Heavy metal content of the soil in the vicinity of the united cement factory in Southern Nigeria

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ABSTRACT

Cement dust deposition on soil has been implicated in the heavy metal (HM) contamination of soil, leading to adverse effects on plants and humans. This study assessed the impact of cement dust deposition on the HM content of the soil samples in the vicinity of a cement factory and its implication on the public health of the host community. Topsoil samples were collected at varying distances and directions in the vicinity of the cement factory and a remote area to the factory (control). The Pb, Cu, Mn, Fe, Cd, Se, Cr, Zn, and As content of the soil samples were determined by atomic absorption spectrophotometry. The HM content of the soil samples in the studied locations were within the safe limits, except for Zn, which was higher in the samples closest to the factory. The levels of Mn, Fe, Zn, Pb, Cu, and Cr were significantly higher in the samples closest to the factory compared to the other locations (P<0.05). Moderate contamination with Cu and Pb and considerable contamination with Cr were observed in the samples closest to the factory. The HM content of the soil samples of all the locations demonstrated minimal enrichment (EF < 2) and average pollution index ($1 < IPI \le 2$). Cement production is associated with the exacerbation of the HM contamination of the surrounding soil, with the degree of contamination depending on the distance from the factory. Moderate soil contamination with HM poses potential risk of deleterious public health effects if appropriate remediation strategies are not implemented.

Keywords: Cement dust, Heavy metals, Soil, Contamination

Introduction

Heavy metal contamination of soil is considered to be a severe public health issue since these metals are indestructible and bioaccumulative and exert toxic effects on the living organisms in the ecosystem. Sources of heavy metals in soil may be natural or anthropogenic, with anthropogenic sources emanating from the smelting of metal ores, mining and agricultural activities, and industrial emissions.¹

Cement production has been described as the major source of soil contamination with several heavy metals, including lead (Pb), copper (Cu), cadmium (Cd), selenium (Se),

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Chromium (Cr), zinc (Zn), and nickel Ni, which may affect the physicochemical properties and crop production in the contaminated soil.² The soil samples in the vicinity of cement factories have been shown to contain higher levels of exchangeable calcium, sodium, hydrogen, and magnesium, as well as soil organic matters, calcium oxide, sulfur oxide, Pb, Zn, and Cd compared to the remote areas to these factories.³ Elevated pH and extremely high levels of chromium, silica, iron, and calcium have been reported in the soil samples in the vicinity of cement factories, with considerable reduction in the contamination levels with the increased distance from the factory.³

Heavy metals exert toxic effects on soil microorganisms, thereby changing the diversity, population size, and overall activity of the microbial communities in soil.⁴ In plants, the uptake of excessive heavy metals has been shown to alter normal metabolic pathways



through disrupting specific cellular enzymes and inhibiting photosynthesis.⁵ According to reports, the leaching of heavy metals from the soil or runoff into aquatic environments and the subsequent contamination of underground and surface water with Pb, Ar, Cd, and Hg above the threshold recommended by the World Health Organization (WHO) for these elements is associated with toxic effects on aquatic plants and animals.⁴

Heavy metal uptake by plants from soil. successive accumulation the in human tissues, and biomagnification through the food chain has been implicated in the development of several chronic diseases, such as cancer, and cardiovascular, renal. hepatocellular, neuromuscular, gastrointestinal, skeletal, hematological, and immunologic diseases in humans.^{5, 6} The regulatory standards for the measurement of heavy metal levels have been established for agricultural soils; however, there is discrepancy in different countries the critical level of regarding each contaminant.7,8

Heavy metals cannot be biodegraded to less harmful components by natural processes. Consequently, the adverse effects of heavy metal pollution on the local environment and organisms may be substantial and long-lasting irrespective of extensive remediation efforts to reduce the pollution level.9 This is further compounded by the poor monitoring of the industrial activities of the factories that are involved in the heavy metal pollution of the environment by appropriate local regulatory bodies, so that the soil contents of heavy metals become higher than the recommended safe limits for a healthy population, which in turn leads to public health epidemics. Therefore, the heavy metal content of the soil in a particular locality may be a practical determinant and reliable index for the assessment of environmental pollution and general health of the living organisms in the locality.

The present study aimed to assess the impact of cement dust exposure on the heavy metal contents of the soil samples in the vicinity of the United Cement Factory and their efficacy in the assessment of environmental pollution.

Materials and Methods *Study area*

This study aimed to assess the heavy metal contamination of the agricultural soil in the vicinity of a cement factory at Mfamosing, located in Akamkpa local government area, which hosts one of the largest cement factories in the country, known as the United Cement Factory in Southern Nigeria. The Mfamosing limestone depot is the major source of raw materials for the production of ordinary Portland cement by this factory. The site is located within five kilometers west to Mbebui village (coordinate: 05.04493oN, 008.298995oE), five kilometers south to Abifan community (coordinate: 05.07591oN, 008.52192oE), two kilometers east to Mfamosing community, and three kilometers east to the main quarry site (coordinate: 05.06993oN, 008.53908oE).¹⁰

Sample collection and preparation

In total, 20 surface soil samples (five from each location) were collected from the quarry site camp at the distance of 100 m from the cement factory, three communities in the vicinity of the factory, including Mfamosing Ι within 2 km east of the quarry site, Mfamosing II within three kilometers south of the quarry site. and Mbebui within five kilometers west of the quarry site, and Calabar metropolis located at the distance of 45 km from the quarry site (north) as the control samples. The soil samples were collected from the upper 10 cm of the topmost soil and placed in labeled plastic bags. Stones and debris were sieved out, and the soil samples were dried for three consecutive days and stored in the dark until analysis.

The soil samples were digested by the addition of 0.5 gram of each sample into appropriately labeled, chemically clean digestion tubes and 10 ml of triacid mixture (HNO₃:HClO₄:HCl ratio: 2:1:2) and incubated in a fume chamber at the temperature of 250 °C for three hours. Following that, each digest was made up to 50 ml with deionized water after cooling, covered with paraffin paper, and

swirled meticulously for proper mixing. The sample solutions were transferred to a set of centrifuge tubes and shaken for 10 minutes, followed by centrifugation at 500 g for 10 minutes.¹¹ The clear supernatant solutions were transferred to a set of plastic vials to measure the concentrations of Pb, Cu, Mn, Fe, Cd, Se, Cr, Zn and As.

Laboratory methods

Estimation of heavy metals via atomic absorption spectrophotometry (AAS 1100 B, Alva, United Kingdom)

Atomic absorption spectrometry (AAS) is based on the principle that a ground-state atom is capable of absorbing light at the same characteristic wavelength as it would emit if excited to a higher energy level. In flame AAS, a cloud of ground-state atoms is formed through the aspiration of a sample solution into a flame of the adequate temperature to convert the element into its atomic state. As a result, the degree of the absorption of the characteristic radiation produced by a proper source will be proportional to the population of the groundstate atoms in the flame, as well as the concentration of the element in the analyte.¹²

Soil pollution indices

In this study, three soil pollution indices were employed to estimate the extent of surface soil pollution with arsenic, Cd, Se, Cr, Cu, Mg, Fe, Pb, and Zn in the vicinity of the cement factory. The indices included the enrichment factor (EF), geoaccumulation index (Igeo), and pollution index (PI).¹³ EF and Igeo are the indicators that are used to the presence and intensity of assess anthropogenic deposition contaminant in surface soil. The mentioned indices of potential contamination were calculated by the normalization of one metal concentration in the topsoil in terms of the concentration of a reference element. A reference element is a relatively stable element, which is often characterized by low occurrence variability, and the most commonly used elements in this regard include aluminum, iron, titanium, silicon strontium, and potassium.¹⁴ In the present, study, iron was used as the reference element.

Enrichment factor (EF)

EF was expressed as follows:

$$EF = \frac{HM(s) / Fe(s)}{HM(b) / Fe(b)}$$

where HM(s) is the concentration of heavy metals in the samples, Fe(s) represents the concentration of iron in the samples, HM(b)shows the concentration of heavy metals in the reference background environment, and Fe(b) is the concentration of iron in the reference background environment.

The numerical results were indicative of various pollution levels. Accordingly, the values of $0.5 \le EF \le 1.5$ suggested that heavy metal contamination may be entirely due to natural weathering processes, and EF>1.5 indicated that a significant concentration of the heavy metals came from anthropogenic sources. Moreover, EF was used to classify the soil quality as EF<2 (deficiency in minimal enrichment), EF=2-5 (moderate enrichment), EF=20-40 (very high enrichment), and EF>40 (extremely high enrichment).¹⁵

Geoaccumulation index (Igeo)

Igeo is used to assess the degree of anthropogenic or geogenic accumulation of the pollutant load through the comparison of the current and pre-industrial contents. In this study, Igeo was expressed, as follows:

Igeo = $\log_2([HM(s)]/[1.5 \times HM(b)])$

where HM(s) is the measured concentration of heavy metals in the samples, HM(b) denotes the geochemical background value for the heavy metals, and the constant 1.5 allows the analysis of the natural fluctuations in the content of a given substance in the environment and detection of minor anthropogenic effects.

Igeo was calculated for each heavy metal and classified as uncontaminated (Igeo ≤ 0 ; class zero), uncontaminated to moderately contaminated ($0 \leq Igeo \leq 1$; class one), moderately contaminated ($1 \leq Igeo \leq 2$; class two), moderately to heavily contaminated ($1 \leq Igeo \leq 2$; class three), heavily contaminated



 $(3 < Igeo \le 4; class four)$, heavily to extremely contaminated $(4 < Igeo \le 5; class five)$, and extremely contaminated $(5 < Igeo \le 6; class six)$.¹⁶

Pollution index (PI)

In the present study, PI was calculated based on the current concentrations of the evaluated heavy metals and their geochemical background based on the following formula:

PI = Cn/Bn

where *Cn* is the concentration of the analyzed element, and *Bn* shows the geochemical background of the analyzed element. According to the obtained results, PI<1 indicated low soil pollution with the heavy metal, $1 \le PI < 3$ denoted average soil pollution, and PI>3 showed severe soil pollution.¹⁷

Integrated pollution indices

The mean PI for the examined heavy metals in the soil sample was expressed as the integrated pollution index (IPI) of the soil. Based on the IPI, the soil samples were classified as low pollution (IPI \leq 1), average pollution (1<IPI \leq 2), high pollution (2<IPI \leq 5), and extreme pollution (IPI>5).¹⁷

Contamination factor (CF)

The contamination factor (CF) was used to assess the enrichment of the heavy metals in terms of the background concentration of these elements in the soil sample based on the following formula:

CF = Cn/Bn

where Cn is the mean concentration of heavy metal n in the soil, and Bn represents the background concentration of heavy metal n. The CFs were classified as CF<1 (low contamination), $1 \le CF < 3$ (moderate contamination), $3 \le CF < 6$ (high contamination), and CF ≥ 6 (extreme contamination).¹⁸

Quality control

Heavy metal contamination was prevented in the process of sampling, extraction, and analysis by rinsing the devices and containers with acidified and deionized water before use. Quality control was assured by performing duplicate analyses on all the samples and using reagent blanks and standard reference soil. The heavy metals with levels below the detection limits of the device were not used.

Statistical analysis

Data analysis was performed in SPSS version 20 (IBM, USA), and the results were expressed as mean and standard deviation (SD). One-way analysis of variance (ANOVA) was used to assess the inter- and intra-group variations of the means, and Fisher's least significant difference (LSD) post-hoc test was applied for the comparison of the multiple group means. In addition. Pearson's correlationto coefficient was used determine the associations between the variables. In all the statistical analyses, P-value of less than 0.05 was considered significant.

Results and Discussion

Table 1 shows the concentrations of the heavy metals in the surface soil samples collected from the camp, west, east, and south of the camp, and north of the camp (control environment) in comparison with the safe limits.¹⁹⁻²³

Table 1. Heavy metal content of surface soil samples from Camp, East, South and West of Camp, North (control) and Safe limits

Element (mg/kg)	Camp 100 m	East 2 km	South 3 km	West 5 km	North (control) 45 km	F-value	p-value	Safe limit
Mn	139.74±1.58	116.17±3.38	104.12±0.89	118.94±2.30	115.32±4.51	18.16	0.000*	44 ¹⁵
Fe	149.33±4.44	113.74±3.62	112.68±2.06	114.34±4.41	117.66±2.22	18.48	0.000*	150 16
Zn	103.41±2.73	87.32±3.937	68.99±1.03	99.18±0.79	81.42±4.18	22.02	0.000*	50-100 ¹⁶
Cu	37.31±2.13	18.23±0.47	18.37±0.18	17.10±0.45	18.40±1.40	57.19	0.000*	50 ¹⁷
Pb	0.255±0.04	0.104 ± 0.001	0.099 ± 0.002	0.099 ± 0.006	0.12±0.002	11.49	0.000*	10-70 18
Cr	0.735±0.049	0.375 ± 0.058	0.225±0.014	0.321±0.016	0.19±0.001	36.14	0.000*	65 ¹⁵
As	0.034 ± 0.003	0.039 ± 0.018	0.033 ± 0.001	0.029 ± 0.002	0.03±0.001	5.26	0.000*	0.5 18
Se	0.047 ± 0.009	0.044 ± 0.004	0.023 ± 0.001	0.037 ± 0.002	0.04 ± 0.002	4.77	0.000*	10 19
Cd	0.056 ± 0.004	0.063 ± 0.004	0.054 ± 0.001	0.060 ± 0.005	$0.05 {\pm} 0.002$	1.76	0.000*	3.0 17

*= Significant at p<0.05



Table 2. Comparison of heavy metal content of surface soil samples from Camp, West, East and South of Camp and North (control) using LSD post hoc analysis

Locations	HM (mag/lage)	Mean difference	F-value	p-value
Comp/West	(mg/kg)	20.904+4.256	19 150	0.000*
Camp/west	IVIII F	20.804±4.256	18.139	0.000*
	Fe	34.985±5.015	18.483	0.000*
	Cu	20.211±1.574	57.188	0.000*
	Pb	0.157±0.027	11.495	0.000*
	Cr	0.414±0.050	36.135	0.000*
Camp/East	Mn	23.571±4.256	18.159	0.000*
	Fe	35.585±5.015	18.483	0.000*
	Zn	16.092±4.261	22.023	0.007
	Cu	19.075±1.574	57.188	0.000*
	Pb	0.151±0.027	11.495	0.000*
	Cr	0.360 ± 0.050	36.135	0.000*
Camp/South	Mn	35.623±4,256	18.159	0.000*
	Fe	36.650±5.015	18.483	0.000*
	Zn	34.425±4.261	22.023	0.000*
	Cu	18.939±1.574	57.188	0.000*
	Pb	0.156±0.027	11.495	0.000*
	Cr	0.510±0.050	36.135	0.000*
	Se	0.024 ± 0.006	4.770	0.005*
Camp/North	Mn	24.417±0.101	18.159	0.000*
	Fe	31.661±5.015	18.483	0.000*
	Zn	21.991±4.261	22.023	0.000*
	Cu	18.903±1.574	57.188	0.000*
	Pb	0.135±0.027	11.495	0.000*
	Cr	0.538 ± 0.050	36.135	0.000*

*= Significant at p<0.05

Table 3. Index of geoaccumulation (Igeo), Enrichment factor (EF), Contamination factor (CF) and Integrated pollution index (IPI) of soil samples from camp, West, East and South of Camp and North (control)

Element	Index	Camp	East	South	West	North (control)
(mg/kg)	macA	100 m	2 km	3 km	5 km	45 km
Mn	Igeo	0.24	0.20	0.19	0.21	0.20
	EF	0.95	1.04	0.19	1.06	1.0
	CF	1.21	1.01	0.90	1.03	1.0
Fe	Igeo	0.25	0.19	19	0.20	0.20
	ĒF	1.27	0.97	0.96	0.97	1.0
	CF	1.27	0.97	0.96	0.97	1.0
Zn	Igeo	0.25	0.22	0.17	0.24	0.20
	ĒF	1.00	0.53	0.88	1.26	1.0
	CF	1.27	1.07	0.84	1.21	1.0
Cu	Igeo	0.41	0.20	0.21	0.18	0.20
	ĒF	1.56	1.00	1.02	0.93	1.0
	CF	†2.03	0.99	1.0	0.92	1.0
Pb	Igeo	0.43	0.17	0.16	0.16	0.20
	EF	1.71	0.91	0.86	0.86	1.0
	CF	†2.12	0.86	0.83	0.83	1.0
Cr	Igeo	0.752	0.38	0.26	0.33	0.20
	EF	*3.13	*3.29	1.99	*2.81	1.0
	CF	•3.75	1.91	1.15	1.63	1.0
As	Igeo	0.24	0.28	0.24	0.21	0.20
	EF	1.14	1.71	1.46	1.27	1.0
	CF	1.21	1.39	1.17	1.03	1.0
Se	Igeo	0.25	0.24	0.12	0.19	0.20
	EF	1.049	1.29	0.68	1.08	1.0
	CF	1.27	1.19	0.62	1.0	1.0
Cd	Igeo	0.22	0.25	0.21	0.24	0.20
	ĒF	0.94	1.38	1.20	1.31	1.0
	CF	1.09	1.24	1.06	1.17	1.0
IPI		1 5 5	1.12	0.96	1.05	

* = moderate enrichment, \dagger = moderate contamination, • = considerable contamination.

According to the table 1, the soil content of the examined heavy metals varied significantly depending on the location of the soil samples and their distance from the cement factory plant. No specific trend was observed in the soil content of the heavy metals in terms of their relative distance from the cement factory plant. However, the heavy metal concentrations of the surface soil samples collected from all the locations were within the recommended safe limits for the heavy metals in soil, with the exception of Zn in the soil samples collected from the closest camp areas to the cement factory, which was observed to be slightly above the safe limit. On the other hand, higher Zn levels were observed in the soil samples collected from this location, which could be due to soil contamination by the cement dust emitted from the cement plant proximal to this location, adversely affecting the microflora and fauna that are beneficial to agricultural practices.

Similar observations have been reported regarding the Zn levels in the soil samples collected from the areas in the vicinity of cement factories. Zinc has been shown to have higher mobility in soil profiles compared to other elements. The highest Zn and Pb levels in the topsoil samples obtained from the depth of 0-10 cm have also been reported in an area close to a cement factory.²⁴ The topsoil in the vicinity of a cement factory has been reported to be enriched with Zn, Pb, Cr, Ca, and Hg, which are released from the air emitted from cement kilns. Contrary to our findings, higher levels of Pb, Cu, Cd, and Cr levels than the recommended safe limits have been reported in the soil obtained from the areas in the vicinity of a cement factory in southwestern Nigeria.²⁵ Zinc is an essential element for normal growth and metabolism in plants, while higher Zn concentrations than the recommended optimal levels often result in zinc toxicity.⁴ Soil zinc levels above the maximum threshold have been implicated in plant growth inhibition, poor flower production, distortion of the cell membranes and organelles, nuclear condensation, inhibition of metabolic activities, photosynthesis, and respiration.²⁶ Furthermore, excess zinc could disrupt the microbial balance of soil, thereby creating a hostile environment



for earthworms and microorganisms. The disturbances in the biological balance of soil caused by excess zinc might be attributed to the disruption of physiological functions, protein denaturation, and destruction of the cell membranes in soil microorganisms.²⁷

Table 2 shows the comparison of the heavy metal concentrations in the surface soil samples collected from the camp, west, east, and south of the camp, and north of the camp (control environment) using the LSD post-hoc analysis. Accordingly, the concentrations of Mg, Fe, Cu, and Cr were significantly higher in the soil samples collected from the camp, which is the closest area to the factory compared to the other locations.

Cement production activities have been described as a major source of the heavy metal contamination of the agricultural soils in the proximity of cement factories.^{1, 28} In a study in this regard, heavy metals in the soils within 0.50-2.0 km of a cement factory have been higher.²⁵ be comparatively reported to Moreover, soil samples in the vicinity of cement factories have been shown to have elevated levels of exchangeable calcium, sodium, hydrogen, and manganese, as well as soil organic matters, calcium oxide, sulfur oxide, Pb, Zn, Fe, Mg, Cd, and Cr, compared to the remote areas³

Heavy metal contaminants are found in the cement dust that is emitted into the atmosphere and dispersed and deposited on surface soil within a distance depending on the size of the emitted particles.²⁹ Therefore, the deposition of heavy metal increases at shorter distances from cement plants. Soil contamination with heavy metals poses multiple risks to humans and animals since the ingestion of the heavy metalcontaminated crops that are planted in heavy metal-contaminated soil is associated with multiple organ toxicities in humans.² The deleterious health consequences associated with exposure to these soil contaminants depend on the type of the pollutants, exposure pathway, and vulnerability of the exposed population (children, adults or the elderly).³⁰

Table 3 shows the Igeo, EF, CF, and IPI of the soil samples collected from the camp, west,

east, and south of the camp, and north of the (control). camp Accordingly, moderate contamination with Cu and Pb (1≤CF<3) and significant contamination with $Cr(3 \le CF \le 6)$ were observed in the soil samples collected from the camp, which was the closest area to the cement factory. On the other hand, moderate enrichment (EF=2-5) with Cr was observed in the soil samples collected from the camp (closest area to the cement factory) and the west and east of the camp. In addition, EF values of >1.5 were observed in case of Pb and Cr in the soil samples collected from the closest area to the cement factory, which indicated that the heavy metal content of the soil was caused by anthropogenic sources, which was exposure to the cement dust emanating from the activities of the cement plant in the current research.

The release of Cr from the linings of the rotaries of the machinery used in cement production due to wear and friction could be another source of Cr contamination in soil.³¹ Cr has been described as a metal indicating geogenic loads as it is released from parent rocks, leading to the rapid weathering of parent rocks and contributing to the high Cr content of the soil in the vicinity of cement factories. However, low Cr levels with very low potential for environment hazard have also been reported in the vicinity of a cement factory in a previous study in this regard.³²

The uptake of heavy metals by plants and the subsequent accumulation in the food chain are considered to be a potential threat to human health. The crops that are cultivated in the soils with elevated levels of heavy metals often show reduced nutrient uptake, plant metabolism disorders, and reduced ability to fixate molecular nitrogen in leguminous plants,³³ which often manifests as inhibited growth, reduced transpiration, chlorosis of leaves, limited seed germination, and deformations of the root system.⁴ In addition, soil contamination with heavy metals in variable quantities and forms has been reported to cause changes in the count of microorganisms and activity of microbial enzymes, which clearly reflect the actual microbiological condition of the contaminated soil.27



Heavy metals cause abiotic stresses by inducing disorders in the metabolism of microorganisms. The diverse effects of heavy metals on individual groups of microbes are resulted from their specific effects on the physiological, morphological, and genetic characteristics of microorganism.^{34, 35} Excessive levels of Cd, Cu, and Zn have been associated with disturbances in the homeostasis of soil microorganisms through interfering with the mechanisms of gene control and inhibition of processes through nitrification, such ammonification, and activities of microbial enzymatic proteins, which in turn disrupt the cellular metabolic pathways and lead to apoptosis and decreased count and diversity of soil microorganisms.²⁷ Moreover, elevated Pb levels have been reported to significantly decrease the activities of urease, catalase, invertase, and acid phosphatase, thereby leading to poor seed germination.

High levels of Cr (VI) have detrimental microbial cell effects on metabolism and shifts the composition of microbial populations, while elevated Cu levels inhibit b-glucosidase activities.^{14, 19} The toxic effects of Cd, Cr, Cu, and Zn on the microbial populations in soil could be minimized by the use of organic and natural fertilizers. Moreover, soil phytoremediation could be performed by the use of microorganisms that are resistant to these heavy metals but enhancing their availability.27

According to the results of the present study, the heavy metal contents of the soil samples from all the examined locations demonstrated minimal enrichment (EF<2) and average pollution index $(1 \le IPI \le 2)$. The effects and concentrations of the emitted dust containing trace metals as pollutants vary depending on the technology employed by cement industries in order to ameliorate environmental degradation.6 The indices of minimal enrichment and average pollution for the heavy metals in the soil samples collected from all the studied locations may be an indication for the improvement of the air pollution control system in the areas in the vicinity of the cement factory.

Conclusion

According to the results, cement production and dispersion of cement dust and its deposition on topsoil led to soil contamination with Pb, Cu, and Cr in the studied area. The degree of contamination was observed to be a function of the relative distance from the cement factory, which may lead to adverse environmental and health consequences. Furthermore, the evaluated soil samples exhibited moderate pollution with Pb, Cu, Mg, Fe, Cd, Se, Cr, Zn, and Ar, which indicated the potentials for more severe detrimental effects on the ecosystem in the future if appropriate remediation strategies are not implemented.

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