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An investigative study on the ecological risk associated with the release of industrial effluents containing anionic contaminants in Chitrapuzha river, Kerala

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The alarming increase in the presence of anionic contaminants in industrial effluents are creating huge destruction to our river ecosystems. In spite of the fact that they are non-toxic to human beings, but still, it has the potential to add pace to eutrophication and thereby causing instability to the ecological cycle in river bodies. The current work emphasis on an Ecological Risk Assessment study based on a river ecosystem polluted by industrial release containing anionic contaminants. The analysis comprises a risk assessment associated with the consumption of water and other river organisms pertained due to these effluent releases. The analysis was conducted for both resident and worker. The water samples for the analysis were collected from Chitrapuzha river located at Ernakulam in Kerala state. This river is a release basin for around a dozen chemical industries. The results from analysis clearly showed a drastic reduction in the quality of water and an alarming rate of various anionic contaminants such as sulphate, nitrate, chloride and fluoride. The risk pertained due to these contaminants by consumption of river water is presented in this work. The future recommendations in light of this assessment are also included.

Keywords: Anionic contaminants, river ecosystems, Ecological Risk Assessment, risk quantification, environmental impact assessment.

Introduction

The release of toxic wastes from industries is causing huge destruction to our water bodies and the ecosystems present within. These releases are usually a mixture of many undesirable contaminants such as heavy metals, oil and grease, coarse and suspended particles etc. The magnitude of destruction caused by these constituents is so unpredictable that it not only reduces the quality of water but also can trigger drinking water crisis. Even the legislation governing these releases seems inadequate in front of the challenges caused by these destructions. The studies are performed by collecting the water samples from Chitrapuzha river located at Ernakulam in Kerala state. This river is an effluent release basin for around a dozen chemical industries. The continuous releases from the industries had seriously affected the water quality and made a notable change to the odour, colour and taste of the water.

One major contributor to this disturbance is the increase of anionic contaminants in rivers and other water bodies due to industrial releases[1,2]. Anions are negatively charged atoms or group of atoms. Their charge is obtained due to the gaining of electrons[3]. The presence of anionic contaminants in river water is highly undesirable especially when the water is a source for consumption by human beings. Anionic contaminants are non-carcinogenic, non-lethal and non-mutagenic to human beings. This is the reason why the industries give less priority in reducing anionic waste levels in their effluents. The inadequate legislations and un-updated permissible limits governing the industrial effluent release are not providing proper guidelines to the industries for installing sophisticated mechanisms or methods for the removal of anionic wastes. At the same time, an increase in the level of anionic contaminants in effluents can cause many ecological imbalances and can also trigger the reduction in water quality. This not only causes drinking water scarcity but also results in the restriction in usage and consumption of fishes and other aquatic organisms. This, in turn, will cause large scale pollution and ecological destruction of the river and its ecosystems. Due to these reasons, the removal of anionic waste from industrial effluents should be given equal importance similar to other priority pollutants. This necessitates the need for the proper assessment and preparation of guidelines for anionic contaminant removal from industrial effluents.

Anionic contaminants

The anionic contaminants can cause lots of harmful effects[4] on both aquatic organisms and human beings. When the anionic wastes are released into rivers, it can cause the increase in the nutrient content of water and has the potential to add pace to the Eutrophication[5], i.e. growth of unwanted algae and other organisms. The abnormal algal growth will reduce the dissolved oxygen content in water and affects the lives of other aquatic organisms. This scenario later results in the mass death of organisms and can cause pollution and reduction in the water quality and as well as destruction[6] to the river ecosystems and ecological cycle associated with it. Consumption of this water and the organisms present within can cause lots of chronic effects in human physiological conditions[7]. It is a fact that anionic species are necessary for human beings in the diet in small quantities, but its abnormal concentration is not at all desirable and recommendable at any circumstances. The present work considers the various anionic contaminants such as sulphate, nitrate, chloride and fluoride in the river water for the risk analysis associated with its consumption.

Sulphates play an integral part in the human diet as glucosamine sulphate which does an important function in the building of tendons, cartilage, ligaments and the thick fluid that surrounds joints[8]. On the other hand, higher sulphate levels can result in catharsis, dehydration and even in the critical case of diarrhea.

Nitrate is useful in the manufacture of fertilizers and also included in the human diet in the form of cured meat, leafy vegetables and even in drinking water[9]. Nitrate helps in reducing hypertension. But its abnormal increase can cause nitrate toxicity in infants which are referred to as Blue baby syndrome. Abnormal nitrate levels can cause lots of adverse effects in pregnant women including Methemoglobinemia.

Chlorides are regularly included in the human diet as sodium chloride or commonly referred to as table salt. But at the same time high and abnormal levels of chlorine can cause hyperchloremia in humans[10]. This results in the dehydration and can cause an imbalance in the functioning of kidneys.

Fluoride is essential for our body at low concentrations and that is the reason why it is purposefully added to drinking water or table salt in low concentrations[11]. It helps in the protection against tooth cavities and decay. But the regular exposure to high concentrations of fluoride can cause many adverse health effects such as skeletal fluorosis and mottling of teeth.

Various international standards and environmental protection bodies are also not providing adequate data showing the maximum permissible limits allowable for these contaminants in drinking water. The United States Environmental Protection Agency (USEPA) and the World Health Organisation (WHO) only provides the maximum permissible value for fluoride and it is recommended as 4 mg/L for USEPA and 1.5 mg/L for WHO. But Indian Standard Institute (ISI) provides more detailed and stringent values for the maximum permissible limits of anionic contaminants. According to the recommendations made by ISI maximum allowable limit of fluoride must be between 0.6–1.2 mg/L. For sulphate and nitrate, the maximum permissible values recommended are 150 mg/L and 45 mg/L respectively. In the case of chloride, the ISI recommends for a much more different approach in which the chloride content should be differentiated by its presence, i.e. whether it is present as salt or as free residual chlorine. This differentiation is explained on the basis of the fact that the free residual chlorine present in the water will react with the organic compounds present in the water which results in the formation of carcinogenic products[12] like trichloromethane commonly known as chloroform. The maximum allowable limit of chloride in the presence of salt is 250 mg/L, but as free residual chlorine is 0.2 mg/L.

However, all these limits are defined by various agencies for the maximum allowable limit in drinking water. No recommendations and guidelines are provided so far regarding the use of water containing anionic contaminants for the purposes other than drinking. But still, the use of anionic contaminated water for the purposes other than drinking is not recommended since clinical studies had claimed that it causes adverse dermal effects[13] on human beings.

Ecological Risk Assessment

Nowadays the chemical industry has bloomed on a very large scale in which it is estimated to be manufacturing more than half a million products every day worldwide. This remarkable growth and consumer satisfactory policy of many industries had created a stigma where the motive for making more profit can justify any illegal and unpragmatic actions against our environment. Due to this reason, the majority of our river ecosystems are under threat and many of them are on the verge of destruction.

The swiftness with which the new chemicals are formulated seems much faster than their hazard potential evaluation, which in turn discloses us with the fact about the existence of a hazard due to those chemicals. And it is clear that the existence of any hazard poses a risk. This risk can be serious due to the potential of hazard and can even cause large scale destruction to our environment if not carefully dealt. So acquiring proper knowledge regarding this risk possess by a hazard is an important task especially in order to frame the safety practices and standards. But usually many of the hazards are found too late or may even it take some adverse instances or accidents to identify the same. Here comes the importance of Ecological quantitative risk assessment. It helps us to analyze, evaluate and quantify the risk pertained due to certain hazard and also help us in making decisions about the safe concentrations and safety procedure which need to be maintained when dealing with it. This also explains the significance of Ecological quantitative risk assessment.

Ecological risk assessment can be defined as the quantification of risk or adverse effect likely to happen on the environment and organisms when exposed to a hazard[14]. Risk is often referred to as a function of hazard and exposure.

The quantitative ecological risk assessment is a step by step process which is illustrated in Fig. 1. The procedure of hazard identification is actually a summation of finding disturbances or destructions in the environment and finding the factor of its cause. This step is initiated with the observation of abnormalities in the function of the environment or in the behaviour of organisms or ecosystems[9]. Once the hazard is identified, we then proceed to obtain two sets of data i.e. the dose-response assessment data and the exposure assessment data.

Dose-response assessment data is obtained using various methods which include the testing of toxic materials in rodents and animals. This step is usually done and is monitored by an authorized governing agency. The clinical data thus obtained is analyzed using various probability functions and is derived into a model. Thus a model is developed for each toxic substances. On the other hand, the exposure assessment data is obtained by considering and studying the exposure pathway of toxic materials to humans and other

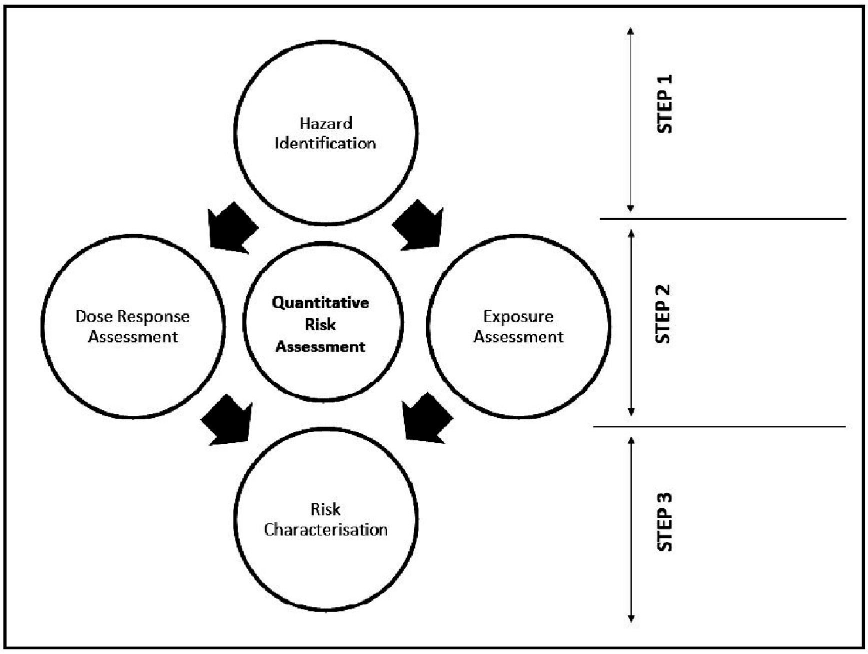

Fig. 1. Schematic illustration of quantitative risk analysis.

organisms. The common exposure pathway of toxic substances for human beings is air, water and soil. The exposure through the air is caused due to the inhalation of toxic particles. The action of wind also triggers this exposure pattern since it carries the particles to different locations even were the toxic particles are absent[15]. The exposure via water is caused mainly by the consumption of water. The chances of having the presence of various toxic particles in the surface water are quite high these days because of the discharge of industrial and domestic waste into the water bodies. The unscientific disposal of solid wastes results in the erosion of leachate into the groundwater which in turn causes toxic contamination in groundwater[16]. The toxicity exposure pathway by soil mainly occurs by ingestion of vegetables which contains the soil particles which are contaminated by the toxic pesticides or other substances. Using these toxicity assessments and exposure assessment data sets we quantify and characterize the risk.

In this work, the quantitative risk assessment of anionic contaminants such as sulphate, nitrate, chloride and fluoride is performed. All these come under the non-carcinogenic category.

Among these contaminants, lots of works are reported regarding the risk assessment due to the presence of fluoride in drinking water. A detailed quantitative risk assessment of fluoride in drinking water was reported by Erdal *et al.*[17], which estimated the average daily consumption of fluoride via all exposure pathways causing the risk of fluorosis in infants and children in various communities in the United States. The health risk assessment of fluoride exposure through food via various ingestion pathways such as water, plants and soil was reported in Chavoshi *et al.*[18] by analyzing the samples collected from Isfahan city of Iran. Yousefi *et al.*[19] describes in detail about the assessment performed to quantify the risk pertained due to the presence of fluoride in drinking water samples collected from Poldasht city of Iran.

While the assessment of risk pertained due to the chloride in drinking water in Hong Kong is well explained in Lee *et al.*[20], which clearly describes the risk and adverse effect caused due to the presence of trihalomethane, an undesirable carcinogenic by-product obtained due to the reaction between residual chlorine and organic matter present in the water. Jameel *et al.*[21] reports about the assessment of risk possessed due to the contamination of sulphates from sugar mill wastes in groundwater in Thiruchirapalli city of India. The detection of nitrate-based fertilizer in groundwater sample collected from Gimpo agricultural area in South Korea and the assessment of risk associated with it is presented in Cheong *et al.*[22]. While a case-based risk assessment was reported in Xiaosi *et al.*[23] which explains the assessment of risk due to nitrate contamination in groundwater due to agricultural wastes in Northeast China.

Materials and methods:

The samples of river water for analysis were collected during the month of July 2019 from the Chitrapuzha river in Ernakulam district of Kerala state. The sampling point was selected 0–5 cm from the surface of the river at the approachable point nearest to the centre of the main flow. 1–2 cm of the top surface layer was avoided in order to collect a dust and oil-free sample. Multiple samples were collected and later mixed uniformly in order to get an average resultant concentration.

Anionic contaminants were quantified using ion chromatography. For analysis, Metrohm 883 Basic IC Plus was used. Sulphuric acid was used as cation and the mixture of sodium carbonate and sodium bicarbonate was used as the anion for elutriation. The neutral agent used for the optimisation of column was Millipore water.

The anionic contaminant quantification analysis was performed three times and the uncertainty in the anionic contaminant quantification is found by calculating the percentage uncertainty given by,

$$\% \text{ Uncertainty} = \left[\frac{\text{Absolute uncertainty}}{\text{True value}}\right] \quad (1)$$

The percentage of uncertainty can be defined as the absolute value of the ratio between absolute uncertainty and true value, where absolute uncertainty is the mean of errors and true value is the mean of experimental values obtained. The error is defined as the absolute difference between the true value and the experimental value.

The anionic contaminants under consideration in this work comes under the non-carcinogenic category. For non-carcinogenic substances, the risk characterization is performed by finding the threshold value below which a body can cope and recover from the exposure easily and safely. On the other hand, they leave no hazard until the next exposure. The procedure for quantitative risk assessment performed is discussed below.

The Intake ratio (I) or also called as Chronic daily intake (CDI) can be defined as the lifetime maximum average daily intake dose of a contaminant which can be taken by an individual. It is calculated in mg/kg/day using the equation[16],

$$\mathrm{CDI} = \mathrm{C}\,\frac{\mathrm{CR}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}} \qquad (2)$$

where C is the average concentration of a contaminant on exposure in mg/L, CR is the contact rate or ingestion rate in L/day, EF is the exposure frequency in days per year. ED is the exposure duration in years, BW is the body weight in kg and AT is the period over which exposure is averaged in days.

The concentration of the contaminant (C) in this work is the concentration of anionic contaminants quantified from river sample using Ion chromatography. United States Environmental Protection Agency (USEPA) provides default values for the remaining parameters provided in the above equation. The default contact ratio (CR) is taken as 2 L/day for a resident and 1 L/day for a worker. For exposure duration (ED) the default values are 350 days/year and 250 days/year for resident and worker respectively. The body weight (BW) is taken as 70 kg by default for both the resident and worker. While exposure frequency (EF) and the actual duration of exposure (AT) is taken as per the actual event of exposure duration faced by an individual under consideration. However, in this work, EF is taken as 70 years and AT is taken as 365 days/year ×70 years for both resident and worker since consumption of water is an inevitable action for the functioning of the body.

The risk characterization of non-carcinogenic substances is determined using a dimensionless quantity called Hazard Quotient (HQ) which is given by[16],

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\mathrm{RfD}} \qquad (3)$$

where CDI is the chronic daily intake and RfD is the reference dose factor. RfD can be defined as the ratio between NOAEL and UF, where NOAEL is the No Observable Adverse Effect Level and UF is the Uncertainty Factor. NOAEL can be defined as the maximum level of exposure of a contaminant on an organism up to which it shows no adverse effects. Uncertainty factors (UF) are nothing but correction factors which are used to compensate the deficiency in knowledge regarding the accuracy of test outcomes or results and also the difficulty in estimating the adverse health effects for different species in different exposure conditions. The USEPA provides RfD values for many contaminants from which the RfD values for sulphate, nitrate, chloride and fluoride was found to be 39 mg/kg, 10 mg/kg, 0.14 mg/kg and 0.06 mg/kg. The RfD values given are the maximum dosage concentration on a daily basis.

The exposure of a toxic substance is found to be safe when the hazard quotient calculated is less than unity i.e. if HQ > 1 then it is unsafe. Hazard quotient is calculated for a single contaminant. For a system with multi contaminant system, we use Hazard Index (HI) which can be defined as the summation of all the hazard quotients in the system under consideration i.e.

$$\mathrm{HI} = \sum \mathrm{HQ} \qquad (4)$$

The system is said to be safe if HI is lesser than unity i.e. if HI > 1 then it is unsafe and that contaminant source should be strictly monitored. It should be either treated before consumption or discarded without use.

Results and discussion

The collected river water sample was analyzed and the concentration of sulphate, nitrate, chloride and fluoride in the sample along with its percentage uncertainty was found to be 9±0.6 ppm, 12.4±0.3 ppm, 12±0.5 ppm and 1±0.2 ppm respectively. The error bar graph for the anionic contaminant quantification is plotted and given in Fig. 2.

Using the obtained anionic component concentration values, the chronic daily intake of each anionic contaminant was calculated using eq. (2). The calculated CDI values calculated separately for the resident and the worker is given in Table 1.

Hazard quotient was calculated using eq. (3) and the calculated HQ values for each contaminant separately for the resident and the worker is given in Table 2. The analysis clearly shows the abnormal hazard quotient value obtained for chlorine for resident which states that the river water with this level of chlorine is not consumable by a resident without proper treatment.

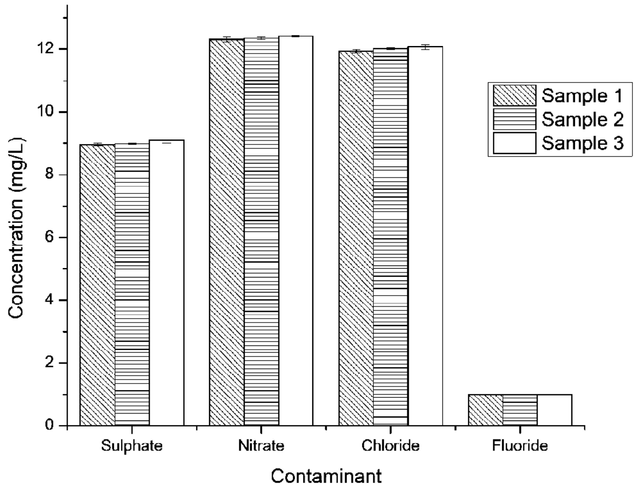

Fig. 2. Error bar graph for the anionic contaminant quantification.

Table 1. Calculated chronic daily intake values of anionic contaminants for a resident and a worker

Contaminant	CDI (Resident)[a]	CDI (Worker)[a]
Sulphate	24.5×10^{-2}	8.7×10^{-2}
Nitrate	33.8×10^{-2}	12.0×10^{-2}
Chloride	32.7×10^{-2}	11.6×10^{-2}
Fluoride	2.7×10^{-2}	9×10^{-3}

[a] In mg/kg/day.

Since the river water sample is a multi-contaminant system with the presence of sulphate, nitrate, chloride and fluoride, hazard index of the river water sample was calculated separately for the resident and the worker and found out to be 2.821 and 0.992 respectively. The hazard index values obtained for the resident is more than 1 and for the worker is almost close to unity. This result shows that river water sample analysed, cannot be recommended to a resident for consumption in any circumstances without proper treatment since the hazard index value is high it is even advisable to discard the use of water from this source. In the case of a worker, it is advisable for consumption only in the absence of other water sources. But this can be allowed only after proper treatment since the hazard index value is almost close to unity.

Table 2. Calculated hazard quotient values of anionic contaminants for a resident and a worker

Contaminant	HQ (Resident)	HQ (Worker)
Sulphate	6.3×10^{-3}	2.4×10^{-4}
Nitrate	33.8×10^{-3}	8.7×10^{-4}
Chloride	2.33	0.831
Fluoride	0.45	0.16

Conclusions

The results from the present study draw us to the conclusion that the continuous releases from the industries into the Chithrapuzha river located in the Ernakulam district of Kerala state had seriously affected the water quality and made a notable change to the odour, colour and taste of the water. The observations clearly showed a drastic reduction in the quality of water and an alarming concentration of chloride and other anionic contaminants such as sulphate, nitrate and fluoride in the river water. The abnormally high level of chlorides can result in the formation of carcinogenic products[12] such as trichloromethane by reacting with the organic compounds present in the water. Its consumption can cause chronic adverse effects on human beings including cancer. The risk pertained due to these contaminants by direct consumption and indirect consumption (via aquatic organisms) are quantified and found to be alarmingly high. This result also shows that the water in Chitrpuzha river cannot be recommended to a resident for consumption in any circumstances without proper treatment, due to its high hazard index value. The higher value even recommends the restriction of its use. But for a worker, it is advisable for consumption only in the absence of other water sources that too with proper treatment since the hazard index value is almost close to unity. This work enables us to draw a clear idea regarding the aftermath and effects of industrial effluent release in our river bodies.

The study also prompts us to provide some future recommendations such as the public should be given proper details regarding the behaviour and characteristics of effluent which is released, and proper awareness must be provided regarding the use of water from river basins were anionic contaminants are released. Proper treatment should be initiated by the water authority when pumping and distributing this anionic contaminated river water to the public for domestic use. The government legal authority should run quality assurance tests on a daily basis. The consumption of various organisms within the contaminated water body should be strictly restricted. The activities such as fishing for consumption and swimming should be restricted until the water quality improvements to satisfactory levels.

The international and national environmental protection agencies, as well as legal authorities, should take at most care in preparing proper guidelines to the industries regarding the treatment, screening and removal of anionic contaminants from its effluent releases. Strict and stringent actions should be made for Implementation of sophisticated techniques for anionic contaminant removal. The legal authorities should frame and implement strict legislature and sanctions against the industries which fail to modify their effluent treatment systems for the removal of anionic contaminants.

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