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Health risk assessment of heavy metals in soil irrigated with paper mill effluent

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ABSTRACT

This study evaluates the health risk caused by selected heavy metals (Cr, Cd, Ni, Co, Pb) from the soils contaminated with paper mill effluent at Manikpara, India. The concentrations of heavy metals were measured using ICPMS and exposure parameters were used to estimate human carcinogenic and non-carcinogenic risks. The hazard index (HI) and hazard quotient (HQ) values for all the investigated heavy metals were less than 1, implying that there is no non-carcinogenic risk exposure from these heavy metals in soils for children and adults in the study region. The main exposure pathway of heavy metals for both children and adults was through ingestion. Among the studied heavy metals, the carcinogenic risks (CR) values for Ni and Cr in the ingestion pathway were higher than the safe value (1×10^{-6}) both for adults and children and has a descending order of Ni> Cr. The lifetime cancer risks (LCR) for Ni (1.75E-04) and Cr (1.54E-04) for children are higher than the LCR for Ni (3.14E-05), Cr (2.77E-05) for adults. This implies that children are at high cancer risk than the adults of this study area.

Keywords: Hazard index, hazard quotient, carcinogenic risks, lifetime cancer risks.

INTRODUCTION

With the progress of industrialization, significant environment deterioration results due to the discharge of untreated waste. Soils are the major sink for these wastes particularly in the vicinity of industrial areas (Jiang *et al.* 2017). Heavy metal accumulation in the soil is a severe environmental threat as they generally do not undergo chemical or microbial degradation for a long time (Kirpichtchikova *et al.* 2006). Thus heavy metals from the soil can be accumulated to the plants, animals, water bodies and finally entered into the human body through the different food chain (Khademi *et al.* 2019). Heavy metal contaminated soil may pose risks and hazards directly or indirectly on human health via ingestion, inhalation and dermal contact (Li *et al.*2014). The living organism requires a definite concentration of essential metals for the functioning of body organs exceeds which may cause toxicity. Cr (III) is an essential element but Cr (VI) compounds are known to be carcinogenic as long term exposure may cause liver and kidney damage (Shil and Pal 2018). Ni, on the other hand, known to cause cancer, hemorrhages and kidney problems (Cameron *et al.*2011). Cu toxicity may lead to liver damage (Nolan, 2003) whereas Zn causes impairment of growth and reproduction (Cao *et al.* 2010).Some other metals with definite oxidation state show toxicity to the human at a particular concentration (Lane and Morel, 2009). Pb is a carcinogen, it induces renal tumors, disturbs the normal functioning of kidneys, joints, reproductive and nervous systems (Ogwuegbu and Muhanga, 2005). Cd is regarded as a carcinogen even at low concentration. Chronic exposure to Cd may result in pulmonary effects, kidney dysfunction and hypertension (Khan *et al.* 2013).

In recent years several studies have been carried out about the heavy metal contamination, their source and distribution pattern on the soil contaminated with the paper mill effluent (Reza *et al.* 2015, Manskinen *et al.* 2011) but an assessment of human health risks are scarce in the literature. The solid waste from the paper mill along with the fly ash accumulates in the nearby soil may also increase the content of heavy metals along with other rare earth elements (Das 2019). Soils near the paper mill waste disposal site displayed higher heavy metal content (Phukan *et al.* 2003). Plants grow in the soil affected with the paper mill effluent shows different content of heavy metals in their different parts (Kumar *et al.* 2015, Borah *et al.* 2017). Therefore, the health of the people residing at the vicinity of paper mill waste disposal site may also be affected with the heavy metals present in the soil and hence human health risk assessment is essential. No studies were executed pertaining to the human health risk assessment associated with the heavy metals in the soil affected with the paper mill effluent at Manikpara. The present study was conducted to evaluate the potential impact on human health risks of selected heavy metals (Cr, Cd, Zn, Pb, Ni, Cu) for both adults and children via ingestion, inhalation and dermal contact in the study region.

MATERIALS AND METHODS

Soil samples irrigated with the paper mill effluent at Manikpara, West Bengal (22^0 $22^'$ N, 87^0 $7^'$ E) at depth 0-15 cm (topsoil) were collected for analysis. Four sampling sites were chosen with a distance of 1 km, 750m, 500m and 250m from the paper mill. The control site (uncontaminated) was located at 3 km from the paper mill. All the prepared (0.05g) soil samples were digested using a mixture of supra pure (3:1) 24 M hydrofluoric acid: 14M nitric acid on a hot plate at 120 °C for two days then evaporated with two repetitions. The metal content of the soil was determined on a Thermo Fisher Scientific iCAP-Q quadrupole Inductively Coupled Plasma Mass Spectrometer (ICPMS) by the method of Das (2019). Statistical analysis was conducted with SPSS 21.0 and Origin Pro 8.5.0 (OriginLab, Northampton, MA, USA).

Health risk assessment of heavy metals in soil: Health risk assessment is an effective model developed to estimate the human health effect that might results from exposure to carcinogenic and non-carcinogenic chemicals (Narsimha and Rajitha 2018). Generally, the human body is exposed to the metals present in the soil through ingestion, inhalation and dermal contact pathways (Deng *et al.* 2019). The chronic daily exposure dose (CDD: mg/kg/day) of toxic metals via ingestion, inhalation and dermal contact for both adult and child may be computed using equation 1,2,3, respectively (US EPA 1989, 2002):

$$CDD_{Ingestin} = \frac{C \times IR_{ing} \times ED \times EF}{BW \times AT} \times CF \text{ .... (1)}$$

$$CDD_{Inhalation} = \frac{C \times IR_{inh} \times ED \times EF}{BW \times AT \times PEF} \text{................ (2)}$$

$$CDD_{Dermal} = \frac{C \times SA \times SAF \times DAF \times ED \times EF}{BW \times AT} \times CF \text{..... (3)}$$

Where, CDD is the chronic daily dose (mg/kg/day), C is the concentration of metal in soil (mg/kg), IR_{ing} and IR_{inh} are the ingestion and inhalation of metal in soil, respectively (mg/day), ED is the exposure duration (year), and EF is the exposure frequency (day/year). BW and AT represent the average body weight (kg) and the average exposure time period (year), respectively. CF is the conversion factor (10^{-6} kg/mg), SA is the exposed skin surface area (cm2), SAF is the skin adherence factor (kg/cm^2 day), DAF is the dermal absorption factor, and PEF is the particle emission factor (m^3/kg). All the exposure factors and values used to estimate the chronic daily dose (CDD) are listed in Table 1. Risk assessments predict quantitatively the potential cancerous and non-cancerous health risk of children and adults in any study area.

Table 1: Reference values of parameters for health risk assessment of heavy metals in soils affected with Paper mill effluent

Factor	Unit	Adult	Children	Reference
IR_{ing}	mg/day	100	200	USEPA (1989, 2002)
IR_{inh}	m^3/day	12.8	7.63	USEPA (2002)
ED	years	30	6	,,
EF	days/year	365	365	,,
CF	kg/mg	10^{-6}	10^{-6}	,,
BW	kg	70	20	Narsimha and Rajitha (2018)
AT	years	8760	2190	USEPA (2002)
SA	cm^2	4350	1600	,,
SAF	mg/cm^2	0.7	0.2	,,
DAF	-	0.001	0.001	,,
PEF	mg^3/kg	1.36×10^9	1.36×10^9	,,

Non carcinogenic risk assessment: Non-carcinogenic risks are characterized by a term Hazard quotient (HQ), which is a unitless number and is defined as the ratio of chronic daily dose(CDD) and the reference dose (R_fD) for a given substance (USEPA 1989) as:

$HQ = \frac{CDD}{R_f D}$ .... (4)

The R_fD is the reference dose (mg/kg/day) for a particular element (Table.2).
The hazard index (HI) indicates the total risk of non carcinogenic elements via different pathways for a particular element which is computed as the summation of HQs as:

$HI = (HQ_{ing} + HQ_{inh} + HQ_{der})$ .... (5)

$HQ_{ing}, HQ_{inh}, HQ_{der}$ are the hazard quotient of ingestion, inhalation and dermal pathways, respectively. Generally the value of HQ < 0.2 is considered acceptable and the value of HQ> 0.2 is considered unacceptable (Johnbull *et al.* 2019). Similarly the value of HI >1 (from various pathways) is considered unacceptable, which indicates that the exposed population may experience adverse health effect and risk management measures should be implemented while the value of HI < 1 indicates no risk of non-carcinogenic effects is believed to occur (USEPA 1989).

Table2: Reference dose (mg/kg/day) and Cancer slope factor (mg/kg/day) of some heavy metals

Metal	Reference dose (R_fD)			Reference	Slope factor (SF)		
	Ingestion	Inhalation	Dermal		Ingestion	Inhalation	Dermal
Cr	3.00E-03	2.86E-05	3.00E-03	USEPA 1989	5.01 E -01[a]	4.20E+01[a]	2.00E+01[a]
Co	2.00E-02	5.70E-06	5.70E-06	Kamunda *et al.*2016	-	9.80E+00[b]	-
Ni	2.00E-02	2.06E-02	5.40E-03	USEPA 1989	1.70E+00[a]	8.40E+01[b]	4.25E+01[a]
Cd	1.00E-03	1.00E-03	2.50E-05	USEPA 1989	-	6.30E+00[a]	-
Pb	1.40E-03	3.52E-03	5.24E-04	USEPA 1989	8.50E-03[a]	4.20E-02[d]	8.50E-06[c]

[a]USEPA 1989, [b]Lu et al. 2014, [c]Johnbull et al. 2019,[d]Kamundaet al. 2016

Carcinogenic risk assessment: The carcinogenic risk is estimated as the possibility of an individual developing any type of cancer over a lifetime as a result of exposure to a potential carcinogenic environment. The carcinogenic risk (CR) for an individual heavy metal over a lifetime is expressed as CR = CDD × SF ... (6)

LCR = ∑ CR (ingestion + inhalation + dermal)............. (7)

Where, SF is the slope factor (mg/kg/day) (Table.2), LCR is the lifetime cancer risk. The acceptable threshold value of CR = 1.0E-04, while the tolerable range for LCR is 1.0E-04 to 1.0E-06 (USEPA 2001).

RESULTS AND DISCUSSION

The mean concentration of heavy metals in the surface soil followed a generalized decreasing order: Cr>Ni>Pb>Co>Cd indicating distinct changes in the concentration (Table 3). The concentrations of all the heavy metals were higher than the control (uncontaminated) site. This indicated that the soils were sufficiently polluted with these heavy metals. The coefficient of variation of heavy metals (%CV) of the surface soils of different locations decreased in the order: Pb>Co>Cr>Ni>Cd. This low value of CV indicated that the concentration of heavy metals did not vary greatly with respect to different sampling locations as the study was conducted in the area within 1 km radius from the paper mill. The skewness of Ni and Pb indicated that these metals positively skew towards lower concentrations whereas other metals negatively skew towards relatively lower concentrations. The presence of Cr in +3 and +6 oxidation states can cause a hazard to the natural environment although it has oxidation state varying from -2 to +6 (Adriano *et al.* 2001). Chromium level in the study area varied from 35.25 ppm to 23.57 ppm, with an average value of 30.65 ppm exceeding the maximum permissible limit (Table 3). The mean concentrations of other heavy metals present in the soil were below the maximum permissible limit. Since soils are originally derived by the rocks consists of different metals with varying concentrations (Morgan 2012). Any deviation in the distribution of metal concentration from the original value in the soil may be expected due to the anthropogenic activity (Zhao *et al.* 2019). Coal fly ashes, green liquor dregs, slaker grits, lime mud derived from the pulp and paper mills are the main source of heavy metals along with other organic pollutants (Monte *et al.* 2009). So without proper treatment of the paper mill effluent may cause to increase the content of heavy metal in the discharged soil. The solid sludge generated by the wastewater treatment process used in the pulp and paper industry also contains heavy metals (Ashrafi *et al.* 2015).

Table3: Descriptive statistics of Soil heavy metal concentration (ppm) and comparison with the soil of South Africa

	Cr	Co	Ni	Cd	Pb
Min	23.57	2.72	8.81	0.08	3.45
Max	35.25	6.50	12.54	0.12	10.01
Mean	30.65	4.75	10.29	0.11	6.06
SD	5.00	1.56	1.67	0.01	2.95
Skew	-1.32	-0.53	1.02	-1.20	0.99
Kurt	2.25	1.54	0.001	1.82	-0.11
%CV	16.33	32.77	16.24	15.85	48.62
Range	11.68	3.78	3.73	0.04	6.56
PL[a]	6.50	300	91	7.5	20
Control	5.030	1.27	4.77	0.05	0.64

Human health risk assessment

Non-carcinogenic health risks

The risk assessment of some selected heavy metals such as Cr, Co, Cd, Pb and Ni in the affected surface soils through possible exposure pathways: ingestion, inhalation and dermal were executed for adults and children. The HQ values for adults and children were calculated based on the R_fD values and the average chronic daily dose (CDD) value of each element are represented in Table 4. In risk assessment, the calculated HQ and HI values were below 1, indicating that adults and children were not at risk of any non-carcinogenic effects from these heavy metals. HQ values both for adults and child follows the following order in different pathways (ingestion, inhalation and dermal): $HQ_{ing}: Cr > Pb > Ni > Co > Cd$, $HQ_{inh}: Cr \approx Co > Pb > Ni > Cd$, $HQ_{der}: Co > Cr > Pb > Ni \approx Cd$

Table 4: Non-carcinogenic risks through ingestion, inhalation and dermal pathways of adults and children in the study region

Metal	Adults				Child			
	HQ_{ing}	HQ_{inh}	HQ_{der}	HI	HQ_{ing}	HQ_{inh}	HQ_{der}	HI
Cr	1.82E-02	1.79E-04	5.56E-04	1.89E-02	1.02E-01	3.01E-04	1.63E-04	1.02E-01
Co	4.24E-04	1.4E-04	4.52E-02	4.58E-02	2.37E-03	2.34E-04	1.33E-02	1.59E-02
Ni	9.19E-04	8.39E-08	1.03E-04	1.02E-03	5.14E-03	1.4E-07	3.04E-05	5.17E-03
Cd	1.88E-04	1.76E-08	2.29E-04	4.17E-04	1.05E-03	2.95E-08	6.73E-05	1.11E-03
Pb	7.72E-03	2.89E-07	6.29E-04	8.35E-03	4.32E-02	4.83E-07	1.85E-04	4.34E-02

The hazard quotient (HQ) of Cr is higher than other heavy metal in all the three pathways except dermal contact. This may be due to the lowest R_fD value (5.70E-06 mg/kg/day) of Co among the other studied metal. As R_fD (ingestion) of Pb < R_fD (ingestion) of Ni the order of HQ_{ing} and HQ_{der} for Pb > Ni. The HI values of the child are greater than the adults for all the metals except Co (Fig.1). This is due to the high value of HQ for adults in both ingestion and dermal pathways for the heavy metal of Co. This indicates that the children are believed to be the most prone to non-carcinogenic effects of these heavy metals.

Carcinogenic Health risks

The lifetime cancer risks (LCR) for adults and children were calculated separately from the average contribution of the individual heavy metals in the investigated soil for all the pathways using Equations (6) and (7) and was plotted Fig.2 and Fig.3. Among the three different pathways (ingestion, inhalation and dermal), only the ingestion pathway contributed more towards the carcinogenic risks. The LCR values of Cr and Ni via ingestion exceeded the safety limit of (1E-06) but in inhalation and dermal pathways, the LCR value of these two metal was below the safety limit both for adults and the child. The LCR values of Cr and Ni for adults via the ingestion pathway were 2.77E-05

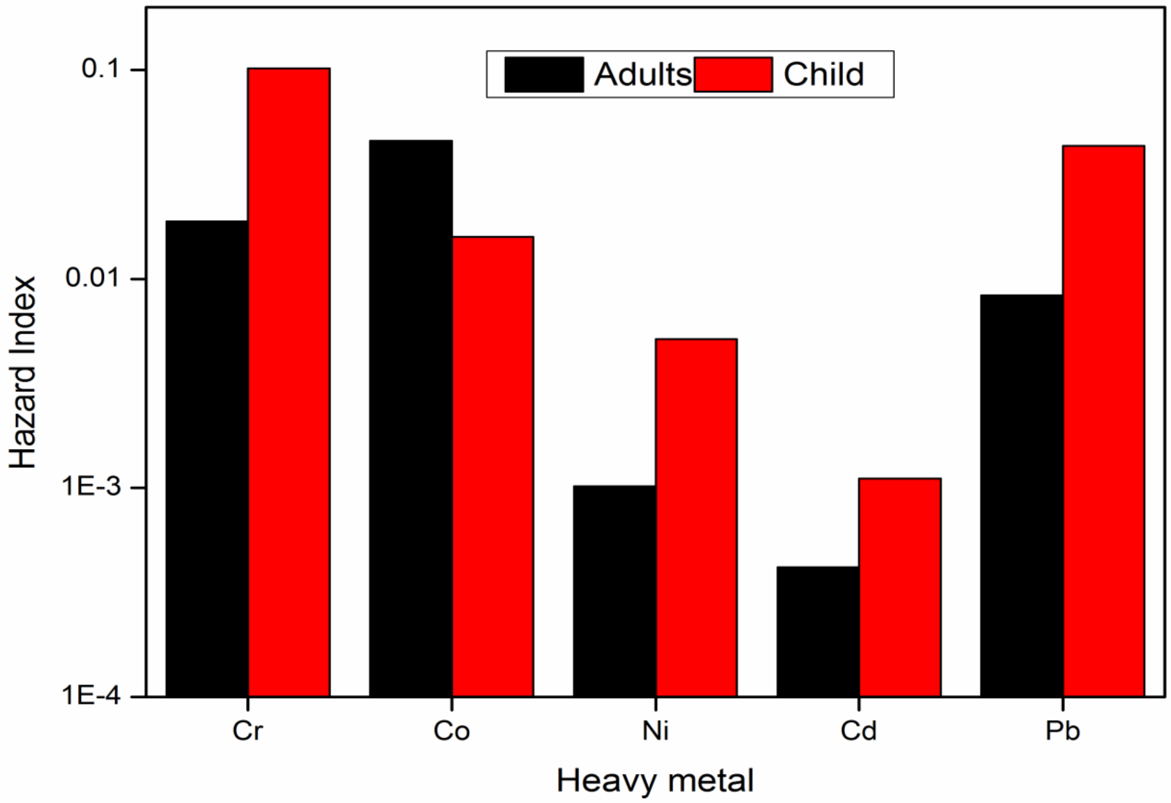

Fig.1 Hazard index (HI) of heavy metals in the topsoil around the paper mill.

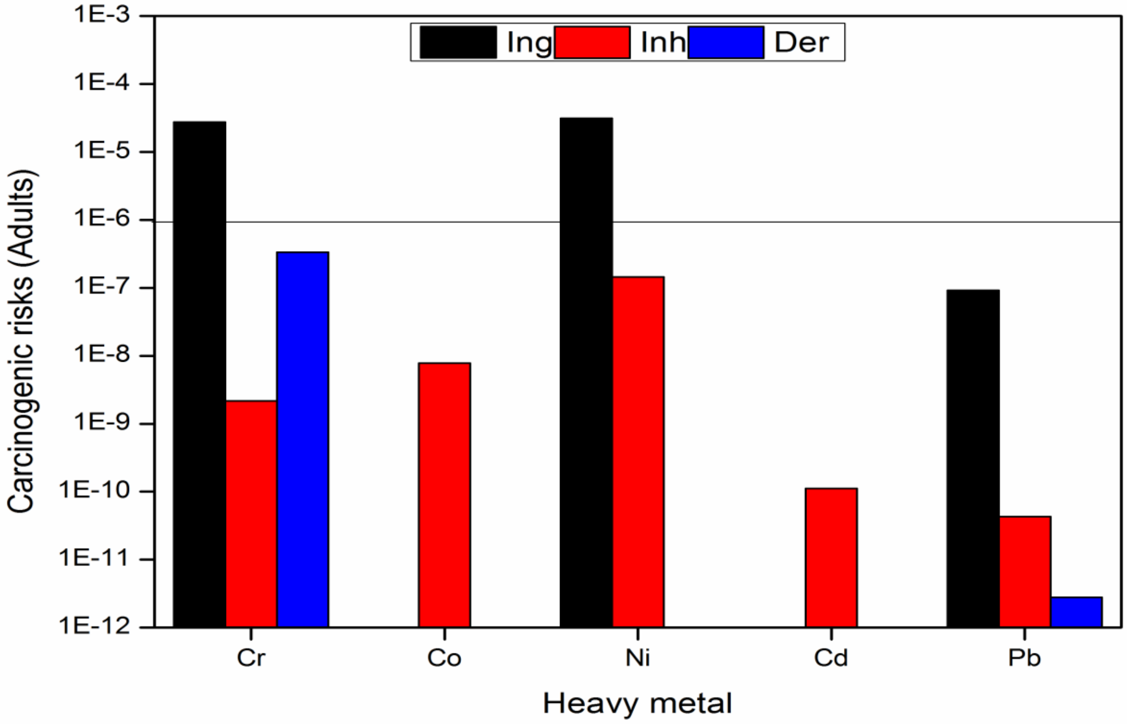

Fig. 2 Carcinogenic risks of heavy metals for adults in soils from paper mill effluent

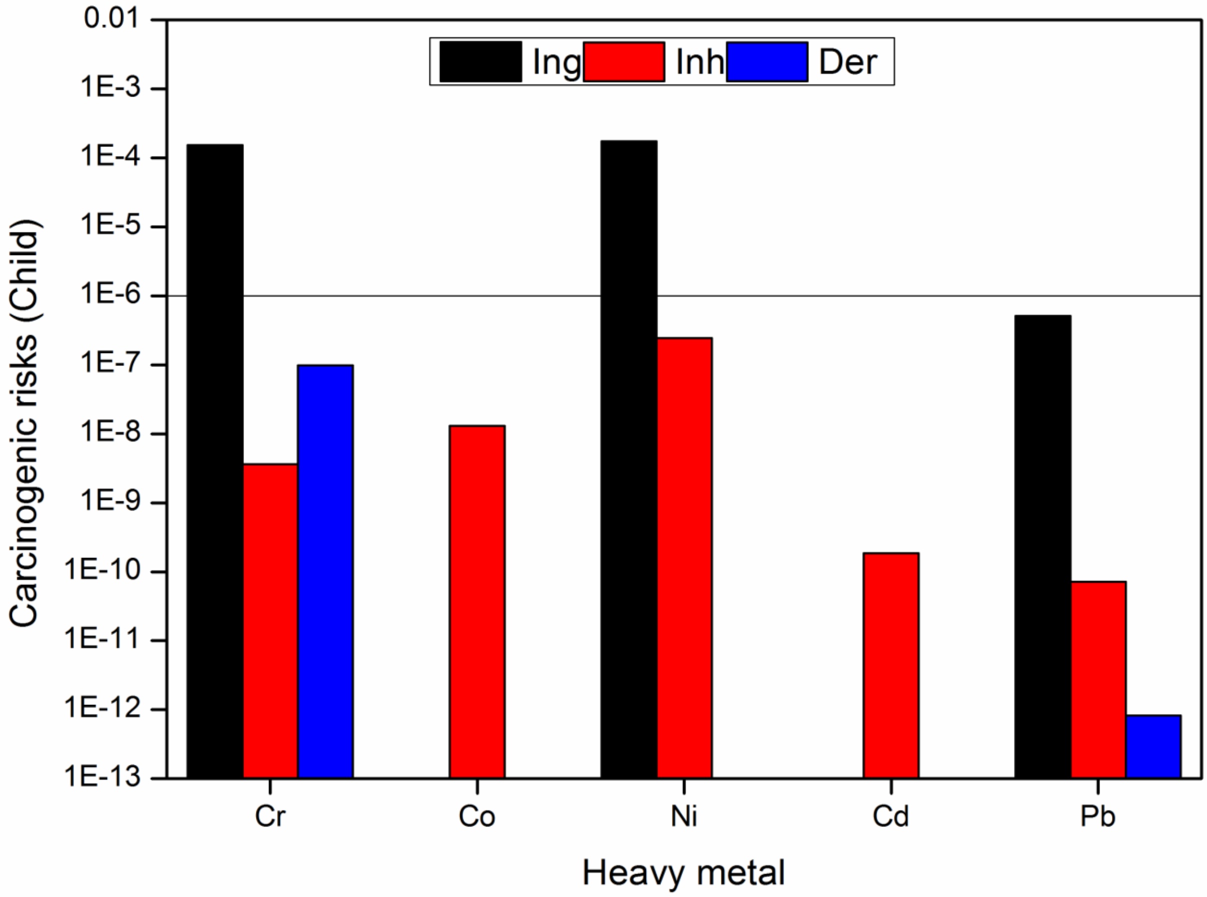

Fig.3 Carcinogenic risks of heavy metals for child in soils from paper mill effluent

and 3.14E-05, respectively whereas the corresponding values for the child were 1.54E-04 and 1.75E-04, respectively (Fig.5). This suggests that there may be a potential health risk associated with Cr and Ni metal via the ingestion pathway of both adults and children in this area. For other studied metals, the LCR values were below the threshold of 1E-06. This indicates that no risks of carcinogenic effect for Pb, Cd and Co for the adults and child in this region are believed to occur. The high LCR value for Cr and Ni compared to the other studied metals may be due to their presence in higher concentration in the affected soil. These results are very similar to the findings of Doabi *et al.* (2018).

From the results it can be concluded that the average heavy metal concentration in soils affected with the paper mill effluent varied significantly and decreased in the order of Cr>Ni>Pb>Co>Cd. Only Cr crosses the maximum allowable limits compared to the other studied heavy metals. The results indicated that, in both adults and children, the ingestion pathway was the greatest contributor to the non-carcinogenic risk followed by the dermal and inhalation pathway for all the metals except Co. For the carcinogenic effect, the ingestion pathway contributed the most to cancer risk followed by the dermal and inhalation pathway in both adults and children. Children are more at cancerous risk than adults in the study area for Cr and Ni. The quantitative evidence demonstrates the critical need to monitor the treatment of the effluent and solid waste generated from the paper mill and their discharge to protect the residents, especially the children from the heavy metal pollution in the environment.

REFERENCES

Adriano. D.C (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals, 2nd edition. SpringerVerlag, New York.

Ashrafi.O., Yerushalmi.L., Haghighat.F (2015) Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management***158**:146-157

Borah. P., Paul. A., Bora. P., Bhattacharyya.P., Karak.T., Mitra.S (2017) Assessment of heavy metal pollution in soils around a paper mill using metal fractionation and multivariate analysis. *International Journal of Environmental Science and Technology***14**(12):2695-2708

Cameron K.S., Virginia Buchner.V. and Tchounwou.P.B (2011) Exploring the Molecular Mechanisms of Nickel-Induced Genotoxicity and Carcinogenicity: A Literature Review. *Reviews on Environmental Health***26**(2): 81–92

Cao, H.; Chen, J.; Zhang, J. (2010)Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China.*Journal of Environmental Science***22**: 1792–1799

Das. T.K. (2019) Variation of REE content in the soil affected with the Paper Mill waste at Manikpara, Jhargram, India. *International Journal of Scientific Research and Reviews* **8**(2): 3853-3865

Das. T.K. (2019) Assessment of heavy metal contamination in soils irrigated with paper mill effluent in West Bengal, India. *Annals of Plant and Soil Research***21**(4): 312-319

Deng, Y., Jiang, L., Xu, L., Hao, X., Zhang, S., Xu, M., *et al.* (2019). Spatial distribution and risk assessment of heavy metals in contaminated paddy fields—A case study in Xiangtan City, southern China. *Ecotoxicology and Environmental Safety* **171**: 281–289

Doabi , S. A., Karami. M., Afyuni M, Yeganeh M (2018) Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran. *Ecotoxicology and Environmental Safety***163**: 153-164

Jiang, Y., Chao, S., Liu, J., Yang, Y., Chen, Y. and Zhang. A (2017) Source apportionment and health risk assessment of heavy metals in soil for a township in Jiangsu Province, China. *Chemosphere***168**: 1658–1668.

Johnbull. O., Abbassi.B., ZytnerR.G (2019)Risk assessment of heavy metals in soil based on the geographic information system-Kriging technique in Anka, Nigeria. *Environmental Engineering Research* **24**(1): 150-158

Kamunda.C.,Mathuthu.M., Madhuku. M (2016) Health risk assessment of heavy metals in soils from Witwatersrand Gold Mining Basin, South Africa. *International Journal of Environmental Research and Public Health***13** (663): 1-11

Shil.K., Pal. S (2018) Metabolic adaptability in hexavalent chromium-treated renal tissue: an *in vivo* study. *Clinical Kidney Journal* **11**(2): 222–229

Khan, K., Lu, Y., Khan, H. (2013)Heavy metals in agricultural soils and crops and their health risks in Swat District,northern Pakistan. *Food and Chemical Toxicology***58**: 449–458.

Khademi, H., Gabarro´n, M., Abbaspour, A., Martı´nez-Martı´- nez, S., Faz, A., Acosta, J. A. (2019) Environmental impact assessment of industrial activities on heavy metals distribution in street dust and soil. *Chemosphere***217**:695–705.

Kirpichtchikova. T.A., Manceau. A., Spadini.L., Panfili.F., Marcus.M.A., Jacquet.T (2006) Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modelling. *Geochimica et Cosmochimica Acta* **70** : 2163–2190

Kumar.V., Chopra. A.K., Kumar. S., Singh. J., Thakur. R.K. (2015) Effects of pulp and paper mill effluent disposal on soil characteristics in the vicinity of Uttaranchal Pulp and Paper Mill, Haridwar (Uttarakhand), India.*International Journal of Agricultural Science Research* 4 (6): 117-125

Lane, T.W., Morel, F.M. A biological function for cadmium in marine diatoms (2009) *Proceedings of the National Academy of Sciences of the United States of America***9**: 462-431.

Li P, Qian H, Howard KWF, Wu J, Lyu X (2014) Anthropogenic pollution and variability of manganese in alluvial sediments of the Yellow River, Ningxia, northwest China. Environ Monit Assess **186**(3): 1385–1398.

Lu.X., Zhang. X, Li. L.Y, Chen. H (2014) Assessment of metals pollution and health risk in dust from nursery schools in Xi'an, *China Environmental Research***128**:27–34

Manskinen. K., Nurmesniemi.H., Pöykiö. R(2011) Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semi-chemical pulp mill**.***Chemical Engineering Journal* **166:** 954-961

Monte, M.C., Fuente, E., Blanco, A., Negro, C. (2009) Waste management from pulp and paper production in the European Union.*Waste Management***29** (1): 293-308

Morgan, R. (2012). Soil, heavy metals, and human health.*Soils and Human Health,* 1st edition, CRC Press pp 59–82

Narsimha A, Rajitha S (2018) Spatial distribution and seasonal variation in fluoride enrichment in groundwater and its associated human health risk assessment in Telangana State, South India. *Human and Ecological Risk Assessment: An International Journal24:2119*–2132

Nolan, K. (2003) Copper toxicity syndrome. *Journal of Orthomolecular Psychiatry***12**: 270–282

Ogwuegbu, M.O.C., Muhanga, W. (2005) Investigation of lead concentration in the blood of people in the copper belt province of Zambia. *Journal of Environment***1**:66–75.

Phukan.S. and Bhattacharyya. K.G., (2003) Modification of Soil Quality Near a Pulp and Paper Mill.*Water, Air, and Soil Pollution***146** (1-4):319-333

Reza.S.K., Baruah. U., and Singh. S.K. (2015) Accumulation and Translocation of Heavy Metals in Soil and Crop Irrigated with Paper Mill Effluents. *Journal of the Indian Society of Soil Science***63**(2): 242-244

USEPA (1989) Risk assessment guidance for superfund.Human health evaluation manual (Part A) (Vol. 1). Washington, DC: Office of Emergency and Remedial Response.

USEPA (2001) Supplemental guidance for developing soil screening levels for superfund sites. OSWER, Washington, DC.

USEPA (2002) Supplemental guidance for developing soil screening levels for superfund sites. Washington: U.S. Environmental Protection Agency, Office of Emergency and Remedial Response.

Zhao, K., Fu, W., Qiu, Q., Ye, Z., Li, Y., Tunney, H., *et al.* (2019)Spatial patterns of potentially hazardous metals in paddy soils in a typical electrical waste dismantling area and their pollution characteristics. *Geoderma* **337**: 453– 462.