# **Identification and Mapping of Chromium (VI) Plume in Groundwater for Remediation: A Case Study at Kanpur, Uttar Pradesh**

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**Abstract:** With only twenty five percent population living in urban areas, India has cities amongst the biggest in the world. Urban growth in most of Indian cities is concomitant with rise in water demand for community, as well as, for industrial purposes. The complex situation resulting from indiscriminate disposal of waste and its severe impact on groundwater quality is set for continuous worsening mainly for want of sustained effort aimed at site-specific remediation.

The study, a prerequisite for actual remediation in an industrial city of Kanpur, India, envisages detailed investigation about pollutant transport, evaluation of concept of Bio-remediation and a range of other options and finally full scale implementation of the best suited. Drilling of piezometers and resistivity survey indicates that the area is constituted of alluvial sands, gravels and their various admixtures. Chemical analysis of water samples collected from piezometers and hand pumps shows the presence of hexavalent chromium rich horizons at various depths. The alarming concentration of this carcinogenic heavy metal of the order of 16.3 mg/l against the permissible concentration (of 0.05 mg/l) for drinking water and high concentration within sediments of the area poses a major threat to the entire ecosystem. The projection of migration contaminant plume of hexavalent chromium as depicted in the paper is indicative of a concentrated extent of core zone existing in shallow alluvial aquifer, which may be targeted for interception by remedial measures.

The present work, elaborating on the source, potential and monitoring the migration of the pollutant plume is the first field scale study of its kind in the country. The findings of these studies are of strong relevance in addressing the ground water pollution due to indiscriminate disposal practices of hazardous waste in areas located within the alluvial zones.

**Keywords:** Groundwater, Hexavalent chromium, Pollutant transport, Kanpur, Uttar Pradesh.

# **INTRODUCTION**

Groundwater – a dependable freshwater resource, constitutes one of the major, strategic socio-economic issues, impacting development in India. This is mainly due to a growing awareness of the potential for further groundwater pollution and subsequent spread of pollutants many negative health effects. In a developing country like India, more than 50% of its irrigation, 80% of drinking water and a sizeable requirement of industries is met by groundwater (CGWB, 2001). With groundwater availability being an important criterion for urban-industrial development, there is an urgent need to ensure judicious groundwater management.

The near-general observation of depleting groundwater table in the country and pervasive pollution of groundwater

by a variety of contaminants, have been documented in the latest published report (NCIWRD, 1999). For several decades, the drainage basin of the Gangetic plain has been used for the disposal of domestic and industrial wastes which have adversely affected the quality of water, sediments and soil of the plain (Ansari et al. 1999).

The Government of India, appreciating the gravity of the alarming status of groundwater resources in the country, has expressed its concern to the Groundwater Authority. However, without a strict code of monitoring backed by enforcement of preventive and regulatory measures, the outcome of efforts to preserve and protect India's groundwater, remains in doubt. The present study envisaged to improve Kanpur's groundwater quality, is a comprehensive investigation invoking latest techniques and

validated tools of modeling. The findings of the study are planned for use in actual remediation and stand to serve as a role model for replication elsewhere.

## **STUDY AREA**

The present study has been carried out in the Kanpur city of Uttar Pradesh (U.P.), which is situated on the right bank of river Ganga covering a Municipal area of 260 sq km. The city is recognized as one of the highly industrialized cities in northern India. It is bounded in the north by river Ganga and in the south by river Pandu (Fig.1). Kanpur has a number of industries mostly that of textiles, leather, jute and chemicals. Although, the pace of industrialization has significantly receded over the years, yet, the unplanned disposal of domestic waste and discharge of untreated or partially treated effluents by industries over the last several years directly on land or river are now resulting in the pollution of surface and sub-surface water resources. Studies have revealed that the process of urbanization is associated with higher concentration of heavy metals in river sediments (Singh et al. 1997), low lying lands and finally into the ground water. This is especially apparent regarding quality of groundwater in the city, which has reported



**Fig.1.** Location map of the area. Inset shows the location of observation wells.

alarming concentrations of Chromium. Groundwater monitoring carried-out by many institutions has confirmed that the Chromium concentration in groundwater and the pattern of land-use in the city are inter-related (CPCB, 1997). Hexavalent Chromium has been detected in the industrial pockets located at Nauriyakhera, Babunia, Rakhi Mandi, Fazalganj localities of the city (CGWB, 2000). Nauriyakhera, the present area of investigation has hexavalent Chromium concentration varying from 0.01 to 16.30 mg/l. A number of chemical industries which have now been closed or shifted had been generating chromiumrich solid waste from production of basic chrome sulphate. The waste had been dumped at several low lying areas.

# **GEOLOGICAL SETUP OF THE AREA**

Geologically, the area is part of Indo-Gangetic alluvial plain. It exhibits a more or less flat topography with a gentle slope running from northwest to southeast. The average elevation of the land surface is 125 m above sea level. The sub-surface stratigraphy shows that the area is predominantly constituted of medium sand and gravel interbedded with silty clay. The micaceous sandy horizons have Himalayan source (Singh and Bajpai, 1989). Based on the bore-hole data, Central Ground Water Board has suggested the presence of granitic basement at a depth of around 502 m around Noriakhera, Panki (CGWB, 2000). The detailed lithounits of the area of investigation are described in Table 1.

In the present area of investigation, thick piles of sediments down to the bed rock broadly constitute a three tier aquifer system. The sands and gravels constitute aquifers. The deeper aquifers at a depth of 250 m bgl, are primary productive zones with discharge ranging between 2000–3000 lpm. Shallow aquifers exist up to a depth of 100 m bgl. Those up to 30-50 m bgl, give a discharge of 400-1200 lpm. The shallower zones occurring in the depth range of 10 to 40 m bgl possess highest concentration of Cr (VI) in groundwater. Out of the three piezometers drilled at different locations, the piezometer #3 showed the presence of Cr (VI) at depth of 8 m and 44 mbgl, whereas the Piezometer # 1  $\&$  # 2 have reported Cr (VI) at depth of 22 m and 26 m bgl respectively (Table 1). Besides these, it is also present in various hand pumps used for domestic water supply.

## **THE GENESIS OF PROBLEM**

Hexavalent Chromium, the known carcinogen is reported in high concentration in ground water from various industrial





cities in India (GDUP, 1994; CPCB, 1997). Normally, such sites have the legacy of disposal of chromium-bearing waste. Availability of safe drinking water in settlements around such areas is a priority issue and of National concern.

In the present area of investigation, the (Cr) anomaly in the groundwater has mainly resulted from indiscriminate on-land burial of Chromium bearing sludge (5-10%  $Cr_2O_3$ by wt) by various industries engaged in the manufacture of Basic Chrome Sulphate (BCS)  $\text{[Cr(OH)}_2\text{SO}_4\text{]}$ , an important input for local tanneries. Such industries existed during the period of 1980 to 1995, thereafter, these were directed to either close or shift to other appropriate locations. The sludge resulting from the initial stage of BCS manufacture is a product of incineration of chromite ore (Fe  $\text{Cr}_2\text{O}_4$ ) and has remnant of Cr (VI) which is water soluble. The leachate of Cr (VI) in the sludge ultimately reached the groundwater. On reaching the groundwater its movement with given velocity formed a plume and migrated down-gradient towards drinking water supply wells. The chromium in groundwater has been in hexavalent state and its concentration varied ranging from 0.01–16.30 mg/l (CGWB, 2000).

The polluted groundwater can be easily identified with strong yellow colour. The higher the concentration of chromium, the stronger the color can be observed. During the initial phases of investigations(CPCB, 1996, 1997), high chromium was observed in the shallow wells/ hand pumps, tapping groundwater from the depth of 8-10 m, whereas, monitoring in successive years has revealed that the influence of (Cr) pollution has been spreading to deeper levels of 35-45 mbgl and also spanning widespread to other areas, unaffected earlier.

#### **METHODOLOGY**

In consideration of the applied approach towards the problem, the study has been comprehensive and aimed at first-hand data generation about specific location of the affected zone of polluted groundwater. The geophysical investigations, hydro-geological characterization and identification of plume migration, being some of the specific aspects addressed in the study, have been helpful in locating the chromium affected zone. The concept of mass transport modeling has been invoked to attain a precise movement of pollutant (Cr-VI) plume. The findings of the study are slated to be further utilized in development of lab-scale as well as actual remedial designs, followed by pilot studies and workout actual cost of full-scale remediation. The exercise of demarcation began with reconnaissance survey, extensive monitoring of groundwater, physical appearance of soil and interaction with local community, which revealed a broad idea of affected zone of pollution and its trend over the years. The detailed investigations carried out are explained as following:

#### **Construction of Piezometers**

Three Piezometers, each of 50 m depth have been drilled in three locations in the study area, to monitor vertical migration of chromium in groundwater by collecting depth specific samples (Fig. 2). It is clearly observed that along the vertical profile of Piezometer #1 and #2, there are two distinct chromium (VI) rich horizons at a depth of 22 to 24 and 28 to 30 m bgl and 16 to 18 and 26 to 28 m bgl respectively. The Piezometer #3 has three such distinct zones located at the depth of 6 to 10, 26 to 28 and 42 to 44 m bgl (Fig. 2). There is a very high concentration of total chromium (32.2 mg/l) as well as Hexavalent Chromium (16.3 mg/l) in the Upper and Lower horizons of Piezometer #3. The chromium concentration in ground water has attained an alarming level and is posing a big threat to the groundwater in the area.

## **Monitoring of Groundwater Quality**

Keeping in mind that the shallow groundwater conditions are relevant for the study, monitoring of groundwater has been carried out mostly for *India Mark-II* Hand pump*s.* These hand pumps, supplying water mainly for domestic usage, derive water from depths around 10- 15 m. In areas, where such hand-pumps are not available, local hand pumps and open dug-wells have been selected for monitoring (Fig.1). Following Clescari et al. (1989), different parameters like Hexavalent Chromium, Trivalent Chromium, Total Dissolved Solids, Electrical Conductivity, pH, Alkalinity and Total Hardness have been measured at 32 locations



Concentration in mg/l.

**Fig.2.** Vertical profile of the area along three Piezometers showing the location of the Chromium rich horizons.

S.No.	Lat $(N)$ deg	Long $(E)$ deg	<b>SWL</b>	$Cr^{+6}$	T-Cr	pH	EC	<b>TDS</b>	Alk	T-Hard.
1	26°27.067'	80°16.014'	13	$\mathbf{0}$	0.535	7.79	1306	863	324	332
$\overline{c}$	26°27.148'	80°16.049'	13.03	1.81	3.275	7.45	1421	938	319	560
3	26°27.190'	80°16.075'	11.7	0.85	1.304	7.99	744	491	193	388
$\overline{4}$	26°27.342'	80°16.104'	13.65	$\boldsymbol{0}$	0.7	8.11	434	286	219	276
5	26°27.168'	80°16.105'	12.6	3.12	4.574	7.58	873	577	193	448
6	26°27.159'	80°16.124'	11.7	3.71	5.187	7.58	1052	695	193	520
$\overline{7}$	26°27.147'	80°16.102'	11.51	2.92	4.765	7.58	868	567	198	446
8	26°27.176'	80°16.130'	11.45	0.11	0.574	7.48	1385	915	258	604
9	26°27.271'	80°16.270'	9.65	0.02	0.04	7.43	854	542	198	432
10	26°27.352'	80°16.024'	10.85	$\boldsymbol{0}$	0.7	8	422	276	198	242
11	26°27.324'	80°15.845'	10.5	$\boldsymbol{0}$	$\boldsymbol{0}$	7.84	440	290	274	280
12	26°27.201'	80°16.102'	11.9	1.39	1.44	7.58	865	546	201	453
13	26°27.126'	80°16.127'	12.35	0.43	0.835	7.66	486	321	230	330
14	26°27.055'	80°16.158'	12.8	$\boldsymbol{0}$	3.743	7.88	394	260	238	240
15	26°27.020'	80°16.146'	12.65	$\boldsymbol{0}$	$\boldsymbol{0}$	7.91	375	248	228	192
16	26°26.994'	80°16.110'	13.56	$\boldsymbol{0}$	$\boldsymbol{0}$	7.62	419	277	253	240
17	26°26.943'	80°16.203'	13.65	$\mathbf{0}$	0.478	8	256	169	143	152
18	26°27.151'	80°16.218'	12.68	10.6	11.65	8.12	998	698	239	654
19	26°26.939'	80°16.096'	13.5	$\boldsymbol{0}$	0.004	7.87	403	267	218	180
20	26°26.930'	$80^{\circ}16.127$	14.15	$\boldsymbol{0}$	0.583	8.04	436	289	258	284
21	26°26.939'	80°16.146'	13.15	$\boldsymbol{0}$	$\mathbf{0}$	8.15	282	186	178	200
22	26°26.955'	80°16.125'	13.55	$\boldsymbol{0}$	0.4	7	1567	1036	620	639
23	26°26.990'	80°16.130'	13.6	$\boldsymbol{0}$	0.404	7.06	1570	1040	605	645
24	26°26.984'	80°15.949'	12.74	$\boldsymbol{0}$	$\boldsymbol{0}$	7.72	1762	1160	409	828
25	26°27.006'	80°16.039'	14.05	$\boldsymbol{0}$	0.487	7.61	481	318	298	268
26	26°26.995'	80°16.001'	13.7	$\boldsymbol{0}$	0.096	7.84	524	346	193	284
27	26°26.426'	80°15.001'	16.5	$\mathbf{0}$	0.255	7.52	561	371	374	276
28	26°26.624'	80°15.105'	15.2	$\boldsymbol{0}$	0.09	7.46	571	377	392	308
29	26°27.049'	80°14.558'	9.8	$\boldsymbol{0}$	0.517	7.54	747	493	470	385
30	26°26.523'	80°15.392'	16.4	$\boldsymbol{0}$	$\boldsymbol{0}$	7.53	1237	816	969	754
31	26°27.321'	80°15.802'	9.5	$\boldsymbol{0}$	$\boldsymbol{0}$	7.6	749	495	384	244
32	26°27.316'	80°15.632'	8.5	$\mathbf{0}$	0.057	7.58	655	433	345	360

Table 2. Groundwater quality at different locations in the study area

SWL - Depth to water table in meter below ground level; EC - Conductivity in micro-semen; all others except pH in mg

(Table 2). It is observed that against the permissible limit of 0.05 mg/l set by the Bureau of Indian Standards (BIS) for drinking water, 10 out of the 32 locations have high to very high concentration of Hexavalent Chromium. At one of the locations (location no. 18, Table 2), the concentration of Hexavalent Chromium has reached to an alarming level of 10.6 mg/l which is about 200 times of the permissible limit.

## **Characterisation of Aquifer Matrix**

Three borings, each of 60 m depth were drilled at different locations in the study area (Table 3). The soil samples analysed at every meter revealed following information:

Hexavalent Chromium exists in the aquifer matrix and its concentration is in the range of  $0.042 - 4.2 \mu g/g$ . It is associated with high concentration of total chromium (15 – 60 µg/g). High content of oxides (nitrate, sulphate and nitrite) combined with low Total Organic Carbon (TOC) and Ammonia-N are further indicative of oxygen rich regime. The oxidized state of Cr in groundwater has been in homogeny with the host aquifer matrix. It may be a point of further investigation to transform the oxygen rich aerobic regime to oxygen deficient anaerobic regime and chemically transform the state of chromium from hexavalent to relatively innocuous trivalent. The chemical characteristics of the aquifer matrix are further summarized in Table 3.

# **Vertical Electrical Soundings**

Vertical Electrical Soundings (VES) have been carried out at eleven different locations in the study area for ascertaining aquifer geometry using Schlumberger

Parameter	Min	Max	Mean	SD.						
Location: Latitude $26^{\circ}27'05''$ N; Longitude $80^{\circ}16'18''$ E Site reference level: 119 m amsl; Average of 30 samples										
pH	7.90	8.51	8.10	0.13						
Conductivity $(\mu S/cm)$	81.7	317.0	160.6	53.8						
Chloride $(\mu g/g)$	30.0	100.1	46.4	14.75						
Fluoride $(\mu g/g)$	1.10	6.84	3.02	1.40						
Sulphate $(\mu g/g)$	56.20	162.00	138.60	21.32						
Phosphate $(\mu g/g)$	8.86	74.59	35.51	15.72						
Nitrate-N $(\mu g/g)$	8.53	57.78	19.60	11.27						
Nitrite-N $(\mu g/g)$	0.884	1.989	1.262	0.30						
Ammonia-N $(\mu g/g)$	0 <sub>0</sub>	294.0	91.0	69.2						
TOC $(\% )$	0.234	0.683	0.462	0.13						
Total Hardness (µg/g)	200.00	480.00	305.33	75.01						
Ca Hardness (µg/g)	140.00	300.00	212.67	54.45						
Mg Hardness $(\mu g/g)$	20.00	200.00	92.67	46.53						
Sodium $(\mu g/g)$	7.34	228.00	30.43	50.41						
Potassium (µg/g)	1.502	10.088	4.473	2.25						
Total Cr $(\mu g/g)$	15.130	51.913	31.248	8.74						
Hexa. Cr $(\mu g/g)$	0.217	4.226	1.039	0.82						

**Table 3.** Aquifer matrix characteristics

Location: Latitude 26°27'13" N; Longitude 80°16'00" E Site reference level: 120.460 m amsl: Average of 30 samples



configuration (Zohdy, 1989). The resistivity information has revealed that the sub-surface is stratified into three distinct layers viz. top soil underlain by sandy clay, sand and clay layers. The Fence diagram prepared for the area shows that the sandy clay as well as sand layers are wedge shaped and are not uniform (Fig. 3). At certain locations in the north eastern part of the area, only sandy clay and clay layers have been encountered.

## **Preparation of Conceptual Model for Mass Transport**

The preparation of conceptual model for (mass transport)



**Fig.3.** Fence diagram depicting the subsurface lithology of the area.

computation of dissolved chemical species in an aquifer at any specified time and space has been undertaken using Visual Modflow-pro ver.3.1 (Guiger and Franz, 1996; McDonald and Harbaugh, 1988; Zheng, 1990). While preparing the model for pollutant transport, it has been considered that the groundwater flow is generally governed by the relations expressed in Darcy's law and the conservation of mass. The theoretical basis for the equation describing pollutant transport has been well documented in the literature (Bear, 1972). Initial period in model simulation has been the period of anthropogenic input of chromium to the environment.

## **RESULT AND DISCUSSION**

The subsurface geological information (CPCB, 1997) furnished by lithologs of state and private tube-wells, reveal disposition of different aquifers. Geologically, the area is underlain by Indo-Gangetic alluvium of Quaternary age, formed by fluvial processes comprising of clay, silts, sands of various texture and kankar. The granitic bedrock sloping towards north by  $1^{\circ}$ -2° is encountered at 503-507 m bgl at Panki. The thickness of alluvium increases towards north (Singh and Bajpai, 1997). The deposits of sands are the main source of groundwater which occurs in unconfined to semi-confined conditions. The principal sources of natural recharge include infiltration after precipitation, stream-flow, tanks and reservoirs, recharge from excess irrigation water, seepage from unlined canals and water courses.

The three piezometers developed in the study area and their logs indicate that ground water exists in three distinct zones (sandy layers). The first zone exists at 8-12 m bgl followed by second clay layer at  $26 - 30$  m bgl and the third sandy zone at 42- 46 m bgl. Groundwater in these aquifer

zones occurs under unconfined and semi-confined to confined conditions.

The present study gives us sufficient data to confirm that the extent of chromium pollution of groundwater is confined in an area of about 4 to 5 sq km. In this affected area, there is a Core area surrounding earlier dump sites of approximately 1 sq km, which has reported high to very high concentration of Chromium (Fig.3). In the affected area, the concentration of hexavalent chromium has been mostly in the range of 0-2 mg/l, whereas, in the core area, the concentration increases up to 16.0 mg/l.



**Fig.4.** Spatial distribution of Cr (VI) in groundwater.

The concentration of chromium is present in all the three zones, however, the first and the third zones are significant. The maximum concentration of hexavalent chromium reported in the first, second and third zones have been 10.60 mg/l, 0.01 mg/l and 16.30 mg/l, respectively. Total chromium concentration in three zones has showed concentration of 21.78 mg/l, 1.51 mg/l and 32.20 mg/l respectively.

The groundwater flow and transport of hexavalent chromium in the subsurface regime in the study area has been simulated using a finite difference model using "Visual Modflow" (Guiger and Franz, 1996) software. The area measuring 2.7 km x 2.7 km has been divided into finite difference grids of 54 m x 54 m.

Based on the borehole logs of piezometers, fence diagram developed using electrical resistivity soundings, the aquifer system has been divided vertically into three layers. The first layer of the aquifer is hydraulically connected to a fresh water (Lower Ganga) canal in the east and River Pandu in the south. These two (perennial) water bodies have been assigned river boundaries.

The recharge to the aquifer varies spatially due to difference in soil type and distribution of rainfall. Boundary conditions have been established to represent, as closely as possible, the conceptual model of the flow system. The



**Fig.5.** Twenty five year perspective model for Total Chromium concentration in Ground water. (Depth w.r.t. Mean Sea Level).

hydraulic conductivity value of 35 m/day has been considered. Constant Chromium concentration of 16 mg/l was registered in the third aquifer at a depth of 45 m bgl. Mass transport for simulation of advection, dispersion and chemical reaction of contaminants in three dimensional groundwater flow system has been carried-out with the help of MT3D computer software. The above model has been calibrated with the groundwater quality data (CPCB, 1997) and validated for the known responses of the period 2005 and 2006.

The advective transport of the pollutant (Cr, VI) is expected to migrate to about 500 m southwest and may reach a depth of about 100 m within a span of 25 years with an average ground water velocity of 20 m / yr as per the present day calibrations (Fig. 5).

# **CONCLUSIONS**

The findings of the study reveal that the problem of chromium in groundwater in Nauriyakhera is mainly due to chromium dumps. The high content in the shallow and deeper zones and near absence in intermediate zones has been mainly due to assimilation in the intermediate clay layer. The inter-zonal variance in chromium content may be attributed to the dilution affect due to fresh water, localized lesser mobility of chromium in soil matrix and leaching of chromium impacted zone. A possible explanation may also be the sequential burial of waste having varying chromium concentrations.

The detailed monitoring of groundwater in terms of chromium and associated ions, their statistical interpretation

followed by digital depiction with reference to surface contours has revealed migration pathways of the pollutants. It has been observed that the resultant migration of groundwater with elevated chromium concentrations has been under the influence of local regime. Dominated by the perennial flow in the Ganga canal in the northeast, hydrostatic gradient and also due to the prevailing hydrodynamic conditions, the predominant migration has been mainly in the horizontal (southwesterly) direction, while the vertical migration being very minimal.

The area of highest chromium zone has been demarcated by interpreting elevated values. It has been conferred to a narrow zone located at Latitude 26°27.15' N and Longitude 80°16.218' E*.* The polluted zone is located at a shallow depth at about 35 to 40 m bgl. This zone may be considered for in-situ remediation either by plume interception or through geo-chemical transformation, apart from other options. Chemical transformation of the pollutant (Hexavalent chromium) in the area of study is likely to bring in an almost irreversible change of chemical state, i.e. from hexavalent chromium to trivalent chromium. The latter is relatively insoluble in water having a tendency to fix in the aquifer matrix.

Groundwater quality as revealed from deeper borings (tube wells) of depth beyond 80 m does not show any appreciable chromium (CGWB, 2000).

The ground characteristics and the regime's affect on the polluted leachate as revealed from modelling are indicative of vertical spread of pollution affect. It would be of great relevance especially in restricting development of deeper borings and excessive withdrawal of groundwater, thereby generating a cone of depression and magnifying the problem which now is of local nature and is of manageable proportions. The present study to understand the spatial distribution of the hexavalent chromium is likely to provide

basic guidelines while attempting an *in-situ* remediation of chromium in groundwater.

The findings and the first hand data generated during the present study can lead to further attempts as discussed below:

- Consider options for excavating and treating affected soil, including dilution of the polluted zone through relatively cost-effective rain water harvesting.
- Isolate the plume in order to restrict its interface with surface (rain) water, thus eliminating the formation of leachate and the migration/magnification of the polluted zone. In this process, assessment of the viability of introducing Reactive Barrier of 'zero valent' iron dust around the polluted site may be carried out.
- Assess options for checking chromium leaching through geo-chemical immobilization of the pollutant in groundwater as well as in the ground (soil). One option involves introducing (injecting) chemicals/gas  $(SO_2)$  into the site.
- The present study is likely to be a reference for similar attempts addressing groundwater remediation issues in general and prevailing problems due to heavy metal pollution in particular.
- $\bullet$  The migration of chromium plume monitored in the present study if not intercepted at the initial stages, is likely to magnify and further contaminate the ground water reservoirs posing a major threat to the entire living community of the area.

*Acknowledgements:* The authors acknowledge support and cooperation extended by Industrial Toxicology Research Centre, Lucknow, India. The grant from the Blacksmith Institute, New York, USA is also thankfully acknowledged.

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*(Received: 1 October 2008; Revised form accepted: 6 January 2009)*