HEAVY METALS CONTENT IN ROADSIDE SOIL FROM A CANYON STREET

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Abstract
The aim of this paper is to test the relationships between vehicle traffic and the content of the two heavy metals, lead and cadmium, in soils. The field study was conducted for a year in a street canyon in Pitesti, a town in the southern Romania, which can be considered hot spot, by comparison with a blank area in Calinesti, a suburban area near Pitesti. Heavy metal content of soils sampled at progressively greater distance from the road was determined using atomic absorption spectroscopy. The horizontal, vertical and time variations of heavy metal content in soil from the two studied areas demonstrate that the vehicle traffic is a major emission source for lead and cadmium pollution. Lead concentrations in the urban soils were particularly high compared with any of the rural sampled sites.

Keywords: atmospheric pollution, lead, cadmium, vehicle traffic

INTRODUCTION

Millions of tones of pollutants are emitted every year into the atmosphere, both from natural sources and especially from anthropogenic sources. There are four categories of emission sources: stationary (industrial processes, industrial and domestic combustions); mobile (road and stationary traffic); natural (volcanic eruptions, forest fires) and accidental pollutions (discharges, fires). (EPA, 2007)

The systemic pollutants such as heavy metals are very dangerous because of their long time retention in soil and their accumulation by plants and animals. These pollutants can combine with minerals and oligominerals becoming blockers for these and the living organisms of these essential elements. The heavy metals do not decay by food preparation; they accumulate in the body and block the intracellular biochemical processes. The heavy metals represent a class of omnipresent pollutants, with toxic potential, in some cases even at low exposure level. They concentrate in each trophic level, because of their weak mobility, so the concentration in plants is higher than in soil, higher in herbivore animals than in plants, higher in carnivores' tissues than in herbivore, the highest concentration being reached at the end of the trophic chain, i.e. in large predators and in humans. (Measnicov, 1998)

In most cases, heavy metal pollution is a problem associated with intensely industrialized areas. However, high vehicle traffic was proven to be one of the important heavy metal emission sources. Zinc, copper and lead are three of the most common heavy metals emitted by vehicle traffic, totaling at least 90% from the total emitted quantity. (EPA, 2000) Also, vehicle traffic is responsible for the emission of some small quantities of other metals, like nickel and cadmium. In populous areas, where vehicle traffic is relatively high, the exposure of people to traffic – related pollution, especially particulate pollution is significant. In the recent years, vehicle traffic has increased especially in urban areas. In cities with densely packed with buildings, placed on both sides of the street, the pollution levels often do not comply with quality standards. (EEA, 2006)

Heavy metals total deposition is the sum of dry (aerosol), wet (via rain, snow or hail) and fog and cloud water deposition. (Geczi, Bodis, 2003) Most heavy metals get into the dust on the road surface. These metals become soluble during rainfall or are cleaned from the road in the same time with the dust. In both cases, the metals get into the soil and/or deposit on the vegetation and are transported by the chemical processes. Most metals have positive charge (are cations), while the organic matter from soil has positive or negative charge.

MATERIAL AND METHODS

The field study was conducted for a year in a street canyon, which can be considered a pollution 'hotspot', by comparison with a suburban area, a blank area: 1. *Nicolae Balcescu Street, Pitesti* – an urban canyon street, with high buildings located both sides along the street the area and high vehicle traffic, that can achieve most times 60.000 transits in 24 hours, especially in the working days. 2. *Calinesti village, Arges County* – a rural area, about 20 Km east from Pitesti, characterized by very low vehicle traffic and away from any industrial influence.

The soils sampling were performed by three campaigns per year (spring, summer and autumn), from the two pedological levels (0-20cm, 20-40cm), at 10m, 20m, 50m away from the street axis. The soil samples were dried and milled till homogenization, digested by pressure disintegration in acid medium and then analyzed using atomic absorption spectroscopy. 4mg of each soil sample were digested with 6ml HNO_3 65% and 2ml HCl 37% in a Berghof microwave oven using the temperature program from Table 1. (Berghof, Application Report)

Table 1

The temperature program used for digestion of soil samples

Step	*Temperature (°C)*	*Ramp time (min)*	*Time (min)*
1	160	6	0
2	180	5	0
3	180	0	14
4	Cooling	-	-

The solutions were analyzed according to the reference method SR ISO 11047/1999 "Soil quality. Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc from soil extracts in regal water. Method by flame atomic absorption spectrometry and electrochemical atomization" (Standard SR ISO 11047/1999) using an AA700 Perkin-Elmer spectrometer with hallow cathode lamp (User's Guide, Atomic Absorption Spectrometer Perkin-Elmer)

RESULTS AND DISCUSSIONS

Heavy metals: theoretical air emissions

The annual quantities of **lead** and **cadmium** emitted by the vehicle traffic were calculated by using the EMEP/CORINAIR Methodology (Group 7-Road Transport), with the input data: the daily average vehicle traffic DAT [number of motor vehicles/24 hours], the average running speed ARS [Km/h] and the annual carburant consumption (ACC) estimated for each motor vehicle class [tonnes/year]. The DAT was determined from the vehicle traffic manual counts made in three-hour intervals in different days along the year. (EEA, 2007) The results are presented in Tables 2 and 3.

Table 2

Heavy metals calculated emissions – Nicolae Balcescu Street

Motor vehicle class	***Carburant***	***DAT [nr/24 h]***	***ARS [Km/h]***	***ACC [tonnes/year]***	***Emission(g/year/km)***	
					Pb	**Cd**
Cars	Gasoline	45500	40	1245	149.5	12.45
	Diesel oil	10800	40	265	0	2.65
Vans (<3.5 t)	Gasoline	4200	40	172	20.6	1.72
	Diesel oil	8300	40	305	0	3.05
Tracks	Gasoline	350	30	43	0	0.43
Buses	Diesel oil	1400	30	215	0	2.15
TOTAL					**170.1**	**22.45**

Table 3

Heavy metals calculated emissions – Calinesti village

Motor vehicle class	***Carburant***	***DAT [nr/24 h]***	***ARS [Km/h]***	***ACC [tonnes/year]***	***Emission(g/year/km)***	
					Pb	**Cd**
Cars	Gasoline	80	50	1.64	0.197	0.0164
	Diesel oil	25	50	0.50	0	0.0050
Vans (<3.5 t)	Gasoline	5	50	0.12	0.014	0.0012
	Diesel oil	10	50	0.27	0	0.0027
Tracks	Gasoline	2	40	0.18	0	0.0018
Buses	Diesel oil	2	40	0.18	0	0.0018
TOTAL					**0.211**	**0.0289**

The vehicle traffic is shown to be an important emission source for heavy metals; in the urban area, the calculated air emissions are particularly higher than in the rural area.

Lead Content

Lead content determination was performed at 283.3 nm wavelength using atomization technique in air-acetylene flame. Values obtained are presented in Table 4.

Table 4

Lead contents in soil (mg/kg dry matter)

Pb (mg/Kg d.m.)	**Nicolae Balcescu Street, Pitesti**						**Calinesti**					
	10 m		**20 m**		**50 m**		**10 m**		**20 m**		**50 m**	
	0-20	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*
March	37.15	40.23	48.23	38.05	32.15	19.06	12.34	10.22	10.06	11.11	10.12	11.82
June	35.31	36.15	44.86	34.45	28.25	16.26	11.46	9.98	9.85	10.62	10.06	11.58
September	46.23	48.02	55.79	43.62	38.86	22.85	11.78	11.15	10.84	11.01	10.84	12.06
Annual average	**40.52**		**44.17**		**26.24**		**11.16**		**10.58**		**11.08**	

Analyzing these results, it can be seen that in the urban area the lead concentrations are significantly higher than in rural area, exceeding the normal value of 20 mg/Kg dry matter, but being under the alert threshold for sensible usage of 50 mg/Kg dry matter, according to the Order 756/1997 for approval of the Environmental Pollution Regulation.(WFEP Ministry, 1997)

The horizontal variation is plotted in Fig. 1 by representation of lead annual averages based on the distance from the street axis.

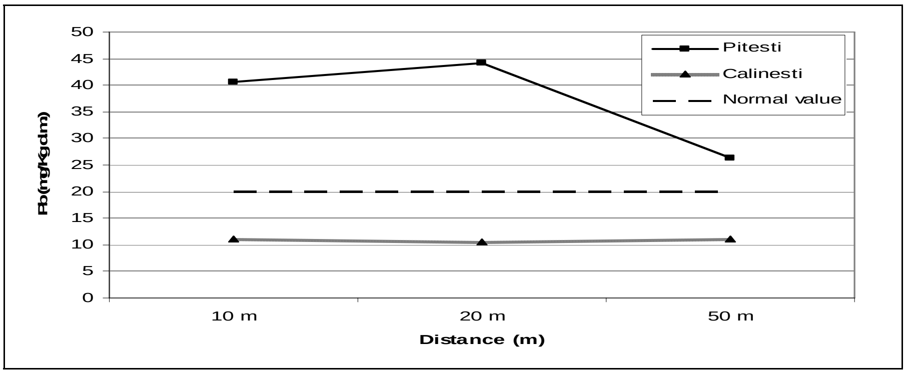

Fig. 1. Horizontal variation of lead concentrations – 2008 annual averages

In the rural area, without vehicle traffic influence, average concentrations obtained are relatively constant at any distance from street axis. In the urban area, the highest lead concentration in soil was determined in the sample at 20m from the road axis. At greater distances from the road, the Pb values decrease, at 50 m being near the 'normal' value. Referring to soil samples at 20m, the time variation is plotted in fig. 2:

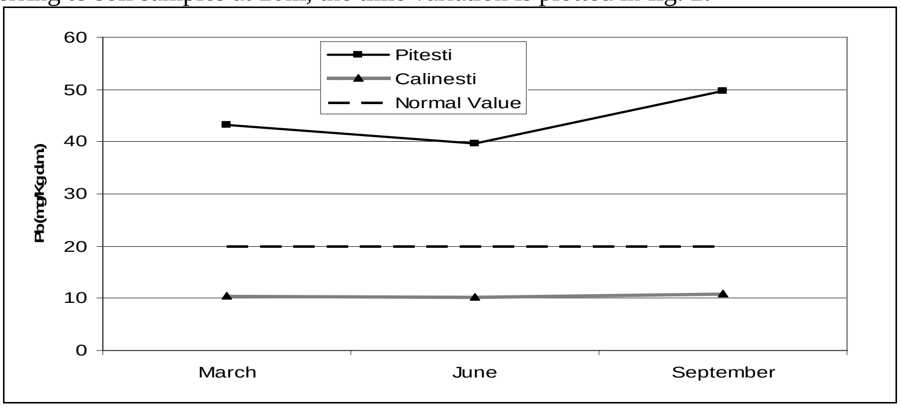

Fig. 2. Time variation of lead concentrations at 20m from street axis – 2008

Again in the rural area, the values are relatively constant throughout 2008, whereas in the urban area, there is a slight decrease in June, while vehicle traffic is higher in this period of year. This variation may reflect the fact that in June low precipitation was recorded (Fig. 3), so the wet deposition is less.

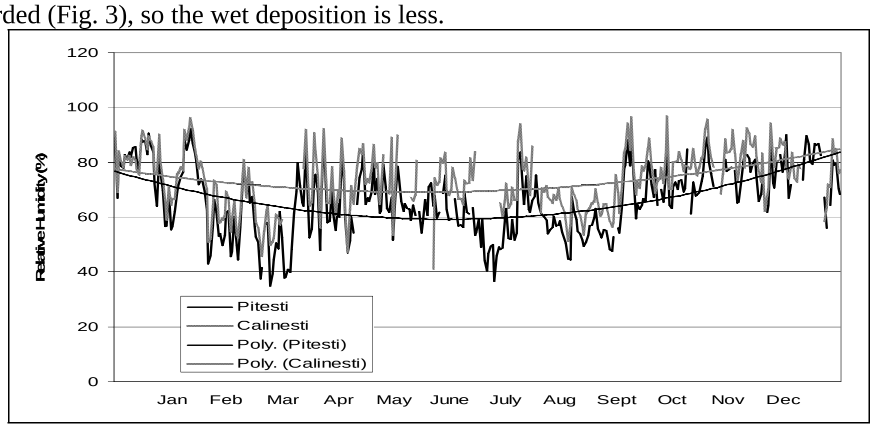

Fig. 3. Relative humidity – 2008

The vertical variation is plotted in Fig. 4 by representation of lead annual averages based on the sampling depth and distance from the street axis.

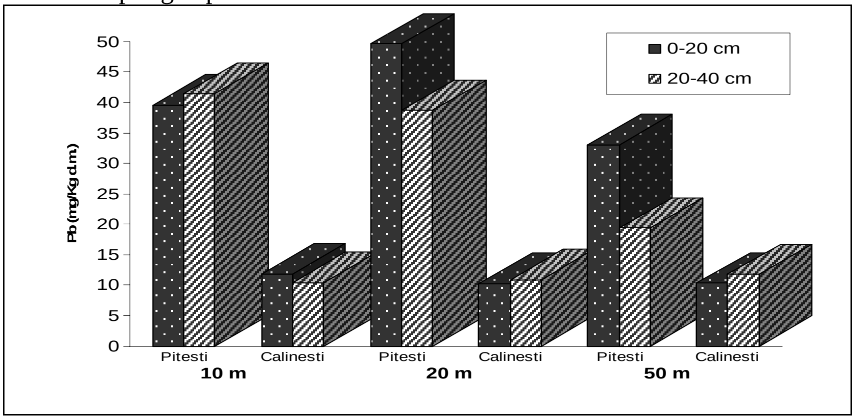

Fig. 4. Vertical variation of lead concentrations based on the distance from street axis

In the rural area, the average concentrations obtained are relatively constant at any depth or distance from the street axis. In the urban area, at 10m from the street axis, the soil contamination increases with depth, while at 20m and 50m it decreases with depth. At the side of the street, the heavy metal deposition was higher through time, deeper into soil. As the distance from the street increases, the soil contamination becomes more superficial.

Cadmium content

Cadmium content determination was performed at 228.8 nm wavelength using atomization technique in air-acetylene flame. Values obtained are presented in Table 5.

Table 5

Cadmium contents in soil (mg/Kg dry matter)

Cd (mg/Kg d.m.)	Nicolae Balcescu Street, Pitesti						Calinesti					
	10 m		20 m		50 m		10 m		20 m		50 m	
	0-20	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*	*0-20*	*20-40*
March	0.80	0.68	0.70	0.64	0.54	0.50	0.11	0.12	0.11	0.10	0.06	0.03
June	0.75	0.54	0.59	0.48	0.46	0.44	0.09	0.09	0.09	0.07	0.05	0.02
September	0.91	0.65	0.68	0.54	0.58	0.59	0.10	0.09	0.09	0.08	0.06	0.03
Annual average	**0.72**		**0.61**		**0.52**		**0.10**		**0.09**		**0.04**	

Analyzing these results it can observe that in urban area the cadmium concentrations are higher than in rural area, but do not exceed the normal value of 1 mg/ Kg dry matter according to the *Waters, Forests and Environmental Protection Ministry Order no. 756/1997 for approval of the Environmental Pollution Regulation*. (WFEP Ministry, 1997)

The horizontal variation is plotted in Fig. 5 by representation of cadmium annual averages based on the distance from the street axis.

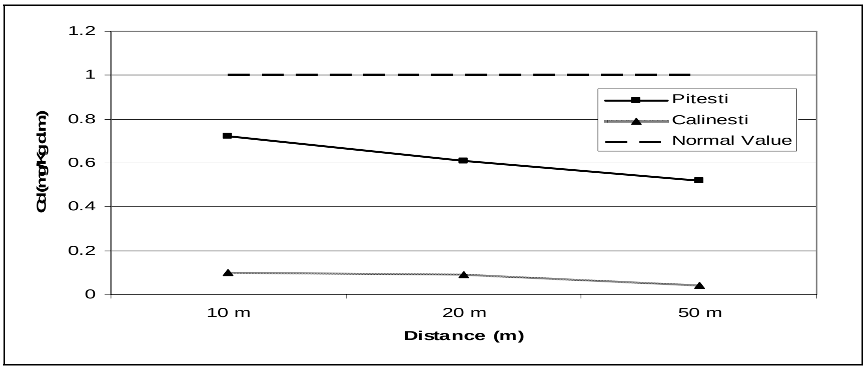

Fig. 5. Horizontal variation of cadmium concentrations – 2008 annual averages

In the rural area, average concentrations are relatively constant, with a slight decrease at 50m. In the urban area, the cadmium concentration in soil decreases proportional with the distance from the street axis.

Referring to soil samples at 20m, the time variation is plotted:

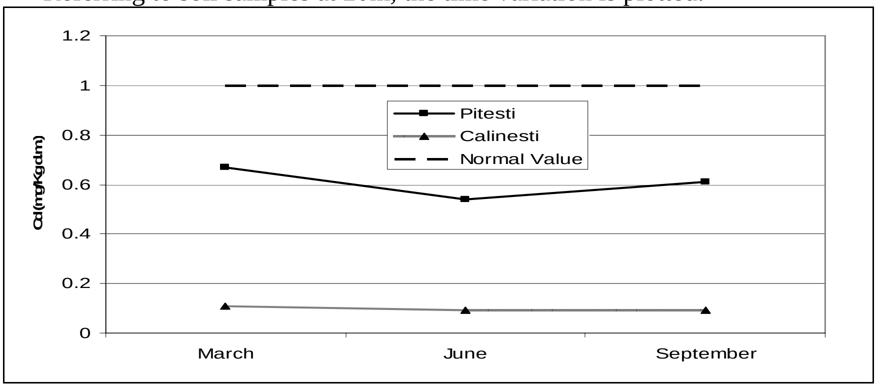

Fig. 6. Time variation of cadmium concentrations at 20m from street axis – 2008

Again in the rural area the values are relatively constant along 2008, whereas in the urban area, there is a slight decrease in June, when vehicle traffic is higher. Like lead, this variation may be due to the low precipitation recorded in June, so the wet deposition is less.

The vertical variation is plotted in Fig. 7 by representation of cadmium annual averages based on the sampling depth and distance from the street axis.

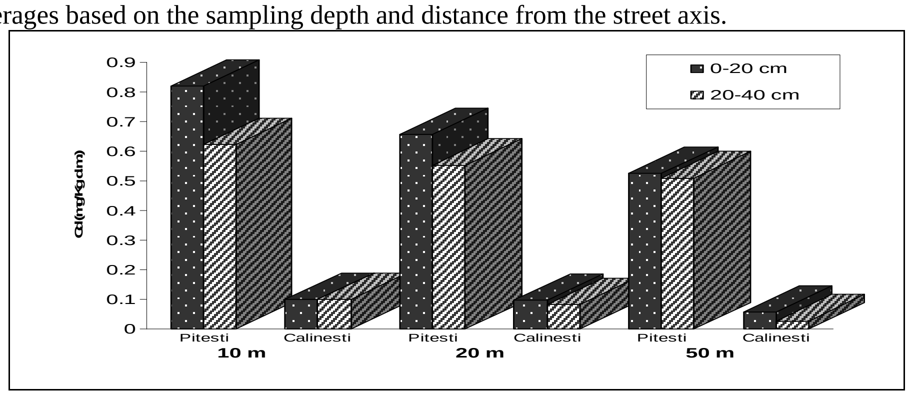

Fig. 7. Vertical variation of cadmium concentrations based on the distance from street axis

In the rural area the average concentrations are relatively constant with a slight decrease at 50m and at 20-40cm depth. In urban area, the soil contamination decreases with depth and distance from street axis. At the side of the street, the soil contamination is more superficial.

CONCLUSION

Lead and cadmium concentrations in soils from rural area do not exceed 'normal' values of 20 mg/ Kg dry matter, and 1 mg/ Kg dry matter, respectively, according to Romanian legislation. They remain relatively constant by vertical, horizontal and temporal distribution.

Lead concentrations in soils from the urban area exceed the 'normal' value, but do not exceed the 'alert' threshold of 50 mg/ Kg dry matter, according to the same Romanian legislation. Analyzing the horizontal distribution, the highest lead concentration was detected at 20 m distance from the street axis; the traffic influence weakens with distance from the road, so at 50 m concentrations decrease significantly, approaching the 'normal' value. In terms of vertical distribution, near the street the deposition of particulate heavy metal has been more intense through time, with higher lead values penetrating deeper into the soils, and as the distance from the street increases, the soil contamination becomes more superficial.

Analyzing the temporal variation, a slight decrease in June is established, although vehicle traffic is more intense during this period of year; this decrease is thought to reflect reduced rainfall and wet deposition of particulate pollutants at this time.

Cadmium concentrations in soils from the urban area are under the 'normal' value of 1 mg/ kg dry matter, recording a decreasing directly proportional to the distance from the street axis and to the sampling depth. Along the year the same decreasing in June was recorded, because of the low precipitation.

REFERENCES

1. ASRO, 1999, SR ISO 11047/1999, Soil quality. Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc from soil extracts in regal water. Method by flame atomic absorption spectrometry and electrochemical atomization
2. Berghof, Application Report, Microwave Pressure Digestion Berghof
3. EEA, 2006, Environment and health Report No 10 (2005), European Environment Agency, Copenhagen, Denmark, On line at: www.eea.europa.eu/publications/ eea_report_2005_10.
4. EEA, 2007, EMEP/CORINAIR Atmospheric Emission Inventory Guidebook, European Environment Agency, Copenhagen, Denmark, On line at: www.eea.europa.eu/ publications/EMEPCORINAIR5.
5. EPA, 2000, Taking Toxics Out of the Air EPA-452/K-00-002, United States Environmental Protection Agency, On line at: www.epa.gov/raf/metalsframework/pdfs
6. EPA, 2007, Framework for Metals Risk Assessment EPA 120/R-07/001, United States Environmental Protection Agency, On line at: www.epa.gov/raf/metalsframework/pdfs /metals-risk-assessment-final-3-8-07.pdf
7. Geczi A, Bodis K, 2003, Regional Examination of Metal Content in Soil
8. Measnicov, M., 1998, Lead Pollution
9. Measnicov, M., 1998, Heavy Metals Pollution
10. Perkin-Elmer, AAnalyst 700, Atomic Absorption Spectrometer User's Guide
11. WFEP Ministry 1997, Water, Forests and Environmental Protection Ministry Order no 756/1997 for approval of the Environmental Pollution Regulation, 303bis of 11/06/97