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Research and Evaluation of the Aromatic Hydrocarbons in the Polluted Wooden Railway Sleepers

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Abstract. Wooden railway sleepers are impregnated with the chemicals that prevent the disassembling of the wood splitter. Such chemical wood impregnator as creosote or shale oil have been widely used to prolong the lifetime of wooden railway sleepers, protecting them from the negative microorganisms and atmospheric effects. These substances are based on aromatic hydrocarbons (powerful carcinogens), phenolic compounds, heterocyclic nitrogen, oxygen, and sulfur compounds. Lithuania formes over 30,000 pieces of wooden sleepers improper for use annually. Based on the existing environmental legislation, used wooden railway sleepers can not be burned anywehere else except hazardous waste inceneration facilities or can not be buried because of their negative impact on the environment and human health, therefore, this unsuitable wooden sleepers are only stored in their collection or storage areas and they are a major threat to the environment. The aim of this articel is to study how the wooden railway sleepers stored in Vilnius city (Lithuania) are contaminated with the aromatic hydrocarbons using the gas chromatography. Wooden railway sleepers were sampled and prepared for chemical analysis.

Keywords: wooden railway sleepers, aromatic hydrocarbons, creosote, oil shale.

Conference topic: Environmental protection.

Introduction

Wooden railway sleepers are impregnated with chemical substances that prevent the disruptors from eroding wood. The chemical substance creosote is used for impregating and is made of coal and sonsists of aromatic hydrocarbons, phenolic compounds and heterocyclic aromatic compounds that are strong carcinogens (Ikarashi *et al*. 2005a; Kukulska-Zając *et al.* 2014; Ghaly *et al*. 2012).

Based on the data of the International Union of Railways (UIC), 160,030 m^3 of wooden sleeper were purchased in 2010 (analysing the data provided by the European countries that cover around 70% of the European railway infrastructure) (Černi *et al.* 2015). There are 3 types of wood most widely used for the manufacture of sleepers in Europe: oak, pine and beech. 94% of used wooden sleepers in Finland, Sweden and Poland are made of pine wood. Switzerland, Germany, Norway, and Austria most widely use beech sleepers (95%) (Černi *et al.* 2015). The major part of the main railway sleepers in Europe are made of concrete (in average 75%). The wooden sleepers make only 23% and only a tiny part (up to 3%) of sleepers is made of steel (Fig. 1).

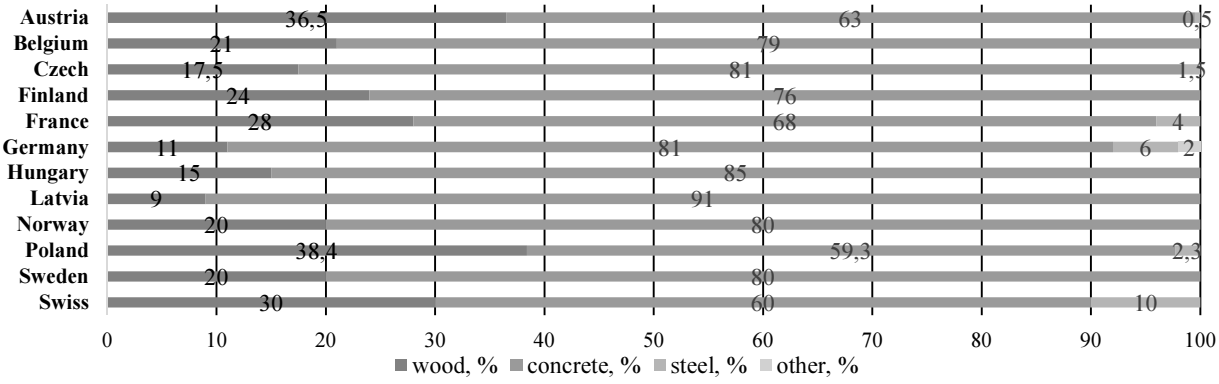

Fig. 1. Percentage of the main railway sleepers (International Union... 2013)

When railways are restored and reconstructed in Lithuania, wooden sleepers are used. Around 30,000 (2,000 tones) of wooden railway sleeper waste are formed annually. The sleepers treated with creosote and made of pine or spruce are the most common (Stankevičius *et al.* 2015).

Based on the valid environmental legislation, the used wooden sleeperes may not be burnt anywehere else except hazardous waste inceneration facilities and they cannot be buried due to their adverse effects on the environment and health. Therefore, a major part of wooden railways unsuitable for use are accumulated in the places of their collection or storage and they pose a major threat to the environment. The aim of this work is to carry out an experimental research on the used wooden railway sleepers stored in Vilnius to evaluate their contamination with aromatic hydrocarbons.

Methodology

Wooden railway sleepers were ground with an electric disc saw, and the sawdust was used for the study. The contamination was researched in 2 types of used sleepers impregnated with creosote: rotten (Fig. 2) and intact (Fig. 3). In total there were four samples researched. They were selected in the way that would reflect the common condition of all sleepers stored in Vilnius (Lithuania) that were taken from the main Lithuanian railways. The first sample was taken from the rotten part of a sleeper where the wood was seriously eroded. The remaining three (second, third and fourth) samples were taken from a used intact sleeper in order: the second sample was taken from a surface layer of the impregnated sleeper, the third was taken from the end of the sleeper and the fourth – from the middle part. The sawdust was homogenised and put in jars. In the laboratory the sawdust samples were additionally miled to powder.

According to the technology of manufacturing sleepers, it is known that they are impregnated with creosote. The most important constituents of creosote are aromatic hydrocarbons, phenolic compounds and heterocyclic aromatic hydrocarbons. In this case, the analysis involved only the following aromatic hydrocarbons: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenzo(a,h) anthracene, and indeno(1,2,3-cd)pyrene (Table 1).

Fig. 2. Rotten used wooden railway sleepers in sampling spot (author's photograph)

Fig. 3. Intact used wooden railway sleepers in sampling spot (author's photograph)

Table 1. Researched aromatic hydrocarbons in the used wooden railway sleepers

Analyte type	Substance name	CAS No.	Hazard class and category codes	Hazard statement codes	Research methodology
Aromatic hydrocarbons	Naphthalene	91-20-3	Carc.2 Acute Tox. 4 Aquatic Acute 1 Aquatic Chronic 1	H351 H302 H400 H410	LST EN 15527:2008
	Acenaphthene	83-32-9	STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H373 H400 H410	LST EN 15527:2008
	Fluorene	86-73-7	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	LST EN 15527:2008
	Phenanthrene	85-01-8	Acute Tox. 4 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H302 H317 H400 H410	LST EN 15527:2008
	Anthracene	120-12-7	Carc.2 Eye irrit. 2 Skin Sens. 1 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H351 H319 H317 H335 H400 H410	LST EN 15527:2008
	Fluoranthene	206-44-0	Acute Tox. 4 Aquatic Acute 1 Aquatic Chronic 1	H302 H400 H410	LST EN 15527:2008
	Pyrene	129-00-0	Eye irrit. 2 Skin irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H319 H315 H335 H400 H410	LST EN 15527:2008
	Benz(a)anthracene	56-55-3	Carc.1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	LST EN 15527:2008
	Chrysene	218-01-9	Carc. 1B Muta.2 Aquatic Acute 1 Aquatic Chronic 1	H350 H341 H400 H410	LST EN 15527:2008
	Benzo(b)fluoranthene	205-99-2	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	LST EN 15527:2008
	Benzo(k) fluoranthene	207-08-9	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	LST EN 15527:2008
	Benzo(a)pyrene	50-32-8	Carc. 1B; Muta. 1B Repr. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350 H340 H360FD H317 H400 H410	LST EN 15527:2008
	Benzo(g,h,i)perylene	191-24-2	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	LST EN 15527:2008
	Dibenzo(a,h)anthracene	53-70-3	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	LST EN 15527:2008
	Indeno(1,2,3-cd)pyrene	193-39-5	Carc.2 Aquatic Acute 1 Aquatic Chronic 1	H351 H400 H410	LST EN 15527:2008

Sleeper samples are prepared for further research in accordance with Standard LST EN 1014-2:2010 Wood Preservatives. Creosote and creosoe-treated wood. Sampling and analysis methods. Part 2. Sampling procedure of creosote samples from creosote-treated wood for further analysis. Finding aromatic hydrocarbons according to Standard LST EN 15527:2008 Characterisation of Waste. Finding polycyclic hydrocarbons in waste using the mass spectrometry of gas chromatography.

The samples used to find multi-cycle aromatic hydrocarbons are extracted with light petroleum in an ultrasonic tub. The analysis of multi-cycle aromatic hydrocarbons is carried out with an effective liquid chromatography applying the fluorescent method of finding effectiveness.

Results and discussion

After the contamination was analysed in the used wooden railway sleepers of 2 types (rotten and intact), a relatively higher contamination with aromatic hydrocarbons was found in the used intact wooden railway sleepers treated with creosote, compared to the rotten sleepers (see Fig. 4).

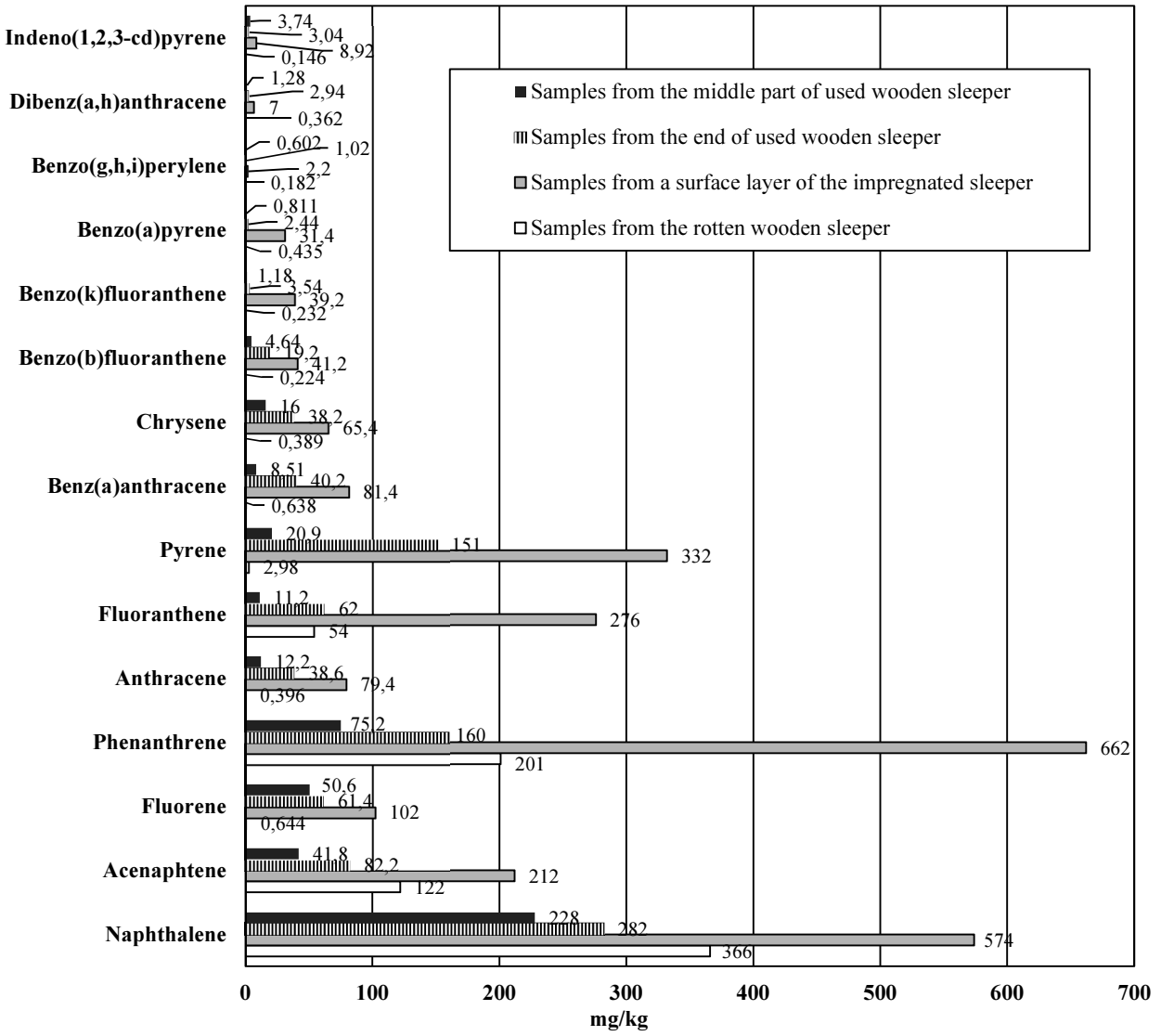

Fig. 4. Concentration of aromatic hydrocarbons in the used rotten and intact sleeper (in sleeper centre, end and surface layer)

After evaluating the contamination with different aromatic hydrocarbons, it was found that the sleepers are most widely contaminated with the following pollutants: phenanthrene, naphthalene, pyrene, fluoranthene, acenaphthene, fluorene, anthracene. The contamination with the mentioned pollutants in the creosote-impregnated intact wooden railway sleeper is as follows: 79.4–662 mg/kg in the surface impregnated layer (Fig. 6), 38.6–282 mg/kg at the end of the sleeper (Fig. 7) and 11.2–228 mg/kg at its centre (Fig. 8). The contamination with the aromatic hydrocardbons in

the rotten wooden railway sleepers is around 3 times lower than the contamination in the surface impregnated layer of railway sleepers intact. The rotten wooden sleepers are mainly contaminated with naphthalene, phenanthrene, acenaphthene, and fluoranthene. This contamination is within the range of 54 and 366 mg/kg (Fig. 5). In comparison, the lowest contamination with the mentioned aromatic hydrocarbons was found in the centre of the creosote-treated wooden sleeper intact. The main contaminators there are naphthalene, phenanthrene, pyrene, acenaphthene, fluoranthene, fluorene, anthracene, etc., and the contamination is between 11.2 and 228 mg/kg (Fig. 8). Apart from the aromatic hydrocarbons mentioned, there were other pollutants found in the used wooden railway sleepers, such as: benz(a)anthracene, chrysene, benzo(b)flouranthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, and indeno(1,2,3–cd)pyrene. The experimental tests showed that the mentioned contaminators were distributed as follows: 2.3–81.4 mg/kg in the surface layer of the impregnated sleeper intact (Fig. 6), 1.02–40.2 mg/kg at the end of the sleeper (Fig. 7) and between 0.62 and 8.51 mg/kg at the centre of the used sleeper intact (Fig. 8).

The lowest concentration of benz(a)anthracene, chrysene, benzo(b)fluouranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene were found in the rotten wooden railway sleepers – 0.146–0.638 mg/kg (Fig. 5). The lower contamination with aromatic hydrocarbons may be conditioned by a long exploitation time when constantly changing environmental conditions (precipitation, ambient temperature, etc.) may have washed out the pollutants, by different technologies of sleeper manufacture, type of wood, etc.

Often these used wooden railway sleepers are reused for the construction of buildings and other structures (e.g. fences), building of gardens/parks, and even as a solid fuel for heat energy. Since the wooden railway sleepers are impregnated with creosote, they are hazardous to the environment and people: during a direct contact with skin they may burn the skinn or cause skin diseases; creosote is also classified as carcinogens (Ikarashi *et al.* 2005a), and when they are improperly utilised, the toxic substances occur in the environment.

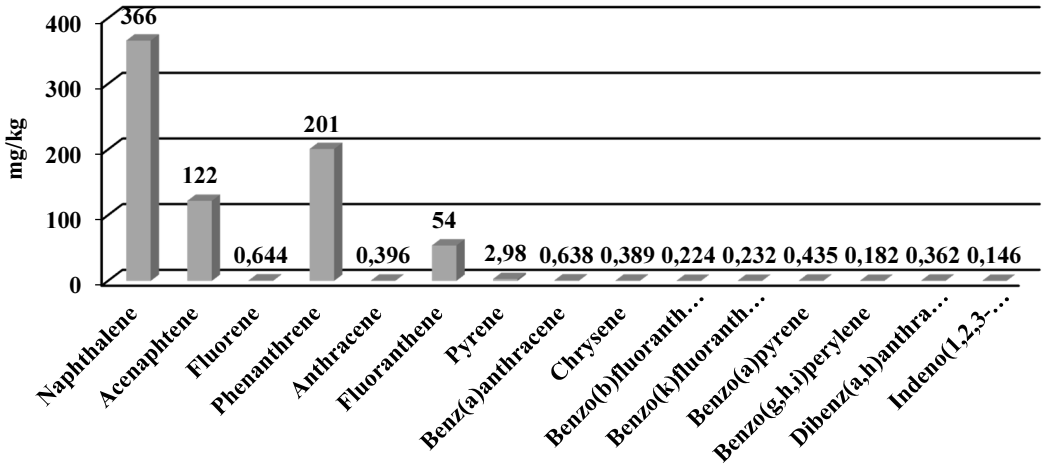

Fig. 5. Results of the concentration of aromatic hydrocarbons in rotten wooden railway sleepers

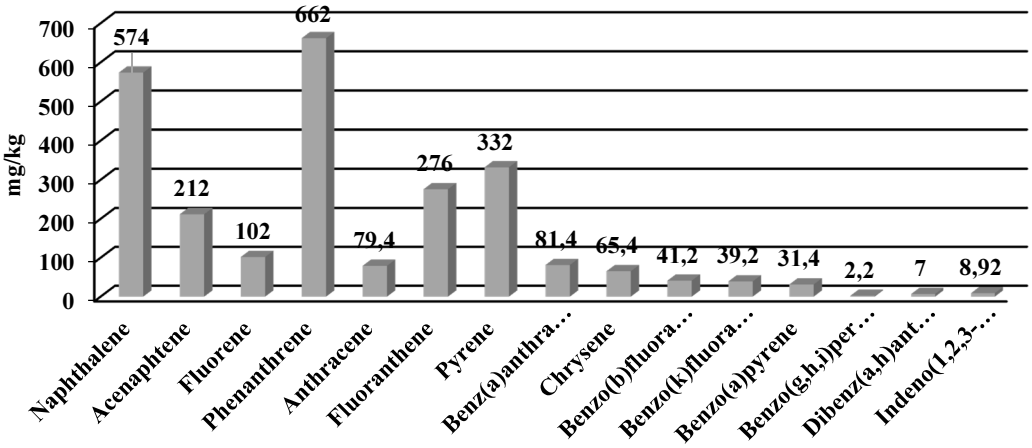

Fig. 6. Results of the concentration of aromatic hydrocarbons in the surface layer of creosote-treated wooden railway sleepers

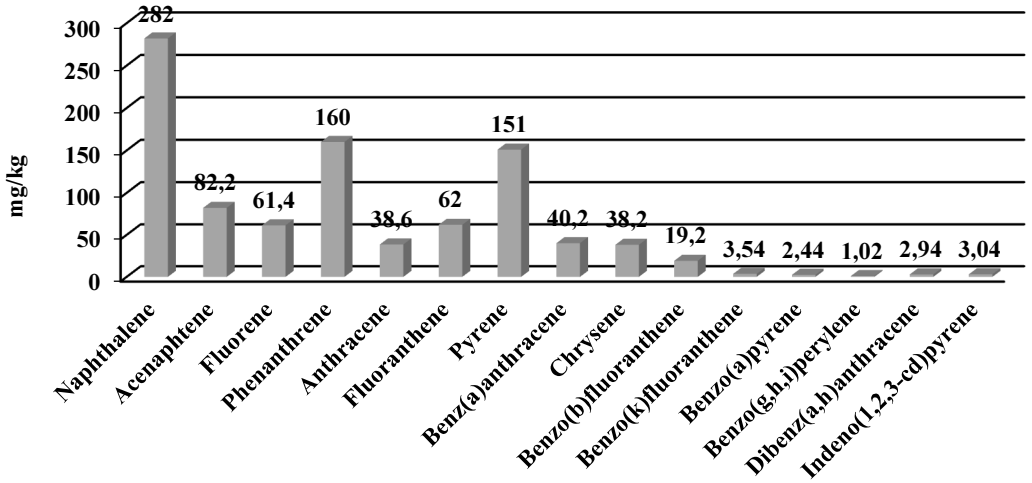

Fig. 7. Results of the concentration of aromatic hydrocarbons at the end of used creosote-treated impregnated wooden railway sleepers

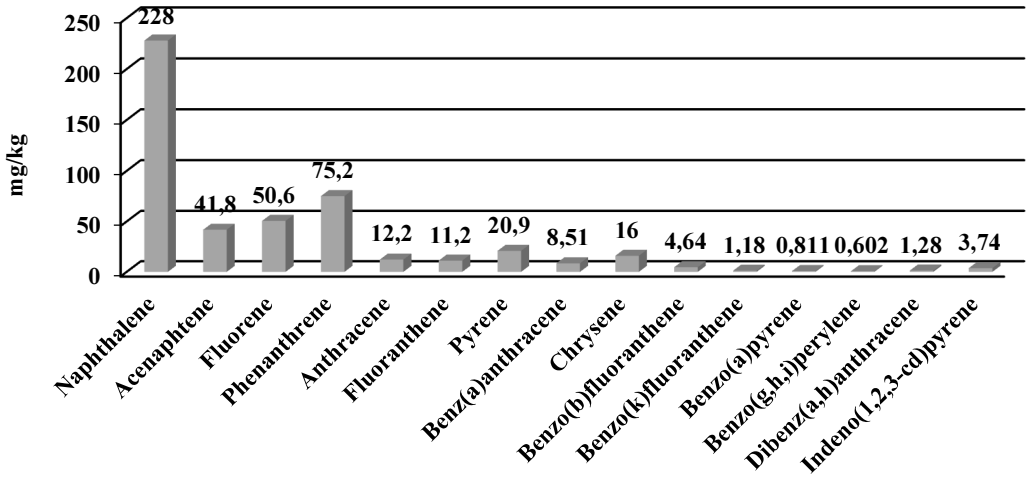

Fig. 8. Results of the concentration of aromatic hydrocarbons at the centre of used creosote-treated impregnated wooden railway sleepers

The results of the research are supported by researches of other scientists (Ikarashi *et al.* 2005a). For example, their studies showed that such wooden railway sleepers have the highest concentration of phenanthrene, also, relatively high amounts of acenaphthene, fluorene, anthracene, and fluoranthene. In the researchers' opinion, different results may be obtained due to the different methods of sleeper manufacture and amount of creosote used for impregnation.

Moret et al. mostly researched the soil pollution with aromatic hydrocarbons in Italy. However, a few samples of the used wooden railway sleepers were collected in two places. The research revealed that wooden creosote-treated sleepers have the higher amounts of phenanthrene, flouranthene and pyrene (Moret *et al.* 2007).

The Swiss scientists carried out the research in order to find the emission of aromatic hydrocarbons from creosote-impregnated sleepers. The sleepers researched were 0.5, 1, 6, 19, 32, and 46 years old. The samples were taken across the sleeper with the distance of 10%, 30% and 50% along the sleeper (Kohler, Künniger 2003). As is the case with the researches from other scientists, the dominating aromatic hydrocarbons are acenaphthene, flourene, phenanthrene, and flouranthene (Kohler, Künniger 2003). Kohler *et al.* (2000) claim that naphthalene and anthracene are eventually washed out of the surface layer of sleepers, and carcinogenic substances, such as dibenzo[a,h]anthracene and benzo[a]pyrene remain and their concentration is higher on the surface than in the deeper layers (Kohler *et al.* 2000). The research carried out supports these results: the higher concentrations of aromatic hydrocarbons were found on the surface layer of creosote-treated wooden railway sleepers (Fig. 6) rather than at their ends (Fig. 7) or centre (Fig. 8).

Sleeper contamination with chemical substances depends on the type of wood, impregnation technology, exploitation time, place, and the intensity (train traffic) of the effects of other environmental components, therefore, their contamination level may differ rapidly. According to the Law on Waste Management of the Republic of Lithuania and

Waste Management Rules, the wooden sleeper waste is classified as hazardous waste. In Annex 1 to the Waste Management Rules, wooden sleeper waste are attributed to section 17 (construction and demolition waste (including the primer dug out of the contaminated areas), waste list code 17 02 04* – glass, plastic and wood containing hazarous substances or having a potential to be contaminated with them.

In accordance with the Waste Management Rules, in case certain substances may be classified as both hazardous and non-hazardous waste, laboratory research shall be carried out in order to identify their hazardousness. Should it be found that the concentrations of the hazardous chemical substances do not exceed limit values in the Commission Regulation (EU) of 2014 December 18 No. 1357/2014, the waste of wooden railway sleepers may be classified as non-hazardous waste (waste code 17 02 01 – wood) and managed as non-hazardous waste. Hence, in order to assess the hazardousness of the wooden railway sleepers, the research of their contamination with aromatic hydrocarbons is not sufficient – the concentrations of heavy metals (Černi *et al.* 2015), phenols (Ikarashi *et al.* 2005b; Kohler, Künniger 2003; Kohler *et al.* 2000) and other hazardous pollutants shall also be analysed.

Conclusions

Based on the provided experimental research results, after analysing the contamination of 2 types (rotten and intact) of used wooden railway sleepers with aromatic hydrocarbons, the relatively highest pollution was found in used creosote-impregnated wooden railway sleepers intact, compared to the rotten sleepers.

During the experimental resarch, it was found that both in the rotten sleepers and the intact sleepers the dominating aromatic hydrocarbons are as follows: naphthalene, pyrene, fluoranthene, acenaphthene, fluorene, and anthracene. The contamination with the mentioned pollutants in the intact used wooden railway sleepers impregnated with creosote is between 11.2 and 662 mg/kg. In comparison to the results of rotten wooden railway sleepers, the contamination there with aromatic hydrocarbons is around three times lower than the contamination on the surface layer of a intact creosote-treated railway sleepers. The same aromatic hydrocarbons dominate in the rotten railway sleepers: naphthalene, phenanthrene, acenaphtene, fluoranthene, etc., and the contamination with these substances is from 54 to 366 mg/kg.

The lowest level of pollution with the studied aormatic hydrocarbons was recorded in the centre of a intact wodden creosote-impregnated sleeper, where the main aromatic hydrocarbons are naphthalene, pyrene, acenaphthene, fluoranthene, fluorene, anthracene, etc., and the contamination with the mentioned chemical substances is 11.2–228 mg/kg. Out of all sleeper types researched, the lowest concentrations of benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, and indene(1,2,3-cd)pyrene were recorded in the rotten wooden railway sleepers. This contamination is between 0.146 and 0.638 mg/kg. Possibly, the lower pollution with aromatic hydrocarbons in the rotten sleepers was conditioned by their long-time exploitation in the environment where the contaminators may have been conditioned by constantly changing environmental conditions (precipitation, ambient temperature, etc).

The results of the research are supported by the research of other scientists. For example, in such wooden railway sleepers, the prominent aromatic hydrocardbon is phenanthrene. There is also a significant amount of acenaphthene, fluorene, anthracene, and fluoranthene.

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