CHEMICAL CONTAMINATION AND TOXICITY OF SEDIMENTS FROM GANGLA BASIN

EXECUTIVE SUMMARY

THESIS SUBMITTED TO THE
H. N. B. GARHWAL UNIVERSITY, SRINAGAR (GARHWAL)
IN FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

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Executive Summary

Ganga cleaning Project has raised public awareness about the quality of Indian rivers. There have been a series of reports and debate in the media about environmental contamination in freshwater system and their ecosystem. However, our river systems continue to receive discharges of contaminants from non-point and point sources, resulting in elevated and biologically significant concentrations of many contaminants in urbanized segments of rivers throughout the country. Traditionally, the management of aquatic resources is focused primarily on water quality. However, the importance of sediments in determining the fate and effects of a wide variety of contaminants has become more apparent in recent years. In addition to providing a habitat for many organisms, sediments are important because many toxic substances found only in trace amounts in water may accumulate to elevated levels in them. As such, sediments serve both as reservoirs and as potential sources of contaminants to the water column. As well as their potential to degrade surface water quality, sediment-associated contaminants have the potential to affect benthic and other sediment-associated organisms directly. Therefore, sediment quality data provide essential information for evaluating ambient environmental quality conditions in aquatic ecosystems.

Therefore, this study was directed to the assessment of sediment quality of Ganga River. Over the past 10 years or so, isolated studies have been conducted on the chemical composition of Ganga sediments that were mostly focused on geochemical aspects. The assessment of these data indicates that numerous areas in the Ganga River from its origin to fall in the Bay of Bengal are contaminated by metals and organic substances. Recently
few reports identified the adverse effects on the quality of crop grown on the dry beds of Ganga River. The study showed accumulation of contaminants from the sediment to crop, thus identifying the problem of sediment contaminations and their adverse biological effects.

It is getting increasingly recognized that sediment chemistry data alone do not provide an adequate basis for identifying or managing potential sediment quality problems. Newer approaches for Biologically-based sediment quality assessment guidelines (SQAGs) are required to interpret the significance of sediment chemistry data.

The combined chemical and biological approach for sediment quality assessment has been adopted in this study and the most polluted segment (i.e., Kanpur where the Ganga River receives effluents from organized and un-organized tannery industries) has been chosen. Primary efforts were to determine chemical contaminants in the sediment due to tannery effluents and subsequently biological significance of sediment-associated contaminants was worked out by using toxicity bioassays.

The purpose of this study was to apply and standardize simple bioassay techniques that can find effective application by the regulatory authorities in assessing efficiently and cost-effectively sediment quality conditions of Indian River system. However, it is to be kept in mind that sediment quality assessment is not to be used in lieu of water quality criteria rather it will indicate the effectiveness of regulatory programs and identify the need for more stringent regulations.

In the introductory Chapter 1, the problem of river pollution, significance of sediment in identifying the pollution status has been described. In addition to that the major polluting industries at the selected study site and their effluent composition have
been examined. In fact, the tannery industry mushrooming in North India has converted the Ganga River into a dumping ground. The tanning industry discharges different types of waste into the environment, primarily in the form of liquid effluents containing organic matters, chromium, sulphide ammonium and other salts. As per an estimate, about 80%-90% of the tanneries use chromium as a tanning agent. Of this, the hides take up only 50%-70%, while the rest is discharged as effluent. Pollution becomes acute when tanneries are concentrated in clusters in small area like Kanpur. Consequently, the Leather-tanning sector is included in the “Red” category of industries due to the potential adverse environmental impact caused by tannery wastes. The Government of India (GOI) has numerous laws in place that affect the leather industry. Tanneries in India are required to comply with the regulations of the Central Pollution Control Boards and concerned State Pollution Control Boards. In 1996, the Supreme Court of India ordered the closure of all tanneries that had not set up pollution control systems. Using government subsidies, the tanneries have built numerous Common Effluent Treatment Plants (CETPs) to treat the toxic wastewater from tanneries. Despite this initiative, many of the pollution problems are still unresolved. The major components of the tannery effluents are the toxic trace metals. Several analyses reveal high concentrations of chromium even in supposedly 'treated' effluents. The majority of chemicals discharged into aquatic system eventually end up in sediments that may act as a sink of pollution as well as a source of pollution. Sediments are ecologically important components of the aquatic habitat which play a significant role in maintaining the trophic status of any water body. Thus, study of sediment helps in the understanding of pollution effect as the residence time of pollutants in sediment of impacted area is long.
The chapter II was dedicated to the methodology adopted in this study. Starting from the sediment collection, transport, storage and the technique for the elutriation of bioavailable contaminants have been described. Sediment samples were collected from the upstream area (Bithoor) and downstream area (Jajmau) at Kanpur segment of Ganga. Sediment samples were also collected from Deoprayag that is the point of origin of Ganga and anthropogenic pollution is not expected. The sample from Deoprayag served as controls to compare with downstream sediment quality. In addition to that a certified sediment samples with known contamination concentration was commercially procured from UK to serve as positive control in sediment bioassays. In general standard analytical methods have been used that were suggested either by the sediment quality assessment guidelines or Standard EPA methods were adopted. Trace metals in sediment and sediment elutriate were analyzed by the atomic absorption spectrophotometer using standards for QA/QC method. The toxicity of the sediment was assayed by bacterial toxicity assay method employing Microtox that uses photobacterium Vibrio fischeri as a test organism. Direct solid phase test was adopted with whole fresh sediment whereas Microtox basic test was used for the sediment elutriates. The other bioassay used was the seed germination and seedling growth assessment on exposure to bulk sediment directly and also sediment elutriates. This test system has been widely used for soil pollution and considered useful in determining the toxicity of sediment and differentiating between highly contaminated and less contaminated sediment.

In chapter III, the data for chemical characterization of sediment sample collected from different locations have been reported. Sediment collected from the upstream and downstream locations of Kanpur segment showed differences in color, texture, moisture
content and chemical composition. The pH of downstream sediment was slightly higher as compared to upstream sediment samples showing increase in alkalinity of sediment. The Total Organic Carbon (TOC) of the sediment from the two locations was not different and their values were comparable with the sediment TOC contents in River sediment reported in literature. The total petroleum hydrocarbons (TPH) were found manifold higher in sediment samples from downstream stations. The possible sources of TPH may be gasoline pumps, spilled on pavement and chemicals used at home and work, used engine oil reaching to the river through municipal discharges and other industrial discharges. Since Ganga River is free from any direct sources of oil pollution, the TPH values were far less than reported in sediment from other parts of the World. Though the values in the sediment obtained in our study were at the lower end of other reports but indicated hydrocarbon contamination in the study area. However, TPH have never received attention in sediment contamination studies reported from Ganga River or for that matter from Indian rivers in general.

Trace metals in the sediment are the most studies fraction considering its presence as natural constituents and as contaminants from anthropogenic sources. Sediments are increasingly recognized as carriers and possible sources of contaminants in the system. Human activities (urbanization, industrialization, mining, etc.) promote the accumulation of polluted sediments in the nearby river system, which is considered to be a safe disposal site for contaminated sediments, thus, sediments are an important source for assessing heavy metal pollution in rivers, as they have a long residence time. In general, trace metal levels in sediment collected from downstream Jajmau area were higher than upstream area. The increase in concentration ranged from 1.5- to 2-fold for most of the metals with
the exception of As and Pb which showed no change and Cr which showed a dramatic increase in concentration in sediment from down stream area. The accumulation of Cr in sediment at Jajmau area was 30-fold higher than in sediment from upstream Bithoor area. In an earlier report of 2001 a 10-fold increase in Cr in sediment from similar areas was found suggesting that sediment contamination is worsened in the last few years.

Trace metals determined in the present study were in the bulk sediment and by comparing the present study results with the average of Indian River System (IRS) all the trace metals were found less in sediment samples from the upstream area Bithoor except Zn. Whereas, in sediment from downstream sampling area Jajmau Cr, Cu and Zn were high, among these metals Cr was extremely high. Same was the scenario when compared with the World River System (WRS). All the values of the present study were on the lower side compared with WRS values except Cr, which also suggests that Cr pollution was very high at down stream area Jajmau due to discharges from tannery wastes.

The comparison of trace metal values obtained in the present study with IRS or WRS suggests that the condition of the Ganga River sediment was in general not alarming, but there are hot spots of contamination like downstream area Jajmau where pollutants accumulated due to the point source discharges from tannery industries. However, the dimension of the impacted area was not determined in this study. Comparison with freshwater sediment quality guidelines provide criteria for the evaluation of trace metal concentration in river sediments in response to adverse affects on the river’s biological components. The levels of various trace metals obtained in the present study were compared with the lowest effect level (LEL) and probable effect level (PEL). In the LEL, sediments are considered to be clean to marginally polluted, where as
no effects on the majority of sediment-dwelling organisms are expected below this concentration. The PEL represents the level above which adverse effects to aquatic biota are predicted to occur frequently. Using above criteria in the present study, Cr was the only trace metal above the PEL and LEL concentrations; whereas Cu is identified only above the LEL concentration.

Numerous studies have shown that organic contaminants persist on solid matrix and becomes increasingly resistant to desorption and biological uptake. Initial sorption of organic contaminants to solid particles is fairly rapid and reversible followed by a prolonged slow sorption phase that leads to chemical fraction that then resist desorption. This process of aging substantially reduces the rate of desorption that correlates with a net reduction in bioavailability of the contaminants.

The assay of chemical contamination in sediment elutriates was conducted in consideration with accessibility of contaminants in water phase from the solid matrix. Sediment elutriates primarily drives the contaminants present in pore water that is the water occupying the spaces between sediment particles. Secondly elutriation process accesses the sorbed contaminants from the sediment that may be released in a situation where re-suspension of sediment may occur. The composition of elutriate depends on the preparation method and the nature and quality of sediment. The elutriation procedure used consists of the vigorous shaking of 1:4 sediment and water ratio to release sorbed pollutants. This mixture was allowed to settle and the liquid phase centrifuged. Elutriates prepared under these experimental conditions showed low quantities of TPH elution in the aqueous medium even in the samples that contained high amount in whole sediment possibly due to hydrophobicity of petroleum hydrocarbon. TOC in elutriates were eluted
only in samples from down stream sediments. Among trace elements detectable elution was observed only for iron, manganese, nickel and zinc whereas the other metals in elutriate were present at their lowest detection levels. Our observations on elutriate composition were in agreement with the results obtained in earlier studies where various trace metals were in elutriate at below detectable levels.

In chapter IV, studies on toxicological characterization of sediment are reported. The toxicity refers to the inherent potential of a substance to cause systemic damage to living organisms. The use of living test organisms is the only way to reliably measure the toxicity of polluted water, sediment or any other chemical pollutant. In this study, sediment toxicity was determined by using two different systems, the first Microtox Solid-Phase Test (SPT) assay and the second seed germination toxicity assay. The selected systems are simple, cost effective, and easy to perform and help to provide the information regarding sediment quality.

In Microtox SPT bioluminescent bacteria *Vibrio fischeri* are exposed to sediment suspension and the effects on light emission of bacteria are evaluated in the liquid phase that remains after removal of the sediment by filtration. The test is getting wide application in environmental monitoring. Several researchers have advocated direct sediment bioassays over indirect assays with pore-water or elutriate. Direct testing has many advantages over indirect testing.

Microtox SPT assay was done with sediment from upstream and down stream areas and also the control samples collected from the point of origin of Ganga River at Deoparyag, as negative control and a certified contaminated sediment commercially procured from UK as a positive control. At the study location the upstream sample
(Bithoor) though exerted some toxic effects on bacteria but EC50 values were >1% sediment (= 10,000 mg/L sediment) and categorized as non toxic according to toxicity classification. The down stream (Jajmau) sediment samples were very toxic to the bacteria from all the locations, the average EC50 value for the sediment from the down stream area was 0.43 % (= 4,266 mg/L sediment) that falls in very toxic category as per toxicity classification. Other reported studies have shown the toxicity of sediment with EC50 values in the range of 0.01-2.06%.

The segment of Ganga River chosen for the present study receives effluent mostly from organized and unorganized tanneries in Kanpur city. The tanning industry, which commonly utilizes “Chrome liquor” in the tanning process discharges the effluent into the environment containing chrome salts in excess of the maximum permissible limit. The chrome discharges chromium however, the vegetable tanneries discharge chromium and phenolics both in high quantity. These are retained in effluent due to its toxic and recalcitrant nature during the activated sludge process which causes environmental pollution. However, the extent of toxicity in different organism has not been well studied except few reports.

Recent studies of untreated and treated tannery effluent collected from the Common Effluent Treatment Plant (CETP) revealed EC50% values of untreated tannery effluent in the range of 3.12-5.09% while with treated effluent the toxicity was greatly reduced and EC50 ranged between 63.49-76.07%. The CETP discharges goes to the Jajmau region the down stream area from where the samples were collected for the present studies. These observations suggest that the toxicity observed with downstream sediments was due to tannery effluent.
In order to assess the leachability of contaminants present in bulk sediment elutriates were prepared and tested for toxicity. Sediment elutriates from downstream areas showed no toxicity to Microtox indicating that toxic principles were not leachable in aqueous medium or their concentration eluted was lower than their toxic levels. Low elutriate: bulk sediment concentrations ratios have been reported in the literature as one of the factor showing no toxicity of elutriates from otherwise toxic sediment and there are numerous results on harbour elutriates showing absence of metal release from sediments. This indicated that the characteristic of sediment from downstream area was of aged sediment. Slow sorption of chemicals on solid matrix over weeks, months and years leads to a chemical fraction that then resist desorption as that found with sediment from this location suggesting polluted sediment accumulation over the years. Sediment geochemical properties determine the type of metal bindings and its trend to desorb, while factors such as pH and salinity can also determine the bioavailability of chemicals bound to sediments. Also organic matter affects metal speciation and plays a major role in binding different contaminants and may be the responsible for the negative elutriate toxicity.

The data obtained with sediment elutriates in our study refutes the claims that elutriates can predict the bioavailability and toxicity of the sediment. Therefore, based on our studies, we suggest that the quality of a given sediment should be assessed by direct sediment toxicity assay of whole sediment and Microtox SPT proved to be an appropriate method in discriminating nontoxic and toxic samples over a wide range of toxicity.

In chapter V the data for seed germination and seedling growth inhibition test are reported. The test was conducted with both bulk sediment and elutriates to see the toxic
effect on direct contact of seed with sediment matrix and the effect of aqueous elutable toxicant from the contaminated sediment as examined with Microtox bioassay. The sediment samples from upstream and downstream areas reduced the viability of seeds from 62.5-66% compared to 100% viability observed in control soil. This shows that irrespective of location there were some toxicants present in Ganga sediments that caused a reduction in seed viability. However, the exposed seeds on germination showed similar root and shoot growth in upstream sediment compared to controls, whereas the sediment from downstream area showed negligible effect on the growth of root but shoot growth was stunted. It was interesting to note that exposure of seeds to elutriate of downstream sediment samples inhibited both root and shoot growth. A decrease of lower magnitude was also occurred in the growth of roots germinated in elutriates from upstream sediment samples whereas shoot growth was not influenced. Since toxic trace metals were poorly eluted and their concentration was very low, the inhibitory effect on the germination of seeds and specially the shoot growth may be attributed to other chemical contaminants possibly present in the sediment. It has been shown in the earlier studies that Ganga soil from the same sampling area contained pesticide contamination and the crops grown on the dry beds of Ganga accumulated higher concentration of pesticides. Bioaccumulation of trace metals in the seedlings was not done in this study; however, risk of the accumulation of some toxic metals especially Cr is possible if any crop is grown in dried beds near the study area as reported earlier. Thus seed germination bioassay could indicate the difference in the toxicity of upstream (less contaminated sediment) and downstream (highly contaminated sediment). Also seed germination could provide indication of the presence of factors other than trace elements present in the downstream sediment due to differential response
observed in shoot growth of seedlings exposed to up- and downstream sediments making the test sensitive assay. The seed germination bioassay is fairly inexpensive requiring simple laboratory facilities, and can be conducted by the manpower after minimal training.

Thus, the present study dealt with the sediment quality assessment of the Ganga River collected from Kanpur region by assessing contaminant load, their bioavailability in aqueous elutriates and the toxic effect employing two biological test systems that effectively differentiated between polluted and non polluted areas. The study also indicated that *Vibrio fischeri* based luminescent test is more sensitive, rapid, cost effective and reproducible and Microtox toxicity testing is useful tool for environmental risk assessment. Considering the LC50 concentration of trace metals determined in direct toxicity of standard solution, the trace metals were present at several fold higher concentration in the sediment. This suggests that the expected toxicity of contaminated sediment is much higher than determined if the total metals present in the sediment are freely bioavailable to the organism. The seed germination bioassay, the other test system used in this study could also effectively differentiate the toxic and non-toxic sediment samples. This test system is also inexpensive and easy to perform even by the semi-skilled worker; hence this bioassay could be widely used in the toxicity testing of the sediment. The discriminatory value of sediment bioassays examined in this study are suggested to be used by the regulatory authorities for primary screening of environmentally degraded areas prior to detailed chemical analysis of priority pollutants. To the best of author’s knowledge this is the first comprehensive study conducted on the sediment quality of Ganga River where chemical estimation of pollutants and the toxicity of sediment were simultaneously measured. These two approaches go hand in hand and complement each other in providing valuable site-specific information.