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COMPLEX CONTAMINATION RESEARCH AND HAZARD ASSESSMENT OF THE WASTE OF THE WOODEN RAILWAY SLEEPER

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Abstract. Before being put to use, wooden railway sleepers are impregnated with creosote to increase their longevity and protect them from any adverse environmental impact. Creosote consists of a number of chemical substances, and some of those substances, namely, the polycyclic aromatic hydrocarbons, phenolic compounds and heterocyclic aromatic compounds, are potent carcinogens. Apart from polycyclic aromatic hydrocarbons and phenolic compounds, during their use, sleepers are mostly be contaminated with heavy metals and petroleum products. Upon railway reconstruction, wooden railway sleepers become the waste, which must be handled by the current legislation of the European Union. After determining the concentration of contaminants with laboratory research, it is possible to identify their hazard level and classify them as hazardous or non-hazardous waste. After conducting laboratory research on the waste of wooden railway sleeper analysed, they are classified as hazardous waste.

Keywords: creosote, hazardous waste, heavy metals, phenols, polycyclic aromatic hydrocarbons (PAH), waste of the wooden railway sleeper (WRSW).

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Introduction

The renovation and reconstruction of railway tracks are performed with the use of railway sleepers. Sleepers are the track elements used to ensure an equal width of tracks and an even load distribution on the ballast (Tuntsev, Safin, Chismatov, Khairullina, Antipova, & Garaeva, 2015). The wooden railway sleepers used in Lithuania are most often impregnated with creosote, which is a complex mixture of over 200 constituents (Moret, Purcaro, & Conte, 2007). Depending on the type of wood, an in the wooden railway sleeper is found contain from 40 kg/m^3 to 175 kg/m^3 creosote. According to scientific studies, polycyclic aromatic hydrocarbons (PAH) are found in wooden sleepers treated with creosote for many years after the impregnation. There are 16 PAH, which are classified as carcinogens and genotoxic compounds (Moret, Purcaro, & Conte, 2007). Apart from PAH, wooden railway sleepers are contaminated with heavy metals (Černi, Kalambura, Jovičić, Grozdek, & Kreč, 2015), phenolic compounds (Ikarashi, Kaniwa, & Tsuchiya, 2005; Kohler & Künniger, 2003; Kohler, Künniger, Schmid, Gujer, Crockett, & Wolfensberger, 2000) and petroleum products. Wooden railway sleepers are contaminated with heavy metals (nickel – Ni, lead – Pb, vanadium – V, cadmium – Cd, and zinc – Zn), which are formed by the friction, which occurs during the breaking of rolling stock or rolling stock friction to the railway (Burkhardt, Rossi, & Boller, 2008).

According to various data, the useful life of wooden railway sleepers is 7–50 years (Thierfelder & Sandström, 2008; Tuntsev, Safin, Chismatov, Khairullina, Antipova, & Garaeva, 2015). Wooden railway sleepers become the waste, which must be handled by the current legislation of the European Union removed from the railway track.

The problem of handling the waste of wooden railway sleepers (hereinafter WRSW) is essential in many countries of the world, such as the USA, where the annual formation of WRSW is about 20 million units (Kim, Lloyd, Kim, & Labbé, 2016), Russia – 2 million units per year (Tuntsev, Safin, Khairullina, Kitaev, & Khayrullina, 2017), France – 50.000 t/year (Marcotte, Poisson, Portet-Koltalo, Aubrays, Basle, De Bort, ... & Blondeel, 2014), Croatia, where waste records show 0.9 million units in total (Černi, Kalambura, Jovičić, Grozdek, & Kreč, 2015), Sweden – 0.18 million units per year (Thierfelder & Sandström, 2008), and Lithuania – 0.03 million units per year (Stankevičius, Maruška, Tiso, Mikašauskaitė, Bartkuvienė, Kornyšova,... & Levišauskas, 2015).

By the Rules on Waste Management, approved by Order No. 217 of 14 July 1999 of the Minister of Environment of the Republic of Lithuania “On Approval of Waste Management Rules”, in case of certain waste are attributed the waste codes of both hazardous and non-hazardous waste, laboratory research is conducted to determine their hazard. If the laboratory research shows the concentrations of hazardous chemical substances do not exceed the limit values established in Commission Regulation (EU) No 1357/2014 and the Council on waste and repealing specific Directives (hereinafter Regulation), WRSW are classified as non-hazardous waste (waste code 17 02 01 – wood), and if the limit values are exceeded, WRSW are classified as hazardous waste (waste code 17 02 04* – wood containing hazardous chemical substances).

The research aims to carry out laboratory research of pine (in Latin *Pinus sylvestris*) WRSW to determine its contamination with PAH, phenols, petroleum products (C10-C40), and heavy metals (Ni, Pb, V, Cd, and Zn). By the *Regulation,* determine whether the sleeper waste is classified as hazardous or non-hazardous.

1. Methodology

The samples are collected in the form of sawdust by sawing WRSW with an electric circular saw (to avoid any additional contamination) vertically from the middle part of a sleeper, surface impregnated layer and the end part (Figure 1). After every cut, the circular saw is cleaned with compressed air flow. Three sleepers are taken in total, selected in such a way as to reflect best the general condition of all sleepers stored in the storage place. The first sample is collected from the surface impregnated layer of WRSW, second – from the end part of WRSW, and third – from the middle part of WRSW. The samples are taken from different parts of WRSW because the sleeper impregnated with creosote soaks it in unevenly (Figure 1). All three samples are homogenised and placed in jars of 1 l capacity. The samples in the laboratory are additionally shredded to powder.

1 – samples from a surface layer of the impregnated wooden railway sleeper;
2 – samples from the end of wooden railway sleeper;
3 – samples from the middle part of wooden railway sleeper

Figure 1. The scheme of a sleeper and its cross-section, impregnated with creosote

Table. Hazardous chemical substances found in the waste of wooden railway sleeper

Type of analyte	**Substance name**	**Number of chemical abstracts service number**	**Hazard class, category code(s) (hazard phrase code)**
Research methodology *LST EN 1014-4:2010 Wood Preservatives. Creosote and Creosoted Timber. Methods of Sampling and Analysis. Part 4. Determination of the Water-Extractable Phenol Content of Creosote*			
Amount of phenols	Phenol	108-95-2	Acute Tox. 3 (H301); Skin Corr. 1B (H314); Muta. 2 (H341); STOT RE 2 (H373)
Research methodology *LST EN 15527:2008 Characterisation of Waste. Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Waste by Gas Chromatography with Mass Spectrometric Detection*			
Polycyclic aromatic hydrocarbons (PAH)	Naphthalene	91-20-3	Carc.2 (H351); Acute Tox. 4 (H302); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Acenaphthylene	208-96-8	STOT RE 1 (H372); STOT RE 2 (H373); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Acenaphthene	83-32-9	STOT RE 2 (H373); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Fluorene	86-73-7	Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Phenanthrene	85-01-8	Acute Tox. 4 (H302); Skin Sens. 1 (H317); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Anthracene	120-12-7	Carc.2 (H351); Eye irrit. 2 (H319); Skin Sens. 1 (H317); STOT SE 3 (H335); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)

Type of analyte	Substance name	Number of chemical abstracts service number	Hazard class, category code(s) (hazard phrase code)
Polycyclic aromatic hydrocarbons (PAH)	Fluoranthene	206-44-0	Acute Tox. 4 (H302); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Pyrene	129-00-0	Eye irrit. 2 (H319); Skin irrit. 2 (H315); STOT SE 3 (H335); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Benz(a) anthracene	56-55-3	Carc.1B (H350); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Chrysene	218-01-9	Carc. 1B (H350); Muta.2 (H341); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Benzo[b] fluoranthene	205-99-2	Carc. 1B (H350); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Benzo[k] fluoranthene	207-08-9	Carc. 1B (H350); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Benzo[a]pyrene	50-32-8	Carc. 1B (H350); Muta. 1B (H340); Repr. 1B (H360FD); Skin Sens. 1 (H317); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Indeno[1,2,3-cd] pyrene	193-39-5	Carc.2 (H351); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Dibenzo[a,h] anthracene	53-70-3	Carc. 1B (H350); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Benzo[ghi] perilenas	191-24-2	Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)

Type of analyte	**Substance name**	**Number of chemical abstracts service number**	**Hazard class, category code(s) (hazard phrase code)**
Research methodology *ISO/TS 17073:2013 Soil quality -- Determination of Trace Elements in Aqua Regia and Nitric Acid Digests -- Graphite Furnace Atomic Absorption Spectrometry Method (GF-AAS)*			
Heavy metals	Vanadium	7440-62-2	Aquatic Chronic 4 (H413)
	Lead	7439-92-1	Lact. (H362); Repr. 1A (H360)
	Cadmium	7440-43-9	Acute Tox. 2 (H300); Muta. 2 (H341); Carc. 1B (H350); STOT RE 1 (H372); Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410); Repr. 2 (H361)
Research methodology *LST CEN/TS 16188:2012 (FAAS) Sludge, Treated Biowaste and Soil. Determination of Elements in Aqua Regia and Nitric Acid Digests. Flame Atomic Absorption Spectrometry Method (FAAS).*			
Heavy metals	Zinc	7440-66-6	Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410)
	Nickel	7440-02-0	Skin Sens. 1 (H317); Carc. 2 (H351); STOT RE 1 (H372); Aquatic Chronic 3 (H412)
Research methodology *LST EN 14039:2004 Characterisation of Waste. Determination of Hydrocarbon Content in the Range of C_{10} to C_{40} by Gas Chromatography*			
Petroleum hydrocarbons C10-C40	Diesel fraction	68334-30-5	Carc. 2 (H351)
	Oil fraction	72623-86-0	Carc. 1B (H350)

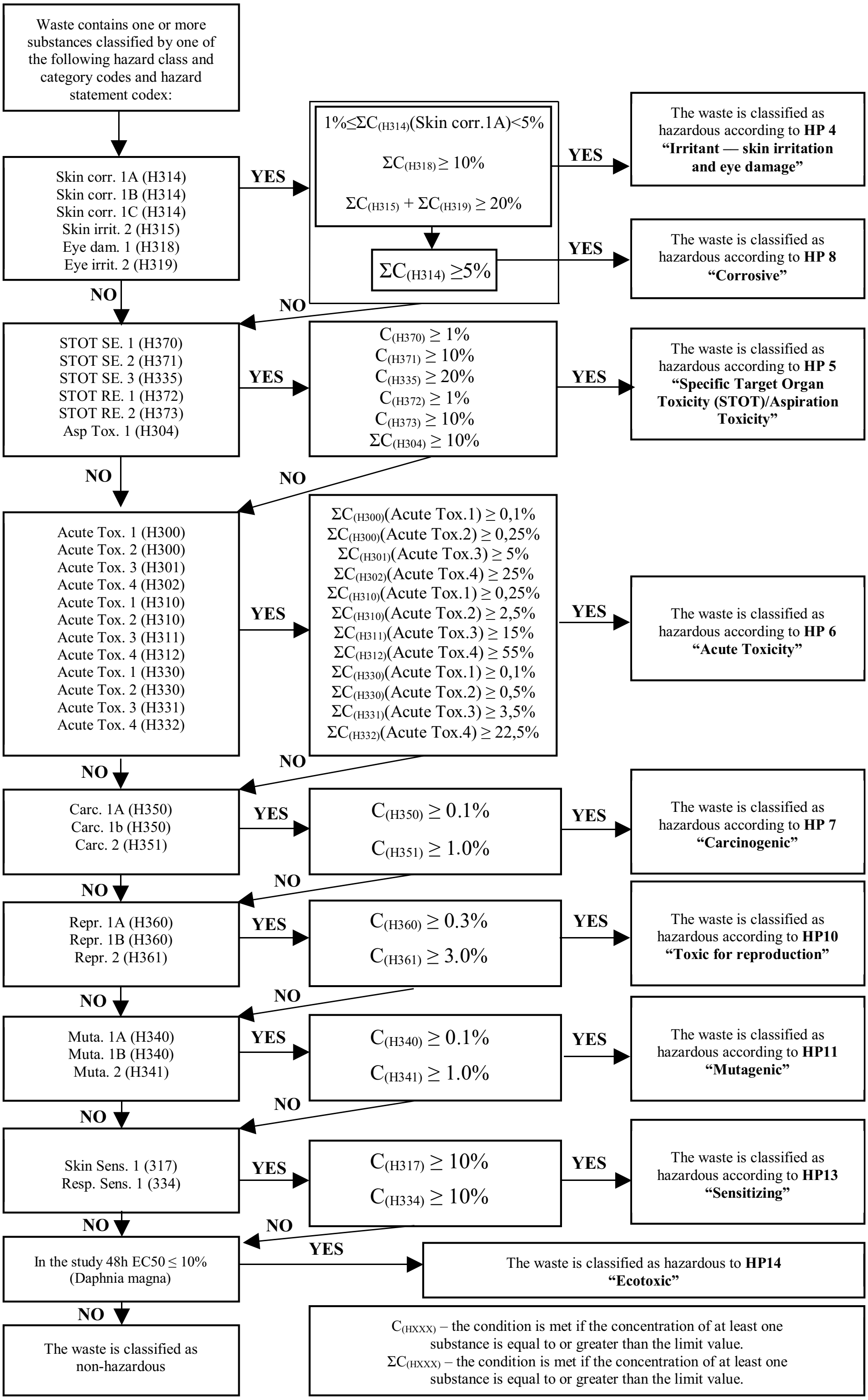

Figure 2. The hazard classification scheme of wooden railway sleepers

The samples tested were collected from the regions of Vilnius, Kaunas, Klaipėda, Utena, Kėdainiai, and Varėna, to assess the overall WRSW contamination in Lithuania. The concentration of PAH, phenolic compounds, heavy metals, and petroleum products are determined by standards of the Lithuanian Standards Board (LST) under the Ministry of Environment (Table).

After the research, the hazard level of WRSW analysed is determined in compliance with the *Regulation* according to the scheme provided in Figure 2. The scheme contains only those limit values and of only those hazardous substances, which are relevant and are found in WRSW.

2. Research results

After evaluating the contamination of WRSW with PAH, the highest contamination was caused by the following contaminants: phenanthrene, naphthalene, pyrene, acenaphthene, fluoranthene, acenaphthylene, fluorene, and anthracene (Figure 3). The highest concentration of PAH was found in the impregnated surface layer of WRSW. The contamination with the mentioned contaminants there varies between 63.88 mg/kg and 621.28 mg/kg. The concentration of PAH at the end part of WRSW is between 47.75 mg/kg and 264.38 mg/kg and in the middle part of sleeper samples – between 40.13 mg/kg and 215.38 mg/kg (Figure 3).

Apart from the mentioned PAH, WRSW contained other contaminants as well, such as 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. During the experimental tests, the concentrations of the mentioned contaminants were observed to be between 1.65 mg/kg and 57.93 mg/kg on the impregnated surface layer of WRSW, 1.56 mg/kg and 48.88 mg/kg at the end of the used WSRW and between 1.0 mg/kg and 43.11 mg/kg in the middle part (Figure 3). The highest PAH concentrations were observed on the impregnated surface of WRSW samples because, during creosote treatment, the sleepers soak in unevenly (Figure 1) and most of the contaminants remain on the impregnated surface.

The results of the tests support the results of research by other scientists. For example, such WRSW have been found to contain the highest concentration of phenanthrene and, also, significant amounts of acenaphthene, fluorene, anthracene, and fluoranthene. According to the scientists, different test results are possible due to different manufacture methods of sleepers and the amount of creosote used for impregnation (Ikarashi, Kaniwa, & Tsuchiya, 2005; Lebow, Woodward, Kirker, & Lebow, 2013; Liu, Wang, Karim, Sun, & Wang, 2014; Liu, Zhang, & Huang, 2014; Lloyd, Brischke, Bennett, & Taylor, 2018; Lu, Ye, Zhang, Cui, Guo, Qi, ... & Yang, 2016; Lu, Ye, Zhang, Dong, & Zhang, 2014; Lu,

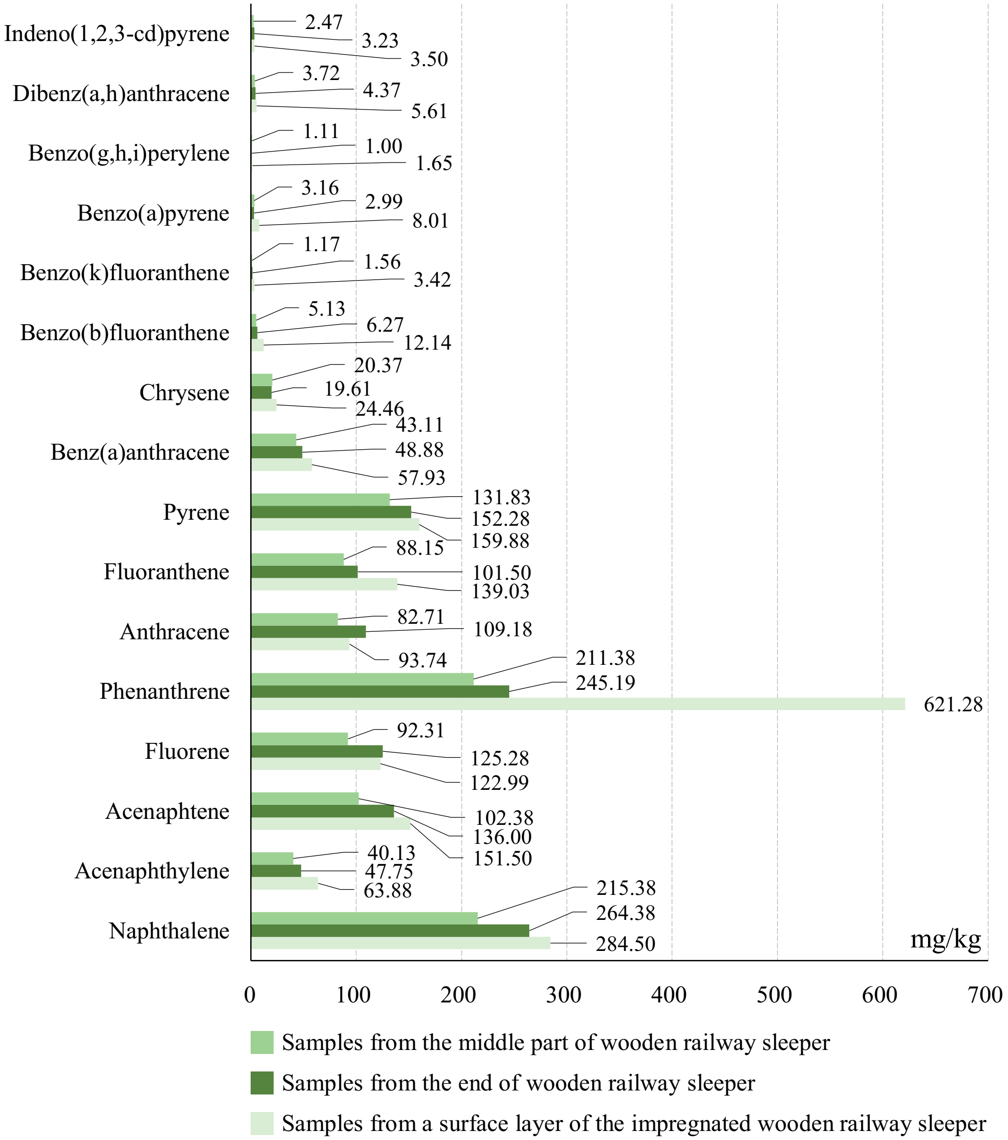

Figure 3. Concentrations of polycyclic aromatic hydrocarbons in a waste of the wooden railway sleeper

Zhang, Yang, Dong, & Zhu, 2013; Lu, Zhang, Ye, Li, Hu, Dong, & Yang, 2017; Rosenbaum, Bachmann, Gold, Huijbregts, Jolliet, Juraske,... & McKone, 2008; Taylor, Bennett, Harper, & Lloyd, 2017; Taylor, Jordan, & Lloyd, 2013).

Moret, Purcaro, & Conte (2007) mainly researched the contamination of soil with PAH in Italy. However, several PAH samples were collected in two areas of study. Based on research, in the wooden railway sleepers treated with creosote, the concentrations of phenanthrene, fluoranthene and pyrene prevail (Moret, Purcaro, & Conte, 2007; Zeta-Tech, 2011; Zhang, Lu, Ye, Li, Zhang, & Dong, 2015).

The Swiss scientists researched to find the emissions of PAH aromatic hydrocarbons from WRSW. The sleepers analysed had been used for 0.5, 1, 6, 19, 32, and 46 years. The samples were collected across the sleeper, by 10%, 33% and 50% distance along the sleeper (Kohler & Künniger, 2003). As in the research of other scientists, the prevailing concentrations are of acenaphthene, fluorene, phenanthrene, and fluoranthene (Kohler & Künniger, 2003; Silva, Martins, Feio, & Machado, 2014).

After considering previous studies, the contamination of WRSW with chemical substances depends on the type of wood, impregnation technology, time of use of wooden railway sleepers, place and rail traffic flow, and impact of other environmental components. Hence, according to the data of various scientific studies, contamination of WRSW with chemical substances is different, and the concentrations of different contaminants differ rapidly, yet the tendency remains similar.

Upon assessing the hazardousness of WRSW, it is found, whether the substance concentrations do not exceed the limit values established in *Regulation*. Therefore, in evaluating the hazardousness of WRSL, it is necessary not only to carry out the studies of contamination with PAH, but also find the concentrations of heavy metals (Černi, Kalambura, Jovičić, Grozdek, & Kreč, 2015), phenols (Bolin & Smith, 2013a, 2013b; Carrasco, Passos, & Mantilla, 2012; Ikarashi, Kaniwa, & Tsuchiya,

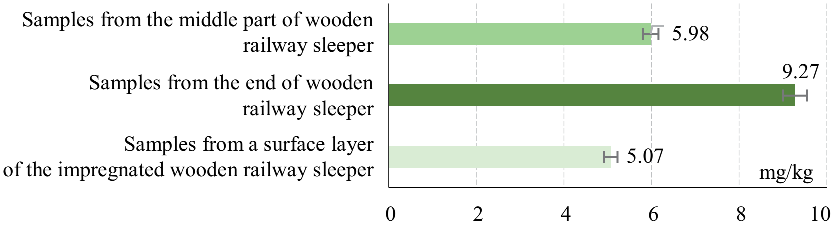

Figure 4. Concentrations of phenols in a waste of the wooden railway sleeper

2005; Kohler & Künniger, 2003; Künniger, Schmid, Gujer, Crockett, & Wolfensberger, 2000) and other hazardous contaminants.

After conducting the research and assessing the contamination of WRSW with phenolic compounds, the highest contamination was determined at the end of WRSW (9.27 mg/kg). The contamination with phenols on the surface reaches up to 5.07 mg/kg and in the middle – up to 5.98 g/kg (Figure 4).

Ikarashi, Kaniwa, & Tsuchiya (2005) also conducted the studies of sleeper contamination with phenols. The research was carried for both impregnated and non-impregnated sleepers. According to research results, both creosote-treated and non-impregnated sleepers have similar concentrations of phenols (Ikarashi, Kaniwa, & Tsuchiya, 2005). The phenol concentrations were determined during the studies are not related to the creosote treatment, and it all depends on the phenolic substances, which are found in the wood or form due to the substance oxidation during the hydrolysis process (Becker, Matuschek, Lenoir, & Kettrup, 2001; Gallego, Roca, Perales, Guardino, & Berenguer, 2008; Gevao & Jones, 1998; Gong, Delahunty, Chui, & Li, 2013).

The scientists of other countries mostly analyse the contamination of WRSW with PAH and phenolic compounds, yet they do not asses the contamination with petroleum products and heavy metals.

After conducting the research and assessment of WRSW contamination with petroleum products, the highest contamination was found in the samples collected from the end of the wooden railway sleepers (43 g/kg) (Figure 5). The contamination with petroleum products on the surface of creosote-treated WRSW reaches up to 38 g/ kg and in the middle of intact WSRW – up to 33 g/kg (Figure 5). The concentrations in different parts of WSRW differ insignificantly.

There was also laboratory research carried out to find the contamination of WRSW with heavy metals (nickel (Ni), lead (Pb), vanadium (V), cadmium (Cd), and zinc (Zn)) (Figure 6). The research and the assessment of WSRW contamination with Ni, the highest

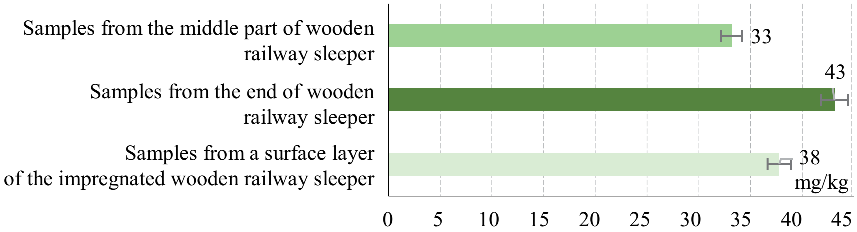

Figure 5. Concentrations of petroleum products in a waste of the wooden railway sleeper

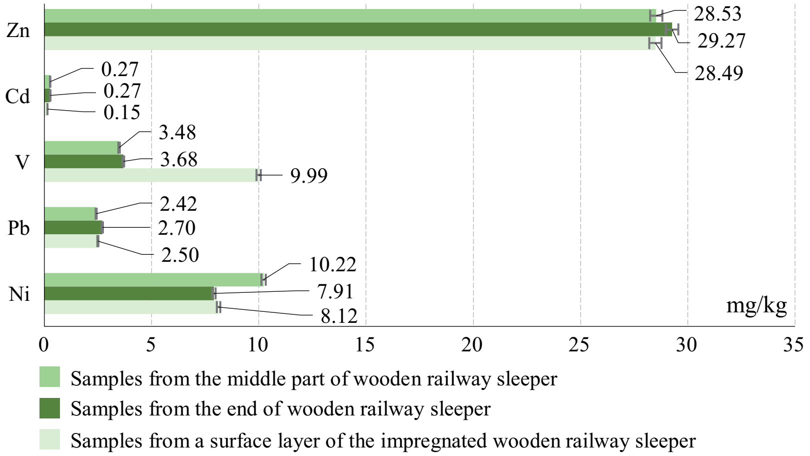

Figure 6. The concentration of heavy metals in a waste of the wooden railway sleeper

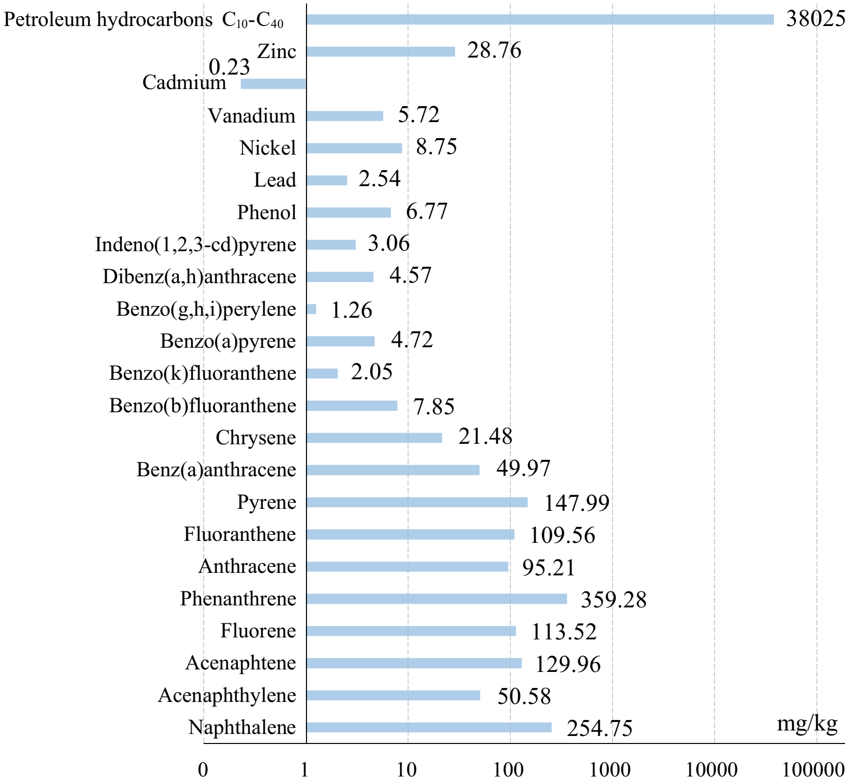

Figure 7. Determined and evaluated concentrations of the contaminating substances

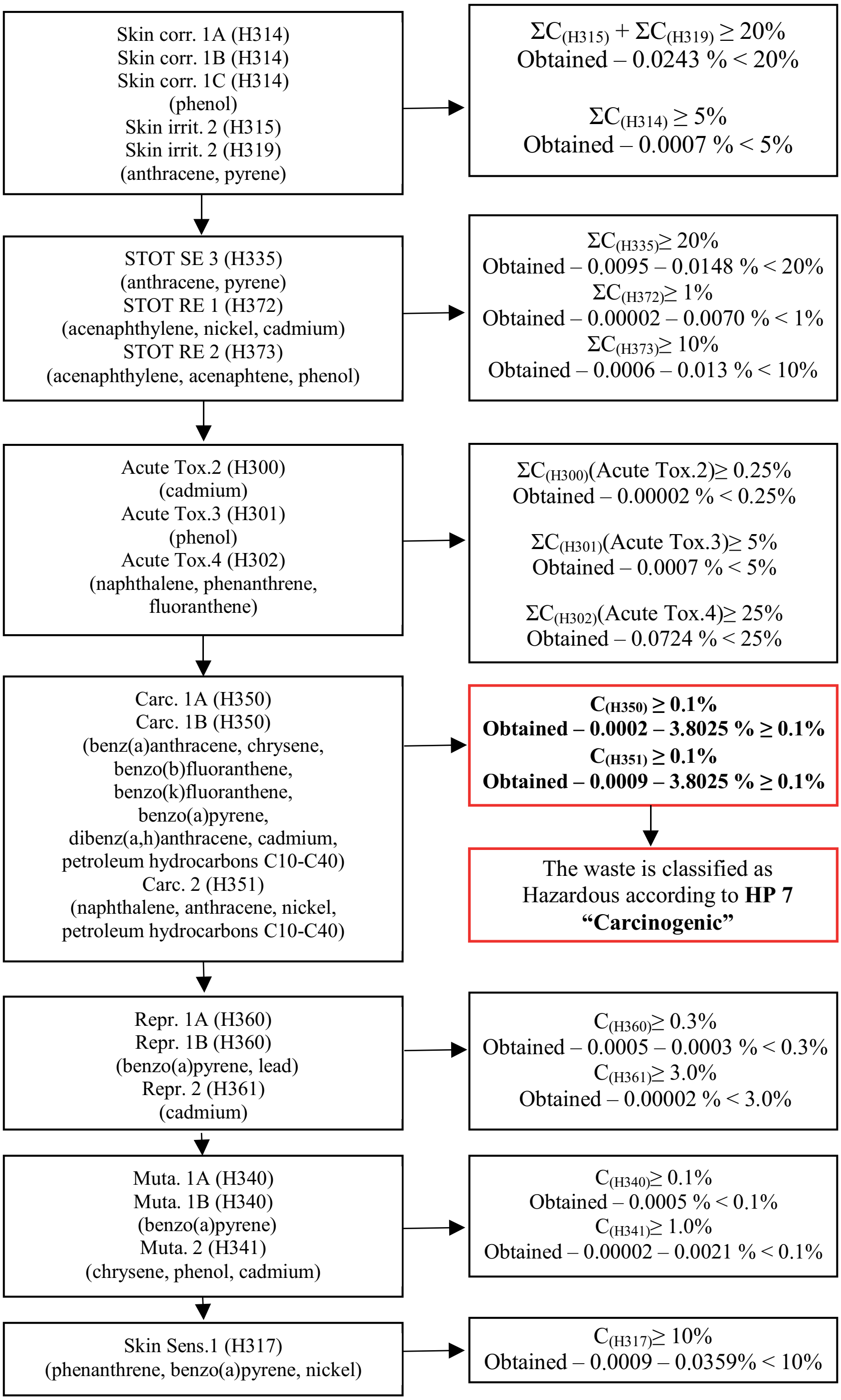

Figure 8. WRSW hazard evaluation

contamination is in the samples collected from the middle part of the railway sleepers reaches up to 10.22 mg/kg. The highest concentration of V was observed in the samples taken from the impregnated surface of intact WSRW was observed to be 9.99 mg/kg. The concentration of Cd in the samples of the impregnated surface reached up to 0.15 mg/kg (Figure 6). The concentrations of WSRW contamination with heavy metals in different parts of WSRW differ insignificantly.

Based on research of Burkhardt, Rossi, & Boller (2008), the heavy metals form due to the friction, which occurs during the breaking of rolling stock or rolling stock friction to the railway. Therefore, the contamination of WSRW with heavy metals is mostly caused by railway transport and traffic flow.

The hazardousness of WSRW is evaluated in consideration of the concentrations of the substances found. Upon evaluating the characteristics of WSRW, which make them hazardous waste, the average concentration was evaluated (of samples from the middle part of sleepers, end part and impregnated surface). The evaluated concentrations of the contaminating substances are provided in Figure 7.

Based on the research results, Figure 8 provides the evaluation of the characteristics of the researched WRSW, which make this waste hazardous. The evaluation was carried out by the scheme in Figure 2 taking into consideration the concentration of every contaminating substance (Figure 7), hazard class, category code, and hazard phrase code (Table 1).

Upon evaluating the WRSW characteristics, which make this waste hazardous, the waste of the researched wooden railway sleepers is classified as hazardous waste with the code HP 7 “Carcinogens” attributed to it (Figure 8). The researched WRSW are hazardous because of the concentration of petroleum products exceeds the limit value and reaches 38.0 g/kg. The concentrations of other contaminants (PAH, phenols, and heavy metals) did not exceed the limit values (Vilniškis & Vaiškūnaitė, 2017, 2018).

WRSW hazardousness according to the property HP14 was not evaluated because the waste researched is hazardous. It is attributed code HP7 “Carcinogens” and must be managed as hazardous waste.

Conclusions

The results have indicated:

1. After the evaluation of waste of the wooden railway sleeper contamination with polycyclic aromatic hydrocarbon, the highest concentrations exist for the following substances: phenanthrene,

naphthalene, pyrene, acenaphthene, fluoranthene, acenaphthylene, fluorene, and anthracene. The results of the tests support the results of research by other scientists. The highest concentration of polycyclic aromatic hydrocarbon was found in the impregnated surface layer of wooden railway sleeper waste treated with creosote. The contamination with the mentioned contaminants there varies between 63.88 mg/kg and 621.28 mg/kg. Based on the results, the contamination with polycyclic aromatic hydrocarbon is mainly prominent in the surface layer of a waste of the wooden railway sleeper impregnated with creosote.

2. According to the studies of other scientists, the contamination of wooden railway sleeper waste with heavy metals depends on the rail traffic and its traffic flow. However, after researching the contamination with heavy metals on the wooden railway sleeper waste, used in different regions of Lithuania.
3. It is also supported by the research of wooden railway sleeper waste contamination with phenols since the concentrations of phenols differ insignificantly on both the wooden railway sleepers used in different regions of the country and on different parts of a sleeper.
4. Upon assessing the hazardousness of waste of the wooden railway sleeper, the researched wooden railway sleeper waste is classified as hazardous waste with the attributed code HP 7 "Carcinogens" because they exceed the limit value of petroleum product concentrations reaching up to 38.0 g/kg. Waste of the wooden railway sleeper was contaminated with petroleum products during the performance of railway rolling stock or events with ecological consequences. The concentrations of polycyclic aromatic hydrocarbon, phenols and heavy metals did not exceed the limit values.

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