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# Heavy metal content in used engine oils depending on engine type and oil change interval

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**Abstract:** The paper presents the results of the analysis of the content of selected heavy metals in used engine oils collected in car service stations during oil change. The main purpose of the research was to determine the difference in heavy metal content (Cr, Cu, Fe, Ni, Pb, Zn, Hg, Cd) depending on the engine type and oil change interval. The analysis comprised 80 samples of used engine oils obtained from passenger cars. The content of heavy metals was tested with use of the HDMaxine analyzer, operating on the basis of HDXRF (High-Definition X-Ray Fluorescence). Upon analyzing the differences in the average content of the examined elements, depending on the type of engine, it can be concluded that in oils coming from diesel engines the following elements showed a higher concentration – Cr (three times), Fe (1/3 times), Ni (two times), Pb (1/2 times), whereas in oils coming from gasoline engines, only the average Cu content was higher (3/4 times). Zinc had a comparable level of concentration. The multi-factor analysis of variance showed that in diesel engines the levels of Fe, Cr, Pb and Ni are statistically significantly different than in the reference group of gasoline engines. The study findings suggest that, depending on the engine type, the content of selected heavy metal elements in used oils varies. Therefore, to ensure proper handling of waste oils and reduce environmental risk, selective collection of used oils depending on the engine type may definitely be considered.

## Abbreviations:

AAS – Atomic Absorption Spectrometry

HDXRF – high definition X-Ray fluorescence

DE – diesel engines

GE – gasoline engines

PAO – polyalphaolefin

PAHs – polycyclic aromatic hydrocarbons

PCBs – polychlorinated biphenyls

ZDDP – zinc-dialkyl dithiophosphate

WLO – Waste Lubricating Oil

Cr, Cu, Fe, Ni, Pb, Zn, Hg, Cd – the analyzed elements

GI, GII, GIII, GIV, GV – five groups created according oil change intervals

GI – oil change interval <10k km

II – oil change interval 10–12k km

GIII – oil change interval 12–14k km

GIV – oil change interval 14–16k km

GV – oil change interval >16k km

## Introduction

Lubricating oils primarily serve to reduce friction between moving parts of various machines and devices and to minimize their wear, which consequently leads to the improvement of their overall efficiency, including energy and fuel savings. Among different lubricants, the most common are engine oils,

and they are generally used for gasoline- and diesel-powered cars. Engine oils are composed of base oils and various refining additives, the content of which may reach up to 20% (v/v). Base oils can be mineral (petroleum vacuum distillation processing products) or synthetic (e.g., PAOs or synthetic esters). During the use of an engine oil, several changes take place and various impurities occur, which gradually lead

to the decrease in oil quality and the loss of its predominant functions. As a result, the oil must be removed from the engine and replaced with a new one. Used oils may pose a serious environmental problem, especially in terms of the logistics of the waste disposal, mainly due to the fact that they are used in small amounts by a large number of users located in different places. The total amount of engine oils changed annually in Europe is large and ranges from 1.7 to 3.5 million tons, according to various estimations. Such substantial quantities of used engine oils have significant economic and environmental consequences. Particularly because approximately 23% of the reported amount of used oils (Kupareva et al., 2013) is in fact outside the waste collection system. It is either illegally burnt or enters the natural environment directly (e.g., through car leaks). The biggest concerns, however, have been raised over deliberate disposal of used engine oils into the eco-system by the workers of service stations and local garages that deal with engine repairs, during which used engine oils are generated, stored, and sometimes intentionally or accidentally dumped into the soil or sewage system (Piecuch et al., 2015; Stout et al., 2018; Vazquez-Duhalt, 1989). The pollution with used engine oils creates environmental hazards due to its permanent nature and the tendency to spread into ground and surface waters. These compounds are refractory to biodegradation, so their presence in waters is a serious problem (Bogacki and Al-Hazmi, 2017; Kryłów et al., 2018).

The chemical composition of waste oils depends on many factors, including the type of base oil, the additives used, physical and chemical changes they were subject to during operation and the conditions in which the oil was operated (Magiera and Głuszek, 2009; Zając et al., 2015). They usually contain polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals (Delistraty and Stone, 2007; Hamawand et al., 2013). Heavy metals found in engine oils cause many concerns, particularly due to their adverse effects on the environment and human health, especially when their concentration is high. There are different sources of metals in used oils. They can be native elements of crude oil, residues from oil processing (most often residues of catalytic processes), refining additives, as well as products of corrosion and wear of the metal surfaces which come into contact. The metals which are general constituents of crude oil are mainly nickel and vanadium. In turn, catalyst residues containing metals are introduced during various processes of catalytic hydrotreating of the oil base (Lynch, 2007); whereas, refining additives include, among others, detergents containing calcium or magnesium salt and zinc dialkyl dithiophosphate (ZDDP) (Stout et al., 2018). Waste engine oils also contain metals which are products of wear of the metal surfaces that contacting themselves, and which occur in the course of oil use (Fe, Cu, Al, Sn, Sb). The concentration of metals in used oils in Europe reaches about 0.7% (w/w) (Magiera, 2006).

An appropriate waste management has become one of the most significant challenges facing the world today. As lubricating oils are generally toxic and not readily biodegradable, extensive disposal of WLO into the environment may pose serious adverse effects to ecosystems, with a high risk of soil, water, and air contamination (Pinheiro et al., 2020). Due to the fact that the composition of waste lubricating oils is not uniform, it is particularly difficult to find

a universal utilization procedure for them (Nerín et al., 2000). That is why, the proper disposal of used lubricating oils is a major challenge today, as inappropriate use of this hazardous waste can pose a direct threat to the environment and human health. However, automotive lubricating oils are an excellent example of waste that can be recycled and turned into useful and valuable products. They can be processed and refined and then used in the production of fuels or serve as a base for lubricating oils (Pawlak et al., 2010; Pinheiro et al., 2020).

The recycling of used lubricating oils involves subjecting them to a series of processes that lead to the elimination of most impurities, including water, oxidation products, and additives; thus, restoring the original properties of the base oil. To achieve this end, the most frequently used processes are vacuum distillation, solvent extraction, aluminum-acid treatment and hydrotreatment (Hsu and Liu, 2011; Jafari and Hassanpour, 2015; Kamal and Khan, 2009; Osman et al., 2018; Salem et al., 2015). Yet, due to their level of contamination, not all used lubricating oils can be re-refined (Nerín et al., 2000). It is estimated that only 60–65% of WLOs can be recycled as they have to meet specific requirements regarding the impurity level and viscosity index (Hsu and Liu, 2011; Sanchez-Hernandez et al., 2020). By far the cheapest method of utilizing waste lubricating oils is burning them (Elnajjar et al., 2019; Nukman et al., 2018). Because of high calorific value of WLOs, they are readily used as on-site boiler fuel, which also eliminates the need for transporting these oils – a rather costly undertaking for many individuals. However, due to combustion processes, the metals accumulated in WLO pass into solid (Nerín et al., 1999) and gaseous (Pinheiro et al., 2020) combustion products. According to data provided by the US Department of Energy, the combustion of WLO releases more than 50% of its lead, cadmium, chromium, and zinc in the form of solid particles (US Department of Energy, 2006). In other words, the combustion of WLO may result in the release of 800 mg Zn and 30 mg Pb into the atmosphere, the amount which is 50–100 times higher than in the case of petroleum-based heating oil (Boughton and Horvath, 2004; Pinheiro et al., 2020). Using WLOs for home heating purposes is especially dangerous if uncontrolled combustion processes take place in boilers that do not have built-in control systems and filtering devices.

Pyrolysis is yet another method that can be applied for the management of used lubricating oils that cannot be refined. However, heavy metals are also found in the oil fractions after the condensation of pyrolysis products from the waste oil. Metals present in lubricating oils (e.g., Pb, Fe, Cu and Ni) are transformed into volatile substances during the process of pyrolysis at a reaction temperature of 600°C and above (Nerín et al., 2000).

Due to high costs associated with the disposal of waste lubricating oils, it is still a relatively common practice of irresponsible users to discard them illegally to sewers and soil; especially, in the absence of clear regulations in this regard or non-compliance to the existing ones (Lam et al., 2016). The introduction of WLO directly into the soil leads, for example, to the accumulation of the following chemical elements: K, Mg, Ca, Fe, Co, Ni, Cu, Zn, Al, Pb, Cd and their possible translocation into plant tissue (Vwioko et al., 2006). In turn, high concentrations of toxic heavy metals may inhibit the

metabolism and growth of most plant species and this may have a detrimental effect on the food chain (Morkunas et al., 2018). Heavy metals can also strongly inhibit coal mineralization, nitrogen transformation, as well as sulfur and phosphorus mineralization (Pinheiro et al., 2020; Srivastava et al., 2017).

Considering the above, it is both purposeful and necessary to determine the level of heavy metal contamination of used lubricating oils, since the data available in the literature relate to either a relatively small number of samples (Zajac et al., 2015), waste oils that were collected from special recycling containers (Kashif et al., 2018) or the data are outdated and inadequate to the current compositions of lubricating oils and their operating conditions (Stout et al., 2018).

Hence, due to insufficient data available in the literature, this paper contributes to filling the research gap by presenting the concentrations of selected heavy metals (Cr, Cu, Fe, Ni, Pb, Zn, Hg, Cd) in used lubricating oils coming from passenger cars of different mileage, and by determining the differences in heavy metal content depending on engine type and oil life.

The results of the study not only expand the literature database with information on the content of selected heavy metals in used engine oils, but they may also facilitate the decision-making process regarding the management of waste oils.

## The environmental impact of the heavy metals tested

On a global scale, there is little risk of contamination of the natural environment with chromium. Nevertheless, if locally introduced into the atmosphere, waters and soils, it may contribute to its inclusion in the bio-geochemical circulation in excessive amounts, which poses a potential risk to human and animal health (Kabata-Pendias and Pendias, 1999). According to Tóth et al., around 2 million ha of Europe's agricultural land is ecologically endangered because of high concentration of chromium in the soil (Tóth et al., 2016). The content of Cr in engine oil is usually associated with the wear of piston rings. A high content of this element may be caused by impurities coming from the air supplying the engine or it may be the result of wear of chromium parts, for instance rings and bushings (Hamawand et al., 2013; Nwosu et al., 2008; Palkendo et al., 2013).

Copper is another element heavily introduced into the environment as a result of human activity, which represents a significant risk of local biological contamination due to the relatively high bioaccumulation factor (Kabata-Pendias and Pendias, 1999). In many cases, uncontrolled precipitation or discharge of copper into the soil may severely undermine its chemical balance, thus leading to soil degradation (Tóth et al., 2016). Toth et al. indicate that the accumulation of copper in soil is mainly of anthropogenic origin, such as mining or industrial activities, although the agricultural use of copper-containing products, especially in pesticides, is also common.

It is not specified how much iron contributes to environmental pollution, as it does not pose a threat to the environment. However, as the most commonly used metal, it may provide information on the impact of some anthropotechnical elements on the natural environment (Zajac et al., 2015). Fe is introduced into the engine oil mainly due

to the wear of various engine parts, such as camshafts and crankshaft, pistons, gears, rings and oil pump. A high content of this element in oil indicates advanced processes of wear of engine parts (Hamawand et al., 2013).

Nickel has immunotoxic and carcinogenic effects, it is also a very strong allergen (Śpiewak and Piętowska, 2006). Despite the fact that this element introduced into water reservoirs is largely absorbed by bottom sediments, it is also bioaccumulated, especially in phytoplankton, which results in its rapid incorporation into the food chain (Kabata-Pendias & Pendias, 1999). What is more, soluble nickel salts easily dissociate in an aqueous environment, which allows metal ions to penetrate cell membranes (ATSDR, 2005). The assessment by (Tóth et al., 2016) indicates that soils throughout Europe are to some extent affected by nickel pollution.

Lead, next to cadmium and mercury, belongs to the group of the most toxic elements for living organisms. Anthropogenic accumulation of lead is observed in most soils as a result of global pollution with this element. In almost all soils, the lead balance is positive and indicates a steady increase in concentration. From the point of view of ecotoxicity or phytotoxicity, even the permissible content or slightly elevated level of lead in soil may pose a threat to humans, and above all to children (Kabata-Pendias and Pendias, 1999). Even a relatively low lead exposure can cause toxic effects. The widespread occurrence of Pb content in agricultural land above the permissible threshold indicates the need for strict control of lead in the environment and ultimately in the food chain (Tóth et al., 2016). The Pb content in engine oil is mainly associated with the wear of plain bearings (Hamawand et al., 2013; Nwosu et al., 2008; Palkendo et al., 2013).

Zinc, just like copper, is more easily extracted from anthropogenic sources than from its natural occurrence in soil (Kabata-Pendias and Pendias, 1999). Due to the high solubility, zinc easily penetrates into groundwater. Excess zinc found in soil can reduce nitrification processes and adversely affect many microbiological processes. Furthermore, zinc is an essential element for both plants and people, but its excess is toxic (Swartjes, 2011). That is why it is very important to control its proper amount in agricultural soils. Large amounts of zinc probably also inhibit copper absorption, which causes symptoms of copper deficiency. The main source of zinc in fresh oil is a package of antioxidant additives, corrosion inhibitors, anti-wear additives, detergents and additives that increase resistance to extremely high pressure (Hamawand et al., 2013; Nwosu et al., 2008; Palkendo et al., 2013).

## Methods of research

The study material consisted of 80 samples of used engine oils collected from passenger cars of different manufacturers. The oils were collected at car service stations during oil change. In the course of sampling, the following information regarding each sample was also gathered: car mileage, oil change interval, and engine type.

The content of heavy metals was tested with the use of the HDMaxine analyzer. It is a multi-element device used for the determination of trace elements in liquid samples on a hydrocarbon matrix, and operating on the basis of high-definition fluorescence (X-ray Fluorescence – HDXRF).

The device has the capability to simultaneously determine the content of Cr, Cu, Fe, Ni, Pb, Zn, Hg, Cd in the ranges corresponding to the concentrations of these elements found in engine oils. The limits of detection of the analyzed elements are summarized in Table 1.

Due to the fact that the analyzer does not require any additional sample preparation, the oil samples were poured directly into measuring cups. The analyses were performed in triplicate for each sample. The quality of the analytical results was tested with the use of the metal-organic standard.

In order to determine the differences in heavy metal content depending on the type of engine and the oil change interval, the oil samples tested were divided, according to the type of car engine they were collected from, into two groups designated as GE (Gasoline Engine) and DE (Diesel Engine). In terms of oil change interval, the samples were divided into 5 groups marked as follows: GI oil change interval <10k km, GII – oil change interval 10–12k km, GIII – oil change interval 12–14k km, GIV oil change interval 14–16k km, and GV >16k km.

To determine the impact of several factors (independent variables – engine type, oil consumption) on the dependent variable (metal content in engine oils), a multifactor analysis of variance was performed. This analytical tool was used to seek answers to the following questions: a) is heavy metal content influenced by the type of engine, depending on the degree of oil consumption, b) does the car mileage (degree of oil consumption) affect the concentration of a given heavy metal regardless of the type of engine, and c) do the car engine type and car mileage affect the heavy metal content?

In addition to the two-way analysis of variance (Two-way ANOVA), the Tukey HSD test was also performed. The significance level of 0.05 was adopted in the analysis. All *p* values below 0.05 were interpreted as indicating significant relationships. The analysis was performed with the use of the R software, version 3.6.1. (R Core Team, 2019)

The obtained results were then statistically analyzed with STATISTICA software. Data mining methods were also used. In each of the analyzed groups (depending on the type of engine and oil change interval) the results were presented with the use of box-and-whisker plot, taking into account the following data: median of measured values, outliers and extreme values, interquartile range (quartiles – 25 and 75 percentile) and whiskers denoting the minimum and maximum non-outlier values. Statistical significance was measured with Student's *t*-test for independent samples.

## Results and discussion

The concentrations of heavy metals in used engine oils, divided into groups according to engine types and oil change intervals, are presented in Table 2. The information regarding average values and standard deviations is provided in Tables 3 and 4, while the information on medians is provided in Figures 1–6.

The obtained data show that the content of particular metals varied quite considerably depending on the type of engine and the oil mileage, which was confirmed by means of statistical analysis.

The average Cr content in DE oil samples was three times higher than in GE oil samples, and so was the median (two times higher). A clearly wider range of outlying concentrations was observed for DE oils – 0.4–4.2 mg·kg<sup>-1</sup> (max value 8.1 mg·kg<sup>-1</sup>), which may suggest that it could be more difficult to predict the Cr content in this type of engine. This was also confirmed by a twice higher coefficient of variation for DE oils (90%). For GE oils, the range of outlying results was 0.3–1.2 mg·kg<sup>-1</sup> (max value 1.9 mg·kg<sup>-1</sup>). Kashif et al. (Kashif et al., 2018) tested used engine oils collected from gasoline-powered passenger cars (GE) by applying the AAS method. They found significantly higher Cr concentration in the range of 16–27 mg·kg<sup>-1</sup>. In turn, Wolak et al., using the AAS method to test engine oils from passenger cars powered by gasoline engines (GE), determined the chromium content in the range similar to the one obtained in this study – 1.47–3.14 mg·kg<sup>-1</sup> (Wolak et al., 2019). Moreover, Zając et al. assessed used oils collected from agricultural tractors powered by diesel engines (DE) by means of the XRF method and obtained the average of 1.4 mg·kg<sup>-1</sup> for chromium (Zając et al., 2015), however, with a wider range (min-max) of the results 0.4–10.7 mg·kg<sup>-1</sup>. A higher content of chromium was also reported by Stout et al. (Stout et al., 2018).

Considering the concentrations of elements in groups established according to oil change intervals (Table 2, Fig. 1), it can be seen that in all of them (GI–GV) the average content of chromium was lower in oil samples collected from GE engines, and also the coefficient of variation for oil samples taken from these engines was lower compared to DE oils. These findings are consistent with those drawn at an earlier stage of the study, where the comparison focused only on different types of engine. Therefore, as a result of oil use (different car mileages), the average, the coefficient of variation and the non-outlier range are higher for DE oils, also when broken down into separate stages of oil use (oil change intervals). The median value in oil samples collected from GE engines was close to their average value.

Having analyzed the lengths of the whiskers for the results obtained for the samples taken from DE engines, it should be stated that the distribution of the variable is characterized by clear right-hand asymmetry (GI–GIV). The highest content of chromium was found in the samples collected from DE engines (groups GI and GII) – 8.1 and 7.8 mg·kg<sup>-1</sup>, respectively. The maximum content of Cr for GE engine oil samples was observed in GII group – 1.9 mg·kg<sup>-1</sup>.

Cu is introduced into engine oils due to wear of bearings and valve guides. The average Cu content in GE oils was 75% higher than in DE oils (25.8, 14.8, respectively), while the median was 40% higher (18.6, 13.3, respectively). Moreover, there was a clearly wider range of non-outlying values in GE oils – 3.1–80.9 mg·kg<sup>-1</sup> (the range from the first

**Table 1.** The limits of detection of the analyzed elements

Metal	Cr	Cu	Fe	Ni	Pb	Zn	Hg	Cd
Limit of detection [mg kg <sup>-1</sup> ]	0.4	0.14	0.7	0.1	0.08	0.14	0.08	0.06



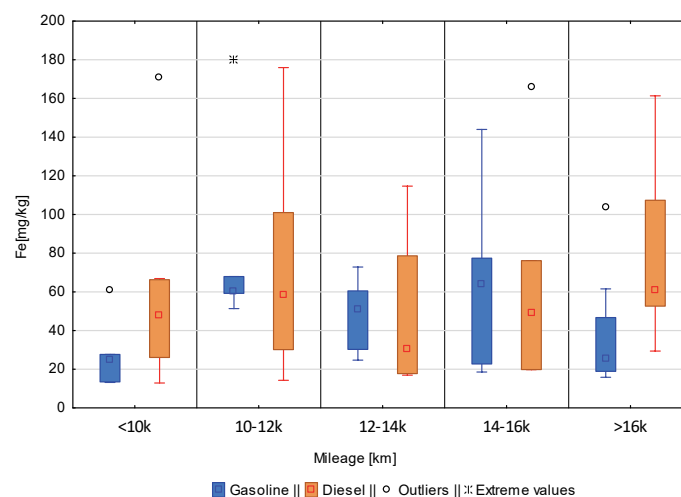
to the third percentile was also wider – 13.3–49.9 mg·kg<sup>-1</sup>). Furthermore, the maximum value was recorded for GE oils as well – 82.0 mg·kg<sup>-1</sup> (GII, GIV). A much higher coefficient of variation for GE oils (75%) compared to DE oils (41%) may indicate a more difficult prediction of Cu concentration in GE oils. For DE oils, the range of non-outlying values was 10.2–16.9 mg·kg<sup>-1</sup>. The Cu content in GE oils obtained in this study was higher than that reported by (Kashif et al., 2018) 4.7–8.5 mg·kg<sup>-1</sup> and (Wolak et al., 2019) 1.8–25 mg·kg<sup>-1</sup>. However, in DE oils the average values obtained were similar

to those reported by (Zajac et al., 2015), with an average content of 18 mg·kg<sup>-1</sup>; however, the maximum content of Cu was 76 mg·kg<sup>-1</sup>. In turn, Stout et al. (Stout et al., 2018) reported a higher average value (33 mg·kg<sup>-1</sup>) compared to that obtained in the study (21 mg·kg<sup>-1</sup>). Considering the distribution of the Cu content in individual groups of oil change interval (Table 2, Fig. 2), it can be seen that the greater differentiation in copper concentration applies to the results obtained for GE oils; in all groups the coefficient of variation was higher for oils coming from these engines. Additionally, the average and median

**Table 2.** Selected positional measures of variability of the heavy metal contents in the oils tested, divided into groups according to engine types and oil change intervals

Metal	value	unit	GE [45]	DE [35]	GI		GII		GIII		GIV		GV	
					GE [7]	DE [9]	GE [6]	DE [9]	GE [7]	DE [4]	GE [13]	DE[7]	GE [12]	DE [6]
Cr	$\bar{x}$	[mg kg <sup>-1</sup> ]	0.7	2.1	0.6	2.3	1.1	2.4	0.7	1.2	0.7	1.4	0.7	2.9
	M	[mg kg <sup>-1</sup> ]	0.7	1.5	0.5	1.5	1.1	2.0	0.6	1.0	0.7	1.0	0.6	3.7
	V	%	44.18	89.7	60.3	106.5	50.5	96.4	31.9	82.6	24.4	71.0	36.3	54.6
Cu	$\bar{x}$	[mg kg <sup>-1</sup> ]	25.8	14.8	21.2	13.0	28.3	13.6	21.2	12.8	25.3	18.6	30.6	16.5
	M	[mg kg <sup>-1</sup> ]	18.6	13.3	18.7	13.1	16.9	13.2	15.4	12.7	21.7	14.1	15.3	14.2
	V	%	75	41.0	36.6	10.0	94.8	17.0	54.0	4.9	71.5	66.1	82.6	30.1
Fe	$\bar{x}$	[mg kg <sup>-1</sup> ]	49.9	64.2	27.3	56.1	79.9	73.9	49.6	48.2	60.3	59.0	36.8	78.7
	M	[mg kg <sup>-1</sup> ]	43.7	52.6	24.7	47.8	60.1	58.4	51.1	30.6	53.2	49.4	25.6	60.6
	V	%	71.1	75.0	58.2	84.4	62.0	72.9	34.7	95.1	67.6	87.9	70.2	60.8
Ni	$\bar{x}$	[mg kg <sup>-1</sup> ]	0.5	1.0	0.4	1.0	0.8	1.1	0.5	0.7	0.5	0.7	0.5	1.3
	M	[mg kg <sup>-1</sup> ]	0.5	0.8	0.3	0.6	0.8	0.9	0.5	0.8	0.4	0.7	0.5	0.9
	V	%	58.2	82.9	67.3	104.7	49.6	84.7	53.4	38.7	66.3	55.2	48.0	68.3
Pb	$\bar{x}$	[mg kg <sup>-1</sup> ]	0.6	0.9	0.4	0.9	1.1	1.4	0.5	0.4	0.6	0.9	0.5	0.6
	M	[mg kg <sup>-1</sup> ]	0.4	0.3	0.4	0.5	0.9	0.7	0.4	0.4	0.5	0.3	0.4	0.3
	V	%	64.0	124.2	21.5	131.0	60.0	95.3	49.1	13.9	45.3	164	61.3	116.9
Zn	$\bar{x}$	[mg kg <sup>-1</sup> ]	872.9	906.6	820.8	894.5	907.6	1027.5	789.2	869.2	962.2	842.9	837.9	842.8
	M	[mg kg <sup>-1</sup> ]	868.3	820	834	823.7	909.3	902.7	828.7	826.8	921.3	786.3	841.0	812.2
	V	%	15.8	31.1	11.6	30.3	12.4	43.6	12.4	15.1	15.8	15.1	15.9	22.5

$\bar{x}$  – arithmetic average, M – median, V – coefficient of variation



**Fig. 1.** The content of Cr in the tested engine oils divided into groups according to engine type and engine oil mileage

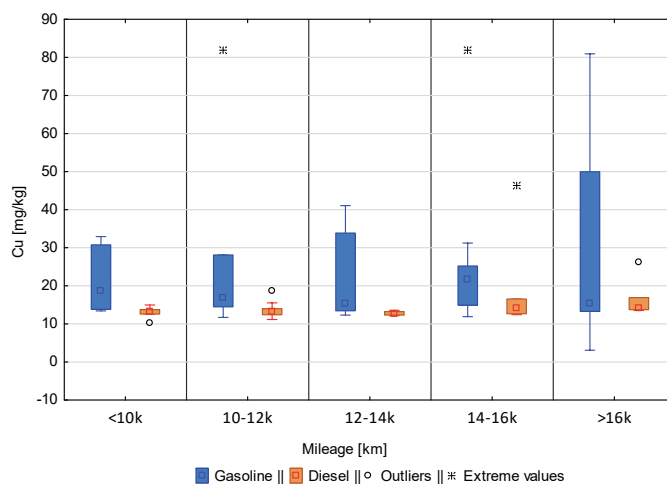
values in individual oil change interval groups were higher for GE oils than for DE oils (Fig. 2). The highest Cu contents of approx.  $80 \text{ mg}\cdot\text{kg}^{-1}$  (GII, GIV, GV) were found for GE oils, whereas the highest concentration of this element for DE oils was lower by almost half –  $46 \text{ mg}\cdot\text{kg}^{-1}$  (GIV).

The average content and median content of Fe in DE oils were higher than in GE oils (29% higher average and 17% higher median, respectively). A narrower range of non-outlying values was observed in GE oils –  $13.2\text{--}104 \text{ mg}\cdot\text{kg}^{-1}$  (DE oils  $12.9\text{--}176.0 \text{ mg}\cdot\text{kg}^{-1}$ ), but the maximum values were similar (GE oils –  $180 \text{ mg}\cdot\text{kg}^{-1}$ , DE oils –  $176 \text{ mg}\cdot\text{kg}^{-1}$ ). The content ranges (min-max) of Fe indicated by (Kashif et al., 2018) were much narrower  $98.5\text{--}138 \text{ mg}\cdot\text{kg}^{-1}$  than those obtained in the study. Also, the average value ( $60.2 \text{ mg}\cdot\text{kg}^{-1}$ ) reported by (Wolak et al., 2019) falls within the ranges obtained in presented study. Moreover, average values indicated for DE oils were similar to those obtained by (Zając et al., 2015) with an average content of  $53.5 \text{ mg}\cdot\text{kg}^{-1}$ . However, (Stout et al., 2018) report an average Fe content of  $256 \text{ mg}\cdot\text{kg}^{-1}$ , which is much higher than the maximums obtained in this study. It therefore follows that on the one hand, it is possible to estimate the increase of Fe after only one period of oil use (10–15k km) at the level of

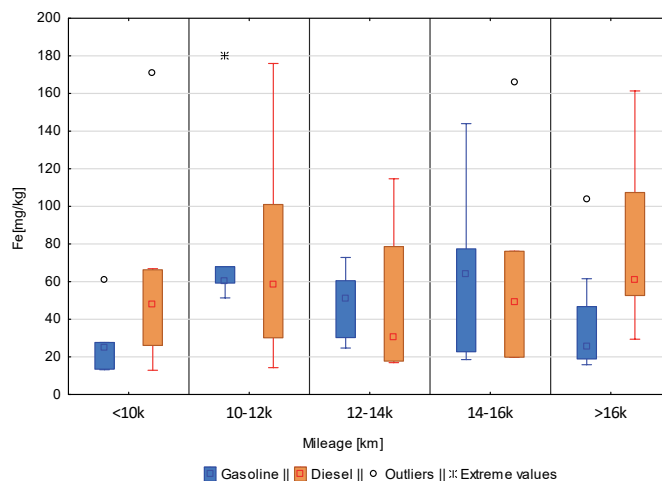
min  $50 \text{ mg}\cdot\text{kg}^{-1}$ ; while, on the other hand, it should be borne in mind that during operation drivers use refills that effectively refresh the oil and reduce Fe concentration (e.g., the average and median for GE-GV) and then the min Fe concentration may decrease to about  $20 \text{ mg}\cdot\text{kg}^{-1}$ .

When analyzing the results obtained in individual oil change interval groups (Table 2 Fig. 3), it can be seen that in the GII group, the average and the median Fe content in GE and DE oils were similar, in the GIII and GIV group – the average and the median were higher for GE oils, while in the lowest and highest mileage groups (GI and GV), the average and the median content for GE oils were lower by half as compared to DE oils. In turn, when analyzing the lengths of the obtained whiskers for DE oils coming from the GII, GIII, GV groups and for GE oils from the GIV group, it should be stated that the distribution of the variable is clearly characterized by a right-sided asymmetry. The maximum content of Fe for both GE and DE engines was found in group GII ( $180$  and  $176 \text{ mg}\cdot\text{kg}^{-1}$ , respectively). In addition, 3 values close to the maxima (above  $160 \text{ mg}\cdot\text{kg}^{-1}$ ) were identified for 3 other DE samples.

The main source of nickel in used engine oils are piston rings and shaft (Palkendo et al., 2013). The average Ni



**Fig. 2.** The content of Cu in the tested engine oils divided into groups according to engine types and engine oil mileage



**Fig. 3.** The content of Fe in the tested engine oils divided into groups according to engine type and engine oil mileage

content in GE oils ( $0.5 \text{ mg}\cdot\text{kg}^{-1}$ ) was half that of DE oils ( $1 \text{ mg}\cdot\text{kg}^{-1}$ ). Also, for DE oils a clearly wider range of non-outlying values was noted –  $0.15\text{--}2.5 \text{ mg}\cdot\text{kg}^{-1}$  with a maximum value of  $3.4 \text{ mg}\cdot\text{kg}^{-1}$ . For both types of oils, the results were characterized by strong variability (58% – GE, 83% – DE); hence, the prediction of Ni concentration in oils may be rather difficult. The Ni contents in GE oils obtained in the tests were lower than those reported by (Kashif et al., 2018), where Ni was determined in the range of  $6\text{--}11.75 \text{ mg}\cdot\text{kg}^{-1}$ . However, in the paper by (Wolak et al., 2019), the content indicated is similar (average –  $0.8 \text{ mg}\cdot\text{kg}^{-1}$ ) to the average content obtained in this study.

The average Ni concentration in DE oils reported by (Zajac et al., 2015) is lower and amounts to  $0.4 \text{ mg}\cdot\text{kg}^{-1}$  with a minimum of  $0.14 \text{ mg}\cdot\text{kg}^{-1}$  and a maximum of  $0.75 \text{ mg}\cdot\text{kg}^{-1}$ . In turn, a higher average content of this element is reported by Stout et al. –  $2.1 \text{ mg}\cdot\text{kg}^{-1}$  (Stout et al., 2018). Considering the Ni concentration in individual groups of oil change interval (Table 2, Fig. 4), it can be observed that the average and median values in GE oils were lower than in DE oils, only in the GII group the values were at a similar level. For DE oils in groups GI, GIV and GV, the distribution of the variable is characterized by a clear right-hand asymmetry. Likewise, for DE engines, the highest content of this element was found to be  $3.4 \text{ mg}\cdot\text{kg}^{-1}$ , while for GE engines this value was 60% lower ( $1.3 \text{ mg}\cdot\text{kg}^{-1}$ ) – GII and GIV.

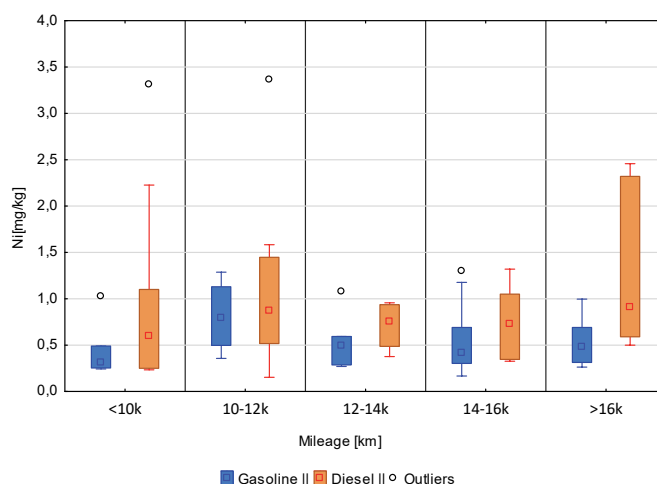
The average Pb content in DE oils ( $0.9 \text{ mg}\cdot\text{kg}^{-1}$ ) was higher than in GE oils ( $0.6 \text{ mg}\cdot\text{kg}^{-1}$ ), with the median higher for GE oils ( $0.3 \text{ mg}\cdot\text{kg}^{-1}$ ) compared to the median for DE oils ( $0.4 \text{ mg}\cdot\text{kg}^{-1}$ ). The range of non-outlying values was the same ( $0.3\text{--}1.1 \text{ mg}\cdot\text{kg}^{-1}$ ) for both types of oils; however, for GE oils the max. content was  $2.2 \text{ mg}\cdot\text{kg}^{-1}$ , while for DE oils it was almost twice as high –  $4.0 \text{ mg}\cdot\text{kg}^{-1}$ . This was confirmed by the coefficient of variation, which for DE oils showed a very strong variability of results (124%), and for GE oils – a strong variability (64%). The Pb contents reported by (Kashif et al., 2018)  $8.5\text{--}12.75 \text{ mg}\cdot\text{kg}^{-1}$  were higher than those obtained in the study, whereas Wolak et al. indicated a very similar range to the one obtained in this study  $0.27\text{--}4.57 \text{ mg}\cdot\text{kg}^{-1}$  (Wolak et al., 2019). Likewise, for DE oils, the average Pb contents reported by (Zajac et al., 2015) –  $3.6 \text{ mg}\cdot\text{kg}^{-1}$  were higher than those

obtained in the study. Conversely, (Stout et al., 2018) pointed to the average Pb content of  $2777 \text{ mg}\cdot\text{kg}^{-1}$ . Yet, it should be noted that in this case such a high Pb value may be due to the fact that Stout reports on oils that cover the period when gasoline containing lead was widely used. Analyzing the lead contents in individual oil change interval groups (Table 2, Fig. 5), it can be observed that the median values in GI, GIII and GV are similar, while in GII and GIV they are clearly higher for GE oils. However, the coefficient of variation is much higher for DE oils (except for group GIII).

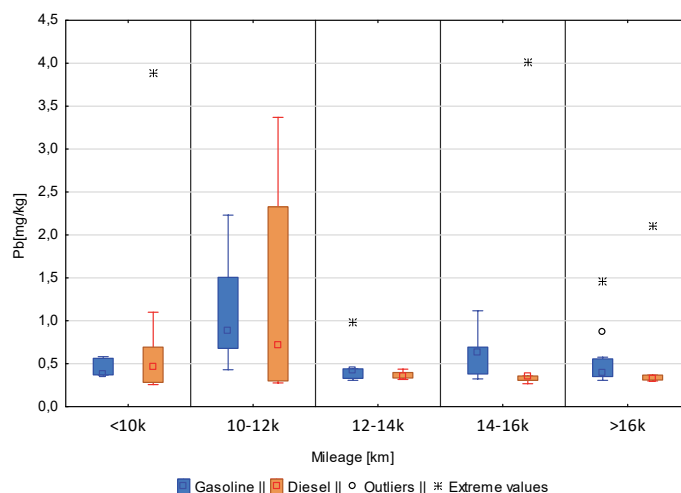
The average Zn content in the tested oils, for both types of engines, was similar (GE –  $873 \text{ mg}\cdot\text{kg}^{-1}$ , DE –  $907 \text{ mg}\cdot\text{kg}^{-1}$ ), with a higher median for GE oils (868 compared to  $820 \text{ mg}\cdot\text{kg}^{-1}$ ). The range of non-outlying values for GE oils was  $729\text{--}1064 \text{ mg}\cdot\text{kg}^{-1}$ ; however, the range of recorded values (min-max) was wider and amounted to  $653\text{--}1431 \text{ mg}\cdot\text{kg}^{-1}$ . Yet, the variability of results for these oils was low (16%). For DE oils, a higher range of non-outlying values  $576\text{--}1383 \text{ mg}\cdot\text{kg}^{-1}$  was found at a maximum value of  $1790 \text{ mg}\cdot\text{kg}^{-1}$  (GII), with an average variation of 31%. On the other hand, in the study by (Wolak et al., 2019), Zn content in the range of  $840\text{--}1112 \text{ mg}\cdot\text{kg}^{-1}$  was obtained. In contrast, in DE oils, the average content reported by (Zajac et al., 2015) was  $1106 \text{ mg}\cdot\text{kg}^{-1}$ . The average value reported by (Stout et al., 2018) was  $873 \text{ mg}\cdot\text{kg}^{-1}$ .

Analyzing the results of lead content in individual groups of oil change interval (Table 2, Fig. 5), it can be seen that the average and median values in the groups GI, GII, GIII and GV for both engine types are similar; the differences are visible in GIV – the average and median for GE oils are clearly higher than for DE oils.

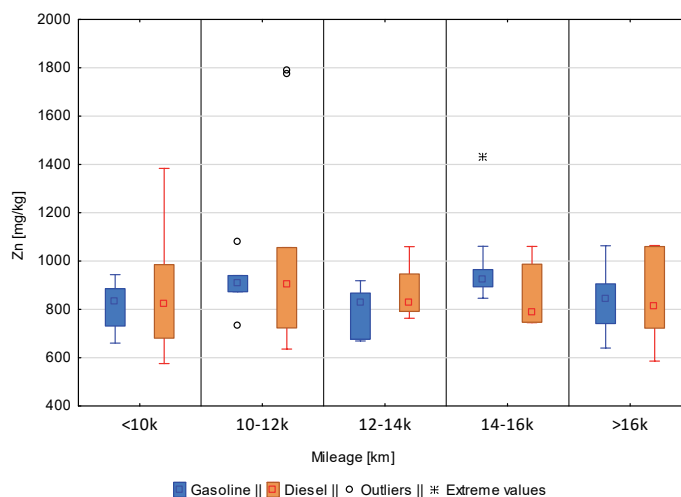
Particular attention is currently paid to pollution of the environment with mercury and cadmium compounds due to the anthropogenic distribution of these elements in the environment and high toxicity. It should be noted that these toxic elements were not detected in the engine oils tested. The obtained Cd and Hg content was below the level of quantification (Table 1). This, however, does not mean that the risk related to the toxic effects of cadmium should be excluded. It is introduced to engine oil as an impurity during use (Hamawand et al., 2013). From the literature it follows that the Cd content in used engine oils is from  $0.27$  to  $1 \text{ mg}\cdot\text{kg}^{-1}$  (Cassap, 2008; Hamawand et



**Fig. 4.** The content of Ni in the tested engine oils divided according to groups of engines and engine oil mileage



**Fig. 5.** The content of Pb in the tested engine oils divided into groups according to engine type and engine oil mileage



**Fig. 6.** The content of Zn in the tested engine oils divided into groups according to engine type and engine oil mileage

al., 2013). However, there is no information about the content of Hg in used and new engine oils, despite the fact that mercury was found in crude oil (Klojzy-Karczmarczyk, 2013). Mercury was not detected in the tested samples, so it can be concluded that the threat posed by this metal is rather insignificant.

Tables 3 and 4 present the mean values, standard deviations and  $p^*$  values for selected elements (Cr, Cu, Fe, Ni, Pb, Zn). Table 3 presents the results for 5 groups, different in terms of oil mileage (GI – <10k km, GII – 10–12k km, GIII – 12–14k km, GIV – 14–16k km, GV – > 16k km). Table 4 presents the results for two groups differentiated in terms of the type of engine to which the engine oil was applied (GE – gasoline, DE – diesel). The threshold for statistical significance was set to 0.05. Any result below the value was considered statistically significant (the values were indicated in bold).  $P$  values ( $P$ -value resulting from the application of Student's  $t$  test for independent samples) below 0.01 were considered highly statistically significant (the values were indicated in bold and underlined).

The analysis of the results presented in Table 3 suggests that the largest number of statistically significant differences

between the mean values (for respective oil groups GI–GV) concerned the concentration of Cr and Zn. In the case of this element, five comparisons showed statistically significant differences. The smallest differences in concentrations of these elements were observed for Cu. Only in two sets (GI vs GIV and GI vs GV), the differences in mean values of these elements were statistically significant.

Analyzing the results presented in Table 4, it was observed that the differences in mean concentrations of elements in various engines (diesel, gasoline) in nearly every case (except Zn) were highly statistically significant ( $p$  lower than 0.01). The largest variation in mean values in the case of different engine types was obtained for Cr. In each case, this difference was two-fold. In the case of the Cr, the average concentration for oils from diesel engine was 3 times higher than the average for gasoline engine oils.

In the next step, a multivariate analysis of variance was performed. It provides much more information than a Student's  $t$ -test. The interaction effect (introduction of another factor) can change the view of a given phenomenon. The Student's  $t$ -test only compares two groups with each other. The results



of the statistical analysis presented in Table 4 show that the type of engine affects the content of the heavy metals tested, but the effect of oil consumption needs to be investigated. In order to be able to draw more comprehensive conclusions, it is necessary to take into account the impact of the type of engine in the context of the degree of oil consumption (oil change interval). Table 5 shows the parameters of ANOVA two-factor analysis.

In the GII group, half of the analyzed elements (Fe, Ni, Pb) showed a statistically significant difference in concentration in relation to the reference group (GI). It should be indicated, however, that it only applies to the basic type of engine (gasoline). The iron concentration in this group is on average higher by 53 compared with the reference group GI. In the GIV group, statistical significance was demonstrated by Fe and Zn. The concentrations of these elements are higher by 33 and 141, respectively, when compared with the reference group. By type of engine, it was shown that in diesel engines the level of Fe, Cr, Pb and Ni is significantly different than in the reference

group of gasoline engines. With the indication that this only applies to the basic oil change interval, i.e., the GI group.

Table 5 also presents the results for both the car mileage and the type of engine analysis. The significance of statistical differences was obtained for GII:DE (Fe) and for GIV:DE (Cr, Zn), which showed lower concentrations of the analyzed elements than in the base GI:GE combination (-35 for Fe, -1 for Cr and -193 for Zn, respectively).

In the next step, various combinations of car mileage groups and engine types were compared using post hoc analysis. The results are shown in Table 6.

For the correct interpretation of the results in Table 6, it is necessary to use the data from Table 5. This makes it possible to compare the sets of variables, taking into account both different engine types (gasoline, diesel) as well as different car mileages/oil change intervals (GI-GV).

The first important observation is that with respect to gasoline engines, when comparing extreme mileages (GV:GE vs GI:GE), none of the analyzed elements showed statistical

**Table 3.** Mean values, standard deviations and p\* values for groups of oils divided based on oil mileage

	[In total]	GI	GII	GIII	GIV	GV	GI vs GII	GI vs GIII	GI vs GIV	GI vs GV	GII vs GIII	GII vs GIV	GII vs GV	GIII vs GIV	GIII vs GV	GIV vs GV
	$\bar{x}$ (s)						p									
Metal	N=80	N=16	N=15	N=11	N=20	N=18										
Cr	1.3 (1.4)	1.5 (2.0)	1.9 (1.9)	0.9 (0.6)	1.0 (0.7)	1.4 (1.4)	0.391	0.056	<b>0.038</b>	0.712	<b>0.003</b>	<b>0.001</b>	0.165	0.438	<b>0.040</b>	<b>0.037</b>
Cu	21.0 (15.9)	16.6 (6.5)	19.5 (17.8)	18.1 (9.8)	22.9 (16.3)	25.9 (21.6)	0.279	0.384	<b>0.011</b>	<b>0.004</b>	0.682	0.297	0.109	0.118	0.051	0.400
Fe	56.1 (41.8)	43.5 (38.9)	76.3 (50.4)	49.1 (28.4)	59.8 (43.5)	50.8 (38.9)	<b>0.001</b>	0.475	<b>0.042</b>	0.344	<b>0.005</b>	0.071	<b>0.005</b>	0.198	0.825	0.244
Ni	0.7 (0.6)	0.8 (0.9)	1.0 (0.8)	0.6 (0.3)	0.6 (0.4)	0.8 (0.6)	0.127	0.279	0.162	0.850	<b>0.004</b>	<b>&lt;0.001</b>	0.106	0.954	0.100	<b>0.041</b>
Pb	0.7 (0.8)	0.7 (0.9)	1.3 (1.1)	0.4 (0.2)	0.7 (0.8)	0.6 (0.5)	<b>0.004</b>	0.093	0.903	0.365	<b>&lt;0.001</b>	<b>0.001</b>	<b>&lt;0.001</b>	0.099	0.118	0.414
Zn	887.6 (212.7)	862.3 (210.1)	979.6 (350.5)	818.3 (111.8)	920.4 (152.0)	839.5 (148.3)	<b>0.047</b>	0.266	0.094	0.520	<b>0.011</b>	0.236	<b>0.008</b>	<b>0.001</b>	0.476	<b>0.005</b>

GI – < 10k km, GII – 10–12k km, GIII – 12–14k km, GIV – 14–16k km, GV – >16k km; N – the number of samples tested,  $\bar{x}$  – arithmetic average, s – standard deviation, p – p-value

**Table 4.** Mean values, standard deviations and p\* values for groups of oils divided based on engine type

	[In total]	GE	DE	GE vs DE
	$\bar{x}$ (s)			p
Metal	N=80	N=45	N=35	
Cr	1.3 (1.4)	0.7 (0.3)	2.1 (1.9)	<b>&lt;0.001</b>
Cu	21.0 (15.9)	25.8 (19.3)	14.8 (6.1)	<b>&lt;0.001</b>
Fe	56.1 (41.8)	49.9 (35.4)	64.2 (48.2)	<b>0.008</b>
Ni	0.7 (0.6)	0.5 (0.3)	1.0 (0.8)	<b>&lt;0.001</b>
Pb	0.7 (0.8)	0.6 (0.4)	0.9 (1.1)	<b>0.003</b>
Zn	887.6 (212.6)	872.9 (138.2)	906.6 (282.3)	0.223

GE – gasoline, DE – diesel; N – the number of samples tested,  $\bar{x}$  – arithmetic average, s – standard deviation, p – p-value

significance. Similar results were obtained for DE engines. In the GIII:GE vs GI:GE and GIV:GE vs GI:GE combinations, statistical significance was found for Fe in two adjacent periods only (GI and GII – GE). Statistically significantly more iron is found in GII for GE [the calculations were done in the following way: the ANOVA parameters from Table 5 are added for each component, i.e., for GI:GE the total is 0 (for GI – there is no indication because it is the base level, for GE – there is no indication because it is the base level, for GI:GE – there is

no indication because it is the base level), for GII:GE the total amounts to 52.535].

When comparing the last period of car use (GV), taking into account engine types (GE, DE), the highest number of statistically significant differences was found (4 elements – Cr, Cu, Fe, Ni). This means that used oils (after GV) contain statistically more Cr, Fe and Ni when the oils come from DE engines, whereas they contain statistically more Cu when the oils come from GE engines. Hence, the content of respective

**Table 5.** Two-factor analysis of variance (ANOVA)

Metal	Linear model (two-way ANOVA) parameters								
	Mileage (ref. level: GI <sup>2</sup> )				Engine (ref.level: GE <sup>3</sup> )	Interactions			
	GII	GIII	GIV	GV	DE	GII:DE	GIII:DE	GIV:DE	GV:DE
Cr	0.484	0.05	0.136	0.044	<b>1.646 *</b>	-0.343	-1.099	<b>-1.004 *</b>	0.626
Cu	7.187	0.019	4.123	<b>9.424 *</b>	-8.138	-6.604	-0.259	1.42	-5.957
Fe	<b>52.535 *</b>	22.233	<b>32.958 *</b>	9.516	<b>28.75 *</b>	<b>-34.705 *</b>	-30.112	-30.074	13.062
Ni	<b>0.393 *</b>	0.102	0.107	0.116	<b>0.6 *</b>	-0.263	-0.407	-0.426	0.148
Pb	<b>0.66 *</b>	0.027	0.13	0.096	<b>0.44 *</b>	-0.161	-0.542	-0.162	-0.354
Zn	86.802	-31.571	<b>141.37 *</b>	17.052	73.709	46.198	6.22	<b>-192.984 *</b>	-68.737

\* statistically significant ( $p < 0.05$ )

<sup>2</sup> Five groups of samples were analyzed. In ANOVA, one of them must serve as a reference group – the GI group was selected; yet, indicating that this does not affect the entire analysis

<sup>3</sup> Two types of engine were analyzed. In ANOVA, one of them must serve as a reference type – the GE engine was selected; yet, indicating that this does not affect the entire analysis

**Table 6.** Tukey HSD post-hoc

Mileage:Engine	Tukey HSD post-hoc p-value					
	Cr	Cu	Fe	Ni	Pb	Zn
GII:GE vs GI:GE	0.971	0.886	<b>0.002 *</b>	0.524	0.169	0.947
GIII:GE vs GI:GE	1	1	0.718	1	1	1
GIV:GE vs GI:GE	1	0.99	0.068	1	1	0.244
GV:GE vs GI:GE	1	0.381	0.997	0.999	1	1
GI:DE vs GI:GE	<b>&lt;0.001 *</b>	0.676	0.272	<b>0.017 *</b>	0.597	0.965
GII:DE vs GII:GE	<b>0.025 *</b>	<b>0.04 *</b>	1	0.666	0.969	0.648
GIII:DE vs GIII:GE	0.97	0.862	1	0.996	1	0.986
GIV:DE vs GIV:GE	0.668	0.807	1	0.984	0.937	0.488
GV:DE vs GV:GE	<b>&lt;0.001 *</b>	<b>0.037 *</b>	<b>0.011 *</b>	<b>0.001 *</b>	1	1
GII:DE vs GI:DE	1	1	0.816	0.998	0.311	0.334
GIII:DE vs GI:DE	0.318	1	1	0.886	0.619	1
GIV:DE vs GI:DE	0.338	0.956	1	0.679	1	0.997
GV:DE vs GI:DE	0.757	0.999	0.682	0.894	0.982	0.998

\* statistically significant ( $p < 0.05$ )

heavy metals in used engine oils varies depending on the engine type and oil mileage.

## Conclusions

Waste engine oils contain metals that may pose a threat to human health and/or to the environment after entering soil and water. That is why it is important to handle used oils in an adequate way. Directive 2014/955/EU explicitly states that WLO (waste lubricant oil) should be classified as hazardous waste and appropriate methods of disposal should be ensured.

By ordering the elements in terms of their decreasing average content in the examined oils, it can be stated that the dominant element was Zn – the average content of this element in both types of oils was at a similar level – 900 mg·kg<sup>-1</sup>, followed by Fe and Cu, the content of which, however, was one order of magnitude lower. In GE oils, the next elements marked in descending order were Cr, Pb and Ni, and their content was below 1 mg·kg<sup>-1</sup>, while in DE oils it was Cr, Ni and Pb. Analyzing the differences in the average content of the examined elements, depending on the type of engine, it can be stated that in oils coming from DE engines the following elements showed a higher concentration – Cr (three times higher concentration), Fe (1/3 times higher concentration), Ni (two times higher concentration), Pb (1/2 times higher concentration). In oils coming from GE engines, only the average Cu content was higher (3/4). In both cases, zinc had

a comparable level of concentration. The multi-factor analysis of variance, taking into account the mileages from the GI group, showed that in diesel engines, the level of Fe, Cr, Pb and Ni is statistically significantly different than in the reference group of gasoline engines. The differences in the content of heavy metals in used lubricating oils, depending on the engine type, suggest that their separate collection may definitely be considered, which will facilitate the proper handling of these oils and reduce the risk to the environment.

In turn, the post hoc analysis, taking into account both different mileage as well as the type of engine, showed that in oil, which was operated for above 16k km in the DE engine, the concentrations of Cr, Fe and Ni are statistically higher, whereas in oil operated in the GE engine – there is statistically more Cu. Mercury and cadmium were not measured in any of the engine oil samples tested. However, based on the literature data, it should be borne in mind that cadmium may appear in the form of impurities during the use of engine oils. Further research should be expanded to include the heavy metal content analysis of used engine oils with significant oil change intervals (over 20k km of mileage). This is due to the possible intensification of the concentrations of wear elements and pollutants after such a time of use, and their potential leakage into the environment. As the authors' own research suggests, car users oftentimes change the oil themselves, especially when its mileage is significant, which raises concerns about non-compliance with the rules for the management of waste oils.

Supplementary data

Code	Car mileage (km)	Oil change interval (km)	Engine type	Cr	Cu	Fe	Ni	Pb	Zn
				mg·kg <sup>-1</sup>					
G_01	53,173	18,440	Gasoline	0.59	56.91	15.86	0.27	0.31	833
G_02	59,988	19,764	Gasoline	0.43	14.73	18.79	0.46	0.58	868
G_03	59,200	8,349	Gasoline	1.36	13.41	27.41	1.02	0.37	944
G_04	20,000	14,000	Gasoline	0.72	15.43	51.08	0.50	0.44	835
G_05	22,301	7,718	Gasoline	0.49	30.78	13.21	0.24	0.37	834
G_06	55,650	14,230	Gasoline	0.76	14.94	63.96	0.57	0.38	894
G_07	7,125	7,125	Gasoline	0.77	18.73	60.65	0.49	0.56	731
G_08	34,537	19,387	Gasoline	1.18	32.84	104.00	1.00	0.87	1035
G_09	117,000	13,000	Gasoline	1.01	12.32	72.88	1.07	0.37	669
G_10	15,150	15,150	Gasoline	0.77	82.04	32.08	0.33	1.12	853
G_11	24,500	14,623	Gasoline	0.53	23.08	20.60	0.42	0.63	907
G_12	72,000	15,200	Gasoline	1.04	19.44	144.00	1.30	0.39	869
G_13	63,212	13,503	Gasoline	0.84	41.07	30.30	0.35	0.31	829
G_14	231,293	18,272	Gasoline	0.93	12.59	23.61	0.26	0.31	1064
G_15	31,182	16,617	Gasoline	0.54	65.69	17.49	0.28	0.38	833
G_16	60,666	19,101	Gasoline	0.66	14.81	27.57	0.34	0.52	853
G_17	30,802	15,000	Gasoline	1.02	21.49	94.25	0.59	0.35	940
G_18	52,916	14,660	Gasoline	0.69	27.48	19.75	0.24	0.33	846

G_19	60,278	19,858	Gasoline	0.66	15.78	19.09	0.49	0.38	849
G_20	103,250	12,500	Gasoline	0.60	13.45	24.71	0.29	0.33	867
G_21	28,218	9,961	Gasoline	0.47	32.94	24.09	0.32	0.37	859
G_22	27,521	8,766	Gasoline	0.59	13.81	27.71	0.32	0.46	832
G_23	39,500	21,754	Gasoline	0.63	80.94	61.57	0.83	0.54	943
G_24	138,000	18,000	Gasoline	0.51	3.08	22.72	0.52	0.33	739
G_25	19,602	19,602	Gasoline	0.92	43.03	54.53	0.94	1.46	744
G_26	300,000	12,000	Gasoline	1.40	14.48	67.95	1.09	1.00	892
G_27	130,000	15,000	Gasoline	0.42	12.47	22.72	0.41	0.38	917
G_28	230,000	12,000	Gasoline	1.87	16.00	59.62	1.29	2.23	1081
G_29	11,000	11,000	Gasoline	1.44	82.00	180.33	1.13	1.51	873
G_30	90,000	15,000	Gasoline	0.94	21.69	122.33	1.18	0.45	1061
G_31	16,000	10,000	Gasoline	0.33	18.56	13.49	0.27	0.38	660
G_32	135,000	17,600	Gasoline	0.39	14.04	38.87	0.55	0.38	653
G_33	25,593	13,000	Gasoline	0.44	14.60	47.12	0.56	0.44	729
G_34	32,600	18,200	Gasoline	0.44	12.55	38.04	0.44	0.42	640
G_35	27,600	14,000	Gasoline	0.58	17.51	60.30	0.59	0.42	677
G_36	25,300	10,800	Gasoline	0.46	17.80	51.34	0.50	0.43	733
G_37	14,200	14,200	Gasoline	0.57	31.23	71.36	0.30	0.96	921
G_38	13,000	13,000	Gasoline	0.44	33.87	60.54	0.27	0.98	919
G_39	12,000	12,000	Gasoline	0.69	11.70	59.23	0.50	0.68	927
G_40	15,000	15,000	Gasoline	0.66	24.29	43.71	0.35	0.63	980
G_41	16,000	16,000	Gasoline	0.74	25.20	53.25	0.30	0.79	925
G_42	12,000	12,000	Gasoline	0.71	28.10	60.71	0.36	0.76	940
G_43	15,000	15,000	Gasoline	0.84	11.90	77.11	0.67	0.69	964
G_44	92,000	9,000	Gasoline	0.27	19.88	24.74	0.25	0.58	886
G_45	125,000	15,000	Gasoline	0.72	13.41	18.60	0.17	0.32	1431
D_01	60,849	19,700	Diesel	0.87	14.38	29.40	0.50	0.37	722
D_02	62,000	12,000	Diesel	2.11	14.00	101.00	3.36	0.71	723
D_03	184,748	16,000	Diesel	0.96	15.12	58.50	0.36	0.36	745
D_04	68,527	18,000	Diesel	4.18	14.09	107.36	2.32	0.30	831
D_05	215,872	19,579	Diesel	3.91	16.90	161.33	2.46	2.11	586
D_06	149,172	14,725	Diesel	1.42	46.21	165.67	0.76	0.35	786
D_07	120,151	17,123	Diesel	0.90	26.30	52.62	0.59	0.31	793
D_08	225,450	13,673	Diesel	1.45	12.88	114.67	0.92	0.36	833
D_09	50,000	10,000	Diesel	3.18	13.14	58.55	0.71	0.46	985
D_10	150,500	14,500	Diesel	2.64	16.55	76.19	1.05	4.01	987
D_11	152,000	16,000	Diesel	0.75	14.06	23.34	1.32	0.31	798
D_12	150,000	14,000	Diesel	0.38	13.59	18.55	0.96	0.44	820
D_13	148,000	12,000	Diesel	0.63	12.84	14.29	0.82	0.28	779
D_14	146,000	10,000	Diesel	0.36	12.55	12.94	0.48	0.28	824
D_15	180,000	10,000	Diesel	0.37	13.75	31.81	0.60	0.43	886
D_16	136,000	16,000	Diesel	0.55	12.66	19.87	0.33	0.35	747
D_17	133,000	15,000	Diesel	0.53	12.45	19.80	0.35	0.27	776
D_18	134,000	14,000	Diesel	0.49	12.14	16.96	0.38	0.35	763
D_19	260,000	12,000	Diesel	3.49	11.16	100.67	1.45	1.47	1791

D_20	400,000	11,000	Diesel	2.02	18.64	120.00	0.88	3.35	917
D_21	180,000	11,000	Diesel	8.06	15.54	176.00	1.58	2.33	1774
D_22	320,000	10,000	Diesel	2.75	14.97	66.90	1.10	3.88	1384
D_23	89,000	10,000	Diesel	7.76	10.21	171.00	2.23	1.10	1247
D_24	10,000	10,000	Diesel	3.35	13.14	66.27	3.31	0.69	806
D_25	64,000	19,000	Diesel	3.53	13.73	63.72	0.95	0.32	1064
D_26	62,000	17,000	Diesel	4.18	13.52	57.51	0.87	0.33	1060
D_27	60,010	15,000	Diesel	2.88	12.90	49.38	0.73	0.31	1061
D_28	58,000	13,000	Diesel	2.52	12.51	42.62	0.60	0.32	1060
D_29	56,015	11,000	Diesel	2.16	12.40	36.26	0.52	0.33	1056
D_30	130,000	10,000	Diesel	1.47	13.90	47.83	0.25	0.54	576
D_31	139,000	10,000	Diesel	0.59	12.95	26.11	0.23	0.26	662
D_32	140,000	11,000	Diesel	0.75	13.21	30.18	0.15	0.30	670
D_33	141,000	12,000	Diesel	0.71	13.27	28.39	0.26	0.30	636
D_34	138,000	8,000	Diesel	0.50	12.58	23.30	0.25	0.28	681
D_35	162,000	11,500	Diesel	1.66	11.36	58.38	1.30	3.37	903

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## Zawartość metali ciężkich w przepracowanych olejach silnikowych w zależności od rodzaju silnika i przebiegu oleju

**Streszczenie:** W pracy przedstawiono wyniki analizy zawartości wybranych metali ciężkich w przepracowanych olejach silnikowych zebranych w warsztatach samochodowych podczas wymiany oleju. Głównym celem przeprowadzonych badań było określenie różnicy zawartości metali ciężkich (Cr, Cu, Fe, Ni, Pb, Zn, Hg, Cd) w zależności od typu silnika i czasu eksploatacji oleju. Analizę przeprowadzono na 80 próbkach przepracowanych olejów silnikowych z samochodów osobowych różnych producentów. Zawartość metali ciężkich badano za pomocą analizatora HDMaxine, działającego w oparciu o fluorescencję wysokiej rozdzielczości (X-ray Fluorescence – HDXRF). Analizując zróżnicowanie średnich zawartości badanych pierwiastków w zależności od rodzaju silnika można stwierdzić, że w olejach pochodzących z silników o zapłonie samoczynnym następujące pierwiastki wykazały wyższe stężenie – Cr (trzykrotnie wyższe stężenie), Fe (o 1/3 wyższe stężenie), Ni (dwukrotnie wyższe stężenie), Pb (o 1/2 wyższe stężenie). Jedynie średnia zawartość Cu była wyższa (3/4) w olejach pochodzących z silników o zapłonie iskrowym. Cynk w obu przypadkach charakteryzował się porównywalnym poziomem stężeń. Wieloczynnikowa analiza wariancji, wykazała, że w silnikach dieslach, poziom Fe, Cr, Pb oraz Ni jest istotnie statystycznie różny niż w referencyjnej grupie silników benzynowych. W żadnej z badanych próbek oleju silnikowego nie oznaczono rtęci i kadmu. Uzyskane wnioski uprawniają do stwierdzenia, że istnieją różnice w zawartości metali ciężkich w przepracowanych olejach w zależności od typu silnika. Można zatem rozważyć selektywną zbiórkę przepracowanych olejów w zależności od typu silnika co może zapewnić właściwe postępowanie z tymi olejami i zmniejszy zagrożenie dla środowiska.