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EFFECT OF PUBLIC TRANSPORT FOR HEAVY METAL CONCENTRATION IN THE SOILS

WPŁYW TRANSPORTU PUBLICZNEGO NA STĘŻENIE METALI CIĘŻKICH W GLEBACH

Abstract: Industrial and agricultural activities in the soil cover of the earth cause more and more noticeable environmental load. Therefore, the natural self-purification ability of soils has been greatly reduced and is decreasing continuously. The soil itself is an essential value as it preserves the traces of land history, the landscape, the cultural and scientific examinations. It is indispensable for the survival of the wildlife, because with the climate it also influences the water cycle and quality. One of the most important environmental factors nowadays is the public transport. The public transport is a polluting source that not only emits greenhouse gases, aldehydes, carbon blacks, dust, but unfortunately also many inorganic toxic substances into the environment. The biggest problem with the various inorganic pollutants is that some of them are essential for living organisms, but some of them are also very toxic at very low concentrations, too. The environmental pressure and pollution caused by heavy metals has become a serious problem since the middle of the previous century. From the point of view of their fate, the soil characteristics are, for example, humus, pH, etc. their role is important. The heavy metal content found in the soil and/or in the soil can easily penetrate to the groundwater, which can be transmitted through the animals and/or the plants to the human food chain. Nowadays, the aero-planes are one of the most important transport devices. The main goal was to have the Budapest "Ferihegy" Airport in this area a detrimental effect on its immediate environment. Therefore, it was our aim to examine the soil of the forest near the former "Ferihegy I". Our investigations were carried out not far from the then active running runway, in the acacia and beside the road, which was not far from this area. Among the heavy metals, the concentration of cadmium, zinc, manganese, lead, copper and iron were measured and then compared to those from control area. The examination of the samples has begun with the proper way of storing, preparing and digesting. From the sieved (2 mm) samples, the pH value and dry matter content were measured. The samples that went through a smoother sieve (0.20 mm) were digested by a Milestone 1200 Mega Microwave digestion system. After the nitric acid digestion were measured the heavy metal concentration in the soil samples by an "ATI UNICAM 939 FAAS" atomic absorption spectrometer, which was carried out for five elements: iron, lead, copper, zinc, manganese and cadmium with Unicam 939 QZ GF90 graphite furnace atomic absorption spectrometer. The measurement results were recalculated to mg/kg of dry matter content. The statistical analysis was performed by ANOVA with three-factor random block design, using SPSS 14.0 software package for Windows.

Keywords: heavy metals, public transport, monitoring, effect of airport and road

Introduction

Industrial and agricultural activities are causing more and more noticeable environmental load in Earth's soil cover. Therefore, the natural self-purification of soils is greatly reduced and is decreasing continuously. Soil itself is an inestimable value as it preserves the traces of land history, the landscape, the cultural and scientific examinations. It is indispensable for the survival of the wildlife, with the climate together also influences the water cycle and quality.

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Among the environmental problems the transport especially the air transport [1-3] was chosen. Transport is a polluting source that not only emits greenhouse gases, aldehydes, carbon blacks, dust, but unfortunately also many inorganic toxic substances into the environment. The biggest problem with the various inorganic pollutants is that some of them are essential for living organisms, but some of them are also very toxic at low concentrations [4-6]. The environmental pollution caused by heavy metals [4] has become a serious problem since the middle of the previous century. From the point of view what will happen to them, the soil characteristics are important, for example humus content, pH, etc. The heavy metal content found in the soil and/or in the soil can be transferred into the groundwater, which can be transmitted through the animals and/or the plants to the human food chain.

The state of our environment is very important. In Budapest Ferihegy Airport was selected to study its environment. It is an important question because the airport uses almost the whole Budapest's airspace. The primary goal was to examine the soil of the shelter belt near Ferihegy. The tests were carried out not far from the runway, in the acacia and beside the roadside. In this little forest, which serves the relaxation of the local habitants a strange spot was found in 2006 on the surface of the soil, where the condition of the plants was much worse than outside of the spot.

One of the reasons for this was excessive amount of heavy metals. In 2006 the heavy metal concentration was measured by us, it was found high Cd contamination (mean: 13.35 mg/kg dry mass (d.m.)). After several years the condition of the shelter belt became much better. The earlier bad-looking vegetation has disappeared and new beautiful vegetation has emerged. The soil was also likely to be replaced, with another soil sampling for this phenomenon. If high heavy metal concentrations can still be detected in the soil, some other contamination can be attributed to previous bad states. If the amount of the heavy metal is reduced in the soil, it can be stated in the literature that high cadmium content is likely to be responsible for the damage to the wildlife, that is to say, changes in the soil spot. Among the heavy metals, the concentration of cadmium, zinc and manganese, lead, copper and iron were measured and then compared to a control area. Nowadays this area is rebuilt once again.

Our secondary aim was to monitor the heavy metal content of soils near the woods, in order to find out whether road traffic could affect the soil of the forest and thus the flora and fauna's living space.

Materials and methods

Sampling

Sampling of different soil samples

First sampling place is shown in Figures 1a and b.

The suspected contaminant source the former runway (Ferihegy 1, Airport in Budapest, Hungary, which does not work nowadays) was considered as the centre, the sampling was made along this area. The polluter source was drawn onto a map with 1:10,000 scales.

Second sampling place is shown in Figure 2.

a) b)

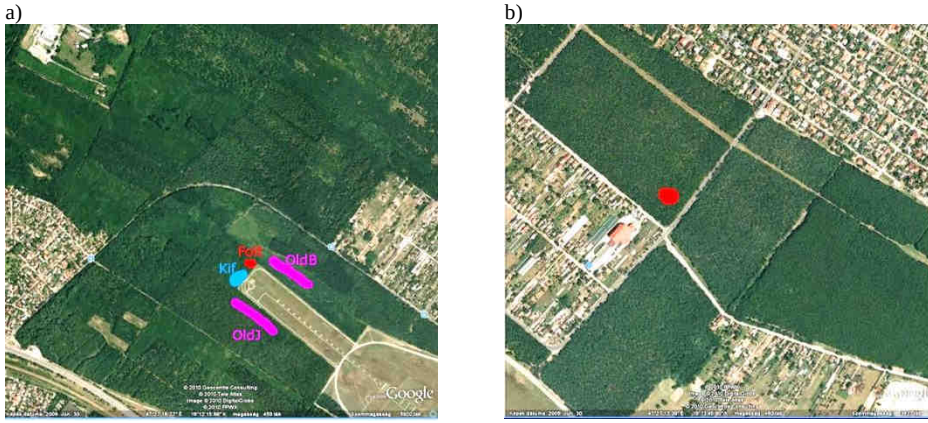

Fig. 1. Soil sampling near Budapest Airport (former Ferihegy 1, nowadays it does not work): a) "Folt", "Kif", "OldB" and "OldJ" are the spots of the soil samples and b) the control (source: Google Earth)

Fig. 2. Soil sampling scheme near road in Budapest not far from Budapest Airport (source: Google Earth)

Soil samples were spot and average samples, they were taken from a 10 cm soil depth. 10 average soil samples (Folt2, Folt5, Folt7, Folt9, Folt 11, Folt14, Folt17, Cont2, Cont, Cont7) and 35 spots were taken from the examined area. The soil was polluted according to the results of the previous studies. From this point of view, spot samples were taken on a rectangular sampling net and linearly from the road (see Fig. 3). The average samples were taken from a homogeneous area and from the same layer. Figure 4 shows the location of average and point patterns.

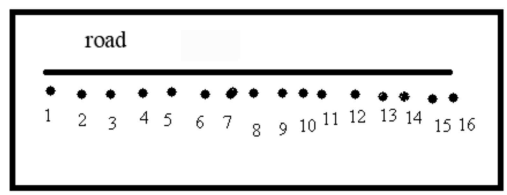

Fig. 3. Point samples taken from the road

Linear emission sampling was applied near road not far from the Airport (see Fig. 3).

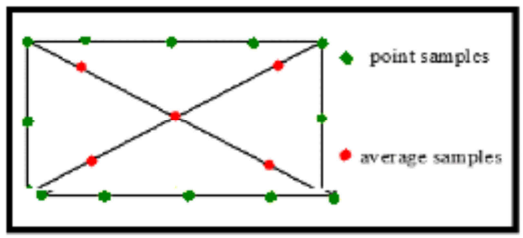

Fig. 4. Location and average and spot patterns

Sample preparing

Preparation of soil: in order to remove pieces of roots, the samples were sifted with sieve (diameter: 2 mm). Then these were left to dry.

Moisture content and pH determination: determination of moisture content and pH were made according to standards No. MSz-08-0205-1978 [7].

All analytical measurements were done in 3 replicates.

Determination of soil pH

The pH value characterized the acidity of the soil's liquid phase. A lot of Hungarian and National standards specify 2.5 : 1 liquid soil rate for water suspensions, and this is used in the present method, too. The advantage of using 1 mole/dm^3 KCl suspension is that the result values are more permanent and more reproducible. The acidity caused by H_3O^+ ions is the real or actual acidity in distilled water medium and the potential acidity can be measured in neutral saline solution (source).

6 g air dry soil was used for the determination of KCl and distilled water pH in test tubes. Soil was measured into 4 test tubes, then 10 cm^3 distilled water was put into 2 test tubes and 10 cm^3 1 mole/dm^3 KCl solution was given to 2 test tubes, then these were homogenized and the method was repeated for all samples. The samples were let to stay 12 hours at room temperature. The measurement was done with ADWA AD8000 pH meter. WTW Technical Buffer (T = 25°C, pH = 4.01), HANNA Instruments HI7007 (T = 25°C, pH = 7.01), HANNA Instruments HI7010 (T = 25°C, pH = 10.01) were used for three point calibration.

Digestion of the soil samples by Milestone 1200 mega microwave oven

Soil microwave digestion: The samples were digested by a MILESTONE 1200 Mega Microwave Digester with the following process:

Digestion of soil samples: about 0.5 g dry matter soil was put into each bomb. Then 5 cm^3 65% HNO_3 and 2 cm^3 30% H_2O_2 were added and let to stay in the solution for half an hour and then put the bombs into the microwave oven for half an hour. After that, the bombs were put into water cooling for half an hour and when they cooled, they were opened under a fume hood. The suspension made was filtered into 25 cm^3 standard flask, then it was filled up with high purity distilled water. The samples were stored in refrigerator

until the instrument measuring. The digestion was done according to the „Cook-book" recipe of Milestone mega 12000 microwave oven. Table 1 contains the recipe of digestion in microwave oven.

Table 1

Digestion program for soil samples

Steps	Time [min]	Process, microwave power [W]
1.	5	Digesting, 250
2.	2	Ventilation
3.	5	Digesting, 400
4.	5	Digesting, 250
5.	7	Digesting, 700

Heavy metal detection

The soil samples were measured for Cd, Cu, Zn, Mn, Fe and Pb. In this paper, the Cd, Cu, Zn and Pb concentrations will be described in different soil samples. The concentration of measured heavy metals was determined by atomic absorption spectrometry (Soil: "ATI Unicam 939 FAAS" and Unicam 939 QZ-GF90).

Statistical analysis

Statistical analysis was done by SPSS 14.0 for Windows.

Results and discussion

The pH value of the soil samples was examined and the results are given in Table 2. All the pH of soils were mostly acidic. Generally it is true, that mobility of the heavy metals increase in soil, if pH is acidic, and more available for the plants. It can be said, that the acidic pH is not favorable from environmental point of view.

Table 2

pH of soil samples

Soil samples	pH_{H_2O}	pH_{KCl}
Folt 2	5.41 ±0.04	4.99 ±0.11
Folt 5	5.89 ±0.02	5.41 ±0.05
Folt 7	7.06 ±0.09	6.68 ±0.06
Folt 9	6.76 ±0.10	6.19 ±0.01
Folt 11	7.70 ±0.03	6.10 ±0.03
Folt 14	5.98 ±0.04	5.07 ±0.03
Folt 17	5.07 ±0.08	4.70 ±0.04
Kif 1	5.30 ±0.04	4.55 ±0.01
Kif 2	5.58 ±0.02	4.99 ±0.01
Kif 3	5.61 ±0.06	5.19 ±0.04
Kif 4	5.26 ±0.01	4.64 ±0.00
Kif 5	6.03 ±0.03	5.79 ±0.03

Soil samples	pH_{H_2O}	pH_{KCl}
Kif 6	5.64 ±0.01	5.16 ±0.03
Kif 7	5.18 ±0.04	4.67 ±0.01
OldB 1	5.02 ±0.01	4.20 ±0.03
OldB 2	5.07 ±0.02	4.60 ±0.00
OldB 3	5.54 ±0.01	5.26 ±0.02
OldB 4	5.34 ±0.04	4.86 ±0.03
OldB 5	5.53 ±0.01	5.24 ±0.06
OldB 6	5.91 ±0.02	5.85 ±0.07
OldJ 1	6.16 ±0.02	6.15 ±0.02
OldJ 2	5.79 ±0.04	5.57 ±0.01
OldJ 3	6.66 ±0.08	6.60 ±0.01
OldJ 4	5.61 ±0.05	5.41 ±0.02
OldJ 5	5.86 ±0.04	5.78 ±0.01
OldJ 6	5.92 ±0.04	5.74 ±0.01
Cont 2	6.89 ±0.08	5.34 ±0.06
Cont3	7.46 ±0.03	7.10 ±0.06
Cont 7	7.78 ±0.10	7.53 ±0.04
Road 1	5.91 ±0.05	5.73 ±0.01
Road 2	6.75 ±0.07	6.74 ±0.03
Road 3	5.89 ±0.06	5.65 ±0.04
Road 4	6.92 ±0.03	6.85 ±0.01
Road 5	6.74 ±0.06	6.52 ±0.01
Road 6	6.94 ±0.06	6.87 ±0.04
Road 7	6.90 ±0.02	6.87 ±0.04
Road 8	7.02 ±0.11	6.97 ±0.11
Road 9	6.18 ±0.01	6.02 ±0.03
Road 10	6.98 ±0.04	6.97 ±0.04
Road 11	6.70 ±0.02	6.68 ±0.02
Road 12	6.92 ±0.09	6.82 ±0.04
Road 13	7.00 ±0.06	6.92 ±0.03
Road 14	7.46 ±0.15	7.33 ±0.02
Road 15	6.94 ±0.06	6.84 ±0.01
Road 16	7.28 ±0.11	7.21 ±0.01

Cadmium concentration in soil samples

The average cadmium concentration was in the soil 0.16 mg/kg d.m. In 2006 it was monitored the same area, that time it was measured the average Cd concentration in the soil 13.35 mg/kg d.m. The Cd concentration of the spot soil samples was 14.20 mg/kg d.m.

Cadmium concentrations of soil samples exceeded the contamination limit (1 mg/kg d.m.). At that time, pollution was 10 times higher than, pollution limit. In 2008 cadmium concentration in the soil samples from the same area was measured under

contamination limit in all cases (Fig. 5a and b). This may be due to a change of the soil state after the measurements in 2006.

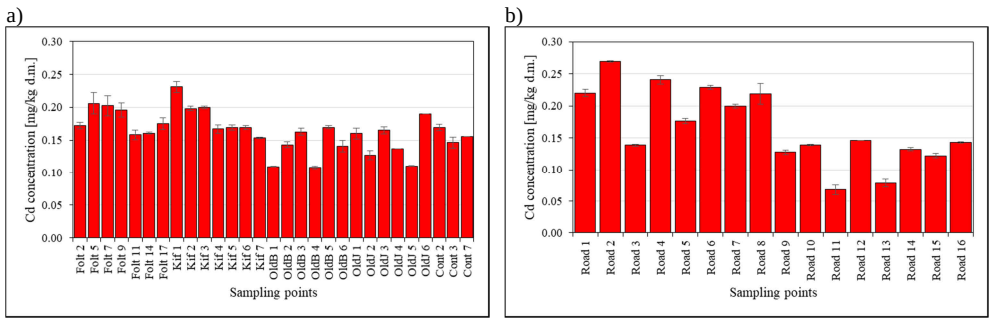

Fig. 5. Cd concentration in different soil samples (contamination limit is: 1 mg/kg d.m.): a) near the Airport, b) near the road

In control samples, it can be stated that while in 2006 the average value was 11.66 mg/ kg. d.m. When measuring soil samples for 2008, it is only 0.16 mg/kg d.m., that was the mean value. This may be due to the fact that a food processing plant near it was closed in 2007 and leakage happened at the nearby landfill site.

The cadmium content of our samples was significantly dependent (p = 5%) on the sampling site $LSD_{5\%} = 0.01$.

The concentration of the samples taken along the Road (Fig. 5b) is largely significantly higher than that of the soils around the runway and the controls. This is probably due to the car tires from the cars.

In soil samples at the beginning of the road (Route 1-Way 8) the concentration of cadmium is higher than in the rest of the road. The soil samples 1-8 next to the road come from the straight section of the road, probably the cars are moving faster than in the bend (Road 9-Way 16). The higher speed is likely to result in higher wear, which is clearly visible in the slightly higher cadmium concentration of soils.

The highest concentration difference was among the following soil samples: Route 1 and Route 11 (0.15 mg/kg d.m.) As well as Route 6 and Route 11 (0.16 mg/kg). The Roads 1 and 6 are derived from the straight section of the road, while the Road 11 is located on the side of the curve.

Copper concentration in soil samples

The average copper concentration in the soil samples was 12.07 mg/kg d.m. Ferihegy 1 samples had a copper concentration from 4.44 to 41.39 mg/kg d.m.

The copper content of the samples depend on significantly (p = 5%) on the sampling points $LSD_{5\%} = 6.38$.

Most noticeably, the copper concentrations of the samples taken along the way were significantly higher than those of the other samples. This phenomenon can be explained by the car's traffic, as wear and tear on lubricants [4] may occur, although the contamination limits are not exceeded. The Road 4 patterns differ from each road except for the Road 10,

the best deviates from Road 9 (35.38 mg/kg d.m.), the least deviating from Road 12 (7.06 mg/kg d.m.). The Road 6 samples of all road patterns are different except for Route 16. Route 8, the most different from Road 7 (20.83 mg/kg d.m.). The least from Road 12 (6. 80 mg/kg d.m.). Road 8 is the best route from 9 samples (26.18 mg/kg d.m.) to the Road 16 samples (16.60 mg/kg d.m.). Road 10 is different from Route 9 (29.29 mg/kg d.m.) and Road 12 (0.97 mg/kg d.m.). The Road is 12 samples from the Road 9 (28.32 mg/kg d.m.). Road 14 is from Road 7 (29.82 mg/kg d.m.) and Road 6 (8.98 mg/kg d.m.). In a clear context such as lead and cadmium it can not be observed that the copper concentration would be higher along the straight section of the road than the curve section. It is probable, that the copper pollution caused by the car's wear does not depend on the speed of the car.

Figure 6. shows, that none of the samples exceeds the copper limit (75 mg/kg of d.m.). However, it was found that Road 4 (41.39 mg/kg d.m.), Road 6 (27.53 mg/kg d.m.), Road 10 (35.39 mg/kg d.m.) and Road 14 (sample 31.51 mg/kg d.m.) have a copper content higher than the other samples.

The control samples have a copper content lower than the average, Cont 2 sample was 4.51 mg /kg d.m., the Cont 3 sample was 6.67 mg/kg d.m., and the Cont 7 sample was 5.22 mg/kg d.m.

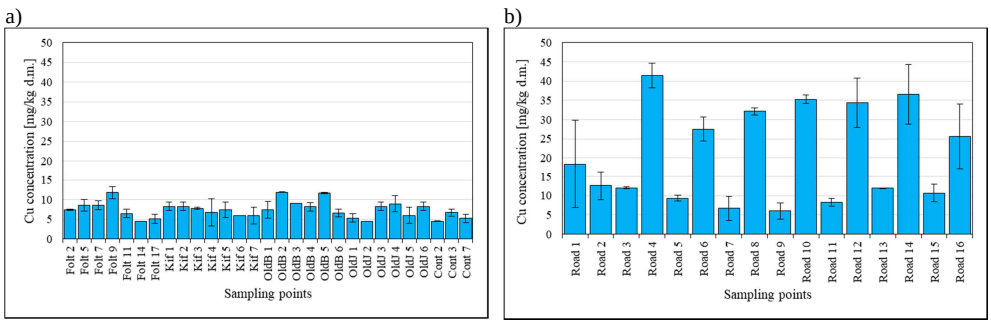

Fig. 6. Copper concentration in different soil samples (contamination limit: 75 mg/kg d.m.): a) near Airport, b) near the road

Zinc concentration in soil samples

The average zinc content of our soil samples was 62.42 mg/kg d.m. The average zinc content of soil samples measured in 2006 was 37.17 mg/kg d.m. The average zinc concentration in the soil was 41.24 mg/kg d.m. in 2006, the sample of special spot was 21.69 mg/kg d.m. in 2010. The average zinc content of control soils was 29.05 mg/kg d.m. in 2006, whereas the control soils had an average zinc content of 20.40 mg/kg d.m. in 2010. These data show, that over two years the concentration of zinc in the soil samples increased on average except in the control area where it decreased (Fig. 7a).

The zinc content of the samples was significantly depend on (p = 5%) the sampling point $LSD_{5\%}$ = 28.58.

The most striking is the Road 4 samples (Fig. 7b), which show a significant difference from all road patterns. The largest differences were between the Road 4 and Road 13

samples (247.37 mg/kg d.m.). The smallest deviation is between Road 4 and Road 8 (123.68 mg/kg d.m.).

Figure 7b shows, that one sample exceeds the limit value for contaminants based on 200 mg/kg d.m. content. This was in the case of Road 4 with a zinc concentration of 276.93 mg/kg d.m.

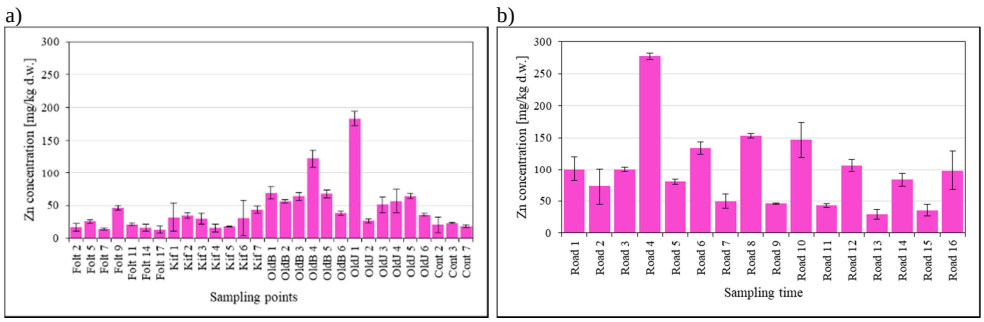

Fig. 7. Zinc concentration in different soil samples: a) near Airport, b) near the road (contamination limit: 200 mg/kg d.m.)

Lead concentration in soil samples

The average lead content of soil samples was 20.75 mg/kg d.m. In forest in Ferihegy 1 and in the road area the lead concentration were between 4.24-79.27 mg/kg d.m. This can be due to the human intervention and the car traffic along the road. It is true, that leaded petrol has been banned in Hungary, but it was still visible in the soil during the measurement.

The lead content of the soil samples is significantly depend on (p = 5%) of the sampling site $LSD_{5\%}$ = 18.08.

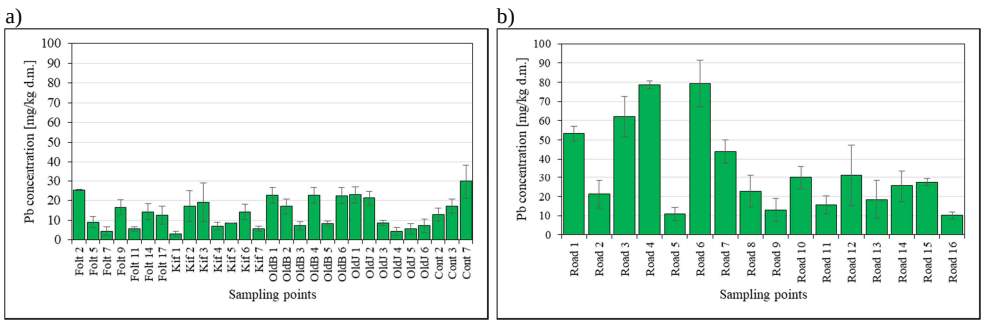

Fig. 8. Lead concentration in different soil samples (pollution limit: 100 mg/kg d.m.): a) near Airport, b) near the road

Most noticeably, the lead concentration of the samples along the road is significantly higher than the other samples. This phenomenon can be explained by the amount of leaded gasoline previously accumulated, although the contamination limits are not exceeded. Road 1 is significantly different from Road 16 (difference is in the Pb concentration (Road 1 - Road 16) is between them 43.48 mg/kg d.m.), Road 6 (difference is in the Pb concentration (Road 1 - Road 6) is between them: 26.20 mg/kg d.m.) and Road 4 is different from Road 16 (difference is in the Pb concentration (Road 4 - Road 16) is between them 69.12 mg/kg) and Road 6 (difference is in the Pb concentration (Road 4 - Road 6) is between them: 0.53 mg/kg). Road 6 is significantly different from the Road 16 (difference is in the Pb concentration (Road 6 - Road 16) is between them 69.65 mg/kg d.m.). The reason for this is, that the track path is winding (Road 9-16), so the vehicles are even faster in the straight (Road 1-8) section, they are slowing down to the bend, so emissions drop. In other road area was found similar results [8].

It can be seen from Figure 8, that the concentration of lead in any sample does not pass through the contamination limit, based on 100 mg/kg d.m.

The samples from other paths lead to a concentration of lead of 2 to 45 mg/kg d.m. It is also apparent, that the winding road sections are otherwise polluted and the degree of emissions of cars is different.

Conclusions

In 2006 was a study at Szent Istvan University, in which was found, that cadmium pollution in soil samples was over contamination limit near Budapest airport runway. Since then, partial pollution removal has taken place, that is why was repeated the monitoring the shelter belt area. It was important to know how successful the rehabilitation was. During the evaluation, it was found, that there was not any soil sample over contamination limit in the forest area. The same was stated for the soil samples taken from the road, except for the content of a Zn soil sample (Road 4 sample: 276.93 mg/kg d.m.).

As the heavy metal contamination found in 2006 existed for a longer period of time, it would be worthwhile to carry out further investigations of the deeper layers of the soil as to how much rainwater contaminated the deeper layers and to what extent. The present studies do not reveal this, and the soil exchange could only take place in the upper layer. Measurement of pH in most soil samples, in most places, showed an acidic effect, which facilitates the mobilization of a large proportion of heavy metals.

During the rehabilitation, the entire forest was cut. By this method, the measurements have resulted in the removal of contamination from the soil. The new forest was installed. The trees are only 20-25 years old and will again become a forest in the area.

Acknowledgements

The authors acknowledge for G. Bernvalner, who called attention to a contaminated area near the airport, which was verified by her measurements still in 2006. The authors acknowledge for help to Cs. Meszaros.

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WPŁYW TRANSPORTU PUBLICZNEGO NA STĘŻENIE METALI CIĘŻKICH W GLEBACH

Abstrakt: Działalność przemysłowa i rolnicza w obrębie pokrywy glebowej powoduje coraz bardziej zauważalne obciążenie środowiska. W związku z tym naturalna zdolność gleb do samooczyszczania się uległa znacznej redukcji i stale się zmniejsza. Sama gleba jest wartością podstawową, ponieważ zachowuje ślady historii Ziemi, krajobrazu, podlega badaniom kulturowym i naukowym. Jest ona niezbędna do przetrwania dzikiej przyrody, ponieważ wraz z klimatem wpływa również na obieg i jakość wody. Jednym z najważniejszych obecnie czynników środowiskowych jest transport publiczny. Jest on źródłem zanieczyszczeń emitującym nie tylko gazy cieplarniane, aldehydy, sadze, pyły, ale niestety również wiele nieorganicznych substancji toksycznych dla środowiska. Największy problem z różnymi zanieczyszczeniami nieorganicznymi polega na tym, że niektóre z nich są niezbędne dla organizmów żywych, ale niektóre są również bardzo toksyczne w bardzo niskich stężeniach. Presja i zanieczyszczenie środowiska metalami ciężkimi stały się poważnym problemem od połowy ubiegłego stulecia. Na ich los mają wpływ cechy charakterystyczne gleby, na przykład zawartość humusu, pH itp. Metale ciężkie z gleby mogą łatwo przedostać się do wód gruntowych, z których przenoszone są przez zwierzęta i/lub rośliny do łańcucha pokarmowego człowieka. Samoloty są obecnie jednym z najważniejszych środków transportu. Głównym celem pracy było zbadanie możliwości ograniczenia szkodliwego wpływu budapeszteńskiego lotniska „Ferihegy" na najbliższe otoczenie, dlatego zadaniem autorów było zbadanie gleby lasu niedaleko byłego lotniska „Ferihegy I". Badania te zostały przeprowadzone niedaleko niegdyś czynnego pasa startowego, na obszarze porośniętym przez akacje i obok pobliskiej drogi. Wśród metali ciężkich oznaczono stężenie kadmu, cynku, manganu, ołowiu, miedzi i żelaza, a następnie porównywano je ze stężeniami metali pochodzącymi z obszaru kontrolnego. Badania próbek obejmowały właściwe ich przechowywanie, przygotowywania i roztworzenie. W przesianych (2 mm) próbkach gleby oznaczono wartość pH i zawartość suchej masy. Próbki, które przeszły przez gęstsze sito (0,20 mm), były mineralizowane w mikrofalowym mineralizatorze Milestone 1200 Mega Microwave System. Po roztworzeniu w kwasie azotowym stężenie metali ciężkich w próbkach gleby oznaczono spektrometrem absorpcji atomowej ATI UNICAM 939 FAAS. Sześć pierwiastków: żelazo, ołów, miedź, cynk, mangan i kadm było znaczonych za pomocą spektrometru absorpcji atomowej z wykorzystaniem kuwety grafitowej Unicam 939 QZ GF90. Wyniki pomiarów przeliczono na mg/kg zawartości w suchej masie. Analizę statystyczną wykonano na planie trójczynnikowej ANOVA z blokami losowymi z wykorzystaniem pakietu oprogramowania SPSS 14.0 dla systemu Windows.

Słowa kluczowe: metale ciężkie, transport publiczny, monitoring, efekt lotniska i dróg