Study of lead and copper accumulation by selected botanical species in urban environment

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Abstract: The aim of this study is to quantify lead and copper concentrations deposited on plant species exposed in different habitats of Abidjan in order to assess air quality of Abidjan. Five species were used *Barleria prionitis*, *Cassia surattensis*, *Duranta repens*, *Ficus benjamina*, *Jatropha interrigima* and exposed in parks, main roads, industrial and residential zones. Leaf samples were collected and the concentrations of copper and lead were carried out by inductively coupled plasma mass spectrometry. Roads generally showed high levels of copper and lead and the highest values reached 13 $mg.g^{-1}$ and 7.5 $mg.g^{-1}$ respectively. While the lowest were found in Parks with the values 2 $mg.g^{-1}$ for Cu and 0.5 $mg.g^{-1}$ for Pb. These results suggest that the major source of pollution were car exhaust. However, *C.surattensis* at roadsides showed the highest deposition of Cu and Pb. A significant positive correlation between lead and copper concentration in three leaves species, *Cassia surrattensis* ($r = 0.974$; $p = 0.0043$), *Duranta repens* ($r = 0.824$; $p = 0.0057$) and *Jatropha interrigima* ($r = 0927$; $p = 0.00001$) were found.

Keywords: lead and copper contents; air pollution; plant leaves; ICP-MS.

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1 Introduction

Lead and copper form part of heavy metals the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water (Hawkes, 1997).

Most of heavy metals may be important trace elements in the nutrition of plants, animals or humans (e.g., Zn, Cu, Mn, Cr, Ni, V), while others are not known to have positive nutritional effects (e.g., Pb, Cd, Hg). However, all of these may cause toxic effects (some of them at a very low content level) if they occur excessively (Spiegel, 2002).

Metals such as lead, cadmium, mercury and copper are cumulative poisons. They have been reported to be exceptionally toxic (Ellen et al., 1990). Lead has been associated with intoxications leading to problems in the kidney and liver, the central nervous system, reproductive organs and anaemia. Although copper is an essential trace element in the functions of the human body, chronic and excessive intake has been linked with digestive tract problems and cirrhosis of the liver (Oskarsson, 1989; Abdulla and Chmielnicka, 1990).

Atmospheric heavy metals pollution is one of the most serious problems facing human and other life forms nowadays. The toxicity of heavy metal depends a great deal on their chemical form, concentration, residence time, etc. (Mielke and Reagan, 1988; Duffus, 2002). Because of these elements do not decay with time, their emission to the environment is a serious problem which is increasing worldwide due to the rapid growth of population, increasing combustion of fossil fuels, and the expansion of industrial activities (Smodiš and Bleise, 2001).

Monitoring and systematic gathering of information on heavy metal levels in the environment are essential components of any pollution-control system.

Air quality can be monitored by direct measurements of air pollution, using special models or by aid of plant species. Physical and chemical methods provide information about emission and transmission in the atmosphere and concentrations near the source as well as level of deposition. This kind of monitoring provides information about potential effects on the environment but it is not possible to evaluate the real frequency and magnitude of these effects (Borowiak et al., 2014).

Plants can effectively be used as cheap and naturally available monitoring systems or bioassays of the level and type of air, soil and water pollution in an area. The type and concentration of a pollutant can be reliably found in the plants. Biological indications of levels and concentrations of pollution support the changes caused by human activity. Biological methods due to their relatively low costs and widespread are used in many places. The usefulness of tree leaves in detecting atmospheric metals was reported by various investigators for various species of trees (Barnes et al., 1976). In tropical regions, some authors (Osibanjo and Ajayi, 1980; Fatoki, 1987) used heavy metal levels in various species of Nigerian tree bark as an indicator of atmospheric pollution.

In recent years, Côte d'Ivoire (Ivory Coast) has achieved significant strides in its quest for rapid economic growth through industrialisation. Thus, a number of factories, have developed, and with increased affluence generated by income from the export of natural resources (Olade, 1987). The problems of urbanisation, population explosion due to the armed conflicts and the increased use of automobiles have become very common. More than 10,000 used cars arrive in Abidjan each year.

Previous studies were performed by our group in Abidjan on leaf-based particulate matter (PM) biomonitoring using saturation isothermal remnant magnetisation method (Barima et al., 2014, 2016) but nothing is known about heavy metals amounts present into (PM) and its origins. This study aims to quantify lead and copper concentrations accumulated in plant species exposed in different habitats of Abidjan.

2 Materials and methods

2.1 Study area and experimental set-up

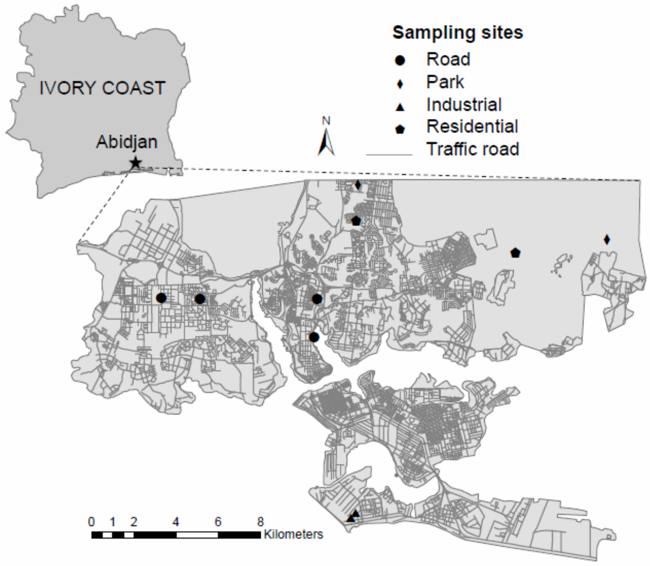
The study was conducted in Abidjan, the largest city in Côte d'Ivoire (5°00'–5°30' N, 3°50'–4°10'W) in West Africa. The city has main automobile fleet constituted in majority of second hand vehicles. All official transport vehicles (about 30,000 in 2010) had diesel engines contain a significant amount of sulphur compared to industrialised countries (UNEP, 2006). The city of Abidjan also contains several parks of which a national park (Banco National Park), a botanical garden, a municipality plants nursery and a centre of floristic. In these green areas, human influence was relatively weak and activities of pollution were more controlled relatively to road traffic. Climate is tropical, hot and humid with a long rainy season from May through July, a small rainy season (September–November) and two dry seasons in between.

2.2 Sampling design

Leaf sampling was performed during two campaigns in February and March 2013 in four habitats: main roads (MR), residential zones (RZ), industrial zone (IZ) and parks. The sampling location is shown in Figure 1. IZ located in south of Abidjan contain companies that are primarily involved in the wood, food, textile. RZ were dormitories and relatively distant from IZ and MR. Parks are botanical gardens. They are intended for scientific and recreational activities. The site of 'Pépinière du district' is relatively close to road relating to 'Jardin Botanique'. Selected MR make up between 4 and 6 traffic lanes in both directions and are the major roads in Abidjan, i.e.: 'Boulevard lagunaire' (Lagoon Blvd.)

and ‘Autoroute du Nord’ (North Highway).To avoid confusion in the main sources of pollution, roads remote to IZ were selected.

Figure 1 Sampling sites and the considered land use classes in the urban environment of Abidjan, Ivory Coast (Côte d’Ivoire)



No rain events occurred five days prior to the sampling campaign and during the campaign itself.

2.3 Species characteristics

The study was performed on five ornamental species used in Abidjan, i.e., *Barleria prionitis* L. (Acanthaceae), *Cassia surattensis* F.Muell. (Fabaceae), *Duranta repens* L. (Verbenaceae), *Ficus benjamina* L. (Moraceae), *Jatropha interrigima* Jacq. (Euphorbiaceae). These plants were grown in 13 litres pots with compost and soil during three months in a municipal garden (municipal plant nursery). After three months of growth, two pots of each studied species, which reached a height of about 1 m, were placed side-by-side in the selected sites and separated from one another of 1 m. In each habitat, these plants have remained exposed to ambient air for three consecutive months.

B. prionitis is an erect, prickly shrub, usually single-stemmed, growing to about 1.5 m tall. The stems and branches are stiff and smooth and light brown to light grey in colour. Leaves are elliptic to oblong, 3 to 10 cm long and 1.5 to 4 cm broad. The base of the leaves is protected by three to five sharps, pale coloured spines.

C. surattensis is a shrub or small tree. The leaves are bipinnate, 12.5–22.5 cm long, rachis with conspicuous stipitate glands between 2–4 lower pairs of leaflets; leaflets from 4 to 10 pairs, 2.5–7.5 cm long are elliptic to oblong and glaucous beneath. The flowers are creamy yellow in axillary corymbose raceme; sepals 8–9 mm long, broadly oblong or suborbicular; petals 1.5–2.7 cm long, broadly oblong, obtuse, shortly clawed.

D. repens is erect to subscandent, usually armed shrub. The leaves 1.5–5 cm long, 1–2 cm broad are obovate-elliptic, serrate to entire, cuneate, very shortly petioled. The racemes are laxly many flowered. The flowers 8–9 mm across, blue or violet, scented; bracts minute; pedicels 2–4 mm long. Calyx-tube 4 mm long, angular, appressedly pubescent. Corolla-tube c. 8 mm long, limb subequally 5-lobed with lobes 3.5–4.5 mm long, pubescent on both sides.

F. benjamina is a tropical evergreen tree reaching a height rarely exceeds 3 m when used as an ornamental plant. Leaves are glossy, oval of 6–13 cm long, with an acuminate tip. *J. interrigima* is an evergreen shrub or small tree with glossy leaves and densely hairy leaves when young. The plant has a rounded or narrow domed form and gets up to 4 m tall with a spread of 3 m or so, although in cultivation it is usually smaller. Leaves are extremely variable; they may be entire and elliptic or oval, or they may be fiddle shaped, or they may have three sharp pointed lobes.

2.4 Heavy metals monitoring

2.4.1 Leaves sampling

At each sampling location, and for each species, six mature undamaged leaves were collected on the same plant and carefully placed in paper envelopes and directly dried at ambient temperature. No discrimination between leaf surface-accumulated and leaf-encapsulated heavy metals were done in order to quantify total lead and copper present on and in leaves

2.4.2 Heavy metals determination

Chemical determination of trace elements (Pb, Cu) was carried out by means of ICP-MS, Perkin-Elmer Elan 6000 (Serveis Científico-Tècnics, University of Barcelona). The ICP-MS were equipped with a Meinhard concentric nebuliser, cyclonic spray chamber, Pt cones and quadruple mass analyser, measuring time 50 ms, integration time 1 s and 3 replicates were used for this study. Typical instrument operating conditions for the ICP-MS were: RF power 1,150 W, plasma Ar flow rate 15 L/min, nebuliser Ar flow rate 0.8 L/min. Leaf samples (100 mg) were digested in Teflon TM containers using HNO_3 (1–2 ml) and H_2O_2 (0.5–1 ml) for 14 h at 90°C. All concentrations are expressed in $mg.g^{-1}$ on a dry weight basis.

The calibration was done with 4 standard solutions Cu (0, 4, 8, 20, 40 ppb) and Pb (0, 2, 4,10, 20 ppb), prepared by dilution of standard solutions 1,000 ppm certified traceable to National Institute of Standards and Technology (NIST). All standards were prepared daily after subsequent appropriate dilution with high-purity deionised water (Millipore, USA). The isotopes used for the measurement were ^{63}Cu and ^{208}Pb, and rhodium (^{103}Rh) was used as internal standard corrector. Rhodium allows us to correct for matrice-induced variation and instrumental drift.

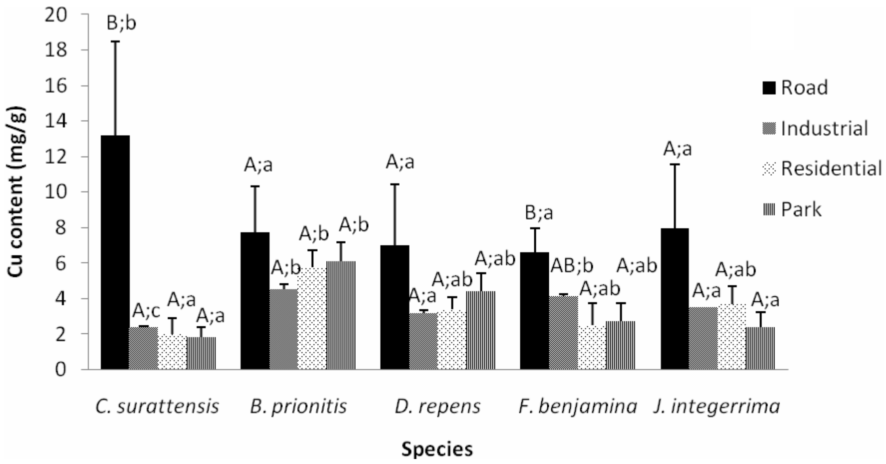
2.5 Traffic density measurement

The number of motor vehicles was determined by field survey with measurement intervals as follow: 06.00–07.00, 12.00–13.00, 16.30–17.30 from Monday to Sunday.

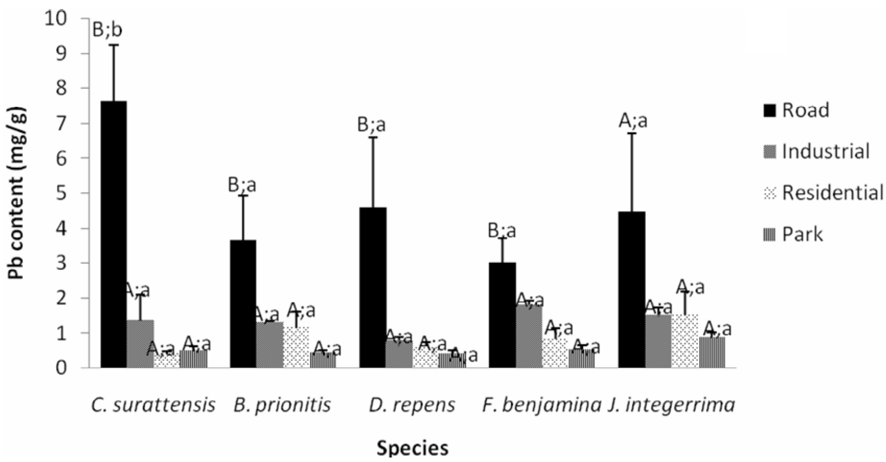
2.6 Statistical analysis

The analyses were performed with Statistica software, version 7.1 (StatSoft. Inc. 1984–2005). Differences in heavy metal (Cu and Pb) in leaves species across site were assessed by one-way analysis of variance (ANOVA) with Fisher-LSD test. Site and species effects on heavy metal deposition were analysed by two-way ANOVAs. The relationship between Cu and Pb content in species leaves was analysed by correlation analysis.

Figure 2 Copper and lead concentrations (mean value ± standard deviation; n = 3) in plant species exposed in different land uses classes (MR, parks, industrial and RZ), (a) copper concentration in plant species (b) lead concentration in plant species



(a)



(b)

Notes: Land uses for each considered species with significant ($p < 0.05$, LSD test) differences to others are marked by different capital letters. Plant species in each land use with significant ($p < 0.05$, LSD test) difference to others are indicated in lowercase letters.

Table 1 Content of heavy metals (Cu and Pb; mg/g) in plant species leaves at all sampling location

Species		*C. surattensis*		*B. prionitis*		*D. repens*		*F. benjamina*		*J. interrigima*	
Land use classes	*Sampling location*	*Cu*	*Pb*	*Cu*	*Pb*	*Cu*	*Pb*	*Cu*	*Pb*	*Cu*	*Pb*
Main roads	Autoroute du nord	6.55^{b}	5.62^{b}	6.58^{a}	3.6^{a}	4.43^{a}	3.56^{ab}	6.21^{bc}	3.4^{c}	4.36^{a}	2.64^{a}
	Boulevard lagunaire	17.59^{c}	8.97^{c}	8.89^{a}	3.67^{a}	12.16^{b}	6.62^{b}	7.07^{c}	2.58^{bc}	11.59^{b}	6.26^{b}
Residential zones	Plateau-dokui	2.92^{a}	0.48^{a}	4.77^{a}	1.61^{a}	4.05^{a}	0.72^{a}	3.75^{abc}	1.14^{ab}	4.71^{ab}	2.19^{ab}
	Riviera-faya	1.03^{a}	0.33^{a}	6.71^{a}	0.69^{a}	2.75^{a}	0.5^{a}	1.25^{a}	0.5^{a}	2.64^{a}	0.84^{ab}
Industrial zones	Vridi canal	2.38^{a}	1.35^{a}	4.55^{a}	1.31^{a}	3.16^{a}	0.78^{a}	4.12^{ab}	1.8^{ab}	3.5^{a}	1.51^{ab}
Parks	Jardin botanique	1.34^{a}	0.21^{a}	5.01^{a}	0.33^{a}	3.38^{a}	0.41^{a}	1.73^{a}	0.41^{a}	1.5^{a}	0.7^{ab}
	Pépinière du District	2.37^{a}	0.64^{a}	7.15^{a}	0.52^{a}	5.4^{a}	0.57^{a}	3.76^{abc}	0.64^{a}	3.23^{ab}	1.03^{ab}

Notes: Mean values on each vertical column marked by the same letter do not differ. Significantly different if ($p < 0.05$).
Different letters a, b,c indicate significant differences between species.

3 Results and discussion

Biomonitoring is common tools for assessing air pollution. Some investigations revealed the usefulness of higher plants for investigating selected heavy metals (Caggiano and Ragosta, 2001). In our study, mean Cu and Pb concentrations measured in four land use classes (MR, Residential, Industrial and Parks) from five plant species leaves (*Barleria prionitis*, *Cassia surattensis*, *Duranta repens*, *Ficus benjamina*, *Jatropha interrigima*) are summarised in Figure 2 and Table 1.

Relating to the land use classes, about levels of Cu and Pb, there is no significant difference in RZ, parks and IZ ($p > 0.05$). However, along roads generally showed high levels of copper and lead, the highest values reached 13 $mg.g^{-1}$ and 7.5 $mg.g^{-1}$ respectively. While the lowest were found in parks with the values 2 $mg.g^{-1}$ for Cu and 0.5 $mg.g^{-1}$ for Pb. The most polluted land use class was MR. These results also suggest that the major source of pollution were car exhaust and confirm those obtained by Bukowiecki et al. (2010), Kardel et al. (2012) in temperate regions also in West Africa by Osibanjo and Ajayi (1980) and Fatoki (1987). The high heavy metal contents in plant samples collected from roadsides are due mostly to the density of traffic. Along the major roads, the sampling site of Boulevard lagunaire (lagoon Blvd) with about 6,000 vehicles per hour recorded higher values than the site of Autoroute du Nord (North highway) (about 4,000 vehicles/h) . The main species in which these values were observed is *C. surattensis*, 17.59 $mg.g^{-1}$ for Cu and 8.97 $mg.g^{-1}$ for Pb. Lagoon Blvd is located in the administrative neighbourhood of Abidjan's City. It communicates to a bridge which separates the South and the North of Abidjan. The high concentrations of heavy metals showed that this road had more traffic density than North highway.

The sources of Pb on roads are automobile emissions of gasoline combustion; Cu from overhead wires and brake pads usury (Pacyna, 1983; Kakareka et al., 2004). The mean heavy metal concentrations of plant leaf samples in Abidjan were found to be at the upper range of values reported in the literature such as Tel-Aviv, Israel (Garty et al., 1977) and Italy (Loppi and Pirintsos, 2003).

High, or at least better, air quality was observed in parks and residential areas as opposed to roads which are in agreement with results of other studies, including those of Weijers et al. (2004) and Serbula et al. (2010). These authors showed that air quality was better within parks and worsened when approaching roads. The recent study published about air quality of Abidjan by Barima et al. (2016) on leaf-based PM biomonitoring using three ornamental plant species (*Jatropha interrigima*, *Ficus benjamina*, *Barleria prionitis*) showed that leaf saturation isothermal remnant magnetisation was two to ten times higher at roadsides than in parks.

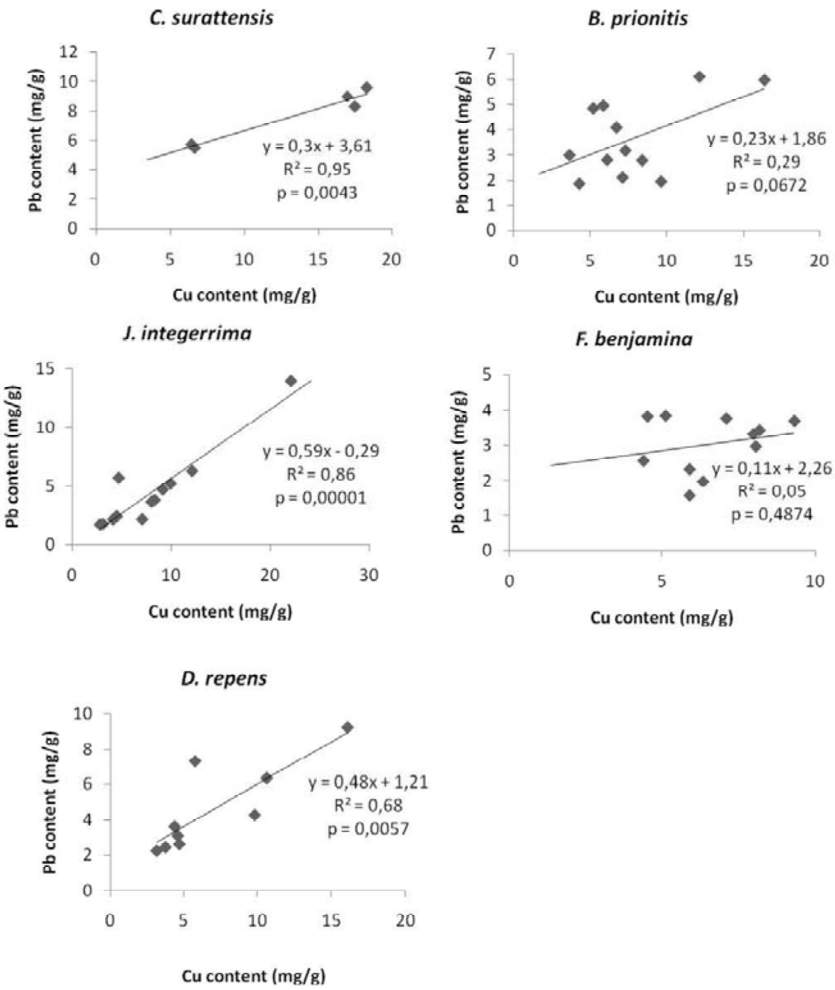
The low pollution in industrial similar to residential and parks may be due to the fact that in the sampling site there were neither refineries nor metallurgical industries.

In the two-way ANOVAs between localities and species, both factors, as well as their interaction, were not significant for Cu and Pb (Table 2). Only sites had significant difference to the pollution ($p < 0.05$). This result confirms that major roads are the main polluted site and it has been demonstrated in previous studies in Abidjan. In our survey, plant species are not source of variation in accumulating heavy metals ($p > 0.05$). Whatever the plant species used leaves would captured heavy metals. However, *C. surattensis* at roadsides showed the highest deposition of Cu and Pb.

Table 2 Two-way ANOVA for species (*C. surattensis*, *B. prionitis*, *D. repens*, *F. benjamina*, and *J. integerrima*) and site (Autoroute du nord, Boulevard lagunaire, Plateau-dokui, Riviera-faya, Vridi canal, Jardin botanique, and Pépinière du District) effects on Cu and Pb concentration in leaves

Variable	*Source of variation*	*df*	*F*	*p*
Cu (mg/g)	Species	4	0.9398	0.449914
	Site	6	17.9496	0.000000
	Species and site	24	1.5552	0.100515
	Error	44		
Pb (mg/g)	Species	4	0.47448	0.754193
	Site	6	14.01535	0.000000
	Species and site	24	1.06904	0.412727
	Error	44		

Figure 3 Correlation between Cu and Pb contents in the studied species



The possible relationship between lead and copper concentration in plant species was analysed and a significant positive correlation between lead and copper concentration in three leaves species, *Cassia surrattensis* (r = 0.974; p = 0.0043), *Duranta repens* (r = 0.824; p = 0.0057) and *Jatropha interrigima* (r = 0.927; p = 0.00001) (Figure 3) were found. These species captured in relatively same amount Pb and Cu present in air.

4 Conclusions

Our study showed that the higher amount of lead and copper accumulated by plant species (*Barleria prionitis*, *Cassia surattensis*, *Duranta repens*, *Ficus benjamina*, *Jatropha interrigima*) exposed in different sites of Abidjan in order to evaluate air quality is mostly dependent on traffic density. However, parks, residential and IZs showed similar deposition trends.

In addition lead and copper were higher on mature leaves of *Cassia surattensis* at MR.

Selected heavy metal concentrations in the five plant species observed in this study were consistently higher than certains showed to another area even in West Africa.

However, a significant positive correlation between lead and copper concentration were found in three leaves species, *Cassia surrattensis*, *Duranta repens*, and *Jatropha interrigima*.

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