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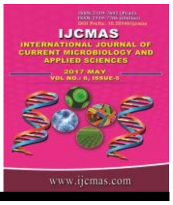

Original Research Article

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Seasonal Variations in Water Quality Parameters of River Yamuna, India

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ABSTRACT

The river Yamuna is one of the most important and sacred rivers of India. During the past few years, the massive pollution has affected its water quality resulting in a foul smelling drain. Seasonal assessment of river water quality would be helpful in evaluating the temporal variations in river pollutants. The present study reports the seasonal and spatial changes in water quality of river Yamuna, India. Surface water samples were collected from three different stretches of river Yamuna i.e. Delhi, Mathura and Agra on seasonal basis from April 2014 to February 2015 and were analyzed for different water quality parameters i.e. water temperature, pH, electrical conductivity, total dissolved solids, total alkalinity, biochemical oxygen demand, chemical oxygen demand, dissolved oxygen, nitrates and phosphates. The mean values of these parameters were used to assess the suitability of river water by comparing with World Health Organisation (WHO) and Indian standards (ISI) for domestic purpose and University of California Committee of Consultants (UCC) and Bureau of Indian Standards (BIS) for irrigation purpose. The sample analysis reveals that river water is not fit for drinking with respect to EC, TDS, TA, BOD and COD, the concentrations of these parameters exceed the permissible limits of WHO and ISI standards whereas for irrigation almost all parameters were found within the permissible limits of UCC and BIS standards. The results suggest urgent need for proper management measures and suitable tools to restore the water quality of this river for a healthy and promising human society.

Keywords

River Yamuna; India; pollution; temporal; water quality; irrigation; parameters.

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Introduction

With heavy industrialisation and expanding urbanisation, rivers are under threat worldwide. The freshwater that Indian rivers carry is often so severely polluted due to heavy pollution load of domestic sewage and industrial poisons that river now threaten the very life they once nurtured. The hydrochemical composition including quality of river water is affected by both the anthropogenic activities and natural processes (Carpenter *et al.*, 1998). Natural processes influencing water quality include weathering of soil and rock, erosion, forest fires and volcanic eruptions whereas anthropogenic activities include urban development and expansion, industrial effluents, mining and refining, agricultural drainage and domestic discharges (Zhao *et al.*, 2014; Basu and Lokesh, 2013) in the rivers. Today, freshwater resource is becoming scarcer and more polluted as the stresses on water quality and quantity due to development and increasing climate change increase every year and are as strongly felt in our country, India, as anywhere else in the world as people of India have always shared a profound and multifaceted relationship with their natural environment. The degradation and deterioration in the water quality of our rivers portends us not only of worsening water shortages and potential conflicts over meager supplies but escalating ecological damage (Mulk *et al*., 2015). All these ultimately, decline the quality of life for many people (Pearce and Turner, 1990) either by reducing the availability of fresh water for consumption or by transmission of germs and carcinogenic substances. Despite the fact that life on earth would be nonexistent without freshwater which is a finite and constant resource, we as humans have disregarded this fact by abusing our rivers and other sources of fresh water. This implies that a fundamental understanding of consistent and comprehensive water quality management is required for proper utilisation and sustainable development of our valuable and vulnerable freshwater resources (Kannel *et al*., 2007).

The river Yamuna is the largest tributary of River Ganga and one of the major rivers in Northern India. The river originates at Saptarishi Kund and traverses a distance of 1376 km from its source in Himalayas, over the states of Delhi, Haryana and Uttar Pradesh, to its confluence with the Ganges at Allahabad. During the last few decades, the Yamuna river, like most of the other major rivers of India, has become increasingly polluted from both point (domestic and industrial wastewater) and non-point (agricultural activities and erosion) pollution sources, especially in the vicinity of the historical urban sectors like National capital territory; Delhi, pilgrimage centre; Mathura-Vrindavan and the world heritage sites of Agra (Haberman, 2006), which are located within a stretch of 200 km on its banks. It is a paradox that these cities, despite river Yamuna being their primary source of water supply, are discharging almost totality of untreated sewage into the river which has severely deteriorated the water quality of the river Yamuna making it unfit for drinking and bathing purposes. The grossly polluted status of river Yamuna has attracted attention of many national and international authorities to take up initiative measures for its water quality restoration and conservation. The Yamuna Action Plan (YAP) under the mega project of the Ganga Action Plan (1985) launched by the Ministry of Environment and Forest (MoEF) majorly funded by Japan Bank of International Cooperation (JBIC) in 1993 is an initiative taken by the Govt. of India to rejuvenate the river Yamuna. Owing to this, several studies have been carried out to evaluate the water quality of river Yamuna (Dubey, 2016; Chopra *et al*., 2014; Upadhyay *et al*., 2011; Sharma and Kansal, 2011 and Mandal *et al*., 2009) In this backdrop, the objective of present study was to assess the pollution status of river Yamuna after it enters the National Capital Territory, Delhi. The prime objective was seasonal assessment of the physicochemical parameters of water to find out the pollution load.

Study Area

The river Yamuna, a snow fed river of northern India, is one of the major rivers of India, originating from the Yamnotri glacier near Banderpunch peak of the lower Himalayas (38^{0} 59$^{\prime}$ N 78^{0} 27$^{\prime}$ E) in the Mussoorie range, at an elevation of about 6,320 m above mean sea level in the Uttarkashi district of Uttarakhand, India. It starts out clear as rainwater from a lake and hot spring at the foot of a glacier, 19,200 feet up in the Himalayas providing basic life support services for countless communities in the South Asian country of India. But for much of its 853-mile length, it is now one of the world's most defiled rivers. With over 50 million people dependent on the water of river

Yamuna along with rapid population growth, it has developed into one of the most polluted rivers in the world. Millions of tonnes of sewage are dumped daily into the river, slowly choking it to death, jeopardizing the lives and livelihoods of millions of people.

The investigation was carried out for one year at selected sites along a 225 km Delhi to Agra stretch of river Yamuna from April 2014 to March 2015.The study area is divided into three stretches viz; Delhi, Mathura and Agra stretch and two sites were selected from each stretch. A brief description of these stretches is as follows:

Delhi Stretch

The Delhi stretch of river Yamuna is located between 28°49′24.39″N and 28°31′50.99″ N and between 77°13′39.92″ E and 77°20′36.8″ E, covering a total of 22 km. The river forms an integral component of water supply source for the state of Delhi contributing around 94 % for irrigation, 4 % toward domestic water supply, and 2 % for industrial and other uses, respectively (CPCB, 2006). It has the largest agglomeration of small and medium-scale industries such as battery, electrical appliances manufacturing, printing, electroplating and steel processing, dyeing, etc. (Mishra and Malik, 2012).

The wastewater generated from these small-scale industries are directly released into the unlined open drains outside the industrial locations which are meant for storm water purposes or into the underground sewerage systems which are ultimately disposed into the river Yamuna (Rawat *et al*., 2010; Mishra and Malik, 2013). Among the total five major segments of river Yamuna viz. Himalayan stretch (172 km), upper stretch (224 km), Delhi stretch (22 km), mixed stretch (490 km) and diluted stretch (468 km), the Delhi stretch is severely polluted and NCR Delhi alone is responsible for 79% of the entire pollution load in the river Yamuna (CPCB, 2006–2007).

Mathura Stretch

The river Yamuna at Mathura is located at latitude of 27^0 29′26.98″N and longitude 77^0 42′18.35″E, 55 km upstream of Agra and 150 km downstream of Delhi. Mathura city with a population of over 0.3 million generates about 43 mld (million liters a day) of wastewater and a high portion of this wastewater is collected by nineteen drains (Kumar, 2004) and discharged into the river.

The water quality of river Yamuna has been continuously degrading all along its Mathura stretch due to the release of harmful and non biodegradable toxic chemicals, dyes, detergents, etc. by a number of small and big industries such as sari printing, metallic works, washing down of chemical fertilizers and pesticides applied for agriculture, dumping of poly bags filled with different kinds of holy material, mass bathing of devotees and direct disposal of burnt or unburnt dead bodies of humans and animals into the river (Bhargava, 2006).

Agra Stretch

The river Yamuna at Agra lies between 27^0 11′2.59″N latitude and 78^0 1′47.58″E longitude at an average altitude of 171 meters or 561 feet above the sea level of central part of India in the Indo-Gangetic plains. The city is famous for its leather industry all over the world that is allegedly discharging untreated wastewater in the river Yamuna, the ultimate source of water for Agraites. Along with tanneries, various other industries like that of metal plating, metal refining and glass industry are also located in the vicinity of the city which adds to the misery of the people.

Methodology

For the seasonal assessment of river water quality, a total of six sampling sites were chosen covering the 225 km stretch of river Yamuna starting from the Wazirabad barrage in Delhi up to the Taj Ghat in Agra. Locations of these sampling sites are shown in Fig1 and their details are listed in Table 1. Surface water samples were collected from April 2014 to February 2015. The whole study period was divided into four fixed seasons i.e summer (April, May and June), monsoon (July, August and September), post-monsoon (October and November) and winter (December, January and February). The samples were analyzed for 10 physicochemical parameters by following standard and recommended protocols of analysis (APHA, 1998). Some of the parameters including water temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO) and total alkalinity (TA) were performed *in situ*. For the determination of the remaining parameters, viz. biochemical oxygen demand (BOD), chemical oxygen demand (COD), phosphate (PO_4^{2-} -P) and nitrate (NO_3^- -N), water samples were collected in polyethylene bottles previously washed with deionised water, acidified with 5ml nitric acid, immediately transported to the laboratory and stored at 4^0 C until their analysis, which was accomplished within one week. The analytical methods employed and instrumentation used for measuring these parameters is tabulated in Table 2. Three replicates for each parameter were taken and mean values were used for calculations.

Statistical analysis

Statistical analysis was done using IBM SPSS® (ver.19.0).Two-way ANOVA was applied to analyze the significant differences in all physicochemical parameters between seasons and sites. Pearson correlation matrix was employed for a better understanding of relationship between the concentrations of different physicochemical parameters of river water.

Results and Discussion

Seasonal variations in the values of selected physicochemical parameters are presented in Table 4-5 for all the selected sampling sites of river Yamuna in terms of their mean and standard deviation.

Water Temperature

Temperature is an important physical property of river systems due to its strong influence on many physical, chemical and biological characteristics of water like the solubility of oxygen and other gases, chemical reaction rates and toxicity, and microbial activity (Dallas and Day, 2004). Increase in water temperature decreases the solubility of dissolved oxygen in water (Perlman, 2013), thus its availability to aquatic organisms which may have an influence on their metabolism, growth, behaviour, food and feeding habits, reproduction and life histories, geographical distribution and community structure, movements and migrations and tolerance to parasites, diseases and pollution. Long-term temperature increase can impact aquatic biodiversity, biological productivity, and the cycling of contaminants through the ecosystem. The mean value of temperature of river Yamuna ranged between 15.00±2.64 to 36.33±3.05 ^{0} C. The maximum value of temperature 36.33±3.05 ^{0} C was recorded at Site5 during summer, whereas minimum 15.00±2.64 ^{0} C was recorded at Site2 during winter. The water temperature showed an upward trend from winter to summer followed by a downward trend from monsoon onwards. Change in water temperature could be attributed to the seasonal changes in air temperatures, sensible heat transfer from the atmosphere, thermal plant effluent discharges into river, convective heat exchange between the free water surface and the atmosphere, the intensity and duration of sunshine. Results from two way ANOVA demonstrate that water temperature had a significant effect between seasons (F= 532.29 p<0.01) and insignificant between sites (F= 0.88) (Table 6).

pH

pH is a measure of acidic and alkaline condition of a water body that affects its productivity (Welch, 1952). It is considered to be of great practical importance as it influences most of the chemical and biochemical reactions. High or low pH values in a river have been reported to affect its biota, impede recreational uses of water and alter the toxicity of other pollutants in one form or the other (DWAF, 1996; Morrison *et al*., 2001). The mean value of pH of river Yamuna varied from 7.50±0.10 to 8.20±0.26 at different sampling sites which show that the water is alkaline in nature. The maximum pH was recorded at Site3 during winter and the minimum was recorded during summer at Site2. Higher values of pH during summer could be due to decomposition of organic matter and high respiration rate of aquatic organisms, thus resulting in production of CO_2 and decrease in pH. Seasonal variations in the pH values did not show much difference. Moreover, the pH values of collected water samples were found within the given limit (6.5-8.5) prescribed by WHO (2004) and ISI (1993) standards for drinking water and CCU (1974) and BIS (1986) for irrigation purpose. Results from two way ANOVA demonstrate that pH had a significant effect between seasons (F= 57.00 p<0.01) as well as between sites (F= 5.66 p<0.01) (Table 6). pH showed significantly negative correlation with temperature (−0.652) (Table 7).

Electrical Conductivity

Electrical conductivity (EC) is a measure of the ability of water to conduct an electric current. It is considered as an indirect indicator of pollution because of its close relationship with the dissolved salt content present in the water column of water bodies that often is associated to sewage discharge and is therefore a well established water quality parameter (Thompson *et al*., 2012). The mean value of electrical conductivity of river Yamuna varied from 1097±117.30 to 1969±31.34 μScm^{-1} at different sampling sites. The maximum electrical conductivity was recorded during summer at Site 2 and the minimum was recorded during winter at Site 3. It is clear that the condition of the water is polluted as the average value of electrical conductivity at most of the sites exceeds 1000 μScm^{-1}which is the threshold value for the water to be called as fresh and unpolluted (Chapman, 1992). High values of EC during summer could be attributed to the presence of domestic sewage, agricultural run-off, industrial effluents and organic matter in water due to an increase in the ionic concentration i.e. Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-} etc. The higher EC values of studied water samples exceeded the WHO (2004) and ISI (1993) guidelines for drinking water. Results from two way ANOVA demonstrate that EC had a significant effect between seasons (F= 223.26 p<0.01) as well as between sites (F= 9.12 p<0.01) (Table 6). EC showed significantly negative correlation with pH (−0.504) (Table 7).

Total Dissolved Solids

Total Dissolved Solids (TDS) is a measurement of inorganic salts, organic matter and other dissolved materials in water (USEPA, 1986). It is a useful parameter in describing the chemical density of water as a fitness factor (Jhingran, 1982). Dissolved solids in water include all inorganic salts, silica, soluble organic matter (Ahipathy and Puttaiah, 2006) and carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates of Ca, Mg, Na, K, and Mn (Mishra and Saksena, 1991). In other words TDS includes anything present in water other than pure water molecules and suspended solids. Kataria *et al* (1996) reported that increase in TDS value reflects the pollutant burden on the aquatic systems originating from both natural as well as extraneous sources like sewage, urban runoff, industrial wastewater and chemicals used in the water treatment processes, and hence, adversely affect the quality of water. High level of dissolved solids in water systems increases the biological and chemical oxygen demand and ultimately depletes the dissolved oxygen level in the aquatic systems (Suthar *et al*., 2009). Total dissolved solids cause toxicity through increase in salinity, changes in the ionic composition of the water and toxicity of individual ions. Waters with total dissolved solids concentration greater than 1000 mg L^{-1} is considered to be "brackish". The mean value of TDS of river Yamuna varied from 1068±131.24 to 2060±144.22 mgL^{-1} at different sampling sites indicating that most of the surface water samples lie within the permissible limits. The maximum TDS were recorded during summer at Site4 and the minimum during winter at Site5. Seasonal fluctuations in the values of TDS at different stations of the river followed the similar trend as that of conductivity. These were maximum in summer and minimum in winter. The maximum value of TDS in summer could be attributed to the increase in the load of soluble salts, mud, humus, nutrients and surface runoff, leaching of fertilizers, faecal matter, and sewage from the catchments area. Due to high concentration of TDS, especially at Site2 in Delhi stretch of river Yamuna, the colour of water for most of the year was found to be grayish black or muddy brown. Results from two way ANOVA demonstrate that EC had a significant effect between seasons (F= 119.74 p<0.01) as well as between sites (F= 5.58 p<0.01) (Table 6). TDS showed significant positive correlation with temperature (0.872) whereas it had a negative correlation with pH (− 0.504) (Table 7).

Total Alkalinity

Total Alkalinity (TA) constitutes an important factor in determining the buffering capacity of a water body (Egleston *et al*., 2010). It is the acid neutralizing capacity of the water that gives primarily a function of the carbonate, bicarbonate and hydroxide content (Tripathi *et al*., 1991) but may include contributions from borate, phosphates, silicates and other basic compounds. Waters of low alkalinity (< 24 ml L^{-1} as $CaCO_3$) have a low buffering capacity and can, therefore, be susceptible to alterations in pH (Chapman, 1992), thus alkalinity is important for fish and aquatic life due to its buffering capacity against rapid pH changes (Capkin *et al*., 2006) that occur naturally as a result of photosynthetic activity of plants. The mean value of alkalinity of river Yamuna varied from 204.66±6.65 to 397.66±28.72 mgL^{-1} at different sampling sites. The maximum alkalinity was recorded during summer at Site2 and the minimum was recorded during winter at Site4. In the present investigation, the maximum total alkalinity was observed in summer and minimum in winter at all the selected sites and was predominantly caused by bicarbonates. Maximum values of total alkalinity in summer could be attributed to accelerated rate of photosynthesis leading to greater utilization of carbon dioxide, disposal of dead bodies of animals, clothe washing station and urban discharge through open drains in the river. Results from two way ANOVA demonstrate that EC had a significant effect between seasons (F= 50.54 p<0.01) as well as between sites (F= 7.03 p<0.01) (Table 6). TA showed a significantly positive correlation with temperature (0.811), EC (0.425) and TDS (0.693) whereas a significantly negative correlation with pH (− 0.743) (Table 7).

Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) is an approximate measure of the amount of oxygen required by the aerobic micro-organisms to stabilize the biochemically degradable organic matter to a stable inorganic form present in any water sample, wastewater or treated effluents, therefore, it is taken as an approximate measure of the amount of biochemically degradable organic matter present in the aquatic systems, which adversely affects the river water quality and biodiversity, the greater the decomposable organic matter present, the greater the oxygen demand and greater the BOD (Ademoroti, 1996). The unpolluted waters usually have BOD value of 2mgL^{-1} or less, whereas those receiving wastewaters may have value up to 10 mgL^{-1} (Chapman, 1992).The major sources of organic contaminants entering the aquatic systems are the municipal sewage treatment plants or the raw sewage which require oxygen for decomposition by bacteria thus, increase the BOD. According to the Central Pollution Control Board (CPCB, 2000), 70% of the pollution in rivers is from untreated sewage, which results in low DO and high BOD (Khaiwal *et al*., 2003). The mean value of BOD of the river Yamuna varied from 8.00±2.66 to 37.34±6.05 mgL^{-1} at different sampling sites. The maximum value was recorded during summer at Site2 and the minimum during monsoon at Site1. Generally, the BOD values recorded in the entire sampling sites crossed the limit prescribed by the WHO (6 mgL^{-1}) standards for drinking water quality criteria (WHO, 2004). The highest value of BOD was recorded in Delhi stretch of river Yamuna where the water quality is influenced by the wastewater, generated from various domestic as well as industrial units, which is directly released into the unlined open drains like Najafgarh and Shahdara drains and ultimately these drains discharge millions of tons of untreated or partially treated effluents per day into the river Yamuna (Rawat *et al*., 2010; Mishra and Malik, 2013). The Najafgarh drain is the largest contributor (BOD Load 76.47 tons/days) as it provide for 31.81% (CPCB, 2004-2005) of the total BOD load of the drains and Shahdara drain also contribute a significant portion of the BOD load i.e; 44.57 tons/days (CPCB, 2004–2005).These two drains alone contributes about 73% of total BOD load and 81% of total discharge of the 18 major drains that join river Yamuna at Delhi. The high values of BOD during summer could be attributed to the acceleration in the metabolic activities of various aerobic micro-organisms in the decomposition of organic matter at high temperature, depleting DO, considerable decrease in water flow and direct discharge of untreated domestic and industrial waste into the river. The low values of BOD in monsoon could be due to dilution by rain in the concentration of dissolved organic matter due to the huge volume of fresh water rains. Results from two way ANOVA demonstrate that EC had a significant effect between seasons (F= 134.50 p<0.01) as well as between sites (F= 10.80 p<0.01) (Table 6). BOD showed a significant positive correlation with EC (0.933) and TA (0.533), while significantly negative correlation with pH (− 0.737) (Table 7).

Chemical Oxygen Demand

Chemical oxygen demand (COD) is one of the most important parameters of water quality assessment employed for estimating the organic pollution of water. The COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in the water bodies. COD determines the amount of oxygen consumed in the chemical oxidation of chemical compounds using a strong chemical oxidant, such as potassium dichromate or permanganate (CSEPA, 1998) under reflux conditions. The mean value of COD of the river Yamuna varied from 16.49±6.91 to 87.92±11.97 mgL^{-1} at different sampling sites. The maximum COD was recorded during summer at Site2 and the minimum was recorded during monsoon at Site4. The higher values of COD in Delhi stretch of river Yamuna indicate water pollution which could be attributed to high organic and significant chemical load of fertilizers, pesticides etc. carried by the major drains viz. Najafgarh and Shahdara drain as they are fed by drains from domestic sewage, industrial units such as electroplating, pharmaceuticals, food manufacturing etc. and agricultural sectors (Bellos and Sawidis, 2005). The COD values recorded in the entire sampling sites crossed the limit prescribed by the WHO guidelines ($10mgL^{-1}$) for drinking water quality criteria (WHO, 2004). The elevated level of COD lowers the concentration of the DO in a water body resulting in a bad water quality and stress to the resident aquatic life (Kannel *et al.*, 2007). Results from two way ANOVA demonstrate that EC had a significant effect between seasons (F= 59.37 p<0.01) as well as between sites (F= 8.70 p<0.01) (Table 6).COD showed a significant positive correlation with EC (0.870), TA (0.590) and BOD (0.945) but significant negative correlation with pH (− 0.738) (Table 7).

Dissolved Oxygen

Dissolved oxygen (DO) has been attributed a great significance as an indicator of water quality assessment since it influences nearly all chemical and biological processes within water bodies. It is an important limnological parameter indicating degree of water quality and organic pollution load in the water body. The main sources of oxygen in an aquatic environment are the gaseous exchange of atmospheric oxygen across the air-water interface and *in situ* production of oxygen, via photosynthesis. The concentration of oxygen in natural waters is largely influenced by physical factors viz. temperature and salinity, dissolved oxygen solubility decreases as temperature and salinity increase. The main anthropogenic activity that leads to the change in dissolved oxygen concentration in the aquatic environment is the addition of organic matter mainly from sewage treatment works together with agricultural run-off, contributing to oxygen demand, also, the nutrient loading of the water bodies promotes the toxic algal blooms and leads to a destabilized aquatic ecosystem. The mean value of DO in the river Yamuna varied from 0.93±0.11 to 6.30±0.81 $mg\ L^{-1}$ at different sampling sites. The maximum DO was recorded during winter at Site1 and the minimum was recorded during summer at Site2. The lowest values of DO were observed in summer and highest values in winter. The DO content sometimes touched zero in Delhi stretch of river Yamuna possibly due to the partially treated and untreated domestic and industrial wastewaters discharged into it through various drains especially Najafgarh and Shahdara drains that have deleterious effects on the water quality of the river. Bellos *et al.*, (2006) and Chopra *et al.*, (2009) have reported that increased industrial activities and sewage from point and non-point sources result in low dissolved oxygen. The low DO values in summer months were possibly due to less oxygen holding capacity of water at high temperature along with increase in DO assimilation for biodegradable organic matter by microorganism. High dissolved oxygen during winter could be attributed to greater dissolution of oxygen in winter at lower water temperature (Khaiwal *et al.*, 2003). Results from two way ANOVA demonstrate that EC had a significant effect between seasons (*F*= 33.55 $p<0.01$) as well as between sites (*F*= 15.36 $p<0.01$) (Table 6). DO showed a significantly negative correlation with most of the parameters viz. temperature (− 0.674), EC (− 0.426), TDS (− 0.714), TA (− 0.745), BOD (− 0.473) and COD (− 0.543) except pH with which it had a positive significant correlation (0.807) (Table 7).

Nitrate−Nitrogen

Nitrate (NO_3^- -N) in surface water is an important parameter for water quality assessment (Johnes and Burt, 1993) to find out the pollution status and anthropogenic load in the river water due to both point and non−point sources. This is a highly oxidized form of nitrogenous compounds and is usually present in surface water as it is the end product of aerobic decomposition of organic nitrogenous matter present in animal waste and concentration may depend on the nitrification and denitrification activities of microorganisms. Unpolluted natural waters usually contain only minute amounts of nitrate (Jaji *et al.*, 2007).

The excessive use of fertilizers in agriculture (Addiscott *et al.*, 1991), urban activities and atmospheric deposition are generally assumed to be a major source of elevated nitrate concentration in freshwater (Carpenter *et al.*, 1998) which cause diverse problems in aquatic systems such as toxic algal blooms that is the most pernicious effects of eutrophication (Anderson and Garrison, 1997), loss of oxygen, fish kills, loss of biodiversity (including species important for commerce and recreation), loss of aquatic plant beds, impairs the use of water for drinking, industry, agriculture, recreation, and other purposes. Elevated nitrate concentrations in drinking water are linked to health problems such as methemoglobinemia in infants, stomach cancer in adults (Wolfe and Patz, 2002) and toxic effects on livestock (Amdur *et al.*, 1991). The mean value of NO_3^--N of river Yamuna varied from 0.85±0.58 to 10.10±1.21 mgL^{-1} at different sampling sites. The maximum value of NO_3^- -N was recorded during monsoon at Site2 and the minimum was recorded during winter at Site1. High value of NO_3^- -N during monsoon could be attributed to the excessive entry of water from agricultural field, decayed vegetable, animal matter, domestic effluents, sewage or sludge disposal, and industrial discharges, leachable from refuse dumps, atmospheric washout and precipitation that enrich river water with nitrogen compounds.

According to WHO (2004), value of nitrate for drinking purpose is 50mg/l and in the respect, NO_3^--N was found under the permissible limit, results from two way ANOVA demonstrate that EC had a significant effect between seasons (*F*= 92.74 $p<0.01$) as well as between sites (*F*= 16.71 $p<0.01$) (Table 6). NO_3^- -N showed significant positive correlation with temperature (0.764), TDS (0.862) and TA (718) and had a negative correlation with pH (− 0.471) and DO (− 0.732) (Table 7).

Phosphate−Phosphorous

Phosphorous as PO_4^{2-}-P is an important parameter to assess the water quality since it is the first limiting nutrient for plant growth in freshwater system (Stickney, 2005) which regulates the phytoplankton production in presence of nitrogen. It is an essential component of the geochemical cycle in water bodies, thus it is often included in basic water quality surveys or background monitoring programmes.

It is available in the form of phosphate (PO_4^{2-}−P) in natural waters and is rarely found in high concentrations as it is actively taken up by plants.

Table.1 GPS location and description of sampling sites of river Yamuna

Stretch	Name of Sampling Site	Site No.	Latitude	Longitude	Location Description
Delhi	Wazirabad Barrage	Site 1	28° 42′ 40.3776″N	77° 14′ 0.0240″E	1 km upstream of Wazirabad barrage.
	Okhla Barrage	Site 2	28° 32′ 50.7624″N	77° 18′ 46.3788″E	1 km downstream from Okhla barrage, Shahdara drain outfall.
Mathura	Vishram Ghat	Site 3	28° 19′ 40.2240″N	77° 41′ 12.7284″E	Main bathing ghat.1 km downstream of the major drain outfall and a minor drain direct outfall.
	Gokul Barrage	Site 4	27° 26′ 42.2448″N	77° 43′ 4.7388″E	8 km downstream of Mathura where water is highly polluted.
Agra	Poiya Ghat	Site 5	27° 15′ 9.7308″N	78° 1′ 9.7308″E	Entry point of Yamuna in Agra. Several nallas join the mainstream here.
	Taj Ghat	Site 6	27° 10′ 37.6248″N	78° 2′ 41.5284″E	Exit point of river Yamuna from Agra. East gate drain outfall.

Table.2 Analyzed water quality parameters, their units, analytical methods and instrumentation used in the study

Parameters	Abbreviation	Units	Analytical Methods	Instruments
Water Temperature	Temperature	^{0} C	Instrumental	Mercury thermometer
pH	pH	–	Instrumental	pH meter (Hanna Instrument, No.S254992).
Electrical Conductivity	EC	μScm^{-1}	Instrumental	Conductivity meter (Hanna Instrument No. S250178)
Total Alkalinity	TA	mgL^{-1}	Titrimetric	Titration assembly
Total Dissolved Solids	TDS	mgL^{-1}	Instrumental	TDS meter (Hanna Instrument No. S98302).
Biochemical Oxygen Demand	BOD	mgL^{-1}	Winkler azide method	BOD incubator and titration assembly
Chemical Oxygen Demand	COD	mgL^{-1}	Dichromate reflux method	Refluxing assembly
Dissolved Oxygen	DO	mgL^{-1}	Winkler iodometric method	Titration assembly
Nitrate	NO_3^--N	mgL^{-1}	Phenol disulphonic acid method	UV−spectrophotometer
Phosphate	PO_4^{2-}-P	mgL^{-1}	Stannous chloride method	UV−spectrophotometer

Table.3 Concentration of various physicochemical parameters (mean ±SD) at six sampling sites of river Yamuna from April 2014 to February 2015

Parameter	Seasons	Site 1 Mean ± SD	Site 2 Mean ± SD	Site 3 Mean ± SD	Site 4 Mean ± SD	Site 5 Mean ± SD	Site 6 Mean ± SD
Temperature (°C)	Summer	35.33±3.05	35.33±2.51	34.33±3.21	35.66±3.21	36.33±3.05	36.00±2.00
	Monsoon	32.00±2.00	32.33±2.08	31.66±2.08	31.33±0.57	31.66±2.08	31.66±0.57
	Post Monsoon	23.33±3.78	21.33±3.78	23.66±5.50	24.66±6.02	23.00±6.55	24.66±5.68
	Winter	15.00±3.00	15.00±2.64	16.33±3.51	15.33±4.04	15.00±3.46	17.66±4.04
pH	Summer	7.70±0.10	7.50±0.10	7.70±0.10	7.6±0.15	7.8±0.10	7.7±0.10
	Monsoon	8.0±0.10	7.90±0.10	7.93±0.05	8.00±0.10	8.06±0.15	7.96±0.05
	Post Monsoon	7.93±0.15	7.83±0.15	7.86±0.05	7.90±0.10	7.90±0.10	7.90±0.10
	Winter	8.13±0.20	7.90±0.10	8.20±0.26	8.00±0.10	8.06±0.11	8.06±0.15
EC (µScm–^{1})	Summer	1848±97.32	1969±31.34	1867±40.50	1894±70.63	1724±95.31	1889±34.11
	Monsoon	1460±96.64	1677±146.87	1384±167.41	1460±123.22	1504±180.13	1452±163.32
	Post Monsoon	1453±93.75	1691±164.07	1438±150.74	1514±103.05	1488±185.30	1538±206.57
	Winter	1109±93.98	1233±79.30	1097±117.30	1129±68.30	1098±84.50	1122±76.86
TDS (mgL–^{1})	Summer	1874±15.86	2058±199.04	1864±157.42	2060±144.22	1895±74.66	1790±268.67
	Monsoon	1789±138.26	2011±44.52	1735±115.49	1771±62.06	1621±118.98	1709±172.25
	Post Monsoon	1481±207.46	1593±216.17	1414±382.58	1729±479.35	1485±383.69	1423±155.02
	Winter	1177±123.78	1282±213.92	1081±29.67	1072±101.07	1068±131.24	1140±132.06
TA (mgL–^{1})	Summer	344.00±23.25	397.66±28.72	343.33±59.53	339.66±33.62	362.00±43.31	359.33±13.57
	Monsoon	301.00±4.35	369.66±40.07	266.00±11.13	287.00±25.51	262.00±43.31	337.33±43.87
	Post Monsoon	255.00±39.28	286.33±33.70	245.66±29.67	229.00±31.04	271.66±26.83	264.33±46.54
	Winter	226.33±13.79	270.66±11.06	212.66±57.27	204.66±6.65	235.33±21.36	233.50±32.48

Table.4 Concentration of various physicochemical parameters (mean± SD) at six sampling sites of river Yamuna from April 2014 to February 2015

Parameter	Seasons	Site 1 Mean ± SD	Site 2 Mean ± SD	Site 3 Mean ± SD	Site 4 Mean ± SD	Site 5 Mean ± SD	Site 6 Mean ± SD
BOD (mgL–^{1})	Summer	25.74±3.47	37.34±6.05	26.51±4.52	30.20±1.37	32.73±6.99	32.91±5.73
	Monsoon	8.00±2.66	12.67±2.82	8.32±2.94	11.05±2.62	10.36±1.89	11.39±2.01
	Post Monsoon	14.71±3.54	20.26±4.70	16.46±4.37	17.72±3.37	16.59±6.18	18.99±6.18
	Winter	16.43±2.76	26.20±5.19	15.97±1.69	15.57±3.25	18.14±3.33	22.66±3.28
COD (mgL–^{1})	Summer	56.15±8.58	87.92±11.97	55.31±6.45	43.76±24.86	64.31±17.68	65.60±9.40
	Monsoon	19.94±7.65	31.11±3.82	22.07±4.82	16.49±6.91	26.81±6.66	22.39±2.97
	Post Monsoon	29.06±1.19	42.65±11.25	33.45±7.14	30.22±7.22	33.61±12.51	36.06±9.98
	Winter	30.26±1.93	48.35±3.68	32.20±8.12	32.20±8.12	38.19±4.53	42.81±8.30
DO (mgL–^{1})	Summer	2.16±0.20	0.93±0.11	2.70±0.20	2.50±0.45	2.70±0.45	2.23±0.49
	Monsoon	3.80±0.20	1.73±0.15	3.10±0.26	3.20±0.10	3.20±0.36	3.80±0.40
	Post Monsoon	4.50±0.78	1.53±0.47	3.80±0.70	3.63±0.40	3.53±0.70	3.86±0.35
	Winter	6.30±0.81	2.40±0.50	5.73±1.05	4.96±0.87	4.76±1.15	4.70±0.72
NO_3^- -N (mgL–^{1})	Summer	3.70±0.52	8.39±0.75	5.25±1.01	5.30±0.94	5.67±0.62	6.58±1.10
	Monsoon	4.73±0.56	10.10±1.21	7.04±1.51	6.88±1.59	7.33±1.03	7.90±1.47
	Post Monsoon	2.63±1.60	5.58±2.77	3.59±1.65	3.19±1.66	4.27±1.72	4.88±3.76
	Winter	0.85±0.58	2.91±0.73	1.65±0.50	1.51±0.60	2.52±0.63	1.22±1.00
PO_4^{2-} -P (mgL–^{1})	Summer	0.78±0.14	1.67±0.07	1.09±0.06	1.25±0.04	0.92±0.05	1.44±0.06
	Monsoon	0.90±0.13	2.04±0.06	1.44±0.11	1.33±0.12	1.09±0.04	1.68±0.14
	Post Monsoon	0.58±0.18	1.37±0.53	1.06±0.23	1.06±0.14	0.94±0.20	1.20±0.27
	Winter	0.39±0.13	0.88±0.13	0.66±0.18	0.68±0.21	0.57±0.13	0.77±0.19

Table.5 Comparison of studied water quality parameters with the standards for drinking and irrigation purposes provided by WHO (2004), ISI (1993), UCC (1974) and BIS (1986)

Sl. No.	Water Quality Parameters	Drinking Water		Irrigation Water		Range in the Study Area
		WHO International Standards (2004)	Indian Standard (ISI 10500, 1993)	University of California Committee of Consultants (1974)	Bureau of Indian Standards(BIS,1986)	
1	Temperature	-	-	-	-	15.00-36.33
2	pH	6.5-8.5	6.5-9.5	6.5-8.4	6.5-8.4	7.50-8.20
3	EC µScm^{-1}	1400	-	700-3000	1164-1986	1097-1969
4	TDS mgL^{-1}	500-1500	500-2000	450-2000	-	1060-2060
5	TA mgL^{-1}	200	-	-	-	204.66-397.66
6	BOD mgL^{-1}	6	-	-	-	8.00-37.34
7	COD mgL^{-1}	10	-	-	-	16.49-87.92
8	DO mgL^{-1}	-	-	-	-	0.93-6.30
9	NO_3^--N mgL^{-1}	50	-	5-30	0-10	0.85-10.10
10	PO_4^{2-}-P mgL^{-1}	-	-	-	0-2	0.39-2.04

Table.6 Two-way analysis of variance (ANOVA) for different parameters

Two way - ANOVA			
S. No.	Parameters	Between Seasons *(F value)*	Between Sites *(F value)*
1	Temperature	532.29*	0.88$^{\#}$
2	pH	57.00*	5.66*
3	EC µScm^{-1}	223.26*	9.12*
4	TDS mgL^{-1}	119.74*	5.58*
5	TA mgL^{-1}	50.54*	7.03*
6	BOD mgL^{-1}	134.50*	10.80*
7	COD mgL^{-1}	59.37*	8.70*
8	DO mgL^{-1}	33.55*	15.36*
9	NO_3^--N mgL^{-1}l	92.74*	16.71*
10	PO_4^{2-} -P mgL^{-1}	43.35*	24.00*

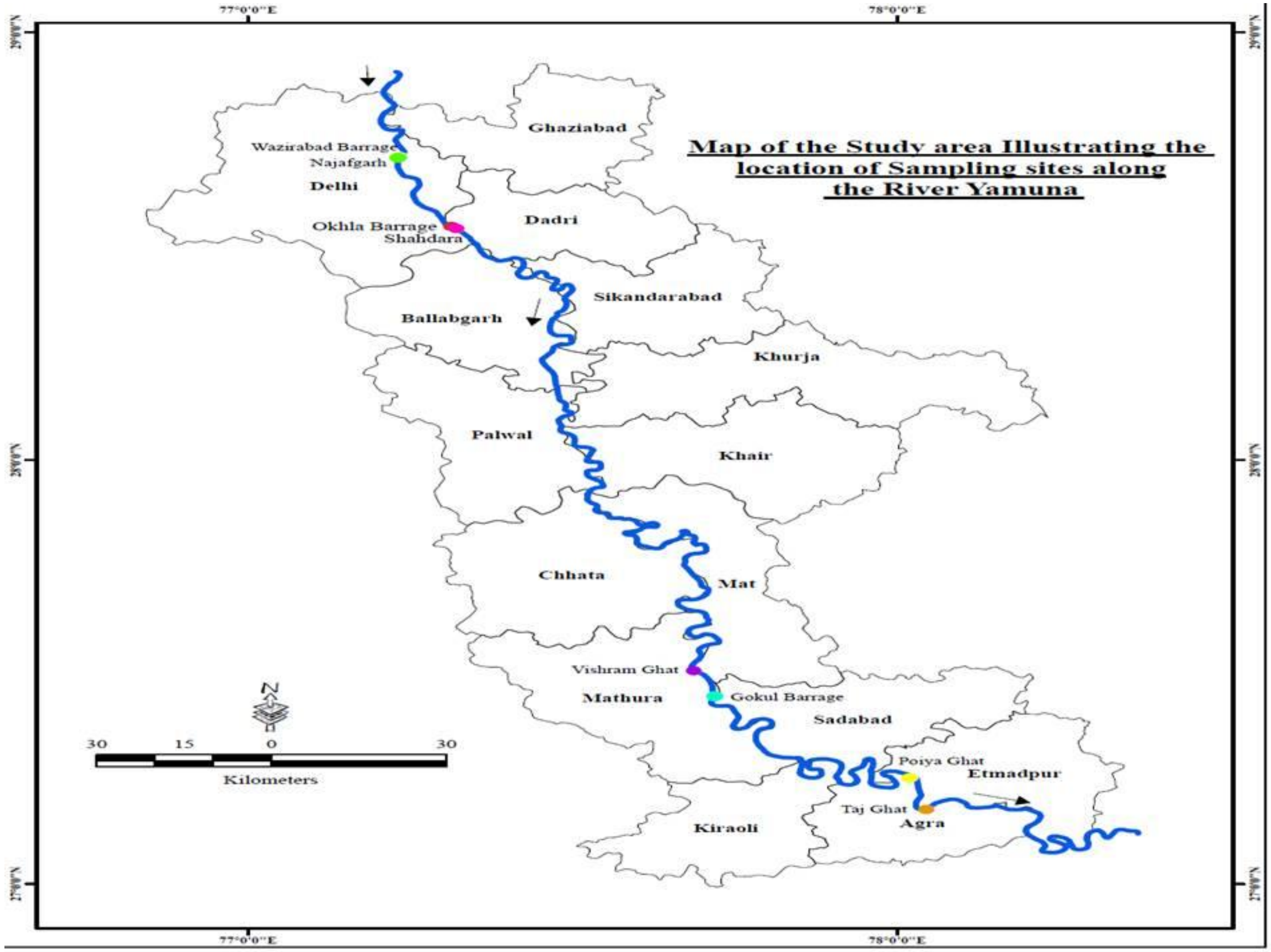
*Significant at $p<0.01$

$^{\#}$ Not significant

Table.7 Correlation matrix for different water quality parameters

Parameter	Temp	pH	EC	TDS	TA	BOD	COD	DO	NO_3^--N	PO_4^{2-}-P
Temp	1									
pH	-0.652^{**}	1								
EC	0.167	-0.756^{**}	1							
TDS	0.872^{**}	-0.504^{*}	−0.088	1						
TA	0.811^{**}	-0.743^{**}	$.425^{*}$	0.693^{**}	1					
BOD	0.270	-0.737^{**}	0.933^{**}	−0.011	0.533^{**}	1				
COD	0.315	-0.738^{**}	0.870^{**}	0.066	0.590^{**}	0.945^{**}	1			
DO	-0.674^{**}	0.807^{**}	-0.426^{*}	-0.714^{**}	-0.745^{**}	-0.473^{*}	-0.543^{**}	1		
NO_3^--N	0.764^{**}	-0.449^{*}	−0.114	0.862^{**}	0.718^{**}	0.020	0.132	-0.732^{**}	1	
PO_4^{2-} -P	0.614^{**}	-0.471^{*}	−0.053	0.747^{**}	0.623^{**}	0.057	0.129	-0.716^{**}	0.916^{**}	1

*Correlation is significant at the 0.05 level ($p<0.05$)
**Correlation is significant at the 0.01 level ($p<0.01$)


Map of the Study area Illustrating the location of Sampling sites along the River Yamuna
77°0'0"E
78°0'0"E
29°0'0"N
28°0'0"N
27°0'0"N
Ghaziabad
Wazirabad Barrage
Najafgarh
Delhi
Okhla Barrage
Shahdara
Dadri
Sikandarabad
Ballabgarh
Khurja
Palwal
Khair
Chhata
Mat
Vishram Ghat
Mathura
Gokul Barrage
Sadabad
Poiya Ghat
Etmadpur
Taj Ghat
Agra
Kiraoli
N
30
15
0
30
Kilometers

Therefore, the enhanced availability of phosphate is an indicative of pollution and a worldwide cause for eutrophication and depletion of DO (Kannel *et al*., 2007) of rivers resulting in a variety of adverse ecological effects. Major source of phosphate in water is effluent discharge from sewage treatment plants, domestic wastewater, runoff that comes from agricultural fields sprayed with phosphate fertilizers, phosphate additives used in detergents for washing clothes. The mean value of PO_4^{2-}-P of river Yamuna varied from 0.39±0.13 to 2.04±0.06 mgL^{-1} at different sampling sites. The maximum value of phosphates was recorded during monsoon at Site2 and the minimum during winter at Site1. In the present study, the high values of PO_4^{2-} -P recorded during monsoon could be correlated to inflow of rain water from catchment area, which brought with it various salts and fertilizers including phosphates into the river. Results from two way ANOVA demonstrate that EC had a significant effect between seasons ($F = 43.35$ $p<0.01$) as well as between sites ($F = 24.00$ $p<0.01$) (Table 6). PO_4^{2-}-P showed significantly positive correlation with temperature (0.614), TDS (0.747), TA (0.623) and NO_3^- -N (0.916) while a significantly negative correlation was found pH (− 0.471) and DO (− 0.716) (Table 7).

In conclusion, the present study along a 225 km stretch of river Yamuna from Delhi to Agra demonstrated that the water quality is degrading that may lead to an increase of at risk situations with regard to potential health impact on humans. For drinking purpose, all the studied physicochemical parameters, except pH, NO_3^--N and PO_4^{2-}-P, were higher than the prescribed limits of WHO and ISI whereas for irrigation purpose all the parameters were found within the permissible limits of CCU and BIS. Therefore, a higher value of these parameters is an alarm for increasing pollution in river Yamuna. Moreover, the river Yamuna at its Delhi stretch has the worst water quality with low DO, high BOD and COD as compared to the river stretch in Mathura and Agra because several drains from different industries of Delhi as well as neighboring states join the river at this segment. At present, the direct discharge of domestic and industrial sewage into the river without treatment is a major threat to water quality of river Yamuna. There is a huge need to undertake water quality monitoring tools for the evaluation of our waterways and future trends prediction. To enhance sewage treatment mechanisms in order to control effluents and untreated waste being discharged from industries, thermal power plants and other point sources of pollution is an urgent need of hour.

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