

Gas chromatographic analysis of polycyclic aromatic hydrocarbons in the disposed creosote treated wooden railway sleepers collected from several storage sites in Lithuania

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The screening of PAH in used wooden railway sleepers treated with coal tar and creosote for their protection against biodegradation has been made. The analysis was based on cold solvent extraction and Soxhlet extraction of PAH using several organic solvents and analysis by GC-MS/GC-FID. For extraction several organic solvents of different polarity, including aromatic solvents, were tested. The results showed that aromatic solvents are the most efficient solvents for cold solvent extraction with the highest recoveries of PAH from wood matrix. Several PAH were identified. Naphthalene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, crysene and benzo[a]anthracene were predominant. Thirty samples from Central Lithuania and twenty from the coastal area were analyzed. Based on the results of chemical analysis the samples were classified using the cluster analysis according to several parameters including age, decay status and chemical composition of the extract of the sleeper. The composition of PAH varies between intact and rotten sleepers. Few sleeper samples differ from others with a strong coal tar odor and a dark color and very high quantities of PAH.

Key words: wooden railway sleepers, coal tar, creosote, polycyclic aromatic hydrocarbons, gas chromatography–mass spectrometry, cold solvent extraction

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INTRODUCTION

Wooden railway sleepers in Lithuania are in use for maintenance and renewal of some railways. According to the infrastructure development directives, Lithuania will use wooden railway sleepers for at least 15 years more until the exploitation of the former technology railways will be completely stopped and replaced with the railways based on the concrete sleepers. About 30 000 units (2 000 tons) of disposed wooden sleepers are accumulated annually. Mostly pine (*Pinus* L.) or fir (*Abies* Mill.) is used for the production of wooden railway sleepers. Wood is impregnated with coal tar or creosote to prevent the decomposition of wood. Impregnation protects wood from microorganism activity, various bacteria or fungi infections. Coal tar contains several hundreds of organic compounds, so it is difficult to define its exact composition. Creosote is a yellow to amber colour product, obtained by the fractional distillation of crude coal tars [1]. Usually it contains higher percentage of polycyclic aromatic hydrocarbons (PAH) than coal tar. Coal tar components can be classified into five groups regarding a chemical composition and mainly depend on the manufacturer and the manufacturing process. Coal tar contains: (1) polycyclic aromatic hydrocarbons – naphthalene and its alkyl derivatives, also higher PAH like phenanthrene, anthracene and pyrene up to 90%; (2) phenols and acids up to 2–17%; (3) heterocyclic nitrogen compounds and aromatic amines 4–8%; (4) heterocyclic sulphur compounds 1–3%; (5) heterocyclic oxygen compounds including dibenzofurans 5–7% [2].

Creosote is analysed using various chromatographic methods, which are suitable to evaluate PAH and phenols quantitatively and qualitatively. PAH are environmental pollutants. The main source of PAH is incomplete combustion of wood [3]. PAH can be found in atmosphere, soil, and environmental waters [4–6]. Some of PAH are highly carcinogenic, e. g. benzo- α -pyrene (BaP). BaP is distinguished from other PAH by high toxicity and carcinogenetic properties. In coal tar it can be found from 0.3 to 6.4 g/kg. The toxic equivalence factor for BaP is 1, compared to other five- or six-aromatic ring PAH, which have the toxic equivalence factor classified from 0.01 to 0.1 [7].

In 2 000 the European Committee for Standardization has issued a standard on the classification and methods of creosote testing. Methods for testing of the chemical composition of creosote are based on a spectrophotometric and chromatographic analysis, namely, liquid and gas chromatography, fluorescence and UV spectrophotometry [8–11]. The European industry was using creosote where the BaP content in the oil distillate was below 0.005% and the content of volatile compounds is low [12].

The European directive upon hazardous waste handling and disposal defines that such waste cannot be buried, burned or utilized without proper control [13]. During the last decades in many countries the out-of-service wooden

railway sleepers have been disassembled and piled in various places close to the railways or stored in special depots. Transportation of the used railway sleepers is not cost-effective [14].

One of the ways to manage the used wooden railway sleepers as waste is an application of bioremediation technology based on the ability of microorganisms to break down phenols and even polycyclic aromatic hydrocarbons with strong carcinogenic properties [15]. For development of bioremediation technologies of this kind of waste the spectrum and content of the pollutants in the disposed railway sleepers should be screened.

The object of the study was screening of the polycyclic aromatic hydrocarbons composition and content in the disposed creosote treated wooden railway sleepers collected from several storage sites in Lithuania. Due to the long-time continuous accumulation of big amounts of used railway sleepers in many countries worldwide, the composition of pollutant residues in the used sleepers is an important characteristic for development of bioremediation technologies of this kind of waste.

EXPERIMENTAL

Chemicals and standards

Extraction of polycyclic aromatic hydrocarbons from impregnated wooden sleepers was performed using different solvents: methanol (gradient grade), acetonitrile and toluene (HPLC grade), benzene (analytical grade) (Lab-Scan, Poland), n-hexane (pure, Lachema, Czech Republic) and n-heptane (pure, Fluka Analytics, Sigma-Aldrich, Germany). A standard mixture solution of sixteen PAH (Cat. No.: ERS-011; Sigma-Aldrich, Germany) was diluted in benzene/dichloromethane 1:1 (v/v) to 500 mg/ml for identification of the compounds. For a quantitative analysis the calibration curve of 8 different concentrations (from 2 to 250 mg/ml) was constructed.

Sampling and sample preparation

Samples were collected from the central region (Kaunas and Čekiškė) and the coastal region (Klaipėda) of Lithuania from disposed wooden sleepers storage yards as presented in Table 1. The sampling of the wooden sleepers was carried out sawing off the outer layer of 2 cm thickness from the sleeper and grinding the material to 4–8 mm particles. Reference sample preparation was carried out according to the standard method LST EN 15527 (Lithuania) [16] based on the Soxhlet extraction as follows: 20 g of the ground sleeper particles was dispersed in 250 ml of 99.9% toluene and extracted at 120 °C for 8 h. After the extraction, the solution was aligned to 250 ml with toluene. Before gas chromatography the sample was diluted up to 10 times.

Organic solvent extraction of all the samples was carried out at ambient (20 °C) temperature reducing extragent and sample amounts 10 times, namely 2 g of dry ground material

Table 1. List and classification of the used railway sleeper samples

No.	Label	Age		Decay level 1 – intact, 2 – medium rotten, 3 – severe rotten	Type of wood 1 – pine, 2 – fir, 3 – not identified soft wood	Sampling site*
		A < 10 years	B > 10 years			
1	K1	A		1	1	Kaunas
2	K2	A		1	1	Kaunas
3	K3	A		1	2	Kaunas
4	K4	A		1	2	Kaunas
5	K5	A		2	3	Čekiškė
6	K6	A		2	3	Čekiškė
7	K7	A		2	1	Kaunas
8	K8	A		2	1	Kaunas
9	K9	A		2	1	Kaunas
10	K10	A		2	2	Kaunas
11	K11	A		2	1	Kaunas
12	K12	A		2	1	Kaunas
13	K13	A		2	1	Kaunas
14	K14	A		2	1	Kaunas
15	K15	A		2	1	Kaunas
16	K16	A		2	1	Kaunas
17	K17	A		2	1	Kaunas
18	K18	A		2	1	Kaunas
19	K19	B		3	1	Kaunas
20	K20	A		3	2	Kaunas
21	K21	A		1	1	Kaunas
22	K22	A		2	1	Kaunas
23	K23	A		2	2	Kaunas
24	K24	A		2	2	Kaunas
25	K25	A		2	2	Kaunas
26	K26	A		2	2	Kaunas
27	K27	A		2	2	Kaunas
28	K28	A		2	1	Kaunas
29	K29	A		2	1	Kaunas
30	K30	A		2	1	Kaunas
31	K31	A		2	2	Kaunas
32	L1	B		3	3	Klaipėda
33	L2	A		2	3	Klaipėda
34	L3	B		3	3	Klaipėda
35	L4	B		3	3	Klaipėda
36	L5	A		2	3	Klaipėda
37	L6	A		2	3	Klaipėda
38	L7	A		2	3	Klaipėda
39	L8	A		2	3	Klaipėda
40	L9	A		2	3	Klaipėda
41	L10	A		2	3	Klaipėda
42	L11	A		2	3	Klaipėda
43	L12	B		3	3	Klaipėda
44	L13	A		1	3	Klaipėda

45	L14	A		2	3	Klaipėda
46	L15	A		2	3	Klaipėda
47	L16	A		2	3	Klaipėda
48	L17	A		2	3	Klaipėda
49	L18	A		2	3	Klaipėda
50	L19	A		3	3	Klaipėda
51	L20	A		3	3	Klaipėda

* Sampling sites GPS coordinates: Klaipėda (55°42'40"N 21°7'50"E); Kaunas (54°53'50"N 23°53'10"E); Čekiškė (55°09'29"N 23°31'30"E).

was extracted adding 20 ml of the solvent and placed in the orbital shaker for 24 hours to proceed.

Instrumentation and analysis methods

A GC2010 gas chromatograph with a GCMS-QP2010 mass spectrometer (GC-MS), Shimadzu (Japan), was used for a qualitative and primary quantitative analysis of the extracts. Extracts were injected using an AOC-5000 auto injector. The analysis was performed using the low polarity, low bleed gas chromatography column RTX-5MS (30 m × 0.25 mm × 0.25 μm, Restek, USA). For a quantitative analysis a Shimadzu (Japan) GC2010 gas chromatograph with a flame ionization detector (GC-FID) and an auto injector AOC-20i was employed and the analysis was performed with the high temperature resistant (maximum temperature 370 °C) column RXI[®]-5HT (30 m × 0.25 mm × 0.25 μm, Restek, USA).

GC-MS method conditions were as follows: injector temperature was set at 280 °C, interface temperature 280 °C, ion source temperature 220 °C. The temperature gradient was as follows: 60 °C maintained for 1 min and raised at 25 °C/min up to 180 °C, then at 5 °C/min raised up to 320 °C and maintained for 10 min. The total analysis time was 43.8 min. The injection of 1 μl volume was used. Carrier gas was helium 5.0 (AGA, Lithuania), flow rate was set at 2.0 ml/min. Analytes were ionized with an electron ionization ion source set at ionization energy 70 eV. Two MS operation modes were used: selective ion monitoring (SIM) and total ion current (TIC).

GC-FID method conditions were as follows: injector and detector temperatures were set at 350 °C. The following temperature gradient was used: 60 °C maintained for 1 min, temperature was increased at 10 °C/min up to 120 °C, at 5 °C/min up to 180 °C, at 10 °C/min up to 330 °C and maintained for 7 min. The total analysis time was 41 min. The injection was 1 μl. Carrier gas was helium, column flow rate was set at 1.4 ml/min, and column head pressure was 171 kPa.

Injection was carried out in a split mode at the ratio 1:10 in both cases. Two injections were performed per sample.

Statistical analysis

The statistical measurements, average, standard deviation and relative standard deviation were calculated using the MS Excel software. The cluster analysis of Euclidean distances was made using the STATISTICA v8.0 software.

RESULTS AND DISCUSSION

Sample preparation method validation

Wooden matrix sample preparation is quite a challenge. There are numerous sample preparation methods for soil, water and air samples developed. However, wood is quite a different material, less dense, therefore bigger volume samples are required for preparation. Extraction solvent selection is an important factor in order to obtain sufficient recoveries. Soxhlet extraction is known as a powerful extraction method, although it is expensive, highly energy consuming and it is of very low throughput. Other extraction techniques can be selected, such as overheated, high pressurized solvent extraction, microwave extraction, sonic enhanced extraction, solid phase microextraction etc. However, none of these methods can be simple and cost-effective. The cold liquid extraction, on the other hand, can save time and energy resources. It is simple, cost-effective and does not require specific equipment. Nevertheless, to reach optimal extraction recovery can be difficult. Therefore proper selection of the extraction solvent is important.

Soxhlet extraction was carried out according to the Standard method EN 15527 [16]. Similar conditions were applied for the ambient temperature organic solvent extraction (24 hours extraction) agitating the sample in the orbital shaker. The advantage of the cold liquid extraction compared to the standard Soxhlet procedure was, firstly, high throughput, since tens of samples can be extracted simultaneously and, secondly, that the extracted sample amount can be reduced up to ten times (depending on the pollutant residue in the sleeper chips) [17]. The choice of the solvent for extraction is always related to the analytical method used. Gas chromatography has high organic solvent compatibility, however, liquid chromatography is limited to

fewer solvents [18]. Different solvents were tested for the extraction, namely, methanol, acetonitrile, n-heptane, n-hexane, benzene and toluene which represent polar, nonpolar and aromatic solvent groups. All extractions were carried out in triplicate and relative standard deviations (RSDs), did not exceed 5.55%. Results showed that benzene and toluene give the highest recoveries of polycyclic aromatic hydrocarbons (PAH) from the wooden sleeper matrix (Fig. 1). This is related to the same aromatic structure of PAH and these organic solvents [19]. Toluene is the mostly used solvent for extraction of these pollutants and is also less toxic compared to benzene [20]. The results showed that 70% of all aromatic compounds can be extracted out of impregnated wood using a cold solvent extraction method with toluene relatively to the high temperature Soxhlet extraction method with the same solvent. Toluene and benzene used for cold solvent extraction were of higher selectivity to both more volatile compounds in the wooden samples, namely, naphthalene (recovery 57.3% compared to the standard Soxhlet extraction method using toluene) and acenaphthene (recovery 51.38%), and less volatile compounds such as anthracene (recovery 63.01%). The recovery of volatile compounds using other solvents was considerably lower, e. g. using aliphatic n-heptane the recovery of naphthalene and acenaphthene did not exceed 15% and the recovery of anthracene was only 4%.

Polycyclic aromatic hydrocarbons are non-polar, hydrophobic substances. Therefore they almost do not dissolve in water. PAH solubility in water decreases with an increase of the molecular weight and decrease of the polarity (solubility limits for naphthalene are 25–30 µg/ml, anthracene 0.03–0.045 µg/ml, phenanthrene 0.99 µg/ml and benzo(α) pyrene 0.004 µg/ml [21]). Two- and three-ring PAH are quite volatile, four-ring and higher PAH have a significant drop

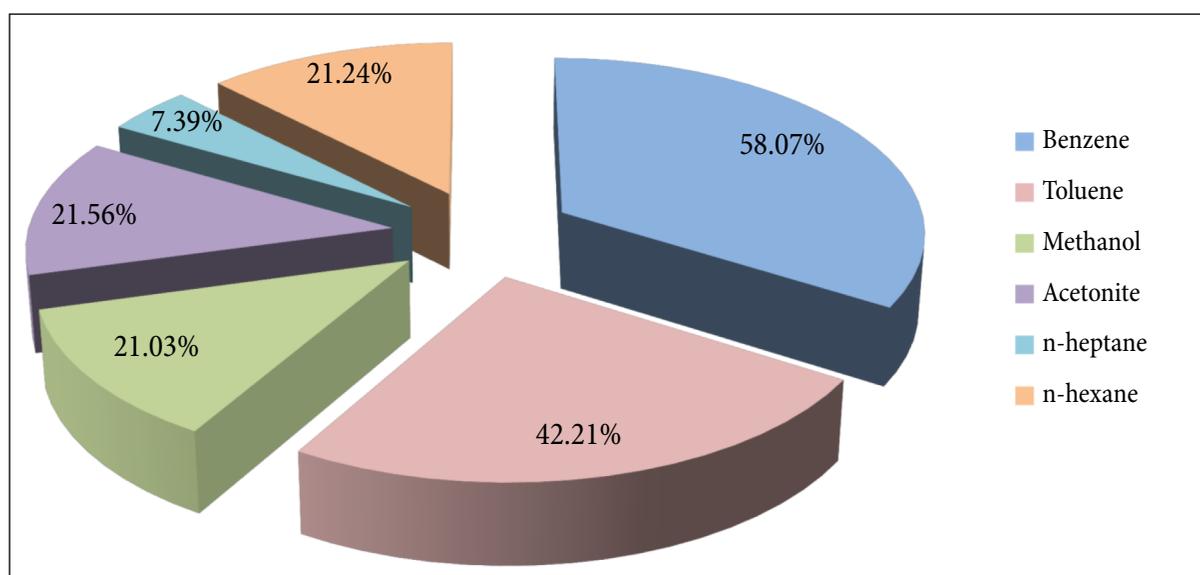


Fig. 1. Recovery of the liquid extraction using different organic solvents in comparison with standard Soxhlet extraction

of volatility. Wide selection of organic solvents can be used for extraction of PAH, however, similar structure aromatic solvents show higher dissolution ability for PAH. The highest recovery of PAH was obtained using benzene or toluene as an extragent (recoveries 86.35 and 70.13%, respectively). The lowest recovery value was obtained using n-heptane (15.82%), acetonitrile and methanol showed similar medium recoveries (28.33 and 23.50%, respectively). Due to carcinogenic and mutagenic properties of benzene a higher homologue, toluene, was used for further extraction of all samples in this study. The sample matrix, namely, its composition, porosity, size and size distribution, also play role in the extraction process. Since the same soft wood matrix was used in all the experiments, this factor can be neglected.

Analysis method validation

For the chromatographic analysis all the samples were injected two times and the average values were used for calculations. For the gas chromatographic analysis repeatability determination five consecutive injections were carried out and RSD for the PAH peak area was calculated resulting in 1.8%. Polycyclic aromatic hydrocarbons were identified using the PAH standard mixture consisting of 16 PAH with the molar mass ranging from 128 to 278 (Fig. 2). Calibration curves were constructed out of 8 concentrations between 2 µg/ml and 250 µg/ml of individual compounds. The limits of detection and quantification (LOD and LOQ), calibration curve regression coefficient R^2 , relative standard deviation RSD were calculated for each of PAH identified. The results obtained are presented in Table 2.

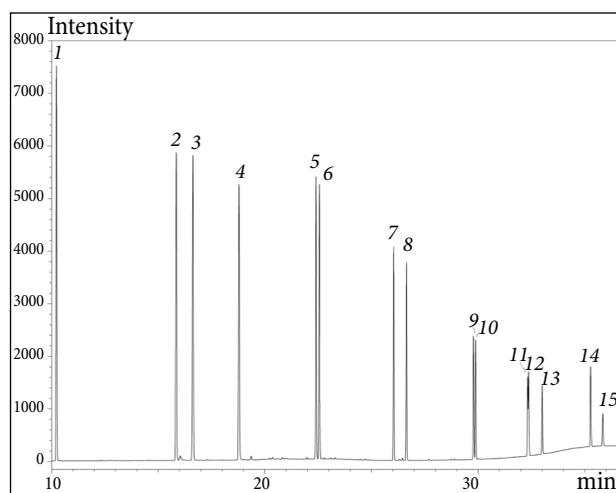


Fig. 2. GC-FID of the standard mixture of 16 PAH, MS mode total scan (TIC): 1 – naphthalene, 2 – acenaphthylene, 3 – acenaphthene, 4 – fluorene, 5 – phenanthrene, 6 – anthracene, 7 – fluoranthene, 8 – pyrene, 9 – benzo(a)anthracene, 10 – chrysene, 11 – benzo(b)fluoranthene, 12 – benzo(k)fluoranthene, 13 – benzo(a)pyrene, 14 – indeno(1,2,3,c,d)pyrene, 15 – dibenzo(a,h)anthracene, 16 – benzo(g,h,i)perylene – not determined

Depending on the gas chromatograph injector construction the higher molecular weight PAH results in lower signal at the same mass concentration [22]. This can be overcome using on-column injection. Otherwise different volatility of the analytes affects the result. This is reflected in lower slope of the calibration graphs, decrease of the regression coefficient R^2 and increase of the standard deviation for higher

Table 2. GC-FID method validation parameters

PAH	Regression equation	Regression coefficient, R^2	LOD, ng/ml	LOQ, ng/ml	RSD% _{0.25} *	RSD% _{0.02} *
Naphthalene	$y = 1515.3x$	0.999	8.81	26.69	0.15%	1.50%
Acenaphthylene	$y = 1372.1x$	0.999	9.73	29.48	0.31%	0.44%
Acenaphthene	$y = 1361.3x$	0.999	9.81	29.72	0.34%	1.04%
Fluorene	$y = 1230.5x$	0.997	10.85	32.87	0.93%	2.31%
Phenanthrene	$y = 976.79x$	0.987	13.66	41.41	0.88%	2.20%
Anthracene	$y = 952.59x$	0.986	14.01	42.46	0.93%	1.79%
Fluoranthene	$y = 664.24x$	0.968	20.09	60.89	0.60%	1.24%
Pyrene	$y = 627.96x$	0.967	21.26	64.41	0.57%	0.77%
Benzo(a)anthracene	$y = 404.68x$	0.971	32.98	99.95	0.15%	1.36%
Chrysene	$y = 388.70x$	0.974	34.34	104.06	0.19%	1.22%
Benzo(b)fluoranthene	$y = 284.11x$	0.982	46.98	142.37	5.55%	6.97%
Benzo(k)fluoranthene	$y = 273.43x$	0.971	48.82	147.93	7.02%	7.54%
Benzo(a)pyrene	$y = 254.25x$	0.981	52.50	159.09	5.49%	5.73%
Indeno(1,2,3,c,d)pyrene	$y = 372.40x$	0.984	35.84	108.61	5.81%	5.48%
Dibenzo(a,h)anthracene	$y = 171.97x$	0.978	77.62	235.20	6.00%	6.08%
Benzo(g,h,i)perylene	n/d**	n/d	n/d	n/d	n/d	n/d

* RSD calculated for different concentrations 0.25 and 0.02 µg/ml.

** n/d – not determined.

PAH. Due to the signal loss, the limit of detection increases and repeatability decreases for higher PAH.

Gas chromatographic analysis

A gas chromatograph with a mass spectrometric detector was used for the optimization of chromatographic method conditions. The optimized GC-MS method was used for identification of pollutants comparing the mass spectra obtained with the spectra from the NIST database 8.0v. The configuration of the equipment and relatively low chromatographic column operation temperature limit (max temperature 320 °C) did not provide a possibility to evaluate higher PAH content efficiently. The latter experiments of quantitative analysis were carried out using the high thermal stability GC column and flame ionization detection. Gas chromatography with flame ionization detection (GC-FID) was carried out for the quantitative and qualitative analysis of PAH in the used creosote impregnated wooden railway sleepers. Screening of the samples was performed using four variables: type of wood, age of the sample, decay level and geographic origin of the sample (Table 1). The type of the wood used for manufacturing of railway sleepers was determined using the microscopic method. Dr. Adomas Vitas has identified from the microscopic observation of the samples that pine (*Pinus*) and fir (*Abies*) were used for manufacturing of the sampled sleepers. They are mostly used to manufacture the railway sleepers, less frequent is oak or larch [23]. The age of railway sleepers was determined according to the ID plate with the manufacturing date or according to the railway company provided data. Commonly a railway sleeper serves ca. 15–20 years before it is replaced. In the intensive traffic districts sleepers can be worn out in 5 years [24]. The decay level of wood depends on many factors, such as meteorological conditions, geographic location, number and variety of microorganisms in the surrounding environment, wood kind and pre-treatment used [25]. Samples were collected in different regions of different climatic conditions influencing the decay of the wood. The coastal area in Lithuania is more humid and climate is milder compared to the central part, therefore it provides better natural biotic conditions for degradation of the sleepers. Higher humidity, more windy and sunny days in the coastal area are the abiotic factors, which affect the loss of PAH, particularly those of higher polarity and volatility. In Table 1 the investigated samples are classified according to age, decay level, wood type and storage site location.

Screening analysis was performed for ca. fifty samples from two different regions of Lithuania (central and coastal) using extraction with toluene at ambient temperature.

The results show that the number and concentration of PAH in the samples are closely related to the condition of the railway sleepers. The most rotten sleepers contained smaller amounts and lower numbers of PAH compared with intact sleepers. This is due to the natural bioremediation process occurring in the open environment [26]. Influence

of the geographic location of railway sleepers sampling and storage sites is expressed on the qualitative and quantitative results. Comparing different locations, from which the samples were taken, it is clear that climatic conditions are a factor of wooden railway sleepers higher decay in more humid (the coastal area of Lithuania) than in arid areas (the central area of Lithuania) thus affecting the residual PAH concentration in the sleepers.

All samples come in great variety and different concentrations of PAH. Samples from the central area (Kaunas and Čekiškė) are summarized in Fig. 3. The most predominant compounds are phenanthrene, fluoranthene and pyrene compared with naphthalene and other smaller molecular mass compounds, which can be reduced due to their volatility or easier natural bioremediation.

Used wooden sleepers collected in the coastal area were more worn-out than those collected in central Lithuania. Some of the collected samples were in a severe decay state. A few samples of less than 10 years old were in good condition and they contained a high concentration of polycyclic aromatic hydrocarbons. All the data for the coastal area samples are presented in the diagram of PAH distribution in wooden sleeper samples in Fig. 4. Approximately 30% of the samples from the coastal area contained only trace amounts of the PAH (below 0.06 g/kg).

Cluster analysis

Cluster analysis was used for the data evaluation to refine characterization of the object properties according to the several factors potential to affect the composition and amounts of residual PAH. As a result, all the samples were spread into three main clusters with two subgroups each (Fig. 5), i. e. the first cluster consisted of group G1, the second cluster consisted of groups G2 and G3, and the third cluster consisted of groups G4 and G5. Each large cluster corresponds to the sleeper condition and age which is reflected in the concentration of PAH found in the extracts. A separate cluster includes high concentration PAH samples, which were intact and not decayed (G1).

The first group (G1) is a small group of screened wooden sleepers, where sleepers from the coastal area are dominating at the ratio 2:1, which is distinguished by the highest concentration of PAH. By appearance these wooden sleepers distinguish for being coated by a dark colour oily layer and having a strong characteristic coal tar odour. The concentration of PAH in this group exceeds the regulated norms more than 10 times.

The second group of wooden railway sleepers screened are similar to the first group qualitatively. The major factor which distinguishes this group from the first group is the presence of several semi-volatile PAH like fluorene and acenaphthene. Additionally, the condition of wooden sleepers from the second group (G2) is somewhat worse than the condition of the first group. Samples from the coastal area and central Lithuania in these groups are represented equally.

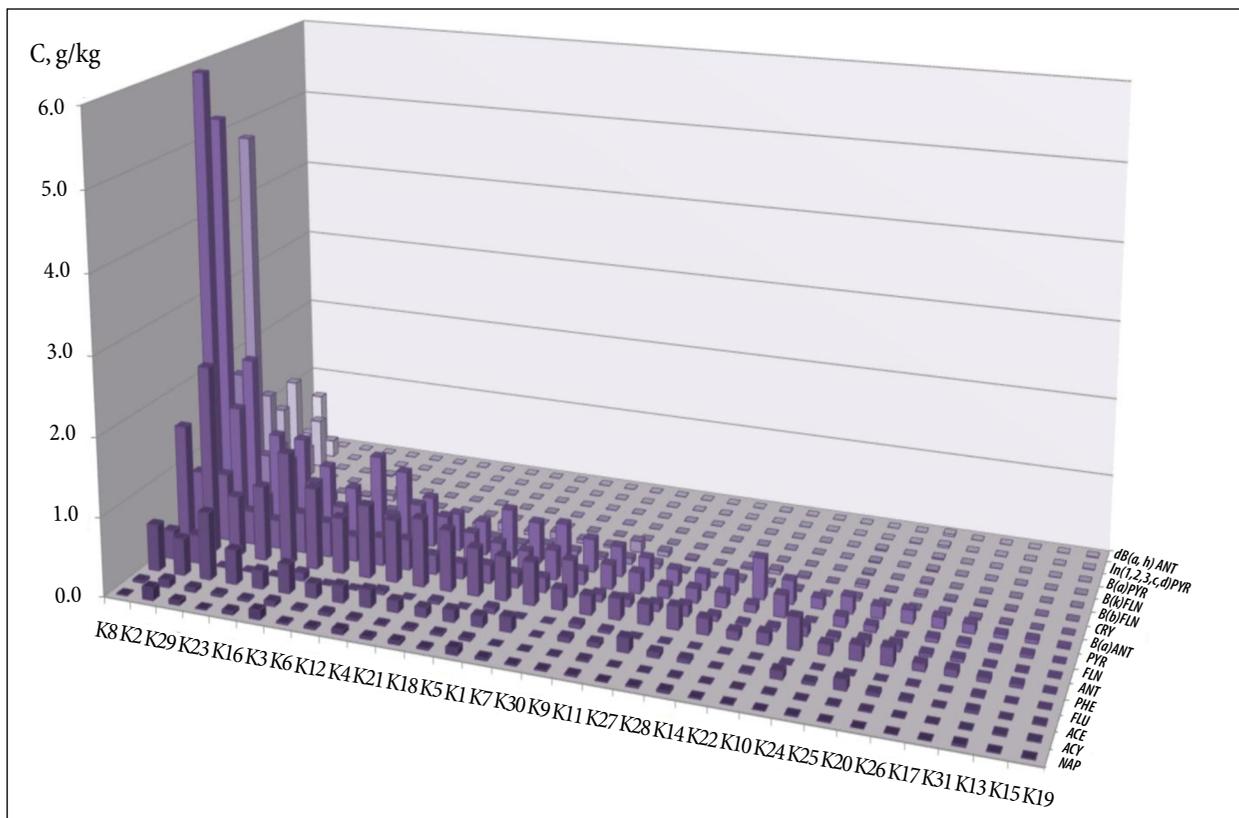


Fig. 3. Diagram of the PAH content (g/kg) in wooden railway sleepers collected in central Lithuania. *NAP* – naphthalene; *ACY* – acenaphtylene; *ACE* – acenaphthene; *FLU* – fluorine; *PHE* – phenanthrene; *ANT* – anthracene; *FLN* – fluoranthene; *PYP* – pyrene; *B(a)ANT* – benzo(a)anthracene; *CRY* – crysene; *B(b)FLN* – benzo(b) fluoranthene; *B(k)FLN* – benzo(k)fluoranthene; *B(a)PYP* – benzo(a)pyrene; *In(1,2,3,c,d)PYR* – indeno(1,2,3,c,d)pyrene; *db(a,h)ANT* – dibenzo(a,h)anthracene (see sample codes in Table 1)

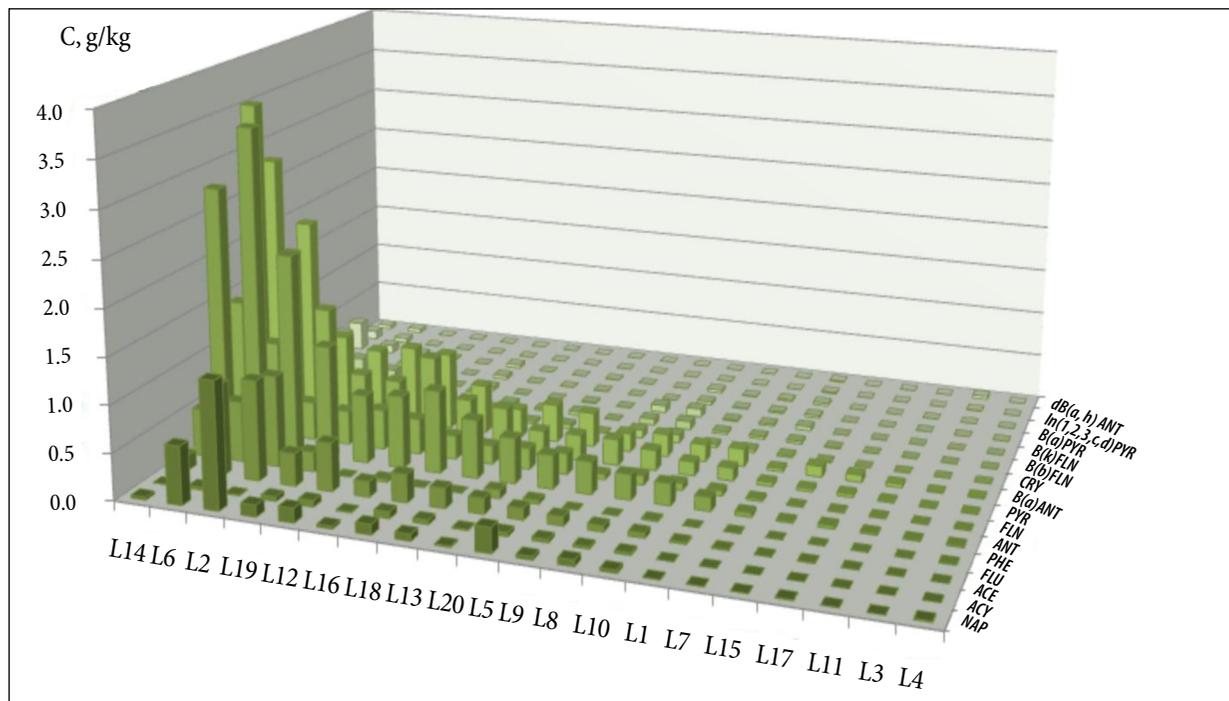


Fig. 4. Diagram of the the PAH content (g/kg) in wooden railway sleepers, collected in the coastal area of Lithuania (abbreviations as in Fig. 3; see sample codes in Table 1)

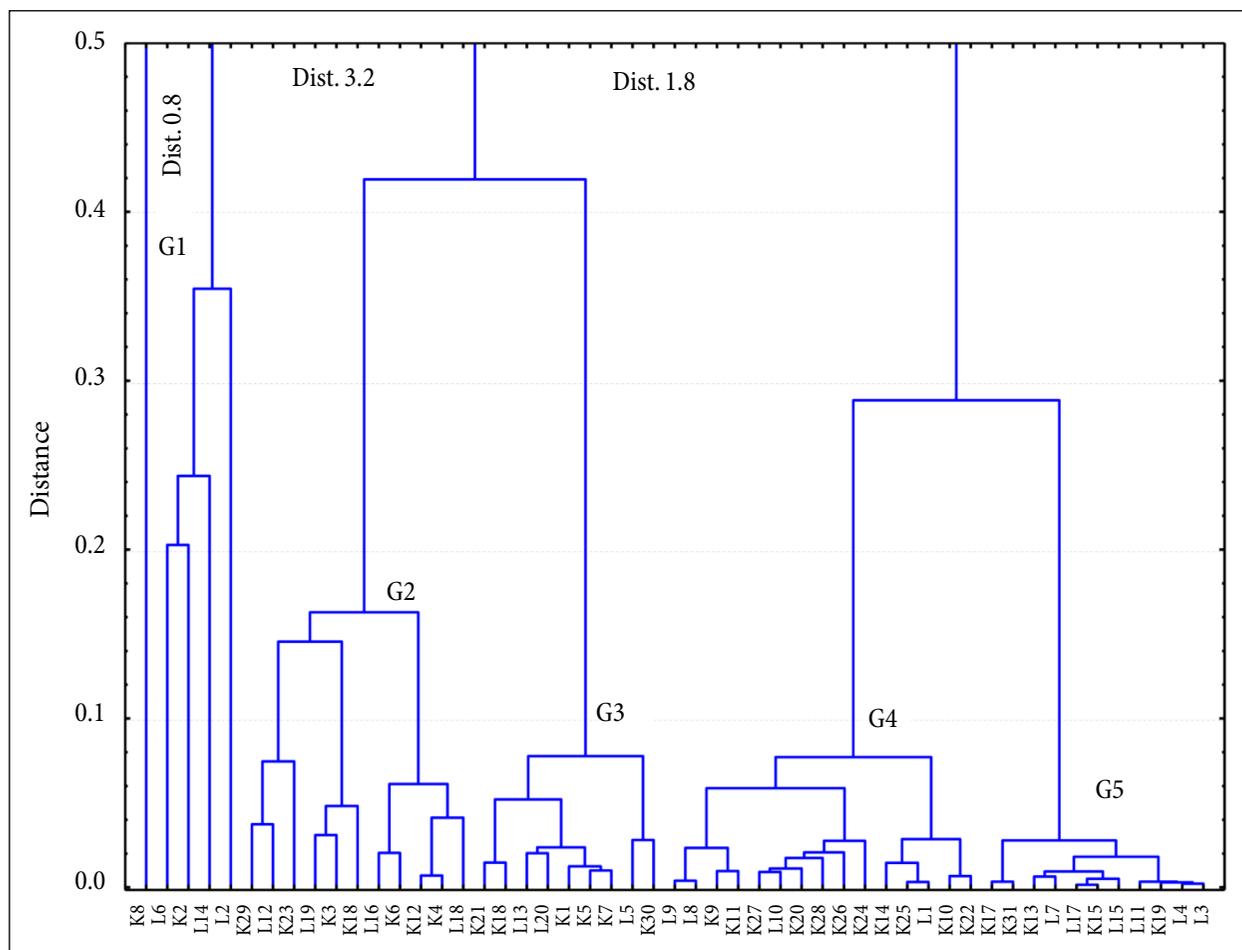


Fig. 5. Classification to the clusters of the tested samples (identification of the samples in Table 1)

Groups 3 and 4 (G3; G4) represent the groups of railway wooden sleepers which are of a medium decay condition and have a specific composition of PAH. In these groups of sleepers PAH with five and six rings were not determined or were determined at the detection limits. The samples from Kaunas were slightly dominating in groups 3 and 4 (G3; G4).

The last group (G5) of the samples corresponds to wooden sleepers, which are ten years or older and are of a medium or higher decay level. Sleepers from the coastal area are dominating in this group at the ratio 2:1. Their composition of PAH differs from other samples by the high variety of environmental pollutants.

The cluster analysis revealed the relation of qualitative and quantitative differences of the PAH composition on the properties of the used wooden sleepers. It showed that the decay level of the sleeper is reflected in the qualitative composition of PAH. Also climatic conditions have influence on the quantitative and qualitative differences of PAH which are obvious comparing samples from central Lithuania and the coastal area. The average annual precipitation in Klaipėda is 750–800 mm while in Kaunas it is 600–650 mm. The average temperature in Klaipėda is 6.5–7.0 °C during a year and in Kaunas it is 6.0–6.5 °C, so higher humidity and slightly

higher temperature provide more favourable conditions for microbiological degradation of the pollutants.

CONCLUSIONS

Organic solvents of various polarity and aromatic properties, namely, methanol, acetonitrile, n-heptane, n-hexane, benzene and toluene were used for extraction of polycyclic aromatic hydrocarbons from wooden railway sleepers. The highest recoveries of polycyclic aromatic hydrocarbons were obtained using benzene, however, due to its lower mutagenic and carcinogenic activities toluene was selected for latter extractions instead. Heptane showed poor ability to extract PAH from wood material, methanol and acetonitrile showed similar moderate recoveries. The optimized extraction method quantitative repeatability provided 5.5% RSD and the extraction recovery was 70.13% compared to the standard Soxhlet extraction method with toluene as an extraction solvent.

Gas chromatography method conditions were optimized for the separation of PAH, the limit of detection was between 30 ng/ml and 90 ng/ml while injection repeatability was up to 2% RSD. Using the external standard method 15 polycyclic aromatic hydrocarbons were identified and quantified.

All types of wooden railway sleepers samples collected were analysed and classified using a cluster analysis. Five groups of the samples were distinguished. The first group (G1) is characterized by an extremely high concentration of PAH, which exceeds the European Union directives for PAH residues in waste by ca. 10 times. The second group (G2) contains fewer semi-volatile PAH like fluorene and acenaphthene and the samples represent sleepers which remained intact. Groups 3 and 4 (G3, G4) represent sleepers which are of a medium decay condition, but have a specific composition of PAH. In this group only PAH with less than five rings were determined. The last group (G5) of the samples corresponds to wooden sleepers which are ten years or older and are of a medium or high level of decay. Their composition of PAH differs from other samples by the extended qualitative variety. Samples from the coastal area are dominating in this group. The geographic sample origin is reflected in the dendrogram clusters. The results show that natural bioremediation occurs in the storage sites and during the exploitation of the sleepers and that the climatic conditions have influenced the decay level of the sampled wooden railway sleepers.

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**POLICIKLINIŲ AROMATINIŲ ANGLIAVANDENILIŲ,
ESANČIŲ KREOZOTU APDOROTUOSE
MEDINIUOSE GELEŽINKELIO PABĖGIUOSE,
SURINKTUOSE SKIRTINGOSE LIETUVOS VIETOSE,
SUDĖTIES IR KIEKIO DUJŲ CHROMATOGRAFINĖ
ANALIZĖ**

S a n t r a u k a

Atliktas policiklinių aromatinių angliavandenilių (PAA) nustatymas panaudotuose mediniuose geležinkelio pabėgiuose, apdoro tuose siekiant juos apsaugoti nuo biologinio irimo skalūnų alyva arba kreozotu. PAA analizei atlikti panaudota skysčių ekstrakcija aplinkos temperatūroje ir Soksleto ekstrakcija bei dujų chromatografija su masių spektrometrine ir liepsnos jonizacijos detekcija. Ekstrakcijai panaudoti skirtingo poliškumo ir aromatiniai organiniai tirpikliai. Rezultatai parodė, kad aromatiniai tirpikliai yra efektyviausi ir lemia didžiausią PAA išgavą, atliekant PAA ekstrakciją iš medienos aplinkos temperatūroje. Buvo identifikuota keletas PAA. Dominavo naftalenas, acenaftenas, fluorenas, antracenas, fenantrenas, fluorantenas, pirenas, krizenas ir benzo[α]antracenas. Išanalizuota 20 Lietuvos centrinėje, ir 30 pajūrio dalyje surinktų bandinių. Panaudojant klasterinės analizės metodą ir cheminės analizės rezultatus bandiniai buvo sugrupuoti pagal keletą veiksnių, įskaitant eksploatacijos trukmę, nusidėvėjimą ir ekstrakto cheminę sudėtį. PAA sudėtis kito priklausomai nuo pabėgių suirimo laipsnio. Keletas pabėgių išsiskyrė iš kitų tamsia išvaizda, intensyviu, būdingu skalūnų alyvai, kvapu ir labai dideliu PAA kiekiu.