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HEAVY METAL CONTAMINATION AND DISTRIBUTION IN THE URBAN ENVIRONMENT OF JELGAVA

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Abstract
The growing economy with following industrialization and urbanization has led to environmental contamination with trace elements worldwide. In urban environment, the large inputs of anthropogenic contaminants in atmosphere are arising from mobile and stationary sources. The snow sample analysis is one of methods to monitor air contamination with heavy metals in urban areas. The aim of this research is to analyse heavy metal contamination and distribution in urban environment of Jelgava city. The samples were collected twice in January and February. Snow samples were collected in 20 urban area sampling plots and one natural area sampling plot with three repetitions taken from 1.0 to 1.5 kg of snow. The concentration of trace elements was estimated in 126 melted and filtrated snow water using inductively coupled plasma spectrometer (ICP-OES). The average heavy metals and nutrients concentrations were calculated for each sample. The concentrations data of trace elements were analysed using agglomerative hierarchical clustering method.
The results show differences between results in January and February. The differences are related to anthropogenic impact intensity differences during the exposition periods of snow. The clustering results of snow samples taken in January show three clusters, but snow samples taken in February show four clusters.
Key words: ICP-AES; air quality; snow; pollution.

Introduction

The growing economic activity leads to more intensive exploitation of natural resources. The mining and industrial use of minerals as well as usage of different chemicals in agriculture and households lead to air pollution with trace elements (Tchounwou *et al*., 2014). The snow geochemistry has become a topic of interest since Antarctica, Greenland and Arctic snow and ice trace elements research results were published (Candelone *et al*., 1996; Gabrielli *et al*., 2005a; Barbante *et al*., 2011; Barbante *et al*., 2003; Shotyk *et al*., 2005). The anthropogenic impact on trace elements distribution are investigated in the Andes (Correia *et al*., 2003) and some studies have been done next to urbanised areas in the European Alps (Van de Velde *et al*., 2000; Schwikowski *et al*., 2004). Snow as an indicator for urban air pollution is used in several studies (Dossi *et al*., 2007; Engelhard *et al*., 2007).

Many of trace elements are hazardous (e.g. Cd, Pb, Ni) for human health and ecosystem (Wiener *et al*., 2003). The major trace elements are associated with both natural and industrial processes (Gabrielli *et al*., 2008). The sources of industrial air pollution trace elements are different: fossil and oil combustion (As, Cu, Co, Cr, V, Ni, Sb, Fe, Mn, Zn, Sn, Mn, Pb, Fe, Ni); waste water management (Pb, Zn); steel production (Cr, Mn, Ni, Co); transport emissions (Pb, Cu, Cr, Sn, Sb) and others (Pacyna & Pacyna, 2001). The concentrations of trace element in troposphere are with high temporal and spatial variability (Melaku *et al*., 2008). Snow samples with short exposition period are analysed in several studies. The trace elements from transport emissions in snow cover at roadsides and crossroads have been analysed (Loranger *et al*., 1996; Engelhard *et al*., 2007; Vasić *et al*., 2012). The significant anthropogenic emissions of trace elements related with industrial gases and energetic sector were found in long term trace element monitoring by Moreno *et al*. (2011).

The aim of this research is to analyse concentrations and distribution of trace elements in urban environment of Jelgava city. The objectives are (1) to analyze the composition of metal in snow in Jelgava city; (2) to analyze the distribution of metals in different places of Jelgava city and to conduct cluster analysis; (3) to compare the concentrations of metals in different places of Jelgava city taken in January and February.

Materials and Methods

Study area

Jelgava city has an area of 60.3 km^2 and more than 57000 inhabitants. The climate in Jelgava is cold and temperate. The yearly average temperature is 6.5 °C and average annual precipitation is 642 mm. Snow cover is normally from November till March, and the length of snow exposition period is impacted by local meteorological conditions such as city heat island influence. The main wind direction is from southwest. The research area is an urban territory of Jelgava city with different urbanisation level. Sampling plots were chosen close to transport corridors, industrial areas and living areas. The additional spot *Mežciems* was chosen in forest area in south west direction from the city centre to identify transboundary air pollution with trace elements. The sampling plots description is presented in Table 1.

Table 1

Sampling plots coordinates and anthropogenic pressure

No	Name of sampling point	X coordinate	Y coordinate	Characteristics of anthropogenic impact
1	Viskaļu str./Lietuvas str.	483086.650	6275689.140	Close to transit street and living area
2	Platones str./Lietuvas str.	482975.520	6276218.310	Close to transit street and living area
3	Savienības str./Lietuvas str.	483293.026	6276805.680	Close to transit street road and
4	Train station	483525.860	6277369.250	Jelgava train station
5	Tērvetes str./railway	481838.609	6276571.000	Transit street and railway
6	Rūpniecības str./Tērvetes str.	482043.660	6276941.400	Transit street and gasoline station
7	Tērvetes str./Pavasara str.	482380.199	6277740.316	Urban area with street canyon
8	Lielā str./Kalpaka str.	482241.609	6278438.223	Open area close to mine street
9	Lielā str./Dobeles str.	481903.940	6278612.119	Between two main streets
10	Aspazijas str./Asteru str.	481388.500	6278423.200	Open area close to school
11	Dobeles str./Satiksmes str.	481436.100	6278707.899	Main street and car roadworthiness test centre
12	Satiksmes str./Ganību str.	481507.072	6279135.466	Main street and gasoline station
13	Ausekļa str./Blaumaņa str.	482801.400	6279119.060	City market and intensive traffic
14	Pasta island	483563.400	6278804.200	Open are between rivers close to main street
15	Rīgas str./Brīvības str.	484290.526	6279236.721	Open are three main streets and gasoline station
16	Prohorova str./Neretas str.	485513.400	6278465.500	Industrial area
17	Garozas str./Rubeņu str.	485772.690	6278788.330	Near to railway
18	Aviācijas str./Lāčplēša str.	485302.390	6279209.020	Industrial area
19	Rīgas str./Loka str.	485437.330	6280722.440	Intensive traffic gasoline station
20	Institūta str./Rīgas str.	484630.350	6279806.980	Intensive traffic car parking area
21	Mežciems	486643.054	6277428.039	Natural area

Sampling strategy

The samples were collected twice in January and February with snow exposition period 7 days. The snowing was on the second of January and seventh of February, and sampling was done on 10^{th} of January and 14^{th} of February. Three snow samples were collected during each sampling period in each sampling plot. Plastic bags and gloves were used to avoid negative artefacts during snow sampling. The snow cover was collected via the use of a pre-cleaned Plexiglas device and a plate. Each snow column was taken from the whole depth of snow.

The concentration of trace elements was estimated in the 126 melted snow water and HNO3 solution samples using inductively coupled plasma spectroscopy (ICP-OES) method. The average concentrations of Cd, Cu, Pb, Ca, Mg, Na, Fe, Zn, Ni, Cr, Mn, K, As, Co, Li, Sr, Ti, Tl, Ba, V, Al, P and Sb were calculated for each sample. The sampling plot average concentrations standardised values for January and February concentrations data were analysed using agglomerative hierarchical clustering method.

Results and Discussion

Snow samples were collected in January and content of 26 trace elements have been analysed using ICP-OES. The concentrations of Cu, Pb, Ca, Mg, Na, Fe, Zn, Ni, Cr, Mn, K, Co, Li, Sr, Ti, Ba, Al, P were different between samples and other elements concentrations were smaller than instrument error, and they were excluded from further analysis. Snow samples taken in January, average trace elements concentration data cluster dendogram is presented in Figure 1.

There are three separate clusters with different trace element concentrations. The first cluster represents areas close to main streets with intensive traffic. The concentrations of Cu, Pb, Fe, Zn, Ni, Cr, Mn, Co, Li, Ti, Ba, Al, P are low and close to natural sample concentrations, see Table 2. The concentrations of Ca (4.5 ± 2.31 mg L^{-1}); Mg (1.6 ± 0.85 mg L^{-1}); Na (13.0 ± 1.49 mg L^{-1}); K (0.8 ± 0.6 mg L^{-1}) and Sr (7.3 ± 2.3 µg L^{-1}) are higher than second and third cluster and significantly higher than that in pristine areas (Shevchenko, 2016).

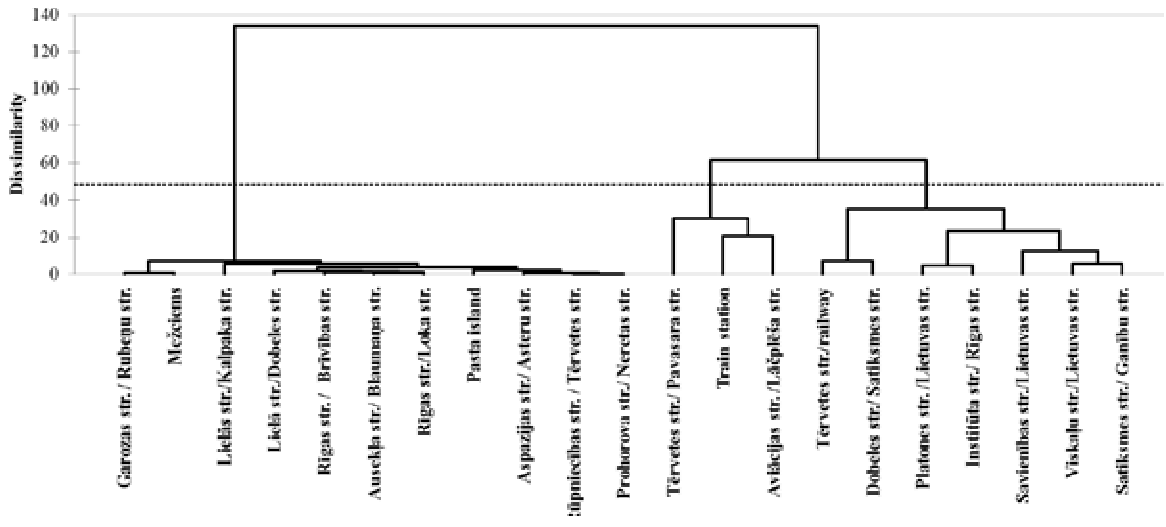

Figure 1. Dendogram of cluster analysis of snow samples taken in January.

Table 2

The mean ad standard deviation of trace elements by cluster for snow samples taken in January

Trace element	Measurement unit	1st cluster			2nd cluster			3rd cluster		
		No. of observations	Mean	Standard deviation (n-1)	No. of observations	Mean	Standard deviation (n-1)	No. of observations	Mean	Standard deviation (n-1)
Cu	μg L^{-1}	21	3.3	0.834	9	28.7	4.220	33	2.4	0.791
Pb	μg L^{-1}	21	1.2	0.669	9	7.3	0.876	33	0.9	0.608
Ca	mg L^{-1}	21	4.5	2.314	9	3.5	1.242	33	1.4	0.515
Mg	mg L^{-1}	21	1.6	0.850	9	1.2	0.531	33	0.5	0.191
Na	mg L^{-1}	21	13.0	1.493	9	10.7	7.918	33	2.7	2.584
Fe	mg L^{-1}	21	0.2	0.107	9	0.3	0.153	33	0.1	0.030
Zn	μg L^{-1}	21	44.5	11.346	9	101.2	23.963	33	32.2	12.535
Ni	μg L^{-1}	21	0.5	0.031	9	0.8	0.099	33	0.5	0.105
Cr	μg L^{-1}	21	0.3	0.103	9	0.6	0.134	33	0.3	0.003
Mn	μg L^{-1}	21	16.8	10.454	9	18.7	2.633	33	7.1	1.980
K	mg L^{-1}	21	0.8	0.643	9	0.3	0.133	33	0.2	0.010
Co	μg L^{-1}	21	0.2	0.025	9	0.2	0.021	33	0.2	0.004
Li	μg L^{-1}	21	0.2	0.033	9	0.2	0.058	33	0.1	0.020
Sr	μg L^{-1}	21	7.3	2.304	9	6.3	1.148	33	3.1	1.118
Ti	μg L^{-1}	21	2.6	0.922	9	3.8	0.994	33	1.1	0.605
Ba	μg L^{-1}	21	8.5	2.194	9	20.2	6.738	33	6.7	3.064
Al	mg L^{-1}	21	0.1	0.015	9	0.1	0.014	33	0.0	0.011
P	mg L^{-1}	21	0.0	0.009	9	0.0	0.021	33	0.0	0.005

Figure 2. Spatial distribution of cluster analysis of snow samples taken in January.

The second cluster includes three sampling plots close to railway and industrial area. This cluster characterises with relatively low concentrations of Ca, Mg, Na, K, Co, Li, Sr, Al, P. The concentrations of Cu (28.7 ± 4.22 µg L^{-1}); Pb (7.3 ± 0.85 µg L^{-1}); Fe (0.3 ± 1.5 mg L^{-1}); Zn (101.2 ± 23.96 µg L^{-1}); Ni (0.8 ± 0.1 µg L^{-1}); Cr (0.8 ± 0.1 µg L^{-1}); Mn (18.7 ± 2.6 µg L^{-1}); Ti (3.8 ± 0.99 µg L^{-1}); Ba (20.2 ± 6.74 µg L^{-1}) are higher than the first and third cluster and significantly higher than in natural areas (Shevchenko, 2016). The higher concentrations of Cu, Pb, Fe, Zn, Ni, Cr, Mn are associated with fossil and oil combustion (Pacyna & Pacyna, 2001).

The third cluster represents relatively clean areas with low concentrations of all trace elements. The snow sample plots classified in the third cluster are mostly open areas with some green infrastructure. The spatial distribution of clusters is presented in Figure 2.

Snow samples were collected in February and the content of 26 trace elements has been analysed using ICP-OES. The concentrations of Cd, Cu, Pb, Ca, Mg, Na, Fe, Zn, Ni, Cr, Mn, K, As, Co, Li, Sr, Ti, Tl, Ba, V, Al, P, Sb were different among samples and other elements' concentrations were smaller than instrument error, and they were excluded from further analysis. Snow samples taken in February average

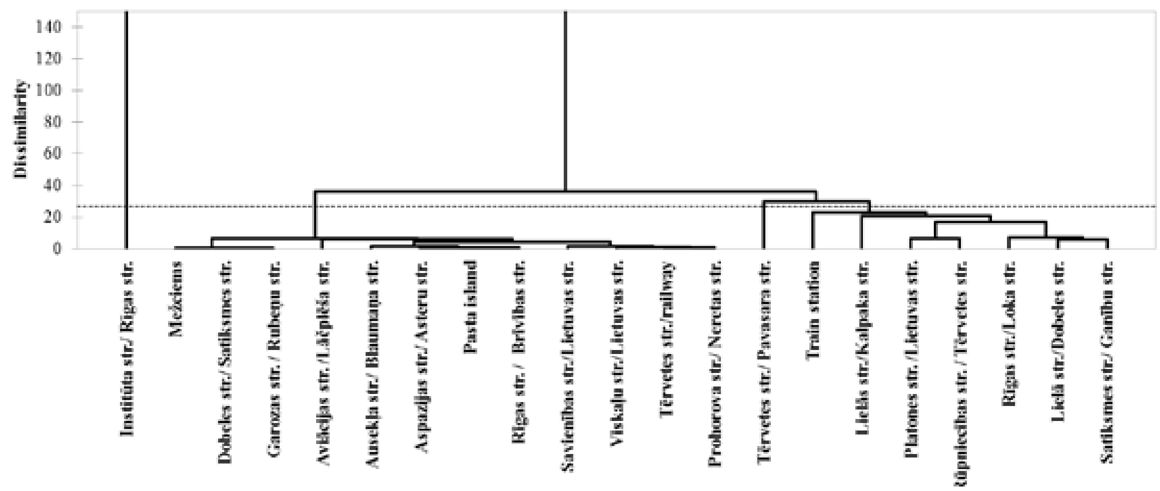

Figure 3. Dendogram of cluster analysis of snow samples taken in February.

Table 3

The mean ad standard deviation of trace elements by cluster for snow samples taken in February

Trace element	Measurement unit	1st cluster			2nd cluster			3rd cluster			4th cluster		
		No. of observations	Mean	Standard deviation (n-1)	No. of observations	Mean	Standard deviation (n-1)	No. of observations	Mean	Standard deviation (n-1)	No. of observations	Mean	Standard deviation (n-1)
Cd	$\mu g\ L^{-1}$	36	0.2	0.000	21	0.2	0.055	3	0.2	0.185	3	0.4	0.185
Cu	$\mu g\ L^{-1}$	36	15.5	16.141	21	29.9	13.677	3	10.4	0.625	3	150.4	0.625
Pb	$\mu g\ L^{-1}$	36	6.0	3.093	21	15.6	6.327	3	24.3	0.780	3	31.9	0.780
Ca	$mg\ L^{-1}$	36	23.0	13.693	21	45.1	34.135	3	14.4	0.025	3	259.6	0.025
Mg	$mg\ L^{-1}$	36	9.0	5.534	21	18.3	13.952	3	5.7	0.002	3	118.5	0.002
Na	$mg\ L^{-1}$	36	9.1	9.558	21	17.4	23.954	3	41.6	0.024	3	20.2	0.024
Fe	$mg\ L^{-1}$	36	1.1	0.588	21	2.7	1.523	3	0.4	0.003	3	14.6	0.003
Zn	$\mu g\ L^{-1}$	36	76.5	39.684	21	204.5	179.944	3	125.9	1.189	3	680.6	1.189
Ni	$\mu g\ L^{-1}$	36	1.4	0.570	21	3.1	1.367	3	0.9	0.309	3	11.8	0.309
Cr	$\mu g\ L^{-1}$	36	1.3	0.626	21	4.1	2.128	3	1.2	0.280	3	14.0	0.280
Mn	$\mu g\ L^{-1}$	36	97.7	51.036	21	178.8	87.448	3	62.8	0.099	3	983.6	0.099
K	$mg\ L^{-1}$	36	0.5	0.325	21	0.6	0.140	3	1.9	0.059	3	1.6	0.059
As	$\mu g\ L^{-1}$	36	1.9	0.000	21	2.1	0.201	3	1.9	1.912	3	3.5	1.912
Co	$\mu g\ L^{-1}$	36	0.7	0.262	21	1.2	0.415	3	0.4	0.216	3	7.5	0.216
Li	$\mu g\ L^{-1}$	36	0.7	0.331	21	1.4	0.840	3	0.4	0.021	3	9.6	0.021
Sr	$\mu g\ L^{-1}$	36	18.4	9.445	21	38.4	20.600	3	29.5	0.104	3	173.5	0.104
Ti	$\mu g\ L^{-1}$	36	16.4	7.802	21	27.9	8.458	3	4.9	0.071	3	192.0	0.071
Tl	$\mu g\ L^{-1}$	36	0.8	0.000	21	0.8	0.006	3	0.8	0.804	3	0.8	0.804
Ba	$\mu g\ L^{-1}$	36	27.4	20.499	21	87.7	83.590	3	32.0	0.581	3	222.1	0.581
V	$\mu g\ L^{-1}$	36	1.3	0.562	21	2.7	0.757	3	0.7	0.394	3	13.5	0.394
Al	$mg\ L^{-1}$	36	0.4	0.174	21	0.8	0.332	3	0.3	0.001	3	4.0	0.001
P	$mg\ L^{-1}$	36	0.1	0.079	21	0.3	0.064	3	1.9	0.003	3	1.2	0.003
Sb	$\mu g\ L^{-1}$	36	1.3	0.030	21	1.7	0.402	3	1.3	1.330	3	3.5	1.330

Figure 4. Spatial distribution of cluster analysis of snow samples taken in February**.**

trace elements concentration data cluster dendogram is presented in Figure 3.

The clustering results are quite different from January clusters, and it is related to extremely high traffic during snow exposition period. The February data are characterised with much higher concentrations of trace elements. The first cluster represents relatively clean areas and all trace elements concentrations are lower than for other clusters (see Table 3). The second cluster represents areas close to main streets; however, the third and fourth clusters consist of one sampling area.

Results show changes of snow contamination with metals affected by atmospheric deposition. Despite similar snow exposition time during winter period traffic and pyrogenic dust and aerosols reaches snow cover. These data strongly correlates with cultural and art events in the city providing increased traffic intensity and therefore emissions from transport.

Conclusions

The cluster analysis of snow samples taken in January and February show different cluster spatial and temporal distribution.

The February data clustering results show high anthropogenic impact related with fossil and oil combustion.

The future research has to concentrate on multidimensional analysis of point source and non-point source pollution impact on heavy metal spatial and temporal distribution in urban areas.

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