Physicochemical Analysis of Discharged Particulate from Power Generating Engines

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ABSTRACT

Engines Soot samples, collected from fuelled with a range of diesel and gasoline have been analyzed. The Particulate carbon, as soot or carbon black of power plants composes one of the more visible and troublesome particulate air pollutants. Analytical result gave vanadium (0.056±0.036), selenium (0.04±0.022) and bismuth (0.04±0.022) with units in ppm for the raw or unburnt diesel. The corresponding values for particulate diesel soot were estimated at values up to 0.04, 0.004 and 0.04ppm respectively. This implies a possibility of volatilization by the hot air current and fragmentation into the near atmosphere. Because of its good adsorbent properties, carbon of gasoline soot was predicted to have adsorbed these metals and presented values as V(0.004ppm), Se(0.004ppm) and higher value for Bi(0.04ppm) which were evidently absent in the unburnt gasoline samples. They may therefore be a carrier of metallic and other particulate pollutants which could be potential environmental and subsequently health threats.

Key words: Particulate, Diesel, Gasoline, Environment, Metals, Soots.

INTRODUCTION

There are disadvantages to burning. The first and most visible disadvantages is the large black smoke plume that burning oil produces .the second is unsuspected deposit of potentially toxic metals embedded in the soot .Soot blowing and air heater cleaning operations were areas of neglect and not taken into account when assessing environmental pollutants [1] in the Diesel particulate pollution from mobile stationary engines is a constituent of regional particulate problems leading to visibility impairment across the country. Fine particles in the lower atmosphere scatter and absorb light, obscuring scenic vistas such as those in national parks. Fine particles also play a major role in creating the "brown clouds" that shroud many western cities, particularly during the winter months [2].The breathtaking range of hazards posed by diesel exhaust stands in stark contrast to the lack of a comprehensive approach to controlling diesel emissions from all their sources. The critical constituents of diesel exhaust include Particulate

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Matter, NO_2 and SO_2, as well as a laundry list of toxic chemicals that cause both public health and environmental dangers [2].

Diesel exhaust occurs as a gas, liquid or solid and is a result of the combustion of diesel fuel in a compression-ignition engine. Its composition varies depending on the type of engine, the operating conditions, fuel characteristics and the presence of a control system, but it always contains both particulate matter and a complex mixture of hundreds of gases, many of which are known or suspected to cause cancer [3, 2]. Diesel engines produce far more particulate pollution than gasoline engines. Depending on operating conditions, fuel quality and emission controls, light-duty diesel engines and heavy-duty diesel engines can emit 50 to 80 times and 100 to 200 times, respectively, more particle mass than typical catalytically equipped gasoline-powered engines. Diesel particulate matter is typically fine (< 2.5microns) or ultrafine (< 0.1 micron) in size [2]. The major pollutants that make up diesel exhaust each pose threats to public health and the environment. In addition, a growing body of research on the hazards of diesel exhaust shows that this particular combination of pollutants causes significant cancer risk and both acute and chronic health problems [2].

Toxic elements are present in trace quantities in coal and other fossil fuels. Since the quantities of these inhaled each year are enormous, the associated quantities of potentially harmful toxic elements are appreciable. For example, assuming 600 million tons of coal burned per year in the United States, with average concentrations for Hg of 0.10 ppm , Pb-20, Cd-0.4, As-5, Se-5, Sb-4, V-25, Zn-200, Ni-100, Cr-20, and Be-2ppm [1].

Emissions of particulate material from industrial sources have received considerable attention for many years. In the past, the interest was related to a number of effects, including visibility reduction. In recent years this interest has increased as a consequence of concerns about the health impacts of fine particles. As a consequence, the issue of fine particulate material is of great current research and community interest, and the sources, formation, and transformations of fine particles in the atmosphere are likely to be the most important issues in air pollutant research in the next 10 years [4]. Diesel vehicles are a major source of fine particle emissions in urban locations, and an accurate characterization of the composition of particulate emissions from diesel vehicles is a high priority [5].

Chemistry of Soot Formation: Soot particles are mostly found as agglomerates of primary particles typically no larger than 500Å. The hydrogen and carbon ratio in soot ranges between 1:8 to 1:10. A typical agglomerate obtained from rich high-temperature methane combustion is shown below [6]. Soot formation cannot be explained by simple thermodynamic equilibrium considerations as suggested in the following overall reaction [6].

$$C_mH_n + \alpha O_2 \rightarrow 2\alpha CO + n/2H_2 + (m-2\alpha)C_{soot}$$
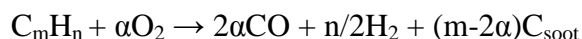
It is concluded that soot formation is a kinetically governed process. The formation process consists of fuel pyrolysis and oxidation reactions, formation of the first ring (benzene) and subsequently polycyclic aromatic hydrocarbons (PAH), inception of the first particles, growth of soot particles due to reactions with gas phase species, particle coalescence, agglomeration and oxidation. This process has been roughly sketched in Figure 1[6].
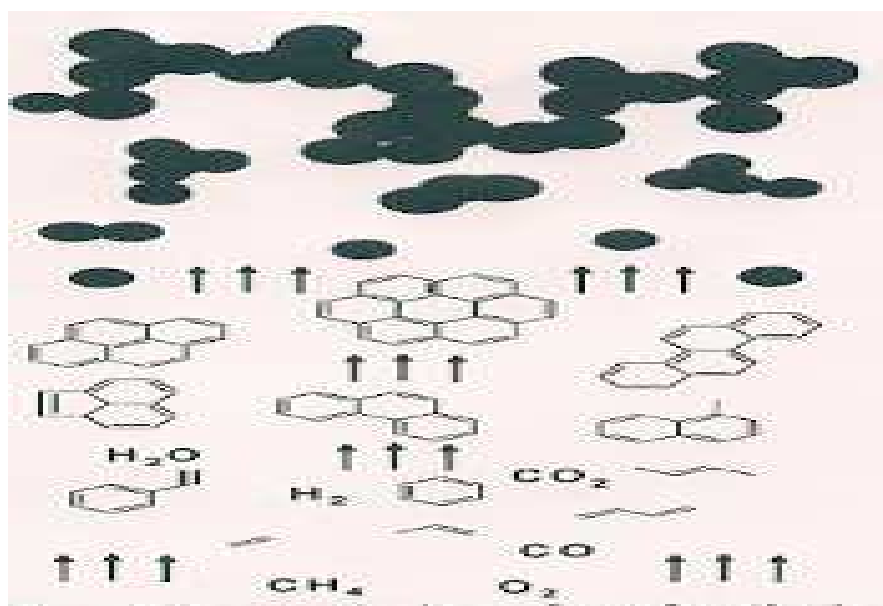
Figure 1: A schematic picture of soot formation in homogenous mixtures. Source: [6]
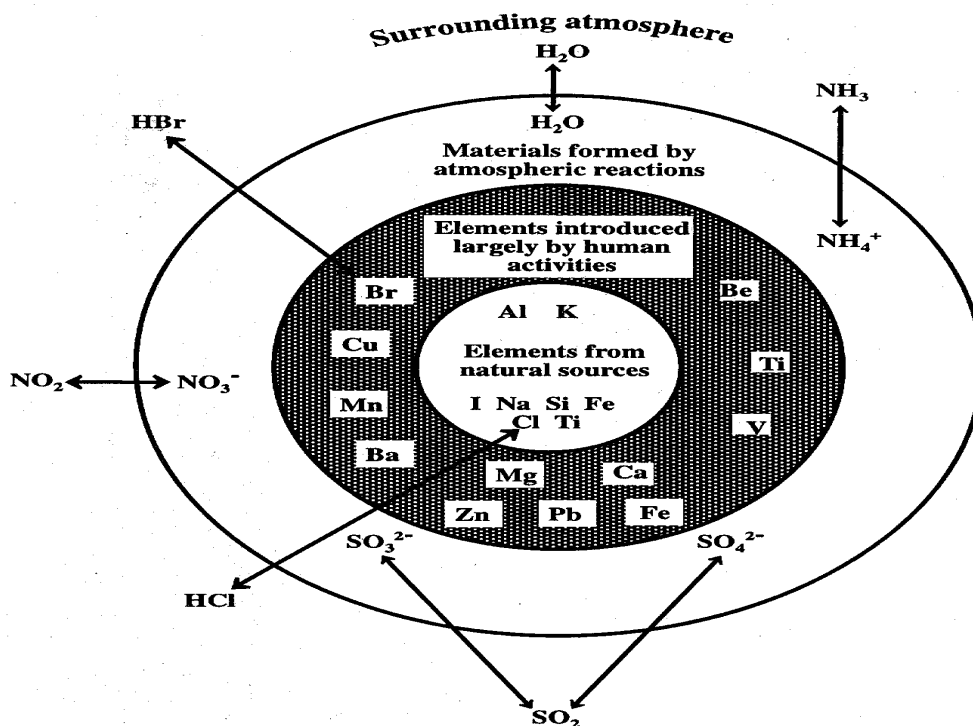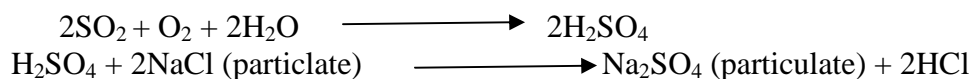

Figure 2: Some of the components of inorganic particulate matter and their origins. Source: [7]

A study of particulate matter emitted by gasoline auto engines (with and without catalysts) and diesel truck engines measured more than 100 compounds quantitatively. The source of particulate matter is reflected in its elemental composition, taking into consideration chemical reactions that may change the composition. For example, particulate matter largely from an ocean spray origin in a coastal area receiving sulfur dioxide pollution may show anomalously high sulfate and corresponding low chloride content. The sulfate comes from atmospheric oxidation of sulfur dioxide to form nonvolatile ionic sulfate, whereas some chloride originally from the NaCl in the seawater may be lost from the solid aerosol as volatile HCl [7]:

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$$
$$H_2SO_4 + 2NaCl \text{ (particlate)} \longrightarrow Na_2SO_4 \text{ (particulate)} + 2HCl$$

Soot particles are very common in polluted atmospheres, so it is very likely that they are strongly involved in catalyzing the oxidation of sulfur dioxide.

Particulate carbon as soot, carbon black, coke, and graphite originates from automobile [7] and truck exhausts, heating furnaces, incinerators, power plants, and steel and foundry operations, and composes one of the more visible and troublesome particulate air pollutants. Because of its good adsorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. Particulate carbon surfaces may catalyze some heterogeneous atmospheric reactions, including the important conversion of SO_2 to sulfate [7]

Selenium, a very volatile element, possibly from the combustion of oil, coal, or refuse while Vanadium Combustion of residual petroleum (present at very high levels in residues from Venezuelan crude oil).Selenium toxicity resembles that of arsenic and tellurium, occurs by inhalation, ingestion and absorption through skin of the metal or its compounds. Selenium concentration in the blood is 19-25 micrograms per 100 millilitres. It is found in the highest concentrations in the kidney, heart, spleen and liver, and to some degree, in all other tissues except fat. Although selenium can be toxic by itself, it also prevents the toxicity of several other metals such as silver, mercury, cadmium, and lead [8]. Acute toxicity include; nervousness, vomiting, cough, dyspnea, convulsions, abdominal pain, diarrhea, somnolence, fall in blood pressure, respiratory failure and death. Garlic-like odor may be present on breath. Selenium oxychloride is a severe vesicant and may cause fatal poisoning [9].

Bismuth is a brittle pinkish metallic element belonging to group 15 (formerly VA) of the periodic table. It occurs native and in the ores bismuthinite (Bi_2S_3) and bismite (Bi_2O_3). The element does not react with oxygen or water under normal temperatures. It can be dissolved by concentrated nitric acid. It is the most diamagnetic of the metals and has less thermal conductivity than any metal except mercury [7]

Most previous works on diesel exhaust speciation have been aimed at characterizing the composition of diesel exhaust, often in great detail. There have however been a number of studies, which report emission rates [4]. This present study was conducted to examine toxic metallic pollutants of accumulated soot particles produced from a variety of fuels and processes, including kerosene (K_{1-6}) and wood (W_{1-6}) which are disposal as atmospheric ultrafine particles from these two locally unsuspected sources.

MATERIALS AND METHODS

Petroleum soot from the exhaust of different power generating plants ware randomly obtained at different locations within Sokoto metropolis including residential areas. About 50g of each sample was randomly procured from the exhaust of each power plant generator into clean sample holders with seals. They were labeled and stored at room temperature. Samples were obtained at specific location from five zones based on population index as related to generator operations. The zones are: 1.UDUTH (Uduth, Kware road, and Gawon Nama), 2.Emir Yahya (Emir Yahaya Market, Sahara Mechanic village and Buzaye), 3.Rima Bassin (Rima basin, Kwannawa, Army Barracks and Old air port), 4.Tudun Wada (Tudun Wada area, Kofar rini, Sokoto Cinema and Kofar Tarauniyya) and 5.Main Markete Zone (Market gate Aliyu Jodi and Dandima).The most

notable soot generating area were identified and the soot were collected from the specified location and the information of the sample are presented in Table 1.

Table 1: sampling and sample information/description

Sampling site	Sample	Fuel Uptake (dm^3)	rated out put	Model/Manufacturers
Uduth	D1	313.8	1500KVA	400series/Parkins England.
Uduth	D2	221.4	1000KVA	4000 series/Parkins Englands
Kware road	D3	60.5	100KVA	200 series/Parkins England
Gawon nama	D4	62.5	200KVA	dd 200/Parkins England
Rima basin	D5	442.8	500-2000KVA	dd 500 Parkins England
Rima basin	D6	30	13.2KW	ll50 China
Kwarnawa	G1	30	6.5 KW	ll8gf series Japan
Barracks	G2	4	5.3 KW	yg30 sereis China
Old airport	G3	30	5.5. KW	fpg7800e
EmirYahaya	G4	4	3.8KW	yg 30 series China
Sahara	G5	30	7.0 KW	fpg 30 series
Duzaye	G6	4	3.0 KW	llf8gf series China

D-Dieseal soot, G-Gasoline Soot, KVA-kilovolt amperes, KW-kilowatts

Sample treatment: Treatment of sample entails breaking of soot lumps into powder. The already carbonized sample were homogenized and taken for the preparation of working solutions. High analytical grade purity chemical reagents and distilled water were used throughout the experiments. The preliminary studies carried out sample include; physical examination, Moisture content, Bulk density, pH and conductivity. Bulk Density was estimated by placing the product into a graduated cylinder and compacted by tapping on the bench top until peculiar volume; V (cm^3) was occupied, by mass (mg). The cylinder was tapped on the bench until the volume of the sample stop decreasing, the mass and volume were recorded and the density was calculated by the formula below. [10], the result was recorded.

0.1g of each sample was weighed into a 25 cm^3 beaker and suspended with 10cm^3 distilled water and the pH was determined directly using pH meter at room Temperature (33^{0}C) [11] .The pH meter was calibrated with buffers solution of pH 4 and 7. The result was recorded.

0.1g of each sample was weighed in a beaker, 30cm^3 of distilled H$_2$O was added and stirred the conductivity was measured by inserting electrode of the conductivity meter into the suspensions. The readings are displayed and recorded. [12, 11].

Apparent colour examination was done with naked eye and were found to be black (Carbonized) powered samples. [11].

Sample Digestion: Sample Digestion using the wet digestion method earlier described by [13,14,15] was followed with slight modification. Exactly 0.2g of each sample was mixed with 0.2g potassium permanganate (Oxidant) after which 2cm^3 Hydrogen peroxide was added the resulting solution was treated with 10cm^3 concentrated Nitric acid the sample was allowed to settle for 1 hour followed by heating at 200-300^{0}c until the content reduced to between 3-5cm^3 [14,15]. The process was repeated until substantial quantity was obtained. The mixture was allowed to cool at room temperature. Filtration was done using fitter paper No 42. About 10cm^3 of each filtrate was diluted to 50cm^3 with distilled water and the sample were labeled for FAAS Analysis [8] The Unicam 969 model AAS was set up according to manufacturers instruction with the wavelength corresponding to that of the element under investigation. The spectrometer was set to zero absorbance using the blank solution. The absorbance of each sample was read

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with an automatic calculation of the average concentration (ppm). Blank solution used to eliminate the contamination was prepared, using the procedure which contains sample volume of the entire reagent used excluding the soot sample [15].

RESULTS AND DISCUSSION

Physicochemical Analysis: pH is a measure of the hydrogen ion concentration in a solution. This implies that a low pH value indicates a high hydrogen ions concentration. Generally, pH all falls within the acidic range for the analyzed soot samples. pH values obtained was presented in ascending order. For Diesel soot; $D_6 > D_5 > D_4 > D_2 > D_3 > D_1$, for gasoline soot; $G_5 > G_6 > G_2 > G_1 > G_4 > G_3$. For kerosene soot; $K_6 > K_4 > K_2 > K_1 > K_3 > K_5$ and for wood soot; $W_6 > W_4 > W_5 > W_3 > W_1 > W_2$. Conductivity values obtained in this analysis ware low. This is an indication that the compounds in the samples are mostly covalent with high carbon contents. However the availability of divalent metals could be critical in explanation for fairly high values (92-229µs/cm) conductance of Diesel engine soot.

Table 2:   pH, Electrical conductivity, Moisture content, Bulk Density. **From Diesel soot engines**

Sample	pH	Conductivity(µs/cm)	Moisture (%)	Bulk Density(g/cm^3)
D_1	3.12	229	5	0.160
D_2	3.30	226	10	0.146
D_3	3.16	218	5	0.140
D_4	3.36	096	20	0.543
D_5	3.41	092	10	0.152
D_6	3.55	101	20	0.484
G_1	3.86	063	20	0.395
G_2	4.58	005	20	0.590
G_3	3.61	059	20	0.185
G_4	3.78	066	20	0.365
G_5	5.25	013	10	0.661
G_6	4.86	017	10	0.407

D-Dieseal soot, G-Gasoline Soot, .Locations; D1-Uduth, D2-Uduth, D3-Kware road, D4-Gawon nama, D5-Rima basin, D6-Rima basin, G1-Kwarnawa, G2-Barracks, G3-Old airport, G4-EmirYahaya, G5-Sahara, G6-Duzaye

Conductance is a measure of relative ease with which ions migrates. The conductivity of electrolytes decreases as the pH increases. From the Table2 it is believed that the statements are true. Hence, these could be a factor to assess the samples and arrange the samples in ascending order; For Diesel soot, $D_1 > D_2 > D_3 > D_6 > D_4 > D_5$. For Gasoline soot; $G_4 > G_1 > G_3 > G_6 > G_5 > G_2$. Bulk Density is the measure of strength / attrition of the soot. In this analysis all the values obtain were less than 1. This is an implication that the soot can be easily spread by air current to the environment. The Gasoline soot presented higher values (0.590 for G_2 and 0.661 for G_5). Table 2 shows the values obtained of the above parameters. Based on the result the samples were rank in ascending order. Moisture content; For Diesel soot. $D_6 = D_4 > D_5 = D_2 > D_3 = D_1$. For Gasoline soot; $G_1 = G_2 = G_3 = G_4 > G_5 = G_6$; For Kerosene soot;

Metal Analysis: Atmospheric selenium, up to a concentration level of 50ppb was reported as too high [16, 17]. Table 3 shows the availability of vanadium, selenium, and bismuth concentrations in (ppm) present in Diesel petroleum engine soot samples. It was found that the mean value concentration in ascending order are; V (0.056 ± 0.036)> Bi (0.04 ± 0.02) >Se (0.04 ± 0.00).Vanadium is high in the series. This is an indication that, vanadium in unburned diesel is higher compared to selenium and bismuth as observed from the reference sample (Dr).

Generally, engines, especially Diesel engines are regulated for smoke capacity, total oxide of nitrogen (NO_X) ,total particulate matter and total hydrocarbon.

Table 3: Vanadium (V) ,Selenium(Se) and Bismuth(Bi) concentrations in Diesel Engine Soot

samples	Potentially toxic metals		
	V	Se	Bi
	(ppm)	(ppm)	(ppm)
D1	0.04	ND	ND
D2	0.04	ND	ND
D3	ND	ND	0.04
D4	0.04	ND	0.04
D5	0.04	0.004	ND
D6	ND	0.004	ND
Dr	0.12	0.004	0.04
Mean	0.056	0.04	0.04
SD	0.035777	0.00	0.021907

ND-Not Detected, D-Diesel, Dr-Diesel reference.Locations; D1-Uduth, D2-Uduth, D3-Kware road, D4-Gawon nama, D5-Rima basin, D6-Rima basin

The magnitude of engine emissions depends on fuels consumptions. This research considers particulate emissions which manly relies on soot carbon and deformed as solid materials collected on the appropriate sites at an ambient temperature because they could be carrier's toxic metals.

From Table 4, the traces of pollutants V, Se and Bi detected in some samples could not be traced to the Gasoline itself Gr (Not detected) but traceable to engine chambers and emissions from other mechanical activities within operation zones. Table 4 presents the concentration (in ppm) of V, Se and Bi in gasoline petroleum soot engine. Availability follows the trend; Se > Bi > V. The Table revealed that V is majorly not detected. Generally the reference sample gave no value.

Table: 3.3.2:Vanadium(V), Selenium(Se) and Bismuth(Bi) Concentrations in Gasoline engine soot

samples	Potentially toxic metals		
	V	Se	Bi
	(ppm)	(ppm)	(ppm)
G1	ND	ND	ND
G2	ND	ND	0.04
G3	0.004	0.004	0.04
G4	0.004	0.004	ND
G5	ND	0.004	ND
G6	ND	0.004	0.04
Gr	ND	ND	ND
Mean	0.004	0	
SD	0	0	

G-Gasoline, ND-Not Detected, BDL-Below Detection Limit and Locations; G1-Kwarnawa, G2-Barracks, G3-Old airport, G4-EmirYahaya, G5-Sahara, G6-Duzaye

Vanadium ,Selenium and Bismuth were respectively analyzed at a mean level of; V (0.056±0.036ppm), Se(0.04±0.00ppm) and Bi(0.04±0.0219ppm) for raw or unburned Diesel samples. These values were considerably higher than those of the corresponding Gasoline samples which was estimated as 0.004ppm each for sample G_3 and G_4 . No such value was obtained for G_1, G_2 and G_5 .This implies that other sources of emission could be responsible for

the values estimated for G_3 and G_4 since the raw gasoline sample (Gr) has no indication for the presence of V, Se and Bi .This is in line with the assumption that the soot particulate is an attractant for pollutants due to the porous nature of the carbon soot [15]. On the contrary, the sources of the metals in Diesel soot could be linked to the reference (un burnt) Diesel, (Dr) which shows indication of volatilization, since value obtained for $Dr > D_{1-6}$.

CONCLUSION

Unlike diesel, the traces of pollutants; V, Se and Bi detected in some samples could not be traced to the original gasoline, Gr (Not detected) but traceable to engine chambers and emissions from other mechanical activities within operation zones. As a result, unimaginable quantities of soot from the partial combustion of petroleum and other combustibles could be a possible threat to the unsuspecting populace when fragmented into the air current and near atmosphere. Generally, particulate carbon surfaces may determine the gaseous, particulate and metal uptake or emissions as made evidence in this research.

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