



Evelina BRANNVALL

**INVESTIGATION OF HEAVY METALS AND
PETROLEUM PRODUCTS IN THE ROADSIDE
ENVIRONMENT AND REMEDIATION
BY NATURAL SORBENTS**

**Summary of Doctoral Dissertation
Technological Sciences,
Environmental Engineering and Landscape Management (04T)**

Vilnius



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VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

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VILNIUS GEDIMINO TECHNIKOS UNIVERSITETAS

Evelina BRANNVALL

**SUNKIŲJŲ METALŲ IR NAFTOS PRODUKTŲ
KELIO APLINKOJE TYRIMAI IR MAŽINIMAS
NAUDOJANT GAMTINIUS SORBENTUS**

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General Characteristic of the Dissertation

Topicality of the problem – the main highway pollutants are heavy metals, non organic salts, aromatic hydrocarbons (petroleum products) and solid particles accumulated in the air or on the highway surface by exploiting them. These pollutants are transported by air streams and washed out from the road surfaces by rain and snowmelt. Surface waters are very sensitive, because of the direct pass of pollutant. Heavy metals occurring naturally in soils usually are as an isomorphic additive of minerals. Also, they can be sorbed by minerals or be in a compound with organic matter. The quantities of heavy metals in Lithuanian soils are small and non hazardous, but there are some very contaminated territories where due to the anthropogenic influence they increase ten or more times and reach the level of risk for biota. One of the most important technogenic sources of heavy metals is transport emission. Therefore heavy metals and petroleum products contaminate the roadside soil near intensive traffic roads as well. Not all cities in Lithuania have bypasses and sometimes highways cross living areas, so a lot of people live in the zone, which is hazardous for the health. In the very close to the road zone people grow vegetables, which accumulate pollutant. Usually to use such vegetables is dangerous for health. Sometimes people collect berries in a vicinity of the road. Roadside grass is used to feed animals. With rainfall or snowmelt part of heavy metals reach the groundwater layer passing through an aeration zone. The groundwater is usually used for drinking, so in such zones the quantities of heavy metals in food chain increase and can be hazardous for the health. Therefore it is very important to find means to remove the pollutant from soil or water and to stop migration into the next ecosystems.

In order to reduce the environmental risks arising from heavy metal and petroleum products pollution of soil and water it is necessary to develop some low cost remediation methods which do not destroy the soil structure and fertility, and are easy to apply. In recent years, attention has focused on the development of *in situ* immobilization methods that are less expensive and disruptive to natural landscape and ecosystems than treatment, excavation and disposal methods are. *In situ* immobilization of metals using inexpensive amendments such as minerals zeolite and vermiculite is a promising alternative to current soil remediation and water treatment methods. This method relies on a fundamental understanding of the natural geochemical processes governing the speciation, migration, and bioavailability of metals in the environment. The main goal of the *in situ* remediation method is to reduce the fraction of toxic elements that is potentially mobile or bioavailable. Pollutants sorbed by natural mineral are immobilized inside and they can't move from contaminated materials to any compartment of soil or groundwater.

Aim and tasks of the work: to define the level of contamination of the roadside soil near the intensive traffic roads and prepare scientifically based pollution minimization recommendations using natural zeolite.

- To evaluate the roadside soil pollution by heavy metals and it's dangerous.
- To evaluate the roadside soil dangerous level of pollution and variation tendencies.
- To carry an experimental study on heavy metal immobilization in soil and removal from runoff by natural zeolite.
- To define the sorption capacity of natural zeolite and vermiculite to sorb heavy metals and petroleum products from runoff.

Scientific novelty

The pollution by heavy metals in the roadside soil alteration tendency was thoroughly investigated by applying the complex experimental and statistical environmental analysis and means for pollution by heavy metals and petroleum products reduction by natural zeolite and vermiculite were evaluated and developed. To reach the novelty it was:

- The roadside soil pollution by heavy metals, it's dangerous and pollution variation tendencies were investigated.
- The suitability of natural zeolite for heavy metal removal from soil and aquatic solutions was proved.
- The suitability of natural zeolite and vermiculite for petroleum products removal from aquatic solutions was proved.

Methodology of research includes soil and water samples analyse by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for metal Cr, Cu Pb and Zn analysis in liquid (analyse was performed at Lulea University of Technology, Sweden); Atomic Absorption Spectrophotometry AAS-ES for metals Cu, Ni, Mn, Pb and Zn analysis in liquid (analyse was performed at Vilnius Gediminas Technical University (VGTU), Lithuania); DC-Arc Emission Spectrometry for Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn and Zr analysis in solid phase (analyse was performed at Institute of Geology and Geography, Lithuania); Infracal TOG/TPH Analyzer, Model HATR-T for petroleum products analyse in liquid (analyse was performed at VGTU, Lithuania).

Practical value. Recommendations for the reduction of roadside soil and runoff pollution by heavy metals and petroleum products were offered. "Runoff-cleaning filter" is created and patented.

Defended propositions:

- The pollution of roadside soil by heavy metals increased recently.
- Natural zeolite is suitable for the heavy metals immobilization in soil and

removal from runoff.

- Natural zeolite and vermiculite are suitable for the removal of petroleum products from runoff.

The scope of the scientific work

The scientific work consists of the general characteristic of the dissertation, 5 chapters, generalization of the work and recommendations, list of literature and list of publications. The total scope of the dissertation – 145 pages, 71 pictures and 14 tables.

Short content of the dissertation

1. Investigations of soil pollution and runoffs, in situ soil remediation

This chapter reviews scientific studies completed previously on the subject of the thesis. After the review of the scientific studies of polluted roadside soil, it was decided to define the level of roadside soil pollution in Vilnius–Kaunas highway by using the same methods of sampling and sample analysis in order to evaluate the pollution dependence on time. To define the level of roadside soil pollution of high and low intensity roads in all territory of Lithuania as well. Runoff treatment system in Lithuania doesn't function properly, so it is very important to create effective and easy applicable runoff water treatment system for Lithuanian conditions. At the present, there are no data about pollutant concentration in runoff; therefore it is not clear, what is the level of pollution in the runoff in Lithuania. But after the review of the roadside soil pollution in Lithuania, it could be concluded that pollutants from motor transport contaminate runoff. Some natural materials for soil remediation and pollutant removal from runoff were reviewed and it was decided to use natural zeolite for heavy metal immobilization in soil and to use vermiculite as well as natural zeolite for runoff treatment. It is important to find out what kind of treatment system (construction) to use in certain conditions.

2. Investigation of heavy metals in the roadside soil

In this chapter investigations of roadside topsoil pollution in 1991, 2002 and 2005 are presented. In 2002 the topsoil samples were collected in the territory of Lithuania in Via Baltica, Vilnius–Druskininkai, Kaunas–Klaipėda, Vilnius–Panevėžys, Panevėžys–Šiauliai and Šiauliai–Palanga by author of the dissertation. The topsoil samples were analyzed by addition of 100 ml of 20 % HNO₃ and boiling for 15 min. by atomic absorption spectroscopy AAS (Buck 210 VGP) in the laboratory of Environmental Protection department of VGTU. In 1991 the topsoil sample were collected in Vilnius–Kaunas highway roadside by researchers of geochemical department of Geological institute of Lithuania. In 2005 the topsoil samples were collected in the same points as in 1991 in Vilnius–Kaunas highway roadside by the author of the dissertation and researchers of geochemical department of Geological institute of Lithuania for the comparison of the topsoil

pollution in 1991 and 2005 and evaluation of pollution variation tendencies. Soil samples were analysed by DC-Arc Emission Spectrometry using a DFS-13 spectrograph, MD-100 microdensitometer.

Median values of all heavy metals defined in the roadside soil sampling profiles were calculated (Table 2.1).

Table 2.1. Median values of heavy metals in 2002 year soil samples, mg/kg

Soil sampling in the roads	Cu	Cr	Zn	Mn	Ni	Pb
Via Baltica	4.6	2.9	2.9	116.4	15.3	23.2
Vilnius–Druskininkai	2.9	1.7	13.2	160.5	9.2	23.2
Kaunas–Klaipėda	11.7	7.0	65.7	124	25.2	42.6
Vilnius–Panevėžys	6.8	7.8	22.8	185	9.5	12.3
Panevėžys–Šiauliai	7.3	4.2	42.5	142.8	21.9	18.5
Šiauliai–Palanga	4.8	4.9	20.5	321	23	29

Comparing all regions with each other, where the soil samples have been taken, it is seen that the highest concentrations of Cu 17.1 mg/kg are in the zone of intensive pollution from transport system from the road edge to 100 metres in Klaipėda transport ring soil and the lowest Cu concentrations 1.91 mg/kg is in Vilnius–Druskininkai. The highest concentrations of Cr 21.0 mg/kg are in the Šiauliai–Palanga road and in Klaipėda – 16.16 mg/kg, and lowest concentration 0.85 mg/kg in Vilnius–Druskininkai roadside soil. Zn mostly accumulated in Panevėžys–Šiauliai open space roadside soil nearby Šeduva city 88 mg/kg, minimal quantity of Zn – 1.18 mg/kg in the 5 km of the road Via Baltica. Although the highest quantities of Zn were determined in the roadside soil of Panevėžys–Šiauliai, but the highest minimal concentration of Zn is in the soil of Klaipėda transport ring 43.5 mg/kg, and the maximum of Zn in this place 72.5 mg/kg. The highest concentrations of Mn are in Vilnius–Druskininkai roadside soil 513.3 mg/kg, the lowest concentration in Klaipėda transport ring soil 21.24 mg/kg. Nickel 36.66 mg/kg is concentrated in the loamy sandy soil of Panevėžys–Šiauliai. Maximum value of lead 66.89 mg/kg is defined in the sandy soil 5 m from the road Vilnius–Druskininkai in the descent of relief.

After the determination of the general heavy metal accumulation tendencies in the roadside soil in 2002, it is obvious that pollutant related to the motor transport emissions accumulate in a vicinity of the road in a distance of 10 m from the edge of the road. Therefore, the factor analyse was performed just for the samples of this zone, which have been taken in 1991 and 2005. 22 trace elements were used for the factor analyse (Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn ir Zr). Technogenical association of heavy metals (Cu, Pb, Zn, Sr, Sn ir Mo) in 2005 soil samples is characteristic to the motor transport pollution and

forms the most important 2nd factor (F22-2) loads (not 3rd like it is in 1991 samples). It shows that pollution by these heavy metals increased recently.

Median values of trace elements, which are characteristic to the motor transport pollution, were calculated according to the roadside zones in 1991 and 2005. It exhibits the variation tendency of motor transport impact on the roadside soil pollution (Fig. 2.1 and 2.2).

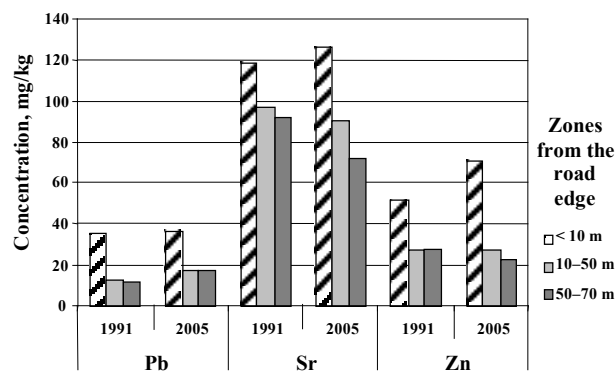


Fig. 2.1. Comparison of median values of Pb, Sr and Zn in 1991 and 2005 year

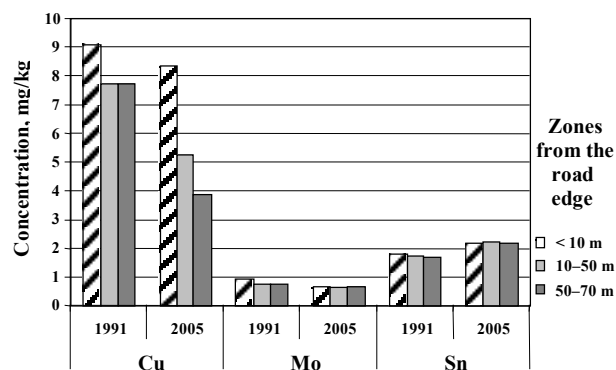


Fig. 2.2. Comparison of median values of Cu, Mo and Sn in 1991 and 2005 year

In 2005, median values of Pb, Sr, Zn and Sn increased in the zone up to 10 m from the edge of the road from 35.4 to 37.0, 119–126.3, 52.1–71.2 and 1.8–2.1 mg/kg respectively. Median values of these trace elements in the vicinity of the road in 1991 and 2005 are pretty higher than in the further zone from the road and it

obviously justifies the impact of motor transport on the roadside soil pollution. Median values of Cu decreased in 2005 from 9.1 to 8.3 mg/kg in the zone closest to the road (< 10 m), 7.7–5.3 mg/kg in the zone of 10–50 m from the edge of the road and 7.7–3.9 mg/kg in the furthest zone from the road. Median values of Mo almost didn't change (0.9–0.7, 0.7–0.6 and 0.8–0.6 respectively to the zones from the edge of the road).

Summarizing the results of the study of roadside soil pollution in 1991 and 2005 total contamination index Z_s was calculated for 6 trace elements (Cu, Mo, Pb, Sn, Sr and Zn) (Fig. 2.3).

Soil samples, which has been taken in the I soil sampling profile, got into the allowable contamination zone. The comparison of the means of the total contamination index Z_s of 1991 and 2005 years shows the increase of soil contamination (from 3.0 to 3.2). Soil pollution in the II soil sampling profile decreased from 6.9 (in 1991) to 3.8 (in 2005) comparing the means of the total contamination indexes. Soil samples collected in the III soil sampling profile in 2005 year belongs to the average contamination level. The means of the total contamination indexes increased 2.3 times – from 2.0 to 4.8. Soil pollution in the IV soil sampling profile decreased from 3.8 (in 1991) to 2.7 (in 2005) comparing the means of the total contamination indexes.

3. Experimental research on heavy metals and petroleum products sorption by natural zeolite and vermiculite

The main idea of the usage of sequential extraction for the soil mixtures with zeolites was to define how zeolite affects metals redistribution in fractions. Three different soils of 100 g and 5 % of zeolite were mixed and left for 1 month in the lab. Natural zeolite – clinoptilolite employed was from a deposit near the village of Sokyrnytsia in the Ukrainian Transcarpathian region. After that the sequential extraction of soil samples was done and analyzed by ICP-OES. A. Tessier (1979) method for sequential extraction was used. Sequential extraction results showed that zeolite increase the quantity of heavy metals in the residual fraction and decrease the mobil fraction of metal in soil. This experiment was performed in the scientific laboratory of Lulea University of Technology, Sweden.

The experiment of the immobilization of heavy metals Cu, Pb and Zn in soil (contaminated by Cu^{2+} , Pb^{2+} and Zn^{2+} nitrates at 3 contamination levels, 50, 100 and 500 mg/kg of each metal) by means of natural zeolite (of 5, 10 and 20 %) showed good results for the Pb immobilization. Natural zeolite immobilised metals in such order: $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. Soil samples were analysed by AAS. Calculating the efficiency of metal reduction and costs of additive, the amount of zeolite in soil should be 10 % if the contamination level of soil is not higher than 500 mg/kg. The highest heavy metal sorption efficiency was for Pb 99.9 %, Zn – 84.6 and Cu – 45.4 %.

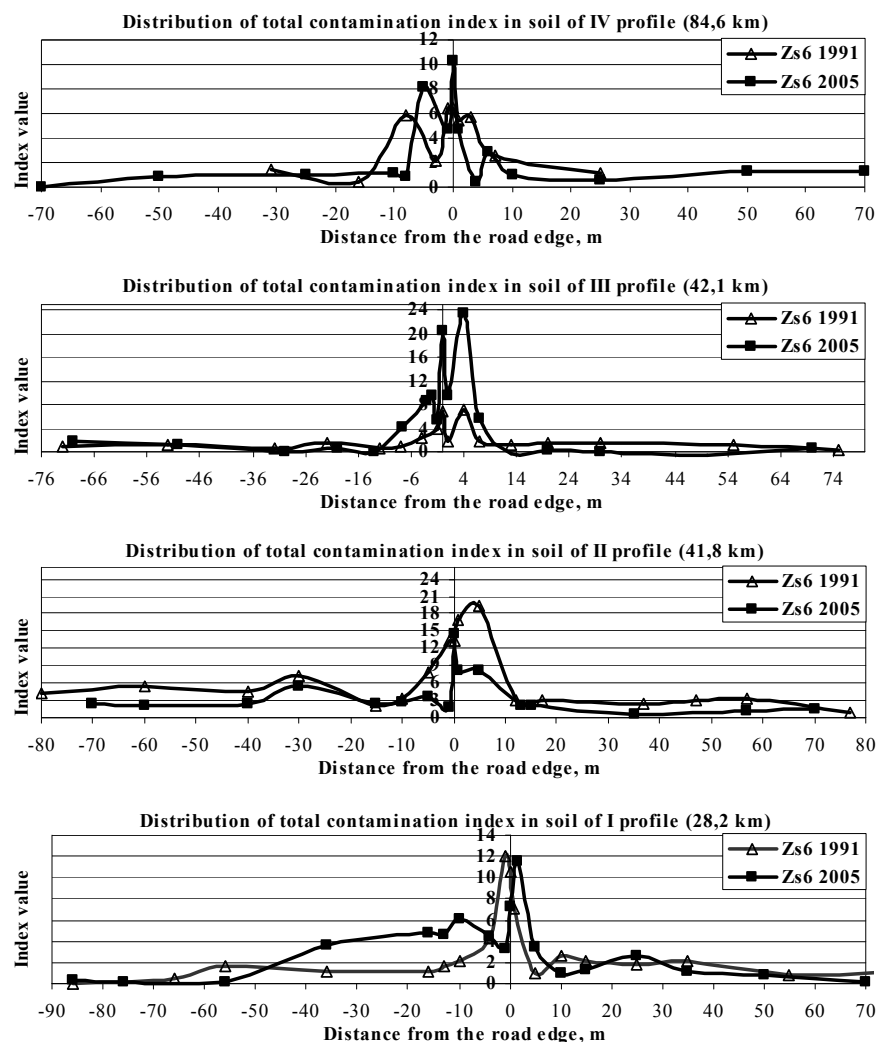


Fig. 2.3. Distribution of total contamination index in Vilnius–Kaunas roadside soil

The purpose of heavy metal sorption from solutions by natural zeolite experiments is to define the sorption capacity of zeolite. To reach this purpose these experiments were carried out: batch leaching test of three metals Pb, Zn and Cu sorption from the single metal solution (analysed by ICP-OES); five metals Pb,

Zn, Cu, Ni and Mn sorption from the single metal solution and the mixture (analysed by AAS); column test of metals Pb, Zn, Cu, Ni, Mn, Ca and Na sorption from solutions by natural zeolite (analysed by AAS).

Batch leaching test showed good results for lead sorption by natural zeolite (Fig. 3.1).

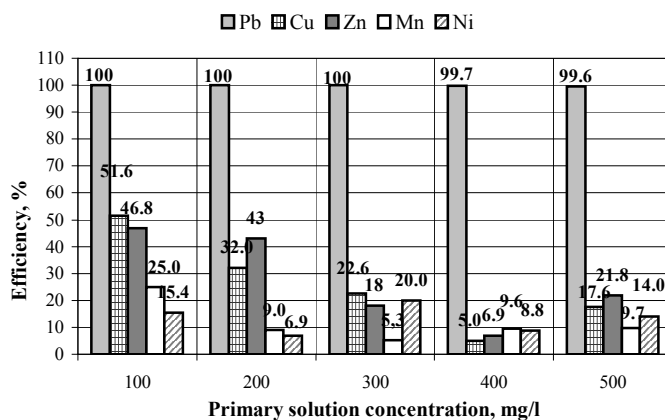


Fig. 3.1. Efficiency of heavy metal sorption by natural zeolite from metal mixture solution (batch leaching test), %

Comparison of the heavy metals sorption from solutions experimental results, showed that natural zeolite sorb Pb better than Cu or Zn and Mn or Ni (Table 3.1).

Table 3.1. Metals sorption by natural zeolite from solutions orders

Metals sorption order	Title of experiment
$Pb^{2+} > Zn^{2+} > Cu^{2+}$	Batch leaching test. Heavy metals Pb, Zn and Cu sorption from single metal solutions by natural zeolite. Experiment was performed in Sweden.
$Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Ni^{2+}$	Batch leaching test. Heavy metals Pb, Zn, Cu, Ni and Mn sorption from single metal solutions by natural zeolite. Experiment was performed in Lithuania.
$Pb^{2+} > Cu^{2+} \geq Zn^{2+} > Ni^{2+} > Mn^{2+}$	Batch leaching test. Heavy metals Pb, Zn, Cu, Ni and Mn sorption from mixture solutions by natural zeolite. Experiment was performed in Lithuania.
$Ca^{2+} > Pb^{2+} > Na^{+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$	Column test. Metals Pb, Zn, Cu, Ni, Mn, Ca and Na sorption from solutions by natural zeolite at the primary concentration 500 mg/l of metals in solution. Experiment was performed in Lithuania.
$Pb^{2+} > Cu^{2+} \geq Zn^{2+} > Mn^{2+} > Ni^{2+}$	Column test. Heavy metals Pb, Zn, Cu, Ni and Mn sorption from solutions by natural zeolite at the primary concentration 1000 mg/l of heavy metals in solutions. Experiment was performed in Lithuania.
$Pb^{2+} > Zn^{2+} > Cu^{2+} > Mn^{2+} > Ni^{2+}$	Column test. Heavy metal Pb, Zn, Cu, Ni and Mn sorption from solutions by natural zeolite at the primary concentration 2000 mg/l of heavy metals in solutions. Experiment was performed in Lithuania.

Heavy metals sorption by natural zeolite from solutions (batch leaching test) order is: $\text{Pb}^{2+} > \text{Zn}^{2+} \geq \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$ (calculating the average percentage). Column test results showed that heavy metal sorption order is: $\text{Pb}^{2+} > \text{Cu}^{2+} \geq \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+}$, when the primary concentration was 1 g/l and $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+}$, when the primary concentration of heavy metals in solutions was 2 g/l. The metal sorption by natural zeolite order is $\text{Ca}^{2+} > \text{Pb}^{2+} > \text{Na}^+ > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$ (column test with heavy metals and Ca^{2+} and Na^+).

An experimental study of the sorption of petroleum products (PP) from aqueous solutions by natural vermiculite and zeolite was carried out. Two different sizes of zeolite particles were used in this study: (0.63–1.0), (1.0–3.0) mm and (2.0±0.71) mm fraction of vermiculite. Zeolite was washed and dried at 105°C temperature in an oven before using it in the filter bed. The amount of 40 l of snowmelt water, 1 l of gasoline and 1 l of diesel passed the filter charged with zeolite and vermiculite. Comparison of the results showed that the highest removal of PP from water solution was obtained by using the finest grain sized zeolite. Removal efficiency was 89.8 % and 76.4 % respectively to (0.63–1.0) mm and (1.0–3.0) mm particle size zeolite. The highest PP removal efficiency of 92.4 % was achieved by using (2.0±0.71) mm particle sized vermiculite.

4. Created equipment and its usage

An experimental investigation on the removal of heavy metals and petroleum products from a solution by natural sorbents zeolite and vermiculite was carried out in a laboratory pilot-scaled test bench (Fig. 4.1). For this purpose a model of a runoff filter, which was invented by the authors was used. 25 kg of natural zeolite and 2 kg of vermiculite were used for the filter charge. An experimental solution of 20 l contained 1 g/l of heavy metals Cu, Pb, Zn, Ni and Mn nitrates and 200 ml of PP gasoline and diesel. The solution was poured into the filter through a funnel and passed over natural zeolite and vermiculite media. The first sample was taken through a sample mixer tap immediately after the contact of the experimental solution with the charge media, the second sample was taken after 5 min, then after 10, 20, 30, 60, 120, 240, 360 and 720 min. TOG/TPH analyser was used for measuring concentration filtrate samples.

The highest efficiency (%) of HM and PP removal from runoff was reached after 720 min of the experimental solution's contact with the filter media and was: Pb – 98.6 %, Zn – 81.8 %, Cu – 86.5 %, Ni – 81.8 %, Mn – 57.5 %, PP – 99.7 %. The runoff-cleaning filter was designed and patented in the Lithuanian Republic Patent Bureau (Fig 4.2).

This runoff-cleaning method could be employed in various branches of industry for treating wastewater and highway runoff contaminated with metal ions and organic compounds (PP).

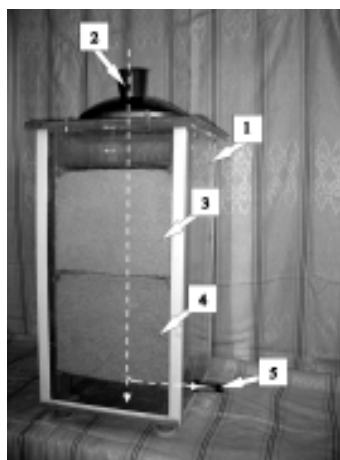


Fig. 4.1. Runoff-cleaning filter model, a pilot test bench:

1 – filter, 2 – funnel, 3 – natural zeolite filter media, 4 – vermiculite filter media, 5 – sample mixer tap

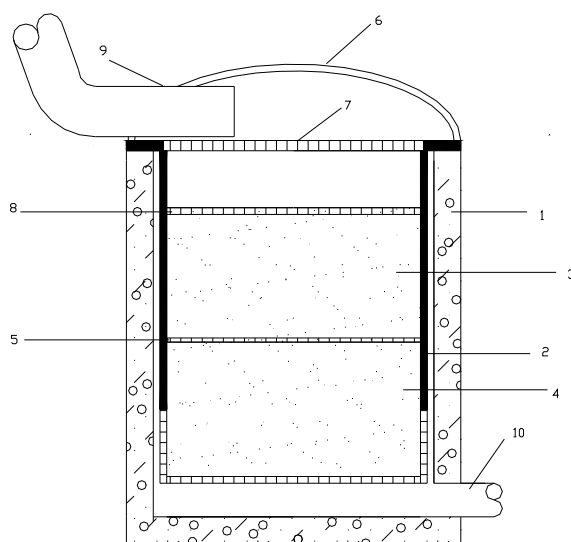


Fig. 4.2. Runoff-cleaning filter scheme: 1 – ferroconcrete frame, 2 – removable cassette

with fenestrated wall (1/4 part) and bottom, 3 – layer of natural zeolite adsorbent, 4 – layer of natural vermiculite adsorbent, 5 – metal grid of < 1 mm mesh diameter, 6 – cap, 7 – metal grid of 30–50 mm mesh diameter, 8 – metal grid of < 2 mm mesh diameter, 9 – water inlet pipe, 10 – water outlet pipe

The point of the proposed runoff-cleaning filter is that pollutants are adsorbed and trapped in a natural mineral medium, which is environmentally friendly, and pollutants don't migrate further. The runoff-cleaning process by the runoff-cleaning filter is further shortly described. Highway runoff runs into water collecting well installed on a roadside. First of all water is cleaned from the bigger branches, leaves, etc, while passing through a grid with large gaps above the well. Then water runs through an inlet pipe (9) into the filter and passes a grid of 30–50 mm mesh diameter (7). Then water filtrates through a cassette (2) with a natural sorbent charge (3, 4) installed in a ferroconcrete frame (1) of the filter.

Natural zeolite (3) is hydrated aluminosilicate mineral of a porous structure with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption. Natural clinoptilolite employed in this study is a zeolite of the heulandite group that is the most abundant in nature. Natural zeolite of 1–3 mm particle size adsorbs Pb, Zn, Cr, Ni, Mn and other metal ions. Vermiculite (4) can be regarded as a micro-pore absorbent, if we consider the interpacked spaces of the crystal as pores. Vermiculite adsorbs PP. Vermiculite of 1–3 mm particle size was used in the filter charge. The layers of sorbents are separated by a metal grid of < 1 mm mesh diameter (5). Both layers of charge are of the same volume, which depends on the composition of runoff and the level contamination with metal ions and organic compounds. The runoff-cleaning filter cassette with a natural mineral sorbent charge is changed, depending on the intensity of highway exploitation and runoff contamination.

Contaminated with petroleum products, heavy metals and other pollutants rain and snowmelt water flows into the roadside drainage ditch. In Lithuania these drainage ditches are not functional and don't protect ground water from the pollution by various pollutants. There are technically and morally obsolete runoff treatment systems from which water of unsufficient quality flows into the surface water.

Therefore improved runoff treatment system was suggested (Fig 4.3). The main idea of the runoff treatment system is the layer of sorbent: sand and 10 % of natural zeolite mixture. The soil surface of the runoff treatment system is overgrown by grass. The efficiency of infiltration-grassy-A-line type runoff treatment system with natural zeolite layer is approximately 10 % higher than ordinary runoff treatment system just with sand layer. It is recommended to use improved runoff treatment system by installing the new construction runoff treatment infiltration-grassy-A-line type system with natural zeolite layer in the roadside.

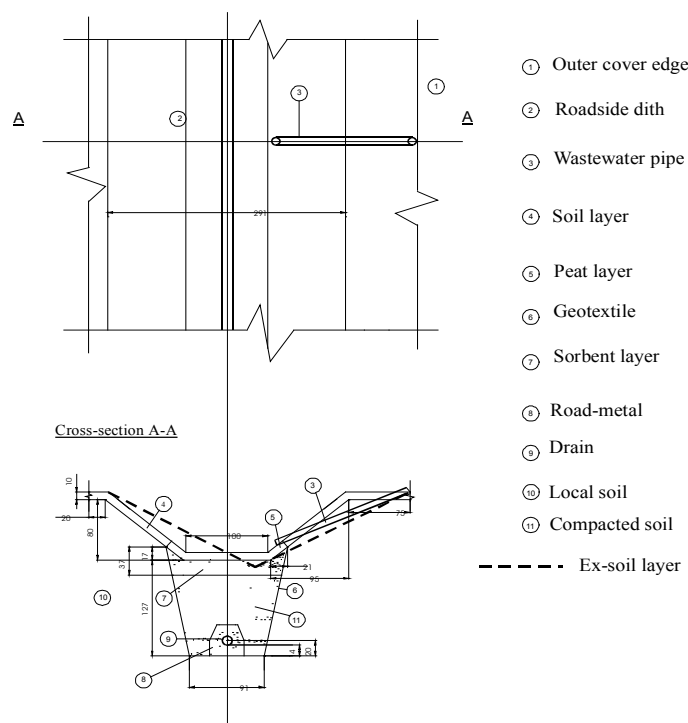


Figure 4.3. Runoff treatment infiltration-grassy-A-line type system with natural zeolite layer

General conclusions and recommendations

1. Investigations of the roadside soil pollution were carried out in 2002 year in the territory of Lithuania in the intensive and low traffic roads and in 2005 year in Vilnius–Kaunas highway showed that the largest quantities of Pb, Cu, Cr, Zn, Ni and Mn accumulates in the road dividing zone and in the vicinity of the road upto 10–15 m from the edge of the road.
2. In all soil sampling perpendicular profiles of Vilnius–Kaunas highway in 2005 year the quantities of heavy metals didn't exceed the MPC (maximum permissible concentration) except the soil samples in the II (41.8 km) and III profiles (42.1 km). The quantity of Pb in the soil of the II soil sampling profile, exceeded MPC 1.04 times in the road deviding zone. The quantity of Pb in the soil of the III soil sampling profile, exceeded MPC 1.4 times in the road deviding zone and in the distance of 5 m in the North eastern side of the highway – 1.5 time.
3. The analyse results of soil samples, which has been taken in the III soil

sampling profile in the 42.1 km of Vilnius–Kaunas highway, where the road is going through the cutting, which doesn't let pollutant to deconcentrate, showed that soil pollution by heavy metals valuating it by the averages of the total contamination indexes Z_{s6} increased about 2.3 times – from 2.0 to 4.8 times of late 14 years. The mean values of the total contamination index Z_{s6} increased 3 times in the zone just upto 10 m from the edge of the road.

4. It has been find out, that heavy metals Cu, Pb and Zn sorption by natural zeolite oder is: $Pb^{2+} > Zn^{2+} > Cu^{2+}$. When the primary heavy metal concentration in soil is 500 mg/kg and the quantity of natural zeolite is 10 %, 82 % of Pb, 47 % of Zn and 30 % of Cu was sorbed by natural zeolite.
5. Heavy metal sorption by natural zeolite from aquatic solutions, showed, that Pb is sorbed the best. Not depending on the fraction of natural zeolite (< 2 mm or 2–10 mm) it sorbed about 99 % of Pb. Both fractions of natural zeolite sorbed about 63 % of Zn. Copper was sorbed less just about 11.4 % by the fraction of less than 2 mm and 9.5 % – by 2–10 mm fraction. Column test showed that natural zeolite sorbed metals in such order: $Ca^{2+} > Pb^{2+} > Na^+ > Cu^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$.
6. The efficiency of petroleum products removal by two fractions (0.63–1.0 mm and 1.0–3.0 mm) of natural zeolite and vermiculite (1.0–3.0 mm) from water has been tested in the experimental study and the results were 96.6, 93.3 and 97.5 % respectively, when the primary concentration of petroleum products was 15 mg/l.
7. Organisational and technical means has to be applied for the reduction of roadside soil and water pollution by heavy metals and petroleum products.

Recommendations

1. It is recommended no to use soil for agriculture activities in the distance of 15 m to the edge of the road, for the purpose to protect the human health. The results of roadside soil pollution study to present for the Ministry of agriculture in order to implement this recomention in practice.
2. It is recommended to build the roads in various aerodynamic traps (the road cutting whith a steep slopes), because they don't alow the pollutant to spread. The results of roadside soil samples analyse of 1991 and 2005 years proves that pollutants don't spread, but accumulates on the steep slopes of the road cutting. To install the runoff-cleaning filter in all already existing aerodynamic traps for pollutant in the road environment.
3. It is recommended to use the designed and patented runoff-cleaning filter (patent No LT 5292 B) was suggested to install in the immediate vicinity of the road. Runoff directed by chamfer into the water collecting well and cleaned from the big branches, leaves and etc. and then through filter charge media.

Water passing through filter media is cleaned from metal ions (HM) and organic compounds (PP). On the other hand, we suggest installing the runoff-cleaning filter after sedimentation ponds where the primary treatment of runoff is executed.

4. It is recommended to use improved runoff treatment system by installing the new construction runoff treatment infiltration-grassy-A-line type system with natural zeolite layer.

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About the author

Evelina Brannvall was born in Vilnius on 22 July 1974. She finished Vilnius Salomėja Nėris Secondary School. In 1992, she entered Vilnius University Faculty of Natural Science. In 1996 graduated the University taking a bachelor degree of geologist and in 1998 a master's degree. In 1996–2001 she worked at the Geological Survey of Lithuania at Ministry of Environment. In 2001 she worked at the Geotechnical department of Vilnius Gediminas Technical University as a junior researcher. In 2002–2005 she worked at the department of Environmental Protection as a research assistant. In 2002–2006 is a PhD student at the department of Environmental Protection of Vilnius Gediminas Technical University. Evelina Brannvall in 2003–2004 was on intership at Lulea University of Technology, Sweden. At present she is a research assistant at the Geotechnical protection department of Vilnius Gediminas Technical University.

SUNKIŲJŲ METALŲ IR NAFTOS PRODUKTŲ KELIO APLINKOJE TYRIMAI IR MAŽINIMAS NAUDOJANT GAMTINIUS SORBENTUS

Mokslo problemos aktualumas – Pagrindiniai automobilių kelių teršalai yra sunkieji metalai, neorganinės druskos, aromatiniai angliavandeniliai (naftos produktai) ir kietosios dalelės, susikaupiančios ore arba kelio paviršiuje. Šie teršalai pernešami oro srautais bei nuplaunami nuo kelių lyjant lietui ar tirpstant sniegui. Paviršiniai vandenys yra ypač pažeidžiami, nes neapsaugoti nuo tiesioginio teršalų į juos patekimo. Dirvožemyje natūraliai yra sunkiųjų metalų, kurie dažniausiai yra mineralų izomorfinė priemaiša, taip pat būna jų sorbuoti ar sudaro junginius su organine medžiaga. Lietuvos dirvožemiuose jų kiekiai yra maži, todėl nepavojingi, tačiau yra vietovių, kuriose dėl antropogeninės veiklos jų kiekiai išauga kelis ar net keliasdešimt kartų ir pasiekia pavojingą biotai lygį. Vienas iš svarbiausių sunkiųjų metalų technogeninių šaltinių yra transporto emisijos, pasižyminčios plačiu sunkiųjų metalų spektru. Dėl to kelio aplinkos dirvožemis

šalia intensyvaus eismo kelių yra užterštas sunkiaisiais metalais (kaip ir naftos produktais). Lietuvoje ne visi magistraliniai keliai turi aplinkkelius ir neretai kerta gyvenamąsias vietas, todėl nemažai žmonių, gyvenančių šalia kelių, patenka į rizikos sveikatai zoną. Dažnai tokiose zonose žmonės, nepaisydami pavojaus sveikatai, augina daržoves sklypuose, nutolusiuose tik kelis metrus nuo kelio važiuojamosios dalies. Į tokias daržoves patenka transporto skleidžiami teršalai. Be to, pakelėse renkamos uogos arba pakelių žolė naudojama gyvuliams šerti. Iš užteršto pakelių dirvožemio dalis sunkiųjų metalų su lietaus ir sniego tirpimo vandeniu migruoja per aeracijos zoną gilyn ir patenka į gruntinį vandenį, kuris dažnai naudojamas maistui. Taigi tokiose zonose maisto grandinėje padidėja sunkiųjų metalų ir kitų pavojingų cheminių junginių kiekis, o tai kelia pavojų žmonių sveikatai. Todėl labai aktualu surasti būdus, kaip sunkiuosius metalus ir naftos produktus pašalinti iš dirvožemio ar vandens, kad jie toliau nemigruotų ir nepatektų į gretimas ekosistemas. Siekiant sumažinti pavojų aplinkai, kylantį dėl dirvožemio ir vandens taršos sunkiaisiais metalais ir naftos produktais, būtina tobulinti pigius vandens ir dirvožemio valymo metodus, kurie nesuardytų dirvožemio struktūros, nesumažintų jo derlingumo ir būtų tinkami taikyti paviršiniame dirvožemio sluoksnyje. Pastaraisiais metais dėmesys sukoncentruotas *in situ* valymo metodams plėtoti, kurie nėra brangūs ir mažiau veikia natūralų kraštovaizdį bei ekosistemas, nei tokie metodai, kaip užteršto grunto iškasimas, laikymas ir valymas atliekų aikštelėse. *In situ* metalų sulaikymas, naudojant gamtinius ceolitus ir vermikulitus, yra perspektyvi alternatyva dabar egzistuojantiems dirvožemio bei vandens valymo metodams. Šis metodas remiasi fundamentaliomis žiniomis apie geocheminius procesus, valdančius metalų migracinių formų susidarymą dirvožemyje, jų migraciją ir *biologinį pasisavinamumą* aplinkoje. Pagrindinė *in situ* valymo metodo esmė yra ta, kad naudojant gamtinius ceolitus, dirvožemyje sumažinama ta toksinių elementų dalis, kuri yra potencialiai mobili arba lengvai *biologiškai pasisavinama*. Metalai, patekę į gamtinį mineralinį sorbentą, sulaikomi jo viduje ir tokiu būdu užkertamas kelias toliau teršalams judėti dirvožemio komponentuose ar patekti į gruntinį vandenį.

Darbo tikslas ir uždaviniai

- Nustatyti intensyvaus eismo kelių aplinkoje esančio dirvožemio užterštumo sunkiaisiais metalais mastą ir parengti mokslškai pagrįstas dirvožemio bei vandens taršos sunkiaisiais metalais bei naftos produktais mažinimo rekomendacijas naudojant gamtinį ceolitą ir vermikulitą.
- Įvertinti kelio aplinkoje esančio dirvožemio taršą sunkiaisiais metalais ir jos pavojingumą.
- Įvertinti kelio aplinkoje esančio dirvožemio taršos pavojingumo laipsnį ir kaitos tendencijas.
- Įvertinti gamtinio ceolito gebą šalinti sunkiuosius metalus iš dirvožemio

bei lietaus nuotekų.

- Įvertinti gamtinio ceolito bei vermikulito gebą šalinti naftos produktus iš lietaus nuotekų.

Mokslinis naujumas

Taikant kompleksinius eksperimentinius ir matematinius statistinius aplinkosaugos tyrimus buvo visapusiškai ištirta kelio aplinkos dirvožemio užterštumo sunkiaisiais metalais kaitos laike tendencija, įvertintos bei sukurtos taršos sunkiaisiais metalais ir naftos produktais mažinimo, naudojant gamtinį ceolitą ir vermikulitą, priemonės. Darbo naujumą rodo:

1. Įvertinta kelio aplinkos dirvožemio tarša sunkiaisiais metalais, jos pavojingumo laipsnis bei taršos kaitos tendencijos.
2. Įvertintas gamtinio ceolito tinkamumas šalinti sunkiuosius metalus iš dirvožemio bei vandeninių tirpalų.
3. Įvertintas gamtinio ceolito bei vermikulito tinkamumas šalinti naftos produktus iš vandeninių tirpalų.

Tyrimų metodika apima dirvožemio ir eksperimentinių tirpalų analizę: induktyviai sužadintos plazmos atominės emisijos spektrometrijos (ICP-OES) metodu atliktą Lulėjo technikos universiteto mokslinėje laboratorijoje, Švedijoje, metalams (Cr, Cu Pb ir Zn) nustatyti skystoje fazėje; atominės absorbcijos spektrofotometrijos AAS metodu atliktą VGTU, Lietuvoje, metalams (Cu, Ni, Mn, Pb ir Zn) nustatyti skystoje fazėje; emisinės spektrinės analizės metodu (DC Arc ES) atliktą Geologijos ir geografijos institute, Lietuvoje metalams (Ag, B, Ba, Co, Cr, Cu, Ga, Li, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn ir Zr) nustatyti kietoje fazėje; Infracal TOG/TPH analizatoriumi naftos produktams skystoje fazėje nustatyti VGTU, Lietuvoje.

Praktinė vertė. Paruoštos kelio aplinkos dirvožemio ir lietaus nuotekų sunkiaisiais metalais bei naftos produktais taršos mažinimo rekomendacijos. Sukurtas ir užpatentuotas „Lietaus nuotekų valymo filtras“.

Ginamieji darbo teiginiai

1. Pastaraisiais metais kelio aplinkos dirvožemio tarša sunkiaisiais metalais padidėjo.
2. Gamtinis ceolitas tinka sunkiųjų metalų šalinimui iš dirvožemio bei lietaus nuotekų nuo kelio paviršiaus.
3. Gamtinis ceolitas ir vermikulitas tinka naftos produktų šalinimui iš lietaus nuotekų.

Darbo apimtis. Darbą sudaro bendra darbo charakteristika, 4 skyriai, darbo rezultatų apibendrinimas ir rekomendacijos, literatūros sąrašas, publikacijų sąrašas. Bendra disertacijos apimtis 145 puslapiai, 71 iliustracija, 14 lentelių.

Darbo rezultatų apibendrinimas ir rekomendacijos

1. Kelio aplinkos dirvožemio užterštumo tyrimai, atlikti 2002 m. Lietuvos teritorijoje intensyvaus ir mažo intensyvumo keliuose bei 2005 m. magistraliniame kelyje Vilnius–Kaunas, parodė, kad didžiausi sunkiųjų metalų Pb, Cu, Cr, Zn, Ni, Mn kiekiai kaupiasi skiriamosioje kelio juostoje bei artimiausioje kelio zonoje iki 10–15 m atstumu nuo kelio briaunos.
2. Visuose magistralinio kelio Vilnius–Kaunas aplinkos dirvožemio mėginių paėmimo 2005 m. skersiniuose profiliuose sunkiųjų metalų kiekiai neviršijo DLK, išskyrus III profilio (42,1 km) dirvožemio mėginius. Šiame skersiniame profilyje skiriamosios juostos dirvožemyje Pb kiekis viršija DLK 1,4 karto, o 5 m atstumu nuo kelio ŠR profilio pusėje – 1,5 karto.
3. Dirvožemio mėginių, paimtų magistralinio kelio Vilnius–Kaunas III skersiniame profilyje (42,1 km), kur kelias eina iškasoje, neleidžiančioje teršalams išsisklaidyti, tyrimais nustatyta, kad dirvožemio užterštumas sunkiaisiais metalais vertinant pagal suminio užterštumo rodiklį Z_{d6} vidurkis padidėjo apie 2,3 karto – nuo 2,0 iki 4,8 kartus per pastaruosius 14 metų. Vertinant dirvožemio užterštumo padidėjimą tik zonoje iki 10 m atstumu nuo kelio briaunos, suminio užterštumo rodiklio Z_{d6} vidurkis padidėjo daugiau nei 3 kartus per pastaruosius 14 metų.
4. Nustatyta, kad sunkiųjų metalų Cu, Pb ir Zn sorbcijos ceolitu iš smėlio dirvožemio seka $Pb^{2+} > Zn^{2+} > Cu^{2+}$. Esant sunkiųjų metalų pirminei koncentracijai 500 mg/kg, o gamtinio ceolito kiekiui mėginiuose 10 %, Pb sorbavo 82 %, Zn – 47 %, o Cu – 30 %.
5. Sunkiųjų metalų sorbcijos gamtiniu ceolitu iš tirpalų eksperimentas parodė, kad Pb sorbuojamas geriausiai. Gamtinis ceolitas, nepriklausomai nuo frakcijos dydžio (< 2 mm ar 2–10 mm), sorbavo apie 99 % Pb. Abi ceolito frakcijos sorbavo apie 63 % Zn. Vario sorbuota mažiau ir tai sudarė 11,4 % mažesnėje nei 2 mm frakcijoje ir 9,5 % – 2–10 mm frakcijoje. Atlikus sunkiųjų metalų ir Na bei Ca chloridų sorbcijos iš tirpalų, naudojant kolonėlę pripildytą ceolitu, eksperimentą, nustatyta tokia sorbcinė eilė: $Ca^{2+} > Pb^{2+} > Na^{+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$.
6. Naftos produktų sorbcijos iš vandens laboratorinio eksperimento metu buvo nustatytas dviejų gamtinio ceolito 0,63–1,0 mm ir 1,0–3,0 mm bei $2,0 \pm 0,71$ mm vermikulito frakcijų NP sorbcijos efektyvumas, kuris atitinkamai siekė 96,6, 93,3 ir 97,5 %, kai pirminė NP koncentracija tirpale buvo 15 mg/l.
7. Kadangi transporto tarša sunkiaisiais metalais bei naftos produktais turi įtakos kelio aplinkos dirvožemiui bei vandens telkiniams, todėl reikia taikyti organizacines bei technines priemones.

Rekomendacijos

1. Rekomenduojama, remiantis dirvožemio mėginių kelio aplinkoje tyrimų rezultatais, žemės ūkio veiklai naudoti plotus, esančius kelio aplinkoje ne arčiau kaip 15 m atstumu nuo kelio briaunos, siekiant apsaugoti žmonių sveikatą. Atliktų tyrimų rezultatus pateikti Lietuvos Respublikos žemės ūkio ministerijai, kad praktikoje būtų siekiama zonoje 15 m atstumu nuo intensyvaus eismo kelio briaunos riboti žemės ūkio veiklą.
2. Rekomenduojama kelius tiesti įvairiose teršalų aerodinaminėse gaudyklėse (pvz. kelio iškasose su stačiais šlaitais), kadangi jos neleidžia teršalams išsisklaidyti. Dirvožemio mėginių, paimtų 1991 ir 2005 m., tyrimų rezultatai patvirtina, kad kelio, einančio iškasa, aplinkoje teršalai neišsisklaido, o nusėda šlaituose. Visose jau esančiose intensyvaus eismo kelių teršalų aerodinaminėse gaudyklėse turi būti įrengtos lietaus nuotekų surinkimo ir valymo sistemos bei lietaus nuotekų valymo filtrai.
3. Rekomenduojama, kelio aplinkos dirvožemio bei paviršinių vandens telkinių taršai mažinti, naudoti sukurta ir užpatentuotą (patento Nr. LT 5292 B) lietaus nuotekų valymo filtrą su gamtinių mineralinių sorbentų įkrova, kurį galima montuoti kelio aplinkoje. Lietaus valymo filtras montuojamas tose kelio vietose, kuriose yra įrengti latakai, nukreipiantys lietaus nuotekas į vandens surinkimo sistemas. Išvalytos lietaus nuotekos pašalinamos lietaus nuotekų surinkimo ir drenažo sistemomis. Lietaus nuotekų filtras taip pat gali būti montuojamas už sulaikomųjų nuotekų tvenkinių, kuriuose vyksta pagrindinis teršalų bei kietųjų dalelių nusodinimas.
4. Rekomenduojama naudoti patobulintą lietaus nuotekų nuo kelių paviršių valymo sistemą, įdiegiant naujos konstrukcijos lietaus nuotekų surinkimo ir valymo infiltracinius-žolinius trapecinius griovius su gamtinio ceolito sluoksniu.

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**INVESTIGATION OF HEAVY METALS AND PETROLEUM PRODUCTS
IN THE ROADSIDE ENVIRONMENT AND REMEDIATION BY
NATURAL SORBENTS**

**Summary of Doctoral Dissertation
Technological Sciences,
Environmental Engineering and Landscape Management (04T)**

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**SUNKIŲJŲ METALŲ IR NAFTOS PRODUKTŲ KELIO APLINKOJE
TYRIMAI IR MAŽINIMAS NAUDOJANT GAMTINIUS SORBENTUS**

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