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Use of Some Trees to Mitigate Air and Soil Pollution Around Oil Refinery, Kingdom of Bahrain

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ABSTRACT

Plants are important bio-indicators for environmental pollution. This study was conducted to assess trees as indicators of environmental pollution near Bahrain oil refinery. Four tree species were located near the refinery were used in this study; Neem (*Azadirachta indica*), *Nerium oleander*, *Phoenix dactylifera* (Date palm) and *Conocarpus erectus*. The same set of trees, located near Arabian Gulf University were used as control. Leaf samples were collected monthly from the trees and analyzed for heavy metals, sulfur, chlorophyll and water content. Results indicated that Air Pollution Tolerance Index (APTI) tend to increase in trees grown in the polluted site, with *Azadirachta* giving the highest APTI followed by *Nerium*. Chlorophyll content is lower in polluted site. *Nerium* and *Conocarpus* significantly accumulated more Chromium than Date palm and *Conocarpus* in the polluted site. *Nerium* accumulated more Cu, Cr, Mn, Mo and Fe than the rest in the polluted site. No differences in Cd and Pb leaf content between tree species or between sites. Sulfate content was higher in the study site compared to the control site in all plant species *Azadirachta* leaves accumulated more sulfates followed by Date palm *Nerium* and *Conocarpus*. This study indicated that trees remove significant amounts of pollutants from the environment and are excellent bio monitors of pollution stress.

1. Introduction

Air Pollution can be defined as the human introduction into the atmosphere of chemicals, particulate matter or biological materials that cause harm or discomfort to humans, or other living organism or damage the environment. Industrialization, urbanization, economic growth and associated increase in energy demands have resulted in a profound deterioration of air quality in many countries. Oxides of nitrogen and sulfur and fly-ash are the major pollutants from industries and automobiles. Chlorophyll is the principal photoreceptor in photosynthesis, the light-driven process by which carbon dioxide is assimilated to yield carbohydrates and oxygen. Air pollutions can directly affect plants via leaves or indirectly via soil acidification. It has also been reported that when exposed to air pollutants, most plant experience physiological changes before exhibiting visible damage to leaves. Urban vegetation became increasingly important not only for social reasons but mostly for affecting local and regional air quality. Response of plants to air pollutants is variable. Plant species can be used as biological indicators of air pollution. The response of plants to air pollution levels can be understood by analyzing the factors that determine resistance and susceptibility [1]. It is possible to estimate the overall effect of a large number of pollutants as total pollution by measuring changes in the plants. Several researchers agree that air pollutants effect plant growth adversely [2, 3].

Trees remove a significant amount of pollution from the atmosphere as part of their normal functioning. Green trees act as sink and living filters to minimize air pollution by various processes like absorption, adsorption, accumulation detoxification, etc. without undergoing serious foliar damage. Trees also improve the air quality by releasing oxygen into the atmosphere. Particulate and gaseous pollutants are generally removed by dry deposition and wet deposition. In dry deposition, pollutants are absorbed or adsorbed on plant surfaces. SO₂ could be absorbed into plant tissues through the stomata and react with water on inner-leaf cell walls to form sulphurous and sulphuric acids. These acids further react with other compounds and ultimately be transported to different parts of the plant.

Sulfur oxides (SO_x) represent the largest amount of discharged gases into the air beside Nitrogen oxides (NO_x) around refineries [4]. Heavy

metals (e. g., cadmium, lead, copper and zinc) and other pollutants (e. g., polycyclic aromatic hydrocarbons and Toluene and Phenol) are also emitted [5]. Sulfur accumulates at high levels in higher plants. Plants in polluted areas are more affected by SO₂ than other living organisms including humans [6]. Plant's leaves take up SO₂ molecules through its stomata and roots. Abdul Wahab and Yaghi [7] found that old leaves accumulate more sulfur than younger leaves and that some plants are more sensitive to sulfur than others. Plants respond to SO₂ exposure either by accumulating more sulfate in their tissues or by showing visible injuries [8]. Many changes associated with SO₂ stress have been reported in plants such as reduction of stem height, and decline of the photo synthetically active tissues.

The response of plants towards air was assessed by air pollution tolerance index. Air pollution tolerance index (APTI) is used by researchers to select plant species tolerant to air pollution. Bioavailability of metals to trees and subsequent metal accumulation in tree tissues can vary largely depending on the source of metal contamination and site conditions. The heavy metal mobility in soils depends on many factors, including pH, redox potential, cation exchange capacity (CEC), presence of organic matter and clay content.

The aim of this study was to determine the APTI values of some plant species near the oil refinery, in Manama, Kingdom of Bahrain. The study also evaluated the ability of some common trees in Bahrain to accumulate heavy metals and sulphates from the environment.

2. Experimental Methods

2.1 Materials and Methods

The plants chosen for this study include: Neem (*Azadirachta indica*), *Nerium oleander*, *Phoenix dactylifera* (Date palm) and *Conocarpus erectus*. The last 3 plant species are already established at the site which is located about 200 meters from BAPCO refinery. Neem trees were established on large pots (200 litres) partially buried in the soil. Plant leaf samples were collected and analyzed for sulfur, and heavy metal content at the laboratories of Arabian Gulf University, Manama, Kingdom of Bahrain. Water content and total chlorophyll was determined by the method described by Maclachlan and Zalik [9] at IFAD labs in Bahrain. A site away from the refinery at Arabian Gulf University with similar ecological conditions was selected as control site (Fig. 1)

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Fig. 1 Map of Bahrain showing study (S) and control (C) sites

2.2 Description of Tree Species

2.2.1 *Azadirachta indica*

A. Juss. is a drought tolerant species belonging to the family Meliaceae. It is a native of India. It is a fast growing tree that can reach a height of 15–20 m when mature. It is an evergreen tree that tolerates extreme temperatures, but may shed its leaves under extreme drought conditions. The crown may reach 15 m diameter in old, free-standing trees. Neem is noted for its drought resistance. It thrives well on minimum water applications of the lowest quality. It is a major shade tree in dry areas and is used successfully for its anti-desertification property. It yields good timber and all parts of the plant are medicinal. *Conocarpus erectus L.*, (green button wood) belongs to *Combretaceae* family and is an evergreen tree having a spreading crown. The tree is used as an ornamental plant and is especially prized for landscaping. *Nerium oleander* is an evergreen shrub or small tree in the family *Apocynaceae*. Oleander is a vigorous grower in warm subtropical regions, where it is extensively used as an ornamental plant in parks and along roadsides. *Phoenix dactylifera*, commonly known as date or date palm is a flowering plant species in the palm family *Arecaceae*, cultivated for its edible sweet fruit, probably originated from lands around Iraq. The species is widely cultivated and is naturalized in many tropical and subtropical regions worldwide.

2.3 Determination of Air Pollution Tolerance Indices (APTI)

The air pollution tolerance indices of the four plants were determined following the method of Singh and Rao, 1983. The formula of APTI is given as:

$$APTI = [A (T+P) + R]/10$$

Where A = Ascorbic acid content (mg/g), T = total chlorophyll (mg/g), P = pH of leaf extract, and R = relative water content of leaf (%).

2.4 Total Chlorophyll Content

Variation in chlorophyll content has been used in many extensively to investigate the effects of pollutants on plants. Chlorophyll was determined by the method described by Maclachlan and Zalik [9]. One gram of fresh leaf samples were macerated in 10 mL of 80% (v/v) acetone and centrifuged at 1000 rpm for 10 minutes to clear the suspension supernatant, which contained soluble pigment and was used for the determination of chlorophyll. One mL of solution was used for detection of chlorophyll content by spectrophotometer, absorbance of the extract was recorded at 663 and 645 nm on spectrophotometer against 80% (v/v) acetone blank. The chlorophyll content was calculated using the formula given below and expressed in mg/g fresh weight.

$$\text{Chlorophyll "a" mg/g} = (12.3D663 - 0.861D645 / d \times 1000 \times W) \times V$$

$$\text{Chlorophyll "b" mg/g} = (19.3D645 - 3.6D663 / d \times 1000 \times W) \times V$$

Where:

D663 = absorbance at 663 nm

D645 = absorbance at 663 nm

W = fresh weigh of leaf sample taken (1 g)

d = length of light path in cm

V = volume of leaf extract (10 mL).

Total Chlorophyll "a+b" = Average chlorophyll "a" + Average chlorophyll "b"

2.5 Relative Leaf Water Content (RWC)

To determine relative leaf water content (RWC) the fresh leaves were weighed and then immersed in water over night, blotted dry and then weighed to get the turgid weight. The leaves were dried overnight in an

oven at 55 °C and reweighed to obtain the dry weight 5 g of the fresh leaves was homogenized in 10 mL deionized water. This was filtered and the pH of the leaf extract determined after calibrating pH meter using buffer solution. Following the method described by Singh [10], leaf RWC was determined and calculated using the formula:

$$RWC = [(FW - DW)/(TW - DW)] \times 100$$

Where, FW = Fresh weight, DW = dry weight, and TW = turgid weight

Fresh weight was obtained by weighing the fresh leaves. The leaves were then immersed in water over night, blotted dry and then weighed to get the turgid weight. Next, the leaves were dried overnight in an oven at 70 °C and reweighed to obtain the dry weight

2.6 Ascorbic Acid

Ascorbic acid content (AA) (mg/g) was measured using spectrophotometric method [11]. One g of the fresh foliage was put in a test-tube, 4 mL oxalic acid - EDTA extracting solution was added, then 1 mL of orthophosphoric acid and then 1 mL 5% tetraoxosulphate(VI) acid added to this mixture, 2 mL of ammonium molybdate was added and then 3 mL of water. The solution was then allowed to stand for 15 minutes. After which the absorbance at 760 nm was measured with a spectrophotometer. The concentration of ascorbic acid in the sample was then extrapolated from a standard ascorbic acid curve.

2.7 Heavy Metals

Sub-samples of the ground plant samples were dry-ashed by placing 1 g of the finely ground material in a silica dish and placed in a muffle furnace where it was burnt to ash at 550 °C for 4 hours. It was then cooled and ash dissolved in 5 mL of 2 N HNO₃, filtered into a 50 mL volumetric flask and diluted to volume with distilled water. A blank was also prepared following the same procedure without the plant sample. Heavy metals were then determined with MS Spectrometer (PerkinElmer 8000 Optima).

2.8 Sulfur

One gram of fine ground dried leaves was digested with concentrated HNO₃ and pre chloric acid in a fumigation chamber. The total sulfate was determined by Ion Chromatography.

2.9 Data Analyses

The data was analyzed using JMP 11.1 statistical software and means were separated at the 5% level of significance.

3. Results and Discussion

The effect of air pollution on chlorophyll content, ascorbic acid. Leaf water content and pH for the four tree species is presented in Table 1. From this data Air Pollution Tolerance Index (APTI) was calculated and presented in Fig. 2.

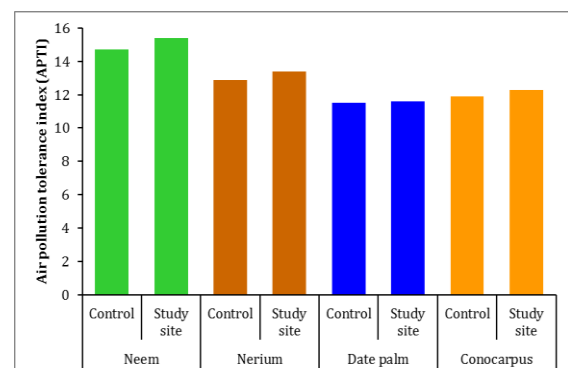


Fig. 2 Air pollution tolerance index (APTI) by tree species and site

All the species showed a decrease in chlorophyll content as compared to sample collected from the control site (Table 1). A similar result was reported by Iqbal, et al. [12] in *Conocarpus* and *Eucalyptus* species. The deposition of particulates particles on the surface of leaves causes clogging of stomata and this clogging ultimately leads to reduction in photosynthetic rate which, in turn, causes a reduction in the contents of sugar, chlorophyll and protein [13, 14]. Results indicated that ascorbic acid tend to increase in trees grown in the polluted site. APTI tend to increase in trees grown in the polluted site.

Table 1 Effects of air pollution on total chlorophyll content (TCh mg/g), ascorbic acid (AA mg/g), leaf water content (RWC %), pH and air pollution tolerance index (APTI) of the four tree species in the control (C) and the study site (S)

Tree species	Site	TCh (mg/g) fr. wt	AA (mg/g) fr. wt	RWC %	pH
Neem	C	7.2	6.5	65.5	5.4
Neem	S	6.6	7.3	65.2	5.6
Nerium	C	5.9	5.5	65.0	5.8
Nerium	S	4.5	6.3	70.2	5.6
Date palm	C	4.8	4.2	72.5	5.2
Date palm	S	4.2	4.8	71.2	5.2
Conocarpus	C	5.6	5.7	56.2	5.5
Conocarpus	S	5.5	6.6	57.3	5.4

3.2 Heavy Metals Content

In the present study, the heavy metal content in tree leaves collected from study and control sites is depicted in Table 2. Cadmium content did not change significantly between tree species and between locations. Regarding chromium, *Nerium* and *Conocarpus* significantly accumulated more than Date palm and *Conocarpus* in the study site. Lowest accumulation of chromium was found in the control site for all tree species. Copper content was significantly higher in *Nerium* leaves in the study site and lowest in *Nerium* leaves in the control site. Similarly, *Nerium* accumulated more Nickel than the rest in the study site. Regarding lead, *Nerium* and *Conocarpus* accumulated more than the rest. *Nerium* also accumulated more molybdenum and manganese than the rest in the study site. *Conocarpus*, Neem and Date palm accumulated more zinc in their leaves. The concentration of heavy metal in tree leaves in the study site is as follows:

Cadmium : No significant differences between tree spp at both sites
 Chromium: *Nerium* > *Conocarpus* > date palm > neem
 Copper : *Nerium*, rest are the same
 Iron : *Nerium* > *Conocarpus* > Date palm > Neem
 Nickel : *Nerium* > *Conocarpus* > date palm > neem
 Lead : No significant differences
 Zinc : *Conocarpus* > Neem > *Nerium* > date palm
 Molybdenum: *Nerium* > *Conocarpus*
 Manganese: *Nerium* > *conocarpus* > date palm > neem

Some of previous works reported that Samples from near the highway showed highest contamination by the metals in Neem leaves especially with the more hazardous metals Pb and Ni. Researchers used neem trees as bioindicator for heavy metals in Borno State, Nigeria. They reported that the concentrations of Pb, Ni, Cr and Cd were not detected away from the highway and that the concentrations of some of the metals in the three sampling points were lower than that of their corresponding controls. They concluded that the Neem tree leaves do not only indicate pollution due to vehicular traffic activities but also other anthropogenic activities.

Table 2 Heavy metal content in the leaves of study trees grown in the study and control sites

Tree species	Cd	Cr	Cu	Fe	Ni	Pb	Mo	Mn	Zn
Neem	0.10 a	0.78 b	7.69 b	214.9 ab	6.1 b	2.1 ab	0.0 b	18.9 bc	50.5 a
<i>Nerium</i>	0.12 a	2.65 a	19.6 a	768.9 a	17.2 a	2.9 a	1.5 a	57.8 a	37.3 bc
Date palm	0.05 a	1.43 ab	9.5 b	429.9 ab	8.5 b	2.6 ab	0.4 b	31.1 c	45.6 ab
<i>Conocarpus</i>	0.09 a	2.06 a	10.8 b	547.9 ab	11.0 b	2.9 a	0.9 ab	48.6 ab	34.7 c
Neem (C)	0.00 a	0.73 b	7.10 b	144.8 ab	5.3 b	1.3 b	0.15 b	9.0 dc	36.0 bcd
<i>Nerium</i> (C)	0.12 a	0.50 b	3.86 c	107.0 ab	3.9 c	1.7 b	0.13 b	8.4 d	29.8 cd
<i>Conocarpus</i> (C)	0.04 a	1.05 b	8.06 b	272.3 b	6.5 b	2.6 ab	0.2 b	27.8 c	51.6 abc
Date palm (C)	0.00 a	0.77 b	7.56 b	188.9 ab	5.7 b	1.5 b	0.1 b	12.9 c	10.6 d
Sig.level	NS	0.0005	0.032	0.0001	0.00012	0.015	0.0001	0.0001	0.0018

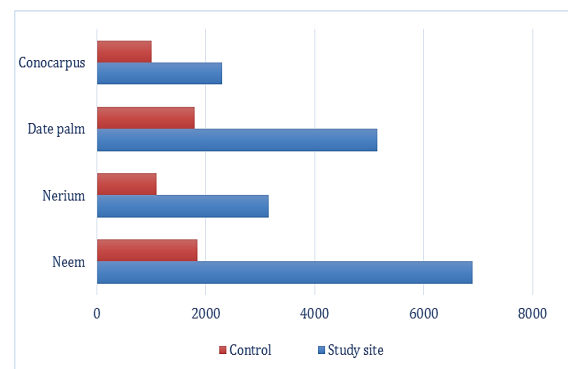
Means followed by the same letter in a column are not significantly different at 5% level

Sharma and Butler [15] reported that plants that are constantly exposed to environmental pollutants absorb, accumulate and integrate these pollutants into their systems. Heavy metals are taken up and Trans located by plants to differing degrees. Many researchers concluded that the presence of these metal ions in plant leaves explain the fact that these plant leaves are good bio indicators and can be used in air pollution monitoring studies in industrial areas [16]. Akan, et al [17] studied the concentration Heavy Metals in Leaf, Stem Bark of Neem Tree (*Azadirachta indica*) and Roadside Dust in Nigeria. The highest concentrations of metals

were found to be higher at the seven sampling points, while the lowest levels were observed in the street dust samples from the control sites. The concentrations of all the metals in plant samples were significantly highest in the leaves of *Azadirachta indica*, while the stem bark shows the least values. Determination of chemical composition of plants is one of the most frequently used methods of monitoring environmental pollution. Various plants have been used as bio indicators to assess the impact of a pollution source on metal accumulation in plants.

3.3 Sulfate Content in Leaves

The analysis of sulfate content in plant leaves shows that it was higher in the study site compared to the control site in all plant species (Fig. 3), Neem leaves accumulated more sulfates followed by Date palm. *Nerium* and *Conocarpus* accumulated less sulfate. The values in Fig. 3 are by far lower than those reported by Al-Jahdali and Bin Bisher [5] for Jeddah refinery in the leaves of *Myoporum pictum* tree (3500-65000ppm sulfate). These levels exceeded the levels reported by Abdul-Wahab and Yaghi [7] in other plant species around Muscat Oil Refinery. This could be explained by the fact that Jeddah Refinery is a very old plant, discharging gases for almost half a century. Desulphurization system in the study site can cut SO₂ emission by up to 90% using seawater as the absorbent to neutralize SO₂ transformation into sulfate, which is a natural compound of seawater.

**Fig. 3** Leaf sulfate content (ppm) in the study and control sites

4. Conclusion

Plants are important indicators of environmental pollution. As the danger of air pollution is increasing, APTI determination becomes more important. Accumulation of heavy metals in plant tissue indicates the very important role of certain plants as Bio indicators of environmental pollution, and can be used for monitoring pollution stress. *Nerium oleander* and Neem are found to be more tolerant to air pollution than date palm or *Conocarpus*. *Nerium* is found to accumulate more heavy metals in its leaves in contaminated areas. Neem trees accumulate more sulfate than the other studied tree species.

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