

Ambient air PM₁₀ particulate levels at Ashaiman near Tema in Ghana

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Authors' contributions

This work was carried out in collaboration between all authors. Author FGO designed the study in consultation with the others. FGO performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript with the assistance of IJKB. SAB supervised the entire work. All authors read and approved the final manuscript.

ABSTRACT

Introduction: Emissions from a variety of air particulate sources have resulted in atmospheric pollution that, in turn, has produced serious problems, causing irreversible reactions in the environment and hence is posing a major threat to our very existence.

Aim: Identify monthly variations of particulate matter mass concentrations in air, the contribution of each size fraction (coarse and fine) to PM₁₀ levels, and the contributions from natural and anthropogenic sources.

Methodology: PM₁₀ ambient air particulates in two size fractions being the coarse (PM_{10-2.5}) and fine (PM_{2.5}) were sampled. Heavy metals and carbonaceous compounds [organic carbon (OC) and elemental carbon (EC)] concentrations were determined. Enrichment factor (EF) was used to identify species of crustal and non-crustal origin in ambient air particulates. The identified elements were used to develop fingerprints for a number of particulate sources.

Results: The mean coarse and fine particulate levels obtained were 89.2 µg/m³ and 21.6 µg/m³ respectively. The maximum and minimum levels occurred in February (dry season) and July (rainy season) respectively. Soil dust was found to be the major source of particulates in the two size fractions (coarse and fine). The sulphur contents in Harmattan (cold dry winds) dust in the dry season was found to be predominantly in the coarse fraction. EF was used to identify species of crustal and non-crustal origin in ambient air particulates. The Enrichment Factor values for the elements Cr, Cu, Zn, Pb, and Br showed that they were mostly from anthropogenic sources.

Conclusion: This study emphasizes the significant impact of seasonal variations, on particulate levels. The problem with air quality is seen to be greatest during the Harmattan when cold dry winds blow soil dust particulates across West Africa.

Key words: PM₁₀, Energy-Dispersive X-ray fluorescence, Organic and Elemental Carbon, Enrichment Factors, Harmattan

1. INTRODUCTION

The influence of the human species on the global ecosystem has increased considerably in the past century. Industrial and technological progress however, has been accompanied by a growing negative impact on the environment in terms of its pollution and degradation. The industrial pollution due to its nature has the potential to cause irreversible reactions in the environment and hence is posing a major threat to our very existence. Air pollution is generally the most widespread and obvious kind of environmental damage. Total worldwide emissions of air pollutants of around 2 billion metric tons per year are released into the atmosphere [1]. The air in a typical industrial city can contain unhealthy concentrations of hundreds of different toxic substances. The health effects of airborne particles have been studied extensively and a strong correlation between human mortality/morbidity and particulate matter (PM) concentrations has been observed [2,3].

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29 Excessive inhalation of pollutants such as particulate matter can affect the functioning of the lungs and may
30 even aggravate asthma [4]. Large quantities of compounds of heavy metals such as Mercury, Zinc, and Lead
31 can lead to a variety of chronic illnesses [5,6]. Polycyclic Aromatic Hydrocarbons (PAH) are also of concern due
32 to their carcinogenic properties [7]. Fossil-fuel power plants constitute one of the major anthropogenic sources
33 of air particulates including polycyclic aromatic hydrocarbons [8]. Air particulates in the atmosphere have both
34 anthropogenic and natural origins. Anthropogenic sources are largely due to combustion processes: motor
35 vehicle emissions, fossil fuel burning, large industrial processes and biomass burning. Natural sources include
36 windblown soils, volcanic emissions, Sea spray and lightning-induced biomass burning. Air particulates have
37 atmospheric residence times of days and weeks depending on the aerodynamic size; hence local emissions can
38 become an issue of regional and even global concern [9], as these particles are able to affect air quality in other
39 countries through transboundary transport and have global climate change implications [10].

40 Ashaiman is among the towns of most rapid population growth in Ghana. Situated to the north of Tema, an
41 industrial and harbour town, the ambient air conditions can be influenced by the industrial emissions. The high
42 number of heavy diesel-powered trucks carrying goods for export and imports to and from Tema coupled with
43 the dual carriage road (Motoway) linking Tema and Accra which also forms part of the Trans-West Africa
44 highway lying about 1.5 km south of Ashaiman can course high levels of vehicular exhaust emissions. As
45 Ashaiman is located downwind of Tema and the highway, it serves as a receptor of the emitted particles.
46 Biomass burning for cooking and open burnings from waste dump sites is quite notable of Ashaiman Township.

47 The objectives of this study are to identify monthly variations of mass concentrations of particulate matter in air,
48 establish the contribution of each size fraction (coarse and fine) to PM_{10} levels, determine the contributions of
49 the particulate matter from natural and anthropogenic sources and also ascertain the possible health effect.



Fig.1: Monitoring Site at Ashaiman

2. MATERIALS AND METHODS

2.1 Study area

Airborne particulates were sampled at the Ashaiman Senior High School campus within Ashaiman township. The Ashaiman township, is located about 10 km from the Tema harbour and about 30 km from central Accra. This site is about 8 km to the northwest of the industrial area at Tema. The town has a population of about 220,000 and identified as the area with the highest population growth rate in Ghana of about 4.6 %. The geographical location of the sampling site is on Latitude 5° 41' 42", Longitude 0° 01' 07" and an altitude of 60 m above Sea level. The climatic conditions of Ashaiman follows the prevailing conditions of most part of southern Ghana. It has a hot humid climate with the major rainfall season occurring mostly from April to June and minor one in September and October. There are two distinct or major seasons, the wet (rainy) and dry seasons (with the Harmattan winds). The major anthropogenic sources of particulate pollution in Ashaiman are fuel wood combustion, biomass burning from bush fires and open refuse dumps (open burning), fossil fuel combustion (from automobile exhaust and industry), dust from construction and re-suspension and particulate emissions from the Tema industrial area. The natural sources are the Sea spray, windblown dust and Harmattan dust. These sources produce both coarse and fine particles.

2.2 Sampling

The sampling instrument was placed at about 2.0 m above the ground level. The GENT air sampler equipment comprises of a GAST pump and Gent Stacked Filter Unit (SFU) that collects two size fractions ($PM_{2.5}$ and $PM_{(2.5-10)}$) of atmospheric aerosol samples at a flow rate of $1\text{ m}^3/\text{hr}$ [11]. Particles with aerodynamic diameters greater than $10\text{ }\mu\text{m}$ are removed from the air sample by inertia separation on a pre-impaction plate with a greased (Apiezon grease) surface. Particles smaller than $10\text{ }\mu\text{m}$ (PM_{10}) are drawn through the tube onto the stacked filter cassette unit containing two filters, but the bigger particles are caught up in the grease. The particles are first directed onto the coarse filter where the coarse particles ($PM_{(2.5-10)}$) settles but the fine ($PM_{2.5}$) particles pass through and continue onto the fine filter. Two samplers were co-located at a separation of about 1.5 m. Both had nuclepore filters for the collection of coarse particles but in the case of the fine particulate collection, nuclepore and quartz fibre filters were used in the separate samplers. The filters used for the particulate collection were all of 47 mm diameter. 24 hours of continuous sampling was done from February to August 2008 capturing 48 days of sampling.

2.3 Sample Analysis

Each sample filter was weighed before and after sampling to determine the net weight (mass) of the collected sample. The filters were earlier conditioned by keeping them in a desiccator and placed in a temperature and relative humidity controlled environment ($22.5\pm0.5^\circ\text{C}$, $40\pm2\%$ RH) for at least 24 hours. The total volume of air sampled was determined from the total volumetric flow rate (l/min) and sampling time in seconds. The mass concentrations of the particulates in ambient air were computed as total mass of collected particulates divided by the volume of air sampled in actual conditions [11].

The nuclepore polycarbonate filters were used for the elemental analysis by employing energy-dispersive X-ray fluorescence technique [13]. The samples were analysed using the Spectro X-Lab 2000 EDXRF system. The tube has a maximum operating power output of 400 W with a Rhodium (Rh) target and a palladium (Pd) end window tube. A 25 mm^2 Si(Li) detector with a beryllium window thickness of $8\text{ }\mu\text{m}$ and X-Ray energy resolution of less than 150 eV measured at the Mn $K\alpha$ line with a high entry count rate ($\sim 40,000\text{ cps}$) was used for the detection of the characteristic X-Ray photons from target sample materials (filters). The primary fluorescence X-ray energies were chosen depending on the analyte element of interest. The data analysis for elemental concentrations was carried out using the fundamental parameters approach. The following were the elements identified; Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb.

The quartz filters were used for the analysis of the carbonaceous compounds (i.e. organic carbon (OC) and elemental carbon (EC)) [14]. The quartz filters were analysed by the Interagency Monitoring of PROtected Visual Environments/ Thermal Optical Reflectance (IMPROVE/TOR) method for eight carbon fractions [14,15]. Organic carbon (OC) fractions were volatilized by four temperature steps (OC1 at 120°C , OC2 at 250°C , OC3 at 450°C , and OC4 at 550°C) in a helium environment. P yrolyzed OC (OP) was oxidized at 550°C in a mixture of

2% oxygen and 98% helium environment until the original intensity of the reflectance is attained. This is followed by elemental carbon (EC) fractions measured in the oxidizing environment (EC1 at 550 °C, EC2 at 700 °C, and EC3 at 850 °C). OP was subtracted from EC1 and utilized as an independent variable in this study since the reported EC1 concentrations in IMPROVE/TOR method include OP concentrations. Thus, EC1 in this study did not include OP.

2.4 Source Fingerprints

The elemental composition and characterization of atmospheric fine particles leads to important information on their sources [10]. The X-Ray fluorescence analysis (XRF) of particulate matter samples provided the opportunity to detect sufficient number of elements with their concentrations to develop fingerprints for a number of particulate sources. It is useful to combine some of these elements and estimate the concentrations of the major compounds such as ammonium sulfate from the measured sulphur concentration. It is also possible to derive combinations of the elements that represent signatures for some interesting aerosol components. These combinations are called pseudo-elements such as “soil” and Salinity, [16,17,18]. Thus, these composite variables and pseudo-elements provide a better understanding of the composition of the air particulates and lead to better estimates of possible sources and their contributions to the average ambient aerosol [16,17,18].

Windblown soil is composed mainly of the oxides of Mg, Al, Si, Ca, Ti and Fe with many other trace elements. The summation of these 5 major oxides account for more than 85 % of the total soil composition [18,19,20].

The equation for soil is: $[Soil] = 2.20*[Al] + 2.49*[Si] + 1.63*[Ca] + 1.94*[Ti] + 2.42*[Fe]$

The square brackets [] signifies concentration values. This equation assumes that the two common oxides of iron Fe_2O_3 and FeO occur in equal proportions. The factor of 2.42 for iron also includes the estimate for K_2O in soil through the $(K/Fe) = 0.6$ ratio for sedimentary soils [18].

Sulphur was one of the major elements measured by EDXRF in both coarse and fine particulate matter. Its origin in the fine fraction is mainly anthropogenic, produced by the burning of fossil fuel from industry, cars and from power plants. Airborne sulphur rarely occurs as pure element but rather as SO_2 gas which readily converts to SO_4^{2-} ions under normal atmospheric conditions. The sulphate ions can exist in the atmosphere as sulphuric (H_2SO_4) acid producing acid rain or be partially neutralized to ammonium bisulphate or be fully neutralized to ammonium sulphate [18,21]. With the assumption that S occurs in the atmosphere in one of these form then clearly the sulphate concentrations can be used to estimate the concentration of any of these sulphate species [17]. For sulphate ions, $[SO_4^{2-}] = 3*[S]$, for acidic sulphate $[H_2SO_4] = 3.063*[S]$, for partially neutralized sulphate (bisulphate) $[NH_4SO_4] = 3.594*[S]$ and for fully neutralized sulphate $[NH_4SO_4] = 4.125*[S]$, where the brackets denote the concentration of the species [17].

Salinity was an estimate of the total Sea salt content on the filter. It included salt of the seven most abundant anions and cations which make up 99.7 % of the salinity found in Seawater, namely Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , SO_4^{2-} and HCO_3^- [16,19]. NaCl is the most abundant salt in Seawater accounting for about 86 % of the total salinity. For this work the total Sodium Chloride (NaCl), sometimes referred to as Sea salt was estimated by $Salt = 1.8*[Cl]$. It was assumed that the majority of the measured Na and Cl were associated with the Sea salt. This was a good assumption since the Na associated with crustal material is typically less than 3 % by weight [17,21].

The ratios of chemical species present in Sea salt can be used to define the non-Seasalt component of various elements. The generally accepted mass ratios of S, K, and Ca relative to Na in Seawater are 0.084, 0.036 and 0.038 respectively [19].

Studies over seven years of S, K and Ca associated with Sea salt in $PM_{2.5}$ size fraction in Tasmania, Australia found that $[S/Na] = 0.029+0.085$, $[K/Na] = 0.032+0.013$, $[Ca/Na] = 0.038+0.025$ in agreement with Weast and Astle (1982) [19]. The non-Sea and Sea salt components of S, K and Ca were obtained from the following;

Non-Seasalt Sulphur $[nsS] = [S_{tot}] - 0.084*[Na]$	Seasalt Sulphur	$[ssS] = [S_{tot}] - [nsS]$
Non-Seasalt Potassium $[nsK] = [K_{tot}] - 0.036*[Na]$	Seasalt Potassium	$[ssK] = [K_{tot}] - [nsK]$
Non-Seasalt Calcium $[nsCa] = [Ca_{tot}] - 0.038*[Na]$	Seasalt Calcium	$[ssCa] = [Ca_{tot}] - [nsCa]$

$[S_{tot}]$, $[K_{tot}]$ and $[Ca_{tot}]$ are the mass concentrations of S, K and Ca respectively.

2.5 Enrichment Factor

The Earth's crust and the Sea are significant contributors to the aerosol composition near the Earth's surface. A comparison of aerosol compositions near the Earth's surface with natural source compositions can reveal elements resulting from human-made sources. This type of comparison is often made by the calculation of "enrichment factors" (EF) for various elements in the aerosol relative to the crust or Sea, normalized to a clear indicator of the source material. The equation for the calculation of enrichment factors to roughly separate trace elements from crustal and non-crustal sources is shown below;

$$EF = \frac{(X_{sol} / C_{sol})}{(X_{crust} / C_{crust})}$$

In the above equation, EF is the enrichment factor [22,23], X_{sol} is the concentration of the element of interest and C_{sol} is the concentration of reference element. X_{crust} and C_{crust} are the upper continental crustal averages of elemental concentrations for the element of interest and reference element respectively [24]. Elements were categorized as "non-enriched," "moderately enriched," and "enriched" if their average enrichment values are less than 3, between 3 and 30, and above 30, respectively [25]. By convention, an arbitrary average EF value of <10 indicates that a trace element in an aerosol has a significant crustal source, and in contrast, an EF value of >10 is considered as a significant proportion of an element with a non-crustal source [23,26].

3. RESULTS AND DISCUSSION

Figure 2 shows the monthly average levels of both coarse and fine particulates at Ashaiman for the sampling period (February to August 2008). Fig 3 shows the monthly average rainfall levels at Ashaiman for the same year. It can be seen that the coarse levels are consistently higher than the fine levels. The mean mass concentration levels for the coarse and fine particulates obtained within the period of investigation were $89.2 \mu\text{g}/\text{m}^3$ and $21.6 \mu\text{g}/\text{m}^3$ respectively (Table 2). The maximum concentrations values for the coarse and fine occurred in February. The month of February falls within the dry season (December-March) when the Harmattan winds carry dust from the Sahara Desert across most part of West Africa.

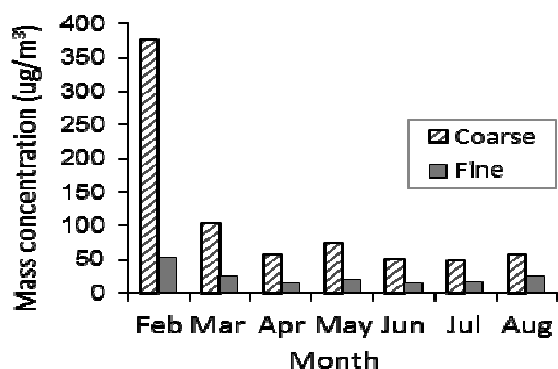


Fig. 2 Monthly variations of coarse and fine particulate levels

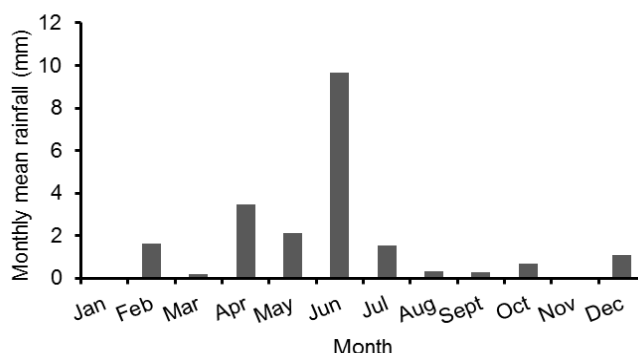


Fig. 3 Monthly mean rainfall levels at Ashaiman

The minimum particulate mass concentration levels for the two size fractions occurred in June and July which falls in the peak of the rainy season in the southern sector of Ghana. The average $\text{PM}_{2.5}$ value of $21.6 \mu\text{g}/\text{m}^3$ obtained for the sampling period was higher than the WHO annual mean value of $10 \mu\text{g}/\text{m}^3$ but less than that of 24-hour mean of $25 \mu\text{g}/\text{m}^3$. The PM_{10} mean value of $110.8 \mu\text{g}/\text{m}^3$ is also higher than WHO 24-hour mean of $50 \mu\text{g}/\text{m}^3$. WHO Ambient (outdoor) air pollution in cities database (2014) states that the world's average PM_{10} levels by region range from 26 to $208 \mu\text{g}/\text{m}^3$, with a world's average of $71 \mu\text{g}/\text{m}^3$. [27]

According to USEPA Air quality index, an ambient air PM_{2.5} particulate level of 21.6 µg/m³ falls within the Moderate Category which ranges from 13 µg/m³ to 35 µg/m³. Similarly, the PM₁₀ level of 110.8 µg/m³ also falls within the Moderate Category which also ranges from 55 µg/m³ to 154 µg/m³. At such moderate conditions for both PM_{2.5} and PM₁₀, people with respiratory or heart disease, the elderly and children are the groups most at risk.

Table 1. Mean percentage of coarse and fine particulates in PM₁₀

Coarse and fine ratios in PM ₁₀			
Month	C/PM ₁₀ (%)	F/PM ₁₀ (%)	C/F
Feb	87.8	12.2	7.3
Mar	81.0	19.0	4.4
April	79.6	20.4	3.8
May	78.4	21.6	3.7
June	77.2	22.9	3.3
July	74.7	25.3	2.8
Aug	69.6	30.4	2.3

Table 1 shows the percentage by mass of coarse and fine particulates in PM₁₀ (coarse + fine) from February to August 2008. On the average, the percentages of coarse and fine fractions in PM₁₀ were found to be 80.5 and 19.5 respectively. The mean contribution by mass of the coarse fraction was approximately 4 times that of the fine. With the exception of February and March which falls in the dry season, the ratio of coarse to fine for the rest of the months did not show significant variations but rather decreased gently to August.

The average mass concentrations of coarse and fine particulates and the identified species can be seen in Table 2. Figure 4 shows the coarse and fine contributions of the species in PM₁₀. The elements Al, Si, Ti, Fe, Rb and Sr known to be mostly of crustal origin had high contributions from the coarse mode in PM₁₀ [28,29,30]. The high contribution of Mg and Ca from the coarse mode to PM₁₀ could be due to both crustal and Sea salt. Chlorine had the maximum contribution from the coarse fraction to PM₁₀ (93.52 %) with Na also having a considerably high contribution (78.92 %) from the coarse fraction. This shows that the Sea spray is mostly of coarse mode. The coarse and fine contributions from S, Ni, Cu, Zn, and Pb did not come with much difference. This shows the possibility of anthropogenic contribution to these elements mostly in the fine fraction. Sulphur in the fine could be coming from Sea salt, fossil fuel, biomass burning and industry. Industry and fossil fuel combustion could be the major anthropogenic contribution to Ni, Cu, Zn, and Pb mostly in the fine fractions [30].

Two stroke engines could also be contributing to Zn in the fine fraction. Ashaiman community is well noted for the use of motorbikes for commuting. Br had a greater contribution in the fine than the coarse fraction. Figures 5 and 6 show the profile of the mass concentrations of Al, Si and S in the fine and coarse fraction respectively. It can be seen from Fig. 6 that Al, Si, and S followed the same profile without much observable variations. Al and Si in the fine mode were seen to follow the same profile but S did not (Fig.5). Al and Si in both coarse and fine modes are known to originate from crust [26]. As S follows in similar profile with Al and Si, in the coarse fraction, it shows that S in the coarse fraction is mostly from crustal origin.

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Table 2. Concentration of species in fine and coarse fractions of PM₁₀ particulates

Species	Fine (PM _{2.5} (ng/m ³))			Coarse (PM _(10-2.5) (ng/m ³))			% Error	MDL
	Mean	STD	Median	Mean	STD	Median		
Na	743	292	690	2960	1460	2770	14.1	15.2
Mg	94.4	74.3	72.4	407	360	332	9.0	8
Al	806	592	670	3450	3270	2480	0.8	94
Si	1160	1530	630	6950	9090	4100	0.5	16
S	390	208	320	452	269	384	0.4	54
nsS	329	196	263	204	212	136	-	-
ssS	62.2	24.4	57.9	248	122	232	-	-
Cl	145	88.9	114	2760	1580	2550	1.2	30
K	487	230	446	1130	1150	791	1.4	22
nsK	460	224	423	1030	1140	669	-	-
ssK	26.8	10.5	24.9	107	52.5	99.7	-	-
Ca	287	260	220	2230	2380	1520	1.4	15
nsCa	259	257	194	2110	2370	1400	-	-
ssCa	28.2	11.1	26.3	113	55.4	105	-	-
Ti	59	46.5	45.2	392	384	2770	2.6	3.7
V	2.9	1.3	2.8	8.9	5.4	8.1	29.2	0.8
Cr	17.3	5	15.9	25.5	8.3	23.8	4.0	6
Mn	27.4	12.4	24.4	93.9	84.7	71.8	2.6	1.4
Fe	987	467	862	5540	3760	4540	1.5	52
Ni	54.4	14.6	51.8	58	15.4	54.5	5.3	14
Cu	180	48	173	187	51	174	2.8	6
Zn	164	109	126	198	120	149	2.6	25
Br	32.4	20.7	29.9	21.9	13.5	17.6	5.1	4
Rb	2.1	1.3	2	6.2	6.8	4.4	44.1	0.6
Sr	7.2	4	6.6	24.5	24.9	18.3	20.4	1.5
Pb	43.9	28	33.6	50.7	28.9	42.8	7.6	8.9
OC ^a	6700	7500	3200	-	-	-	-	-
EC ^b	2010	1900	1300	-	-	-	-	-
OM	9366	5780	13600	-	-	-	-	-
Soil	7600	6700	5700	42700	43100	30700	-	-
Salt	270	101	239	7530	3710	7040	-	-
(NH ₄) ₂ SO ₄	257.36	800	1090	-	-	-	-	-
Mass	21600	12900	17700	89200	86700	66700	-	-

^a OC = OC1+OC2+OC3+OC4 ^b EC = EC1+EC2+EC3

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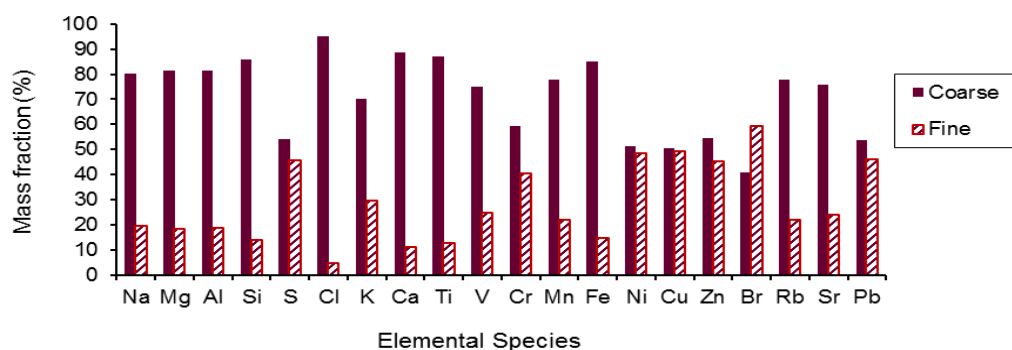


Fig.4 Coarse and fine mass fractions of species in PM₁₀

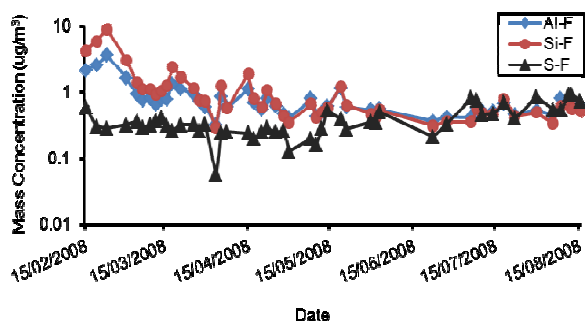


Fig. 5 Profile of Al, Si, and S in fine particulates.

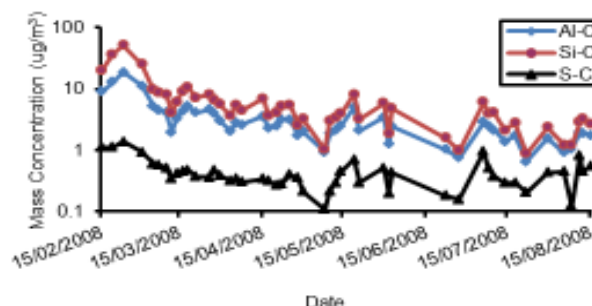


Fig. 6 Profile of Al, Si, and S in coarse particulates.

Tables 3 and 4 show a good correlation between Al and Si in both coarse and fine particulate fractions ($r = 0.99$) respectively. S correlated quite well with Al in the coarse mode ($r = 0.83$) but poorly in the fine ($r = 0.10$). It can be seen in Figs 5 and 6 that during the Harmattan period in February, S levels in the coarse fraction increased with Al and Si but rather decreased in the fine. It can therefore be deduced that S in the Harmattan winds are to the greater extent present in the coarse fraction. Sulphur in the fine fraction of the Harmattan dust was found to be present in insignificant quantities. The profile of the concentration levels of Al and Si in coarse and fine modes show a decreasing trend from February to June. As Al and Si are of crustal origin this shows that the contribution of crustal dust to ambient particulate levels is greatest in the Harmattan season and decreases gently to June and July in the peak of the rainy season in southern Ghana.

Interest is also placed on sources of soil, salt and sulphur which could be generated locally or may have major long range transport components. Malm *et al.* (1994) [17] defined soil as oxides of five major elements; Al, Si, Ca, Ti and Fe (Table 2). The correlations between each of these five major elements shown in Tables 3 & 4 were strong; Si-Al ($r = 0.99$), Si-Ca ($r = 0.99$), Si-Ti ($r = 0.99$) and Si-Fe ($r = 0.93$) for coarse and Si-Al ($r = 0.99$), Si-Ca ($r = 0.99$), Si-Ti ($r = 0.99$) and Si-Fe ($r = 0.92$) for fine fractions. This gives a good demonstration that they can indeed be used to define soil fingerprint in the standard way [16,28,30] for the sampling area. Silicon was the major dominant fraction of this soil estimate (Table 2). The metals Cu, Ni, Zn and Pb did not show good correlations with Al and Si in both coarse and fine fractions (Tables 3 & 4). The contribution of these elements from sources other than soil is therefore significant. Cu, Ni, Zn and Pb are typical indicators of industrial (e.g. metal industries) and vehicular emissions [29,30]. Resuspended dust, mostly from vehicular movements and construction could also contribute to crustal elements in both coarse and fine. Na and Cl showed no good correlation with the crustal elements. However, they showed some correlation with Cr, Cu, Ni and Zn particularly in fine fraction. Na had good correlations with these four elements in the fine, indicating significant anthropogenic contribution to Na in the fine.

260 Ashaiman is about 10 km from the Sea, hence the ambient air particulates will contain some considerable
 261 amount of Sea salt. Dry weight of Sea salt is reported to contain about 90 % of Sodium Chloride (NaCl) with
 262 [Cl/Na] = 1.54 [29]). Inspection of Table 2 shows that the Cl/Na ratio for coarse and fine were 0.93 and 0.2
 263 respectively.

264 Table 3 Correlation between elements in coarse fraction

Elements	Na	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Na	1.00														
Al	0.27	1.00													
Si	0.25	0.99	1.00												
S	0.63	0.83	0.82	1.00											
Cl	0.97	0.27	0.24	0.61	1.00										
K	0.31	0.99	0.99	0.88	0.30	1.00									
Ca	0.29	0.99	0.99	0.83	0.29	0.99	1.00								
Ti	0.28	1.00	0.99	0.84	0.28	0.99	0.99	1.00							
Cr	0.53	0.84	0.81	0.82	0.50	0.83	0.83	0.84	1.00						
Mn	0.28	0.99	0.99	0.84	0.26	0.99	0.99	0.99	0.85	1.00					
Fe	0.36	0.96	0.93	0.85	0.37	0.94	0.94	0.97	0.90	0.95	1.00				
Ni	0.55	0.47	0.45	0.55	0.49	0.46	0.46	0.47	0.83	0.50	0.54	1.00			
Cu	0.56	0.39	0.36	0.51	0.50	0.38	0.38	0.38	0.79	0.42	0.48	0.97	1.00		
Zn	0.28	0.09	0.08	0.18	0.23	0.10	0.09	0.09	0.39	0.17	0.21	0.50	0.52	1.00	
Pb	0.12	0.17	0.15	0.22	0.13	0.17	0.16	0.18	0.33	0.22	0.29	0.31	0.30	0.59	1.00

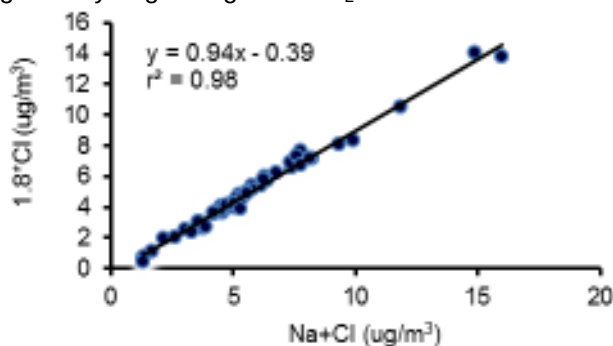
265 Table 4 Correlation between elements in fine fraction
 266

Elements	Na	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Na	1.00														
Al	0.31	1.00													
Si	0.23	0.99	1.00												
S	0.54	0.08	0.11	1.00											
Cl	0.77	0.41	0.35	0.21	1.00										
K	0.57	0.40	0.36	0.74	0.54	1.00									
Ca	0.32	0.98	0.99	0.07	0.43	0.40	1.00								
Ti	0.27	1.00	0.99	0.11	0.38	0.38	0.98	1.00							
Cr	0.73	0.54	0.43	0.22	0.65	0.39	0.50	0.49	1.00						
Mn	0.62	0.82	0.78	0.03	0.65	0.40	0.81	0.80	0.71	1.00					
Fe	0.49	0.96	0.92	0.02	0.56	0.44	0.94	0.95	0.69	0.90	1.00				
Ni	0.76	0.44	0.33	0.29	0.64	0.37	0.41	0.38	0.96	0.65	0.60	1.00			
Cu	0.76	0.34	0.23	0.28	0.65	0.33	0.32	0.29	0.92	0.58	0.52	0.95	1.00		
Zn	0.76	0.05	0.02	0.12	0.75	0.14	0.06	0.02	0.56	0.54	0.26	0.59	0.63	1.00	
Pb	0.37	0.03	0.07	0.01	0.40	0.03	0.01	0.05	0.29	0.34	0.11	0.31	0.36	0.60	1.00

267
 268 The percentage chlorine loss was determined from the following equation; % Cl loss = $100 \times (1.54 - [\text{Cl}/\text{Na}]/1.54)$
 269 [28]. Chlorine losses in the coarse and fine fractions were 39% and 87% respectively. The Chlorine loss can be
 270 due to the possible conversion of NaCl into Na₂SO₄ and NaNO₃ in the course of reaction with H₂SO₄ and HNO₃
 271 respectively in the atmosphere [31,32]. This could be expected as there is a harbour and industries at Tema.
 272 Plots of 1.8*[Cl] against Sodium plus Chlorine (Na+Cl) concentrations for the coarse and fine fractions showed
 273 linear relationship with gradients of 0.94 ($r^2 = 0.98$) and 0.38 ($r^2 = 0.74$) respectively (Figs 7 and 8). Sea salt can
 274 be estimated as 1.8*[Cl]. The degree of correlation gives a good picture of the level of Cl loss from the sum of
 275 Na and Cl (Na+Cl) in air. The low gradient of 0.38 observed in the graph (Fig 8) of the fine fraction together with
 276 the significant reduction in the correlation between Na and Cl in the fine as compared with that of the coarse
 277 (Tables 3 and 4) confirm the significant chlorine loss (87%) in the fine fraction.

278 Tables 5 and 6 show the correlation between S, K and Ca in their salt and non-salt components for the coarse
 279 and fine fraction respectively. Strong correlation was observed between the non-salt components (nsS, nsK and
 280 nsCa) in the coarse fraction (Table 5). This was quite expected as the non-salt components of these three
 281 elements in the coarse fraction are predominantly from crustal origin. Similarly, there was strong correlation

282 between the Sea salt components (ssS, ssK and ssCa). Sulphur in the fine fraction occurs as secondary sulfate
 283 generally originating from SO₂ emissions. It has several significant sources which include automobiles, fossil



284
 285 Fig 7 1.8*[Cl] verses Na+Cl for coarse fraction
 286

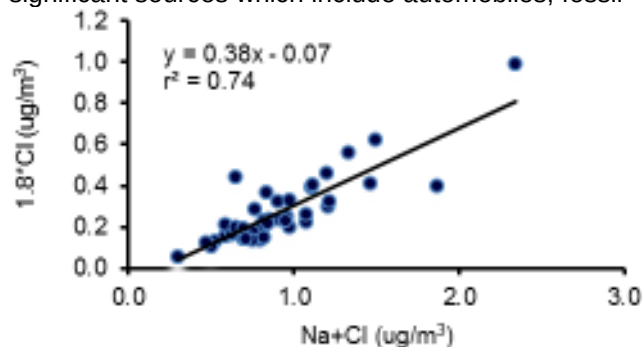


Fig 8. 1.8*[Cl] verses Na+Cl for fine fraction

287 fuel fired power stations and industrial emissions. Table 4 shows possible correlations of fine sulphur with 12
 288 other measured elements. The correlations were not so clear cut as several different source types could be
 289 involved. Total S in the fine only correlated moderately with K which was expected as they could come from soil
 290 and combustion process. K is well known to be a fingerprint of biomass burning [33,34]. SO₄²⁻ showed a good
 291 correlation with non-salt K in the fine fraction which can be traced to combustion process but had moderate
 292 correlation with Na and the salt components of K, and Ca (Table 6). The moderate correlation of the salt
 293 components with SO₄²⁻ could be due to the presence of the harbour.

294
 295
 296 Table 5 Correlation between salt and non-salt components of S, K, and Ca in coarse fraction

	Na	Cl	Salt	nsS	ssS	nsK	ssK	nsCa	ssCa
Na	1.00								
Cl	0.97	1.00							
Salt	0.97	1.00	1.00						
nsS	0.24	0.23	0.24	1.00					
ssS	1.00	0.97	1.00	0.24	1.00				
nsK	0.33	0.32	0.33	0.93	0.33	1.00			
ssK	1.00	0.97	1.00	0.24	1.00	0.33	1.00		
nsCa	0.29	0.28	0.29	0.88	0.29	0.99	0.29	1.00	
ssCa	1.00	0.97	1.00	0.24	1.00	0.33	1.00	0.29	1.00

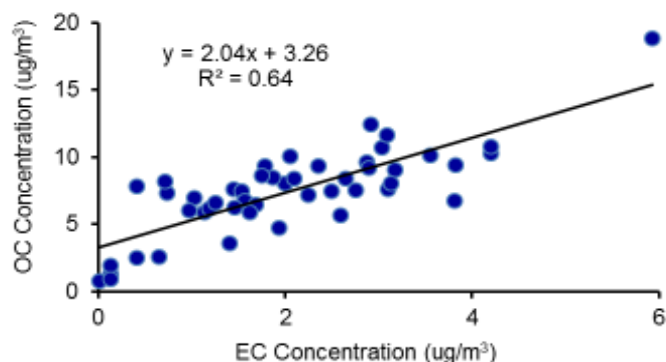
297
 298 Figure 9 shows the organic and elemental carbon concentrations levels for PM_{2.5} particulates. The mean ratio of
 299 total carbon (OC+EC) to PM_{2.5} mass was 40.3 % indicating that total carbon makes up approximately 40 % of
 300 the fine (PM_{2.5}) mass. Elemental carbon (EC) to organic carbon (OC) ratio on the average was approximately 26
 301 %. The minimum and maximum ratios occurred in the months of February and July. The months of February
 302 and July falls within the dry Harmattan and rainy seasons respectively. The dry Harmattan season is usually
 303 characterized by bush fires and this shows that OC is more produced than EC in biomass burnings. In general,
 304 higher ratios of EC to OC (e.g. from diesels combustion) are more likely to result in positive and larger net
 305 forcing (warming) compared to lower ratios [35,36].

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316 Table 6 Correlation between salt and non-salt components of S, K, and Ca in fine fraction

	Na	Cl	Salt	nsS	ssS	SO ₄ ²⁻	nsK	ssK	nsCa	ssCa
Na	1.00									
Cl	0.77	1.00								
Salt	0.77	1.00	1.00							
nsS	0.45	0.13	0.13	1.00						
ssS	1.00	0.77	0.77	0.45	1.00					
SO ₄ ²⁻	0.54	0.21	0.21	0.99	0.54	1.00				
nsK	0.54	0.52	0.52	0.72	0.54	0.74	1.00			
ssK	1.00	0.77	0.77	0.45	1.00	0.54	0.54	1.00		
nsCa	0.28	0.40	0.40	-0.13	0.28	-0.09	0.38	0.28	1.00	
ssCa	1.00	0.77	0.77	0.45	1.00	0.54	0.54	1.00	0.28	1.00

317



318

319 Fig.9 Organic and elemental carbon concentrations in PM_{2.5}

320

321 Table 7. Enrichment factors of elements in the coarse
322 and fine fractions

Element	Coarse			Fine		
	Mean	Max	Min	Mean	Max	Min
Na	4.6	15.4	1.0	4.0	8.0	1.1
Mg	0.5	1.1	0.3	0.4	0.6	0.3
Al	1.0	1.0	1.0	1.0	1.0	1.0
Si	0.5	0.8	0.3	0.4	0.7	0.2
S	38.8	115	17.3	146	473	18.4
Cl	633	2310	141	119	289	39.2
K	1.3	2.3	0.6	2.8	7.0	0.4
Ca	1.2	1.5	0.8	0.7	0.9	0.5
Ti	1.6	1.8	1.1	1.0	1.2	0.9
V	2.1	3.7	1.0	2.9	6.6	0.8
Cr	8.2	22.2	2.5	20.7	30.8	5.8
Mn	2.5	4.3	1.9	3.3	8.2	1.8
Fe	2.6	3.4	1.6	2.0	2.6	1.2
Ni	24.6	85.3	4.8	80.5	115.9	20.8
Cu	111	382	19.7	375	547	93.3
Zn	98.6	333	16.7	296	1020	55.3
Br	287	511	71.4	1700	7270	2760
Rb	1.6	3.8	0.9	2.8	6.7	1.2
Sr	1.7	3.1	1.1	2.2	4.1	1.0
Pb	123	485	21.9	409	879	68.0

323

324 Table 7 gives the enrichment factors (EF) for the elements with Al as the reference element. Aluminum was
325 chosen as the reference element because of its high abundance in the aerosol samples, had negligible
326 anthropogenic contributions and was easily determined by EDXRF analysis. Generally, the EFs for most
327 elements were found to be higher in the fine than the coarse fraction. For most elements of crustal origin (Si, Al,
328 Fe, Ca, Ti, Rb, Sr etc.), the EFs for the coarse and fine fractions were quite low and similar (EF<3) [23]. The

elements Na and Cl well noted to be mostly of marine origin had relatively higher enrichment factors in the coarse than the fine fraction. This indicates that Sea salt is more of coarse than fine fraction. Na had lower EF compared with Cl which could mean that some amount of Na had crustal origin. Br was the most enriched with mean EF value of 287 and 1700 for coarse and fine fractions respectively. The high enrichment of Br could be attributed to Sea salt and vehicular exhaust emissions. It was realized that elements of anthropogenic pollution origins, like Zn, Pb, Ni, Cu, are highly enriched as compared with that of crustal composition. Some toxic and harmful elements, particularly Cr, Cu, Zn, Pb, and Br are highly enriched in both size fractions with fine fraction being higher than the coarse by multiples ranging between 2 to 5. Sulfur enrichment in fine fraction was approximately 4 times that in coarse.

4. CONCLUSION

This work has looked at the variations in ambient air particulate levels for PM₁₀ in coarse and fine fractions in a sub-urban township with contributions from industrial emissions. The contribution of each size fraction (coarse and fine) to PM₁₀ mass and the ratio of coarse to fine were determined. The mean PM₁₀ mass concentration value was 110.8 µg/m³ with maximum and minimum values of 377.17 µg/m³ and 49.80 µg/m³ occurring in February and July respectively. This mean value is higher than WHO 24-hour mean of 50 µg/m³. The mean value of PM_{2.5} was 21.6 µg/m³ and is higher than the WHO annual mean value of 10 µg/m³ but less than 24-hour mean of 25 µg/m³. The maximum and minimum PM_{2.5} levels were 72.73 µg/m³ and 11.1 µg/m³ respectively also occurring in February and July respectively. Coarse fraction contributed an average of 80.5 % to PM₁₀ which is about 4 times the mass of the fine. The problem with air quality is therefore greatest during the Harmattan (the dry season) when cold dry winds blow across West Africa from December to March.

The average composition of soil, salt, ammonium sulphate, organic matter and black carbon in the ambient fine particulate pollution were 35.02%, 1.26%, 1.71%, 43.56%, 9.30% respectively. The remaining missing mass (9.15%) could be nitrates and possibly absorbed moisture. The average composition of soil and salt in the coarse particulate fraction were 47.9% and 8.44% respectively. Soil dust was found to contribute significantly to the particulates in the two size fractions (coarse and fine). Sulphur in the fine fraction of Harmattan dust was present in insignificant quantities. Results of the enrichment factors showed that the elements Cr, Cu, Zn, Pb, and Br present in the ambient air are mostly of anthropogenic origins.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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