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Air Pollution Tolerance and Heavy Metal Accumulation of Selected Tree Species at Swamp Forest Research Station, Onne, Rivers State

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Abstract

Trees improve air quality through the accumulation of air pollutants in their leaves; however, the responses of different tree species to air pollution varies. Hence, this study evaluated the responses to air pollution of selected tree species in the Swamp Forest Research Station, Onne. Ten tree species (*Cola pachycarpa, Khaya grandifoliolia, Irvingia gabonensis, Garcinia kola, Chrysophyllum albidum, Treculia africana, Dacryodes edulis, Tectonia grandis, Gmelina aborea,* and *Nauclea diderrichii*) were selected based on their abundance in the area. Leaves were collected from all sides in 3 replicates for each tree species. Laboratory analysis was carried out using standard procedures. Portable Multi Gas Detector was used to determine the concentrations of air pollutants. One-way analysis of variance was employed to test for significant difference ($p \leq 0.05$) in biochemical parameters among the tree species while Pearson's correlation was utilized to determine the level of association between different biochemical parameters and APTI; heavy metals and APTI. Results showed high concentration of PM_{10}, CO, moderate concentration of NO_2, $PM_{2.5}$, and VOC, and low concentration of ground O_3. Heavy metals - Cadmium, Mercury, Lead, Nickel and Copper were all present in the tree species at varying rates. There were significant differences in the biochemical parameters and APTI values. *C. pachycarpa* exhibited the highest APTI value (89.88), while *D. edulis* had the lowest APTI value (8.24). *C. pachycarpa*, *K. grandifoliolia*, *C. albidum, G. kola, T. africana,* and *N. diderrichii* were identified as tolerant tree species to air pollution. *G. aborea, T. grandis,* and *I. gabonensis* were considered intermediate tolerant species, while *D. edulis* was the only tree species sensitive to air pollution. Ascorbic Acid, Chlorophyll, Hg and Ni had positive correlations with APTI; Cd and Cu had negative association with APTI at the 0.05 significance level. *C. pachycarpa, T. africana, K. grandifoliolia, C. albidum, N. diderrichii* and *G. kola*, are recommended for planting in pollution-prone areas.

Key Words: tree species, air quality, pollution, heavy metals, phytoremediation, onne

Introduction

Air pollution refers to the emission of chemicals, particulate matter, or biological gaseous materials into the atmosphere by human activities. These substances have the potential to cause impairment or discomfort to both humans and other living species, as well as to inflict damage upon the natural environment (Ali and Athar 2010). The atmos-

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phere is a complex and dynamic natural system that performs a vital role in supporting life on planet earth. However, it has been polluted as a result of environmental degradation linked to industrialization and urbanization of the 21st century (Ali and Athar 2008).

Atmospheric pollution is a critical global issue that occurs from the fluctuating levels of some gases and trace metals in the environment, principally caused by anthropogenic activities such as vehicular traffic, road transport, and industrialization (Jahan and Iqbal 1992; Joshi and Swami 2009). The principal forms of these atmospheric pollutants are gaseous compounds, suspended particles, heavy metals, noise and various forms of ionising radiation. The gaseous compounds include various oxidised and reduced forms of carbon, such as carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). The gaseous forms of nitrogen include nitric oxide (NO), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O4), ammonium ions (NH_4^+) and ammonia (NH_3). Other instances of gaseous forms include volatile phenols, sulphur dioxide (SO_2), vapours of benzene (C_6H_6), ozone (O_3), chlorine gas (Cl_2) and mercury (Hg). The particle forms are the particulate matter, such as PM_{10} and $PM_{2.5}$. The main sources of air pollution caused by anthropogenic activities are various industrial processes, including gas flaring, smelting, mining, combustion of fossil fuel petrol foundries and waste incinerators (Mukhopadhyay 2002). These emissions can have detrimental effects on the environment, including vegetation and human health.

The presence of air pollutants has detrimental impacts on the majority of plant species. These pollutants can induce direct toxicity or indirectly affect plants by altering soil pH levels, thereby influencing the solubility of toxic metal salts such as aluminum. Particulate matter for instance, exerts detrimental mechanical effects on plants, as it accumulates on the leaf blade, diminishing the infiltration of light and impeding the stomata openings (Liu and Ding 2008).

However, different plant species have distinct responses to air pollutants. Some tree species demonstrate vulnerability to even little levels of air pollution, resulting in a distinctive damage to their leaves (Escobedo et al. 2008). Such plant species have the potential to be used as bio-indicator species for the purpose of assessing the existence of air pollution within a specific geographical region. There are other several plant species that exhibit resistance to low to medium levels of air pollution. These plants are commonly referred to as tolerant species and are typically suggested for the purpose of greenbelt development, environmental sanitization, and pollution mitigation (Aksoy et al. 2015). In other words, diverse tree species exhibit difference responses to atmospheric pollutants. Therefore, the careful selection of plant species plays a crucial role in pollution treatment initiatives implemented in areas with elevated height of pollution, as well as in the establishment of greenbelts (Malakootian et al. 2009).

Singh and Rao (1983) developed an index referred to as the Air Pollution Tolerance Index (APTI) for the purpose of assessing the tolerance levels of various tree species towards atmospheric pollution. The index was established by the integration of various essential biochemical and physiological parameters of plants, including the pH of leaf extracts, relative water content, ascorbic acid levels and total chlorophyll content (Liu and Ding 2008; Gharge and Menon 2012; Bakiyaraj and Ayyappan 2014). The authors added that the APTI values were categorized into four distinct groups or levels. Plant species with APTI values ranging from 30 to 100 are considered as tolerant species. Those with APTI values between 17 and 29 are categorized as intermediately tolerant species. Tree species with APTI values ranging from 1 to 16 were classified as sensitive species, while those with APTI values less than 1 were considered as very sensitive species. APTI is therefore a proficient tool to identify pollution tolerant plant species which can be used for development of green belts and environmental sanitation from the sensitive tree species, often used as bio-indicators.

However, the responses of tree species to air pollution are understudied. The poor knowledge on the air pollution tolerance and sensitive levels of tree species makes it challenging to select suitable tree species for pollution treatment projects in polluted areas, greenbelt development, and general environmental sanitation. This contributes to the increase in air pollution we often experience today. Hence, this study was designed to assess the Air Pollution Tolerance Index (APTI), and heavy metal concentration of ten (10) selected tree species in the industrial hub of Port-Harcourt City, to examine the responses of the various tree species to air pollutants in order to identify the tolerant and the sensitive tree species to air pollution. This information will be useful for environmental planners and policymakers to make informed decisions on selecting appropriate tree species for planting in areas with high levels of air pollution and greenbelt development. It is anticipated that the adverse impacts of air pollution can be mitigated, thereby fostering improved air quality and a healthier environment through the careful selection of appropriate tree species.

Materials and Methods

Study area

The research was carried out in an even-aged mixed plantation at Swamp Forest Research Station, Onne, Eleme Local Government Area of Rivers State, Nigeria. It is located within the latitude 4.7238-4.7443N and longitude 7.0353-7.1516 E (Fig. 1) and surrounded by many production companies as listed below. Onne is an industrial hub located in the southern part of Nigeria, and it is home to several companies involved in the oil and gas industry, maritime industry, and other manufacturing and power generating industries. Some of the companies located around the study area include:

1. Onne Power Plant: a gas-fired power plant owned and operated by the Nigerian Agip Oil Company (NAOC).
2. Notore Chemical Industries: one of the leading fertilizer and agro-allied companies in Africa.
3. Lafarge Africa PLC: a Cement manufacturing company located at Onne, Rivers State, Nigeria
4. Indorama Eleme Petrochemicals Limited: one of the largest producers of petrochemicals in Africa.
5. Port Harcourt Refining Company: a Company involved in the refining of crude oil into petroleum products.
6. Onne Port Complex: a major seaport in Nigeria that serves as a hub for maritime activities in the region.

These companies are major sources of air pollution, as they release emissions such as sulfur dioxide, nitrogen oxides, heavy metals and particulate matter (Omoko et al. 2021).

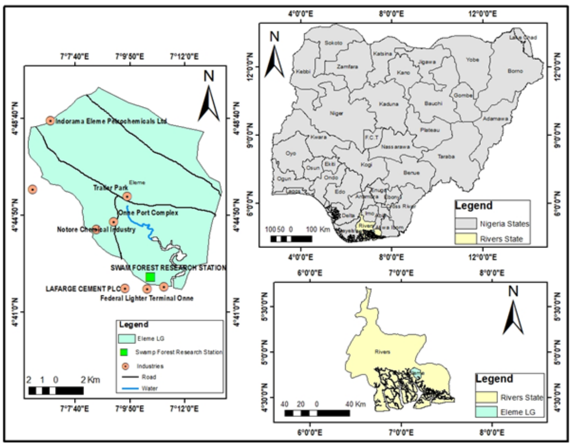

Fig. 1. Map of Eleme local government showing the study area and companies within the area.

Sample collection

Ten tree species (Table 1) in an even-aged mixed plantation were selected for the assessment based on their abundance and commonly distributed tree species of ecological and economical values in Nigeria. The leaves from every side of the tree canopy (north, south, east and west) directions, above and inside the tree canopy were collected in 3 replicates for each tree species. Leaves from each individual tree were bulked, arranged in a zip bag, and moved to the laboratory for determination of Ascorbic Acid (AA), pH of leaf extract, Total Chlorophyll Content (TCC), Relative Water Content (RWC), Cadmium, Nickel, Mercury, Copper and Lead using standard laboratory procedures as used by Irshad et al. (2020). The choice of the selected heavy metals were based on metals associated with vehicular traffic and industrial emissions.

Table 1. Selected tree species under study

S/No	Botanical name	Family	Genus
1	*Irvingia gabonensis*	Irvingiaceae	Irvingia
2	*Cola pachycarpa*	Malvaceae	Cola
3	*Treculia africana*	Moraceae	Treculia
4	*Garcinia kola*	Clusiaceae	Garcinia
5	*Chrysophyllum albidum*	Sapotaceae	Chrysophyllum
6	*Dacryodes edulis*	Burseraceae	Dacryodes
7	*Tectonia grandis*	Lamiaceae	Tectona
8	*Gmelina arborea*	Lamiaceae	Gmelina
9	*Nauclea diderrichii*	Rubiaceae	Nauclea
10	*Khaya grandifoliolia*	Meliaceae	Khaya

Determination of biochemical parameters

Ascorbic acid determination

This was done using Visual Titration Method according to Keller and Schwager (1977) and Bajaj and Kaur (1981), as expressed below:

$$AA = \frac{[Eo - (Es - Et)]\,V}{W \times V1 \times 1{,}000} \qquad \text{Equation 1}$$

where, E0, Es, and Et=optical densities of the blank sample, plant sample, and sample with ascorbic acid, respectively, V=total volume of the solution (mL), V1=volume of the supernatant solution (mL), and W=weight of the leaf sample (g).

PH of leaf extract

Crushed leave (0.5 g) was homogenized in 50 mL of deionized water, and centrifuged at 4,000 rpm at room temperature for about 5 minutes. The sample was filtered and the pH of leaf suspension was gauged using a pH meter (Singh and Rao 1983).

Total chlorophyll content (TCC)

TCC was done according to the general method often used by many researchers (Agbaire and Esiefarienrhe 2009; Abida and Harikrishna 2010; Shrestha et al. 2021; Shahrukh et al. 2023).

$$TCC = \frac{(20.2\,D645) + (8.02\,D663)\,V}{d \times 1{,}000 \times W} \qquad \text{Equation 2}$$

where D645 and D663 are the absorbance of leaf extract at 645 nm and 663 nm respectively; V is the Volume of leaf extract (mL), W=fresh weight of leaves (g), d=length of light path in cm.

Relative water content (RWC)

RWC was determined using the equation as expressed by Agbaire and Esiefarienrhe (2009); Harikrishna (2010); Shrestha et al. (2021); Shahrukh et al. (2023).

$$RWC = \frac{Fw - Dw}{Tw - Dw} \qquad \text{Equation 3}$$

where Fw is the fresh weight of the leaves, Dw is the dry weight, while Tw is the turgid weight.

Air pollution tolerance index (APTI)

The APTI was determined using (4) biochemical parameters documented by Singh and Rao (1983): and has been employed by many researchers in similar works (Achakzai et al. 2017; Irshad et al. 2020). The ranges of APTI values according to Liu and Ding (2008); Gharge and Menon (2012); Bakiyaraj and Ayyappan (2014) are shown in Table 2 below.

$$APTI = \frac{[A(T+P)+R]}{10} \qquad \text{Equation 4}$$

Heavy metal determination

The collected leave samples were rinsed twice in deionized water to get rid of any dirt or adhesive materials. They were placed into individual paper bags and labeled. The leave samples were maintained at 70°C in an oven until they were entirely dry. A clean electric grinder was used to crush the leaves of the dried plants into a fine powder in order to prepare the samples for additional analysis. A Pyrex beaker containing 2 grams of powdered leaves and 10 milliliters of pure HNO_3 was kept overnight at room temperature. After heating the sample on a hot plate, cooling it down, drying it out, and adding 5 mL of HClO4, the sample was ready for use. After filtering the digested material into a fresh volumetric flask and adding double-deionized water, the flask's volume was raised to 50 mL. The amounts of heavy metals–Cadmium (Cd), Nickel (Ni), Lead (Pb), Copper (Cu) and Mercury (Hg) in the acid extracts were measured using an atomic-absorption spectrophotometer

Table 2. Four distinct categories of APTI threshold

S/No	APTI Range	Remarks
1	<1	Very sensitive
2	1-16	Sensitive
3	17-29	Intermediate tolerant
4	30-69	Tolerant
5	70-100	Very tolerant

(AAS) (Nawaz et al. 2023; Shahrukh et al. 2023).

Air quality measurement

Air quality parameters such as Ground-level Ozone (O_3), Particulate Matter 2.5, and 10, temperature, humidity, Carbon monoxide (CO), Nitrogen dioxide (NO_2) and Volatile Organic Compounds were measured using Particle Counter and Portable Multi Gas Detector.

Statistical analysis

One-way analysis of variance was employed to test for significant difference ($p \leq 0.05$) in biochemical variables among the 10 tree species while Pearson's correlation coefficient (r) was employed to assess the level of relationship between different biochemical parameters and APTI; heavy metals and APTI. APTI threshold was used to evaluate the tolerance and sensitivity of the tree species to air pollution.

Results

Mean concentration of pollutants

The concentrations of the air pollutants in (Table 3) shows that $PM_{2.5}$ had mean value of 23 $\mu g/m^3$, PM_{10} had mean value of 81 $\mu g/m^3$; CO, NO_2, O_3 and VOC had 43.89 $\mu g/m^3$, 121.00 $\mu g/m^3$; 0.011 $\mu g/m^3$ and 389.08 $\mu g/m^3$ concentration respectively. Whereas the temperature and relative humidity were 30.77°C and 76.21% respectively.

Biochemical parameters of the tree species

The comparative results of biochemical parameters and APTI of the tree species under investigation are shown in Table 4. There was no significant difference in the water content of the 10 tree species except for *Gmelina arborea* at 0.05 level. Similarly, the pHs of the tree species were not significantly different except *Nauclea diderrichii*, which was significantly different when compared with other tree

Table 3. Mean concentration pollutants and environmental conditions of the study area

Air parameters	Units	Values	Who limits	Averaging time
$PM_{2.5}$	$(\mu g/m^3)$	23	25 $(\mu g/m^3)$	24-hour mean
PM_{10}	$(\mu g/m^3)$	81	50 $(\mu g/m^3)$	24-hour mean
CO	$(\mu g/m^3)$	43.89	30 $(\mu g/m^3)$	1-hour
NO_2	$(\mu g/m^3)$	121.00	200 $(\mu g/m^3)$	1-hour
O_3	$(\mu g/m^3)$	0.011	100 $(\mu g/m^3)$	8-hour mean
VOC	$(\mu g/m^3)$	389.08	N/A	N/A
TEMP	(°C)	30.77		
RH	(%)	76.21		

Table 4. Mean values of biochemical parameters and APTI of the selective tree species

Tree species	WC	pH	TCC	AA	APTI
Irvingiagabonensis	49.3 ± 0.4^{a}	5.4 ± 0.3^{ab}	1.8 ± 0.2^{b}	20.3 ± 0.2^{g}	19.7 ± 0.2^{d}
Cola pachycarpa	44.8 ± 0.2^{a}	5.3 ± 0.2^{ab}	3.8 ± 0.2^{a}	94.0 ± 0.2^{a}	89.9 ± 0.3^{a}
Treculiaafricana	46.8 ± 0.3^{a}	5.8 ± 0.2^{ab}	1.0 ± 0.2^{de}	56.4 ± 0.2^{d}	42.8 ± 0.3^{c}
Garcinia kola	50.3 ± 25.8^{a}	5.5 ± 0.2^{ab}	2.2 ± 0.2^{b}	52.9 ± 0.3^{d}	45.5 ± 0.3^{bc}
Chrysophyllumalbidum	48.7 ± 0.2^{a}	5.5 ± 0.2^{ab}	0.5 ± 0.2^{f}	77.3 ± 0.2^{b}	51.1 ± 0.2^{bc}
Dacryodes edulis	50.3 ± 0.3^{a}	5.0 ± 0.2^{ab}	1.1 ± 0.3^{cd}	5.3 ± 0.2^{h}	8.2 ± 0.2^{f}
Tectoniagrandis	49.8 ± 0.2^{a}	5.8 ± 0.2^{a}	0.6 ± 0.2^{f}	29.3 ± 0.2^{f}	23.7 ± 0.2^{d}
Gmelina arborea	36.3 ± 0.2^{b}	5.8 ± 0.2^{a}	0.9 ± 0.2^{ef}	33.4 ± 0.2^{e}	26.7 ± 0.1^{d}
Naucleadiderrichii	58.2 ± 0.2^{a}	4.2 ± 0.2^{c}	0.9 ± 0.2^{def}	58.5 ± 0.2^{d}	35.5 ± 0.1^{g}
Khaya grandifoliolia	56.9 ± 0.2^{a}	5.1 ± 0.2^{b}	3.5 ± 0.2^{a}	71.2 ± 0.2^{c}	66.6 ± 0.6^{e}
p-value	0.001	0.000	0.000	0.000	0.000

Means on the same column with the same alphabet are not significantly different ($p \leq 0.05$).

species. The TCC of *Chrysophyllum albidum, Tectonia grandis, Gmelina arborea, Treculia Africana* and *Nauclea diderrichii* were not significantly different at 0.05 levels; *Cola pachycarpa* and *Khaya grandifoliolia* were not significantly different, *Irvingia gabonensis* and *Garcinia kola* were not significantly different; but were significantly different from other tree species at 0.05 levels. The Ascorbic Acid of *Nauclea diderrichii, Garcinia kola* and *Treculia africana* were not significantly different but were significantly different from other tree species; while other tree species were significantly different from each other. The APTI values of *Treculia africana, Chrysophyllum albidum* and *Garcinia kola* were not significantly different; *Irvingia gabonesis, Tectonia grandis* and *Gmelina arborea* were not significantly different; however, *Cola pachycarpa, Dalcryodes edulis, Nauclea diderrichii* and *Khaya grandifoliolia* were significantly different when compared with other tree species.

Heavy metal concentration of the tree species

The mean concentrations of heavy metals in the leaves of the 10 tree species are shown in (Table 5). *G. kola* had the highest concentration of Pb (17.55), followed by *I. gabonensis* (9.59), *K. grandifoliolia* (4.60), *N. diderrichii* (2.98), *G. arborea* (1.33), *T. africana* (0.25) had the lowest concentration of Pb, while other tree species had Pb concentration $>$ 0.25 and $<$ 1. *C. pachycarpa* had the highest concentration of Ni (17.12), followed by *G. kola* (8.20), *K. grandifoliolia* (2.44), *T. africana* (0.19) had the lowest concentration of Ni, while other tree species are within the range of 0.26 and 1.08. The highest concentration of Cd was observed in *D. edulis* (11.63), *T. grandis* (7.77), *G. arborea* (7.29), the least concentration was recorded in *K. grandifoliolia* (0.09), while other tree species were within the range of 0.27 and 6.80. *D. edulis* also had the highest concentration of Cu (8.93), followed by *G. arborea* (4.10), *T. grandis* (5.32); *T. africana* (0.31) had the least concentration of Cu, followed by *C. albidum* (0.40), while other tree species ranges between 0.61 and 2.48. For mercury (Hg), *C. pachycarpa* (6.90) had the highest concentration, followed by *K. grandifoliolia* (6.17); *G. kola* (0.02) had the lowest concentration, other tree species had Hg concentration less than 1.

Table 6. Air pollution tolerance indexand responses of the ten tree species

S/No	Tree species	APTI	Response
1	*Irvingiagabonesis*	19.69	Intermediate
2	*Cola parchycarpa*	89.88	Very tolerant
3	*TreculiaAfricana*	42.78	Tolerant
4	*Garcinia kola*	45.45	Tolerant
5	*Chrysophyllumalbidum*	51.14	Tolerant
6	*Dalcryodes edulis*	8.24	Sensitive
7	*Tectoniagrandis*	23.66	Intermediate
8	*Gmelina aborea*	26.26	Intermediate
9	*Naucleadiderrichii*	35.51	Tolerant
10	*Khaya grandifoliolia*	66.55	Tolerant

Table 5. Heavy metal concentration of the tree species

S/No	Tree species	Pb (mg/g)	Ni (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Hg (mg/g)
1	*Irvingiagabonensis*	9.59	1.08	1.17	0.61	0.69
2	*Cola pachycarpa*	0.67	17.12	0.49	1.56	6.90
3	*Treculiaafricana*	0.25	0.19	6.44	0.31	0.35
4	*Garcinia kola*	17.55	8.20	6.80	1.38	0.02
5	*Chrysophyllum albidum*	0.37	0.45	0.27	0.40	0.22
6	*Dacryodes edulis*	0.64	0.26	11.63	8.93	0.28
7	*Tectoniagrandis*	0.29	0.37	7.77	5.32	0.34
8	*Gmelina arborea*	1.33	0.65	7.29	4.10	0.62
9	*Naucleadiderrichii*	2.98	1.03	3.09	2.48	0.37
10	*Khaya grandifoliolia*	4.60	2.44	0.09	1.02	6.17
FAO/WHO maximum permissible value (mg/kg)		3.00	1.63	0.30	10.00	0.001

Air pollution tolerance indices and responses of the ten tree species

Table 6 shows the APTI and responses of the tree species. The APTI ranged from 8.24 to 86.88; *Cola parchycarpa* had the maximum APTI (89.88), followed by *Khaya grandifoliola* (66.55), *Chrysophyllum albidum* (51.15), *Garcinia kola* (45.45), *Treculia africana* (42.78), *Naulea diderrichii* (35.51), *Gmelina aborea* (26.26), *Tectonia grandis* (23.66), *Irvingia gabonensis* (19.69), and *Dacryodes edulis* (8.24) had the least APTI value. Table 2 further showed the responses of the tree species to air pollution. It was recorded that five tree species (*Khaya grandifoliola*, *Chrysophyllum albidum, Garcinia kola, Treculia africana*, and *Nauclea diderrichii* were tolerant to air pollution; *Cola pachycarpa* was highly tolerant, three tree species (*Gmelina aborea, Tectonia grandis* and *Irvingia gabonensis* were intermediately tolerant, while only *Dalcryodes edulis* was sensitive to air pollution.

Correlation between APTI and biochemical parameters, APTI and heavy metals

The correlation assessment presented in Table 7 showed the relationship between the APTI and the biochemical parameters. Ascorbic acid exhibited a very strong positive/direct relationship (0.9432) with APTI. TCC had a moderate linear relationship (0.7300) with APTI. Relative water content exhibited a very weak correlation (0.0519) with APTI while pH (-0.0498) exhibited a very weak negative or inverse relationship with APTI. Ni (0.75) and Hg (0.82) had positive correlation with APTI, while Cd (-0.68) and Cu (-0.59) had negative correlation with APTI. Some heavy metals also exhibited some level of association with each other. Hg had positive correlation with Ni; Cd had positive correlation with Cu, and negative correlation with Hg (Table 8).

Discussion

Air quality of the study area

The concentration of air pollutants in the study area revealed the status of air quality in the area. $PM_{2.5}$ concentration was high but within the permissible limit of WHO; while PM_{10} concentration was above the permissible limit of WHO. The mean $PM_{2.5}$ recorded was higher than mean $PM_{2.5}$ of 16.25 $\mu g/m^3$ recorded in Rumuolumeni, 22.75 $\mu g/m^3$ in EIeme, 5.5 2 $\mu g/m^3$ in Omuanwa, but slightly lower than 26.17 $\mu g/m^3$ in Oginigba according to Akinfolarin et al. (2017). Alani et al. (2021) also recorded higher $PM_{2.5}$ of 45.74 $\mu g/m^3$ at Onike and 38.12 $\mu g/m^3$ at Okobaba. However, the PM_{10} (67.23 $\mu g/m^3$ and 43.96 $\mu g/m^3$) recorded at same location were lower than the

Table 7. Correlation between APTI and biochemical parameters of tree species

Parameters	APTI	RWC (%)	pH	TCC (mg/g)	AA (mg/g)
APTI	1	-	-	-	-
RWC	0.0519	1	-	-	-
pH	-0.0498	-0.7156	1	-	-
TCC	0.7300	0.1218	-0.1479	1	-
AA	0.9432	0.1126	-0.1139	0.49044	1

Table 8. Correlation between APTI and heavy metal concentrations of tree species in the study area

Parameters	APTI	Pb	Ni	Cd	Cu	Hg
APTI	1					
Pb	0.06	1.00				
Ni	0.75**	0.20	1.00			
Cd	-0.68**	-0.15	-0.32	1.00		
Cu	-0.59**	-0.36	-0.26	0.79**	1.00	
Hg	0.82**	-0.04	0.73**	-0.55**	-0.26	1

PM_{10} recorded in this study. The discrepancies could be as a result of varying human activities in the various locations and periods of study. According to Wang et al. (2020), burning of fossil fuels, industrial activities, mining, power generation, transportation and residential heating are the major factors of particulate matter into the atmosphere. However, the high concentration of the particulate matter in the study area could be linked to the various industrial activities, vehicular movement within the study area.

The mean CO, NO_2, O_3 and VOC in the study area were within the permissible limit of WHO, except for CO. Carbon monoxide is one of the major products of incomplete combustion of hydrocarbons or fossil fuel, hence the concentration is mostly high around areas in close proximity to manufacturing industries and construction companies. This was in agreement with the report of Omoko et al. (2021); they recorded high concentration of CO ranging from 45.22 $\mu g/m^3$ to 59.47 $\mu g/m^3$ in some parts of Onne, and attributed the elevated concentration of the CO to high industrial activities around the area. They also recorded high concentration of NO_2, comparable to the NO_2 of this study; while Alani et al. (2021) recorded higher concentration of NO_2 (145.75) at Okobaba, and lower concentration of 84.08 at Onike. The high concentrations of PMs, CO, and NO_2 indicate poor air quality in the study area, and this poses series of health risks to humans, plants and animals in the area. More so, the presence of volatile organic compounds also highlights the complexity of pollution sources and the need for targeted mitigation strategies. The environmental implications of these findings include reduced air quality, ecosystem degradation, and climate change.

Heavy metal concentrations of the tree species in the study area

Heavy metal pollution has remained a subject of global concern, due to the toxicological threats that such metals pose to human health (Ayodeji and Olorunsola 2011). Though the metals are essential for living organisms, however, they become toxic when bioaccumulation occurs (Elekes et al. 2010). Shahrukh et al. (2023), documented in a similar study that the concentrations of heavy metals in deposited particulate matter on the leaves vary among the tree species. In agreement to the assertion, the heavy metal concentrations of the tree species under study were significantly different from each other. For instance, the concentration of Pb was very high in *G. kola* and *I. gabonensis* when compared with the Pb concentration in *C. albidum* and *T. africana*. The concentration of lead in *Dacryodes edulis, Garcinia kola, Cola pachycarpa, Irvingia gabonensis* were higher than the Pb concentration of (0.46 mg/kg) and 0.22 mg/kg in *Mangifera indica* and *P. americana* respectively (Chima et al. 2021). Shahrukh et al. (2023) revealed that Pb concentrations in leaves is associated with traffic activity and industrial processes. The study area has common boundaries with many petrochemical industries, seaports and other activities that cause traffics on daily basis, hence could be the reason for high concentration of Pb in the area. The concentration of Nickel and cadmium also varied among the tree species, with very high concentration in *Cola pachycarpa* and *Dacryodes edulis* respectively. The concentration of Cu also varied among the tree species, however the concentrations were all below the concentration of Copper in *M. indica* (9.95 mg/kg) and *P. americana* (22.60 mg/kg) as reported by Chima et al. (2021) at Eleme, Port Harcourt. Copper is an essential element for plant growth, however, according to Borkert et al. (1998) it causes toxic effects when shoots or leaves accumulate Cu levels exceeding 20 ppm. Mercury is generally considered as one of the most toxic metals found in the environment Nickens et al. (2010). According to the authors, the major source of mercury is the natural degassing on earth crust including land areas, rivers and the ocean and is estimated to be in the order of 25,000 to 15,000 tons per year. This study recorded high concentration of Hg in *Cola pachycarpa* when compared with other tree species under study.

FAO/WHO maximum permissible limit

Heavy metals are essential elements for plant growth, however, they become toxic when the permissible limits recommended by FAO or WHO exceeded. For instance, Copper is one of the essential trace element necessary for many enzymes activities, growth and development. However, Khan et al. (2008) revealed that bioaccumulation of Cu can result in hair and skin discoloration, dermatitis, respiratory tract diseases and some other chronic diseases in humans. The tree species under study contained minute concentration of Copper, and it's below the permissible limit of plant leaves by FAO and WHO. In other words, the leaves of the tree species in the study area are safe for both human and animal consumption.

Nickel (Ni) is also an essential element for plants and animals. It helps in the regulation of lipid contents in tissues and for the formation of red blood cells, however high concentration of Ni becomes toxic and has many consequences such as loss of vision, loss of body weights, heart and liver failures as well as skin irritation (McGrath and Smith 1990). In this study, the concentration of Ni in *Cola pachycarpa* and *Garcinia kola* were higher than the permissible limit by FAO/WHO. Hence, consumption of such leaves in any form are not encouraged.

Lead (Pb) is one of the non-essential trace elements that functions neither in plants nor human body. According to (Jabeen et al. 2010), it causes chronic or acute poisoning that result in adverse effects on vital organs such as kidney, liver, vascular and body immune system. Rehman et al. (2017) added that high level accumulation of Pb in the body causes anemia, colic, headache, brain damage, and central nervous system disorder (Rehman et al. 2017). The lead concentration of the tree species were less than the maximum permissible permit of FAO/WHO except for *Garcinia kola* and *Irvingia gabonensis*. In other words, the consumption of leaves from these two plant species in the study area should be discouraged.

Cadmium is also one of the non-essential trace elements. According to Hunt (2003), a slight amount of Cd is extremely toxic, and has the ability to cause disability and hyper-activity in children. It can also affect the key organs of the body such as kidney, immune system and liver. The FAO/WHO maximum permissible limit for Cd is as low as 0.21 mg/kg, however, only *Chrysophyllum albidum* had Cd concentration less than the permissible limit; other tree species contained higher Cd above the permissible limit. Hence, consumption of leaves from such species in the study area could be injurious to both human and animals.

Mercury is generally considered to be one of the most toxic metals found in the environment (Nickens et al. 2010). It affects the central nervous system; causes mental retardation, cerebral palsy and convulsions in children, and can bring about genetic defects. Consequently, the permissible maximum limit of Hg according to FAO/WHO is as low as 0.001 mg/kg. However, this study revealed that all the tree species in the study area had Hg concentration higher than the permissible limit.

Air pollution tolerance index (APTI)

The Air Pollution Tolerance Index (APTI) of the ten tree species under investigation was evaluated based on the following parameters: relative water content, pH, total chlorophyll content, and ascorbic acid. The study revealed that the parameters exhibited variations among different tree species, indicating that the parameters are contingent upon the specific species. This finding exhibited similarities to the study carried out by Radhapriya et al. (2012), wherein notable fluctuations in the parameters were observed among the various species examined. The RWC of the tree species was moderately low when compared with relative water content recorded by Shrestha et al. (2021) for *Syzygium cumini* (98%) and *Ficus* species (85%), but higher than 32.56% of *Pongamia pinnata* and 24.56% of *Saraca indica* recorded by Abida and Harikrishna (2010). The elevated RWC in the plant's body aids in the maintenance of its physiological balance in stress situations such as exposure to air pollution when the transpiration rates are usually high (Verma 2003). The presence of high relative water content is known to perform a vital role in supporting the proper functioning of biological processes (Meerabai et al. 2012). Additionally, it promotes the capabilities of plants to survive drought and resist pollution. As a result, plants exhibit increased tolerance in response to stress conditions caused by air pollution (Randhi and Reddy 2012). This explains why *Khaya grandifoliolia* with high relative water content and other tree species of moderate RWC are tolerant to air pollution. However, *Dalcryodes edulis* with moderate relative water content was susceptible to air pollution, judging by the APTI.

The pH values of the leaf extract gotten from the selected tree species exhibited relatively lower levels in comparison to the pH values recorded by Shrestha et al. (2021) in a similar research on *F. benjamina* (8.44), *Thuja* sp. (7.69), *C. camphora* (7.71), *S. pueckleri* (7.66), *Ficus* sp. (7.29), *P. guajava* (7.58), and *N. oleander* (5.94). Singh et al. (1991) reported that plants demonstrating leaf extract pH levels of greater than or equal to 7 expresses greater tolerance to air pollution compared to those with lower pH levels. According to Karmakar et al. (2021), plants exposed to acidic pollutants such as SOx, CO_2, and NOx, show a decrease in the pH of their leaf extracts. The comparatively reduced pH level recorded in this research is an indication of the presence of acidic pollutants within the locality of the study site probably due to its heavily industrialized nature.

The total chlorophyll serves as a dependable signs for assessing photosynthetic activity, growth, and biomass productivity, as highlighted by studies executed by Josh and Swami (2009) and Pavlovic et al. (2014). Therefore, the utilization of reduced photosynthetic pigments as a sign of air pollution has been extensively employed, with a decrease in chlorophyll content serving as evidence of heightened plant susceptibility to air pollution (Pavlovic et al. 2014). Put simply, as the chlorophyll content of plants reduces, it results in a decline in their productivity and thus reduces their ability to survive air pollution. This observation agrees with the findings of this study, the two tree species (*Cola pachycarpa* and *Khaya grandifoliolia*) that showed elevated tolerant response to air pollution were the two species with the maximum value of total chlorophyll content. Furthermore, according to the findings of Josh and Swami (2009), the existence of air pollutants such as carbon dioxide, sulphur dioxide, nitrogen dioxide, and suspended particulate matter can lead to a decrease in chlorophyll content. This occurs as these atmospheric pollutants penetrate plant tissues through stomata, resulting in a partial denaturation of chloroplasts.

According to Shrestha et al. (2021), ascorbic acid is an antioxidant that offers resistance to plants under stress conditions. This substance acts as a potent reductant and electron donor (Pandey et al. 2015). It also functions as a scavenger of free oxygen radicals, helps in the conversion of sulphite to hydrogen sulphide, and mitigates the toxicity of SO_2. Pandey et al. (2015) documented that plants demonstrating high levels of AA expresses a heightened strength to survive the detrimental impacts of air pollution, particularly in relation to sulphur dioxide (SO_2), thus improving their effectiveness in combating air pollution. This study yielded comparable results, indicating that plant species with elevated antioxidant activity expressed resistance or tolerance to air pollution, whereas species with moderate to low AA expressed intermediate levels of vulnerability or sensitivity to air pollution.

The vulnerability or resistance of tree species to atmospheric pollution is dependent upon various factors, including the abovementioned parameters (WC, pH, TCC, and AA). The parameters have effects on the total evaluation of APTI. Plants expressing a higher APTI are generally recognized as tolerant species. They have the capacity to efficiently capture and retain dust particles or smog, mitigate gaseous emissions, absorb heat from pollutants, and ultimately enhance the overall quality of the surrounding air environment. Shrestha et al. (2021) and Randhi and Reddy (2012) opined that these particular plant species be cultivated in urban areas with high pollution levels, such as along roadways and in proximity to industrial zones. This cultivation strategy aims to establish a more conducive environment that may effectively absorb pollutants and act as a protective barrier against their detrimental impacts on the surrounding environment. On the other hand, reduced values of the Air Pollution Tolerance Index (APTI) signify that the plant exhibits vulnerability or sensitivity towards air pollution. Molnar et al. (2020) and Kanwar et al. (2016) have opined that the sensitive plant species have promise as a potential bio-indicator for evaluating air pollution levels. This research examined the response of diverse tree species to air pollution. Six (6) tree species, that is *Cola pachycarpa, Khaya grandifoliola, Garcinia kola, Chrysophyllum albidum, Treculia africana,* and *Nauclea diderrichii,* expressed tolerance to air pollution. Concersely, three tree species, *Tectonia grandis, Irvingia gabonensis,* and *Gmelina aborea,* expressed intermediate levels of tolerance whereas only *Dalcryodes edulis* was observed to be sensitive to air pollution. In a research executed by Joshi and Bora (2011), they evaluated the Air Pollution Tolerance Index (APTI) values of 8 varying tree species. The results of the research discovered that *Ficus religiosa* expressed the maximum APTI value of 20.94, while *Eucalyptus* spp. expressed the lowest APTI value of 13.41 among the tree species investigated. In the same way, Panigrahi et al. (2012) reported that a considerable proportion of the tree species evaluated expressed vulnerability to atmospheric pollution, whereas only a few number of tree species expressed tolerance with APTI value; such as *Mangifera indica* (17.81), *Ficus religiosa* (22.44), *Zizipus* spp (24.76) and *Anacardium occidentalis* (17.39). In a research carried out by Radhapriya et al. (2012), it was reported that out of the 27 tree species examined, 33% expressed sensitivity to air pollution, 5% expressed intermediate sensitivity, and 37% expressed tolerance. Remarkably, this group of tolerant plants included *Psidium guajava*, *Bougainvillaea* spp and *Mangifera indica*. In another research by Thambavni and Maheshwari (2012), *Ficus religiosa* and *Mangifera indica* were identified as the most resistance tree species out of the fifteen species evaluated. As a result, they proposed the growing of these specific tree species in areas associated with pollution, roadside locations, and heavy traffic. Similarly, Oyedeji et al. (2019) revealed that *Terminalia catapa, Tectona grandis,* and *Anacadium occidentale* expressed an intermediate level of tolerance to atmospheric pollution in their research. This is similar to the present research findings, which recorded an intermediate level of tolerance for *Tectona grandis*.

Correlation between APTI and biochemical parameters

The correlation assessment between APTI and biochemical parameters of tree species in the research area showed a significant positive correlation between ascorbic acid and APTI, as well as a fair linear link between ascorbic acid and total chlorophyll content. Numerous researches, encompassing Shrestha et al. (2021), Meerabai et al. (2012) and Verma (2003) have proved that AA plays a fundamental function in evaluating the tolerance and sensitivity of tree species to air pollution. This was in line with the findings of this study. In other words, an increase in the absorption of AA leads to a resultant increase in both the APTI and the level of tolerance to air pollution. A comparable pattern was recorded in relation to TCC, as supported by several studies by Shrestha et al. (2021), Yadav and Pandey (2020) and Madhumanjari and Mukherji (2000). There was a negative connection between pH and APTI. This implies that a rise in pH will have an inverse impact on the APTI value. Kaur and Nagpal (2017) and Das and Prasad (2010) reported that the buildup of particulate matter (PM) has effect on the alkalinity of leaves as a result of the breakdown of compounds that are connected with PM particles. The rise in leaf pH enhances the conversion of hexose sugar into AA, thus enhancing the plants' ability to tolerate air pollution. This research disagrees with the previous study. However, the discrepancies could be linked to variances in geographic location, diverse tree species, and seasonal factors. The findings of Shrestha et al. (2021) revealed the influence of site variations, tree species, and seasonal variations on the biochemical parameters of the Air Pollution Tolerance Index (APTI).

Correlation between APTI and heavy metals

The correlation analysis revealed the intricate relationship between APTI and the heavy metals. The positive correlation between APTI and Hg as well as Ni is an indication that tree species with high APTI values will accumulate high amounts of Hg and Ni. This explained why most of the tree species with high APTI had high concentration of Hg and Ni. For instance, *C. pachycarpa* with highest APTI value in the study area had the highest concentration of Hg and Ni. Nawaz et al. (2023) also recorded a similar relationship between Ni and APTI. In other words, such tree species with high APTI could be planted in pollution sites associated with high Hg and Ni. Conversely, the research recorded moderate negative correlation between APTI and Cd as well as Cu. This suggests that as the concentration of Cd and Cu in the air or tree species increases, the air pollution tolerant level of the tree species will decrease. In other words, tree species with high concentration of Cd and Cu will have low APTI values and thus will be sensitive to heavy metal pollution. The low APTI values in *D. edulis, T. grandis* and *G. arborea* could be linked to high concentration of Cd and Cu, as the 3 tree species had the highest concentration of Cd and Cu among the 10 tree species.

Conclusion

The tree species expressed significant variations in the biochemical parameters, heavy metals and the APTI values. The 10 tree species evaluated contained Pd, Cd, Ni, Hg and Cu at varying rates. The concentration of some heavy metals were within the permissible limits of WHO in some tree species and some exceeded the permissible limits. The moderate to high concentrations of $PM_{2.5}$, PM_{10}, CO, NO_2, VOC and O_3 in the air shows the poor air quality staus of the area.

Out of the 10 tree species evaluated, *Cola pachycarpa, Khaya grandifoliola, Chrysophyllum albidum, Garcinia kola, Treculia africana,* and *Nauclea diderrichii* exhibited higher degree of tolerance to air pollution. As a result, they are the most suitable for the purpose of developing green belts, establishing vegetative traffic barriers, and extenuating pollution in various areas. *Gmelina aborea, Tectonia grandis*, and *Irvingia gabonensis* were recorded as tree species with intermediate tolerance to air pollution; whereas *Dacryodes edulis* is sensitive to air pollution.

Hg and Ni had positive correlation with APTI while Cd and Cu had negative correlation with APTI. These research findings will provide valuable guidance to environmental and urban planners, as well as policymakers, in making well-informed decisions on the choice of most suitable tree species for planting in regions characterized by increased levels of air pollution, as well as for the development of greenbelts. The mitigation of air pollution's adverse effects and the subsequent enhancement of air quality and environmental well-being can be achieved through the careful selection of appropriate tree species.

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