TOTAL SUSPENDED PARTICULATES FROM CRUDE OIL SPILL

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Abstract: Total suspended particulates emitted during crude oil spill were investigated using laboratory simulation experiments. This was with a view to establishing the toxicity potentials of emitted particulates. Climatic and spill media conditions similar to those obtainable in real life were created in an environmental chamber and the total particulates emitted during spills involving three crude oil samples of Nigerian origin were measured with Quick Take sampler. The toxicity potentials of the emitted particulates were subsequently determined by dividing the 24- hour averaging period concentrations of the particulates by the statutory limit. The statutory limits used were those of Nigeria's Federal Ministry of Environment (FMENV), World Bank and the World Health Organization (WHO). For temperatures between 15 ºC and 35 ºC and spill media (over fresh water, sea water and soil), the extrapolated 24 – hour averaging period concentrations ranged between 186.79 – 584.28 μgm^{-3}, 186.98 - 584.48 μgm^{-3} and 247.40- 350.21 μgm^{-3} for sample A; 183.44 – 571.99 μgm^{-3}, 183.63 -572.19 μgm^{-3} and 244.05-337.92 μgm^{-3} for sample B and 178.41 – 566.96 μgm^{-3}, 178.61 - 567.16 μgm^{-3} and 332.89- 280.60 μgm^{-3} for sample C. The observed TSP concentrations breached the WHO (lower limit) and World Bank limits at all temperatures and over all spill media and consequently the toxicity potentials exceeded 1.0 which were indications of hazards to human health. The study concluded that particulate emissions during crude oil could be high enough to pose threats and suggested adequate protection for cleaning up workers.

Keywords: oil spill, total suspended particulates, toxicity potential

1. INTRODUCTION

The increasing interest in ambient particulates is as a result of their deleterious effects on human and environmental health [1 - 4]. The toxicity of ambient particulates can be by intrinsic properties or by combining with other harmful pollutants [5 - 7]. Particulates by nature have intrinsic properties of being dangerous due to their size, roughness

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and surface area. When in the respiratory track, they can cause difficulty in breathing and damage to respiratory organs [8, 9]. Depending on size, they get deposited at different depth in the human body ranging from nasal cavity to bronchi and the alveoli [10, 11]. They may be transported to the cardiovascular system and the rest of the body [8, 9]. Inhalation of particulates has been reported to cause oxidative stress, aggravate heart disease, mortality etc. [12 - 14]. They can also serve as conveyors for other hazardous pollutants [15]. According to the studies by [15] and [16], particulates can provide surface for adsorption of pollutants like polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs) and a host of other harmful pollutants. The sources of ambient particulates are ubiquitous and include natural and anthropogenic activities. Natural sources of particulates include volcanic eruptions, sea sprays, sand storm, natural crude seepage etc. Most anthropogenic sources of particulates are combustion related.

In Nigeria, there have been several studies on ambient air particulates (PM) from anthropogenic activities. The effects of vehicular emissions on ambient air PM have been investigated by [5]. The impacts of gas fired thermal plants for electricity generation on air pollutants including PM have been studied by [17]. Others include particulates from general fuel combustion, gas flaring, petroleum refining, vegetation burning and biomass burning, municipal waste burning, sawdust burning, industrial processes [18 - 24]. However, the state of information on the extent of total suspended particulates from crude oil spill is still not sufficient most especially in Nigeria. While studying fine particulate emission from Deep Water Horizon crude oil spill, previous authors [25] had reported that the emitted particulates were in multiple folds greater than the background concentration of the environment. By nature, particulates from crude oil spill will contain organic pollutants such as benzene, toluene etc. making them of greater human health concern. The properties of the crude oil, media over which spillage occurs and the prevailing climatic conditions of temperature and humidity at the time of spill can influence particulate emissions and their spread. Nigerian crudes are generally classified at light crude on the basis of their API gravities [26]. Light crude oils have many advantages, but they are also susceptible to emission of air contaminants including particulates during spill.

The frequency of crude oil spill in the Niger Delta region of Nigeria is high with the potential to affect public health. As earlier pointed out, studies on ambient particulates are many in Nigeria but information on the specific contributions of crude oil spill to their ambient concentrations as well as their toxicities is yet to be reported.

The present study is therefore centered on the measurement to total suspended particulate (TSP) concentrations from laboratory crude oil spill simulation experiments. The simulation experiments help to eliminate the interference of particulates from other sources in the measured data and hence make it possible to isolate crude oil spill as the sole contributor to the measured concentration of particulates. The toxicity potentials of the emitted particulates were also determined to establish the health risk implications.

2. EXPERIMENTAL SETUP

Prior to the measurement of TSP emitted during crude oil spill, the properties of the crude oil samples (relative density, API gravity and viscosity) and those of the spill media (soil porosity, bulk density, organic matter content, pH of water) were determined. The determination of relative density and API gravity was in accordance with these references [26, 27] while that of viscosity followed ISO 9001, ASTM D444 and ASTM D52515 standard methods using Cannon-Fenske reverse flow viscometer [28, 29]. Soil sampling and determination of its properties were in accordance with the methods used by [30 - 33]. The environmental chamber (0.6 m x 0.6 m x 1 m) used for the study was equipped with 1000 W, 0.25 Hp and 1000 RPM heating, cooling and fan respectively while Kestrel 4500 weather tracker was used for measurement of micro climatic conditions (temperature, humidity and wind speed) within the chamber. The chamber test conditions, crude oil, soil and water properties are as summarized in Table 1, Table 2 and Table 3. About 593 mL of three different crude oil samples of Nigerian origin were spilled in the test box under four variations of climatic conditions and the total suspended particulates (TSP) concentrations were measured with a Quick Take portable sampler. The sampler is a portable and battery operated equipment with flow rate of 30 L/min and several options of run time mode (5 min, 10 min and 15 min) for either intermittent sampling or continuous run sampling. Individual particles are counted by deployment of an inbuilt scattered laser light while the corresponding mass concentration is determined with a proprietary algorithm and displayed on the screen.

Table 1. Simulated environmental chamber climatic conditions.

	*T1	*T2	*T3	*T4
Temperature (ºC)	15	25	35	45
Relative Humidity (%)	80	71	68	49

*T1-T4 (Test conditions)

Table 2. Soil and Water Properties.

Soil properties		Water properties	
Bulk density	1.25 ± 0.02 g/cm^3	pH of fresh water	6.9
Porosity	51.10 ± 3.50%	pH of sea water	7.8
Particle density	2.68 ± 0.10g/cm^3	-	-
Organic matter content	2.48 ± 0.03%	-	-

Table 3. Properties of Crude Oil Samples.

Crude oil samples	Density (ρ) g/mL	Specific gravity	Viscosity (μ) mm^2/s	API gravity
A	0.85 ± 0.06	0.83	7.17 ± 1.12	38.00
B	0.87 ± 0.04	0.84	7.23 ± 1.50	34.00
C	0.88 ±0.02	0.86	7.41 ± 1.21	32.00

Subsequently, the toxicity potential (TP) which is the ratio of measured ambient concentration (MTSP) of a pollutant to the statutory concentration limit (STSP) set for that pollutant in ambient was determined following methods earlier used by [5, 34, 35] as captured in Equation 1. The statutory limits adopted include those set by Nigeria's Federal Ministry of Environment (FM), World Bank (WB) and the World Health Organization (WHO) as reported in [36-38].

$$\mathrm{TP} = \frac{\mathrm{MTSP}}{\mathrm{STSP}} \tag{1}$$

Prior to the deployment of equation 1, the measured 3-hour averaging period concentrations (C_i) were first extrapolated to 24-hour averaging period concentration (C_d) with an atmospheric stability formula proposed by [39] as show in equation 2 and equation 3, respectively:

$$\mathrm{C_d} = \mathrm{C}_i \times \mathrm{F} \tag{2}$$

$$\mathrm{F} = \left(\frac{\mathrm{t}_i}{\mathrm{t}_d}\right)^n \tag{3}$$

where C_d is concentration at the desired averaging period (t_d); C_i - measured concentration at the averaging period (t_i); F - factor to convert from the averaging period t_i to the averaging period t_d; n - the atmospheric stability dependent exponent and was assumed to be 0.28.

3. RESULTS AND DISCUSSION

The 3-hour averaging period measured TSP concentrations and their corresponding 24-hour averaging period extrapolated concentrations at temperatures between 15 ºC and 35 ºC for spillage of the three crude oil samples over sea water (SW), fresh water (FW) and soil (S) are as summarized in Table 4, Table 5 and Table 6. The 3-hour averaging period measured concentrations of TSP emitted by sample A were between 334.37 - 1045.9 μgm^{-3}, 334.71 - 1046.25 μgm^{-3} and 442.87 - 626.9 μgm^{-3} for spill over sea water, fresh water and soil respectively while the corresponding 24 – hour averaging period extrapolated concentrations were 186.79 – 584.28 μgm^{-3}, 186.98 - 584.48 μgm^{-3} and 247.40- 350.21 μgm^{-3}.

Table 4. Measured and extrapolated TSP concentrations from sample A (μgm^{-3}).

Climatic Condition	*Sea Water (SW)	Extrapolated (SW)	*Fresh Water(FW)	Extrapolated (FW)	*Soil (S)	Extrapolated (S)
15 ºC, 80 %	334.37	186.79	334.71	186.98	452.17	252.60

25 ºC, 71 %	445.97	249.14	446.32	249.33	442.87	247.40
35 ºC, 68 %	406.23	226.94	406.58	227.13	626.9	350.21
45 ºC, 49 %	1045.9	584.28	1046.25	584.48	533.3	297.92

Table 5. Measured and extrapolated TSP concentrations from sample B (μgm^{-3}).

Climatic Condition	*Sea Water (SW)	Extrapolated (SW)	*Fresh Water (FW)	Extrapolated (FW)	*Soil (S)	Extrapolated (S)
15 ºC, 80 %	328.37	183.44	328.71	183.63	446.17	249.25
25 ºC, 71 %	439.97	245.78	440.32	245.98	436.87	244.05
35 ºC, 68 %	348.23	194.54	384.58	214.84	604.9	337.92
45 ºC, 49 %	1023.9	571.99	1024.25	572.19	511.3	285.63

Table 6. Measured and extrapolated TSP concentrations from sample C (μgm^{-3}).

Climatic Condition	*Sea Water (SW)	Extrapolated (SW)	*Fresh Water(FW)	Extrapolated (FW)	*Soil (S)	Extrapolated (S)
15 ºC, 80 %	328.37	183.44	328.71	183.63	446.17	249.25
25 ºC, 71 %	439.97	245.78	440.32	245.98	436.87	244.05
35 ºC, 68 %	348.23	194.54	384.58	214.84	604.9	337.92
45 ºC, 49 %	1023.9	571.99	1024.25	572.19	511.3	285.63

*Measured concentration

For sample B, the 3-hour averaging period measured concentrations of TSP emitted were between 328.37 -1023.90 μgm^{-3}, 328.71 -1024.25 μgm^{-3} and 446.17-604.90 μgm^{-3} while the corresponding 24-hour averaging period extrapolated concentrations were 183.44 – 571.99 μgm^{-3}, 183.63 -572.19 μgm^{-3} and 244.05-337.92 μgm^{-3} for the same spill media and temperature range respectively. In the same vein, the 3-hour averaging period measured concentrations of TSP emitted were between 319.37 - 1014.9 μgm^{-3}, 319.72 - 1015.25 μgm^{-3} and 427.87- 595.9 μgm^{-3} for sample C while the corresponding 24-hour averaging period extrapolated concentrations were 178.41 – 566.96 μgm^{-3}, 178.61 - 567.16 μgm^{-3} and 332.89- 280.60 μgm^{-3} for the same spill media and range of temperature respectively.

Due to crude oil property factors (viscosity, API and specific gravity), the least and maximum emitted concentrations of TSP were obtained from sample A and sample C respectively. This is expected since the viscosities of the samples were in the order A < B < C. Generally, it was observed that increase in temperature from 15 ºC to 45 ºC favoured the emission of particulates across all spill media for the three crude oil samples. This may also be associated with the reduction in viscosity as temperature rises. The maximum emitted TSP of 1,046.25 μgm^{-3} was obtained from the spill of sample A over fresh water at 45 ºC.

To put the results into proper perspective, the extrapolated concentrations were compared with the regulatory limit set for the pollutant in ambient air. The national standard set for TSP by Nigeria's Federal Ministry of Environment (FM) is 250 μgm^{-3} [36]. For sample A, the extrapolated TSP concentrations breached the recommended limit for offshore (sea water and fresh water) spill at 45 ºC and onshore spill at 15º C, 35 ºC and 45 ºC as earlier presented in Table 3. In the case of sample B, the recommended limit was also exceeded for offshore spill at 45 ºC and onshore spill at 35 ºC and 45 ºC as presented in Table 4. Similar observations as experienced for sample B were observed for sample C (Table 6).

When the lower limit value of 150 μgm^{-3} recommended by WHO (WHO_{LL}) was used as the basis for comparison, the 24-hour extrapolated concentrations of TSP exceeded the limit at all temperatures and across all spill media, an indication that the ambient air might not be really safe especially for people having history of respiratory disease when oil spill occurs. The situation was a bit different when the WHO's upper limit (WHO_{UL}) of 230 μgm^{-3} for TSP was applied. The number of exceedances was 11 times more than when Nigeria's national standard was applied.

The toxicity potentials of total suspended particulates emitted by crude oil samples A, B and C are summarized in Table 7, Table 8 and Table 9 respectively. When stringent regulations (WHO lower limit and World Bank limit) were applied, the toxicity potentials exceeded 1.0 at all temperatures and over all spill media. Previous authors [5, 34, 35] had reported that toxicity potential value that is greater than or equal to 1.0 is an indication that dwellers

around that airshed are exposed to serious health risks. Even with more relaxed statutory limits such as 230 μgm^{-3} and 250 μgm^{-3} which represent the upper limit set by WHO and Nigeria's national standard respectively, the toxicity potentials still exceeded 1.0 in several instances and at 45 ºC, the air condition with respect to suspended total particulates was highly toxic irrespective of the pollutant statutory limit used.

For samples A, B and C, the largest toxicity potential values of 7.3, 7.15 and 7.09 were obtained over fresh water at 45 ºC while the least values of 0.73, 0.75 and 0.71 were obtained over the sea water at 15 ºC. Temperature and crude oil properties were observed to be the predominant factors influencing the emission rates and consequently the toxicity potentials of ambient suspended particulates.

Table 7. Toxicity potentials of total suspended particulate for spillage of sample A over different media.

Climatic Condition	FM (SW)	WHO_{LL} (SW)	WHO_{UL} (SW)	WB (SW)	FM (FW)	WHO_{LL} (FW)	WHO_{UL} (FW)	WB (FW)	FM (S)	WHO_{LL} (S)	WHO_{UL} (S)	WB (S)
T = 15 ºC RH = 80 %	0.75	1.25	0.81	2.33	0.75	1.25	0.81	2.34	1.01	1.68	1.10	3.16
T= 25 ºC RH = 71 %	1.00	1.66	1.08	3.11	1.00	1.66	1.08	3.12	0.99	1.65	1.08	3.09
T= 35 ºC, RH = 68 %	0.91	1.51	0.99	2.84	0.91	1.51	0.99	2.84	1.40	2.33	1.52	4.38
T= 45 ºC RH = 49 %	2.34	3.9	2.54	7.3	2.34	3.90	2.54	7.31	1.19	1.99	1.30	3.72

Table 8. Toxicity potentials of total suspended particulate for spillage of sample B over different media.

Climatic Condition	FM (SW)	WHO_{LL} (SW)	WHO_{UL} (SW)	WB (SW)	FM (FW)	WHO_{LL} (FW)	WHO_{UL} (FW)	WB (FW)	FM (S)	WHO_{LL} (S)	WHO_{UL} (S)	WB (S)
T = 15 ºC, RH = 80 %	0.73	1.22	0.80	2.29	0.73	1.22	0.80	2.30	1.00	1.66	1.08	3.12
T = 25 ºC, RH =71 %	0.98	1.64	1.07	3.07	0.98	1.64	1.07	3.07	0.98	1.63	1.06	3.05
T = 35 ºC, RH = 68 %	0.78	1.30	0.85	2.43	0.86	1.43	0.93	2.69	1.35	2.25	1.47	4.22
T =45 ºC, RH = 49 %	2.29	3.81	2.49	7.15	2.29	3.81	2.49	7.15	1.14	1.90	1.24	3.57

Table 9. Toxicity potentials of total suspended particulate for spillage of sample C over different media.

Climatic Condition	FM (SW)	WHO_{LL} (SW)	WHO_{UL} (SW)	WB (SW)	FM (FW)	WHO_{LL} (FW)	WHO_{UP} (FW)	WB (FW)	FM (S)	WHO_{LL} (S)	WHO_{UP} (S)	WB (S)
T = 15 ºC, RH = 80 %	0.71	1.19	0.78	2.23	0.71	1.19	0.78	2.23	0.98	1.63	1.06	3.05
T = 25 ºC, RH = 71 %	0.96	1.61	1.05	3.01	0.96	1.61	1.05	3.01	0.96	1.59	1.04	2.99
T = 35 ºC, RH = 68 %	0.84	1.40	0.91	2.62	0.84	1.40	0.91	2.62	1.33	2.22	1.45	4.16
T = 45 ºC, RH = 49 %	2.27	3.78	2.47	7.09	2.27	3.78	2.47	7.09	1.12	1.87	1.22	3.51

4. CONCLUSIONS

Nigerian being a major oil and gas nation frequently experiences crude oil spill along its production corridors with potentials to emit particulates. Emissions of particulates under different climatic conditions and over three spill media have been investigated using three separate samples of Nigerian crude oil.

Results showed that considerable amount of particulates were emitted during spill over fresh water, sea water and soil. The WHO (lower limit) and World Bank statutory limits set for TSP were exceeded in all cases. The 250 μgm^{-3} limit set by Nigeria's Ministry of Environment was also exceeded in many instances.

The toxicity potential of particulates associated with crude oil spill in Nigeria is thus considered to be a major air quality hazard. Adequate protection of cleaning up workers and sensitization of the public are considered top priorities and are therefore recommended in event of crude oil spill.

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