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Der Chemica Sinica, 2012, 3(5):1329-1336

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Heavy metals assessment of soil in the vinicity of fuel filling station in some selected local government areas of Benue State, Nigeria

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ABSTRACT

The determination of Cd, Co, Cu, Mn, Ni, Pb and Zn in soils within fuel filling stations in some selected local government areas of Benue state were carried out with Flame Atomic Absorption spectrophotometric technique. The method developed by the United State Environmental Protection Agency for (total sobbed) heavy metals in soils, sediments and sludges was used in the preparation of the soil samples for the determination of total metal content in this study. Generally, the ranges and mean concentrations (µg/g) of metals in the soil samples were 4.00-4.80 (4.37±0.27), 1.07-1.85 (1.51±0.26), 41.40-68.13 (58 .00±7.13),200.67-295.33 (260.00±32.30), 14.00-19.83 (17.13±1.94), 216.00-276.67 (242.67±18.29) and 100. 33-162.33(134.75±21.93) for Cd, Co, Cu, Mn, Ni, Pb and Zn respectively. The concentration of Pb was the highest. The degree of contamination by each metal was estimated by the enrichment factors. The enrichment factors obtained for Cd, Co, Cu, Mn, Ni, Pb and Zn in fuel filling stations were 15.46, 1.87, 3.20, 1.80, 1.96, 73.74 and 13.43, respectively. The inter-element correlation was found among metals in the soils of fuel filling stations using Pearson's correlation co-efficient. There were positive correlations among the metals determined. Metals such as Pb, Cd, and Zn shows high degree of contamination, while Co, Cu, Mn and Ni shows low degree of contamination in the study sites.

Keywords: Heavy Metals; Fuel Filling Station; Benue State.

INTRODUCTION

Heavy metals are released into the environment by both natural and anthropogenic sources. The main natural sources of metals in soils are chemical weathering of mineral. The anthropogenic sources are associated mainly with industrial, agricultural, mining and domestic activities, urban storm, water runoff, landfill leachate, mining of coal and ore, atmospheric sources and inputs rural areas [1, 2]. Soil pollution by trace heavy metals is an important factor in both geochemical cycling of metals and in environmental health. The existence of heavy metals in soil has led to serious concerns about their influence on plant and animal life. While some of these trace metals (Cu, Zn, Mn, Fe, etc) are essential nutrients that are required in enzymatic biochemical activities in the body, Some others like Cd, Pb, As and Hg are extremely toxic even at low concentration [3,4].

Mining, smelting industrial and the associated activities are one of most important sources by which soils, plants and surface waters are contaminated [5, 6, 7]. In addition, there may also be safety risks for people working in mines and smelters or for those living close by with the risk of habitual destruction .It is estimated that the median value of

worldwide emission of Cd, Cu, Pb and Zn, into soils were 22, 954, 796 and 1,372 10^6kg yr^{-1}, respectively, more than half of those metals were associated with base metals mining and smelting activities [8].

Environmental soil pollution has been aggravated by marked increase in global population, poverty, increased industrialization and urbanization in developed countries since the beginning of this century [9]. An environment can be polluted by toxic organic and inorganic wastes/chemicals which are always released into the environment through human (directly or indirectly) activities [10].

As population increases progressively, the environment of the areas (urban and rural) become more polluted. However, urban environment is more likely to be polluted than rural environment. This could be as a result of establishment of modern industries, trade wastes and auto-mobile exhaust which generate waste products such as heavy metals and organic chemicals as their by products, co- products and final products [11]. Apart from the modern industries, the establishments of cottage industries like fuel filling stations especially in cities also compound the pollution of the environment to the various ways [12]. Improper disposal of wastes, engine oil, transmission oil, brake fluid in the vicinity of fuel filling stations contributes immensely to soil contamination; this may possibly have adverse impact on human health [13]. As fuel filling stations increase, measures must be taken to know the source, significance and concentration of this pollutant "heavy metals" and necessary research work should be carried out in order to get a clean society that will match the ever increasing fuel filling stations [14].

This research is therefore based on the study and determination of various concentration of metals such as Cd, Co, Cu, Mn, Ni, Pb and Zn in fuel filling stations in Otukpo, Gboko and Makurdi Local Government Areas of Benue State since most of these fuel filling stations serve as open market where fruits and vegetables and other food items are marketed.

MATERIALS AND METHODS

Sampling spots of about 20-30 m apart from each other were mapped out for soil sample collection within each sampling sites. Samples were collected using clean stainless steel trowel from about 0-15cm depth. A soil sample for each control sites were also collected from where farming, mining and industrial activities were absent. The collected soil sub-samples were thoroughly mixed, pooled together to make a composite of each soil sample.

The collected soil samples were air-dried for some weeks to remove excess moisture. Large soil clods were also crushed to facilitate the drying. The dried soil samples were crushed in a porcelain mortar with a pestle. The crushed soil sample were sieved through a 2.mm sieve made of stainless steel, for analyzing soil pH and particle size, some portion of the individual sieved soil samples were further pulverized to a fine powder and passed through a 0.5mm sieve for analyzing organic carbon and total metal content. The pH of the soil samples was determined with pH meter Hanna (Model H1991000) according to standard analytical methods. Organic matter was determined using the chromic acid oxidation method [15]. Particle size distribution was determined by the hydrometer method as described by Bauyocos [16]. The exchangeable cation was determined by the method described by Hendershot [17].

The method developed by the United States Environmental Protection Agency for (total sobbed) heavy metals in soil, sediments and sludged (USEPA SW-846, method 3050) [18], was used in the preparation of the soil samples for the determination of total metal content in this study. One gram (1g) of the soil sample was weighed into a beaker for acid digestion. Analar grade nitric acid, hydrogen peroxide (about 30%) and concentrated hydrochloric acid were used for the digestion. The digest was filtered through whatman filter paper. Each filtrate was collected in 100ml volumetric flask and deionized water was used to rinse the filter paper into volumetric flask. Each filterate was later made up to 100ml with deionized water. Standards were prepared with serial dilution techniques within the range of each metal determined. The standards used were Analar grade; the instrument was first calibrated with stock solutions of the prepared standards before analyzed using Flame Atomic Absorption Spectrophotometer. After every five samples analyzed using FAAS, the first sample was repeated for quality check. Only when the result was within 10% of earlier readings did the analysis proceed further. The data obtained in the study were analyzed using Pearson correlation analysis. The enrichment factors for soils were calculated according to the following equation

$$EFc = (Cx/C_{Fe})soil/(Cx/C_{Fe})Earth's\ crust$$

Where (Cx/C*Fe*) soil is the ratio of concentration of the element being determined (Cx) to that of Fe (C*Fe*) in the soil sample and (Cx/C*Fe*) earth's crust is the ratio in the reference Earth's crust [19,20,21]. Enrichment factors were calculated for each sample relative to the abundance of the elements in the Earth's crust [22], choosing Fe the reference element due to the crust-dominated element. The iron content of soils does not change owing to its high levels in the Earth's crust, example; 0.5-10%, unless there is a large point source around a specific environment. An enrichment factor of unity would indicate that the relative concentration of a given metal is identical to that which is present in unpolluted soil.

RESULTS AND DISCUSSION

Soil Characteristics

The pH values ranged from 6.50-7.10, 6.40-7.20 and 6.90-7.20 for Otukpo, Gboko and Makurdi fuel filling station soil samples respectively (Tables 1-4). All the soils studied from the fuel filling station either weakly acid or neutral. The soil organic carbon concentrations ranged from 0.65-1.45, 0.95-1.50 and 0.75-1.50 for Otukpo, Gboko and Makurdi respectively. The soils from the three study areas were generally low in organic carbon contents. Most of the soil samples studied from Otukpo, Gboko and Makurdi fuel filling station soil samples have organic carbon values of less than 2.00%. The clay contents ranged from 8.20-12.20%, 13.40-14.60% and 13.40-16.60%, for Otukpo, Gboko and Makurdi fuel filling station soils respectively. The cation exchange capacity ranged from 14.50-18.20 meq/100g, 11.20-16.20 meq/100g and 15.50-20.20meq/100g, for Otukpo, Gboko and Makurdi respectively.

Table 1: Soil Characteristics of Otukpo Fuel Filling Station

Sample sites	pH	O.C	Sand (%)	Silt (%)	Clay (%)	C.E.C meq/100g
A	6.80	0.87	72.10	15.70	12.20	14.50
B	6.90	0.98	72.10	15.70	12.20	16.20
C	7.10	0.65	72.10	16.70	11.20	18.20
D	6.80	0.96	74.10	17.70	8.20	17.20
E	6.50	1.45	76.10	15.70	8.20	15.50
cont1	7.20	0.60	74.40	10.40	15.20	14.20
cont2	6.10	0.95	71.40	10.40	18.20	13.40
cont3	6.90	0.94	72.40	13.40	14.20	12.80

Table 2: Soil Characteristics of Gboko Fuel Filling Station

Sample sites	pH	O.C	Sand (%)	Silt (%)	Clay (%)	C.E.C meq/100g
A	6.40	0.95	70.70	15.90	13.40	11.20
B	6.60	0.96	72.70	13.70	13.60	13.20
C	7.20	0.72	74.70	11.70	13.60	14.20
D	6.90	0.99	70.90	13.50	15.60	15.50
E	6.80	1.50	70.70	14.70	14.60	16.20
cont1	6.90	0.98	69.40	12.40	18.20	14.50
cont2	7.20	0.85	70.40	13.40	16.20	16.20
cont3	7.40	0.60	70.70	14.90	14.20	15.60

Table 3: Soil Characteristics of Makurdi Fuel Filling Station

Sample sites	pH	O.C	Sand (%)	Silt (%)	Clay (%)	C.E.C. meq/100g
A	7.20	1.30	72.70	13.90	13.40	17.20
B	6.80	1.50	70.70	15.90	13.40	15.50
C	6.90	0.75	72.70	10.70	16.60	18.20
D	6.80	0.95	70.70	14.70	14.60	17.50
E	7.20	0.96	74.70	10.70	13.60	20.20
cont1	7.20	0.85	70.70	13.70	15.60	17.20
cont2	7.00	0.70	70.90	13.50	15.60	16.20
cont3	6.90	0.94	73.70	9.60	16.70	15.60

The results of heavy metal concentrations in the fuel filling station soil samples are presented in Tables 5-8. The soil samples from fuel filling station sites in the three major cities (Otukpo, Gboko and Makurdi) of Benue state revealed a clear elevated levels of these heavy metals (Cd, Co, Cu, Mn, Ni, Pb and Zn). The mean concentrations of heavy metals obtained from the control sites were much lower than those obtained from the soils of the fuel filling station under consideration. This reflects a general and diffuse contamination of soils of this fuel filling station by heavy metals. Out of the heavy metals considered, lead shows the highest pollution in the three urban areas studied. The

overall results ranged from 4.00-4.80,1.07-1.85,41.40-68.13,200.67-295.33,14.00-19.83,216.00-276.67 and 100.33-162.33µg/g for Cd, Co, Cu, Mn, Ni, Pb and Zn respectively.

Table 4: The ranges and mean of soil properties of fuel filling station in the study area

		Parameters					
Town		**pH**	**O.C**	**sand**	**silt**	**clay**	**C.E.C**
OTUKPO	Range	6.50-7.10	0.65-1.45	72.10-76.10	15.70-17.70	8.20-12.20	14.50-18.20
n=5	Mean	6.82	0.98	73.3	16.3	10.4	16.32
	S.D	0.22	0.29	1.79	0.89	2.05	1.44
Gboko	Range	6.40-7.20	0.95-1.50	70.70-74.70	11.70-15.90	13.40-14.60	11.20-16.20
n=5	Mean	6.78	1.02	71.94	13.9	14.16	14.06
	S.D	0.3	0.29	1.76	1.56	0.93	1.97
Makurdi	Range	6.80-7.20	0.75-1.50	70.70-74.70	10.70-15.90	13.40-16.60	15.50-20.20
n=5	Mean	6.98	1.09	72.3	13.18	12.32	17.72
	S.D	0.2	0.3	1.67	2.37	5.05	1.7
All soil	Range	6.40-7.20	0.65-1.50	70.70-76.10	10.70-17.70	8.20-15.60	11.20-20.20
n=15	Mean	6.86	1.03	72.51	14.46	12.29	16.03
	S.D	0.24	0.28	1.72	2.11	3.35	2.22

n=number of soil within the site
S.D= standard deviation

Table 5: Total Metal Contents (µg/g) of Otukpo Fuel Filling Station

Sample sites	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
A	4.60	1.60	58.20	226.67	17.57	266.00	103.67
B	4.73	1.73	50.40	292.67	18.33	276.67	126.67
C	4.33	1.33	65.80	295.33	19.83	224.67	133.33
D	4.00	1.56	68.13	233.33	14.63	224.00	143.00
E	4.80	1.80	60.87	289.33	17.30	216.00	100.33
Cont 1	0.35	0.80	18.00	145.00	8.20	3.80	10.50
Cont2	0.30	1.00	17.50	144.80	7.80	3.60	11.20
Cont3	0.20	1.00	17.80	143.50	9.50	3.50	11.80

Table 6: Total Metal Contents (µg/g) of Gboko Fuel Filling Station

Sample sites	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
A	4.13	1.85	58.27	228.00	15.43	272.00	119.00
B	4.13	1.32	59.72	274.64	17.47	249.23	161.67
C	4.33	1.33	58.60	281.67	14.30	235.33	151.67
D	4.73	1.75	51.67	247.33	19.20	224.67	162.33
E	4.33	1.83	53.13	284.67	19.47	240.00	150.67
Cont1	0.80	0.80	19.20	142.50	9.50	3.50	9.50
Cont2	0.37	0.60	17.20	140.80	8.10	3.00	8.50
Cont3	0.25	0.90	17.90	144.20	7.90	2.50	10.00

Table 7: Total Metal Contents (µg/g) of Makurdi Fuel Filling Station

Sample sites	**Cd**	**Co**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
A	4.20	1.20	61.13	271.67	19.23	257.33	149.23
B	4.07	1.07	73.07	280.67	18.00	240.00	135.33
C	4.67	1.65	50.87	200.67	16.43	238.67	160.33
D	4.20	1.20	50.67	283.33	14.00	234.67	100.33
E	4.33	1.40	49.40	210.00	15.80	240.00	123.67
Cont 1	0.35	0.80	17.90	146.20	9.00	3.50	9.70
Cont2	0.30	0.60	18.90	145.50	10.00	3.20	8.60
Cont3	0.20	0.80	18.60	144.10	8.60	3.00	10.50

Generally, in the three urban area studied, the concentrations of the heavy metals were extremely high especially Pb, Cd and Zn. This is an indication that these heavy metals are the primary contaminant in the soil of the fuel filling station which was also reflected in the low level of these heavy metals obtained from the control sites in comparison with those obtained from the study sites. Also, the degrees of heavy metals pollution in fuel filling station soils

which were determined by its enrichment factors were also high. From the mean results and enrichment factors, there is a clear indication that Pb, Cd and Zn are the great contaminant in the studied soils where exhaust from vehicles and gasoline combustion primarily cause air pollution with the heavy metals especially lead particles reaching soils through dry and wet depositions [19]. Studies have shown that motor vehicles constitute principal source of this metal [20, 21]. Soil Pb concentrations greater than 1.0mg/kg generally indicate a local source of pollution [22].The high lead contents in fuel filling station soil samples could further be linked up with the automobile tail-pipe which account roughly two-thirds emission of Pb into the atmosphere. It was reported that Nigeria still run gasoline of Pb concentrations of 0.66g per litre and it is estimated that about 2800 metric tones of vehicular gaseous Pb emission is deposited to urban areas in Nigeria annually [12]. Although the mean concentrations of Mn were found to be very high in the fuel filling station soils, this metal may not be regarded as a primary contaminant in the study area. This is reflected in their enrichment factor which primarily determines its extent of contamination. The enrichment factors of Mn in the motor park soils were 1.82, 1.85 and 1.72 for Otukpo, Gboko and Makurdi respectively. Also the mean concentration of Mn obtained from all the sites (260.00±32.20µg/g) falls within the acceptable limits proposed by E.U,ICRCL and UNEP limits. Hence it could be said that Mn originates from parent material in the soil.

Table 8: Summary of total metal contents(µg/kg) of fuel filling station in the study area

Town	metal	range	mean/S.D
Otukpo	Cd	4.00-4.80	4.49±0.33
	Co	1.33-1.80	1.60±0.18
n=5	Cu	50.40-68.13	60.68±6.96
	Mn	226.67-295.33	267.47±34.35
	Ni	14.63-19.83	17.53±1.90
	Pb	216.00-276.67	241.47±27.74
	Zn	100.33-143.00	121.40±18.67
Gboko	Cd	4.13-4.73	4.33±0.24
	Co	1.32-1.85	1.62±0.27
n=5	Cu	51.67-59.73	56.28±3.62
	Mn	228.00-284.67	263.26±24.62
	Ni	14.30-19.47	17.17±2.28
	Pb	224.67-272.00	244.25±17.86
	Zn	119.00-162.33	149.07±17.66
Makurdi	Cd	4.07-4.67	4.29±0.23
	Co	1.07-1.65	1.30±0.23
	Cu	49.40-73.07	57.03±10.13
n=5	Mn	200.67-283.33	249.27±40.47
	Ni	14.00-19.23	16.69±2.02
	Pb	234.67-257.33	242.13±8.77
	Zn	100.33-160.33	133.78±15.28
all soil	Cd	4.00-4.80	4.37±0.27
	Co	1.07-1.85	1.51±0.26
	Cu	41.40-68.13	58.00±7.13
n=15	Mn	200.67-295.33	260.00±32.30
	Ni	14.00-19.83	17.13±1.94
	Pb	216.00-276.67	242.67±18.29
	Zn	100.33-162.33	134.75±21.93

n= number of soil
S.D= standard deviation

Copper is not regarded as soil contaminant in the fuel filling station soils. Its mean concentrations and enrichment factors were found to be very low in the fuel filling station soil samples (Table 9). The mean concentration of Zn in the fuel filling station soil samples was 134.75±21.93µg/g. This was also found to be very high in comparison with those obtained from control sites. This clearly shows that Zn, which seem, to be mainly associated with traffic auto-mobile source can also be derived from tyre consumption .Zn can also be considered as one of the heavy metals, which are components of tyres and engines, and which can be released during abrasion and wears. However, Zn cannot also be regarded as one of the prominent contaminants like Pb in the fuel filling stations soil because the mean metal content obtained for Zn in the fuel filling station soils falls below some of the proposed ranged for Zn values in uncontaminated soil. The accumulation factor of Zn was much lower than that of Pb.

The concentration of Cd in fuel filling station soil samples ranged from 4.00-4.80µg/g. This was also found to be very high. The high Cd levels obtained from the soil samples of fuel filling station sites may be ascribed to activities such as construction, vehicle exhaust as well as fuel combustion. Furthermore, the average Cd concentration of 4.37±0.27µg/g obtained in fuel filling station soil samples are higher than E.U and ICRCL limits of 1-3 and 0-1mg/kg in the soil.

The concentrations of Cu, Ni and Co were very low in fuel filling station soil samples so also their enrichment factors which does not have much variation. From these observations, Cu,Ni and Co does not contribute much towards the contamination of areas under study. The correlations were established among the various metals under consideration (Table 10). There were positive correlations between pairs of Cd/Co, Mn/Ni, Cu/Pb, Mn/Zn, Mn/Cu, Cd/Cu, Ni/Cu and Pb/Zn in fuel filling station soils confirming their probable common origin.

Table 9: Factors of accumulation of heavy metals in fuel filling station in the study site.

Town	metal	Rainy season
	Cd	16.04
Otukpo	Co	1.72
n=5	Cu	3.41
	Mn	1.82
	Ni	2.06
	Pb	66.46
	Zn	10.87
Gboko	Cd	15.46
	Co	2.10
n=5	Cu	3.11
	Mn	1.85
	Ni	2.02
	Pb	81.45
	Zn	15.97
Makurdi	Cd	15.32
	Co	1.79
	Cu	3.09
n=5	Mn	1.72
	Ni	1.81
	Pb	74.89
	Zn	13.94
all soil	Cd	15.46
	Co	1.87
n=15	Cu	3.20
	Mn	1.80
	Ni	1.96
	Pb	73.74
	Zn	13.43

Enrichment factors

If an enrichment factor is greater than unity, this indicates that the metal is more abundant in the relative to that found in the earth's crust. However, enrichment factors less than 5 may be not considered significant although they are an indicator of metal accumulation, because such small enrichments may arise from differences in the composition of local soil material and the reference earth's crust used in EFc calculations. If the EFc values are greater than 5, in this case they are considered to be soil pollution for related metals. Pb,Cd and Zn have the highest EFc values i.e 73.74, 15.46 and 13.43for Pb,Cd and Zn respectively. These high EFc value indicate that the source of accumulation of Pb,Cd and Zn originates mainly from anthropogenic contributions. The Pb showed high EFc which may be a pollution indicator for soils polluted by Pb to some extent, mainly originated from traffic, since soil samples were collected from fuel filling stations. The important contributors of Pb in soils are the parent geological materials from which soils are derived, smelters, coal combustion and the widespread use of leaded petrol. Pb mainly enters soils by means of atmospheric dry and wet depositions and the disposal of sewage sludge. As a consequence of Pb and materials containing Pb, substantially elevated levels of this element may be found in some local soils [23].

Cd and Zn also have high EFc values. There is much concern about the levels of Cd present in the environment, since it's a cumulative poison for mammals. Its main ways of entering the environment as a waste product are especially from metal refining and electroplating, and also from the chemical and paint industries [24]. Zn is also surface contaminant of studied soil samples from motor parks. Its accumulation may occur from atmospheric deposition originating from smelting activities (in association with lead),galvanized iron and steel,alloys,batteries, brass, rubber manufacture, mining and old tyres [10]. Enrichment factors for Co, Cu, Mn and Ni varied from 1.80-3.20, which indicates that the soils were not polluted by these metals. However Co, Cu,Ni and Mn have EFcs somewhat higher than unity i.e. 1.87, 3.20, 1.80 and1.96, respectively, but these may not be a pollution indicator for the soils under investigation.

Table 10: Elemental correlation coefficient in fuel filling station

Town	metal	Cd	Co	Cu	Mn	Ni	Pb	Zn
Otukpo	Cd		-0.655*	-0.782*	0.457	0.473	0.398	-0.803*
	Co			-0.591*	0.059	-0.325	0.235	-0.563*
	Cu				-0.278	-0.345	-0.834*	0.399
	Mn					0.678*	-0.142	-0.004
	Ni						0.223	-0.189
	Pb							-0.14
	Zn							
Gboko	Cd		0.251	-0.827*	-0.066	0.493	-0.821*	0.508*
	Co			-0.646*	-0.547*	0.445	0.211	-0.495
	Cu				0.049	-0.780*	0.601*	-0.299
	Mn					0.129	-0.492	0.618*
	Ni						-0.434	0.492
	Pb							'-0.841*
	Zn							
Makurdi	Cd		-0.989*	-0.644*	-0.863*	-0.222	-0.202	0.512*
	Co			-0.695*	-0.922*	-0.255	-0.215	0.461
	Cu				0.596*	0.697*	0.318	0.227
	Mn					0.165	0.191	-0.435
	Ni						0.829*	0.710*
	Pb							0.503*
	Zn							

**indicates the significance value*
Correlation is significant at 0.05 level

CONCLUSION

The results obtained from the analysis of topsoils collected from fuel filling stations in various locations in Otukpo, Gboko and Makurdi areas of Benue state in Nigeria indicated that the concentrations of Cd, Co, Cu, Mn, Ni, Pb and Zn were higher than those of control soil metals contents. The degree of contamination of Pb was the highest. Cd and Zn also showed high degree of contamination in fuel filling station soils. From this reason, it could be predicted that the contaminations of Pb, Cd and Zn are probably from anthropogenic sources, while those of Co, Cu, Ni and Mn may be from parent material in the soil. The only observed contaminants were Pb, Cd and Zn and their concentrations and enrichment factors were high in all the soils studied. The results do not provide information about changes in the levels of inorganic soil contaminants over time, but they do provide baseline data for comparisons in the future. Hence, overall, levels of Pb, Cd and Zn contaminations are those which call for closer monitoring in sites under considerations.

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