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INFLUENCE OF BELL-METAL INDUSTRY ON THE CONCENTRATION AND SPECIATION OF LEAD (PB) IN THE PLAYGROUND SOIL OF KHAGRA, WEST BENGAL

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ABSTRACT

Total 48 samples were collected from 16 different playground soil in Khagra, West Bengal. The samples were analyzed for potential toxic element Lead (Pb). The mean total concentration of Pb in the playground soil samples was 63.7 ± 144.7 mg kg^{-1}. Site 13 which is surrounded by bell metal industry, indicated very high contamination due to Pb. Sequential speciation was performed for Pb to evaluate the bio-available fraction. Pb was mostly associated with Fe-Mn oxide phase (F3). Mean mobility factor (MF) for Pb in playground soil of Khagra was 61.1%. Geo-chemical indices such as Enrichment Factor (EF), geo-accumulation index (Igeo) and contamination Factor (CF) were stated moderate pollution level. Ecological risk indicated maximum risk in site 13. The non-carcinogenic health risks of Pb was calculated with mobile fraction, which indicated actual risk due to PTEs was less (HI<1). Mobile fractions of PTEs must be considered for routine risk assessment.

Keywords: Playground, Lead, Geo-accumulation indices, Mobility Factor, Ecological Risk, Health Risk

INTRODUCTION

Over the last few decade a numerous number of research work have been carried out to investigate the exposure of children to urban playground soil particulate since the children were exposed to potentially toxic elements (PTEs) in recreational areas (during playing at school recess and in public playgrounds after school) (Reisa et al., 2014; Okorie et al., 2011; Costa et al., 2012). Soils in playgrounds were subjected to both geogenic as well as anthropogenic depositions of PTEs from rock weathering, soil erosion and road construction (e.g., asphalt, concrete and road paint), vehicular or non-vehicular exhaust (e.g., tire and brake wear and tear, body rust and tail pipe exhaust), industrial inputs and atmospheric depositions (Adachi and Tainosho, 2005).Soil assists as both a sink and a source for soil borne contaminants in the terrestrial environment. Excessive accumulation of PTEs in topsoil of urban playground soils may consequence of not only in PTEs contamination to the soils but also augmentation of human exposure to those PTEs due to their close vicinity to human activities (Sun et al., 2010).

Presence of high concentrations of Pb in urban soils had become a potential threat to children because Pb had become widely distributed in the urban environment through different anthropogenic activities (Laidlaw and Taylor, 2011). Ingestion of soil borne contaminants was an important route of exposure to environmental contaminants in children which deliberate hand-to-mouth movements, or unintentionally by eating food that has dropped on the floor (US EPA, 2011). Children absorb higher percentages of PTEs through the digestive system into the blood stream than adults (Oomen, 2000). In addition, presence of high concentration of lead (Pb) and prenatal exposures to relatively low levels of Pb (e.g. geometric mean value of 80 mg kg^{-1}) may cause chronic health effects, such as disturbances to cognitive development and damage to the central nervous system in children (Johnson and Bretsch, 2002; Elhelu et al., 1995). Subsequently for children, ingestion of soil particle was reflected a major exposure pathway for Pb, absorption and harmfulness of ingested Pb had been studied extensively (Oomen, 2000).

The present study was therefore conducted to investigate of 16 Pb polluted soil that accumulate on outdoor playground surfaces in urban areas of Khagra. The objectives of this study were to: 1) measure total and bioavailable Pb using sequential extraction, 2) determine contamination status of Pb using different pollution indices, 3) assess potential non-carcinogenic health risk. Thus, present study may help to develop methodology to predict Pb bioavailability during risk assessment of Pb-contaminated soils.

MATERIALS AND METHODS

Study area, sampling and sample preparation

Khagra is a major commercial town since the medieval period famous for its bell metal and brass utensils and have a traditional demand in local markets and some are also exported. The bell metal industry in Khagra is a cottage industry, where 100% of the work is handmade, where no machine is used. The main raw material used by the industry are coal, clay, wax, castor oil, firewood, coconut shells, coconut husk, and cow dung. Besides metal industries highway, ferry, tourist spot is also there in present study area. Khagra is neighbourhood of Berhampore in Murshidabad (Fig. 1) district on the East bank of the Bhagirathi-Hooghly River. This area is frequently flooded by the river Bhagirathi, a tributary of river Ganga.

Top soil samples (0-20cm) were collected through stainless steel corer in the playground from sixteen locations at Khagra (Fig. 1) during pre-monsoon season i.e. February, 2014. A total of 48 soil samples (3 samples from each playground) were collected from different playground within the city of Khagra, Berhampore. Three randomly collected samples from each playground were homogenized and made a composite sample. After collection of soil sample, were dried in hot air oven at <40°C.

Sequential Extraction

In case of digestion and extraction for total PTEs did not deliver enough information about degree of contamination and availability of that PTEs to biological substances. Sequential extraction was used to assess the metal fractions, which could be associated to chemical species, as well as to potentially mobile, bioavailable or eco-toxic phases of a sample (Jena et al., 2013). The sequential extraction (Tessier et al., 1979) was employed to partition Pb in the playground soil into five fractions: exchangeable (F1), bound to carbonate phase (F2), bound to Fe-Mn oxides (F3), bound to organic matter (F4), and residual (F5). Sequential extraction was achieved to govern the mobility of potentially mobile fractions of the Pb. The sequential extraction process includes treatment of a soil sample with a sequence of reagents having a different chemical properties in order to partition the PTEs (Rao et al., 2008).

Assessment of contamination and ecological risks

Assessment of contamination was performed by the calculation of enrichment factor, geo-accumulation index, contamination factor and ecological risk.

Geo-accumulation index

$$I_{geo} = \log_2(C_i \;/\; 1.5 \times B_{ref})$$

Where C_i is the measured concentration of element and B_{ref} is the natural background concentration. The index of geoaccumulation index (I_{geo}) was used as a measure of metal concentration (Bai et al., 2008). The factor of 1.5 is a background matrix correction factor that includes possible variations of the background values due to lithogenic effects.

Enrichment factor (EF)

$$\mathrm{EF} = \frac{{C_i}/{C_{ref}}\ of\ Sample}{{B_i}/{B_{ref}}\ of\ background}$$

The EF for each element was calculated to evaluate the anthropogenic influences on heavy metals using the previous formula suggested by Kim and Kim (1999), Zhuang and Gao (2014) and

Mohammad et al. (2015). C_i is the concentration of samples B_i is the concentration of the background, respectively, while $C_{ref}$and B_{ref} are used to normalize the heavy metals. The crustal elemental concentration used in this study is replaced by soil background values that remove the effects of natural geochemical variability (Zhang et al., 2012).

Contamination factor

A contamination factor (C_f^i) to describe the contamination of a given toxic substance in a lake or a sub-basin suggested by Håkanson (1980) is

$$C_f^i = \frac{C_i}{C_{ref}}$$

According to Cabrera et al., (1999), C_i is the content of metal *i* instead of mean content from at least 5 sample sites; $C_{ref}$is the reference value or baseline level value. The level of contamination according to their value (Tomlinson et al., 1980; Mohiuddin et al., 2010) such as, C_f^i<1 represents low contamination, 1 ≤ C_f^i< 3 as moderate contamination, 3 ≤ $C_f^i \leq 6$ as considerable contamination and C_f^i> 6 as very high contamination respectively.

Ecological risk factor

An ecological risk factor (*Eri*) to quantitatively express the potential ecological risk of a given contaminant also suggested by Hakanson (1980) is

$$Er^i = Tr^i . C_f^i$$

Where Tr^i is the toxic-response factor for a given substance, and C_f^i is the contamination factor. The Tr^i value (5) of Pb was given by Hakanson (1980). The following terminologies are used to describe the risk factor: Er^i<40, low potential ecological risk; 40≤ Er^i<80, moderate potential ecological risk; 80≤ Er^i<160, considerable potential ecological risk; 160≤ Er^i<320, high potential ecological risk; and Er^i ≥320, very high ecological risk.

Mobility Factor (MF)

The mobility factor (MF), for Pb in soil was determined by using the following equation (Narwal and Singh, 1998):

$$MF = [(F1+F2+F3) / \sum F] \times 100$$

Here F1, F2, F3, F4 and F5 are the concentration of elements in exchangeable, carbonates, Fe-Mn oxides, organic matter and residual fractions respectively.

Human health risk assessment

The health risk assessment was employed to investigate the probability, occurrence and importance of the contaminants and their connections, which is the relationship between a contaminant, pathway, and the receptor. Probable health risk assessment of urban playground soil is extensively used to enumerate both carcinogenic and non-carcinogenic hazards to human via three exposure pathways i.e., ingestion, inhalation and dermal contact. This approach employed for the health risk assessment was established on the guidelines and Exposure Factors Handbook of US Environmental Protection Agency (USEPA 1989; 2001). The average daily intake (ADI) of PTEs through those pathway was calculated as the following equations,

$$ADI_{ing} = A_m \times \frac{R_{ing} \times F_{exp} \times T_{exp}}{ABW \times T_{avg}} \times 10^{-6}$$

$$ADI_{inh} = A_m \times \frac{R_{inh} \times F_{exp} \times T_{exp}}{PEF \times ABW \times T_{avg}}$$

$$ADI_{dermal} = A_m \times \frac{SAF \times DAF \times A_{skin} \times F_{exp} \times T_{exp}}{ABW \times T_{avg}} \times 10^{-6}$$

Where ADI_{ing}, ADI_{inh}, ADI_{dermal}, are the average daily intake (mg Kg−1 day^{-1}) through ingestion, inhalation and dermal contact respectively. Exposure factors (in equation) and values used to estimate are given in Table 1. In this present study, non-carcinogenic health effects of PTEs were evaluated using the hazard quotient (HQ), hazard index (HI) through following equation,

$$HI = \sum HQ = \sum \frac{ADI}{RfD}$$

The HQ is the ratio of the ADI (ADI_{ing}, ADI_{inh}, ADI_{dermal}) of a PTEs to its reference dose (RfD) for the same exposure pathway(s) (USEPA 1989). The reference dose (RfD) (mg Kg−1 day^{-1}) is the maximum daily dose of a PTE from a specific exposure pathway, for both children and adults, that is assumed not to lead to an considerable risk of toxic effects to sensitive individuals throughout lifetime (Qing et al. 2015). The hazard index (HI) is the sum of hazard quotient (HQ) and depicted of the total risk of non-carcinogenic PTEs through exposure pathways for single PTE. If the value of HI<1, no risk of non-carcinogenic effects is supposed to happen, whereas HI>1 specified a possibility of adverse health effects, and likelihood to increase with the increase of HI values (US EPA, 1989, 1996; Kumar et al. 2014; Qing et al. 2015).

Instrumentation

PTE (Pb) content in the playground soil samples were analyzed by Inductively Coupled Plasma–Optical Emission Spectroscopy (iCAP 6300 Duo; M/s Thermo Fisher Scientific, UK). After every tenth sample during analysis, the calibration standards were analyzed to check the analytical accuracy. Blank reagent and standard reference material were analyzed intermittently, to verify the accuracy and precision of the digestion procedure.

Statistical analysis

All graphs were prepared with the Microsoft Excel 2013 and Origin pro 8 statistical package. Contour maps were prepared through Surfer 11 by plotting coordinate with concentration.

RESULTS AND DISCUSSIONS

Table 2 summarizes the statistical data of physio-chemical parameters and also contains total contents of Pb in playground soil. Fig. 2 shows the contour map plotting through the co-ordinates of various sampling locations depicted total concentration of Pb. The total concentration of lead was varying from 10.8 to 602 mg kg^{-1} with the average value of 63.7 ± 144 mg kg^{-1} in soil samples, which was listed in Table 2. The maximum Pb concentration was found in site 13 due to the bell metal industries are surrounded near the playground. In case of bioavailable Pb the concentration of Pb ranged from 3.51 to 431 mg kg^{-1} with an average of 39.4±105 mg kg^{-1}. Fig. 3 showed the comparison between both total and bioavailable Pb in playground soil. The maximum bio-availability for Pb was also located in site 13. Pb was largely associated (Fig. 4) with Fe-Mn oxides (F3) and organic fraction (F4) (35% and 31%, respectively) followed by the carbonate fraction (F2) (26%). The exchangeable fraction (F1) and residual fraction (F5) contain about 0.36% and 6.84% of Pb, respectively. the average mobility factor of Pb was 45%, and in S13 site it was 71% which indicated that it could be originated from primarily anthropogenic sources such as industrial activities and traffic, which can lead to damage of gastrointestinal tract, kidneys, and central nervous system (Raymond et al., 2011; Olafisoye et al., 2013). Maximum percentage of the Pb present in the bioavailable fraction suggested that the studied soil can easily be taken up by plants and also human beings. According to Rodriguez et al. (2006) normal concentrations of Pb were between 10 to 40 mg kg^{-1} and values greater than 70 mg kg^{-1} can be attributed to pollution. Studied result suggested that though the concentration of Pb in the present study was less, the concentration of mobile fraction was found to be at on higher side. It could also concluded that Pb might be loosely bound by electrostatic force to the soil particle which created potentially bioavailable (Aikpokpodion et al., 2012). Result of this study is similar with the form of lead inter relationship with fraction reported by Kabata-Pendias and Pendias (1992), Ramos et al. (1994) and Yusuf (2007) who reported Pb being largely associated with Fe-Mn oxide and organic fractions. The average Pb contents of all the sites were, F3 (35.31%) > F4 (31.29%) > F2 (26.20%) > F5 (6.84%) > F1 (0.36%).

In this present study, the I_{geo}, contamination factor (CF), enrichment factor (EF), and ecological risk factor (ER) were applied to assess the degree of heavy metals contamination in playground soil. The calculated I_{geo} values of Pb in playground soils are presented in Table 3. The I_{geo} value ranged from -0.79 to 5.01 for Pb. S13 playground soil fall on class 5 category which indicated that the soil of S13 playground soil was strongly to extremely polluted with Pb. The main cause of degree of pollution of Pb in playground soil was deposition of Pb from nearby bell metal industry as well as vehicular exhaust.

CF was introduced to measured heavy metals in topsoil samples. CF for topsoil of playground clearly indicated the role played by dry deposition. According to Table 3, CF for Pb showed moderate to considerable contamination in all the playground except S13 playground. S13 site indicated very high contamination than all others playground sites. Most of the small scale bell metal industry resided nearby S13 playground. So Pb was deposited through atmospheric deposition, wind action or surface runoff.

The Enrichment Factor (Table 3), basically calculated as per earth crust normalization, found that the soils of the area are enriched with Pb. EF value of metals >5 are represented to be contaminated with that particular PTEs. Pb showed moderate to significant enrichment in all studied playground soil except S4 and S13 playground. S4 site had very high enrichment with Pb whereas S13 playground exhibited extremely high enrichment value which clearly indicated the anthropogenic inputs into playground soil of site S13 i.e., from bell metal industry and S4 which is a tourist place (Hazardoari).

Ecological risk (ER) suggested the sensitivity of biota to PTEs and determined the probable potential ecological risk triggered by the various PTEs (like Pb) (Islam et al., 2015; Li et al., 2014). The ER index for PTEs specified that the severity of pollution of Pb. Low potential risk was there for Pb in all of the sampling sites except site 13 which indicated considerable ecological risk due to Pb.

Health risk assessment

Health risk assessment was done with bioavailable fractions (F1+F2+F3) of Pb in the soil collected from different playgrounds in Khagra. For non-carcinogenic risk (Fig 5 and 6), ingestion of soil particles appears to be the main exposure route for Pb to children, followed by dermal contact (Zheng et al., 2010) and inhalation compared to adults. Children were found to have higher risk from ingestion of soil in comparison with adults. HQ values (Fig. 5) of all the studied sites were higher due to ingestion for both child and adults. Risk assessment was calculated from the first three fractions of sequential extraction (F1+F2+F3) as these are highly mobile and can be accessed or absorbed easily. From table 4, it is very clear that the exposure risk was very much lower when we consider the risk of highly mobile first three fractions. In case of dermal exposure also, children were found to be at higher risk compared to adult. HI values (Fig. 6) for Pb were below 1 in all playground sites of Khagra (Table 5). So all the sites have no chance of occurrence of non-carcinogenic effects due to Pb. So for Pb, the actual risk is less than what we measure normally with the total metal concentration.

CONCLUSION

Playground soils of Khagra is moderately polluted with Pb except site 13 which indicated very high contamination and revealed high input of anthropogenic activity. In general, total concentration of Pb was low but bio available fraction showed higher mobility in Khagra. CF, EF, I_{geo} and ER showed that all sites hold moderate to considerable amount of Pb and may lead to contamination if deposition of

Pb by human continues. Risk assessment based on mobile fraction showed ‘no risk’ for Pb. Though HI was <1 for child and adults both, the children have got higher risk than adults. Risk assessment with total metal fraction over estimates, which is not the actual risk because the metal concentration found in mobile phases has a direct effect on human beings. Thus metal content in mobile fractions must be considered for routine risk assessment.

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Table 1 . Reference value of different factor for health risk assessment of PTEs in urban soils

Factor	Definition	Unit	Child	Adult	References
R ingestion	Rate of ingestion	mg/day	200	100	US EPA 2011
R inhalation	Rate of inhalation	m^3/day	10	20	Van den Berg 1995
Fexp	Exposure frequency	day	365	365	Hu et al. 2011
Texp	Exposure duration	Yr.	6	24	US EPA 2001
Askin	The skin area	cm^2	2800	5700	US EPA 2001
SAF	Skin Adherence Factor	mg/cm^2/hr.	0.07	0.7	US EPA 2001
DAF	Dermal Absorption Factor	Unit less	0.001	0.001	US EPA 2001
PEF	Particle Emission Factor	m^3/kg	1.36E+09	1.36E+09	US EPA 2001
ABW	Average Body Weight	kg	18	60	US EPA 2011
Tavrg	Average time for non-carcinogen	day	2190	8760	US EPA 1989

Table 2. Physico-chemical parameters of playground soil of Khagra

Sites	Sand (%)	Silt (%)	Clay (%)	pH	Cond. (µS/ cm)	OM (%)	Pb (mg Kg^{-1})
S1	55	31	14	6.61	503	2.25	27.72
S2	52	35	13	6.38	316	2.32	20.48
S3	54	31	15	6.47	302	1.65	21.98
S4	56	28	16	6.62	440	2.62	68.84
S5	60	27	13	6.25	261	2.08	10.88
S6	62	27	11	5.74	164	1.95	16.64
S7	57	29	14	7.01	408	1.58	13.42
S8	61	27	12	6.85	339	2.72	58.33
S9	52	32	16	7.04	296	2.59	27.14
S10	63	27	10	6.68	260	2.08	15.93
S11	54	31	15	7.28	741	1.88	18.18
S12	59	29	12	7.15	151	1.18	13.53
S13	63	27	10	6.48	364	2.22	602.24
S14	62	27	11	6.20	238	2.42	49.82
S15	57	29	14	6.17	291	2.69	42.25
S16	61	27	12	7.10	236	1.08	11.90
Minimum	52	27	10	5.74	151	1.08	10.88
Maximum	63	35	16	7.28	741	2.72	602.24
Mean	58	29	13	6.63	332	2.08	63.70
Median	58	28	13	6.62	299	2.15	21.23
Std. Deviation	3.86	2.39	1.97	0.43	143	0.51	144.70

Table 3. Geo-accumulation indices of Pb in playground soil of Khagra

	Index of geo-accumulation			
Sites	$\mathbf{I_{geo}}$	**CF**	**EF**	**ER**
S1	0.56	2.22	11.43	11.09
S2	0.13	1.64	7.00	8.19
S3	0.23	1.76	6.74	8.79
S4	1.88	5.51	30.13	27.53
S5	-0.79	0.87	4.30	4.35
S6	-0.17	1.33	7.04	6.66
S7	-0.48	1.07	5.56	5.37
S8	1.64	4.67	20.68	23.33
S9	0.53	2.17	11.68	10.86
S10	-0.24	1.27	5.25	6.37
S11	-0.04	1.45	8.48	7.27
S12	-0.47	1.08	6.01	5.41
S13	5.01	48.18	214.58	240.89
S14	1.41	3.99	16.21	19.93
S15	1.17	3.38	15.01	16.90
S16	-0.66	0.95	4.39	4.76

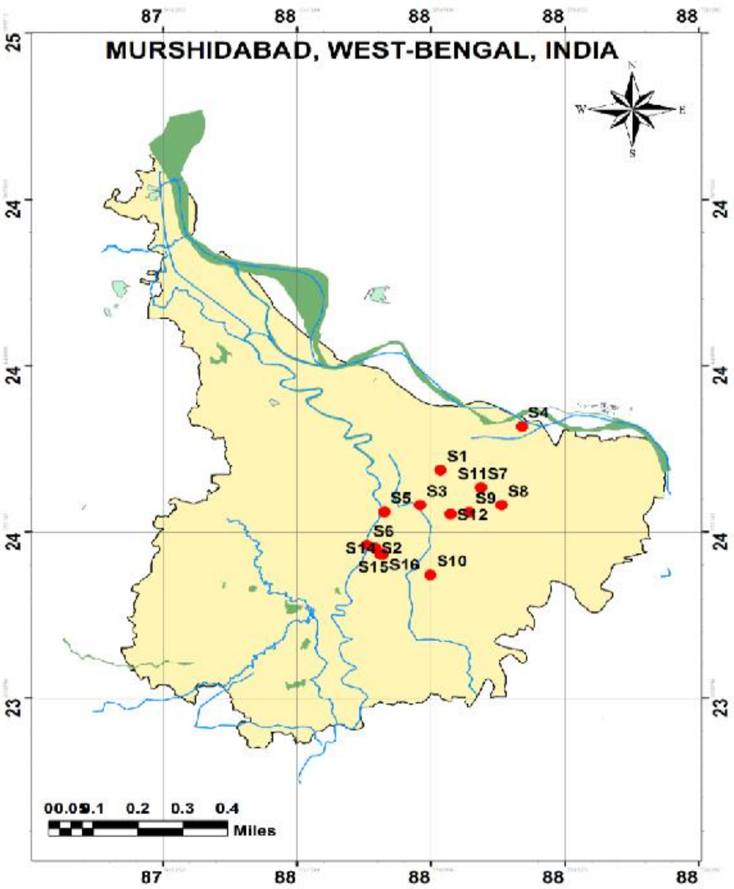

Fig. 1. Sampling sites from different playgrounds at Khagra, Murshidabad

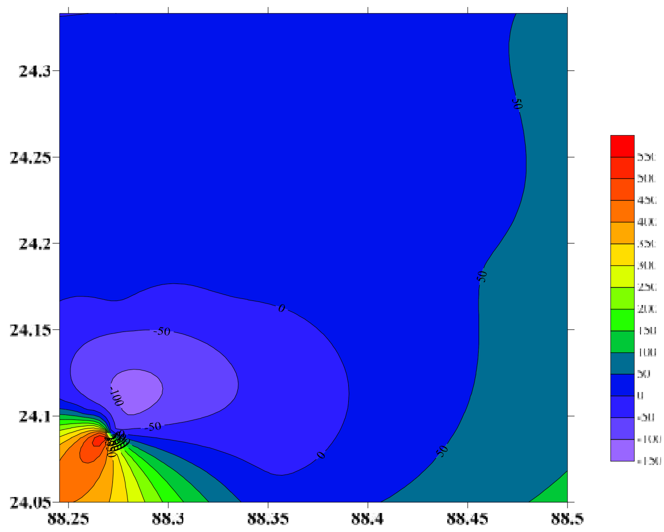

Fig. 2. Contour map showing concentration of Pb in playground soil

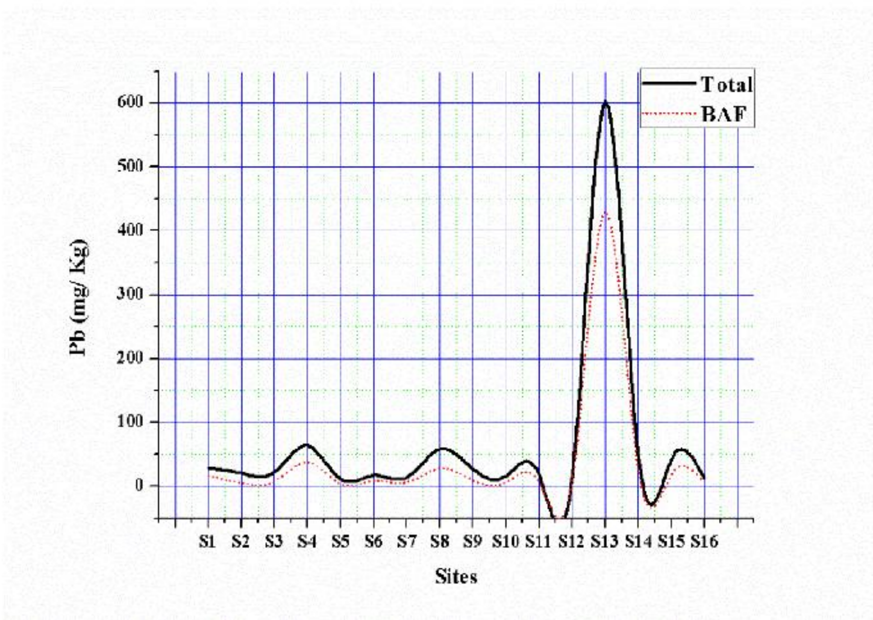

Fig. 3. Comparison between total and bioavailable fraction of Pb in playground soil

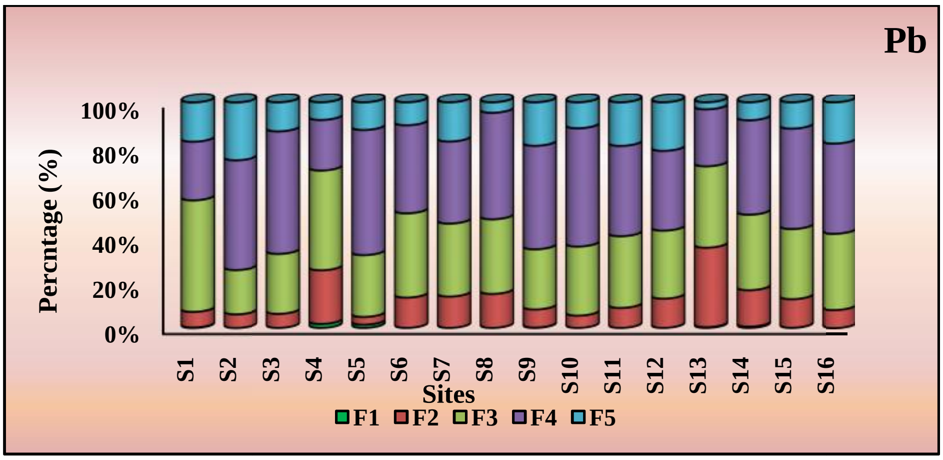

Fig. 4. Distribution of Pb in the fractions (%) of the sequential extraction from each sampling site

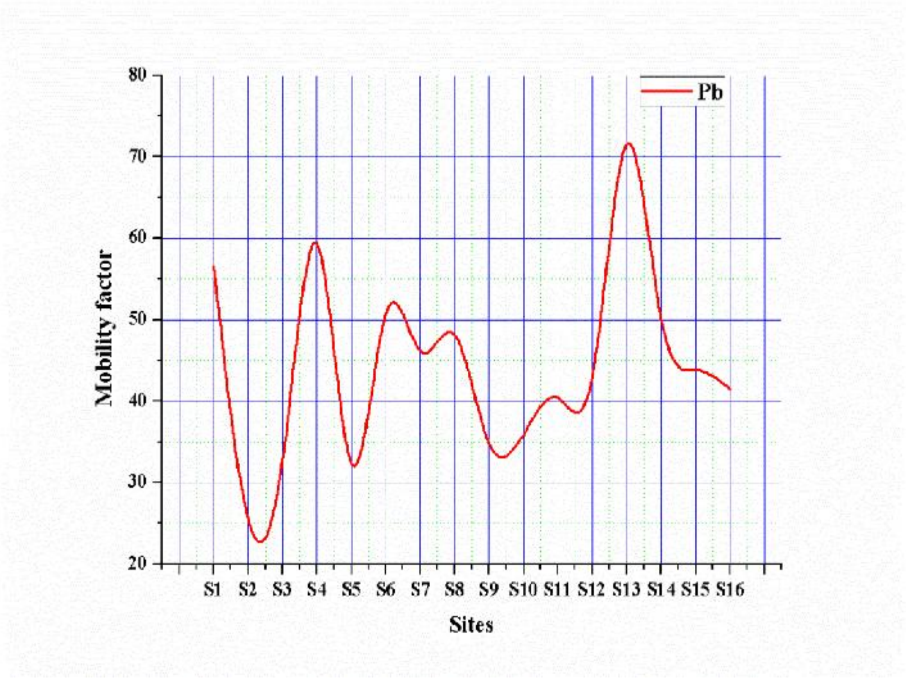

Fig.5. Mobility factor (%) of Pb in playground soil of Khagra

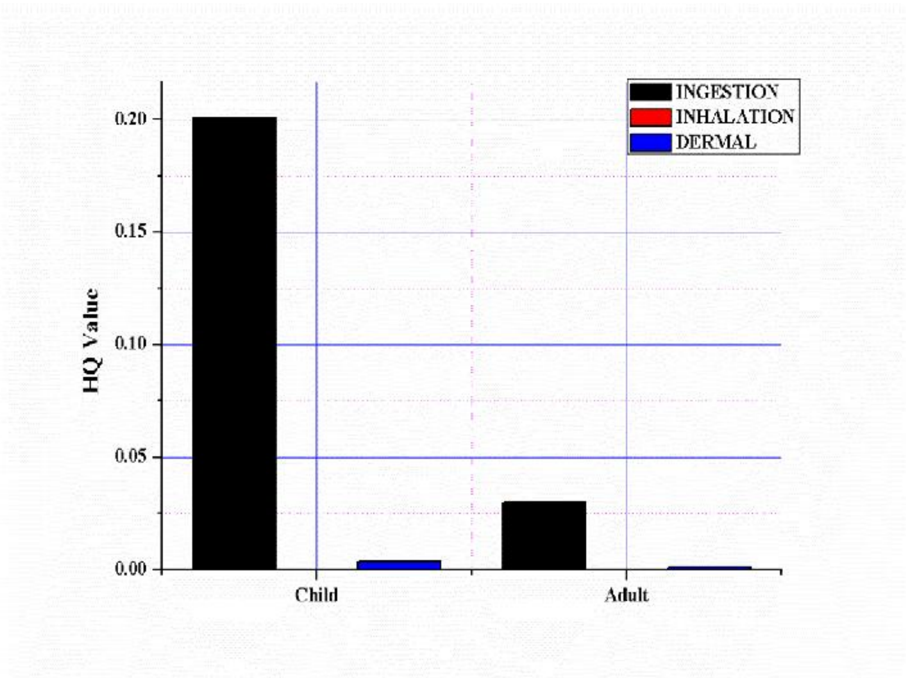

Fig.6. Hazard Quotient (HQ) values of Pb for both children and adult

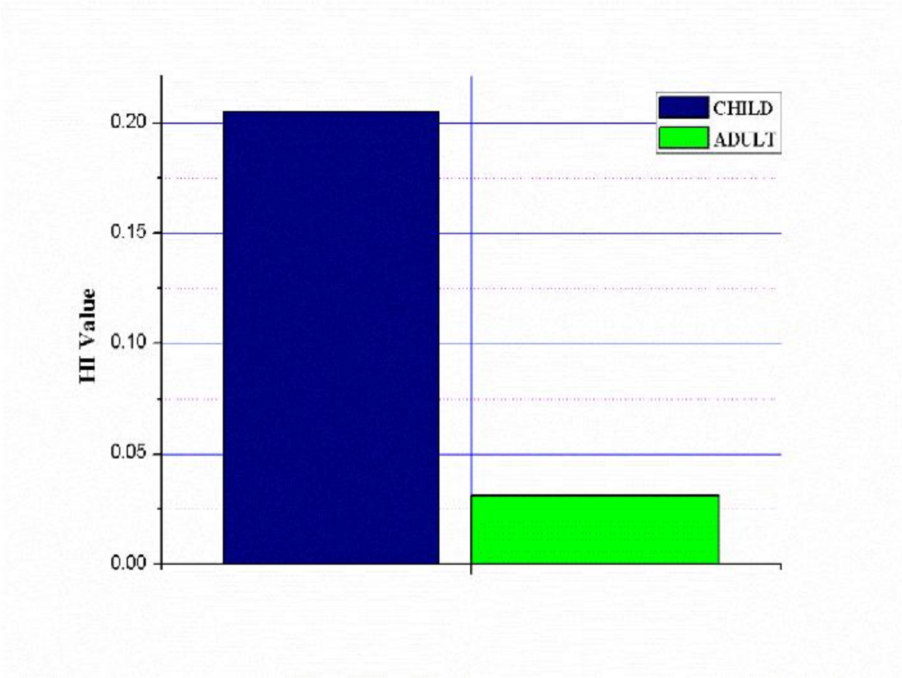

Fig. 7 Hazard Index (HI) of Pb for both children and adult

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