European Journal of Sustainable Development (2017), **6**, 4, 126-136 ISSN: 2239-5938
Doi: 10.14207/ejsd.2017.v6n4p126

Seasonal Assessment of Heavy Metal Pollution in Street Dust of Nicosia City in North Cyprus

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Abstract
Heavy metals concentration is increasingly becoming health concern in the world, particularly on street dust of urban cities with high density traffic. Road dust samples were analyzed for determination of concentrations of the environmentally sensitive elements As, Co, Cr, Cu, Ni, Pb, and Zn in fraction of dust smaller than 100 μm. The dust particles were collected during winter and summer seasons from highways, residential and industrial areas representing different activities across the Nicosia city. The dust samples were measured for their contamination levels and particles size distribution. The assessment of pollution was based on single pollution indices, integrated pollution indices and Pearson moment correlation in order to determine their possible source, spatial distribution and seasonal variations. Single Indices include Contamination Factor (Cf), Index of Geo-accumulation (Igeo) and the integrated indices include degree of contamination (Dc) and Pollution Load Index (PLI). The general pattern of occurrence of heavy metals follows the order of Cr>Zn>Cu>Ni>Pb>Co>As. The highest levels of Cr, Zn and Cu were found in the high traffic density area, and strong positive correlations were found between these metals, implying that automobile exhausts are the dominant source of these metals.

Keywords: Heavy metals, pollution indices, particles size distribution, seasonal variation.

1. Introduction

Air pollution nowadays is a significant issue for contemporary urban centers. Improving contamination stages due to fast urbanization and development in exhaust relevant to vehicle transport are now a cause of significant issue. Pollution of the habitat by pollutants is a global issue because these materials are unbreakable and some of these components at high stages can mean toxicological threats (Domingo J.L., 1994).
Road surfaces receive different quantity of pollutants by the process of environmental buildup, through wet and dry deposition, sedimentation, impaction and interception (Li X. and Poon C. S., 2001). Particularly in cities, the top soils and street dusts are often signs of heavy metal contamination from environmental buildup. Traffic and industries, exploration activities, smelters and construction are some of the main anthropogenic sources of heavy metal pollution. The traffic source contains automobiles; e.g. tire wear, braking mechanism designs, energy burning, etc. (Pagotto, et al., 2001). Road dust is one of the major source contributors for metal contamination in urban environment. Long-term exposure to the polluted road dust would cause severe damage through of inhalation, ingestion, and dermal contact (Lu X, et al. 2010). Heavy metals are conservative pollutants because they tend to bio accumulate, over a period of time; the concentrations of heavy metal within a biological organism can be higher than that of the environment.

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Little interest has been focused on the related field along major roadways in Nicosia city. Hence, there is a need to identify the levels of toxic contaminations in the urban roads because of their association with human health effect. It has been revealed that the average area of asphalt is 3,296,146 m² considering that the average width is 8.22 m (27 feet) in Nicosia city (Ziya B., 2013). The objective of this study is to determine and assess contamination levels of some toxic heavy metals such as; As, Co, Cr, Cu, Ni, Pb and Zn in road dust along the major road sections, to provide the risk factor for each road dust category and to evaluate the status of heavy metal pollution in road dust due to different activities along the roads in Nicosia city.

1.1 Dispersion of Road Dust Particles

Particles deposited on vicinity of the road, are often referred to as road dust, these particles may be restrained, or resuspended into atmosphere. The factors that are affecting road dust emissions depend on various environmental and meteorological conditions. The ability of the dust to be resuspended, due to traffic activity, is directly proportional to particle size (Nicholson et al., 1990).

Large particles usual have less ability to resuspend due to the effect of gravitational force. Fine particles with a smaller diameter may remain suspended in air indefinitely, while particles larger than about 200 μm settle easily and may not travel far from their sources of release (Sioutas et al., 2005). The exhaust gas from vehicle into the atmosphere generally involves cooling and dilution of particle matter, which may alter their properties including particle number, sizes, surface area and chemical composition.

Northern Cyprus is the second highest after the United States (rated as 842 vehicles per thousand people) in terms of the number of vehicles per capita in the world with 823 vehicles per thousand people, 238,839 de-facto number of the registered vehicles. Luxembourg is a close follower of Northern Cyprus with 697 vehicles per thousand people (Ucar, H., 2011).

1.2 Transportation in North Cyprus

There are three modes of transportation in Nicosia of North Cyprus these are;

- Road transport system this involve usually the used of min bus popular known as "Dolmus".
- Air transport system which is done through the Ercan Airport via Turkish international airports.
- Sea transport is usually carried out through the use of ferry boats and sea-buses, travelling from Turkey to Kyrenia and Famagusta port of North Cyprus.

Among all the means of transport listed, the inland transport is the most common which is mostly covered by vehicle passenger cars. The total green in the North Nicosia is estimated to be 1,123,695 square meter which include water bodies as one third of the area and the remaining two third as a plain soil (Ziya B. 2013). The asphalt is approximately 3,296,146 square meters considering the average width of 8.22 meters carriage way according to Ziya B., 2013. The air pollutants linked with vehicle exhaust are particulate matter and volatile organic matter. The amount of particulate matter in Nicosia is 64μ g/m3, which is above annual limit value set by the EU of 40μ g/m3 (Baki et al., 2010). However, volatile organic in benzene is below the limit value of 5μ g/m3.

2. Experimental Work

2.1 Field Sampling and Sample Preparation

Nine roads across the Nicosia city were selected in order to compare the contamination levels of heavy metals and to study their distributions, using sediment quality guideline. The sites for the road dust measurements represent different types of activities affecting the city (i.e. residential, heavy traffic road and industrial road) as shown in Figure 1.

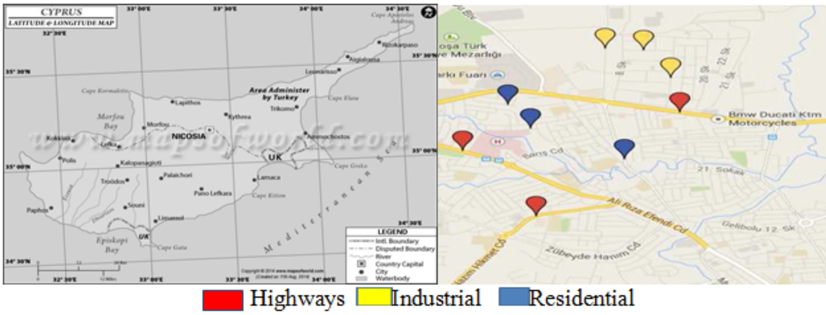

Figure 1: Map of North Cyprus and Sampling points in the Nicosia City

Sampling sites are characterized by different traffic density, number stop point and speed zone, location of the road. Chosen sampling sites include:

(a) Three sites within the residential road area (relatively low traffic),

(b) Three sites in the highways (the busiest with high volume traffic),

(c) Three sites representing the main industrial road (medium traffic volume).

The samples were taken in two different seasons of the year (winter and summer). The samples in winter period were mostly wet samples because of the rain, whereas the summer samples were absolutely dry. At each sampling point, approximately 150 g of dust particles were collected on pavement surfaces of the road, with a clean plastic dustpan and a brush. The dust was then transferred to self-sealing polyethylene bags, ready for the laboratory analysis. The samples were left to dry at room temperature for ten days (winter sample). The fraction of the dust that passed through sieve sizes between 62.5 μ m – 100μm is used for the analysis.

The following Analytical and statistical methods were applied to make the required analyses.

- **XRF (X-Ray Fluorescence) Analysis**
- **PSD (The particles size distribution) Analysis**
- **Single Indices: Contamination Factor (C_f), Index of Geo-Accumulation (I_{geo})**
- **Integrated indices: Degree of contamination (D_c), Pollution Load Index (PLI**

3. Results and Discussion

3.1 Laboratory Results

3.1.1 XRF (X-Ray Fluorescence) Analysis

The concentrations of all the seven heavy metals were analyzed (As, Co, Cr, Cu, Ni, Pb, and Zn) using X-ray fluorescence method. The concentrations are presented below, where nine roads are considered for the sampling, which include Highways, Residential Roads and Industrial Roads. Three dust samples per road are collected during two different seasons of the year (i.e. winter and summer). The seasonal and average concentrations are presented in Table 1 and the results for the average are presented in Figure 2.

Table 1: Winter and Summer Concentration of Heavy Metals (mg/kg)

elements	H1	H2	H3	R1	R2	R3	I1	I2	I3	WHO	EPA
Cu (W)	50.7	41.1	56.7	56.7	40.7	44.7	59.0	62.6	58.5		
Cu (S)	224.9	30.6	61.9	46.3	54.1	36.9	41.5	57.1	46.7	25.0	16.0
Cu (avg)	**137.8**	**35.9**	**59.3**	**51.5**	**47.4**	**40.8**	**50.3**	**59.9**	**52.6**		
Ni (W)	81.3	57.0	46.0	51.5	80.1	72.7	57.0	45.6	42.4		
Ni (S)	52.6	37.7	41.4	39.6	40.5	86.8	62.9	66.8	64.8	20.0	16.0
Ni (avg)	**67.0**	**47.3**	**43.7**	**45.5**	**60.3**	**79.8**	**59.9**	**56.2**	**53.6**		
Cr (W)	420.4	296.9	269.5	279.1	297.6	288.4	345.9	321.5	330.7		
Cr (S)	289.0	303.8	209.2	256.5	232.9	626.1	388.2	409.8	398.5	25.0	25.0
Cr (avg)	**354.7**	**300.3**	**239.4**	**267.8**	**265.2**	**457.3**	**367.1**	**365.6**	**364.6**		
Co (W)	29.8	14.6	0.0	8.5	11.0	0.0	2.8	5.7	9.6		
Co (S)	0.0	12.8	9.5	11.1	10.3	32.3	0.0	15.3	10.3	NA	NA
Co (avg)	**14.9**	**13.7**	**4.7**	**9.8**	**10.7**	**16.2**	**1.4**	**10.5**	**9.9**		
Zn (W)	587.5	85.5	120.5	110.8	76.7	80.7	109.8	125.2	185.6		
Zn (S)	65.9	51.5	53.8	52.7	53.2	41.4	82.3	91.6	83.1	123.0	110.0
Zn (avg)	**326.7**	**68.5**	**87.1**	**81.8**	**65.0**	**61.0**	**96.0**	**108.4**	**134.3**		
As (W)	6.8	5.7	0.0	0.0	0.0	6.4	4.3	1.4	2.1		
As (S)	4.9	0.0	0.0	0.0	0.0	15.3	0.0	8.0	0.0	10.0	10.0
As (avg)	**5.90**	**2.80**	**0**	**0**	**0**	**10.90**	**2.10**	**4.70**	**1.10**		
Pb (W)	18.1	26.5	51.2	53.4	34.3	17.6	33.5	50.9	46.8		
Pb (S)	20.0	35.9	27.8	31.9	29.9	0.0	34.3	14.4	31.6	NA	40.0
Pb (avg)	**19.0**	**31.2**	**39.5**	**42.6**	**32.1**	**8.8**	**33.9**	**32.6**	**39.2**		

W=winter S=summer

It was very obvious that Cu, Cr and Zn were the most abundant heavy metals found in all classes of streets in the city (WHO standards). While the concentrations of Pb and As are within the limit values, that of Co were not reported by the standard. In this study there are two major contributors of pollution in street dust: these are anthropogenic and lithogenic. The lithogenic effects come from origin of the material while anthropogenic effects come from vehicles exhaust and industrial waste.

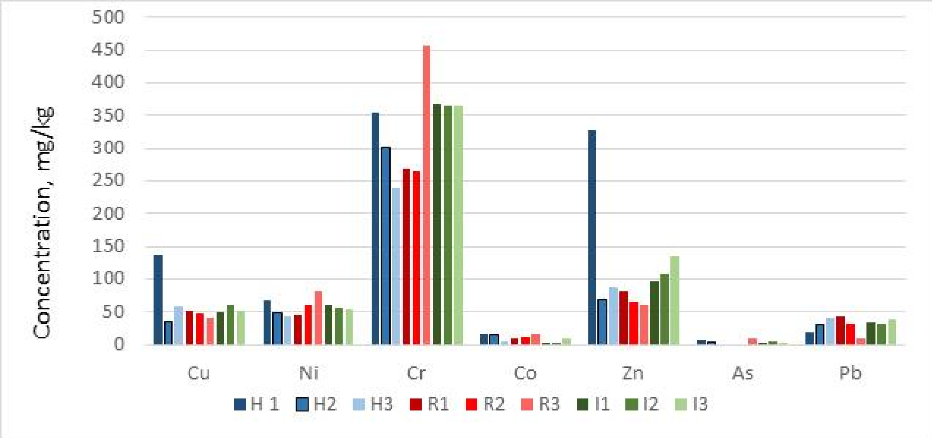

Figure 2. Average Heavy Metals Distribution in Nicosia

Among all the studied areas, highways were found to have the highest average concentrations, followed by industrial and residential roads. This shows that traffic volume is the major contribution to pollution. The metals follow the decreasing order of Cr>Zn>Cu>Ni>Pb>Co>As. Cu, Cr, Co and As are larger in summer and Ni and Zn are larger in winter.

3.1.2 PSD (Particles size distribution) Analysis

The particle size of street dust is an important parameter in the analysis of heavy metals concentration. Particle size is usually described by the diameter of the particle. In this work the Mastersizer2000 Laser diffraction device is used for the analysis. The degree of harmful effect of inhaled street dust is often related with dust particle size. The particle size distribution curves of samples show correlative distribution patterns manifested by the overlapping curves. Figure3 is residential, Figure4 is highway and Figure5 is industrial dust analysis for their particle sizes. The graphs were used to deduce the values of d10, d30 and d60. The definition of the di is as follows: d10 = grain diameter at 10% passing, d30= grain diameter at 30% passing, d60= grain diameter at 60% passing.

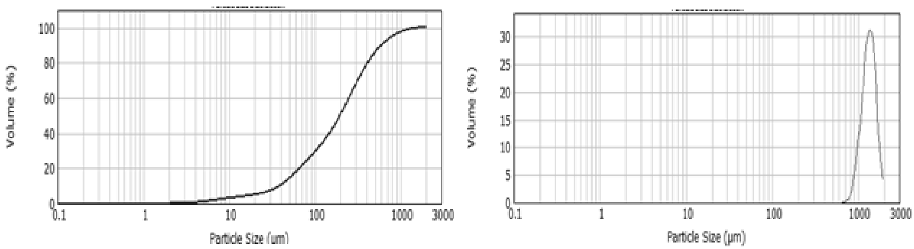

Figure 3: Residential Dust Particle Size in Winter (a) and Summer (b)

The Figure 3a shows that in summer the particles distribution of the dust sample is immediate between fine and coarse particles class.. On the other hand Figure 3b shows that the particles are evenly distributed with a high percentage of coarse particles in sample dust. This indicates the dust is not well graded

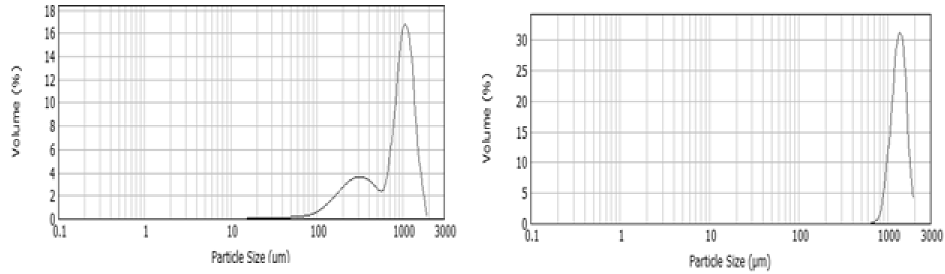

Figure 4: Highways Dust Particle Size in Winter (a) and Summer (b)

Figure 4 for the highways in winter shows that finer particles between 0 to 800µ m are more or less absent in this dust sample site. Coarse particles are within a range of 850µ m to 2500µ m this show that the soil is more of coarse particles In summer**,** the same pattern is observed with a very slight difference.

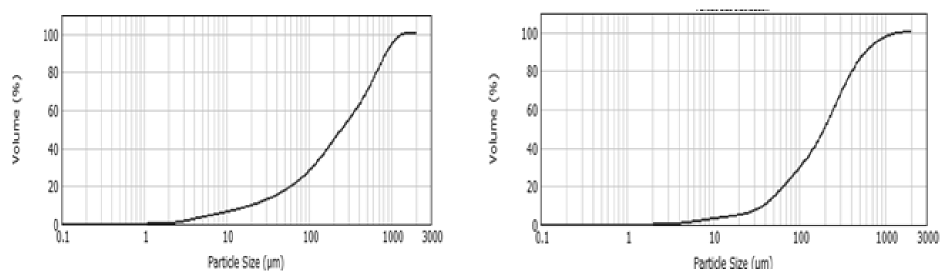

Figure 5: Industrial Dust Particle Size in Winter (a) and Summer (b)

Figure 5 shows that the particles are evenly distributed with a high percentage of coarse particles in samples both in Summer and Winter.

3.2 Single Indices

3.2.1 Average Seasonal Contamination Factors (C_f)

A Contamination Factor is an indicator used to describe the toxic nature of substances in a lake or sub basin (Hakanson 1980). It is defined as the ratio of heavy metal concentration obtained to the ratio in sediment or background samples.

$$Cf = \frac{Ci}{Bn}$$

where

C_i= mean concentration of substance,

B_n=background sample response value (mg/kg),

C_f <1 low contamination factor, 1≤ C_f <3, moderate contamination factor, 3≤ C_f <6 considerable contamination factor, C_f ≥6, very high contamination factor.

In Table 2 the background sample response values are given for Nicosia, from a previous work. Table 3 below shows the base average values obtained from four different sediments in the inland by Duman et al. 2012.Contamination factor (C_f) of the seven studied heavy are present in Table 2, Cu, Zn and Pb are ***moderately polluted***, pollution of Ni, Co and As are very low while that of Cr is ***considerable high***. The degree of contamination in winter reveals that the entire roads chosen in this research work are ***"moderately polluted"*** with exception of H1 and R3 which are ***"considerable polluted".***

Table 2: Background samples response value in mg/kg

Element(ppm)	Cu	Ni	Cr	Co	As	Pb
pre industrial (Bn) 1	45.000	68.000	90.000	19.000	13.000	20.000

*(1) Duman 2012 (2) Hakanson 1980

Table 3: Average Seasonal Contamination Factors (C_f)

Roads	CuW	CuS	NiW	NiS	CrW	CrS	CoW	CoS	ZnW	ZnS	AsW	AsS	PbW	PbS
H1	1.1	5.0	1.2	0.8	4.7	3.2	1.6	0.0	6.2	0.7	0.5	0.4	0.9	1.0
H2	0.9	0.7	0.8	0.6	3.3	3.4	0.8	0.7	0.9	0.5	0.4	0.0	1.3	1.8
H3	1.3	1.4	0.7	0.6	3.0	2.3	0.0	0.5	1.3	0.6	0.0	0.0	2.6	1.4
R1	1.3	1.0	0.8	0.6	3.1	2.8	0.4	0.6	1.2	0.6	0.0	0.0	2.7	1.6
R2	0.9	1.2	1.2	0.6	3.3	2.6	0.6	0.5	0.8	0.6	0.0	0.0	1.7	1.5
R3	1.0	0.8	1.1	1.3	3.2	7.0	0.0	1.7	0.8	0.4	0.5	1.2	0.9	0.0
I1	1.3	0.9	0.8	0.9	3.8	4.3	0.1	0.0	1.2	0.9	0.3	0.0	1.7	1.7
I2	1.4	1.3	0.7	1.0	3.6	4.6	0.3	0.8	1.3	1.0	0.1	0.6	2.5	0.7
I3	1.3	1.0	0.6	1.0	3.7	4.4	0.5	0.5	2.0	0.9	0.2	0.0	2.3	1.6
Avg.	1.3		0.8		3.7		0.5		1.2		0.2		1.6	

Low contamination | Moderate cont. | High cont. | Considerable cont.

3.2.2 Geo-Accumulation Index (Igeo)

Index of geo accumulation was originally defined in 1969 in order to determine and define heavy metal contamination in sediments.

$$Igeo = log_2\{\frac{Ci}{1.5Bn}\}$$

where

Ci= mean concentration of substance, Bn= sample background value

$I_{geo} \leq 0$ un-polluted, $0 \leq I_{geo} < 1$, un-polluted to moderate polluted, $1 \leq I_{geo} < 3$ moderate to strongly polluted, $I_{geo} \geq 3$, extremely polluted

For the street dust, the concentration of Cu, Ni, Co, Zn, As, Pb are considered to be "***unpolluted"*** on this indice for the two seasons and the concentration of Cr is ranging from ***"upolluted to moderate polluted".*** Based on this indice, the concentration of the heavy metals in the remaining samples unchange throughout the seasons.

Table 4: Index of Geo-Accumulation of Samples

Road	CuW	CuS	NiW	NiS	CrW	CrS	CoW	CoS	ZnW	ZnS	AsW	AsS	pbW	pbS
H1	-0.4	1.7	-0.3	-1.0	1.6	1.1	0.1	-4.8	2.0	-1.1	-1.5	-2.0	-0.7	-0.6
H2	-0.7	-1.1	-0.8	-1.4	1.1	1.2	-1.0	-1.2	-0.7	-1.5	-1.8	-4.3	-0.2	0.3
H3	-0.3	-0.1	-1.1	-1.3	1.0	0.6	-4.8	-1.6	-0.2	-1.4	-4.3	-4.3	0.8	-0.1
R1	-0.3	-0.5	-1.0	-1.4	1.0	0.9	-1.7	-1.4	-0.4	-1.4	-4.3	-4.3	0.8	0.1

R2	-0.7	-0.3	-0.3	-1.3	1.1	0.8	-1.4	-1.5	-0.9	-1.4	-4.3	-4.3	0.2	0.0
R3	-0.6	-0.9	-0.5	-0.2	1.1	2.2	-4.8	0.2	-0.8	-1.8	-1.6	-0.3	-0.8	-4.9
I1	-0.2	-0.7	-0.8	-0.7	1.4	1.5	-3.3	-4.8	-0.4	-0.8	-2.2	-4.3	0.2	0.2
I2	-0.1	-0.2	-1.2	-0.6	1.3	1.6	-2.3	-0.9	-0.2	-0.6	-3.8	-1.3	0.8	-1.1
I3	-0.2	-0.5	-1.3	-0.7	1.3	1.6	-1.6	-1.5	0.4	-0.8	-3.2	-4.3	0.6	0.1
Avg. Igeo	-0.3		-0.9		1.2		-1.6		-0.7		-2.6		-0.2	

Low pollution Moderate pollution High pollution Considerable pollution Extreme pollution

3.3 Integrated Indices

3.3.1 Degree of Contamination (D_c)

The Degree of Contamination can be defined as the sum of all contamination factors in the sample for give site.

$$\boldsymbol{Dc = \sum_1^n Cf}$$

where

C_f =single contamination factor,

n= The count of the studied heavy metals

D_c <n : Low pollution, n≤D_c<2n: Moderate pollution, D_c> 4n : Considerable pollution

The values are presented in Table 5 below.

3.3.2 Pollution Load Index (PLI)

Pollution load index (PLI) for the sediments at each site was evaluated by the method of Tomilson et al. (1980), this method provides basic understanding of a component in the environment. Pollution load index of a single site is defined as the nth root of n number of multiplied Contamination factor (C_f) values.

$$\boldsymbol{PLI = \{C_{f1} x C_{f2} x C_{f3} x \ldots\ldots\ldots\ldots x C_{fn}\}^{1/n}}$$

PLI=0 Not Polluted

PLI=1 Moderate pollution

PLI>1 Considerable pollution

In summer H3 and R2 had "*low degree of contamination*" while the rest have "*moderate degree of contamination*". The pollution load indices in winter shows that "H1 and I3 *are polluted*" and in summer only road "I2 *is polluted*".

Table 5: Degree of Contamination (D_c) and Pollution Load Indices (PLI)

Road	Dc	Winter	Dc	summer	PLI	Winter	PLI	Summer
H1	16.18	Considerable	11.05	moderate	1.62	polluted	0.00	Not polluted
H2	8.48	Moderate	7.62	moderate	1.00	polluted	0.00	Not polluted
H3	8.76	Moderate	6.77	low	0.00	Not polluted	0.00	Not polluted
R1	940	Moderate	7.19	moderate	0.00	Not polluted	0.00	Not polluted
R2	8.50	Moderate	6.98	low	0.00	Not polluted	0.00	Not polluted
R3	7.49	Moderate	12.37	moderate	0.00	Not polluted	0.00	Not polluted
I1	9.30	Moderate	8.75	moderate	0.88	Not polluted	0.00	Not polluted
I2	9.91	Moderate	9.90	moderate	0.87	Not polluted	1.94	Not polluted
I3	10.55	Moderate	9.42	moderate	1.01	polluted	0.00	Not polluted

3.4 Pearson Moment Correlation

Pearson's moment correlation (r) is a statistical tool used for the examining the relationship between two variables that are measured on the same interval or ratio scale. In metal analysis, positive correlation indicates strong relationships between contaminants, while negative correlation indicates weak relationship (different source) between the contaminants. The correlations of the 7 heavy metals were analyzed by using the Pearson Product Moment correlation coefficient Table 6. The analysis shows that correlations between heavy metals is in decreasing order of the coefficient: positive correlation (Cu/Zn)>(As/Cr)> (As/Ni)>(Ni/Cr)>(As/Co), Negative correlation: (Pb/Co)>(Pb/Cr)>(Pb/Ni) >(Pb /As).

Table 6: Pearson Product Moment correlation coefficient

Elements		Cu	Ni	Cr	Co	Zn	As	Pb
Cu		**1**						
Ni		0,228	**1**					
Cr		0,059	**0,809**	**1**				
Co		0,225	0,469	0,362	**1**			
Zn		**0,972**	0,237	0,160	0,261	**1**		
As		0,186	**0,834**	**0,851**	0,621	0,204	**1**	
Pb		-0,275	**-0,903**	**-0,719**	-0,658	-0,271	**-0,929**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

The correlation coefficient between copper and zinc (r=0.972) which is quiet in agreement with research of this type, indicating the highest correlation. Other major correlation include chromium and arsenic (r=0.851), arsenic and nickel (r=0.834), chromium and nickel (r=0.809), arsenic and cobalt (r=0.621). Cu, Zn, Ni, As, and Cr are usually generated from anthropogenic sources (Kim CH et al. 2010). Lead (Pb) shows negative correlation with Ni, Co, Cr, and As; this indicates that the presence of lead in streets does not necessary come from vehicle exhaust as a result of regulation imposed in the use of unleaded fuel. On the other hand Cr present in soil dust mostly comes from diesel (Kittelson D.B., 2001). Cu and Zn are usually from tire and engine part corrosion (Adachi K and Tainosho Y, 2010).
During sampling in winter, Nicosia had witnessed a diurnal temperature variation of 10 degree Celsius and a high relative humidity of 78% and a wind speed of 2m/s. This condition favored some accumulation of pollutants in the streets such as zinc and copper which can easily react with soil in the presence of moisture to form zinc oxide and copper oxide. In summer the average temperature is relatively high (33 degree Celsius) and a very low relative humidity of 42% with a wind speed of 3m/s. This condition is less favorable when compared to winter season.

4. Conclusion

The concentrations and particle size distributions of heavy metals were measured using XRF and the Mastersizer2000, respectively. The fractional size of street dust between 62.5μm to 1mm is used for the XFR measurements. Seasonal variation was observed in three zones of environment (Highways, Residential and Industrial area). Both single and integrated pollution indices were studied in order to determine the possible contamination of heavy metals by vehicles exhaust. Single Indices include Contamination Factor (C_f), Index of Geo-accumulation (I_{geo}) and the integrate indices include degree of contamination (D_c) and Pollution Load Index (*PLI*). Seasonal variations in soil texture were also observed: residential and industrial street soil changes from "Fine Sand in winter to Medium Sand in summer", whereas for the busy traffic no significant change was observed throughout the seasons.

The contamination factor for the studied samples indicates Ni, As and Co had "***low contamination factor"***, Cu, Pb and Zn had "***moderate contamination factor"***, and Cr had "***Considerable contamination factor***". The factor follows the decreasing of Cr>Pb>Cu>Zn>Ni> Co>As. Highways in winter and Residential roads in summer had "***high pollution"***.

Index of Geo-accumulation reveals that seven elements are categorized as "unpolluted sample" with exception of Cr which is moderately polluted sample. The work did not reveal statistical differences on the levels of Cr, Zn and Cu between seasons. Winter average values for Pb, Zn and Ni exceeded corresponding summer values. In arid regions opposite patterns were observed. In general contamination of heavy metals, in all sites studied, were statistically not different from each other, except at high traffic site. The street dust should be continually monitored over time. The aim of monitoring would help in putting adequate measures in vehicle emission control. Alternative means of transportation should be provided by the government so that number of vehicle per capita can be reduced drastically e.g. buildup a rail ways system across the city.

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