Evaluation of Zinc Accumulation in Moss (*Pylaisia polyantha*) Growing Near Intensive Traffic Street Based on Modelling and Experimental Data

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Abstract: *Pylaisia polyantha* moss growing near intensive traffic in Geležinis Vilkas street at Vingis Park (Vilnius) was selected as an indicator of environmental pollution. Two models were applied for the study: the Gaussian plume model – for zinc emission from automobiles calculation and mathematical model – for recalculating the zinc emission from transport to zinc concentration in moss. Moss samples were collected during spring, summer and autumn. There were no significant changes in Zn concentrations between these periods. Zn emission dispersion from pollution source was calculated only for one vehicle, in order to reach relationships between environmental conditions and dispersion of Zn emission from vehicle exhaust fumes pipe. It was detected that the concentration of Zn tends to decrease with the distance from the pollution source. It was observed that there was a strong relationship between wind speed and Zn concentration – the slower the wind speed, the higher concentration of zinc in moss.

Keywords: zinc, moss, atomic absorption spectroscopy, Gaussian plume model

1. Introduction

Pollution of environment is increasing now. Transportation is one of main polluters of the environment, which emits various pollutants to the environment. Transportation emits various heavy metals (HM). Zinc is not the most dangerous among other heavy metals, but its emission from transportation is one of the highest. Heavy metals and other pollutants in moss are currently the focus of attention in various countries, as moss is an excellent indicator of environmental pollution (Koz et al. 2014, Oishi 2019, Oishi 2018, Parmar et al. 2016, Pīrāga et al. 2017, Salo 2014, Sujetovienė & Galinytė 2016, Špirić et al. 2014, Urošević et al. 2018, Vuković et al. 2015, Zhu et al. 2018). HM are potentially toxic substances that enter foodstuffs from the environment, enter the human body through food, and are readily integrated into the biological cycle. Each region

has its own pollution specific, which means that the total amount of HM in the moss is highly dependent on the area. Research needs to have as much comprehensive data as possible on the migration and accumulation of heavy metals in the environment and their effects on ecosystems and humans. Studies have shown that the quantity of heavy metals in moss depends on their location and distance to sites that emit heavy metals. From the air, heavy metals settle on the various surfaces. The main sources of anthropogenic pollution in the atmosphere are transportation; industry and energetics. Car emissions account for 60-70% of total emissions. The atmosphere, as a source of metals, is unique in that it has a very short life span, from day to week (I don't understand what you are trying to say, please check). However, even in such a short time, metal particles can travel long distances. Also, metal compounds released into the atmosphere are deposited on the plants at a distance of 10 to 40 km from the source of pollution. The sources of Zinc emissions are many: metalworking industry, transport, energy, fertilizers, and pesticides. It belongs to the intensive accumulation of technogenic dust (Radzevičius et al. 2004). According to Blok (2005) the emissions of zinc along roads originate from: wearing of brake lining; losses of oil and cooling liquid; wearing of road paved surface; wearing of tyres; corrosion of galvanized steel safety fence and other road furniture. The aim of the research was to use moss as an indicator for the assessment of environmental pollution by zinc near intense traffic street, to calculate emission of zinc from cars and to compare experimental results with modelling results.

2. Materials and methods

2.1. Study site

Vingis Park, the largest park in Vilnius, is located at the bend of the Neris River in Vilnius and covers an area of 160 hectares (Vingis park).

The area of investigations (54⁰40'28" N; 25⁰14'32" E) is situated between the park of Vingis and Geležinis Vilkas street (Fig. 1). All samples of moss (*Pylaisia polyantha)* were taken in this order: 5, 10, 15, 20, 25 meters from the Geležinis Vilkas street (Fig. 1).

Control samples of moss, in order to evaluate background level of zinc concentration in moss were taken around 500 meters from Geležinis Vilkas street at Vingis park. Samples of moss were taken on 7th of March, on 21st of August, on 14th of November. According to the methodology of moss sampling for EU surveys, samples should be taken in all seasons, except winter, because in winter mosses are covered with snow. During all three samplings of moss there was no rain or snow.

Fig. 1. Sampling places in Vingis park (Vilnius), near Geležinis Vilkas street

2.2. Climate conditions of study site

The pollutant emissions are transported to different distances, depending on the geographic area, its geology and the local meteorological factors: fog, wind, rains, thermal inversions (Dobra et al. 2006). The climate of Vilnius region is considered as humid continental or hemiboreal by Köppen climate classification. The average annual temperature is $+6.1°C$, in January the average temperature is $-5.8°C$, in July it is $+17.4°C$ (Climate-data). The average precipitation in Vilnius is about 655 millimetres per year (Climate-data). Dominant wind direction – southwest, speed 2.5-4 m/s (Lithuanian Hydrometereological Service).

2.3. Morphological identification of moss

Closely related moss species are often difficult to distinguish from each other than other plants, but it is easy to sample and collect (Banienė 2001, Rowantree et al. 2010). In Lithuania there are 350 species of moss, they all belong to 33 families (Banienė 2001). Each moss species, though much alike in terms of stems and leaves, tends to have different types of capsules (Tiny Shag Moss).

2.4. Sampling of moss

Most methods in heavy metal monitoring employ moss as bioaccumulators (Stihi et al. 2006). Sampling and sample handling was carried out using plastic gloves and bags. All forest debris from moss must be removed (Aboal et al. 2008). Moss samples were stored at room temperature until preparation for analysis.

2.5. Calculation of moisture content

Moisture content was calculated in moss:

$$M_n = \frac{(W_w - W_D)}{W_D} \cdot 100 \tag{1}$$

where: M_n – moisture content of sample, %, W_w – wet weight of the sample, g, W_d – weight of the sample after drying, g (moisture content).

2.6. Reagents and equipment

All chemicals and reagents were of analytical grade or higher purity and they were obtained from Sigma Aldrich (Germany) and used in the experiments as received without further purification. The solutions were prepared by mixing appropriate standards in deionized water from the water purification system (Demiwa 3 ROI). Metal standards made in VWR Chemicals (England) were used for GFAAS and FAAS calibration. The concentration of Zn (II) in used standard solution was equal to 1000 mg/L in 2% of HNO_3. All volumetric flasks used in the experiments were soaked for 24 h with 5M HNO_3 and then rinsed 3-4 times carefully with deionized water. All the volumetric flasks used were of the highest accuracy class. High accuracy analytical balance AS 60/220.R2 (Radwag, Poland) was used to weigh moss samples.

2.7. Sample preparation for metal analysis

The moss samples collected were prepared by a high-temperature dry oxidation method. Each moss sample (about 20 g) was dried in a muffle furnace until constant weight at 100 ±5°C. After that the temperature was gradually raised from (100°C/1h) to 500 ±20.0°C in a muffle furnace for 2 hours. The resulting ash was cooled to room temperature. The aqua regia (3:1, v/v, HCl to HNO_3) digestion procedure was used for analysing total-recoverable heavy metal (Zn) content in ashes. Concentrations of acid used for digestion of moss samples were the following: 36.5% (HCl) and 63% (HNO_3). The digestion of the moss samples (about 0.5 g) was performed by using microwave digestion system Milestone Ethos Touch Control (Milestone SRL, Italy) for about 50 min in Teflon containers. After cooling to room temperature, the solution was filtered through a 0.45 μm PTFE membrane filter, transferred quantitatively to a 50 mL volumetric flask and supplemented with deionized water to the mark. Deionized water used in experiments meets requirements of ISO 3696:1987 (Water for analytical laboratory use – Specification and test methods) standard. After, its concentration of Zn was analysed with an atomic absorption spectrophotometer, model 210 VGP, Buck Scientific (USA), equipped with a Buck Scientific model 220-GF graphite furnace atomizer and acetylene-air flame. 0.7 nm slit was selected for measurement of zinc concentrations in solutions. 213.9 nm wavelength was

used during measurements. The content of Zn in moss ash (mg/kg) was calculated by formula (2):

$$C = \frac{Ce \cdot V \cdot k \cdot 1000}{m} \qquad (2)$$

where: C – the concentration of analyte in sample, mg/kg, C_e – the concentration of the analyte in solution, mg/mL, V – the volume of the sample, mL, k – the dilution factor, m – the amount of moss ash taken for the test, g.

Zn analysis method used for the moss was validated by using a recovery analysis. The percentage recoveries were calculated by using the following equation (Sarker et al. 2015):

$$\text{Percentage recovery} = \frac{C_E}{C_M} \cdot 100 \qquad (3)$$

where: C_E – the experimental concentration that was determined from the calibration curve, C_M – the spiked concentration.

According to the European Commission (2003), a method can be considered accurate and precise when the accuracy of the data is between 70 and 110%. Experimental result meets these requirements.

2.8. Quality control and statistical evaluation

The concentration of Zn in used standard solution was equal to 1000 mg/L in 2% of HNO_3. Working aqueous standard solutions containing Zn was prepared by serial dilution of the certified reference metal standard solution for atomic absorption spectroscopy with deionized water. Three samples of moss were taken from each place. All experiments were conducted in triplicate. Two blanks (without Zn ions) were used for each zinc concentration determination. Statistical analysis of data was carried out using Excel and Statistica software. Arithmetic average, standard deviation, confidence intervals and Pearson coefficients were estimated at $p < 0.05$.

2.9. Theoretical calculation

60 km/h – allowable speed at Geležinis Vilkas street in Vilnius near Vingis park. It was assumed that for 100 km, vehicle uses 10 l of petrol in the city, e.g. 1 automobile consumed 6 l of petrol per hour. Traffic intensity at Geležinis Vilkas street is 1200 vehicles per hour. Total fuel consumption per hour in investigated area will be 7200 l. The density of fuel (in this model only petrol fuel was evaluated) is 770 g/L (What are the types of fuel). Zinc emission factor for vehicles in mg/kg is equal to 1 for passenger car (Road transport). Total emissions of zinc per 1 hour in investigated area is equal to 0.00154 g/s.

2.10. Mathematical modelling

In a Gaussian plume, the spatial distribution of concentration along a transverse axis is Gaussian in shape. The following steady state 3-dimensional model describes the concentration at any point in a coordinate system where the wind is moving parallel to the x-axis (Gaussian plume model):

$$C(x,y,z) = \frac{Q}{2\pi \cdot u \cdot \sigma_y \sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2} \right) \right] \exp\left[-\frac{1}{2}\left(\frac{H^2}{\sigma_z^2} \right) \right] \tag{4}$$

where: C – concentration of contaminant, g/m^3, x, y, z – distance from origin in x, y, z coordinates, m, H – effective stack height, m, Q – rate of emission of gas, g/s, σ_y, σ_z – horizontal and vertical plume standard deviations (m), each a function of x, u – wind speed at effective stack height, m/s.

The input data of the model are presented in the Table 1.

Table 1. Input data for mathematical modelling of Zn dispersion in atmosphere

Input data	Value
Stack height, m	0.3
Stack diameter, m	0.1
Emission	
Zn emission rate, g/s	0.00154
Gas velocity in the pipe of car, m/s	1.0
Gas temperature in the pipe of car, °C	200
Atmospheric condition	3 – slightly unstable
Ambient average temperature, °C	
Spring	6.2
Summer	16.8
Autumn	7.1

The emission of zinc downwind from the vehicle (in this case vehicle is a stack) was simulated. Input parameters needed for simulating, are as follows: the height of the stack above the ground (in meters); the diameter of the opening of the stack (in meters); the velocity of the gas emitted from the stack (in meters per second); the temperature of the gas as it exits the stack (in degrees Celsius); the rate at which pollution is emitted from the stack (in grams per second); the atmospheric stability; the number of wind velocities that you wish to investigate; the wind velocities; the number of distances downwind to calculate; the actual distances downwind. The atmospheric stability categories accounts for

the fact that a parcel of air changes temperature as it changes in altitude. With this input data, it is possible to calculate the concentration of the pollutant at various locations downwind from the stack, usually measuring from 0 kilometers (the base of the stack) down to 100 km from the stack (Gaussian plume model).

3. Results and discussion

3.1. Moisture content in moss

18 samples were taken from Vilnius Vingis park, near Geležinis Vilkas street. The average results from three seasons of moisture content in samples of moss are presented in Fig. 2.
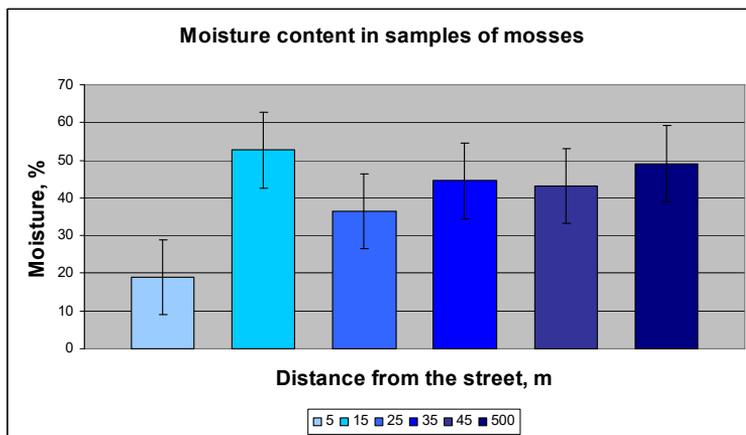
Fig. 2. An average results from three seasons of moisture content in moss

In moss which were located 5 meters from the street, the moisture content was determined as 18.96%. In collected *Pylaisia polyantha* moss which were located at the distance of 15 meters from the street - the average moisture content was 52.65%. In moss which were collected 25 meters from the street the moisture content was 36.44%. In moss located at a distance of 35 meters from the street the moisture content was 44.55%. In samples of moss which were collected at 45 meters from the street the moisture content was 43.22%. In the control samples 49.07% of moisture content was detected.

3.2. Zn concentration in sample of moss

Zn concentration was determined in samples of *Pylaisia polyantha* moss, along the high intensive traffic Geležinis Vilkas street in Vilnius. Zinc concentrations in moss (*Pylaisia polyantha*) growing near Geležinis Vilkas street are presented in Fig. 3. (in spring, in summer and in autumn).

There is a direct relationship between the Zn content found in moss and the distance from the Geležinis Vilkas street. It was observed that Zn content in all samples of moss tends to decrease with the distance from the Geležinis Vilkas street.

a)

b)

c)
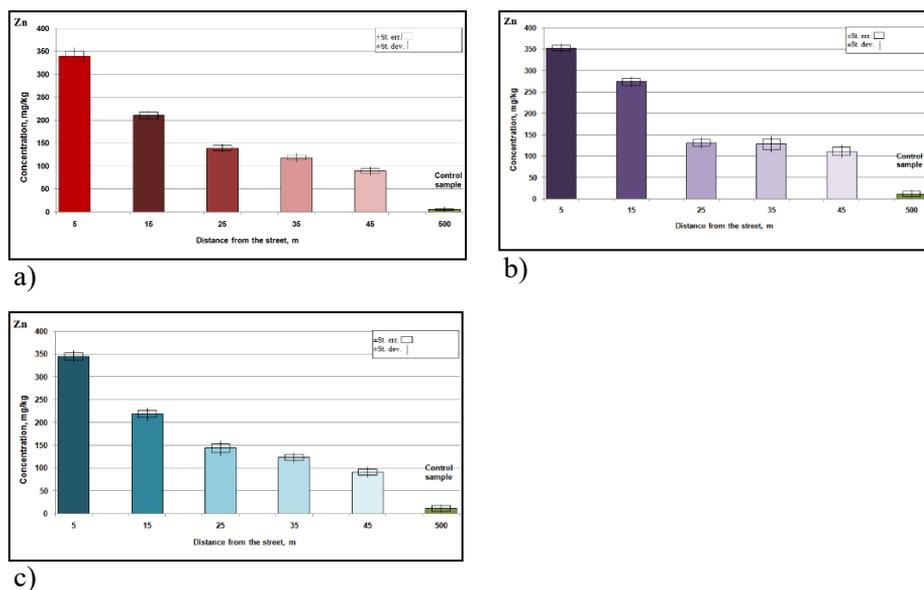
Fig. 3. Zinc concentrations in moss near Geležinis Vilkas street: a) in spring, b) in summer, c) in autumn

At the distance 5 and 15 meters from the Geležinis Vilkas street Zn concentrations were considerably high and it reveals that the moss near intensive traffic were heavily polluted (Fig. 3). At a distance of 5 meters from the street, the highest concentration of zinc – 339.96 ±10.72 mg/kg in dried moss (Fig. 3) was observed. In samples of moss at 15 meters distance from the street, the concentration of zinc was lower – 210.47 ±7.24 mg/kg. In 25 meters from the street zinc concentration decreased till 139.47 ±5.24 mg/kg. In 35 meters from the street, zinc concentration decreased till 118.44 ±5.37 mg/kg. The lowest concentration of zinc in samples of moss was observed at the 45 meters from the intensive traffic – 89.52 ±5.34 mg/kg. In control sample quite low concen-

tration of Zn was determined – 6.03 ±2.15 mg/kg. Control sample was 41 times lower in concentration of zinc than the sample located at 5 meters from the street. It can be stated that Zn emission source could be high around intensive traffic flow in Geležinis Vilkas street (Fig. 3a).

At a distance of 5 meters from the street it was observed that the highest concentration of zinc – 352.14 ±6.52 mg/kg in dried moss (Fig. 3b) was in summer. In samples of moss at a distance of 15 meters from the street, the concentration of zinc was lower – 273.75 ±8.40 mg/kg. In 25 meters from the street, the concentration of zinc was equal to 128.01 ±11.98 mg/kg. The lowest concentration of Zn was observed at 45 meters from the Geležinis Vilkas street – 110.74 ±10.15 mg/kg. In control sample of moss small concentration of Zn was determined – 7.49 ±7.133 mg/kg, it was 47 times lower than closer to the (in 5 meters) pollution source (Fig. 3b).

At a distance of 5 meters from the street, it was observed that the highest concentration of zinc – 344.65 ±7.84 mg/kg in dried moss (Fig. 3c) was in autumn. In samples of moss at a distance of 15 meters from the street, the concentration of zinc was lower – 217.82 ±7.81 mg/kg. At a distance of 25 meters from the street, zinc concentration decreased till 143.71 ±9.52 mg/kg. In 35 meters from the street, zinc concentration decreased till 123.19 ±6.38 mg/kg. The lowest concentration was observed at 45 meters from the Geležinis Vilkas street – 90.88 ±6.86 mg/kg. In the control sample small concentration of Zn was determined – 6.17 ±6.13 mg/kg – 56 times lower concentration than in distance of 5 meters (Fig. 3c).

3.3. Zinc emissions from transport into atmosphere

Emission of zinc from transport in Geležinis Vilkas street is presented in Fig. 4. (in spring, in summer and in autumn).

The highest emission of zinc was calculated at 5 meters from the pollution source, this congruous (I don't understand what you are trying to say, please check) with the results from collected samples of moss, moreover, concentration tends to decrease from the source in both (real and modelled) cases in spring. According to the Lithuanian Hydrometeorological Service under Ministry of Environment, an average of annual wind speed in Vilnius is 4 m/s. Accumulation of Zn has a strong relationship with the speed of wind. The highest concentrations of Zn near emission pollution source in the atmosphere were detected when wind speed was low (Fig. 4 a).

a)

b)

c)
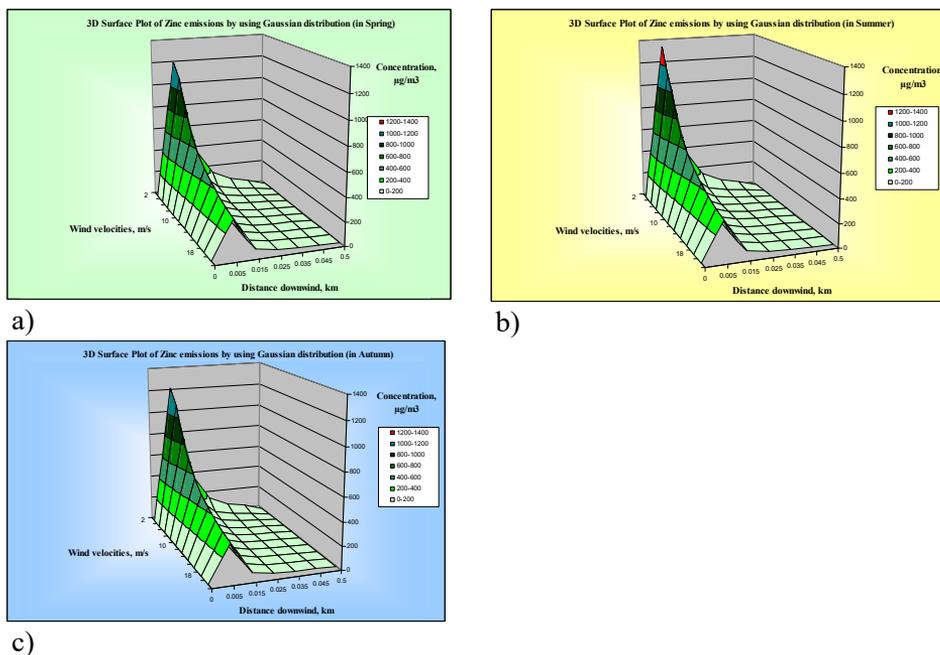
Fig. 4. 3D surface plot of Zn emission based on Gaussian distribution: a) in spring, b) in summer, c) in autumn

In summer, the situation is almost the same like during the spring period. Zn emission had the tendency to decrease with the distance from pollution source. The relationship of wind and zinc concentration is also the same. During summer modelling, one more relationship was observed. The concentration tends to increase with higher temperature, comparing with spring and autumn. This relationship is presented in Fig. 4b, where concentration of zinc at 5 meters reaches more than 1200 $\mu g/m^3$ (in red colour) when the wind speed was 2 m/s. This tendency is similar to results of analysed samples, where Zn concentration was slightly higher in summer period than in spring. Moreover, the highest concentrations of Zn were found during the summer period.

The situation in autumn was almost the same like in spring (Fig. 4c). This was due to the similarity of average ambient temperature (spring 6.2°C and autumn 7.1°C). Strong relationship between wind speed and Zn concentrations near pollution source was observed. Lowest concentrations of zinc were simulated when the speed of wind is higher. Concentration of Zn had the tendency to decrease with the distance from the pollution source – Geležinis Vilkas street.

3.4. Correlation of experimental and modelling data

Correlations between experimental and modelling data were performed by the Excel and software STATISTICA (Fig. 5).

For determination of correlation, Pearson coefficient was used. Correlation between experimental data and modelling results was determined. The calculated Pearson correlation coefficient for zinc was high – r = 0.8738.
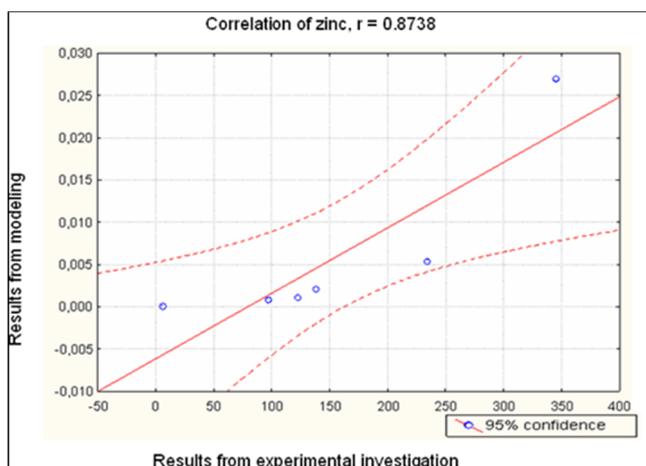
Fig. 5. Correlation between experimental and simulated results for zinc

This shows, that real results and modelling results have strong relationships, moreover, this helps to prove, that high concentrations of zinc were determined due to pollution from intensive traffic (Fig. 5).

3.5. Comparing of modelling and experimental data

After modelling, experimental data and simulated results were compared. The hypothesis of this calculation was such that traffic influences Zn concentration in moss, therefore in order to get clear result of transport impact, from all concentrations at different distances it is necessary to make a subtraction of background pollution, for this case:

Concentration in moss - concentration of control sample = Concentration of HM caused by transport. This mathematical equation was suggested:

$$C_{in\ moss} = K \cdot (C_{modelled\ results})^n \tag{5}$$

where: $C_{in\ moss}$ – concentration of Zn in moss from modelling results, K – empirical coefficient, which converts results from mg/m^3 to mg/kg, n – empirical coefficient.

The empirical coefficients K and n (K = 300 and n = 0.346) was calculated. All results and formulas for calculations are presented in Table 2.

From Table 2 it can be seen, that simulated results are quite similar to investigation results, differences vary from 0.01 to 25%. In order to evaluate investigation results, a mathematical model based on Gaussian plume was performed. All data analysis were made in three main steps: mathematical modelling, calculation of correlation and, finally, in order to make sure that results from mathematical modelling and experimental results can be compared, error of calculation for Zn was calculated.

Table. 2. Comparison of experimental and modelled results of zinc concentrations

Distance	(t, v)	Real results from experiment	Modelled results, mg/m^3	Error	Converted results from modelling
m	°C; m/s	mg/kg	mg/m^3	%	mg/kg
				$f = (d\text{-}g\text{-}m) \cdot 100 /(d\text{-}m)$	$C_{in\,moss} = K \cdot (C_{modelled\,results})^n$
Spring period					
5		339.96	1.08857	-1.85908	339.83347
15		210.47	0.22379	3.70181	196.59083
25	6.2; 4	139.47	0.08475	-5.51755	140.49345
35		118.44	0.04389	0.20111	111.89152
45		89.52	0.02674	-13.3082	94.26109
500		6.33	0.00023	–	–
Summer period					
5		352.14	1.13358	-1.11259	344.63114
15		273.75	0.22480	24.97441	196.89790
25	16.8; 4	131.55	0.08489	-16.9061	140.57256
35		128.01	0.04393	4.10017	111.92373
45		110.74	0.02675	5.19154	94.27753
500		5.08	0.00023	–	–
Autumn period					
5		344.652	1.09489	-2.15008	340.51526
15		217.816	0.22394	4.78291	196.63470
25	7.1; 4	143.71	0.08477	-6.11661	140.50475
35		123.188	0.04390	-0.01084	111.89612
45		90.877	0.02675	-18.4616	94.263436
500		6.17	0.00023	–	–

Simulation model showed few strong important relationships with conditions of the atmosphere. First is wind speed – the slower the speed – the higher the concentration of Zn near the emission source. Second is – the higher the temperature – the higher the concentration of Zn, especially near pollution source. That is why the model from summer period had the highest concentration of Zn. On the other hand, model does not include rain and snow precipitation. Emission factor simulated for Zn was calculated and other input data was chosen according to an average for one passenger automobile, which is the main reason why it was difficult to expect accurate results.

It is important to note that the mathematical model was prepared for one passenger car, in order to get main relationships between Zn dispersion and atmospheric conditions. The results would be very inaccurate results if they were simulated for all 1200 vehicles, because all vehicles have different technical characteristics – age, type of vehicle (passenger, bus, etc.) engine and fuel type, different speed, different situations in traffic (peak hours, etc.).

4. Conclusions

For monitoring of zinc atmospheric deposition, it is popular to apply terrestrial moss, because moss do not have any roots, their surface is large, they grow in wide-spread population in groups, they have long life cycle, they survive in the high-polluted environment, they are able to obtain nutrients from wet and dry deposition and clearly reflect the atmospheric deposition. All these environmental characteristics prove that moss is a good indicator in airborne pollution monitoring, especially in HM monitoring.

Samples of moss accumulate high amounts of precipitation, according to the calculations, moisture in *Pylaisia polyantha* moss were in the range of 13.82-60.07%. Results of moisture content show that it is important to take large amount of samples during sampling process, because after the drying of moss, the sample can be lost due to underweight. According to the measurement, the ratio of mass - loss in samples of moss was 73.28-83.18%.

Investigation results of this work clearly present a strong traffic-related gradient - zinc concentrations in samples of moss tends to decrease with distance from the source of pollution – Geležinis Vilkas street. At the distance 5 and 15 meters from the Geležinis Vilkas street Zn concentrations were considerably high and it reveals that the moss *Pylaisia polyantha* near intensive traffic are heavily polluted.

Sample of moss were collected three times in different sessions (spring, summer, autumn). There were no significant changes in Zn concentrations between these periods. Results of different seasons vary in range of 3-10 mg/kg for Zn. This insignificant variation could be due to short period of investigation.

The highest concentration of zinc accumulated in samples of *Pylaisia polyantha* was recorded at 5-meter distance from the street. The highest concentration of zinc was found during summer season – 352.14 ±6.52 mg/kg. At the distance of 15 meters from the street the highest concentration of zinc was also found in summer season – 273.75 ±8.40 mg/kg. At 25 meters from intensive traffic Zn concentration in autumn season was 143.71 ±9.52 mg/kg. The highest concentration of Zn at the 35 meters from intensive traffic flow was 128.01 ±11.98 mg/kg. At 45 meters from the street moss contain 110.74 ±10.15 mg/kg of zinc and this was the highest concentration, which was determined in summer season. In sample of control at 500 meters was found 6.325 ±2.13 mg/kg of Zn.

Mathematical modelling results based on Gaussian plume is presented. Zn emission dispersion from pollution source was calculated only for one vehicle, in order to reach as clear as possible relationships between environmental conditions and dispersion of Zn emission from vehicle exhaust fumes pipe. It was not possible to calculate total pollution, caused by highly intensive traffic, because there are no accurate data about different types of vehicles, for example: engine type, fuel type, age and other factors, which could have an influence on the modelling results. It was observed during modelling, that the concentration of Zn tends to decrease with the distance from pollution source. The same trend was observed in the experimental research. Moreover, a strong relationship between wind speed and Zn concentration was observed – the slower the wind speed, the higher the concentration of zinc in moss near pollution source.

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