Precursors Influencing Tropospheric Ozone formation and Apportionment in three districts of Ilupeju Industrial Estate, Lagos

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OUTLINE

- INTRODUCTION
- SAMPLING METHODS
- RESULTS AND DISCUSSION
- CONCLUSION

- Air pollution in developing countries and cities

- Tropospheric ozone – formation: photo-oxidation of the precursor gases such as CO, CH_4 and non-methane hydrocarbons in the presence of sufficient amount of nitrogen oxide (NO_x) (Volkamer et al., 2010; Kgabi and Sehloho, 2012)

$$NO_2 + \text{UV photons } (h\nu) \longrightarrow O + NO$$

$$O + O_2 \longrightarrow O_3$$

- Effects of tropospheric ozone – highly corrosive, irritant to lung, respiratory inflammation, impairment of photosynthesis (Nair et al., 2002, Olajire and Azeez, 2014)

Sampling location

- Ilupeju Industrial Estate is one of the industrial estates established in Lagos in Oshodi-Isolo, Local Government Area. Industries situated in the districts are shown on the map

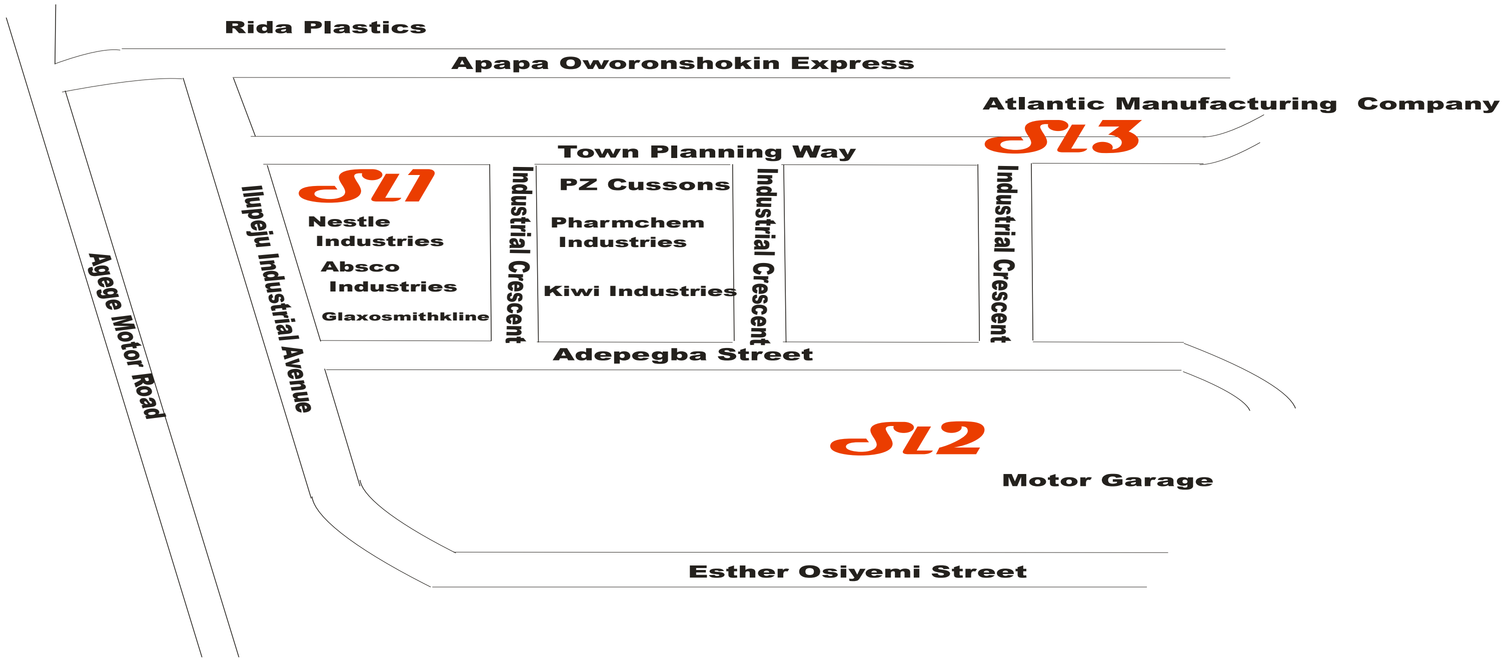

Figure 1: Map of Ilupeju Industrial estate showing sampling locations

- Measurement and analyses of hazardous pollutants, meteorological parameters, ozone and volatile organic compounds were done according to the methods of Olajire et al., (2011); Olajire and Azeez (2014)

RESULTS AND DISCUSSION

Table 1: Average concentrations of toxic pollutants and meteorological parameters

Pollutants	SL1	SL2	SL2
	Mean	Mean	Mean
NO_2 (ppm)	1.1 ± 0.23	0.56 ± 0.03	0.98 ± 0.29
NO (ppm)	0.2 ± 0.01	0.08 ± 0.02	0.23 ± 0.05
SO_2 (ppm)	0.52 ± 0.13	0.32 ± 0.19	0.81 ± 0.21
CO (ppm)	14.6 ± 1.73	13.90 ± 3.30	15.59 ± 1.07
O_3 (ppb)	17.2 ± 1.40	17.0 ± 1.10	18.8 ± 2.50
TVOC (ppm)	8.22 ± 0.13	6.86 ± 0.05	7.08 ± 0.12
Wind speed (ms^{-1})	0.74 ± 0.04	1.00 ± 0.16	1.26 ± 0.22
Temperature (°C)	32.84 ± 0.99	32.22 ± 0.49	32.68 ± 1.04
Pressure (hPa)	14.15 ± 0.07	14.52 ± 0.14	14.59 ± 0.61
Heat Index (°C)	35.40 ± 3.95	36.70 ± 1.74	36.22 ± 2.49
Humidity (%)	66.26 ± 1.48	66.14 ± 1.87	64.88 ± 2.13
$TVOC/NO_x$	6.32	10.72	5.85

NO_x – Nitrogen oxide, SO_2 – Sulphur dioxide, CO – Carbon monoxide, TVOC – Total volatile organic compounds

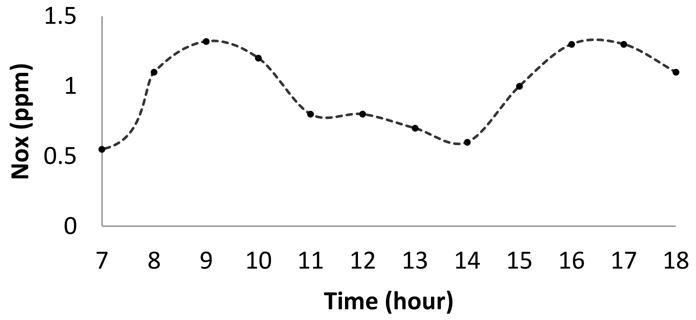

Figure 2a: Diurnal variations of nitrogen (IV) oxide (NO_2)

- Two peaks shown could be as a result of vehicular activities coinciding with rush hours (Wang et al., 2002; Duan et al., 2008

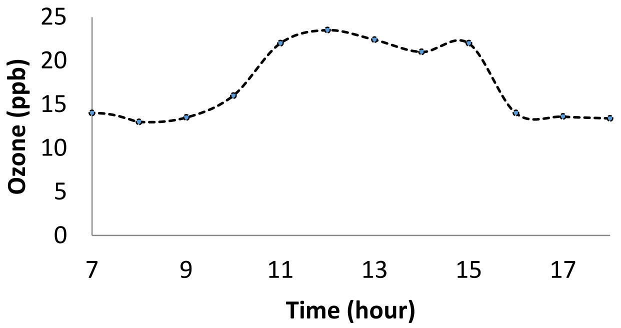

Figure 2b: Diurnal variations of ozone (O_3)

- Diurnal pattern shows two peaks; 11.00 – 13.00 and 15.00. High peaks of O_3 observed in the noon could be due to the formation of ozone from photo-oxidation of the precursor gases such as CO, CH_4 and non-methane hydrocarbons in the presence of sufficient amount of nitrogen oxide (NO_x) (Nair et al., 2002

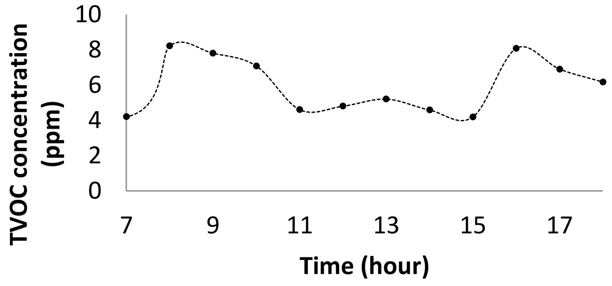

Figure 2c: Diurnal variations of total volatile organic compounds (TVOC)

- Peaks of TVOC coincided with rush hours

Table 3: Factor analysis of toxic pollutants and meteorological parameters

Pollutants	Component			Communalities
	F1	F2	F3	Extraction
Nitrogen oxide	0.882			.850
Sulphur (IV) oxide	0.512			.945
Carbon (II) oxide	0.618		0.617	.839
Pressure		0.850		.795
Wind speed	0.899			.842
Temperature		0.610	0.568	.903
Ozone		0.919		.930
TVOCs	0.710		0.799	.653

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Only factor loadings ≥ 0.5 listed

Table 4: Average concentrations and ozone formation abilities of VOC species

VOC	Concentration (μgm^{-3})			MDL (μgm^{-3})	MIR[a]	O_3 formation (μgm^{-3})		
	SL1	SL2	SL3			SL1	SL2	SL3
Alkane H/C								
Ethane	10.39±0.50	7.89±0.13	11.70±2.14	0.64	0.25	2.60	1.97	2.93
Propane	9.22±0.76	7.61±0.28	7.47±0.69	0.1	1.15	10.60	8.75	8.59
Butane	12.09±0.27	13.27±1.12	10.03±0.23	0.1	2.54	30.71	33.71	25.48
Pentane	8.46±0.49	10.55±1.45	5.66±0.27	0.1	3.94	33.33	41.57	22.30
Hexane	2.19±0.31	7.12±0.61	4.41± 0.04	0.1	5.61	12.29	39.94	24.74
Heptanes	5.58±0.52	2.64±0.05	5.51±0.08	0.2	7.15	39.90	18.88	41.38
Octane	4.81±0.15	9.33±0.99	2.53±0.19	0.3	8.68	41.75	80.98	21.96
Decane	2.65±0.45	6.03±0.13	3.88±0.22	0.3	11.60	30.74	69.95	45.01
Alkene H/C								
Ethene	6.88±1.01	5.27±0.47	8.05±0.16	0.13	8.52	58.62	44.90	68.59
Propene	13.97±2.70	17.15±0.40	12.75±1.72	0.6	26.30	367.41	451.05	335.33
Aromatic H/C								
Benzene	8.45±0.27	8.82±0.84	9.18±0.50	0.19	1.23	10.39	10.85	11.29
Toluene	13.39±0.03	15.58±0.19	15.06±3.20	0.47	5.96	79.80	92.86	89.76
Ethylbenzene	6.32±0.10	4.88±0.12	6.78±0.66	0.82	7.10	44.87	34.65	48.14
m,p-Xylene	28.53±5.29	20.76±0.17	22.36±0.81	0.51	19.00	542.07	394.44	424.84
o-xylene	10.97±2.52	11.51±3.15	8.01±0.28	0.29	13.70	150.29	157.69	109.74
Chlorinated H/C								
TCE	9.94±0.32	13.06±0.30	7.35±0.55	0.14	0.64	6.36	83.58	4.70
TeCE	21.39±0.75	16.61±1.14	18.26±0.72	0.66				
B/T	0.63	0.57	0.61					
Toluene/ m,p-xylene	0.45	0.75	0.67					
Σ Xylene/CO	2.71	2.32	1.95					
TCE/CO	0.68	0.94	0.47					
TeCE/CO	1.47	1.19	1.17					

Alkane H/C – Alkane hydrocarbons, Alkene H/C – Alkene hydrocarbons, Aromatic H/C – Aromatic hydrocarbons, Chlorinated H/C – Chlorinated hydrocarbons, O_3 formation (μgm^{-3}) = [a][VOC]×MIR, MDL – Method detection limit

- Benzene to toluene ratio has been used to identify VOCs sources. A *B/T* ratio of 0.5 has been reported to be characteristic of combustion from vehicular activities while higher values have been reported for bio-fuel burning, charcoal and coal burning (Barletta et al., 2002; Zhao et al., 2004)

- *B/T* ratios (table 4) of 0.63, 0.57 and 0.61 for SL1, SL2 and SL3 respectively suggest that vehicular activities were the major VOC contributors to aromatic hydrocarbons emission in this study. The ratios in this study are in agreement with results obtained by (Barletta et al., 2005).

- Other ratios that can be used as markers to identify VOC emission sources are *toluene/m,p-xylene, xylene/CO, TCE/CO and TeCE/CO* (Wang et al., 2002; Zhang et al., 2012; Olajire and Azeez, 2014). These ratios are therefore indicators of solvent use relative to combustion sources. Low ratios (table 4) calculated for all locations suggest solvent evaporation. This agrees with results obtained by Zhao et al., 2002; Zhang et al., 2012)

Table 5: Factor analysis of VOC species

Compounds	Component			Communalities
	F1	F2	F3	Extraction
ethane				0.922
propane		0.948		0.956
butane	0.969			0.945
pentane	0.969			0.942
hexane				0.949
heptane		0.674		0.997
octane	0.950			0.991
decane	0.574			0.953
ethene				0.915
propene	0.835			0.892
benzene			0.900	0.819
toluene			0.775	0.709
ethylbenzene				0.890
m/p-xylene		0.947		0.900
o-xylene	0.765			0.821
TCE	0.977			0.987
TeCE		0.962		0.961

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Only factor loadings ≥ 0.5 listed

Ozone Formation and Apportionment

- The ratio of *VOCs/NO$_x$* can be used to evaluate whether the production of O_3 is VOC-sensitive or NO_x-sensitive (Carter, 1994). Morning *VOCs/NO$_x$* ratios lower than 10 were equated with VOC-sensitive peak ozone and Morning *VOCs/NO$_x$* ratios greater than 20 correspond to NO_x-sensitive peak ozone (Sillman, 1999; Pudasainee et al., 2006). In this study, TVOC to NO_x ratios (table 1) are lower than 10 in SL1 and SL3 while it is higher than 10 at SL2. This indicates that at all locations, O_3 formation is VOCs sensitive.

- Photochemical reactivity of measured VOCs were estimated using maximum incremental reactivity (MIR). The results are presented in table 4. m/p – xylene was the highest contributor to O_3 formation at SL1 and SL3 while propene had highest contribution at SL2. Ethane contributed the least to O_3 formation

Conclusion

In this study, we have reported the concentrations of toxic pollutants, volatile organic compounds and meteorological parameters measured in three locations of Ilupeju indusrial Estate. Concentrations of toxic pollutants such as CO, NO_2 and SO_2 were higher than acceptable limits and were dependent on meteorological parameters such as temperature, pressure, humidity and wind speed. Majority of VOCs ratios revealed solvent related and unburned fuel emissions from these locations except *B/T* ratio which indicated a traffic related emission. m,p - xylene and propene were the major contributors to O_3 formation at SL1, SL2 and SL3 respectively. Ozone determined was VOC sensitive at all locations. PCA of the results showed traffic related emission sources for toxic pollutants and solvent use as sources for VOCs.

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