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# Biomonitoring of Distribution of Nickel and Vanadium using *Calotropis procera* L. in Jeddah City, Saudi Arabia

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## Abstract

The aim of this study was to investigate the ability of *Calotropis procera* L., as a biomonitoring technique for airborne Vanadium (V) and Nickel (Ni) pollution distribution at four different areas in and around Jeddah city, Saudi Arabia. Concentrations of V and Ni varied significantly between sites. The maximum concentrations of V were 68.06, 40.91 and 25.04 mg $kg^{-1}$ for soil samples, unwashed plant samples (UWS) and washed plant samples (WS), respectively in the industrial area. However, Ni concentrations were 42.73, 39.09 and 22.40 mg $kg^{-1}$ for the same samples, respectively in the roadside area. The results indicated that V concentrations were at the order of: roadside > industrial area > residential area. This was not the case with Ni as the order industrial > roadside area > residential area. There was a significant correlation between the V and Ni concentrations in soil and plant samples. The study also showed that the concentrations of V and Ni on the unwashed leaves were higher than those on the washed leaves and this magnified the effect of airborne fall dust on the ambient air quality in Jeddah City. Based on the results of this study, it was recommended that the *Calotropis procera* plant can be used as a biological technique for the airborne heavy metals bio monitoring, especially in the arid land region countries.

**Keywords:** Air borne heavy metals bioinidcators; Biomonitors; *Calotropis procera*

## Introduction

Airborne heavy metal pollution became of a great concern due to rapid development of many countries. Heavy metal contamination has continued to gain global attention, mainly because of the toxicological risks posed by such metals to human health [1]. Energy, transport, production of construction materials and metallurgy processes are the main source of gas and dust which produce the heavy metal in the atmosphere. Precipitation and natural sedimentation are the way through which heavy metals, except mercury, go to atmosphere and deposit to soils in the form of aerosols. The other sources of the excess heavy metal in atmosphere and soils include the extensive use of fertilizers and pesticides, atmospheric deposition, irrigation with wastewater, the activities of mining improper stacking of the industrial solid wastes. Although some metallic elements are often essential for living organisms, they become toxic when present at high concentrations [2]. This fact is also belongs the tested elements in this study where that nickel (Ni) and vanadium (V) are essentially for human and animal's body (but toxic at higher levels). The existing studies reported that heavy metals may pass in to the human body through dust inhalation and absorption by skin, and thus the direct damages are happened, specially, for children's health. Urban environmental quality is affected and human health is damaged indirectly by heavy metals through polluting the water, food and atmosphere. Heavy metals which are persistent pollutants and non-biodegradable environmentally can be adsorbed and taken up in to the vegetables tissues by the deposition on the plant parts surfaces exposed, environmentally, to the polluted air and contaminated soils [3-6]. Widespread distributions of nickel as metal in the environment is known and there are about 100 of nickel minerals are also known and these minerals are essential materials for the commercial and industrial uses. Occupational and non-occupational population can be affected by nickel and its minerals and many health risks can be happened to them [7]. Plants which play an important role in water, air and land purification need heavy metals in small quantities as of essential nutrients as their need to the macronutrients for grow and their life [8]. Plants can also be a good solution for cleaning up the atmosphere of heavy metals which taken up by plants though several pathways like soil and water [8]. The plant property of heavy metal accumulation is very important for cleaning the polluted sites and in this matter, the plants are different in their abilities of heavy metals accumulation. The plants can be classified in this field to three groups: plants can accumulate metals in the shoot "accumulators", plants reflect the metal content in the environment "indicators" and plants exclude and restrict the heavy metal transferring in to shoots regardless their concentrations are high in the roots or the environment. So the remove of heavy metal and other pollutants from air, water or soil can be done by using these indicators or accumulator plants [9]. Hyper-accumulator plants are the plants that accumulate heavy metals in hundreds to thousands times than normal plants. For many years, biological indicators had been used for the accumulation, deposition and distribution detection of heavy metal pollution [10]. The monitoring of the levels of atmospheric trace metallic concentration by using different types of biological monitors and various vegetation have been reported by different researchers [11]. The use of leaves of higher plants as heavy metal bio-monitoring has been increased during the past near decades [12]. Plants are differing in heavy metal quantities through different paths from soils or air. An investigation by Shaheen [13] on heavy metals in different locations with the industrial area south of Jeddah City, KSA, found the Nickel concentration means in soil ranged from 82.06 mg/kg to 94.80 mg/kg and they also, found the Nickel concentration means in the leaves of three different trees associated with the soil locations ranging from 2.63 g/kg to 4.86 mg/kg. For both Ni and V, Krishm [14] analyzed soil samples from the industrial area of Surar city in India and found 79.0 mg Ni/kg of soil and 380 mg V/kg of soil. Moller [15] found that the average of Ni content in soil collected from Damascus City, in Syria was 39.0 mg/kg. The Ni content ranged from 12.40 to 72.10 mg/kg and the average was 29.14 mg/kg in urban soils collected from different countries [2]. *Calotropis procera* was checked for Ni concentrations uptake in a study by Obiajunwa EI [16] the results showed that this plant leaves Ni concentration mean was 235.2 mg and for Vanadium, in another study on Nigerian medicinal plant they found that V concentration was 339.9 mg/kg in the plant leaves of *Alchornea cordifolia*. Li and Huang [17] found that the soil Ni concentration mean was 72.10 mg/kg in the city of Baoji. Han [18] found that Ni concentration in soil was 57.00 mg/kg in America whereas Huang [19] found 38.50 mg/kg of Nickel in Yangzhou. Alyazouri et al. [20] found 50.0 and 39.0 mg/kg of Ni in *Dactyloctenium aegyptium* and *Heliotropium calcareum*, in dry foliage of dry plants growing in suspected contaminated sites and for soil samples from the suspected contaminated soils (industrial) in Arab United Emirates ranged from 340–680 mg/kg but in two sites in Ajman Deseret and Ajman city were 100 and 30 mg/kg respectively. Soil samples collected from 10 locations in the Hafr Al Batin Area near the Saudi/Kuwaiti border following the Gulf War contained V at concentrations ranging from 2.00 to 59.00 mg/kg soil; the vanadium concentrations decreased with increasing distance from the border [21]. V concentration ranging from 5 to 140 mg/kg has been reported in different soils, and concentrations can reach very high levels (up to 400 mg/kg) in soils polluted by fly ash [11]. The geometric mean vanadium concentrations in 40 samples of urban soils collected in Aviles, Northern Spain were 34.1 mg/kg, ranging from 22.0-67.0 mg/kg [22]. The objective of this study was to investigate the ability of *Calotropis procera* L., as a bio-monitoring technique for airborne Vanadium (V) and Nickel (Ni) pollution distribution at four different areas in and around Jeddah city, Saudi Arabia.

## Materials and Methods

### Study area

Samples were gathered from different locations within Jeddah city, Saudi Arabia. This city is located in the western costal region of the country at 20' 30" to 22' 30" on the Red Sea. Jeddah city is the second Saudi biggest city and it is the main commercial center in the country.

Over the last three decades the city growth has been increased, rapid and still going up to date. In 2010 the population of Jeddah city was around 3,513,000 and it is expected to increase to more than 4,542,000 in the year of 2020 [23].

### The statistical design

Completely randomized design (CRD) with five replications and four treatments was used to conduct this work.

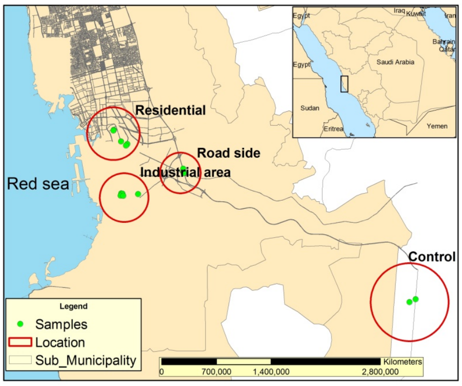


**Figure 1:** Study area and samples locations on Jeddah Map.

### Sampling and analysis

**Sample collection:** *Calotropis procera* (Aiton) WT Aiton. (Family: Asclepiadaceae) is one of the important native species of Saudi Arabia. It is a large shrub or small tree with multi-stems can grow to up 5 m. The leaves are grey to green, broadly ovate to obovate and size 10 × 15 cm. When cutting the branches trickle an abundant milky sap is produced. The roots are growing up to 4 m. and the cross section in the midrib of the leaf shows that the epidermis is single-layered in the upper and lower and covered with thick cuticle (1 mm in thickness) [24]. It is spread in arid and semiarid regions with high-temperature ranges from 20 to 30°C, it cannot frost resistant and precipitation 150–1000 mm or less [25]. *Calotropis procera* is a wild plant growing in the arid region abundance and is distributing as a common plant in all seasons in and around Jeddah city, it is an adaptable plant with the region soil and climatic condition and for these reasons, it was selected for the airborne V and Ni bio-monitoring. During July 2014 five plan leave samples and soil associated samples were collected from different sites within each of the four studied areas as it is shown in Figure 1. The targeted areas were: Jeddah industrial area, the roadside area (Along with the east highway), (3) the central residential area and (4) the background area "control or clean area" about 30 km from the center of the city towards the east south of Jeddah city. All plant leaves samples were saved in brown paper bags and the soil samples were saved in black plastic bags and after that all, samples were transferred to the laboratory for the physical and chemical analysis work.

**Sample preparation:** The laboratory work started by dividing the plant samples into 2 groups: the first group was named as washed (WS) for a half minute with running tap water for each sample then with zero water for dust particles removing and the second group was saved as unwashed (UWS). At room temperature and for 3 days, all plant samples were dried then they were put in an oven drier with 70°C for forty eight hours. By using an electrical grinder, fine powder of each plant sample was prepared. In parallel, soil samples taken from each plant sample location on the depth of (0-20) cm were cleaned of herbs and strange materials, after that they were dried in the same way of plant samples and finally they were sieved by using 2 mm metal sieve. In labeled zip plastic bags, all plant and soil samples were packed and kept till analyzing stage.

**Physical and chemical analysis of soil samples:** As it is listed in Table 1 all physical and chemical characteristics of the soil samples from the studied location were analyzed in the soil laboratory, at Arid land Agriculture department at King Abdulaziz University, Saudi Arabia. All analysis was done according to Pansu and Gautheyrou [26].

**Chemical analysis of plant and soil samples:** An electronic sensitive balance was used to take an extract weigh of 0.5 g of the plant and soil dried powder accurately and this weighs were transferred to usual glass digestion flasks of 100 mL for the wet digestion process. Then 10 mL of digestion mixture (3:5 by volume) of concentrated Perchloric and Nitric acids ($HCLO_4$ + $HNO_3$), respectively were added to each digestion flask which then heated thermally by using an adjusted hot plate.

Heating continued to the point in which 1 mL of the digestion mixture with a white color residue remained at the bottom of each flask. After cooling of the flasks, their contents were filtered and transferred to 50 mL volumetric flasks and by addition of deionized water, the volume was completed to 50 mL for each flask in the same way.

**Determination of V and Ni concentrations:** Inductively Coupled Plasma optical emission spectrometry (ICP-OES) was used to determine V and Ni concentrations. According to AOAC guidelines 1998, all necessary precautions were adopted to avoid any possible cross pollution.

The objective of this study was to assess pollution with heavy metals (Ni and V) in ambient air of Jeddah city by using *Calotropis procera* plant as a bio-monitor through the estimation of their concentrations in soil and plant samples gathered from 4 different areas in the city.

## Statistical Analysis

The study data were organized for statistically analyzing according to the experiment design used which is (CRD). For statistical comparing of means, the Least Significant Differences (LSD) test was used at $p \leq 0.05$ after application of the analysis of assumption of variance [27] by using the program of SAS [28].

## Results

### Soil characteristics

The characteristics of collected soil samples such as organic carbon, organic matter, sand, silt, clay and sorting values are identified and reported in Table 1.

| Location | pH | EC (mmos) | O.C % | T.O.C % | O.M % | Texture |
|---|---|---|---|---|---|---|
| Industrial | 6.84 | 5.03 | 1.08 | 1.44 | 2.49 | Sandy Loam |
| Road side | 7.24 | 2.2 | 0.44 | 0.58 | 1 | Loamy Sand |
| Residential | 7.08 | 12.77 | 0.52 | 0.69 | 1.2 | Sandy Loam |
| Control | 7.62 | 0.381 | 0.08 | 0.11 | 0.19 | Sand |

**Table 1:** Physical and chemical characteristics of soil samples.

### Significance of the obtained results

The concentrations of Vanadium and Nickel in plant leaf samples, WS or UWS, and in associated soil samples were determined and the obtained results were statistically analyzed.

Analysis of variance (ANOVA), shown in Table 2, revealed that there were high significant effects of the different polluted areas on the V and Ni concentrations in plant leaves samples (WS and UWS) and in associated soil samples.

| ANOVA | | | | | | | |
|---|---|---|---|---|---|---|---|
| Source of variance | Df | MS | | | | | |
| | | Vanadium | | | Nickel | | |
| | | WS | UWS | Soil | WS | UWS | Soil |
| Areas | 3 | 339.5955** | 855.536075** | 30.63**** | 254.5329** | 739.876075** | 17.09** |
| Error | 16 | 2.234 | 11.639 | 3.17 | 6.6707 | 12.598 | 1.69 |
| **:Significant at p ≤ 0.01 | | | | | | | |

**Table 2:** Analysis of variance of V and Ni in *Calotropis procera* leaves and associated soils under the effects of different areas in Jeddah city.

### The statistical comparison of means

Table 3 included the V and Ni concentration means in the plant leaves (WS and UWS) of *Calotropis procera* gathered from different sites in each of the four polluted areas and in the soil samples collected from the same sites of plant leaves in each of the studied area.

The least significant difference test (LSD) was used for the comparison of concentration means of the tested heavy metals in this study.

The LSD test used for the statistical comparison of means showed high significant differences between Ni and V means in plant leaves, both of WS and UWS leaves, at $p \leq 0.05$ and under the different studied areas effects.

On the other hand, the same significant effects of the studied areas on the Ni and V concentration means in associated soil samples were found.

### Vanadium and nickel levels in plant leaves

**Vanadium (V):**As it is shown in Table 3, the statistical comparison of V concentrations in the plant leaves under the different studied areas showed significant differences between the four areas. The highest concentration in washed leaves (25.04 mg/kg) was found under the roadside area followed by industrial area (19.12 mg/kg), residential area (16.39 mg/kg) and the least was the control (0.16 mg/kg). The V concentrations in unwashed leaves similar responded to the locations of sampling, but the values were around twice the values in the washed leaves. The Vanadium level order was: Roadside > Industrial > Residential > Control and this style of the order was the same for both plant and associated soil samples.

| Means mg/kg | | | | | | |
|---|---|---|---|---|---|---|
| Treatments | V | | | Ni | | |
| | WS | UWS | Soil | WS | UWS | Soil |
| Industrial | 19.12 b | 31.05 b | 53.25 b | 22.40 a | 39.09 a | 42.73 a |
| Roadside | 25.04 a | 40.91 a | 68.06 a | 14.05 b | 24.70 b | 38.56 b |
| Residential | 16.30 c | 23.26 c | 47.68 c | 11.69 b | 19.80 c | 31.20 c |
| Control | 0.16 d | 1.21 d | 4.30 d | 0.08 c | 1.06 d | 3.18 d |
| *Means followed by the same letter (s) for each metal in WS, UWS or soil are not significantly different according to LSD at p ≤ 0.05. | | | | | | |

**Table 3:** Means of V and Ni in plant and soil samples under the effects of the studied areas in Jeddah city.

**Nickel (Ni):** The statistical comparison Ni concentrations in the plant leaves under the different studied areas showed significant differences between the four areas (Table 3). 22.40 mg Ni/kg of plant leaf of washed samples was absorbed by the leaves of the tested bio-monitor plant in the industrial area locations whereas the concentration mean of Ni absorbed was 39.09 mg/kg of dried unwashed samples in the same area. The minimum Ni concentration mean was 0.08 mg/kg was found in WS leaves of controls samples and 1.06 mg/kg was found in UWS control leave samples. The maximum Ni concentration mean was found in the plant samples gathered from the industrial area locations of 39.09 mg/kg of UWS samples and 22.40 mg/kg of WS samples. The maximum Ni level was mainly found by the industrial area, the second area was the roadside and the third area was the residential and the background came as the last area had the lowest Ni concentration mean. All Ni concentration means in each studied area were in the same range (10-100 mg/kg of dry plant tissue) toxicant standard suggested by WHO/FAO [29] for nickel in plants. It is important to mention here that the washing process of the leaves reduced the V and Ni concentrations significantly in all the sites.

### Vanadium and nickel levels in soil

**Vanadium (V):** As shown in Table 3, the statistical comparison of V concentration means using the (LSD) test showed significant differences between the V concentration means of the soil samples under the effect of the 4 studied areas. (68.06, 53.25, 47.68 and 4.30) mg V/kg of soil samples collected from roadside, industrial, residential and control areas, respectively. The maximum V concentration mean was found in the roadside soil samples, it was significantly the highest among the other three investigated areas. On the other hand, the samples gathered from the control area showed the lowest Vanadium values.

**Nickel (Ni):** At $p \leq 0.05$ and under the effect of the used studied areas "treatments" it was found that the Ni concentration means of soil samples were significantly different. As it was shown in Table 3, the total nickel concentration means in soil samples ranged from 3.18 mg/kg of soil samples in the samples from the control area to 42.73 mg/kg soil samples in the industrial area. All nickel concentrations were found lower the value of 75 mg/kg for soils which it is the Ni toxic limit in soils stated by the European Union [30].

### Percentage of V and Ni resulting from airborne fall dust

The fall dust represents the main factor of air pollution problem in all polluted cities and it determined by the calculation of the quantities of any pollutant removed off the plant leaves by the leaves washing process.

| Sites | Industrial | Roadside | Residential | Control |
|---|---|---|---|---|
| V | 38.4 | 39.0 | 29.0 | 88.7 |
| Ni | 42.6 | 43.1 | 39.4 | 92.5 |

**Table 4:** Total percentage (%) of V and Ni removed from the leaves of *Calotropis procera* by washing process.

In the current study, the values of V and Ni listed in Table 4 represent the effect of leaves washing process. These concentration levels are the amount of V and Ni resulted by the airborne dust falling on each of the studied areas. The fall dust containing Ni was determined on plant samples collected from industrial area was higher than those collected from the residential and roadside sites, this also indicates that atmospheric deposition of Ni was not the same in the studied areas which are different in rates of gases and particles emissions containing Ni. Concerning the V, the deposition in the roadside was higher than the other studied areas.

## Discussion

The study results revealed that the same concept where, for instance, concentrations of Vanadium and Nickel reached to the residential area and even to the clean area "control" at about 30 km. south east Jeddah City and this only can be considered as airborne heavy metals deposition. The study results listed in Table 3 showed significant differences between studied areas "treatments" on the tested heavy metal concentrations and as a result of this, there were significant differences between the V and Ni concentration means and this could be due to the differences existing normally between those areas themselves, in other meaning, traffic, industrial activities and other pollution sources and loads. These results were supported and similar to many studies in world parts such the study conducted by Aksoy [31] in Turkey and with another study by Al-Dhaibani [32] in KSA. Also, the obtained results listed in Table 3 indicated that by increasing urbanization activities "traffic and industry" an increasing in concentrations of Vanadium and Nickel metals resulted. For Vanadium, it was showed that V mean concentrations were higher in the roadside soil samples and plant samples than in residential area, industrial area, and un urban area and this can due to the traffic emissions on roads which referred as an important source of heavy metal pollution on the roads surrounding areas and also this was supported by Onder [33] who found that for both soil and grass samples, the highest mean value of vanadium was at the Alaeddin Hill "heavy traffic area". For Nickel, the current study results showed the Ni mean concentrations were higher in the industrial area soil and plant samples than in roadside area, residential area and un urban area and this can due to the industrial activities dealing with or producing

Nickel salts and to fuel oil burning emissions produced in the industrial plants and can due to traffic emissions from motor vehicles running on petroleum and diesel fuel in the industrial area. The other important probable source of Nickel overcomes the industrial area should not be neglected, it is the fall dust contains Nickel metal comes with wind from the roads and highways surrounding the industrial area because it is located in the down wind direction in the south of Jeddah city. The same interpretation was mentioned by Ibrahim [34] who found similar results in Jeddah city locations; they found that the elevated concentrations of nickel in soils and plant samples collected form Jeddah could be attributed to emissions from motor vehicles that use nickel gasoline and by abrasion and corrosion of nickel from vehicle parts. Similar results were found by Aissa [35] about the determination of heavy metal pollution in Mascara by using *Casuarina equisetifolia* in Algeria. Concerning to the soils contents of the studied metals, the results of this study found elevated levels of Vanadium and Nickel concentrations in the soils associated with plant samples and these findings also, were the same with those obtained by Kadi [36], who found high levels of some heavy metals such Vanadium and Nickel in soils of industrial and urban areas in Jeddah and he reported that the reasons were due to the significant influence of the traffic and industrial activities in the mentioned areas. The nickel levels in the four studied areas followed the trend of: industrial > roadside > residential area > control and this sequence were in agreement with Aksoy [12] who found that the heavy metal concentrations in industrial were > roadside areas > urban area and suburban areas, and significantly were higher than in the rural areas. Generally, *C. proceara* plants accumulated low concentration (%) from V and Ni under the control compared with high concentration under the different areas and this is due to that area "control" is far away from the effects of the heavy metal pollution sources either industries, traffic or other human polluting activities. Many previous studies reported that high levels of heavy metals were found in the plant leaf samples and soil samples gathered from the urban areas, roadside areas and the industrial areas, as mentioned in the studies conducted by Scerbo [37]. From the point view of toxicity, this study indicated that the Ni concentrations in all plant samples were in safe range but all nickel concentration in *Calotropis procera* plant samples collected from polluted areas, except control, exceeded the normal limit 0.5–5.0 mg/kg concentration in plants and this may contributed to the growing environment subjected to the man-made pollution sources effect.

## Conclusion

Vanadium and Nickel pollutants were found in high concentrations in plant samples and associated soil samples taken from locations in the industrial area, roadside area and even residential area and the main reasons are the traffic emissions and the industrial activities. The positive relation was clear between V and Ni concentrations in plant leaves and associated soil samples so that this situation can participate in worsen Jeddah ambient air quality and this would negatively effect on people. For the traffic roads, it is strongly recommended to check out all cars and trucks for adjusting gases emissions and also it strongly recommended to plant suitable shrubs and trees all over the road sides and around the industrial plants to eliminate or at least reduce and avoid the health effects of these emissions on people either at homes and streets or labor within industrial area facilities and also to reduce the pollution loads on air, soil and ground water resources all over Jeddah and its surroundings. The wild plant, *Calotropis procera* growing abundance and which was used in this study is recommended to be used as a significant option for use in environmental studies as a heavy metals bio-indicator and a good heavy metals bio-monitor.

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