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Original Research

Designation of Chosen Heavy Metals in Used Engine Oils Using the XRF Method

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Abstract

Taking into consideration the fact that used oils are considered hazardous and extremely toxic, their subsequent use creates a real threat to the environment. The only effective measure for protecting the natural environment from used oil contamination is collection and controlled utilization. Only appropriate used oil management can guarantee minimal environmental contamination and prevent its irreversible degradation.

The aim of our study was to determine the content of select heavy metal elements in used engine oils originating from agricultural tractors and agricultural machines of varying mileage. The tests were carried out by using the HD XRF method. The researched samples showed a high content of zinc remaining at 726-1,389 mg·kg^{-1}. The contents of molybdenum, iron, and copper also were high, at Mo 360-689 mg·kg^{-1}, Fe 16.5-267 mg·kg^{-1}, and Cu 4.63-76.87 mg·kg^{-1}. Low nickel, manganese, chromium, and lead contents were found in the ranges: Ni 0.14-0.75 mg·kg^{-1}, Mn 0.41-4.27 mg·kg^{-1}, Cr 0.36-10.66 mg·kg^{-1}, and Pb 0.9-13.71 mg·kg^{-1}. Mercury and cadmium were not found in the tested oils.

Keywords: used engine oils, heavy metals, lubricating oil analysis

Introduction

In recent years the problem of the contamination of soil and water with petroleum products has become ever more increasing [1, 2]. Such products mainly contain aliphatic and aromatic hydrocarbons, but also – generally in small quantities – heavy metal ions such as lead, tin, arsenic, mercury, germanium, antimony, thallium, vanadium, and iron. Used engine oils are particularly dangerous for the environment due to their contamination with products of thermal decomposition and mechanical impurities. The above products become hardly biodegradable and have carcinogenic properties, therefore, information on the content of trace elements in these products are crucial, taking into account the environmental aspect.

The chemical composition of used oil depends on the type of the base oil, the applied refining additives, physicochemical conversion that the oil underwent in the course of operation, as well as from any possible impurities occurring during the collection and storage of the used oils [3].

Metals occurring in used oils originate from various sources. For the main part, these are the products of corrosion and wear of mating metal surfaces and functional additives. The content of metals in European used oils amounts to approximately 0.7% (m/m) [3, 4].

It is estimated that in European countries, where consumption of lubricating greases amounts to 4.5 million Mg, approximately 600,000 Mg permeates soil or groundwater. In Poland, from 300 to 350 thousand Mg of fresh oils are annually put on the market, with engine oils constituting over 50% of that amount. Used oils constitute about 60% of the initial mass, which makes up from 180 to 210 thousand

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Mg of hazardous waste every year. It is estimated that the current level of used oils management equals approx. 60% (over 50% of which is directed for re-refining, about 20% for recycling, and the rest for warehousing); the remaining 40% of used oils remains outside the collection system [5].

A significant dispersion of oils connected with a large number of users, who use the oils only in small quantities, poses a serious environmentally relevant problem. Such oil is replaced by new oil after the expenditure of a certain amount of mileage or passage of time. The disposal procedure concerning the changed oils varies. In the case of passenger cars, the change of oil usually takes place at service facilities where used oil is collected by companies servicing the cars. Ever more frequently the charge for the engine oil and oil filter replacement is included in the product price, which encourages users to change oil at such service points. However, the situation is different when it comes to tractors and agricultural machines, where oil service is performed on the spot, in the agricultural holding or farm, and usually the used oil remains there and is reused by the farmers for other purposes. Taking into consideration the fact that used oils are considered to be hazardous and extremely toxic waste, their subsequent use creates a real threat to the environment.

The aim of our study was to determine the content of select heavy metals (Cd, Pb, Hg, Cr, Sn, Zn, Cu, Ni, Fe, Mn, Mo) in used engine oils originating from agricultural tractors and machines of varying mileage. Used engine oils should be managed in compliance with legal provisions; if not, they can pose a serious threat to the environment. Therefore, it is of utmost importance to specify and estimate the risk that such actions can involve.

Material and Methods

Twenty samples of used engine oils from agricultural tractors and machines by different manufacturers available on the market were analyzed. The samples were collected during oil replacement upon varying mileage. These were obtained from service companies dealing with agricultural tractor maintenance, as well as from individual farmers within the Lubelskie Voivodeship.

The collected oil samples were divided according to the mileage of the tractors and the machines: A1-8 are oils from tractors of low mileage (up to 300 work hours), B1-8 are oils from tractors of medium mileage (300-900 h), and C1-4 are oils from tractors of high mileage (more than 900 h).

The research was carried out using of the HD Maxine analyser by XOS, a multi-element analyser that determines trace elements in liquid samples in hydrocarbon matrices using high definition x-ray fluorescence (HDXRF). The device enables simultaneous determination of Cd, Pb, Hg, Cr, Sn, Zn, Cu, Ni, Fe, Mn, and Mo contents within ranges corresponding to the concentrations of these elements occurring in engine oils. The device's configuration is intended for the petroleum industry.

Since the device does not require any sample preparation, the sample was dosed directly into the sample cups. The analysis was carried out in three repetitions for each sample.

The results obtained were subject to statistical analysis with the use of STATISTICA. Data mining methods were used, while the non-parametric Kruskal-Wallis one-way analysis of variance was used to test the impact of tractor engine mileage on the content of heavy metals in used engine oils.

Results and Discussion

The results of surveys conducted in companies dealing with agricultural tractor servicing show that hardly 15% of used oils from the agricultural sector is collected by service facilities and managed in line with applicable provision of the law. The remaining part stays directly at the farm. The surveys carried out among the farmers from Lubelskie Voivodeship show that used engine oil is utilized for the maintenance of agricultural machines or wood (35%), reutilized as lubricating grease (i.e., for the lubrication of chain saws, or older tractors; 60%), for space heating (12%), and stored on the farm for other purposes (3%).

None of the above-mentioned methods of used oil management is in compliance with the relevant legal regulations [4]. Moreover, such management poses a potential environmental threat [6]. The utilization of used oil as a preservative agent for wood or machine causes its permeation into the soil as a result of, for instance, washing off through precipitation. Reutilized oils also pose a serious threat to the environment. Reutilization usually means using the oil in agricultural tractors with a high level of operational wear, which entails leakage and permeation into the soil during operation or when parked. Utilization of used oils for lubricating chain saws is equally reprehensible. Used oil combustion, if carried out in controlled conditions, is not dangerous to the environment. However, in agricultural holdings it is combusted by adding to fine coal, or combusted in agriculturally prepared burners. Such conduct causes the creation of post-combustion toxic wastes and emissions of heavy metals into the atmosphere [7-9].

Heavy metals in soil consist of the source of the threat to plants and underground water, and in consequence these can become incorporated into the food chain. Furthermore, heavy metals that contaminate the soil impede the development of microorganisms functioning therein, which leads to the disturbance of basic physiological functions, and above all processes connected with decomposition and transformation of organic matter [10, 11].

The results of the designation of particular heavy metal elements in used engine oils are shown in Table 1. The obtained data indicate that the content of individual metal was quite diversified with respect to the type of machine, the type of oil, and mileage. Fig. 1 presents the distribution of characteristics, the mean, the outliers, and the extremes.

The majority of analytical methods of designating heavy metals in lubricating oils that are described in literature are based on atomic spectrometry techniques such as:

Table 1. Results of analysis of trace metals in oil using XRF.

Sample ID	Metal concentrations [mg·kg^{-1}]										
	Zn	Mo	Fe	Cu	Pb	Cr	Mn	Ni	Sn	Cd	Hg
A1	1,269	378	36.23	27.83	2.24	0.92	1.76	0.28	n.d.	n.d.	n.d.
A2	1,106	383	18.25	25.35	4.02	0.51	3.34	0.14	n.d.	n.d.	n.d.
A3	1,001	608	16.5	10.45	3.74	0.53	2.05	0.20	n.d.	n.d.	n.d.
A4	726	472	112	14.96	4.33	1.47	4.27	0.23	60.78	n.d.	n.d.
A5	1,104	372	19.03	7.04	2.29	0.36	0.41	0.18	n.d.	n.d.	n.d.
A6	986	689	23.51	76.87	5.31	0.77	2.38	0.57	n.d.	n.d.	n.d.
A7	935	655	19.57	13.34	5.8	0.66	2.11	0.69	n.d.	n.d.	n.d.
A8	1,079	606	25.5	7.53	1.33	0.53	0.53	0.61	59.92	n.d.	n.d.
B1	1,165	443	33.51	6.23	1.46	0.59	1.34	0.50	n.d.	n.d.	n.d.
B2	1,070	371	44.22	23.46	6.92	0.59	1.34	0.41	107	n.d.	n.d.
B3	1,216	431	41.19	6.78	0.90	0.73	0.57	0.45	n.d.	n.d.	n.d.
B4	1,140	616	47.35	43.88	4.78	0.53	2.17	0.60	n.d.	n.d.	n.d.
B5	1,374	402	24.25	4.63	1.06	0.58	0.65	0.25	n.d.	n.d.	n.d.
B6	1,200	449	19.45	20.34	2.30	0.62	2.76	0.24	n.d.	n.d.	n.d.
B7	1,106	383	18.25	25.35	4,02	0.51	3.34	0.14	n.d.	n.d.	n.d.
B8	1,221	403	51.73	15.03	1.84	1.16	1.14	0.27	n.d.	n.d.	n.d.
C1	1,389	360	144.33	7.51	2.61	10.66	1.29	0.54	n.d.	n.d.	n.d.
C2	1,017	425	39.24	5.96	1.87	0.59	0.65	0.32	n.d.	n.d.	n.d.
C3	1,144	388	69.58	5.85	1.42	2.91	1.51	0.32	n.d.	n.d.	n.d.
C4	887	425	267	11.75	13.71	3.47	2.19	0.75	n.d.	n.d.	n.d.
Mean	1,106.7	462.95	53.53	18.00	3.59	1.43	1.79	0.38			
S.D.	158.22	107.05	60.08	17.14	2.93	2.31	1.06	0.19			
Median	1,106	425	34.87	12.54	2.45	0.60	1.63	0.32			
Min	726	360	16.5	4.63	0.90	0.36	0.41	0.14			
Max	1,389	689	267	76.87	13.71	10.66	4.27	0.75			
C.V.	14.3%	23.1%	112.2%	95.2%	81.6%	161.6%	59.4%	49.6%			

n.d. – not detected

F-AAS, ET-AAS, DC-OES, ICP-OES, ICP-MS, and AFS [12-15]. However, the methods require special sample preparation, which are usually laborious [15]. An attractive alternative to those mentioned above is x-ray fluorescence (XRF), which does not require complicated sample preparation [16-20]. Pouzar et al. proved that there is no statistically important difference between the results of XRF and ICP-OES [17]. Similar conclusions were formulated by Sagi [18] and Yang et al. [20], who compared XRF and ICP-AES, and by Simbolon [19], who compared XRF and AAS methods.

The quantity designation of heavy metals in used lubricating oils can be used for a quality control of oils and engine diagnosis. Less often it can be used for assessment of wasted oil environment influence [13]. Therefore, accessible literature concerns mostly such elements as Zn, Fe, Cu, and Pb. Table 2 shows the concentration values of heavy metals under analysis presented in literature [20-23] in reference to concentration ranges obtained in our own research. Yang et al. [20] researched the presence of select heavy metals in used oils from vehicle service stations maintaining passenger cars working on petrol only by using the XRF method. Hamawand et al. [21] researched the content of select heavy metals in used engine oil from passenger cars using the AAS method. Cassap [22] analysed new and used engine oils from passenger cars using the IPC-OS method. Hamad et al. [23] analysed used oils collected from automotive repair shops using the IPC and AAS methods.

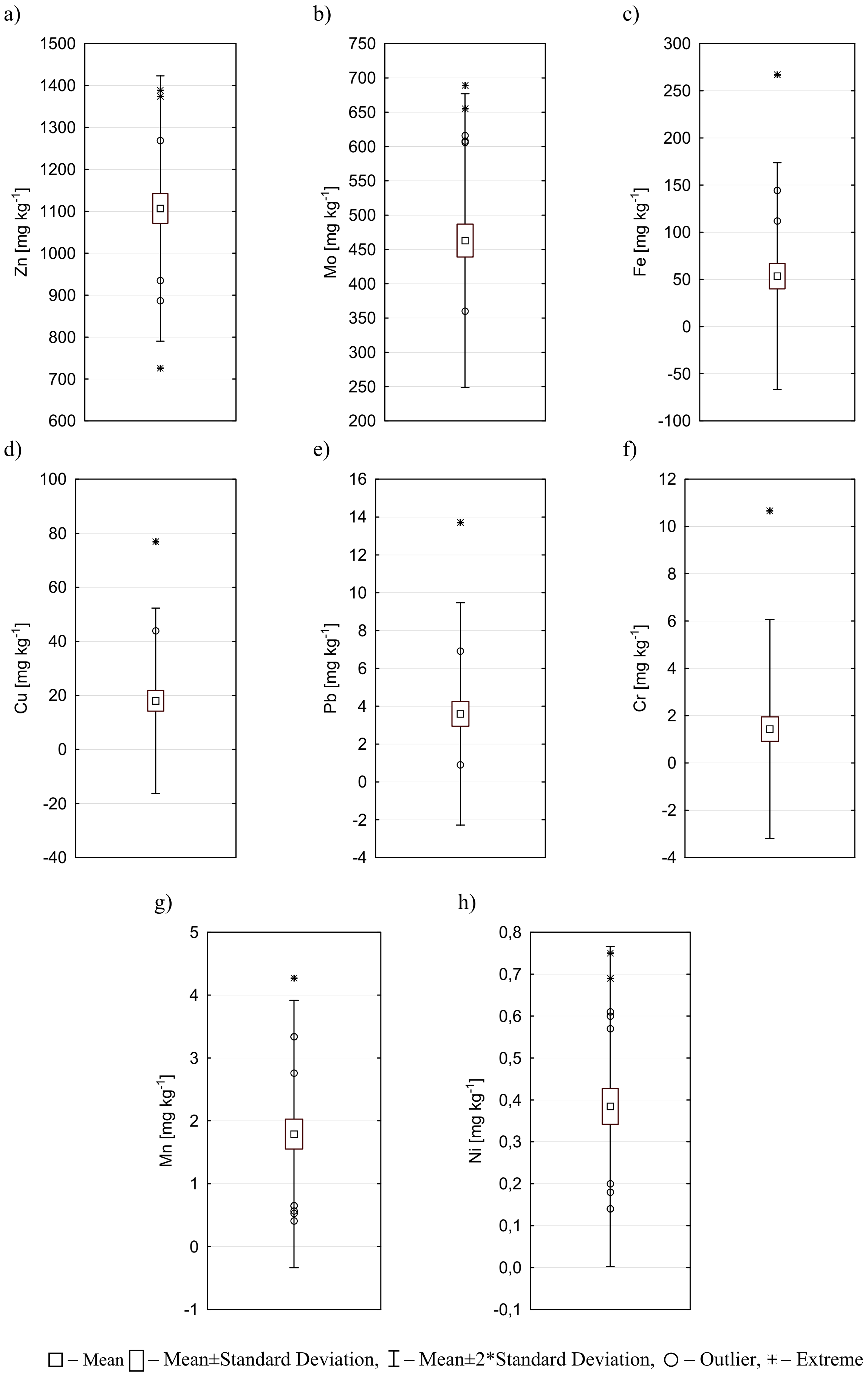

Fig. 1. Box plots for specified elements.

Table 2. Values reported in literature [mg·kg^{-1}].

Elements	Own resarch	References			
		[20]	[21]	[22]	[23]
	Method				
	HD XRF	XRF	AAS	ICP-OS	ICP
Zn	726-1,389	n.r.	1,280	1,106	701
Mo	360-689	n.r.	n.r.	0.38	6
Fe	16.5-267	21	72	30.8	76
Cu	4.63-76.87	18.2	4.6	3.49	13
Pb	0.9-13.71	15.8	14.6	8.0	946
Cr	0.36-10.6	n.r.	1.5	2.54	n.r.
Mn	0.41-4.27	n.r.	1.5	0.89	2
Ni	0.14-0.75	n.r.	n.r.	0.48	1
Cd	n.d.	n.r.	1	0.27	<1
Sn	59.92-107	n.r.	1.6	2.53	1
Hg	n.d.	n.r.	n.r.	n.r.	n.r.

n.d. – not detect, n.r. – not reported

Particular attention is currently being paid to environmental contamination with mercury and cadmium compounds given the anthropogenic distribution of these elements in the environment and their high toxicity. The potential threat of the contamination of the natural environment with cadmium is high, since it is subject to both anthropogenic concentration and exceptionally easy bioconcentration. Permanent control of the level of environmental pollution is necessary – in particular when it comes to food products – because this metal displays a high level of toxicity for humans and animals [24]. None of the analysed samples of the used engine oils showed the presence of cadmium. This, however, does not mean that the cadmium threat should be ruled out. Published references specify values ranging from 0.27 to 1 mg·kg^{-1} (Table 2). Scientific studies found in the literature do not provide information on the content of Hg in new and used engine oils, although the presence of mercury in crude oil was stated [25], the analysed samples were not tested for the presence of mercury; therefore, it may be concluded that the risk posed by this metal is minimal.

Due to the global atmospheric range of lead contamination, its anthropogenic accumulation is noticed in the majority of soils. In nearly all soil the balance of lead is positive and indicates a steady increase in content. Even though these are admissible amounts when it comes to ecotoxicity and phytotoxicity, the elevated content of lead in the soil may pose a threat to human beings, and especially to children [24]. Lead is removed from base oils, hence its presence in used oils is mainly connected with bearing wear [26, 27], but the contamination source may also be fuel. This, however, pertains mainly to petrol-fuelled engines [28]. The analysed samples were collected from diesel-fuelled engines. Therefore, it can be concluded that the established content of lead is connected with the wear of engine parts. The average content of lead in the samples amounted to 3.59 mg·kg^{-1}. The lowest value was noted for the B3 sample (0.9 mg·kg^{-1}) and the highest for C4 (13.71 mg·kg^{-1}). Such a high content of Pb in the C4 sample caused an extremely high value of variation coefficient, which exceeded 80%. The range obtained in the course of the research is similar to data provided by Yang [20] (15.8 mg·kg^{-1}), Hamawand et al. [21] (14.6 mg·kg^{-1}), and Cassap [22] (8 mg·kg^{-1}).

Nickel compounds are classified as hazardous and carcinogenic substances. Nickel, when introduced into water reservoirs, is significantly absorbed by sediments. However, it also is subject to strong bioaccumulation, particularly in phytoplankton, which effects its fast incorporation into the food chain [24]. In used oils nickel mainly comes from the piston rings and the shaft [27]. The content of nickel found in the analysed samples ranged from 0.14 to 0.75 mg·kg^{-1} (on average 0.38 mg·kg^{-1}). In half of the analysed samples the content of nickel did not exceed 0.32 mg·kg^{-1}. Variability in the content was characterized by a high level of differentiation, amounting to almost 50%. The content of nickel in used oils stated in the literature is comparable with results obtained in the research (Table 2).

Tin is entirely removed from base oils since it is considered contamination, therefore its presence in used oil results from the wear of the shaft, bearings, guides, and sleeves [26, 27]. In the analysed oils tin was noted in three samples. The highest concentration for this element was determined for sample B2 (107 mg·kg^{-1}), and the lowest for A8 (59.9 mg·kg^{-1}). Designation of tin in only three samples indicates that its presence in oil is the result of the specific wear processes of engine parts. The values obtained in the research are much higher than those provided by Hamawand et al. [21] at 1.6 mg·kg^{-1} and Cassap [22] at 2.53 mg·kg^{-1}.

Due to the relatively high copper bioconcentration factor and high level of its anthropogenic deployment, it poses a significant threat of local biological contamination [24]. Copper in used oils comes mainly from the wearing products of the bearings, rings, and valve guides; in smaller quantities it is introduced in the form of additives [26, 27]. The content of copper in the analysed samples ranged between 4.63-76.87 mg·kg^{-1} (on average 18 mg·kg^{-1}), with a standard deviation of 17.14 mg·kg^{-1}. The content of Cu in one of the samples caused an extremely high value of variation coefficient, which exceeded 95%. The data about content of copper in used oil found in the literature (Table 2) shows that it remains within the range obtained in the presented research.

Similar to copper, zinc comes mostly from anthropogenic sources [24]. It is the basic active element of high-temperature antioxidation additives. It can also be found in the composition of antiwear additives or corrosion inhibitors added to engine oils [26, 27]. The increase in the content of zinc in used oils in comparison with fresh oil may be the result of the presence of wearing products.

A high concentration of Zn was found in the analysed samples, ranging from 726 to 1,389 mg·kg^{-1}. The average content of Zn in a sample equalled 1,106.7 mg·kg^{-1}, and the standard variation was 158.22 mg·kg^{-1}. In half of the analysed samples the content of zinc did not exceed 1,106 mg·kg^{-1}. The coefficient of variation of Zn in the samples was small at 14%. The values obtained found its confirmation in the literary data. Hamawand et al. [21] determined Zn in used oils to be 1,280 mg·kg^{-1}. A similar value was established by Cassap [22] at 1,106 mg·kg^{-1}, while the lowest was obtained by Hamad et al. [23] at 701 mg·kg^{-1}.

Although there is no risk of global contamination of the natural environment by chromium, its local introduction into the atmosphere, water, and soil may cause excessive incorporation into biogeochemical circulation, thus posing a threat to human and animal health [24]. The presence of chromium in engine oil is usually traced to the wear of engine parts. The high level of chromium may indicate excessive wear of chromed components such as rings and sleeves [26, 27]. The content of chromium in the analysed samples ranged from 0.36 for the A5 sample to 10.66 mg·kg^{-1} for sample C1. The average content equalled 1.43 mg·kg^{-1}, whereas in half of the analysed samples the content of chromium did not exceed 0.6 mg·kg^{-1}. As a result of extremely high content of this element in one of the samples, the coefficient of variation amounted to as high as 161%. The presented values can be confirmed by the data found in the literature (Table 2).

In general, the share of iron in the overall contamination of the environment is not specified since it does not pose a threat to the environment. However, as a most commonly used metal, it may provide information on the impact of some anthropotechnical elements on the natural environment. Iron is the most typical engine wear product present in engine oil. Therefore, its concentration in used oil mainly depends on lubricating conditions inside the engine. In the analysed samples the lowest established content of iron was 16.5 mg·kg^{-}1 for sample A3, and the highest was 267 mg·kg^{-1} for sample C4. The variation between the minimum and maximum value was 250.5 mg·kg^{-1}. In half of the analysed samples the content of iron equalled 34.87 mg·kg^{-1}. A very high content of Fe in two of the samples (exceeding 100 mg·kg^{-1}) caused variability of the results exceeding 112%. Values quoted by Hamad et al. [23] (76 mg·kg^{-1}), Hamawand et al. [21] (72 mg·kg^{-1}), Cassap [22] (30.8 mg·kg^{-1}), and Yang [20] (21 mg·kg^{-1}) remain within the range obtained in the course of the research.

A high bioaccumulation of manganese fulfils an important role in its geochemical circulation. Contamination of the environment with manganese is mainly connected with the metal industry, as well as its emissions bound with coal and liquid fuel combustion [24]. Manganese is introduced into engine oil through the wear of cylinder liners, valves, and shafts. The content of manganese in the analysed samples ranged from 0.41 to 4.27 mg·kg^{-1} (on average 1.79 mg·kg^{-1}); in the half of analysed samples the content did not exceed 1.63 mg·kg^{-1}. The content of manganese in the analysed samples was characterized by quite a high differentiation factor amounting to almost 60%. The values obtained remain within the range obtained by the other authors (Table 2).

Molybdenum is subjected to high bioaccumulation, thus its concentration in some coal beds, crude oil, and bituminous shale. It is difficult to establish the amount of molybdenum that is introduced directly to biogeochemical circulation. Coal and crude oil combustion introduces into the environment approx. 2000 Mg *per annum* [24]. Molybdenum in used oil mainly comes from additives used in the oil and it may come as the result of the wear of piston rings [26, 27]. Its average content in the analysed samples was 462.9 mg·kg^{-1}. The maximum content was 689 mg·kg^{-1}, while the minimum was 360 mg·kg^{-1}. The content of Mo in a sample differed from the average value by about 107 mg·kg^{-1}. The variation coefficient reached up to 23%. In this case the content of Mo established in the samples significantly differed from cases noted in the literature. Cassap [22] determined Mo at the 0.38 mg·kg^{-1} level, while Hamad et al. [23] measured it at the 6 mg·kg^{-1} level. The differences may reflect the fact that used oils analysed by the above-mentioned authors come from passenger cars fuelled with petrol, which influences the wearing character, as well as the composition of engine oil additives.

The age structure of the tractors may be significant, taking into consideration the posed threats. In engines with high mileage the wearing processes runs at a much higher intensity level, therefore the content of elements typical for wearing processes, i.e. Fe, Cu, Pb, Cr, Mn, Ni, and Sn in oils can increase. In order to determine the impact of wearing processes and the age of tractors on the concentration of the elements, the Kruskal-Wallis study was carried out. The test demonstrated that the concentrations of Fe and Cr depended significantly on engine mileage. The average content of these elements in oil samples with mileage exceeding 900 h was significantly higher than in samples with lower mileage. For the remaining elements no statistically significant differences were revealed.

Conclusions

The only effective way to protect the natural environment from used oil contamination is their collection and controlled utilization. Only appropriate used oil management can guarantee minimal environmental contamination and prevent its irreversible degradation.

The issue of waste management is regulated by a range of legal provisions, although these alone will not suffice for the proper management of such waste. A combination of precise and well-construed legal regulations along with a high ecological awareness of society may only allow for the extent of pro-environmental actions.

On the basis of the conducted research and discussion, we formulated the following conclusions:

1. In none of the analysed used engine oils were mercury and cadmium found. However, based on the literary data the presence of cadmium in used oils from agricultural tractors cannot be ruled out. In the analysed sam-

ples a high content of Zn was indicated at the 726-1,389 mg·kg^{-1} level. The contents of Mo, Fe, and Cu in the analysed samples were also high: Mo 360-689 mg·kg^{-1}, Fe 16.5-267 mg·kg^{-1}, and Cu 4.63-76.87 mg·kg^{-1}. The lowest contents of Ni, Mn, Cr, and Pb were stated at the levels of: Ni 0.14-0.75 mg·kg^{-1}, Mn 0.41-4.27 mg·kg^{-1}, Cr 0.36-10.66 mg·kg^{-1}, and Pb 0.9-13.71 mg·kg^{-1}.

2. The concentrations of metals that are introduced into oils along with refining additives (Zn, Mo) are characterized by low variability, while elements present in the oil as a result of engine parts wear (Fe, Cu, Pb, Cr, Mn, Ni, Sn) demonstrate large diversity. Therefore, it is difficult to precisely estimate their amount in the oils, and at the same time determine potential environmental threats.
3. The statistical analysis of the research results indicated statistically significant dependence of the concentrations of iron and chromium in used engine oils from engine mileage. In the case of the other investigated elements no statistically significant dependences were noted according to varying mileage. The age structure of agricultural tractors is significant, taking into consideration the threats posed to the environment. In engines with high mileage, wearing processes run at a much higher intensity level and so the increase of the elements content is typical for wearing processes.

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