the creeks around the Blackbird mining area are heavily contaminated with As from local mining operations.

An ecological survey conducted to evaluate the effects of a disused copper-lead-zinc mine in Australia (Weatherley and Dawson, 1973) revealed that the area remains disfigured by slime dumps, although the mine closed down in 1962. The mining area situated at Captain Flat, 50 km from Canberra, is drained by the Molonglo River. At Rum Jungle in Northern Australia, 64 km south of Darwin, uranium and copper have been mined since the mid 1960s. An estimated 1300 tons of copper had been released and dispersed on the River Finniss floodplain, in addition, 90 curies of radium, whose fate is still uncertain, had been leached from the tailing dump (Watson, 1975).

In New Zealand investigations were performed by Ward et al. (1976) on the distribution of copper, cadmium, lead and Zinc in waters and natural vegetation around the Tui Mine, Te Aroha, and on the silver content of soils, stream sediments, waters and vegetation near a silver mine and treatment plant at Maratoto, Coromandel region (Ward et al., 1977). Metal levels in soils increased near the treatment plant and also in natural vegetation growing over the ore deposits, the metal content of stream waters and stream sediments, though anomalous near the deposits, decrease progressively with increasing distances from the source.

2.3 Industrial Effluents

The disposal of industrial wastes is often conducted without critical appraisal of the losses incurred usually no consideration is taken with regard to the deleterious environmental impact upon the receiving water body.

There are numerous sources of industrial effluents leading to heavy metal enrichment of the aquatic environment. The classical example is the discharge of the catalyst methylated mercury chloride into Minamata Bay from a factory manufacturing plastics. Contrary to expectations, microorganisms converted the sedimented compound to monomethyl-mercury, which led to an enrichment of this most toxic compound in fish consumed by the local fisher-folk.

The major industrial uses of various economically important heavy metals have been compiled in Table 2 (Dean et al., 1972). An inspection of this table reveals that most heavy metals under consideration are employed in widely diversified fields such as petroleum refining, steal and fertilizer production, etc. On the other hand several industries function on a basis where only one specific heavy metal is involved, for example, the use of chromium in the tanning industry. However, in general, the multipurpose uses of numerous heavy metals may lead to difficulties in tracing the source of origin of water pollution conclusively.

The principal source of chromium results from discharges of industries using large amounts of chromates and dichromate as in the textile industry and the leather tanning industry. In the tanning industry the preliminary treatment is by means of alkali solutions used to remove the outer skin and dirt from hides. The second stage known as tanning is directed toward conditioning the hide to keep it from becoming rough or brittle. Chromium(III) compounds are frequently employed for this process. Polish tannery wastes from chrome tanneries have been reported to vary between 9 and 140 mg/L (Koziorowski and Kucharski, 1972). When considering effluents with inorganic pigments content resulting from the paint industry, the great variety of raw materials makes it impossible to approach the problem in a general manner. One possible source is illustrated by an intensive investigations into the cause of cadmium enrichment of sediments from the Nickar River flowing through Heidelberg, West Germany. Water analysis conducted upstream and downstream from the city revealed a maximum cadmium concentration of 220 µg/L at the confluence of the Enz and Neckar Rivers. Subsequently, the investigators were able to trace the source of cadmium solution of the Enz River. In this particular case the discharges contained high enough cadmium levels so that the source of pollution could be traced by means of water analysis (Forstner and Muller, 1974).

Table 2. Heavy metals employed in major industries
(Dean et al., 1972)

	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sn	Zn
Pulp, papermills, paperboard, building paper, board mills		x	x		x		x	x		x
Organic chemicals, petrochemicals	x	x		x	x		x		x	x
Alkalis, chlorine, inorganic chemicals	x	x		x	x		x		x	x
Fertilizers	x	x	x	x	x	x	x	x		x
Petroleum refining	x	x	x	x			x	x		x
Basic steel works foundries	x	x	x	x	x		x	x	x	x
Basic nonferrous metalworks, foundries	x	x	x		x		x			x
Motor vehicles, aircraft-plating, finishing	x	x	x		x			x		
Flat glass, cement, asbestos products, etc.		x								
Textile mill products		x								
Leather tanning, finishing		x								
Steam generation power plants		x								x

Fuller et al. (1990) conducted a reconnaissance survey of the extent of metal contamination in the Rio Grande de Tarcoles river system of Costa Rica in Central America. The Rio Grande de Tarcoles is formed by the confluence of the Rio Virilla, the main drainage in the central vally and the Rio Grande, which drains a sparsely populated rural area to the north. This river system has been impacted heavily by the discharge of untreated sewage, agricultural and industrial effluents (Hartshorn et al., 1982). Several large leather tanneries that use chromium sulfate in the tanning process discharge waste effluent directly into tributaries of the Rio Virilla. A previous study of metal pollution in this river system focused on dissolved metal concentration in the rivers of the central vally, with concentrations generally less than 0.01 mg/L of Cr, Cu, Pb and Zn (Ramirez et al., 1985).

Contamination of drinking water supplies by mercury from fungicides and industrial effluent, such as from chlor-alkali plants, has been a major concern for many years and has been studied extensively (Hem, 1970; Davis, 1972; Jensen and Jernelov, 1972; Amstrong, 1975; Waldbott, 1973). In general, it was found that inorganic mercury is relatively immobile, but transformation to organic form, primarily by bacterial action, will substantially enhance mercury uptake and mobility (Hamdy, 1977; Bernard and Perdue, 1984; Renfro et al., 1974).

Huynh-Ngoc et al. (1988) studied the distribution of cadmium in the Rhine river using differential pulse anodic stripping voltametry. In another study (Kneip et al., 1974) cadmium and nickel enrichment was found in an aquatic system in the marshes and coves along the eastern side of the Hudson River, N.Y. Discharges of these metals were attributed to wastes waters from a nickel cadmium battery plant - which again illustrates the wide diversification of industrial sources of toxic heavy metals. Zhang and Huang (1993) studied the dissolved trace metals in the Huanghe, the most turbid large river in the world.

The environmental pollution from Cd and Zn discharged from a Braun tube (used in TV sets) factory in Japan was investigated by Asami (1974). The slag at the waste water outlets and settling tank was 4820-4500 and 15,500-37,500 ppm respectively for Cd and Zn concentrations.

A typical example of pollution caused by the iron and steel industry is presented by the steelworks near the Tees Estuary, Scotland (Prater, 1975). It was found that iron and manganese had the highest mean concentration, the blast furnaces and the ferro manganese plant respectively being the major contributors. Zinc and lead occurred at similar concentration levels.

2.4 Domestic Effluents

Metal enrichment which results from residential areas is treated in accordance with its source of origin. Thus, on the one hand there are domestic effluents which are usually discharged from a relatively well defined point source. On the other hand, urban storm water runoff is characterised by a diffuse drainage pattern - only partially contributory towards the metal contents of domestic effluents - and together with the rural areas belongs to the most important non point sources of metal loads in inland waters.

Domestic wastewaters constitute the largest single source of elevated metal values in rivers and lakes.

Domestic effluents consist of (1) untreated or solely mechanically treated wastewaters, (2) substances which have passed through the filters of biologic treatment plants, (3) waste substances passed over sewage outfalls and discharged to receiving water bodies - often the sea in coastal residential areas.

Solid wastewater particles may cause appreciable metal enrichment of the suspended load in waters. A clue as to the magnitude of these effects is obtained by comparing the normal values for sewage sludges with the corresponding metal levels in crustal rocks - the letter data serving as natural occurring metal levels in solid substances in Table 3.

Table 3. Comparison of metal concentrations in sewage sludges

	Average sewage sludge (mg/kg) (a)	Average crustal rocks (mg/kg) (b)	Ratio (a)/(b)
Nickel	60	80	0.8
Chromium	240	200	1.2
Copper	700	45	15
Lead	450	15	30
Zinc	2600	65	40
Cadmium	10	0.2	50
Silver	20	0.1	200

(a) Sweden: Berggren and Oden, 1972; England and Wales: Berrow and Webber, 1972; Michigan: Blakeley, 1973; Median-value from Page (1974), and average crustal rocks. (b) Mason, 1958.

From an inspection of these values it is evident that hardly any enrichment can be expected for nickel and chromium. By contrast, the concentrations of copper, lead, zinc, cadmium and silver reveal a marked influence of domestic effluents. These elevated levels of Cu, Pb, Zn, and to a lesser degree Cd, are due to corrosion within the urban water supply network; the high values of silver mainly result from its photochemical use i.e., partly an industrial source (Preuss and Kollmann, 1974).

Similar metal enrichment may also be expected to result from metal species contained in solution. However, due to the localised nature of the hydrochemical conditions, it is more complicated to define the situation than in the case of solid substances. A typical example stems from the presence of detergents in domestic effluents.

The use of detergents also creates a possible pollution hazard, since common household detergent products can affect the water quality. Angino et al. (1974) found that most enzyme detergents contained trace amounts of the elements Fe, Mn, Cr, No, Co, Zn, Sr, and B. Moreover, spectrographic evidence for the presence of arsenic was found in three enzyme presoaks, three heavy duty enzyme detergents, one heavy duty detergent and one detergent aid. The presence of high arsenic levels for these detergents was found to vary between 31 and 45 ppm As, with the enzyme presoak containing between 51 and 73 ppm. Since waste waters containing detergents enter the urban water drainage system and many sewage or waste effluent plants do not remove arsenic, the maximum concentration of 8 ppb, found in the Kansas River at Topeka, is very close to the permissible level of 10 ppb, and may thus be regarded as a potential health hazard.

Kaplan et al. (1987) studied the distribution of trace heavy metals (Zn, Cd, Pb and Cu) along the treatment path of domestic wastewater in stabilization ponds.

With regard to pollution resulting from urbanised areas, there is an increasing awareness that urban runoff presents a serious problem of heavy metal contamination. Heavy rainfall in urban areas is no longer regarded as only a downpour of "rainwater" (Sartor et al., 1974) since they often contain shock loads of contaminants. The runoff frequently presents insurmountable problems especially with regard to the local sewage works, which may become overloaded and thus overflow (Field and Lager, 1975). A statistical summary (Bradford, 1977) revealed that urban stormwater runoff has long been recognized as a major source of pollutants to surface waters.

Potential contamination may occur during periods of storm runoff, whereby trace elements resulting from atmospheric emissions and subsequently deposited on various surface material may be transported to the nearby drainage system. The stormwater discharge and combined sewage overflows from urban areas present problems of ever increasing importance. Whipple and Hunter (1977) have recommended treatment of urban runoff and sewage overflows in combination with detention storage. In their investigations they found that the problem has not really been seriously considered with respect to heavy metals. After monitoring heavy metals from two heavily urbanised watersheds at Lodi, New Jersey, they established high concentrations of lead, zinc and copper after a storm event. The highest concentration usually occurred within the first 30 min of storm runoff which reveals that the first flush carries exceptionally high loads.

From many investigations it is known that urban stormwater contains metal concentrations which vary extremely with regard to locality and time of sampling (Malmquist, 1975). This is not surprising in the light of the aforementioned findings, which are, of course, valid for all pollutants in storm water. No significant predictions as to the quality of stormwater can be made without a knowledge of the pollutant sources.

In the United States almost 97% of the total land area is essentially rural in nature (McElroy et al., 1975). Commercial forest, grassland and cultivated agricultural areas are, on the basis of land area, potentially large contributors of nonpoint sources leading to environmental pollution in aquatic systems.

It is of special interest to note that soil cultivation has been estimated to be responsible for 95-99% of soil erosion (McElroy et al., 1975). The sediment resulting from soil erosion is today recognised as being the largest single pollutant affecting water quality.

2.5 Atmospheric Sources

Natural and man-made processes have been shown to result in metal-containing airborne particulates. Depending on prevailing climatic conditions, these particulates may become wind-blown over great distances; nonetheless they are subjected to the fate that they are ultimately returned to the lithosphere as precipitations by rain or snowfall.

The atmospheric precipitations may lead to a considerable enrichment of heavy metals in the environment. According to Shiomi (1973) 15-36% of the Pb entering Lake Ontario from the Niagara River was attributable to atmospheric precipitations. Since the beginning of the industrial era there has been a considerable increase in the use and redistribution of lead in the environment.

Direct atmospheric deposition generally represents a major source of trace metals to surface waters (Salomons, 1986). In lakes, for example, atmospheric deposition commonly accounts for about half the supply of Pb and Zn, the remainder coming mainly from river runoff (Eisenreich, 1980; Hamilton-Taylor and Wills, 1990). In terms of labile component, dissolved and readily soluble, atmospheric inputs are likely to be of even greater relative importance. On a global scale, the contents of atmospheric particles are predominantly anthropogenic in origin for a range of trace metals (Puxbaun, 1991). A number of previous studies have examined the solubility characteristics of atmospheric aerosols and coal-derived fly ashes, taken to represent a common source of metal in the atmosphere (Crecelius, 1980; atathan and Chester, 1988; Theis and Wirth, 1977; Williams et al., 1988).

In the United States it was found that lead in gasoline is the largest single source of air pollution (Patterson et al., 1976). Tatsumoto and Patterson (1963) attributed high concentrations of lead in surface seawater of the Los Angeles Basin. Patterson (in Duce et al., 1974) found that the atmospheric deposition of Pb in Southern California accounted for approximately 45% of the pollutant lead input, the remaining 55% arising from wastewater, stormwater runoff and river input. In a study of trace metals on the New York bight, Duce et al. (1975) estimated that approximately 13% of the input of Pb was from atmospheric fallout, the rest originated from barge dumping, runoff, sewage and river input (Winchester and Duce, 1977).

Despite the high efficiency of modern electrostatic precipitation, lignite-burning power plants are a typical source of trace metals. Heinrichs (1977) has shown that this is locally of particular interest in the lower Rhine district near Cologne, where about 90% of the total brown coal tonnage of the F.R.G. is fired in as few as six power plants.

Another source of atmospheric pollution has been described by Brumsack (1977). Here comparison of trace metal contents in plants and soils downwind and upwind from brickworks indicate characteristic anomalies for TI, Bi, Hg, Pb, Cd, and Zn.

Fallout from fossil fuels and geothermal emissions are important sources of atmospheric pollution. Especially coal-fired electric power plants have recently come under scrutiny as potential sources of mercury and other heavy metal pollution. Since the amount of mercury in coal was not well known, 36 American coals were analyzed some years ago to establish their mercury content; it was found that the values were generally $<$ 1 ppm. However, 11 samples contained mercury concentrations ranging from 1.5 to 33 ppm. Although the concentration of mercury in most coals appears small, coal is consumed at such an enormous rate that an estimated

3000 metric tons of mercury are released annually in the U.S. - a figure which is comparable to that emitted from industrial processes-far exceeding the upper limit of mercury released by weathering processes where 230 metric tons/annum are released (Joensuu, 1971).

Atmospheric pollution occurs during the metallurgical process known as smelting, a process whereby an ore or ore-concentrate is fused with suitable fluxes (i.e., material added to a furnace charge to combine with the gangue and form a fusible slag). Obviously, smelting operations cause the emission of particulates which often contain toxic constituents that precipitates and high refractory-lined stacks in accordance with modern technological advances, the problem of pollution and smelting operations has not yet been overcome.

Smelting operations have long been known to contain toxic substances. During the late 18th and early 19th centuries industrial workers suffered from arsenic poisoning caused by dust emitted from smelting operations (Luh et al., 1973). Despite modern technological advances, smelting operations continue to contaminate the environment. This is illustrated by numerous examples, such as the large copper smelter at Tacoma, Washington, which has been revealed as a major anthropogenic source of arsenic and antimony to Puget Sound (Crecelius et al., 1975).

Sources of heavy metal pollution resulting from smelting operations are widely diversified. For instance, lead pollution has been localized to a battery smelter in Western Canada (John, 1971), and a zinc smelting plant near Odda, Norway was found to discharge large quantities of solids and solutions to the nearby fjord; the respective amounts of copper, lead, and zinc are 300, 4500 and 6000 kg/day (Skei et al., 1973).

3.0 DESCRIPTION OF THE AREA

The river Kali, which flows in western districts of Uttar Pradesh (U.P), is a perennial river. It is a small water stretch having basin area of about 750 square kilometers. The river originates from Doon Vally and after routing through the districts of Saharanpur, Muzaffarnagar and Meerut, finally met with the river Hindon near village Atoli.

The area under study is part of indogangetic plains and lies between latitude 29°32'N to 29°21'30" N and longitude 77°42' E to 77°41'15" E in the Muzaffarnagar district of Uttar Pradesh.

3.1 Physiography

Physiographically the area is generally flat except Siwalik hills in the north and north east. The area is devoid of relief features of any prominence except from deep gorges cut by nalas and rivers flowing through the area. The district is bound by river Yamuna in the west and river Ganga in the east.

3.2 Drainage

Regarding the drainage of the area, the rivers generally flow from north to south. These rivers during most of the non-monsoon season carry water drained into them from ground water storage. Some of the important rivers of the area are, the Ganga, Yamuna, Hindon, Krishni and the Kali(West). Apart from these rivers, the Western Ganga Canal and Eastern Yamuna Canal also drain the area.

3.3 Climate and Rainfall

The climate of the area as that of the greater part of Indian subcontinent is characterised by moderate type of subtropical monsoonic climate. In general, the average normal monsoon rainfall in the area is about 485.6 mm. The temperature ranges from 8°C in winter to 40°C in summer. Major part of the rainfall (about 75%) is received during the monsoon period. It has been observed that the rainfall is heaviest in the northern region of the district, close to foot hills of Himalayas and becomes lesser southward.

3.4 Geology

The Area under study is a part of west Indogangetic plain which is mainly composed of pleistocene and subrecent alluvium brought down by river action from the Himalayan region. In other words alluvium is made up of recent unconsolidated fluviatile formations comprising of sand, silt, clay and kankar with occasional beds of gravel. The deposits of sand beds of varying thickness are the main source of ground water in the area.

3.5 Geohydrology

The groundwater conditions in all alluvial parts are considerably influenced by the varying lithology of the subsurface formations. As the general fluviatile nature of deposits of Indogangetic plains it has been observed that the strata exhibit great variation both laterally and vertically. The main source of water which sustains groundwater body in fine to coarse grained sands is rainfall. Other sources of groundwater replenishment are infiltration from rivers, canals and return flow from irrigation, and inflow from the neighboring areas.

The most common groundwater structures in the area are shallow and deep tubewells. Dug wells are also used as source for drinking water as well as irrigation, but to a lower extent.

Based on the lithological logs and water table fluctuation data two types of aquifers have been delineated in the area. The upper one is the shallow unconfined aquifer which generally extends to depths around 25 m. The deeper aquifers are confined to semi-confined in nature and located at depths around 30 to 140 m, below ground level separated by three to four aquifers at average depths of 30 to 55 m, 65 to 90 m and 120 to 140 m. Water table contours in the area indicate the southward trend of ground water flow both in unconfined and confined aquifers.

3.6 Sources of Pollution

The main sources which create pollution in river Kali include, municipal waste of Muzaffarnagar city, industrial waste from variety of industries (such as steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper and loundaries) and Mansurpur sugar mill and distillery waste. The wastes from variety of industries such as steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper and laundries etc. transfer their wastes through Muzaffarnagar main drain into the river.

3.7 Sampling Stations

A general plan of the sampling stations with respect to different outfalls of municipal and industrial wastes in river Kali is shown in Fig. 1. The locations of main sources of pollution have also been indicated in the same figure. In all, 6 stations were selected for sampling - four from the outfalls of waste disposals and one each from upstream and downstream sections of the total stretch under study.

Sampling stations selected in the present study stretched over 25 km. Sampling station I and II are situated in the upstream and downstream sections of the stretch under study, while the other four stations, a to d, are located in the waste outfalls/drains in the river. Each station can be characterised as follows:

Station I (Malira bridge), is located in the relatively unpolluted river water zone near village Malira and upstream of the discharge of municipal and industrial wastes into the river. At this point the banks are high with sandy soils

Station a (Wastewater outfall), is located in the wastewater outfall near village Nayajupura where a part of municipal waste of muzaffarnagar city is discharged into the river.

Station b (Wastewater outfall), is located in the municipal wastewater outfall near Shamli Bus stand, downstream of bridge over Muzaffarnagar-Shamli road.

Station c (Industrial drain), is located in the Main Muzaffarnagar drain, downstream of the bridge near village Begharazpur, through which the mixed waste from variety of industries and municipal areas is discharged into the river.

Station d (Sugar mill drain), is located in the sugar mill effluent drain near Mansurpur village on the National Highway.

Station II (Mansurpur bridge), is situated near village Pur Balian on Mansurpur - Shahpur road about 4 km from Mansurpur, after the outfall of sugar mill waste. The colour of the water is black and the soil is sandy mixed with some black material.

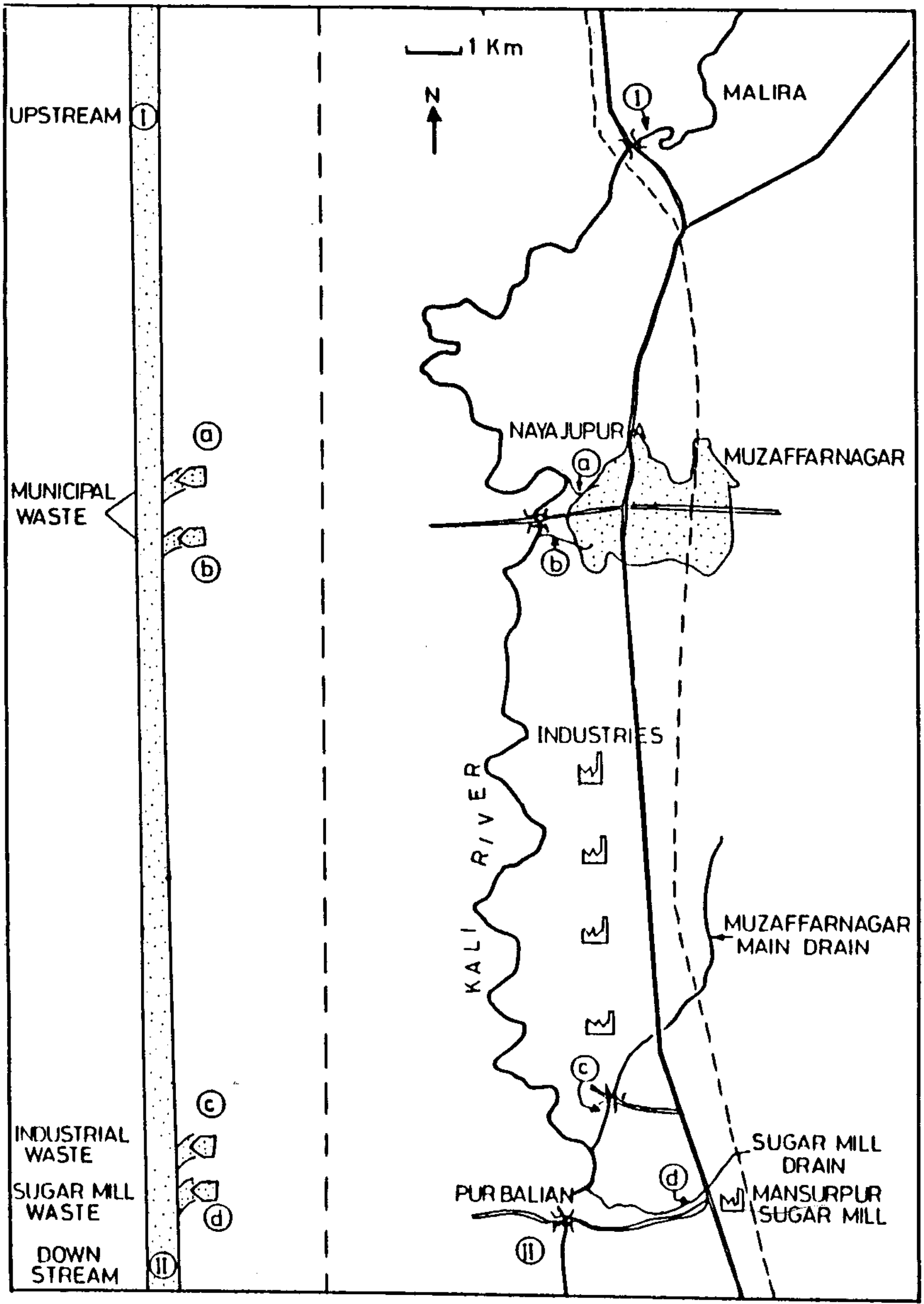

FIG. 1 GENERAL PLAN OF SAMPLING LOCATIONS

4.0 METHODOLOGY

4.1 Sampling and Preservation

For the pollution survey of the river, six sampling stations were chosen as described in the previous chapter.
Two surveys were conducted for collection of water and effluent samples during October and December 1994. The discharge at all the six sampling stations was also determined during each survey.

The water and wastewater samples were collected in polyethylene bottles fitted with screw caps. Water samples were collected from the upper 50 cm of the water surfaces. All containers used were washed with nitric acid and rinsed with deionized water. After collection, water samples were filtered through a standard type 0.45 µm pore diameter membrane filter. The samples were then preserved by acidifying with concentrated nitric acid (A.R. grade) to pH 2 and stored at 4°C in polyethylene bottles.

4.2 Materials and Reagents

All glassware was thoroughly cleaned by soaking in detergent followed by soaking in nitric acid for 24 hrs. and finally rinsed with deionized water. All chemicals used were of Analar grade. Stock solutions of 1000 mg/L were prepared as follows :

Fe stock solution : Fe stock solution was prepared by dissolving 1.0 g iron wire in 50 mL of (1+1) HNO_3 and diluting to 1 liter with deionized water.

Zn stock solution : Zn stock solution was prepared by dissolving 1.0 g zinc metal in a minimum volume of (1+1) HCl and diluting to 1 liter with 1% (v/v) HCl.

Cu stock solution : Cu stock solution was prepared by dissolving 1.0 g copper metal in a minimum volume of (1+1) HNO_3 and diluting to 1 liter with 1% (v/v) HNO_3.

Pb stock solution : Pb stock solution was prepared by dissolving 1.598 g lead nitrate in 1% (v/v) HNO_3 and diluting to 1 liter with 1% (v/v) HNO_3.

Cd stock solution : Cd stock solution was prepared by dissolving 1.0 g cadmium metal in a minimum volume of (1+1) HCl and diluting to 1 liter with 1% (v/v) HCl.

4.3 Sample Analysis

Trace elements (Fe, Zn, Cu, Pb and Cd) were determined by flame atomic absorption spectrometry using Perkin-Elmer Atomic Absorption Spectrometer (Model 3110) as per standard methods. Operational conditions were adjusted to yield optimal determination. Consequently, the results represent filtrable (dissolved) metals. Quantification of the metals was based upon calibration curves of standard solutions of metals.

4.4 Hydrometric parameters - load, water flow and velocity

Load (L) of a particular substance is calculated by using the formula:

$$L = Q \cdot C$$

where Q = flow, and
C = concentration

The flow (Q) of a water course is measured via the water velocity by means of the formula:

$$Q = \bar{v} \cdot A$$

where $\bar{v}$ = mean velocity, and
A = cross-sectional area

In this case the cross-sectional area (A) is measured and the mean velocity is determined by measuring the time (t) needed for a float to reach a certain point:

$$\bar{v} = S/t$$

where S = distance between two points.

5.0 RESULTS AND DISCUSSION

The river Kali is a typical receiving water course for untreated municipal and industrial effluents. The river basin contains towns and villages surrounded by agricultural areas (Fig. 1). The quality of river water has been affected by discharge from municipal and industrial areas but also by extensive drainage from agricultural areas. Detailed hydrochemical studies on the river has been reported earlier (Jain, 1992).

In this study two surveys (October and December 1993) were conducted during the course of investigations to see the extent of metal contamination in the river. The flow values were also determined at each sampling stations and are given in Table 4. As evident from Table 4, the increase in flow between station I and II is brought about by the outfalls of municipal waste at Muzaffarnagar, combined industrial waste through Muzaffarnagar main drain and Mansurpur sugar mill waste.

5.1 Trace Elements in Kali River

Tables 5 and 6 contain the upstream/downstream data for trace elements (iron, zinc and copper) for the two surveys conducted on the river Kali. As evident from Tables 5 and 6, the metal contamination in the downstream section was found to be 3-4 times than the upstream section (background level) for both surveys. The concentrations of iron, zinc and copper were found to be 0.41, 0.04 and 0.015 mg/L respectively in the upstream section during october survey. The same were found to be 0.56, 0.07 and 0.016 mg/L for iron, zinc and copper respectively during december survey. However the concentration of lead and cadmium were found to be nil during both the surveys.

5.2 Indirect Measurement of Sources

Effluent samples, collected from the municipal waste of Muzaffarnagar city, combined industrial waste from variety of industries (such as steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper and laundries) and Mansurpur sugar mill waste, were also analysed for trace elements and the results are discussed below. The major portion of the municipal wastewater of Muzaffarnagar city flows through a system of open nalas and is discharged into the river at two points. One portion of the waste having discharge of about 0.3 m^3 s^{-1} is discharged into the river near village Nayajupura while another portion of the waste having almost the same flow is discharged near Shamli bus stand, downstream of the bridge. At both the points, lot of people and domestic animals (cows and buffalos) take bath and cloth washing activities are common just upstream of the outfalls of the municipal waste. From the point of view of pollution of the river and the deterioration of water quality in the bathing areas, the discharge from these drains have been most critical. The physico-chemical characteristics of the waste collected from both the locations were reported earlier (Jain, 1992).

Estimation of loadings from non-point sources is usually accomplished either empirically through unit area loadings which are based on intensive sampling of a small area and then extrapolation of the resulting loading on a per unit area basis to the entire watershed, or deterministically through loading models which uses such factors as rainfall, soil type, land use, etc. to calculate the loading contribution available from a particular watershed and then estimate the fraction delivered to a water body. Indirect monitoring using upstream/downstream sampling locations provide a viable alternative. This report gave an account of the advantages of using upstream/downstream river water quality data to estimate the load to the river and detect changes in the water quality characteristics within the river system.

If one is willing to give up information of constituents in individual sources, then indirect measurement of the sum of the sources is possible in the receiving water using the following equation :

$$Q_D C_D - Q_U C_U = \sum_{i=1}^{n} L_i$$

where Q_D and Q_U are downstream and upstream flows
C_D and C_U are the downstream and upstream concentrations in the receiving water
and $\sum_{i=1}^{n} L_i$ is the sum of all individual loadings to the receiving water

This simple equation is really a mass budget and can be used to design a study that will result in a much more accurate estimate of $\sum_{i=1}^{n} L_i$ than that likely to be obtained from summing the individual loadings.

The $\sum_{i=1}^{n} L_i$ term is not really the sum of loadings entering the receiving water body, but really the net effect of the loadings plus any loss or generation within the water body. For any contaminant that undergo significant volatilization or degradation, this approach will not give an accurate loading summation unless the time of travel between downstream and upstream is small compared to the rate constants for losses. The same is true for substances that settle from the water column.

The above mentioned indirect approach using upstream/downstream water quality data has been used in the present study and the results have been summarised in Tables 5 and 6 for the two surveys conducted on the river. For the october survey the differential loadings for iron, zinc and copper were found to be 637, 56 and 23 kg per day respectively while for december survey the loadings are 743, 45 and 23 kg per day. This approach is useful for measuring the changes in the differential concentration and/or load to the river from year to year. El-Shaarawi (1987) derived a test for comparing the probabilities of observing higher concentrations at the downstream station than that upstream and determined the frequency of sampling needed within each year, along with the number of years required to detect a linear trend in the probabilities. The upstream/downstream approach is very important in this regard since the difference in the concentration is of interest, which is likely to be free from seasonality. Another approach is to use seasonal Spearman's rank correlation to test for the existence of a trend when the data are available over a long period of time (El-Shaarawi et al., 1983)

5.3 Application of Mass Balance to Upstream/Downstream Data

One of the most important aspect of water quality engineering is the determination of the input mass loading, that is, the total mass of a material discharged per unit time into a specific body of water. For defined sources with continuous flow, the input load is given by the equation :

$$L(t) = Q(t)\ C(t)$$

Where $C(t)$ is the concentration of the input $[M/L^3]$, $Q(t)$ is the input flow $[L^3/T]$ and $L(t)$ is the mass rate (load) of input $[M/T]$, all quantities occurring simultaneously at given time t. In metric units, the concentration and flow are often expressed in mg/L and m^3/s respectively. Also, for almost all practical purposes;

$$1\ mg/L = 1\ g/m^3 = 10^{-3}\ kg/m^3$$

Then, $L = Q \cdot C$

Where L is in g/s, Q in m^3/s and C in mg/L (= g/m^3)

The basic idea in describing the discharge of material into a river is to write a mass balance equation for various reaches of the river. The principal statement for the mass balance assuming complete mixing is:

Load of substance upstream + Load added by outfalls
= Load of substance immediately downstream from outfall

Recalling that the load is the product of flow and concentration, the mass balance is therefore given by:

$$Q_U C_U + \sum_{i=1}^{n} L_i = Q_D C_D$$

Where Q_U and Q_D are upstream and downstream flows,
C_U and C_D are upstream and downstream concentrations in the receiving water,
and $\sum_{i=1}^{n} L_i$ is the sum of all individual loadings to the receiving water.

For understanding the relationship between the water quality found and the sources of natural and man-made pollution, the drawing up of mass balance for certain water constituents is of great help. This is done by determining the load of selected substances, i.e. the weight of the substance transported through a cross-section of the river bed per second.

Tables 7 to 12 contain loadings of trace elements for the major outfalls that enter river Kali. These values are semi-quantitative because they are based on one or two sample during survey period. Thus, the loadings may be summed to provide an estimate of total loadings, but no confidence interval may be given.

As suggested above, the loadings were summed to indicate the total point source loadings (Tables 7 to 12). For the october survey, the estimated differential loadings for iron, zinc and copper are 637, 56 and 23 kg day^{-1} respectively (Table 5) which compares favorably with point source loadings of 392, 32 and 15 kg day^{-1} (Tables 7-9) for iron, zinc and copper respectively considering that the latter does not take into account direct nonpoint loadings to the river. Therefore, it can be argued that the difference of 245, 14 and 8 kg day^{-1} in iron, zinc and copper loadings may be mainly due to the contribution of nonpoint sources of pollution. By far the largest contribution of iron and zinc is the industrial drain which carry effluents from variety of industries such as steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper and laundries. The results of december survey also shows the same trends.

For the december survey, the estimated differential loadings for iron, zinc and copper are 743, 45 and 23 kg day^{-1} respectively (Table 6) which compares favorably with point source loadings of 497, 35 and 18 kg day^{-1} (Tables 10-12) for iron, zinc and copper respectively considering that the latter does not take into account direct nonpoint loadings to the river. The difference of 246, 10 and 5 kg day^{-1} in iron, zinc and copper loadings may be attributed mainly due to the contribution of nonpoint sources of pollution. Again the largest contribution of iron and zinc was observed from the industrial drain which carry effluents from variety of industries.

The mass balance for some trace elements (Fe, Zn and Cu) for river Kali have been drown and the results of mass balance calculations are presented in Table 15 and 16 for the two survey conducted. When two or more rivers come together at one point, the sum of the loads carried by the streams above the confluence must be equal to the load of the river downstream of this point. Mass balance calculations conducted for iron, zinc and copper (Table 15 and 16) indicate that differences found in load along the river may be mainly due to the contribution of non-point sources of pollution due to agricultural activities. The difference may also be attributed due to some point sources of pollution which could not be identified in the course of investigations.

Table 4. Flow values through various sampling stations

Station	Flow Values (m^3 s^{-1})	
	October	December
I. Upstream Section	5.66	5.10
a) Wastewater Outfall Near Village Nayajupura	0.33	0.30
b) Wastewater Outfall Near Shamli Bus Stand	0.35	0.34
c) Industrial Drain	0.46	0.46
d) Sugar Mill Drain	0.12	0.23
II. Downstream Section	7.29	6.74

Table 5. Upstream/downstream data for trace elements for river Kali - October 1993

Element	Downstream			Upstream			Diff.
	Flow m^3 s^{-1}	Conc. mg/L	Load kg D^{-1}	Flow m^3 s^{-1}	Conc. mg/L	Load kg D^{-1}	Load kg D^{-1}
Fe	7.29	1.33	838	5.66	0.41	201	637
Zn	7.29	0.12	76	5.66	0.04	20	56
Cu	7.29	0.047	30	5.66	0.015	7	23

Table 6. Upstream/downstream data for trace elements for river Kali - December 1993

Element	Downstream			Upstream			Diff.
	Flow m^3 s^{-1}	Conc. mg/L	Load kg D^{-1}	Flow m^3 s^{-1}	Conc. mg/L	Load kg D^{-1}	Load kg D^{-1}
Fe	6.74	1.70	990	5.10	0.56	247	743
Zn	6.74	0.13	76	5.10	0.07	31	45
Cu	6.74	0.051	30	5.10	0.016	7	23

Table 7. Point source loadings of iron to river Kali - October 1993

Point source	Flow $m^3 s^{-1}$	Conc. mg/L	Load kg D^{-1}
a) Wastewater Outfall Near Village Nayajupura	0.33	1.41	40
b) Wastewater Outfall Near Shamli Bus Stand	0.35	1.12	34
c) Industrial Drain	0.46	7.19	286
d) Sugar Mill Drain	0.12	3.12	32
Total	1.26		392

Table 8. Point source loadings of zinc to river Kali - October 1993

Point source	Flow $m^3 s^{-1}$	Conc. mg/L	Load kg D^{-1}
a) Wastewater Outfall Near Village Nayajupura	0.33	0.34	10
b) Wastewater Outfall Near Shamli Bus Stand	0.35	0.27	8
c) Industrial Drain	0.46	0.30	12
d) Sugar Mill Drain	0.12	0.16	2
Total	1.26		32

Table 9. Point source loadings of copper to river Kali - October 1993

Point source	Flow $m^3 s^{-1}$	Conc. mg/L	Load kg D^{-1}
a) Wastewater Outfall Near Village Nayajupura	0.33	0.212	6
b) Wastewater Outfall Near Shamli Bus Stand	0.35	0.131	4
c) Industrial Drain	0.46	0.072	3
d) Sugar Mill Drain	0.12	0.212	2
Total	1.26		15

Table 10. Point source loadings of iron to river Kali - December 1993

Point source	Flow $m^3 s^{-1}$	Conc. mg/L	Load kg D^{-1}
a) Wastewater Outfall Near Village Nayajupura	0.30	1.61	42
b) Wastewater Outfall Near Shamli Bus Stand	0.34	1.49	44
c) Industrial Drain	0.46	7.98	317
d) Sugar Mill Drain	0.23	4.74	94
Total	1.33		497

Table 11. Point source loadings of zinc to river Kali - December 1993

Point source	Flow $m^3\ s^{-1}$	Conc. mg/L	Load kg D^{-1}
a) Wastewater Outfall Near Village Nayajupura	0.30	0.37	10
b) Wastewater Outfall Near Shamli Bus Stand	0.34	0.28	8
c) Industrial Drain	0.46	0.27	11
d) Sugar Mill Drain	0.23	0.28	6
Total	1.33		35

Table 12. Point source loadings of copper to river Kali - December 1993

Point source	Flow $m^3\ s^{-1}$	Conc. mg/L	Load kg D^{-1}
a) Wastewater Outfall Near Village Nayajupura	0.30	0.216	6
b) Wastewater Outfall Near Shamli Bus Stand	0.34	0.133	4
c) Industrial Drain	0.46	0.074	3
d) Sugar Mill Drain	0.23	0.232	5
Total	1.33		18

Table 13. Values of flow and trace element concentrations at different sampling stations - October 1993

	Station	Flow ($m^3 s^{-1}$)	Fe (mg/L)	Zn (mg/L)	Cu (mg/L)
I.	Upstream Section	5.66	0.41	0.04	0.015
	a) Waste Water Outfall Near Village Nayajupura	0.33	1.41	0.34	0.212
	b) Waste Water Outfall Near Shamli Bus Stand	0.35	1.12	0.27	0.131
	c) Industrial Drain	0.46	7.19	0.30	0.072
	d) Sugar Mill Drain	0.12	3.12	0.16	0.212
II.	Downstream Section	7.29	1.33	0.12	0.047

Table 14. Values of flow and trace element concentrations at different sampling stations - December 1993

	Station	Flow ($m^3 s^{-1}$)	Fe (mg/L)	Zn (mg/L)	Cu (mg/L)
I.	Upstream Section	5.10	0.56	0.07	0.016
	a) Waste Water Outfall Near Village Nayajupura	0.30	1.61	0.37	0.216
	b) Waste Water Outfall Near Shamli Bus Stand	0.34	1.49	0.28	0.133
	c) Industrial Drain	0.46	7.98	0.27	0.074
	d) Sugar Mill Drain	0.23	4.74	0.28	0.232
II.	Downstream Section	6.74	1.70	0.13	0.051

Table 15. Loadings and mass balance calculations for various elements - October 1993

Station	Load (kg D^{-1}) Fe	Zn	Cu
I. Upstream Section	201	20	7
a) Waste Water Outfall Near Village Nayajupura	40	10	6
b) Waste Water Outfall Near Shamli Bus Stand	34	8	4
c) Industrial Drain	286	12	3
d) Sugar Mill Drain	32	2	2
Sum { I + (a to d) }	593	52	22
II. Downstream Section	838	76	30

Table 16. Loadings and mass balance calculations for various elements - December 1993

Station	Load (kg D^{-1}) Fe	Zn	Cu
I. Upstream Section	247	31	7
a) Waste Water Outfall Near Village Nayajupura	42	10	6
b) Waste Water Outfall Near Shamli Bus Stand	44	8	4
c) Industrial Drain	317	11	3
d) Sugar Mill Drain	94	6	5
Sum { I + (a to d) }	744	66	25
II. Downstream Section	990	76	30

6.0 CONCLUSION

From the study conducted on river Kali, it is concluded that the river is subjected to varying degree of metal contamination due to numerous outfalls of untreated municipal and industrial wastes. The discharge of municipal and industrial wastes into the river at regular intervals do not allow any self purification to occur.

Estimation of loadings from non-point sources is usually accomplished either empirically through unit area loadings which are based on intensive sampling of a small area and then extrapolation of the resulting loading on a per unit area basis to the entire watershed, or deterministically through loading models which uses such factors as rainfall, soil type, land use, etc. to calculate the loading contribution available from a particular watershed and then estimate the fraction delivered to a water body.

This report gave an account of the advantages of using upstream/downstream river water quality data to estimate the load to the river and detect changes in the water quality characteristics within the river system. Indirect monitoring using upstream/downstream sampling locations provides a viable alternative. An additional advantage of this approach is the substantial reduction in cost.

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