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Inorganic chemical composition of dust deposited on oleander (*Nerium oleander L.*) leaves

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Abstract Elemental composition of dust deposited onto leaf surfaces was analysed in this study. Leaves of oleander (*Nerium oleander* L.) were collected for testing the environmental quality from Tripoli (Libya), Tajura (suburban of Tripoli) and Ghadames (remote area). Elemental analysis was carried out by ICP-OES. Principle component analysis (PCA) and enrichment factors were used for characterizing and estimating the level of the pollution. Samples from Tripoli were found to have higher contents of Pb, Zn, Cu in comparison with suburban (Tajura) and remote (Ghadames) areas. Our results demonstrated that the leaves of *Nerium oleander* were useful indicator to assessment of atmospheric deposition. Only limited information is available on environmental issues in Libya and the results reported here may contribute significantly to the assessment of the quality of the environment in this country.

Keywords Dust · Biomonitoring · ICP-OES · Heavy metal · Sahara

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Introduction

The analysis of the inorganic components of the dust is an efficient way of obtaining information on the current environmental state over large areas (Divrikli et al. 2003). Various methods have been developed and used to collect dust samples e.g. containers or funnels, some of them dry others filled with water or liquid paraffin (Adetunji et al. 2001; McTanish and Walker 1982; McTanish et al. 1997; Tiessen et al. 1991), different types of plates, bowls and mats made of different materials (Breuning-Madsen and Awadzi 2005; Moberg et al. 1991; Tiessen et al. 1991) or using a canopy drip method (Stoorvogel et al. 1997). Biological monitoring is also an effective way to measure the level of air pollutants (Baranyai et al. 2015; Osma et al. 2016; Rai and Panda 2014). It has definite advantages when compared to other techniques. Using plants is a low-cost method and suitable for long-term monitoring over large areas without deploying sophisticated and high maintenance sampling equipment (Tingley 1989).

The small particulate matter originating from scarcely vegetated soils is a main common feature of arid ecosystems (Sharifi et al. 1997). Dust may deposits on the surface of the plants, e.g. leaves, twigs and barks for extended periods of time. This is especially true in desert environments where low rainfall frequency prevents the removal of settled dust particles from leaves and other plant surfaces. Due to the physical properties of the epicuticular wax, the leaves are capable to retain the dust particles. High temperature further enhances the attachment of dust to the leaf surfaces (van Heerden et al. 2007).

Various tree and shrub species have been used to investigate the composition of dust in arid area. The leaves of the oleander (*Nerium oleander* L.) were found to be suitable biomonitors of metal pollution in arid and mediterranean environments (Seaward and Mashour 1991; van Heerden et al.

2007). It was shown in many studies that leaves from higher plants can be used as dust trap (Aksoy and Öztürk 1997; Bu-Olayan and Thomas 2002; Shams and Ali Beg 2000).

We collected leaf samples of *N. oleander* in Tripoli, in Tajura and Ghadames. Libya lies along one of the main dust transport routes. Aerosols are transported over Libya from Saharan sources northwards and northeastwards during the spring months. Samples were taken on 23–25 February 2006, shortly after a major dust storm occurred. The chemical composition of dust was investigated. The aim of this paper is to characterize the dust deposited in urban, suburban and remote areas considering the effects of dust outbreaks and anthropogenic sources.

Methodology

Study area

Libya is located in the central part of North Africa, has a 1900 km long Mediterranean coast and covers an area of 1,775,500 km^2, most of which is dominated by desert (O'Hara et al. 2006). Samples were collected from the following areas: Tripoli, Tajura and Ghadames.

Tripoli is characterized by a typical Mediterranean climate with hot dry summers and mild winters and some modest rainfall. It is a rapidly growing city and its present population is estimated to be around 1.68 million and it has an area of 400 km^2. The city is located in the northwest of the country on the edge of the desert, on rocky land facing the Mediterranean Sea along a bay. Tripoli is a commercial, industrial, administrative and transportation center and the principal sea port of Libya. Main manufacturing activities produce processed food, textiles, tobacco products, and woven goods. There is considerable pollution from road and air traffic and ships in the harbour. The main means of transportation in Tripoli are automobiles which use leaded gasoline. Tajura is a suburb of Tripoli. It is a city on the Mediterranean coast, 14 km east of Tripoli. Ghadames lies southwest about 600 km of Tripoli, in the Ghadames Basin (Fig. 1). Its population is estimated to be around 10,000. This city lies in the desert and anthropogenic pollution is negligible.

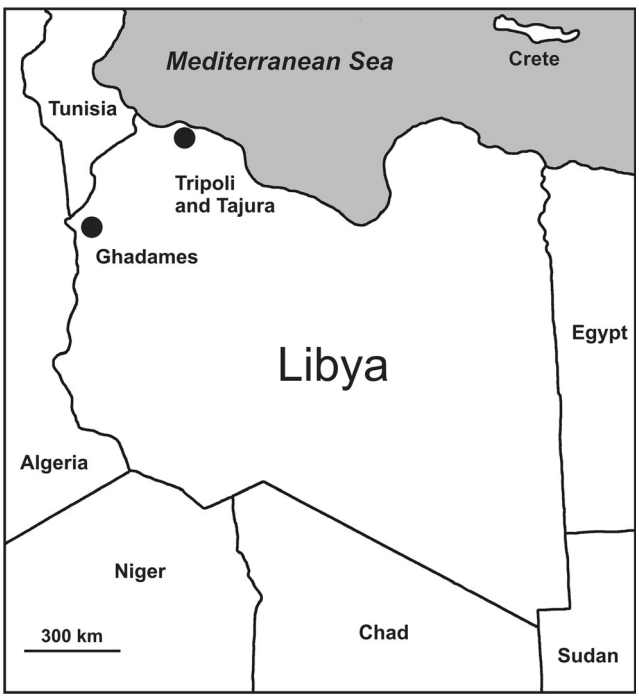

Fig. 1 Map of the sampling sites

Nerium oleander L.

Oleander (*Nerium oleander* L.) is widespread in arid environment, allowing further geographic extension of investigations. Oleander is an evergreen sclerophyllous shrub forming clumps up to 6 m tall and usually occurs with a spread of 2.5–4.5 m. The leaves are in pairs or whorls of three, thick and leathery, dark green, narrow lanceolate, 5–21 cm long and 1–3.5 cm broad, and with an entire margin (Davis 1978; Little and Martin 1972;). It occurs widely in both urban and rural areas. It is easy to identify and distinguish from other species, making sample collection easy and inexpensive. The morphology, canopy structure and the dust preserving epicuticular wax on the leaf surface of these species are appropriate for monitoring environmental pollution by dust.

Sample collection and preparation

Leaf samples were collected at ten locations in Tripoli, Tajura and Ghadames each on February 2006. A large dust storm broke out on 23–25 February was an unintended event during our field trip in Libya. This dust storm swept across northeastern Africa and reached the eastern Mediterranean and Middle East countries. A cloud of dust spanned across several hundred kilometers from Libya and Egypt over the Mediterranean Sea. Faint tendrils of dust reached as far as to the east of Israel (NASA 2006) Ghadames, Tripoli and Tajura were considerably affected by this event.

Samples were collected from different parts of the towns, urban, suburban, highway, rural and industrial sites. The leaves contained dust either deposited during the storm or previous non-dusty period.

The surface area of the leaves was determined using a flat bed scanner. The calibration was performed by using black images with known surface areas. Black and white images were taken by a resolution of 300 dpi. The numbers of black pixels were proportional to the area. The total leaf surface of each sampled location represented 10–12 dm^2. Each plant sample was stored in a clean paper bag.

Table 1 Instrumental conditions for ICP-OES elemental analysis

Background correction	Dynamic mode
Number of replicates	2
Pump speed (rpm)	2.77 mL/min
Rinse time/s	40
Nebulizer flow	32 PSI
Analysis pump rate	1.85 mL/min
Wavelengths and order (nm)	Al: 396.152{085}
	As: 189.042{177}, 189.042{178}, 193.759{173}
	Ba: 230.424{145}, 230.424{146}, 233.527{144}
	Ca: 183.801{182},183.801{183}, 315.887{106}
	Cd: 214.438{156}, 228.802{147}
	Co: 228.616{146}, 228.616{147}, 230.786{145}
	Cr: 206.149{163}, 283. 563{118}
	Cu: 221.458{152}, 221.458{153}, 224.700{150}
	Fe: 238.204{141}, 239.562{140}, 240.488{139}
	K: 766.491{44}
	Li: 670.784{50}
	Mg: 279.079{120}, 285.213{117}
	Mn: 257.610{130}, 260.569{128}, 294.921{114}
	Na: 588.995{57}
	Ni: 216.556{155}, 218.461{154}, 221.647{151}
	Pb: 216.999{154}, 220.353{153}
	S: 182.034{184}
	Sr: 346.446{97}, 407.77{82}
	Zn: 202.548{166}, 213.856{157}
ICAP view	Low WL range axial; High WL range radial
Low WL range	30s
High WL range	10s

Chemical analysis

The dust deposited on the surface of leaves was removed by washing with double deionized water. The samples were placed into 500 ml plastic vessel and shaken with 250 ml water using a shaker machine for 10 min and sonicated in an ultrasonic bath for 1 min. The suspension was passed through a plastic sieve with 200 μm mesh size. The water content of the suspension was reduced by evaporation in a microwave oven. The rest of the suspension was transferred into a 50-ml beaker and the residue of water was evaporated in a drying oven at 105 °C. The amount of dried dust was weighted.

Dust samples were digested with 5 ml of 65 % (m/m) HNO_3 and subsequently were heated in the same beaker on a hot plate at 80 °C. After the evolution of fumes had ceased, the mixture was evaporated almost to dryness and mixed with 2 ml of 30 % (m/m) H_2O_2. The mixture was evaporated to dryness. The samples were dissolved in 10 ml of 0.1 mol/L nitric acid (Alfani et al. 1996; Margitai and Braun 2002).

The elemental analysis was performed by an ICP-OES IRIS Intrepid II XSP. We used a seven-point calibration procedure with multi-element calibration solution (Merck ICP multi-element standard solution IV). The analysis was performed using two or three atomic or ionic lines of the corresponding elements. In the case of alkaline metals (e.g. Li, Na and K), we used single lines. The selected lines were free of spectral interferences in these sample matrixes. The limit of quantification values (LOQ) are given in mgL^{-1}; Al: 0.02, As: 0.001, Ba: 0.006, Ca: 0.008, Cd: 0.001, Co: 0.004, Cr: 0.002, Cu: 0.003, Fe: 0.09, K: 0.003, Li: 0.002, Mg: 0.001, Mn: 0.001, Na: 0.002, Ni: 0.004, P: 0.10, Pb: 0.013, S: 0.10, Sr: 0.002 and Zn: 0.003. Other parameters used in this analysis are shown in Table 1.

Statistical analyses

Analytical results were evaluated by using SPSS/PC+ program. Data were log-transformed prior to principal component analysis (PCA) to reduce the influence of high data. PCA was performed using Pearson's correlation matrix. Varimax rotation was applied and factors were considered with eigenvalue larger than one (Norušis, 1990). The elemental concentrations of deposited dust in the studied areas (Tripoli, Tajura and Ghadames) were compared with ANOVA. In case of significant differences, Tukey's Multiple Comparison test was used. The difference of EF value from 10 was tested with one sample *T* test (Zar 1996).

Results and discussion

Elemental compositions of dusts deposited in cities are usually characterized by anthropogenic and local geological sources. However, storms may have a significant effect on dust composition in the Mediterranean region. Dust events occur frequently between December and March in Libya resulting an elevated rate of deposition. Monthly deposition rate of dust is typical in range between 3 and 90 g m^{-2} in Tripoli (O'Hara et al. 2006).

After the storm thick brownish dust covered everything and the amount of dust deposited onto the oleander leaves was clear visible. In our case 2–6 g m^{-2} dust was found on leaf surfaces of *Nerium oleander*. It should be pointed out that leaves of this plant can filter out significant amount of dust. Particle deposition on leaf surfaces may also be affected by the particle size and mass, wind velocity, leaf orientation, size and moisture level (Bache et al. 1991). In case of leaves, the length of deposition time can also be hardly defined exactly. Thus, these results should not be compared to monthly deposition rates provided by dust collectors or traps.

Table 2 Elemental concentration of dust (mg kg^{-1} dry weight) according to the three different areas (mean ± CI 95 %). Different letters indicate significant differences among studied areas at the $p < 0.05$ level

Elements		Studied areas		
		Tripoli	Tajura	Ghadames
Macro	Ca	78,517 ± 20147a	53,615 ± 16452b	75,812 ± 16649a
	K	25,184 ± 17,408	23,826 ± 25,423	14,722 ± 12,863
	S	19,742 ± 7646a	11,100 ± 2630b	14,492 ± 6167b
	Mg	13,452 ± 1431	12,556 ± 3590	13,260 ± 3154
	Fe	10,279 ± 2642	10,342 ± 2527	9952 ± 2713
	Na	11,505 ± 6421a	7939 ± 11631b	6250 ± 9269b
	Al	7703 ± 1456	7776 ± 1508	7415 ± 1755
	P	1494 ± 387a	1551 ± 1520a	3065 ± 2498b
	Mn	194 ± 110	194 ± 36	190 ± 42
Toxic	Ba	212 ± 51a	77 ± 154b	170 ± 51a
	Zn	135 ± 57a	72 ± 36b	86 ± 16b
	Pb	77 ± 19a	27 ± 19b	38 ± 9c
	Cu	31 ± 16a	15 ± 6b	14 ± 4b
	Cr	22 ± 6	20 ± 5	19 ± 4
	Ni	16 ± 6	18 ± 2	17 ± 7
	Co	5.9 ± 1.3a	7.9 ± 1.1b	6.5 ± 1.8a
	As	3.4 ± 1.1a	2.4 ± 0.4b	3.0 ± 0.8a
	Cd	0.6 ± 0.2a	0.7 ± 0.1ab	0.6 ± 0.4b
Non-toxic	Sr	345 ± 162a	238 ± 58b	272 ± 43b
	Li	17 ± 3	17 ± 4	21 ± 16

Grain size analysis reported by O'Hara et al. (2006) of trapped dust in the area of Tripoli showed bi-modial, tri-modial and multi-modial distribution, usually dominated by silts, with both clay (<2 um) and fine sand (90–100 um) components. The sampling height of *Nerium oleander L.* was between 1 and 2 m which means that larger particles can be also trapped on leaf surfaces. The contribution of resuspended soil particles may also be considered to be significant.

Elemental concentrations in dust

The elemental concentration of dust samples were divided into three main groups: macro elements, toxic elements and non-toxic elements. In the case of macro elements, the following order of concentrations was found: Ca > K > S > Mg > Fe > Na > Al > P (Table 2.), except for Tripoli region, where the Na concentration was higher than Fe, while in Tajura region, the concentration of Mg was higher than the S. Concentrations of Al, K, Mg, Fe and Mn were did not differ significantly in the three areas. Concentrations of S and Na were significantly higher in Tripoli than in Tajura and Ghadames ($p < 0.05$). Significantly higher Ca concentrations were found in Tripoli and Ghadames than in Tajura ($p < 0.001$). The concentration of P was significantly higher in Ghadames ($p < 0.001$) than in Tripoli and Tajura ($p > 0.05$). More details are reported in Supplementary data, Table S1.

The concentrations of Al, K, Mg, Fe and Mn showed equal chemical composition, suggesting basically similar geological origin in dust samples from different areas (Supplementary Material Table S1). Local differences were found in the case of Ca, Na and S. Large concentrations of Na and S reflect the importance of deposits arriving from the sea and from the salty sediments which are common in the North of Libya (O'Hara et al. 2006). Dust samples of the three locations contained remarkable amounts of Ca. Intense foaming during the sample digestion also indicated the rich calcium carbonate content. Dust originating from Libya is usually characterized by lower but still significant carbonate content (Scheuvens et al. 2009). Sulfate concentration of these samples was also considerable. African dusts can be characterized by the ratio of Fe_2O_3/CaO. Low ratio of Fe_2O_3/CaO was found (0.15–0.2) in Tripoli, Tajura and Ghadames. Low values are typical for the Atlas region (Grousset and Biscaye 2005).

In the case of non-toxic elements, significant differences were not found in the concentrations of Li in the studied areas ($p > 0.05$) (Table 2.). However, the concentration of Sr was significantly higher in Tripoli ($p < 0.05$). Similarly, the highest concentration of Ca was measured in this city.

In the group of toxic elements, the order of concentrations was Ba > Zn > Pb > Cu > Cr > Ni > Co > As > Cd (Table 2). The concentrations of Cr and Ni in the dust samples were not significantly different in the three areas ($p > 0.05$) (see, Supplementary data Table S1). The concentrations of Zn and

Cu were significantly higher in Tripoli than in Tajura and Ghadames ($p > 0.05$). The concentrations of Ba, Co and As were lower in Tajura than in Tripoli and Ghadames, but difference was not found between Tripoli and Ghadames (Table 2). The highest Pb concentration was found in Tripoli and the lowest concentration was in Tajura ($p < 0.001$). The three areas differ significantly from each other. In the case of Cd, the concentrations measured in Tripoli and Tajura did not differ ($p > 0.05$) and no difference was found between Tripoli and Ghadames ($p < 0.05$) either.

Concentration of toxic elements in dust collected from plant leaf surfaces has not been available in this region. Results of similar analyses by using tree leaves collected in European cities are available. In spite of these locations are out of Mediterranean region, these data can be used by evaluation of anthropogenic effects.

Concentrations of Pb and Zn in Tajura and Ghadames fall within the natural geological limits (Pb 59 mg kg^{-1}, Zn 81 mg kg^{-1}) measured in dust samples over a wide region in Africa by Moreno et al. (2006). In the case of Cu, the concentration was similar to the geochemical limit of Cu (41 mg kg^{-1}). The use of gasoline was typical with a high lead content (0.6–0.8 g L^{-1}) for a long period in Libya (Lovei, 1998; Elgrni et al., 2007). Due to the intense use of leaded fuel, the concentrations of Pb in soils were between 500 and 800 mg kg^{-1} in Tripoli according to El Hinshery and Kumar (1992). Concentration of Pb is 77 ± 19 mg kg^{-1} measured in Tripoli, which is significantly higher than those measured in Tajura (27 ± 19 mg kg^{-1}).

Concentrations of Pb in dust deposited on leaf surface were 145 ± 56 mg kg^{-1} in Antwerp (Belgium), 355 ± 214 mg kg^{-1} in Varna (Bulgaria), 41 ± 10 mg kg^{-1}in Debrecen (Hungary) (Margitai and Braun 2002) and 18 ± 2 mg kg^{-1} in Vienna (Austria) (Simon et al. 2011). The level of Pb measured in Tripoli was higher than the normal geological background and indicates human impact, respectively. However, dust entrainment also can be attributed to vehicular traffic and construction work (O'Hara et al. 2006). The concentration of Pb in Tripoli was significantly lower in our study than it was reported by El Hinshery and Kumar (1992), Khairy et al. (2011), Al-Khashman et al. (2011). Contaminated road dust may be swept out by strong wind and freshly deposited dust could dilute the local materials.

Elevated levels of Zn in urban and suburban and highway areas show the effects of the pollution sources such as traffic volume and tire wear from the vehicles. Concentration of Zn was 135 ± 57 mg kg^{-1} in Tripoli which is significantly higher than those were in Tajura (72 ± 36 mg kg^{-1}) or in Ghadames (86 ± 16 mg kg^{-1}). Corresponding concentrations of Zn in dust deposited on leaf surface were 374 ± 226 mg kg^{-1} in Antwerp (Belgium), 388 ± 96 mg kg^{-1} in Varna (Bulgaria), 215 ± 27 in Debrecen (Hungary) (Margitai and Braun 2002) and 311 ± 53 mg kg^{-1} in Vienna (Austria) (Simon et al. 2011). The concentration of Zn measured in Tripoli showed small urban effect similar to the Pb concentration.

The source of copper in the street dust was ascribed to corrosion of the metallic parts of cars, such as engine wear,

Table 3 Rotated principal component matrix for data of Libyan dust (PCA loadings are >0.4 are shown in italics)

Element	Component				
	1	2	3	4	5
Pb	*0.955*	0.031	−0.089	0.208	−0.004
Zn	*0.903*	0.003	−0.112	0.288	−0.006
Ca	*0.862*	0.052	0.296	−0.274	−0.101
Ba	*0.815*	−0.088	0.398	0.074	0.116
Sr	*0.815*	0.164	−0.072	−0.155	−0.230
Cu	*0.809*	0.094	−0.355	0.353	−0.064
S	*0.725*	0.186	0.118	0.010	−0.405
As	*0.656*	*0.441*	0.315	0.254	−0.162
Mg	*0.584*	0.015	−0.166	−0.373	0.396
Al	0.024	*0.938*	0.172	0.123	0.074
Fe	0.165	*0.878*	0.077	−0.126	0.166
Mn	0.079	*0.845*	0.051	−0.154	0.005
Cr	*0.455*	*0.790*	−0.195	0.142	0.151
Co	−0.593	*0.632*	−0.087	−0.242	0.239
P	−0.016	−0.061	*0.949*	0.045	−0.088
Li	0.042	0.172	*0.821*	0.090	0.024
Na	0.191	0.088	−0.011	*0.796*	−0.138
K	0.019	−0.209	0.165	*0.766*	0.197
Ni	−0.150	*0.411*	0.061	0.028	*0.728*
Cd	−0.293	*0.543*	−0.226	0.055	*0.565*
Eigenvalue	6.85	4.40	2.30	1.79	1.02
% of variance explained	34.24	22.00	11.50	8.97	5.10
% of cumulative variance	34.24	56.24	67.74	76.72	81.82

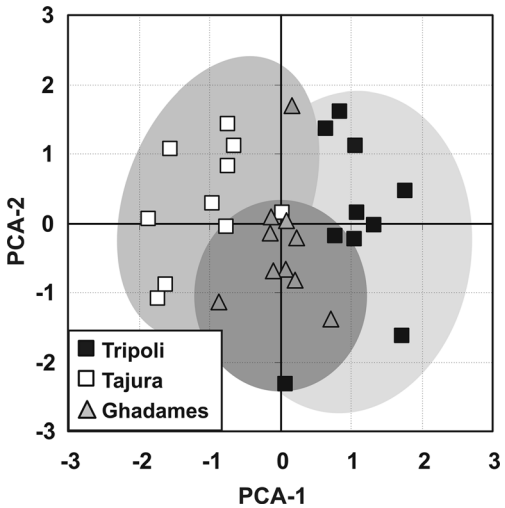

Fig. 2 Comparison of dust samples using the first and second principal component scores

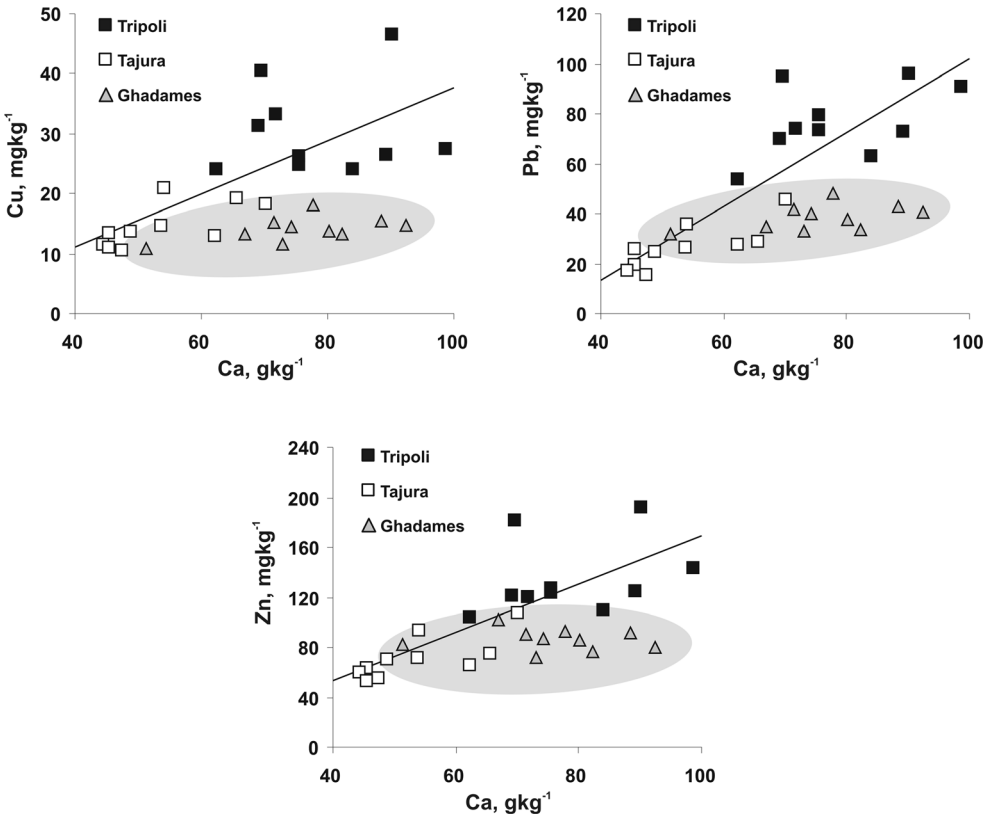

Fig. 3 Pairwise correlation between Ca and Cu, Pb and Zn

thrust bearing and brush wear (Al-Khlaifat and Al-Khashman 2007) The concentration range of Cu in Tripoli (31 ± 16 mg kg^{-1}) was similar to those in Vienna (Austria) 30 ± 5 mg kg^{-1} (Simon et al. 2011). Higher concentrations of Cu were obtained in other cities, 70 ± 62 mg kg^{-1} in Antwerp (Belgium), 110 ± 23 mg kg^{-1} in Varna (Bulgaria), 59 ± 7 in Debrecen (Hungary) (Margitai and Braun 2002). Higher Cu concentration was found in Jordan (80 mg kg^{-1}) (Al-Khashman 2011) and in the Delta region in Egypt (Khairy et al. 2011) than our findings.

Principal component analysis

Principal component analysis (PCA) was applied to characterize the possible sources of heavy metals and to compare the investigated areas based on the inorganic composition of dust. Principal components with an eigenvalue higher than one were considered. Varimax rotated factor loadings, communalities and eigenvalues are given in Table 3. Sampling locations were compared by biplot of the first two principal scores (PCA1 and PCA2) calculated for the individual samples (Fig. 2.). These two components accounts for 56.24 % of the total variance. Dust deposited in Tripoli, Tajura and Ghadames showed different chemical compositions, consequently they were separated by the PCA1. Smaller differences were observed among the three sites in axis PCA2.

The number of principal components with an eigenvalue over one was five. They explain 81.82 % of the total variance. The first factor (PCA1) explains 34.24 % of the total variance and correlates with Pb, Zn, Cu, As, Cr, Ca, Mg, Ba, Sr and S. PCA1 mainly represents the anthropogenic source, because of the presence of toxic elements in this factor. The second principal component (PCA2) is dominated by Al, Fe, Mn and Co. This factor represents the crustal matrix of the natural materials in the dust of the investigated areas and probably related to soil resuspension. In the case of the oxides of Al, Fe, Ca and Mn the second PCA unambiguously indicate the crustal geological origin which is the major mineral constituents of Saharan dust (Vanderstraeten et al. 2008). Toxic elements (As, Cr, Ni and Cd) which were loaded with higher weight into other factors (such as PCA1 or PCA5) were represented

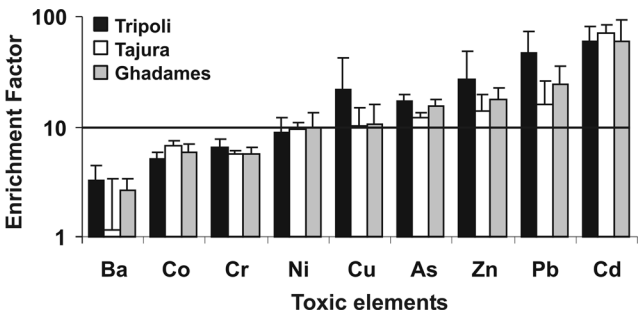

Fig. 4 Average enrichment factors of elements in Tripoli, Tajura and Ghadames

Table 4 Rotated principal component matrix for Enrichment Factor data

Element	Component	
	1	2
EF_{Pb}	*0.964*	−0.198
EF_{Zn}	*0.962*	−0.065
EF_{Cu}	*0.934*	−0.007
EF_{Cr}	*0.840*	0.199
EF_{Ba}	*0.765*	−0.419
EF_{Cd}	−0.016	*0.909*
EF_{Co}	−0.498	*0.705*
EF_{Ni}	0.147	*0.660*
EF_{As}	0.624	*−0.637*
Eigenvalue	5.11	1.99
% of variance explained	56.76	22.10
% of cumulative variance	56.76	78.87

Significant correlations are in italic face

in high weight in PCA2, respectively. The third principal component (PCA3) is loaded primarily by P and Li accounting for 11.50 % of the total variance. The P loaded into a separate factor and showed correlation only with Li. Principal component analysis of chemical composition data of Khamasen dust showed similar result because P also formed a separate factor in that case (Abed et al. 2009). North Africa and the Eastern Mediterranean are well known to accumulate one of the most extensive phosphorite provinces in the world. The fourth principal component (PCA4) is dominated by Na and K representing 8.97 % of variance. This may indicate the effects of sea and salty deposits which are common in Libya, especially around Ghadames. The last principal component (PCA5) correlated with Cd and Ni and its variance was 5.10 %.

Based on principal component analysis, the typical indicators of human impact (Pb, Zn and Cu) showed a strong correlation with Ca, which is an important major metal in the dust. This relationship was further investigated by pairwise comparisons. While the correlation matrix in PCA was calculated from the entire set of the results, in this case the data for Tripoli and Tajura were combined and the results for Ghadames were investigated separately (Fig. 3). Strong correlation was found between Ca-Zn (r = 0.794), Ca-Pb (r = 0.863) and Ca-Cu (r = 0.721). In the case of Ghadames, the distribution of Zn, Pb and Cu was independent of Ca, paired correlation coefficients were not significant: Ca-Zn (r = −0.098), Ca-Pb (r = 0.131) and Ca-Cu (r = 0.566).

Tripoli and Tajura are located near to each other in similar geological areas while Ghadames located in a remote area in the desert. Pollution derived through emission from industrial, vehicular and urban activities are different in the three sites. Our results also show that the pollution caused by industrial activities and emissions from traffic similar to other studies (Al-Khashman 2007; Chen et al. 1997). Dust originating from Libya is characterized by a lower but still significant carbonate content (Scheuvens et al. 2009). Ca, Sr, Mg and Ba were also loaded into the first PCA indicating that the sedimentary rocks play important role in the formation of dust. Strong relationship was found among the anthropogenic indicator elements (Cu, Pb and Zn) and the sedimentary geological factors. The concentrations of Cu, Pb and Zn were close to the geological background, which indicates low urban effect. However, toxic elements e.g. Cd, Cu, Zn and Pb were found highly enriched in the dust samples of the western Mediterranean and Europe in comparison with the Eastern Mediterranean (Herut et al. 2001; Kubilay and Saydam 2001) because the western Mediterranean and Europe are much more industrialized than North Africa and the Eastern Mediterranean countries (Herut et al. 2001).

Enrichment factors

Enrichment factors (EF) are often used to establish the principal sources of heavy metals. Element enrichment factors (EF) were initially proposed to predict the origin of elements in the atmosphere, precipitation or seawater. Index elements of the crust sources may be the Si, Al, Fe, Ti and Sc or Zr. Al and they are frequently used as crustal indicator to calculate the elements of EF (Tanner et al. 2008). In this study, Al was also chosen due to its small variation among the investigated locations. Chester and Stoner (1973) suggested using the following equation:

$$EF_x = \left(c_x / c_{Al}\right) / \left(c_{xc} / c_{Alc}\right)$$

where c_x is the measured concentration of element x and c_{Al} is the measured concentration of Al in the dust samples, while c_{xc} and c_{Alc} are the average crustal concentration of element x

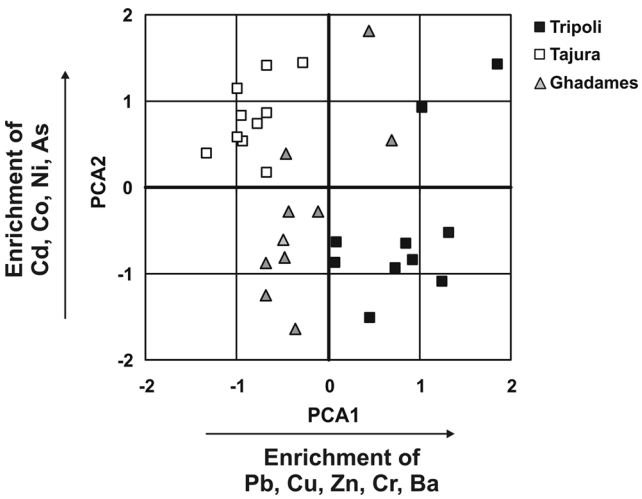

Fig. 5 Comparison of dust samples using principal component scores calculated from Enrichment Factor data

and Al (Mason 1966). In our study, we used the average crustal concentration of elements published by Wedepohl (1995). A value of EF_x >10 for a given element indicates an artificial or industrial source, whereas a value of EF_x <10 indicates a crustal origin (Meza-Figueroa et al. 2007; Wedepohl 1995).

Enrichment factors of toxic elements in dust from the three studied areas are presented in Fig. 4. Enrichment factors of Cd, Pb, Zn and As were significantly higher than 10 in the three settlements ($p < 0.05$). Enrichment of Cu was significantly higher than 10 in the case of Tripoli. Enrichment factors of Ba, Co, Cr and Ni were lower than 10, thus these elements are characterized by crustal origin. The enrichment of Cd, Ni and Cr was not significant in the three locations ($p > 0.05$). Enrichment factors of Ba, Cu Pb and Zn were significantly higher in Tripoli than in those in the other two locations.

Correlation structure of enrichment factors (EF) was investigated by principal component analysis (PCA). Enrichment factors of Pb, Zn, Cu, Cr and Ba loaded into the first principal component (PCA1), while the other group of toxic elements e.g. Cd, Co, Ni and As formed an independent group (PCA2). PCA1 explained 51.9 %, PCA2 26.9 % of the total variance. Results of PCA are given in Table 4. The three investigated locations were separated on scatter plot of PCA1 and PCA2 (Fig. 5.). Similar enrichment was reported by Herut et al. (2001). The strong correlation among the EF of Pb, Zn, Cu, Cr and Ba probably indicates industrial and vehicular effects.

Conclusions

The elemental composition of dust deposited in arid and mediterranean environment could be analysed using *Nerium oleander L.* leaves. This plant is widespread and the dust deposited on oleander leaf surfaces could be easily removed in sufficient amount for the analysis. The results of this study showed that elements indicating of anthropogenic activities (e.g. Pb, Zn and Cu) were measured in higher concentration in Tripoli than in suburban (Tajura) and remote (Ghadames) areas. However, elements of crustal origin (e.g. Al, Fe, K, Mn, Mg) showed similar distribution in the three investigated settlements.

Principal component analysis was an effective tool in identifying the sources of metals in dust samples and characterizing the settlements. Strong relationship was found among the Pb, Zn and Cu indicating vehicular source. These elements correlated with Ca, which is a major geological compound of dust. The mean Pb concentration in Tripoli was found to be much lower than that previously reported by El Hinshery and Kumar (1992). Since leaded gasoline still in use in Libya, the decrease in the concentration of Pb should be explained by other factors. This shows how the dust storm acts as dilatants of many elemental concentrations. The concentrations of other toxic elements (As, Cd, Co, Cr, Ni) were also in the range of geological background. Dust with anthropogenic pollutant may be swept out by strong wind and freshly deposited dust could dilute the local materials. In spite of diluting effect of dust storm, anthropogenic impact on dust composition could be pointed out using multivariate analysis of concentration and enrichment data.

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