Effects of road traffic on photosynthetic pigments and heavy metal accumulation in tree species of Kumasi Metropolis, Ghana

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Abstract

This study was undertaken to examine changes in the content of pigments and accumulation of metals from vehicular pollution in selected species of roadside trees under vehicular pollution. A major arterial road with heavy vehicle emissions in the Kumasi Metropolis was designated as the polluted site, while Kwame Nkrumah University of Science and Technology Campus was designated as the control site. Four tree species (*Terminalia catappa*, *Mangifera indica*, *Ficus platyphylla* and *Polyalthia longifolia*) selected for the study were well distributed and abundant in the polluted and control sites. Photosynthetic pigments and levels of heavy metals (Pb, Cu, Cd and zinc) were assessed in their leaves. Chlorophyll and carotenoid contents were determined by absorption spectrometry, while the metal accumulation index (MAI) was used to determine the total metal accumulation capacity of the tree species. We observed a reduction in photosynthetic pigments in the leaf samples from the polluted site. *Ficus platyphylla* had the maximum reduction in total chlorophyll (49.34%), whereas *Terminalia catappa* recorded the lowest reduction (33.88%). Similarly, the largest decrease (31.58%) of carotenoid content was found in *Terminalia catappa* trees and the lowest in *Polyalthia longifolia* (16.67%). The *Polyalthia longifolia*, *Ficus platyphylla* and *Terminalia catappa* leaf samples collected at the polluted site recorded a higher ratio of chlorophyll a/b. Heavy metal (Cu, Pb, Zn and Cd) accumulation in leaf samples was higher in the polluted site than in the control, as expected. The highest metal MAI value was recorded in *Mangifera indica* (5.35) followed by *Polyalthia longifolia* with 4.30. The findings from this study specifically demonstrate that air contamination induced by vehicles decreases the level of photosynthetic pigments in trees subjected to roadside emissions. It is clear that both chlorophyll a/b and chlorophyll/carotenoid ratios will act as very useful stress-level markers. Elevated heavy metal levels in the tree species along arterial roadsides indicate that they serve as heavy metals sink. The change in MAI resulting from different pollution burden is an indication that the removal capabilities of the tree species differ from each other. We therefore suggest *M. indica* and *P. longifolia* as potential species to be used in air pollution reduction plans in the city.

Keywords Heavy metal · Photosynthetic pigment · Urban trees physiology · Vehicular air pollution

1 Background

Because of the rapid economic growth, social linkage and spread activities, transportation is now the pillar of accessibility systems. It is a decisive factor of economic growth and social interactions in most countries. Regrettably, the antagonistic consequences of transportation exhibit an

overbearing influence on the natural and human environment. At the regional and global levels, vehicular emissions have been considered the major source of air pollution in the cities. Motor vehicles emit significant amounts of CO, SO_x, NO_x, VOCs, HC, NO_x, Cu, Cd, Co, Cr and Pb, responsible for 60–70% of urban air pollution [15, 18, 49]. Most of these pollutants found in the cities can be removed from

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air by plants through absorption, adsorption, detoxification, aggregation and additionally metabolization to the urban population [61]. Once inside the leaves, these contaminants contribute to a decrease in the concentration of chlorophyll pigments that directly influence the plants productivity [29]. Agyemang-Bonsu et al. [4] calculated emissions of ten vehicles pollutants and reported that in Kumasi Metropolis, all of which increased progressively over five years due to increase of autopollution.

In polluted area, plants show several changes in morphology, physiology and biochemistry of leaves [21, 23, 56]. Plant leaves have considerable ecological significance as heavy metals pollution biomonitors [81]. Trees in urban areas participate in the filtration of surrounding air through heavy metal removal and adsorbing of particulate matter [19, 44]. Researchers have carried out experiments on the effects of air pollution cause by vehicles on plant biochemistry, anatomy and physiology [26, 64, 82], in the different parts of the world.

In accordance with [48], the analysis of chemical composition variations in plants from clean and contaminated habitats is aimed at determining the impact of sources of contamination. Analysis of concentrations of heavy metals in urban plants will lead to the natural ecosystem management and provide objective advice for policy decisions on urban greening species [25].

Many plants may be used as traffic-based air quality biomonitors [53, 57, 72, 73]. In regions of heavy traffic, such as urban centers, heavy metal emission is considered to be reasonably high [11–14, 70–72, 84]. Plants are also used as biomonitors to track the accumulation of heavy metals. The tree leaves were widely used as indicators of atmospheric pollution [35, 58]. Therefore, the usage of plant leaves as heavy metal pollution biomonitors is of considerable environmental significance [8, 43, 88]. Plants are essential component of the environment in the reduction of pollution levels [9] and can also be utilized as biological indicators of air pollution [23]. The exhibition of different noticeable changes in relation to the pollution level is an indicator of leaf sensitivity to air pollution [32]. Most roadside plant studies were performed in other countries, such as Turkey [36], India [63], Thailand [79], China [90] and Nepal [91]. Little to no research on tropical city of Kumasi, Ghana's fully grown roadside tree plants has been carried out. In order to support planning and management of urban trees in the city of Kumasi, Ghana, we evaluated the capabilities of air pollution removal of four main tree species in the city, while evaluating their tolerance to high pollution concentrations.

2 Methods

2.1 Study area

Kumasi is the capital of Ashanti region and is located in South Central Ghana. Kumasi is situated between latitude 6.35°–6.40° and longitude 1.30°–1.35° and is subdivided into ten Sub-Metropolis. The city is located in domain of the tropical rain forest with a bi-modal pattern of rainfall. The average temperature is 26.4 °C [42], and average annual rainfall is 1250 mm [52]. Kumasi is Ghana's second largest and fastest growing town with an average population growth rate of 5.4%. It is a key transit point for travelers from inside and outside Ghana and hosts West African free market [1]. Two sampling sites [Offinso road and Kwame Nkrumah University of Science and Technology (KNUST) Campus] in Kumasi Metropolis were selected for this study. Offinso road, in Suame Sub-Metro, is situated between 6°43'52.65"N latitude and 1°37'40.74"W. It has a road length of 6.1 km and average daily traffic per lane of 24, 269 vehicles and thus undergoes severe traffic congestion. Therefore, traffic is the main source of air pollution in this site. In view of these pollution sources, Offinso road was chosen as the polluted site for study. Conversely, KNUST campus was selected as a control site for having an area of about seven square miles in a suburban area with low local traffic. KNUST campus in Oforikrom is situated between 6°41'5.67"N latitude and 1°34'13.87"W longitudes.

2.2 Air quality monitoring in the sampling sites

The SO₂, NO₂, CO and VOC concentrations as well as temperature and relative humidity were measured at the sample sites using the Aeroqual Series 500 (S500) gas detection device (Aeroqual Limited, Auckland, New Zealand). For each site, the surrounding air quality was monitored for 6 days in one week, from 7 am to 3 pm.

2.3 Selection of tree species

A survey of trees frequency and density was carried out with a view to define the dominant species in the study site. *Mangifera indica* L, *Polyalthia longifolia* (Sonn.) Thw, *Terminalia cattapa* L and *Ficus platyphylla* Del which are in abundance and well spread in the roadsides were selected for the study.

2.4 *Terminalia catappa* L.

Terminalia catappa belongs to the family Combretaceae. It is a tall, obvious semi-deciduous tree that grows best in tropical climate. *T. catappa* is an erect tree reaching 15–25 m tall, with maximum diameter of 1–1.5 m and frequently buttressed base. The tree throws a substantial shade that is valuable in greenery enclosures, schools or urban zones. *Terminalia catappa* quick development makes the tree important as an ornamental species. It is used as natural medicine and water conditioner <http://tropical.theferns.info/viewtropical.php?id=Terminalia+catappa>

2.5 *Mangifera indica* L.

Mangifera indica is grouped in the family Anacardiaceae. It is an extensive evergreen tree reaching up to 20 m tall with a dull green, umbrella-formed column. The different parts of the plant are used as an antiseptic, laxative, diuretic and laxative product. (http://apps.worldagroforestry.org/treedb/AFTPDFS/Mangifera_indica.PDF).

2.6 *Ficus platyphylla* Del

Ficus platyphylla belongs to the family Moraceae. It is a deciduous tree 10–25 m tall and column spreading. The leaves are large and stiff, long and oval, 15–26 cm long, 10–20 cm across, edge wavy, tip blunted or pointed. Latex harvested from the tree is used as a base for chewing gum. Bark decoction is sometimes used in the treatment of leprosy and stomach pins. A decoction of the tips leafy branch is an antidote to arrow poisoning (<http://tropical.theferns.info/viewtropical.php?id=Ficus+platyphylla>).

2.7 *Polyalthia longifolia* (Sonn.) Thw.

Polyalthia longifolia belongs to the family Annonaceae. It is a tall nice looking, evergreen tree with a funnel-shaped column. Flowers are yellowish green, in fascicles or short umbels from the axils of fallen leaves; petals are subequal, straight, spreading, decreasing to a point. Leaves are 7–20 cm long, lanceolate with wavy edges. The leaf decoction is used in the treatment of fever [27].

2.8 Sample collection

Twenty (20) fully developed leaves were collected per specimen from each of the four tree species (three individuals per species) making a total sample size of 240 leaves per sampling site. Leaves were obtained from all sides of the crown and pooled for a representative sample of each tree. The harvested leaves were placed in self-sealing black

polythene bags labeled accordingly. They were placed in a polystyrene box containing ice and sent to the laboratory for further analysis. Samples for pigment quantification were stored at -40°C in a deep freezer. The quantification of chlorophyll *a*, chlorophyll *b*, total chlorophyll and carotenoid of the leaf samples were carried out within 24 h of their harvesting.

2.9 Estimation of chlorophyll and carotenoid contents

The spectrophotometric method by [6] was used in chlorophyll and carotenoid content determinations. Leaf samples (3 g) were placed and homogenized in 10 ml of 80% acetone solution using mortar and pestle for 15 min. The homogenate was transferred to another test tube and centrifuged at 2500 rpm for 3 min. The supernatant was transferred with a pipette to a cuvette, and the absorbance readings were taken against a blank using CECIL 8000 UV-Visible spectrophotometer at wavelength 645 nm, 663 nm and 480 nm.

The amount of chlorophyll and carotenoid was measured as follows:-

$$\text{Chlorophyll } a = 12.7(A_{663}) - 2.69(A_{645}) \times V/1000 \times W \text{ mg/g}$$

$$\text{Chlorophyll } b = 22.9(A_{645}) - 4.68(A_{663}) \times V/1000 \times W \text{ mg/g}$$

$$\text{Total chlorophyll} = 20.2(A_{645}) - 8.02(A_{663}) \times V/1000 \times W$$

$$\text{Carotenoids} = A_{480} + 11.4(A_{663}) - 6.38(A_{645}) \times V/1000 \times W$$

where *A* = extract absorbance, *V* = total chlorophyll solution volume (ml) and *W* = tissue extract weight (g).

2.10 Heavy metal analysis

Leaf samples for heavy metal determination were washed thoroughly with distilled water and dried overnight in an oven at 40°C for heavy metal analysis. In total, 0.25 g was digested wet at 120°C in HNO_3 and then diluted with deionized water to 25 mL [33]. The residue was transferred after digestion to a 100-mL volumetric flask and was made up to the mark using distilled water. For reference, a blank digestion solution was made. For the purpose of calibration, a standardized solution for each heavy metal under study was prepared. Heavy metal (Pb, Cu, Cd and Zn) concentrations on the leaf samples were determined by the use of atomic absorption spectrophotometer (model AA240FS). Pb, Cu, Cd and Zn hollow cathode lamps at specific wave lengths were used. All the samples were analyzed in triplicates.

2.11 Metal accumulation index (MAI)

To evaluate the general metal deposition on the tree species, metal accumulation index (MAI) was adopted by using the formula below.

$$MAI = (1/N) + \sum_{j=1}^N I_j$$

where N is the total number of metals analyzed, $I_j = x/d_x$ is the subindex for variable j , obtained by dividing the mean value (x) of each metal by its standard deviation (d_x) [40].

2.12 Statistical analysis

The data generated were subjected to descriptive statistics (mean and standard error), and independent t test was used to evaluate the changes in photosynthetic contents and heavy metal levels in the leaves of the studied tree species among the observational sites. Correlations among different metal concentrations and metal and pigment variables were analyzed by bivariate correlation test with Pearson's correlation coefficient and two-tailed test of significance parameters at a significance level $p \leq 0.05$ and 0.001 using SPSS 23 software.

Percentage variations were calculated using the formula used by [7]

$$\text{Percentage variation(\%)} = C - P/C * 100$$

C = mean value for leaf samples of control site; P = mean value for leaf samples of polluted site.

3 Results

The temperature of the polluted sites was 2.17% higher in comparison with the control, while relative humidity of the control site was 1.70% higher than the polluted site. Carbon monoxide concentration (6.68 ppm) was 87.28% higher at the polluted site as compared to control site. The SO_2 concentration (0.19 ppm) was also recorded at the polluted sites, which was 63.16% higher than the control site. An elevated NO_2 concentration

(0.09 ppm) was also recorded at the polluted site and was 33.33% higher as compared to control site (Table 1).

3.1 Photosynthetic pigment content

The variations in chlorophyll pigments observed in the tree species located in the polluted and control sites are presented in Table 2. The photosynthetic pigments in the leaves of all the four tree species at the polluted site were lower and significantly different from those at the control site except for Carotenoid contents in *Ficus platyphylla* and *Polyalthia longifolia* ($p < 0.05$). There was a reduction of chlorophyll 'a' content at polluted sites as compared to the control site as follows: *Polyalthia longifolia* 43.48%, *Mangifera indica* 39% and *Ficus Platyphylla* 36.39%. The percentage reduction of chlorophyll 'b' content in the leaves of the studied tree species is in this order: *Ficus Platyphylla* 63.23%, *Polyalthia longifolia* 46.51%, *Terminalia catappa* 39.13% and *Mangifera indica*, 35.85% (Table 2). A reduction in total chlorophyll content in the samples from polluted sites was observed with *Polyalthia longifolia* having 47.42% reduction, *Mangifera indica*, a decrease of 35.85%, *Terminalia catappa* having 33.88% reduction, *Ficus Platyphylla* 21.05%. Similarly reductions of 23.53%, 21.05% and 16.67% in the concentration of carotenoid pigment in the *Ficus Platyphylla*, *Polyalthia longifolia*, *Terminalia catappa* and *Mangifera indica* leaf samples from polluted were recorded (Table 2).

The changes in the assimilation of pigments of selected tree species that are exposed to vehicular air pollution in Kumasi Metropolis are presented in Table 3. In the *Polyalthia longifolia*, *Ficus Platyphylla* and *Terminalia catappa* leaf samples collected at the polluted site, the chlorophyll a/b ratio was higher at the polluted site except for *Mangifera indica*, which recorded a higher chlorophyll a/b ratio (1.87) at the control. Chl $a + b +$ carotenoid ratio of *Polyalthia longifolia*, *Ficus Platyphylla* and *Terminalia catappa*, was decreased at the polluted sites relative to the control site. Thus, at the polluted site there was also lower chlorophyll $(a + b)/\text{carotenoid}$ ratio for *Polyalthia longifolia*, *Terminalia catappa*, *Mangifera indica* and *Ficus Platyphylla*.

Table 1 Ambient air quality at the sampling sites during the study period

Sampling sites	Parameter					
	CO (ppm)	SO_2 (ppm)	NO_2 (ppm)	VOC (ppm)	Temperature ($^{\circ}\text{C}$)	Relative humidity
Control	0.85	0.07	0.06	0.01	35.12	52.40
Polluted	6.68	0.19	0.09	0.09	35.90	51.51
% Increase	87.28	171.43	33.33	88.89	2.17	− 1.70

(−) = Values indicate that value of control site is higher than polluted site

Table 2 Changes in the photosynthetic pigment contents of selected tree species exposed to vehicular air pollution in Kumasi Metropolis

Tree species	Photosynthetic pigments								
	Sampling sites	Chlorophyll 'a' (mg/g)	<i>p</i> value	Chlorophyll 'b' (mg/g)	<i>p</i> value	Total chlorophyll (mg/g)	<i>p</i> value	Carotenoid content (mg/g)	<i>p</i> value
<i>Terminalia catappa</i>	Control	0.75±0.02	0.036*	0.46±0.00	0.154*	1.21±0.02	0.045*	0.19±0.01	0.035*
	Polluted	0.52±0.07		0.28±0.08		0.80±0.14		0.13±0.02	
	% R	30.70		39.13		33.88		31.58	
<i>Mangifera indica</i>	Control	1.00±0.01	0.042*	0.53±0.00	0.059*	1.53±0.02	0.048*	0.17±0.01	0.050*
	Polluted	0.61±0.09		0.34±0.05		0.94±0.14		0.13±0.01	
	% R	39.00		35.85		38.56		23.53	
<i>Ficus platyphylla</i>	Control	0.84±0.01	0.075**	0.68±0.01	0.000*	1.52±0.01	0.017*	0.19±0.01	0.008*
	Polluted	0.53±0.11		0.25±0.04		0.77±0.10		0.15±0.02	
	% R	36.91		63.23		49.34		21.05	
<i>Polyalthia longifolia</i>	Control	0.92±0.01	0.022*	0.48±0.01	0.000*	1.41±0.00	0.003*	0.18±0.02	0.205**
	Polluted	0.52±0.11		0.23±0.01		0.74±0.10		0.15±0.01	
	% R	43.48		46.51		47.42		16.67	

* = significant different, ** = not significantly different, *p* = probability value, % *R* = percentage reduction

Table 3 Changes in assimilating pigments of selected tree species exposed to vehicular air pollution in Kumasi Metropolis

Tree species	Chl <i>a/b</i> ratio		Chl 'a' + Chl 'b' + Carot-enoid		Chl (<i>a + b</i>)/Carotenoid	
	Control	Polluted	Control	Polluted	Control	Polluted
<i>Terminalia catappa</i>	1.67	1.86	1.4	0.93	6.37	6.15
<i>Mangifera indica</i>	1.87	1.79	1.69	1.08	8.94	7.31
<i>Ficus platyphylla</i>	1.24	2.12	1.71	0.93	8.00	5.20
<i>Polyalthia longifolia</i>	1.92	2.26	1.58	0.90	7.78	5.00

3.2 Heavy metal contents

The variations in heavy metal concentration (Mean + SE, mg/kg) and metal accumulation index (MAI) of leaves sample from different sampling locations are presented in Table 4. The heavy metal content in the leaves of all the four tree species at the polluted site was higher and significantly different from those at the control site ($p < 0.05$).

3.3 Lead

Pb accumulations at the control site ranged between 1.28 ± 0.01 and 1.78 ± 0.01 (Table 4). Pb accumulation (4.68 ± 0.02) was highest in *Polyalthia longifolia* followed by *Mangifera indica*, *Terminalia catappa* and *Ficus platyphylla*. At the polluted site, the maximum increase in Pb accumulation was observed in *Polyalthia longifolia* (265.63%); it was followed by *Ficus platyphylla*. There was a significant difference in the Pb accumulation of tree species between the polluted sites and the control ($p < 0.05$).

3.4 Copper

Copper accumulations ranged between 5.90 ± 0.00 and 7.23 ± 0.01 in the control site (Table 4). The maximum Cu amounts were found in *Polyalthia longifolia* (24.00 ± 0.00 µg/g) leaves in the polluted site and the lowest Cu accumulation 5.90 ± 0.00 detected in *Mangifera indica* in the control site. Even though the highest Cu accumulations were found in *Polyalthia longifolia*, the accumulation of Cu in *F. platyphylla* was higher (123.97%) than the control site. It was followed by *M. indica* (123.39%) and *T. catappa* (120.06%). It was also observed that statistically significant increases were found in all the tree species between the polluted sites and the control ($P < 0.05$).

3.5 Cadmium

Cadmium accumulation of leaf samples obtained at the control site ranged from 0.03 ± 0.01 to 0.13 ± 0.01 (Table 4). The highest Cd accumulations in all tree species were found in polluted sites. Among the studied tree species, *Polyalthia longifolia* accumulated the highest Cd

Table 4 Heavy metal concentration (mean $\pm$ SD, mg/kg) and metal accumulation index (MAI) of leaves sample from different sampling locations

Tree species	Heavy metal									MAI
	Sampling sites	Pb	<i>p</i> value	Cu	<i>p</i> value	Cd	<i>p</i> value	Zn	<i>p</i> value	
<i>Terminalia catappa</i>	Control	1.78 $\pm$ 0.68	0.000*	6.53 $\pm$ 3.08 ^a	0.000*	0.13 $\pm$ 0.07 ^a	0.000*	0.56 $\pm$ 0.44 ^a	0.254*	1.97
	Polluted	3.21 $\pm$ 1.01		14.37 $\pm$ 5.04 ^b		1.08 $\pm$ 0.55 ^b		1.96 $\pm$ 0.85 ^a		2.58
	% V	80.34		120.06		369.56		71.43		
<i>Mangifera indica</i>	Control	1.75 $\pm$ 0.00	0.000*	5.90 $\pm$ 0.00	0.000*	0.05 $\pm$ 0.02	0.000*	0.06 $\pm$ 0.04	0.000*	2.9
	Polluted	3.41 $\pm$ 1.03		13.18 $\pm$ 4.03		0.21 $\pm$ 0.08		1.46 $\pm$ 0.12		5.35
	% V	54.20		123.39		320		2333.33		
<i>Ficus platyphylla</i>	Control	1.60 $\pm$ 0.40 ^a	0.000*	7.05 $\pm$ 3.00	0.000*	0.03 $\pm$ 0.00	0.001*	0.05 $\pm$ 0.01	0.001*	2.85
	Polluted	3.02 $\pm$ 0.98 ^b		15.79 $\pm$ 4.01		0.28 $\pm$ 0.00		0.74 $\pm$ 0.12		3.37
	% V	88.75		123.97		833.33		1380		
<i>Polyalthia longifolia</i>	Control	1.28 $\pm$ 1.00	0.000*	7.23 $\pm$ 3.03	0.000*	0.05 $\pm$ 0.03 ^a	0.000*	0.07 $\pm$ 0.02	0.007*	2.21
	Polluted	4.68 $\pm$ 1.04		24.00 $\pm$ 7.00		0.23 $\pm$ 0.10		1.18 $\pm$ 0.16		4.30
	% V	265.63		93.64		360		1585.71		

Mean $\pm$ SE in the same column with different letters in superscript are significantly different ($p < 0.05$)

* = significantly different; *p* = probability value; % V = percentage variation

polluted site. The Cd values reported in this study were lower than that of Cd values of plant leaves in the polluted localities of Antakya [13]. Compared with control, the highest increment in Cd (833.33%) was found in *F. platyphylla* (Table 4). Cd content showed statically significant difference ($p < 0.05$) between the polluted and control sites in all the tree species (Table 4).

3.6 Zinc

Zn contents at the control site ranged between 0.05 ± 0.00 and 0.56 ± 0.26 (Table 4). The highest Zn amounts were found in *T. catappa* (1.96 ± 0.90) leaves in the polluted site and the lowest Zn accumulation (0.05 ± 0.00) detected in *Ficus platyphylla* in the control site. The highest Zn accumulations were found in *Terminalia catappa*. However, the accumulation of Zn in *M. indica* was higher (2333.33%) than the control site. It was followed by *Polyalthia longifolia* (1585.71%) and *Ficus platyphylla* (1380%). In the polluted site, there were significant ($p \leq 0.05$) increases in the other tree species except for *Terminalia catappa*.

3.7 Metal accumulation index (MAI)

Metal accumulation index value of **5.35** was highest in *Mangifera indica* at the polluted site followed by *Polyalthia longifolia* (**4.30**) (Table 4), while at the control site, *Mangifera indica* also recorded highest MAI value of

2.9 and the least MAI value of 1.97 found in *Terminalia catappa*.

3.8 Relationship between photosynthetic pigments and heavy metal concentrations

Total chlorophyll content showed a high negative correlation with the concentrations of Pb, Cu and Cd in the leaves of *T. catappa* and also very highly negative correlation with Pb, Cd and Zn concentration in *Mangifera indica* except for Cu. It was also observed that total chlorophyll content had a very high negative correlation with Pb, Cu and Cd concentrations in *F. platyphylla* and *P. longifolia* except for Zn (Table 5).

Carotenoid content showed high negative correlation with Pb, Cu and Cd concentrations in the leaves of in *T. catappa* and very high negative correlation with Pb, Cu and Cd contents in *Ficus platyphylla*. Carotenoid content did not reveal any relationship with Pb, Cu, Zn and Cd accumulation in *P. longifolia* and *Mangifera indica* (except for Pb) (Table 5).

It was observed that the concentrations of Pb and Cu, as well as for Pb and Cd, were positively correlated in *Ficus platyphylla*, *Polyalthia longifolia*, *Terminalia catappa* and *Mangifera indica*, while Pb and Zn concentrations were positively correlated for all species but *Terminalia catappa* (Table 5).

The concentrations of Cu and Cd were also positively correlated in *Mangifera indica*, *Terminalia catappa*, *Polyalthia longifolia* and *Ficus platyphylla* and were positively correlated. Also there was a positive correlation between Cu and Zn contents in *Polyalthia longifolia*, *Mangifera*

Table 5 Relationship among metal–metal and metal–photosynthetic pigments in studied tree species under vehicular pollution

	<i>Terminalia catappa</i>	<i>Mangifera indica</i>	<i>Ficus platyphylla</i>	<i>Polyalthia longifolia</i>
Metal–metal correlations				
Pb×Cu	0.999**	1.000**	1.00**	1.00**
Pb×Cd	0.999**	0.993**	0.997**	0.983**
Pb×Zn		0.996**	0.970**	0.987**
Cu×Cd	0.999**	0.992**	0.997**	0.982**
Cu×Zn		0.995**	0.971**	0.985**
Cd×Zn		0.995**	0.967**	0.971**
Metal–photosynthetic pigments correlations				
Pb×Total Chl	−0.820*	−0.910*	−0.966**	−0.950**
Cu×Total Chl	−0.823*	−0.907	−0.965**	−0.954**
Cd×Total Chl	−0.838*	−0.925*	−0.963**	−0.937**
Zn×Total Chl		−0.910*	−0.899*	−0.899*
Pb×Carotenoid	−0.844*	−0.847*	−0.926**	
Cu×Carotenoid	−0.843*		−0.926**	
Cd×Carotenoid	−0.857*		−0.935**	
Zn×Carotenoid			−0.862*	

indica and *Ficus platyphylla*. In all tree species with the exception of *Terminalia catappa*, significant positive correlations were found between Cd and Zn concentrations (Table 5).

4 Discussion

The conditions recorded in both sampling sites were not different and, therefore, did not affect the results of the photosynthetic pigments and metal concentrations in the leaves. Thus, differences observed here are to a large extent related to the distinct exposure to vehicular pollution.

The accumulation of heavy metal has also been stated to be directly related to the air entering the stomata and the amount of heavy metal taken into the leaf. These contaminants may affect the photosynthesis in plants [73]. Analysis of chlorophyll is a powerful tool for determining the effect of air pollution on plants as it plays a significant role in plant metabolism and any reduction of chlorophyll content is closely associated with plant growth [86]. Hence, the quantity of chlorophyll in the leaf and carotenoids should have valuable physiological information. The chlorophyll pigments experience certain photochemical reactions, namely: oxidation, reduction, phaeophytinization and reversible bleaching during stress condition as the pigment exists in a highly organized condition [62, 74]. There have been significant changes in the concentration of the studied tree species photosynthetic pigments that have resulted in the reduction of chlorophyll 'a', chlorophyll 'b' and total chlorophyll content in the polluted sites. This reduction in plant pigments is independent from local

climate conditions and most likely due to the high vehicular pollution found in the polluted site. Such findings are consistent with the results of [21, 22, 26] but contrary to Mukherjee and Agrawal [47] whose result indicates an increased in the content of Chl *a* and Chl *b* with a rise in air pollution load in the concentrations of *M. indica* and *P. longifolia*. In *M. indica*, elevated total chlorophyll content was also found at higher pollution loads by [80]. Chlorophyll 'a' was higher in this study than chlorophyll 'b'. This result is similar to [87], who reported lower values of chlorophyll 'a' than chlorophyll 'b' in *Quercus petraea* polluted woodland with SO₂. Nayak et al. [51] reported a greater decrease in chlorophyll 'b' than chlorophyll 'a' and in some cases similar decrease in chlorophyll 'a' and chlorophyll 'b'. Chlorophyll pigment oxidation may also be induced by the activity of SO₂ and NO₂ on the chlorophyll metabolism [38], all of which are components of automotive pollution. The decrease of the active photosynthetic leaf region arising from deposits of particulate matter and visible injury symptoms on the leaves of the studied tree species may be another explanation for decreased chlorophyll content [75]. Mondal et al. [45] observed that air pollutants penetrate the leaves through the stomata, resulting in partial chloroplast denaturation and reduction of pigment content in the leaves of polluted sites. These researchers attributed this to the replacement of Mg²⁺ with two atoms of hydrogen and the degradation of chlorophyll to phaeophytin.

Carotenoid plays an important role in the photosynthetic process and protects chlorophyll from photoxidative reaction. In this study the amount of carotenoid was reduced compared to the control. Other studies obtained similar results [17, 21, 22, 26, 30]. Swami et al.

[78] recorded a major decrease in carotenoid content from *Shorea robusta* and *Mallotus philippinensis* due to roadside pollution from vehicles. Agrawal [3] also reported a decrease in the carotenoid content of various plants due to gaseous pollutant exposure. Singh and Pal [76] also reported the low carotenoid content in roadside plant species due to the accumulation of dust particles on the leaf surface as compared to the control site. Our finding, however, was inconsistent with [47], who reported significant increases in carotenoid content in parks with higher pollution loads across all plant species.

Chlorophyll 'a' is found in the pigment antenna and in photosystem I and II reaction centers, while Chlorophyll 'b' originates entirely in the pigment antenna system. Consequently, an enlargement of the PS II antenna system leads to a reduction of the Chlorophyll *a/b* ratio [80]. Chlorophyll *a/b* ratio provides a degree of tree tolerance index, and higher plant species typically produce more Chlorophyll 'a' than Chlorophyll 'b' [85]. A high ratio is an indication of better air pollution tolerance, and the low ratio indicates sensitivity [34]. A higher ratio of chlorophyll *a/b* in the *Polyalthia longifolia*, *Ficus Platyphylla* and *Terminalia catappa* leaf samples collected at the polluted site suggests that these tree species are more tolerant to vehicular air pollution, while *Mangifera indica* is more sensitive to vehicular pollutants. Mukherjee and Agrawal [47] recorded a decreased ratio of Chlorophyll *a/b* in all other species, except for *P. guajava* in areas with higher pollution loads.

The weight ratio of Chlorophyll a and b to carotenoids $(a + b)/(x + c)$ is one measure of greenness of plant. The lower values of $(a + b)/(x + c)$ ratio are an indicator of senescence, stress and damage to the photosynthetic system indicated by a faster chlorophyll breakdown than carotenoids. A decrease in these ratios is an indicator of the stress and harm caused by air contaminants in automobiles.

Pb natural, normal and toxic limits are 3, 10 and 30–300 mg/kg, respectively, for plants [5, 28, 33]. Pb accumulation in the leaf samples of *T. catappa*, *M. indica*, *Ficus platyphylla* and *P. longifolia* trees collected from the polluted site was higher than the natural limits in plants. The highest lead content in leaf of the studied tree species was observed at the polluted sites. Similar results were obtained by [2, 7, 17, 37, 41, 50, 66]. The translocation of Pb from the root of plants is not the main path for the uptake of Pb; however, plants can easily pick up Pb from the atmosphere through the leaves [29, 83]. Also, [67] stated that the high Pb value in plants was due to the uptake from the above-ground parts (leaves stem and seeds) due to air-borne Pb. It has been reported that an increase in lead content in the atmosphere occurs due to anthropogenic behavior, primarily due to the past combustion of leaded fuel, and the persistence of Pb in the environment. Lead has also been considered as one of the most

distinctive heavy metals attributable to vehicular pollution [59, 77]. Pb is one of the most common elements in polluted areas; excessive lead produces detrimental effects on plant morphology, development and photosynthetic processes [10, 60].

Cu is a micronutrient related to the growth process in plant tissue, but it is toxic when it is in excess concentration. According to 75, 59 most plant species can accumulate substantial amounts of copper under different natural and anthropogenic conditions. The phytotoxic level is 30 ppm, while the acceptable limit of copper for plants is between 2 and 20 ppm [28, 54]. In this study, Cu concentrations were within the acceptable limits, but higher in the polluted sites. The high concentrations of Cu at polluted sites could be caused by corrosion of metal parts of cars derived from engine wear, brushing and metal bearing [4]. Similar result was obtained by [17, 25 and 66].

Among other metals in this study, cadmium had the lowest concentrations. According to Hu et al. [25], Cd puts up in low concentrations in particulate matter, thus the likelihood of low Cd concentrations in the plant samples. The amount of Cd in all the studied tree species at polluted and control sites was lower than the acceptable limit levels of Cd ($> 10 \mu\text{g g}^{-1}$) in plants [43, 81], except for *Terminalia catappa* that exceeded the maximum toxic level of $0.5 \mu\text{g g}^{-1}$ for plant foods [46], an indication that it is not safe for its usage for medicinal purposes. Liu et al. [40] stated that fossil fuels combustion, vehicle tire wear and vehicle lubrication oil, and combustion are the main sources of airborne Cd to the environment.

Zinc is a vital constituent of plant protein that performs an essential function in biosynthesis [69]. Zinc originates mostly from atmospheric deposition; it may also be obtained from traffic [16]. The acceptable levels of Zinc in plant have the ranges between 10 and 150 mg/kg [54]. It was also observed that Zn increases were found in the other tree species in the polluted site compared to control except for *Terminalia catappa*. Our result agrees with [25] report of an increased Zn concentration in polluted sites. In their study, the highest Zn concentration was contained in *S. matsudana* from the polluted site, while the minimal concentration was observed in *F. chinensis* of the control. Similarly, [17] reported elevated Zn accumulation in leaf tissues of all plant species the polluted localities in Antakya region in comparison with the control. Bargagli [8] recorded an increase in the concentration of zinc by *Populus* at the urban areas than in the control sites. Studies have shown that trees which accumulate Cd do not accumulate Zn [17, 65]. Our result is in agreement with this assertion; hence, zinc accumulation in all the studied tree species was higher than the cadmium in the studied sites. The microclimate factors (temperature and humidity) to a very large extent affect the pollutant process for on

road vehicles [68]. Higher relative humidity brings about lower concentrations of air pollutants such as NO_x, SO₂, HC and particulate matter [39]. The concentration of air pollution may also vary according to the local temperatures, as air quality decreases as temperature increases. Studies have shown that emissions significantly increase above 2.25 ppm under high temperature [20]. However, this effect is not expected to bias the results presented in this study as local climate conditions are rather similar between control and polluted sites.

Significant relationships were also observed between the concentrations of different metals in the leaves and between their concentrations and the content of photosynthetic pigments. This relationship may have accounted for the metal-specific effects on the chlorophyll and carotenoid biosynthesis [55]. There is simultaneous accumulation of different elements in the leaves of plant species [40]. Metal accumulation index relies upon different factors such as atmospheric chemistry of the local environment and meteorology [25], including height of the sampled trees, sampling time and plant characteristics [24, 89]. In this study the MAI value (5.35) was highest in *Mangifera indica* at the polluted site followed by *Polyalthia longifolia* (4.30) (Table 5). There were changes in MAI in all the studied tree species resulting from different pollution burden and an indication that the removal capabilities of plant species differ from each other [31]. This result agrees with Liu et al. [40], report of higher MAI values of plant species collected from the distance of 1–9 m from the road, while the plant species obtained from 10 m had lower MAI values. Similarly, maximum MAI values were recorded at the Barjora forest surrounded by different pollution zones and minimum MAI values at a Wildlife Sanctuary in West Bengal, India, a control site without human activities. Hu et al. [25] also reported elevated metal accumulation index values at Yan'an, China. In the present study, the maximum MAI value found in *Mangifera indica* (5.35) and *Polyalthia longifolia* (4.30) reveals that they possess good accumulation in heavy metal when growing in a polluted condition. Thus, it could be used as buffer between contaminated and susceptible areas [25, 31, 48]. Owing to the complexities of the parameters of environment it has been challenging to calculate harmful concentrations and the effects of heavy metals in natural ecosystems [81]. Deposition of heavy metal and translocation occurs in plants via the roots and leaves [29, 69], so the precise quantity of elements from air or soil is impossible to differentiate. It is evident that plants in polluted areas are rich in heavy metals relative to plants in stable conditions by comparing the results of the control site and others, independent of the absorption process [25].

5 Conclusion

This study established that the studied tree species situated at the polluted sites (arterial roadsides) were negatively affected by higher vehicular air pollutant concentrations as compared to the control. A higher ratio of chlorophyll *a/b* in the *Ficus Platyphylla*, *Polyalthia longifolia* and *Terminalia catappa* leaf samples collected at the polluted site suggests that these tree species are more tolerant to vehicular air pollution, while *Mangifera indica* is more sensitive to vehicular pollutants. A higher metal accumulation index value found in *Mangifera indica* and *Polyalthia longifolia* reveals that they possess good accumulation in heavy metal while growing in polluted environments. The usage of urban trees as bioindicators is a cost-effective and simple strategy and thus provides a sustainable ecological method for the conservation of urban habitats.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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