DETERMINATION OF HEAVY METALS CONTENT IN SOILS AND INDOOR DUSTS FROM NURSERIES IN DUNGUN, TERENGGANU

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Abstract

Concentrations of Cu, Mn, Cd, Pb, Zn, Fe and Al in indoor dusts and outdoor soils from nurseries located in industrial, town and village area of Dungun district were determined by Atomic Absorption Spectroscopy (AAS) following the acid digestion of the respective soil and indoor dust sample. The range of metals observed in soils were 0.46-46.9 µg/g, 23.2-338 µg/g, below detection limit (BDL) -4.66 µg/g, 2.26-130 µg/g, BDL-91.7 µg/g and 5310-114000 µg/g, for Cu, Mn, Cd, Zn, Pb and Al respectively. Although the results showed a relatively low contamination in general, the village areas had appreciably higher level of toxic metals compared to both town and industrial areas for outdoor soils. Atmospheric depositions and the distance from the main roadside appeared to have an influence on the Pb distribution in soils. Industrial areas on the other hand exhibited higher mean concentration of Cu, Mn, Fe, Pb and Zn in their indoor dust compared to town and village areas. Evaluation of enrichment factors suggest that possible sources of Cu, Mn and Zn in indoor dusts could be from internal source.

Abstrak

Jumlah logam berat yang terdapat di dalam tanah dan zarahan di dalam bangunan di kawasan pusat penjagaan kanak-kanak di sekitar daerah Dungun telah ditentukan melalui kaedah spektroskopi penyerapan atom (AAS) setelah dicerna oleh asid. Kajian kepekatan logam berat Cu, Mn, Cd, Pb, Zn, Fe dan Al yang terdapat dalam tanah dan zarahan telah dijalankan di kawasan perindustrian, bandar dan juga kampung. Dari keputusan analisis, julat kepekatan bagi Cu, Mn, Cd, Zn, Pb dan Al di dalam tanah adalah 0.46-46.9 µg/g, 23.2-338 µg/g, di bawah had pengesanan (BDL) -4.66 µg/g, 2.26-130 µg/g, BDL-91.7 µg/g dan 5310-114000 µg/g masing-masing. Walaupun keputusan yang diperolehi menunjukan kepekatan yang rendah secara keseluruhannya, namun begitu kawasan kampung mempunyai kepekatan logam toksik yang tinggi berbanding dengan kawasan bandar dan industri. Untuk Pb, pemendapan udara dan jarak dari jalan raya didapati mempengaruhi agihan kepekatan Pb dalam tanah. Di kawasan industri, purata kepekatan bagi Cu, Mn, Fe, Pb dan Zn dalam zarahan adalah lebih tinggi banding dengan kawasan bandar dan kampung. Nilai faktor perkayaan bagi Cu, Mn dan Zn dalam zarahan menunjukan logam-logam ini berkemungkinan berpunca dari keadaan dalaman bangunan.

Introduction

The incidence of heavy metal contamination from both natural and anthropogenic sources has increased concern about the health effects of chronic low-level exposures, particularly people living in urban environment who are more likely to be exposed to this threat. Natural and anthropogenic sources of soil contamination are widespread and variable. Heavy metals occur naturally in rocks. But most of the heavy metals occurrences in urban soils tend to originate from anthropogenic sources such as industrial, urban development and transport activities. Many researchers have shown that urban soils received a load of contaminants usually greater than surrounding sub-urban or rural area due to the concentration of anthropogenic activities of urban settlements [1-6].

There is an increasing concern about heavy metals contamination in indoor environment since most of people spend a great extent of their time indoors (office, workplace, house etc). A number of studies [4-6] have suggested that there is a possibility that contaminated soil or dust, ingested either directly or indirectly as a result of hand-to mouth activity, may represent a significant pathway of environment toxic metals to humans, with children representing the main sector of the population at highest risk. Children, especially toddlers, can easily ingest soils or indoor dusts unintentionally when they put contaminated toys in their mouth, pick up foods with dirty hands etc, thus making them susceptible to toxic metals poisoning. In addition, adults may also be exposed to similar threat since inhalation is the most common pathway for toxic metals to enter our body.

Indoor heavy metal sources may derive from many sources including infiltration of outdoor particles, dust, soils, internal ventilation system, cooking smoke, old paint and furniture material.

Currently there is a need to study heavy metals contamination particular in indoor dust as such study are still limited in Malaysia. The aim of the present study was to investigate the mass concentration levels and the heavy metals composition of indoor suspended particulate matter and soil outside nursery school playing parks or gardens. The nursery schools surveyed were located in district of Dungun, Terengganu. The indoor suspended matter and outdoor soils were assessed in relation to major activities carried out in the indoor microenvironments or the elevation from surrounding activities.

Experimental

Sampling Site

The study was conducted in the district of Dungun (4'45'' N, 103'25'' E), one of the coastal towns located in Terengganu, Malaysia. With a population of about 135,000, Kuala Dungun serves as the capital of the district. Kuala Dungun town used to be an iron mining town in the 1940s. Iron ores were actually mined in a small town called Bukit Besi located to the west, while Kuala Dungun served as the port where the ore was transferred onto ships. This "golden" era of Kuala Dungun ended in the middle of 70s. When the mines were gradually closed-down, Bukit Besi has now emerged as government-financed plantation estates. Nowadays, there are still fishing and small scale farming activities and some people involved in small businesses, while a large part of the population are involved with the petroleum industry concentrated in another township in the south, Paka. In this study, a total of 18 nursery schools with differences in general land use backgrounds were chosen; each land use background represents industrial, town and village setting, respectively. The first group of sampling locations, representing township setting was located at center of the town and near heavily frequented urban traffic routes. The second group sampling site for industrial area was situated in the south of the town in a region with a high density of petroleum chemical industry, power plant and main roads with heavy traffic load. The third sampling group (village) was at the edge of the urban area, in a quiet residential district with a low volume of traffic and negligible industry.

Sample Collection and Analysis

Soil samples were collected from the 0-20 cm layer using a plastic ladle. The soils samples were stored in zip plastic bags and transferred back to laboratory for further analyses. The soils samples were first air-dried, ground and passed through a stainless steel mesh of 0.6 mm in diameter. About 0.25 mg of the fine-fraction of the soils were then digested with an acid mixture of HNO3: HCl: HF (9:3:2, v/v) in a Teflon beaker and heated in a microwave oven at 150^{o}C for 10 minutes. After cooling, 9 ml of 10% boric acids were added to remove the fluoride residue. Walkley and Black method was used for the determination of organic carbon contents in soil while the soil pH was determined by glass electrode method. Cation exchange capacity (CEC) was determined using pH 7 ammonium acetate extraction method as described by Ross [7].

In the case of indoor particulate sampling, three pre-weighed acid washed polypropylene Tupper wares were placed in each nursery school; the location of the collector was at a height unreachable by the children, and was away from the kitchen as well as the ventilation system. After two months of collection period, the dust loaded Tupper wares were sealed and taken back to laboratory for further analyses. The three dust samples from each nursery were mixed into one composite sample representing the 3 dusts samples where they were colleted. The dust loaded Tupper wares were first put in the desiccators to remove moisture. The actual mass of indoor particulate was determined by gravimetric method using a microbalance to an accuracy of ±0.0001g. The particulate matter was transferred to Teflon beaker using dilute nitric acids and DI water. The resultant slurries were then heated in a microwave oven at 150^{o}C for 10 minutes to complete the digestion.

Heavy metals (Cu, Mn, Cd, Pb, Zn, Fe and Al) concentrations in both soils and indoor dusts were determined using a simultaneously atomic absorption spectrometer (FS 220A, VARIAN). All chemicals used were of analytical-reagent grade and deionized water was employed throughout for dilutions and washing.

Results and Discussion

Soil Parameters

Table 1 shows the mean, median, standard deviation, range values and number of samples of soil characteristics for all the 3 sampling profiles. Soil pH in village soil is most acidic followed by industrial and town soils. Generally, the soils pH is acidic or neutral, only few samples of soils taken from town and industrial areas showed pH values greater than 7. The organic matter (SOM) contents of soils taken in the village were generally higher than the soils of industrial and town areas. The CEC content in the town soils was significantly lower compared to the other two soil profiles. Correlation study showed that pH was negatively associated with both CEC ($p= 0.05$, $r = -0.63$) and soil organic matter ($p=0.05$, $r=-0.73$). However, there is no relation between CEC and SOM. Most of the heavy metals show no significant correlation with SOM and CEC except for Al and Fe which showed moderate positive correlation with both parameter; Cu, Al and Fe on the other hand exhibit a significant negative correlation with soil pH.

Heavy Metals in Soil

Table 1 illustrates the mean, median, standard deviation, range values of Mn, Zn, Cd, Cu, Pb, Fe and Al in soils according to different zones. The world average concentration proposed by Ure and Berrow [11] were also given in the same table for comparison purposes. The data clearly showed that Cd and Pb were enriched in Dungun nursery soils compared to world average values described by Ure and Berrow. In addition Al and Fe values in village soils also exhibited higher values compared to the value reported by them. When the metals content of the different soil zones were compared, it was found that the village soil profiles had higher mean values of all metals except for Cd. The highest mean value of Cd was found in the town soil profile, which exceeded the overall mean value by 67%. Tables 2 summarizes the comparison of metals concentration found in this study with other similar studies reported by other researchers [9, 10]. The variation of heavy metals concentration between the study areas could generally be attributed to differences in population densities and the degree of the industrial activities in the respective area.

Basically, most of the metals contents except Pb, Zn and Cd in town and industrial areas are lower compared to soils in the village areas. Lead and Cd are anthropogenic metals and they are normally not abundant in upper layer soils [8, 15]. The level of these metals in the soils of three areas with the exception of Zn from industrial area are within similar range suggesting they might be derived from common input since all the samp ling areas were near busy roadside.

Heavy Metal in Indoor Dust

Table 3 summarizes the relevant descriptive statistics of five sampled heavy metals (Cu, Mn, Pb, Fe and Zn) values in three different nursery dusts profiles. With the exception of Zn the mean values in all types of dust profiles increased in the following order: town < village < industrial area. The highest mean concentration of Zn was recorded in industrial dusts (783μg/g) followed by town dusts (558 μg/g) and village dusts (337 μg/g). Table 4 gives the comparison between metal contents values obtained in Dungun nurseries indoor dust with those reported in literature i.e. Riyadh (Saudi Arabia) [12], Hong Kong [13] and Zarqa, Jordan [14]. Generally, almost all heavy metal contents in the present study were much lower compared to Riyadh, Hong Kong and Zarqa with the exception of Zn (738 μg/g and 558 μg/g, respectively) concentrations in industrial and town areas which were slightly higher than Zn level (547 μg/g) in Riyadh community center. The observed differences could be the results of environmental setting of each study location which might exert influence on the metal level in the indoor dusts. For example, in Hong Kong the sampling locations were located in urban residential communities with high traffic density, tall building and high industrial activity. The study in Jordan on the other hand, based on indoor dusts of offices located in petroleum refinery complex. For Riyadh, the sampling location was situated in a community center with high population and high density of vehicles as the condition was quite similar with Hong Kong setting. The indoor metal concentrations in Dungun nursery were closer in values to that reported in Zarqa, Jordan compared to Hong Kong and Riyadh. This could be attributed to the fact that Dungun and Zarqa locations were less influence by (1) restricted air flow cause by tall surrounding building and (2) high density of population community.

Table 1: Heavy metals content and soil parameters in town, industrial, village soil samples

Location	Cu µg/g	Mn µg/g	Cd µg/g	Pb µg/g	Fe Wt%	Al Wt%	Zn µg/g	pH	%C	CEC
Industrial										
Range	1.3-15	28-89	ND-2.8	ND-88	0.08-2.7	1.3-7.6	2.3-32	4.6-7.4	1.0-4.0	0.01-1.6
Mean	5.9	59	2.0	58	0.69	2.9	17	5.63	2.0	0.5
Median	4.3	59	1.9	69	0.25	2.0	16	5.33	1.6	0.5
S.D	5.2	20	0.6	38	0.99	2.4	11	-	1.2	-
N	6	6	6	6	6	6	6	6	6	6
Town										
Range	0.5-20	48-124	ND-4.7	ND-74	0.1-1.5	0.5-5.8	9.8-130	5.0.-7.5	0.7-3.0	0.4-2.3
Mean	7.4	92	2.5	59	0.66	1.8	56	6.53	1.6	1.2
Median	4.1	91	2.4	58	0.51	1.1	60	6.57	1.3	0.7
S.D	7.9	31	2.1	11	0.5	1.8	43	-	0.8	
N	7	7	7	7	7	7	7	7	7	7
Village										
Range	16-47	23-338	0.54-3.2	26-92	1.5-7.6	4.8-11	13-74	3.6-4.9	2.4-4.5	2.1-10
Mean	30	246	1.9	63	4.5	7	52	4.21	2.8	6.3
Median	23	307	1.6	64	3.8	6	59	4.09	2.4	3.0
S.D	15	132	1.1	24	2.7	3	23	-	0.9	
N	5	5	5	5	5	5	5	5	5	5
Overall										
Mean	13	121	1.5	47	1.7	3.5	41	5.6	2.1	2.3
Median	7	79	1.4	56	0.62	2.2	28	5.3	2.0	0.9
N	18	18	18	18	18	18	18	18	18	18
World Average[11]										
Mean	25.8	761	0.62	29.2	3.2	6.7	59.8	-	-	-

S.D., standard deviation
ND, below detection limit
-, no data

Table 2: Metals values of Dungun nursery soils in comparison with mean/median from various authors (in µg/g)

Metals (µg/g)	Dungun			New Orleans, USA [9]	Uppsala, Sweden [10]		
	Town nursery	Industrial nursery	Village nursery	School Community	City center playground	Industrial playground	Rural playground
Cu	7.4	5.9	30	19	28.9	21.1	23.9
Mn	92	59	246	132	591	459	518
Cd	2.5	2	1.9	2.4	0.25	0.17	0.23
Pb	59	58	63	81	31.6	19	23.7
*Fe	0.66	0.69	4.5	-	2.78	2.46	2.54
*Al	1.8	2.9	7	-	2.1	1.9	2.0
Zn	56	17	52	160	109	78.7	79.6

- No data
* Concentration in Wt (%)

Table 3: Heavy metals content in town, industrial and village indoor dust samples

Location	Cu µg/g	Mn µg/g	Pb µg/g	Fe Wt%	Zn µg/g
Industrial					
Range	8-301	11-196	ND-417	0.06-2.3	32-2687
Mean	71	51	116	0.55	783
Median	39	22	55	0.15	519
S.D	104	67	148	0.85	889
n	6	6	6	6	6
Town					
Range	3-28	1-84	15-92	0.05-0.45	135-930
Mean	20	35	51	0.26	558
Median	21	32	52	0.24	681
S.D	9	29	32	0.13	336
N	7	7	7	7	7
Village					
Range	8-122	10-85	19-110	0.08-0.51	68-701
Mean	42	46	67	0.32	337
Median	27	44	62	0.31	311
S.D	42	24	32	0.15	271
N	5	5	5	5	5

S.D, standard deviation
ND, below detection limit

Table 4: Metals values of Dungun nursery indoor dusts in comparison with mean/median from other reported studies (in µg/g)

Metals µg/g	Dungun			Riyadh, Saudi Arabia [12]	Hong Kong [13]		Zarqa, Jordan [14]
	Industrial	Town	Village	Community center	Home	School	office
Cu,	71	20	42	271	981	247	92
Pb	116	51	67	639	220	200	60
Zn	738	558	337	547	2005	2293	640
Mn	51	35	46	-	259	224	-
*Fe	0.55	0.26	0.32	-	-	-	0.013

- No data
* Concentration in Wt (%)

Since there was no significant correlation between heavy metals content in soil and dust samples it could be argued that the surrounding soils were not the main contributing factor to the indoor dust's heavy metal content. To identify the most likely source(s) of indoor particles, enrichment factors were calculated for individual elements over the average elemental composition of the upper continental crust [16, 17]. Typically, the enrichment factor (EF) of an atmospheric element expressed by the equation:

$$EF = ([M]_{atm}/[Al]_{atm})/([M]_{soil}/[Al]_{soil}),$$

where $[M]_{atm}$ and $[Al]_{atm}$ is the concentrations of the chemical element and Al in the atmosphere, while $[M]_{soil}$ and $[Al]_{soil}$ are the mean concentrations of the chemical element and Al, respectively, in the earth's crust. Aluminum is frequently used as a reference element assuming that its anthropogenic sources to the atmosphere are negligible. In this study Al were substituted by Fe as references element. Basically, as the EF value increases, the contribution from non-crustal sources also increases [18]. Based on Al-Momani hypothesis [19], If EF approaches 1; the earth's crust is the predominant source. However, if EFs values are in the range of 1-10, the metals are considered to be not enriched because of the differences between chemical elements composition of local soils and reference crustal compositions. Metals with EFs range between 10 to100 are considered as moderate enriched, thus indicating particular metals in atmosphere would be derived from the crustal material. Finally EFs with the value greater than 100 showed high enriched conditions that indicating a severe contamination due to human activities.

Table 5: Enrichment factors of Cu, Mn, Pb and Zn in indoors dust

Metals	Enrichment Factors (EFs)			Significant site differences
	Town	Industrial	Village	
Cu	9.1	16	16.4	Town<Industrial˜ Village
Mn	0.59	0.4	0.56	Industrial<Village˜ Town
Zn	112	76	57	Village<Industrial<Town
Pb	20.8	23	23.1	Town<Industrial˜ Village

Table 5 shows the metals EFs calculated for indoor dusts. With the exception of Mn which showed no enrichment < 1, all other metals exhibited moderate enrichment in the dust samples. Since there was no significant correlation between indoor metal contents with outdoor soils, the EF values were indicative of possible sources of heavy metals coming from internal sources such as building paint residues, ventilation behavior, furniture scrub materials, roofing and building material rather than infiltration from outdoor soils.

Conclusion

Results obtained from this study showed that some nursery schools in Dungun have high levels of heavy metals content in soils and indoor dust. Data analyses suggest that road vehicular emission is the major source of these heavy metals in soils. The enrichment factors of metals content in indoor dust for all areas are within the range of moderate enrichment according to Al-Momani hypothesis. Since no correlation between heavy metals content in soil and dust samples, thus the moderate enrichment factor exhibited by indoor dust were indicative of possible sources of heavy metals may came from internal sources such as building paint residues, ventilation behavior, furniture scrub materials, roofing and building material. In order to reduce children exposure to heavy metals poisoning caused by contaminated dust, more attention should be directed towards the general cleanliness of the schools environment, such as good house keeping practice, good maintenance of ventilation systems and children should be encouraged to wash their hand frequently to reduce ingestion of contaminated dusts.

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