# Heavy Metals Contents in *Ziziphus* Tree Leaves Under the Effect of Different Industrial Activities

Mohamed Abdulraheem Shaheen[1], Fathy Saad El-Nakhlawy[1], Fahd Mosallam Almehmadi[2] &
Abdulmohsin Rajeh Al-Shareef[3]

[1] Arid Land Agriculture Dept., Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia

[2] Environmental Sciences Dept., Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia

[3] Geography and Information System Dept., Faculty of Arts and Humanities, King Abdulaziz University, Jeddah, Saudi Arabia

Correspondence: Fathy Saad El-Nakhlawy, Arid Land Agriculture Dept., Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia. E-mail: falnakhlawi@kau.edu.sa

## Abstract

Effects of 3 industrial activities on the concentrations of toxic metals (Cd, Cr, Ni and Pb) and micro-nutrients elements (Fe, Cu, Zn and Mn) in the leaves of 2 and 4 years old *Ziziphus* trees grown closed to these industrial areas were studied during March 2013. The highest Cd, Cr, Ni and Pb concentrations in the *Ziziphus* leaves were found in the trees closed the paints, chemical and paper industrial sectors with values of 4.56, 8.69, 6.15 and 48.47 mg/kg, respectively, while the trees in the control area had 1.09, 1.16, 1.34 and 6.27 mg/kg, respectively. The sector of mineralization, plastic and building materials was the highest in Fe, Cu, Zn and Mn emission pollutants accumulated and absorbed by the tree leaves. The 4-years old tree leaves were significantly higher than the 2-years old tree in all studied toxic and micro-nutrients elements.

**Keywords:** emission, industry activity, industry pollution, micronutrient, pollutions, toxic elements, *Ziziphus*

## 1. Introduction

Industrial air pollutants are very dangerous and serious on plant, animal and human in the world. Industrial emissions in air are the main source of air pollution. Many studies indicated serious effects on the plants grown near the industrial factories (Silvola, 1975; Bagatto & Shorthouse, 1991; Shevtsovas, 1998; Malkonen et al., 1999). Most pollutants of heavy metals are the mineralization, paints, dyes, chemicals and paper industries (Zayed & Terry, 2003).

The highest heavy metals concentration in the tree leaves were found in the leaves of the trees near the industrial factories and they were (120±5.4 Pb), (2.6±0.56 Zn), (35±5.7 Ni) and (3.9±0.2 Cr) was found by Al-Khlaifat and Al-Khashman (2007). The type of the industry significantly affects the type and concentrations of pollutants in the nearest plants (Uhlig et al., 2001 and Monni et al., 2000). The toxicity of heavy metals on the plants depends on the plant species, age and element chemical composition and concentration (Nagajyoti et al., 2010). Significantly reducing in photosynthetic rate and chlorophyll content in plant leaves as a result of the pollution with Cu, Ni, Cd and Pb was observed by (Becerril et al., 1989; Angelova et al., 1993; Bishnoi et al., 1993; Pandolfini et al., 1996).

High percentages of Ni, Cu, Zn, As and Cd are emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Ni, Cd, Zn and Pb (Samara et al., 2003). Trees are very efficient at trapping atmospheric particles (Mingorance & Rossini, 2006). Trace elements air pollution leads to physiological disturbance in plants and affects the biological balance and stability of their habitats (Verma & Singh, 2006). Air industrial pollution affects structural leaf properties and lead to lower photosynthesis (Pourkhabbaz et al., 2010). Trees are very efficient in trapping atmospheric particles, mostly on their foliage (Peachey et al., 2009; Qiu et al., 2009).

The aim of this study is to investigate the effects of different industrial sectors air pollutants on heavy metals contents of 2 ages Ziziphus trees closed Jeddah industrial zone.

## 2. Material and Methods

This study was conducted on the *Ziziphus* trees (*Ziziphus jujuba*) grown around the industrial sectors in the industrial zone of Jeddah and the control location (non polluted) was the Agricultural Research Station, Hada Al-Sham, King Abdulaziz University at a distance of 120 km north-east of Jeddah city Saudi Arabia. Three sectors of industrial activities as their distribution and concentration in the industrial zone of Jeddah was studied (Table 1) as sources of air pollutants accumulated and absorbed by closed *Ziziphus* trees of 2 and 4 years old.

Table 1. The studied industry sectors and their industries

| Industry sector | Industries |
| --- | --- |
| **1** | Food |
| **2** | Plastic, Mineral formatting, Isolated materials, Building materials |
| **3** | Paints, Chemical and paper |

### 2.1 Experimental Design

Factorial experiments in a completely randomized design with 4 replications was used, where the industry sector and tree age were the studied factors.

### 2.2 Sampling

Two random samples of leaves of the center position of the 3rd branch of the studied trees with 10 leaves were collected as a sample size from each of the 32 trees in the experiment.

### 2.3 Heavy Metals Determination

Heavy metals concentrations of cadmium (Cd), chromium (Cr), Nickel (Ni), Lead (Pb), Ferric (Fe), Cupper (Cu), Zinc (Zn) and Manganese (Mn) were determined in the leaf samples according to Chapman and Pratt (1961) using ICP Optical Emission Spectrometer Model Varian 720-Es. Sampling time was done at the end of March, 2013 (this date is the end of the active working of the industrial factories in Jeddah).

### 2.4 Statistical Analysis

Statistical analysis of the obtained data were statistically analyzed through analysis of variance and mean separation procedures after the assumption of the analysis of variance were tested and applied according to El-Nakhlawy (2010) using SAS (2006).

## 3. Results and Discussion

### 3.1 Effect of Industry Sectors

3.1.1 Toxic Metals

Means ± SD of toxic metals (Cd, Cr, Ni and Pb) and micronutrients (Fe, Cu, Zn and Mn) of the *Ziziphus* leaves under the effects of the 3 studied industry sectors emissions and the non-polluted site (control) were statistically compared by LSD (0.05) and presented in Table 2.

The highest concentrations of the Cd, Cr, Ni and Pb in the *Ziziphus* leaves were showed under the effect of the 3rd sector (paints, chemicals and paper) with values of 4.56, 8.6, 6.15 and 48.47 mg/kg followed by the 2nd sector (plastic, mineralization and building materials),with significant difference. According to the toxic metals standards and their toxicity in plants as estimated by European Union (EU 2000), the concentrations of Cr, Ni and Pb in tree leaves in the 2nd and 3rd sectors were laid in the toxicity range. Food sectors (sector 1) was significantly lower than the 2nd sector in Cd, Cr, Ni and Pb. Leaf contents from these elements were 1.71,1.93, 2.17 and 20.74, respectively in the sector 1.The unpolluted area (control) was significantly lower than the 3 industry sectors in the 4 toxic elements in the *Ziziphus* leaves. Hada Al-Sham (control) *Ziziphus* leaves had around 24, 13, 22, and 13% from the Cd, Cr, Ni and Pb, respectively from the sector 3 leaf contents. The significance differences between the 3 industrial sectors might be due to the type of their industries and their emissions according to the type of industry and energy power used, accordingly the food industry effect was the lowest but all industrial sectors produced significant values from the 4 toxic metals higher than the control area (Zayed & Terry, 2003, Al-Khlaifat & Al-Khashman, 2007, Uhlig et al., 2001; Samara et al., 2003).

Table 2. Means ± SD of the toxic metals (mg/kg) in/on *Ziziphus* leaves under the effect of emission pollutants of area

| Industry sector | Means ± SD | | | |
|---|---|---|---|---|
| | Cd | Cr | Ni | Pb |
| 1 | 1.71±0.07 c[*] | 1.93±0.09 c | 2.17±0.15 c | 20.74±0.74 c |
| 2 | 3.56±0.14 b | 6.62±0.29 b | 5.03±0.33 b | 39.96±2.56 b |
| 3 | 4.56±0.16 a | 8.69±0.43 a | 6.15±0.40 a | 48.47±3.01 a |
| Control | 1.09±0.03 d | 1.16±0.06 d | 1.34±0.07 d | 6.27±0.37 d |

[*]: Means followed by the same letter are not significantly different according to LSD at p≤0.05.

± SD: ± standard deviation.

Industry sector: 1: food sector, 2: plastic, mineral formatting, isolated materials and building materials, 3: paints, chemicals and paper, Control: no polluted area (Hada Al-Sham Agric. Res. Sta.).

3.1.2 Micro-Nutrients

Statistically comparisons between the micro-nutrients (Fe, Cu, Zn and Mn) in *Ziziphus* leaves under the effects of the industry sectors and control (Table 3) indicated that the highest pollutants in the tree leaves were showed under the $2^{nd}$ sector followed by the $3^{rd}$ sector, then the $1^{st}$ sector, while the lowest was the control site. Micro-nutrients concentrations in the leaves in the $2^{nd}$ sector were 788, 17.36, 32.62 and 89.94 mg/kg, while under the control were 115, 1.78, 5.16 and 14.41 mg/kg for Fe, Cu, Zn and Mn, respectively, as shown in Table 3.

Type of industry activities in the $2^{nd}$ sector included the mineralization, plastic and building materials reflected the highest emission from the 4 micro-nutrients and the rate of their accumulation and absorbation in the plant leaves (Meerabai et al., 2012; Qiu et al., 2009; Sridhar et al., 2007; Uhilg et al., 2001; Monni et al., 2001).

Table 2. Means ± SD of the micro-nutrients (mg/kg) in/on *Ziziphus* leaves under the effect of emission pollutants area

| Industry sector | Means ± SD | | | |
|---|---|---|---|---|
| | Fe | Cu | Zn | Mn |
| 1 | 123±7.38 c[*] | 5.25±0.29 c | 3.90±0.30 c | 20.92±1.21 c |
| 2 | 768±48.86 a | 17.36±0.92 a | 32.62±2.61 a | 89.94±5.39 a |
| 3 | 547±35.01 b | 15.37±0.79 b | 26.77±1.66 b | 65.43±4.32 b |
| Control | 115±6.91 c | 1.78±0.09 d | 5.16±0.31 c | 14.41±0.96 d |

[*]: Means followed by the same letter are not significantly different according to LSD at p≤0.05.

± SD: ± standard deviation.

Industry sector: 1: food sector, 2: plastic, mineral formatting, isolated materials and building materials, 3: paints, chemicals and paper, Control: no polluted area (Hada Al-Sham Agric. Res. Sta.).

*3.2 Effect of Tree Age*

3.2.1 Toxic Metals

As shown in Table (3) the highest and significant Cd, Cr, Ni and Pb concentrations in *Ziziphus* leaves were found in the 4-years old plants. The 4 toxic metals concentrations of the 4 years-old were 3.66, 5.77, 4.65 and 34.52 mg/kg, respectively. The concentrations in the 4 years old tree leaves were higher than their concentrations in the 2 years-old trees by around 214, 168, 171 and 149%, respectively. These results indicated the high accumulation of the 4 toxic metals on the tree leaves during 4 years, besides the absorbtion rate of these pollutants through the stomata during the plant age (Meerabai et al., 2012; Nagajyoti et al., 2010; Mingorance and Oliva, 2006; Qiu et al., 2009).

3.2.2 Micro-Nutrients

Accumulation and absorption of the micro-nutrients on and in the *Ziziphus* tree leaves of 2 and 4 years old resulted in the micro-nutrients concentrations of 2 and 4 years old leaves are presented in Table 3. Significant differences were found between the 2 and 4 years old trees in their contents from micro-nutrients. The 4 years old trees had 538, 16.09, 20.70 and 60.89 mg/kg from Fe, Cu, Zn and Mn, respectively, compared with 248, 3.79, 13.53 and 34.46 mg/kg, respectively in the 2 years old tree leaves.

The old trees received, absorbed and trapped more micro-nutrients emissions during the 4 years old than the 2 years old trees (Mingorance & Oliva, 2006, Qiu et al., 2009; Nagajyoti et al., 2010; Gostin, 2009; Meerobi et al., 2012).

Table 4. Means ± SD of the toxic metals (mg/kg) in/on *Ziziphus* leaves of 2 and 4 years old trees

| Age (year) | Means ± SD (mg/kg) | | | |
|---|---|---|---|---|
| | Cd | Cr | Ni | Pb |
| 2 | 1.71±0.07 b[*] | 3.43±0.21 b | 2.72±0.13 b | 23.19±1.62 b |
| 4 | 3.66±0.15 a | 5.77±0.32 a | 4.65±0.32 a | 34.52±2.34 a |

[*]: Means followed by the same letter are not significantly different according to LSD at p≤0.05.

± SD : ± standard deviation.

Table 5. Means ± SD of the micro-nutrients (mg/kg) in/on *Ziziphus* leaves of 2 and 4 years old trees

| Age (year) | Means ± SD (mg/kg) | | | |
|---|---|---|---|---|
| | Fe | Cu | Zn | Mn |
| 2 | 248±14.14 b[*] | 3.79±0.26 b | 13.53±1.01 b | 34.46±2.30 b |
| 4 | 538±32.28 a | 16.09±1.09 a | 20.70±1.55 a | 60.89±4.08 a |

[*]: Means followed by the same letter are not significantly different according to LSD at p≤0.05.

± SD: ± standard deviation.

## 4. Conclusion

High toxic metals and micro-nutrients pollutants were accumulated and absorbed in the *Ziziphus* tree leaves during its grown closed the industry activities. The highest Cd, Cr, Ni and Pb concentrations were found in the leaves of the trees closed the sectors of paints, chemicals and paper, while the highest concentrations of Fe, Cu, Zn and Mn were showed in the leaves of *Ziziphus* trees closed the mineral formatting, plastic and building materials sectors.

The lowest heavy metals concentrations in the industrial areas ere found in the trees closed the food industries sector. In all industrial sectors, the pollutant concentration in the leaves was higher than in the control area. The 4 years old *Ziziphus* trees accumulated and absorbed around 2 times or more from the heavy metals. As a result of the high heavy metals accumulated and absorbed by *Ziziphus* leaves, it can recommend to use these trees as a phytoremediator of heavy metals, especially in the industrial zones.

### References

Al-khlaifat, A. L., & Al-khashman, O. A. (2007). Atmospheric heavy metal pollution in Aqaba city, Jordan, using Phdenix dactyl liferal Leaves. *Atmospheric Environment, 41*, 8891-8897. http://dx.doi.org/10.1016/j.atmosenv.2007.08.028

Angelova. M., Tsonev, T., Uzunova, A., & Gaidardjieva, K. (1993). $Cu^{2+}$ effect upon photosynthesis, chloroplast structure, RNA and protein synthesis of pea plants. *Photosynthetica, 28*, 341-350.

Bagatto, G., & Shorthouse, J. D. (1991). Accumulation of copper and nickel in plant tissues and an insect gall of lowbush blueberry, Vaccinium angustifolium, near an ore smeller at Sudbury, Ontario, Canada. *Canadian Journal of Botany, 69*, 1483-1490. http://dx.doi.org/10.1139/b91-192

Becerril, J. M., Consalez-Murua, C., Munoz-Rueda, A., & De Felipe, M. R. (1989). Changes induced by cadmium and lead in gas exchange and water relations and clover and Lucerne. *Plant Physiology and Biochemistry, 27*, 913-918.

Bishnoi, N. R., Sheoran, I. S., & Singh, R. (1993). Influence of cadmium and nickel on photosynthesis and water relations in wheat leaves of different insertion level. *Photosynthetica, 28*, 473-479.

Chapman, H. D., & Pratt, F. P. (1961). Ammonium vandate – molybdate method for determination of phosphorus. In: *Methods of analysis for soil , plants and water* (1st ed., pp. 184-203). California: California University, Agrculture Division.

El-Nakhlawy, F. S. (2010). *Experimental Design and Analysis in Scientific Research*. Sci. Pub. Center, King Abdulaziz University, Jeddah, Saudi Arabia.

EU (European Union). (2002). *Heavy Metals in Wastes, European Commission on Environment*. Retrieved from http://ec.europa.eu/environment/waste/studies/pdf/heavy metals report. pdf

Gostin, I. N. (2009). Air Pollution Effects on the Leaf Structure of some Fabaceae Species. *Not. Bot. Hort. Agrobot. Cluj., 37*(2), 57-63.

Malkonen, E., Derome, J., Fritze, H., Helmisaari, H. S., Kukkola, M., Kyto, M., … Salemaa, M., (1999). Compensatory fertilization of Scots pine stands polluted by heavy metals. *Nutrient Cycling in Agroecosystems, 55*, 239-268. http://dx.doi.org/10.1139/b91-192

Meerabai, G., Venkata Ramma, C., & Rasheed, M. (2012). Effect of air pollutants on leaves of pigeon pea, a pulse crop of Fabaceae growing in the vicinity of a silicon industry. *World Rural Observations, 4*(2), 19-21.

Mingorance, M. D., & Rossini, S. R. (2006). Heavy metals content in N. oleander leaves as urban pollution assessment. *Environ Monit. Assess., 119*(1-3), 57-68. http://dx.doi.org/10.1007/s10661-005-9004-9

Nagajyoti, K., Lee, D., & Streekanth, T. V. M. (2010). Heavy metals; occurrence and toxicity for plants; a review. *Environ chem. Lett, 8*, 199-216. http://dx.doi.org/10.1007/s10311-010-0297-8

Pandolfini, T., Gabbrielli, R., & Ciscato, M. (1996). Nickel toxicity in two Durum wheat cultivars differing in drought sensitivity. *Journal of Plant. Nutrition, 19*, 1611-1627. http://dx.doi.org/10.1111/j.1399-3054.1997.tb00016.x

Peachey, C. J., Sinnett, D., Wilkinson, M., Morgan, G. W., Freer-Smith, P. H., & Hutchings, T. R. (2009). Deposition and solubility of airborne metals to four plant species grown at varying distances from two heavily trafficked roads in London. *Environ Pollut., 157*(8-9), 229-299. http://dx.doi.org/10.1016/j.envpol.2009.03.032

Pourkhabbaz, A., Rastin, N., Olbrich, A., Langenfeld-Heyser, R., & Polle, A. (2010). Influence of Environmental Pollution on Leaf Properties of Urban Plane Trees, Platanus orientalis L. *Bull Environ Contam Toxicol., 85*(3), 251–255. http://dx.doi.org/10.1007/s00128-010-0047-4.

Qiu, Y., Guan, D., Song, W., & Huang, K. (2009). Capture of heavy metals and sulfur by foliar dust in urban Huizhou, Guangdong Province, China. *Chemosphere, 75*(4), 447-52. http://dx.doi.org/10.1016/j.chemosphere

Samara, C., Kouimtzis, T., Tsitouridou, R., Kanias, G., & Simeonov, V. (2003). Chemical mass balance source apportionment of PM10 in an industrialized urban area of Northern Greece. *Atmospheric Environment, 3*(1), 41-54. http://dx.doi.org/10.1016/S1352-2310(02)00772-0

SAS. (2006). SAS Institute Inc. Cary Nc., USA ( Soft Ware Statistical Program).

Shevtsova, A. (1998). *Responses of subaractic dwarf shrubs to climate change and air pollution*. Annals Universitations Turkuensis Ser. AII, 113. Doctoral thesis.

Sridhar, B. B., Han, F. X., Diehl, S. V., Monts, D. L., & Su, Y. (2007). Effects of Zn and Cd accumulation on structural and physiological characteristics of barley plants. *Braz. J. Plant Physiol., 19*(1), 15-22. http://dx.doi.org/10.1590/S1677-04202007000100002

Uhlig, C., Salemaa, M., Vanha-Majamaa, I., & Derome, J. (2001). Element distribution in Empetrum nigrum microsites at heavy- metal contaminated site in Harjavalta, *Western Finland, Environ Poll., 112*, 435. http://dx.doi.org/10.1016/S0269-7491(00)00140-8

Verma, A., & Singh, S. N. (2006). Biochemical and Ultrastructural Changes in Plant Foliage Exposed to Auto-Pollution. *Environmental Monitoring and Assessment, 120*(1-3), 585-602. http://dx.doi.org/10.1007/s 10661-005-9105-5