EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology 2021, 22(5), 119–125
https://doi.org/10.12912/27197050/139345
ISSN 2719-7050, License CC-BY 4.0

Received: 2021.06.15
Accepted: 2021.07.10
Published: 2021.08.01

Toxicity of Water After Short-Term Contact with PVC Materials Depending on the Temperature and Components of the Polymer Composition

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ABSTRACT

This work shows a paradoxical fact: a highly plasticized PVC sample containing the maximum amount of the plasticizer di(2-ethylhexyl) phthalate (DEHP) compared to medium- and low-plasticized polymers turned out to be the least toxic. This was confirmed in express bioassays for the pre-lethal reactions of *Paramecium caudatum* Ehrenber and *Escherichia coli* M-17 when determining the acute toxicity for mortality of *Daphnia magna* Straus and *Ceriodaphnia affinis* Lilljeborg, as well as in chronic tests for *D. magna*. The migration of DEHP from the tested PVC samples into water was confirmed by the mass spectrometry method. It was shown that the contact of PVC materials with hot water (70 °C) led to a significant increase in the toxicity of the extracts compared to cold extraction (20 °C). The search for safe composition of PVC materials must be carried out in the direction of the optimal ratio of PVC-polymer, plasticizer and heat stabilizer, as well as replacing the components of the composition with safe substances.

Keywords: polyvinyl chloride, bioassay, acute toxicity, chronic toxicity, toxicant migration, di(2-ethylhexyl) phthalate.

INTRODUCTION

High molecular weight compounds (HMC) represented by plastics, rubbers, synthetic fibers are widely used in everyday life, industry, medicine and other spheres of life. Among the whole variety of HMC, polyvinyl chloride (PVC) Polyvinyl chloride (PVC) can be distinguished. PVC is a polymer that, like polyethylene, is especially used both in industry and in everyday life (Pham et al., 2021). PVC is used as insulating materials, protective cable sheaths, chemically resistant gasket or sealing materials, finish materials, as well as for the manufacture of water pipes, children's toys, food containers and other products that are significant for the population (Wypych 2020).

The most dangerous components of PVC materials are heat stabilizers and plasticizers. For example, organotin compounds are often used for thermal stabilization, these compounds may lead to neurodegenerative diseases in humans (Pompili et al., 2020). Various degrees of plasticity of polymers are most often achieved by adding di(2-ethylhexyl) phthalate (DEHP) to the PVC composition. It is known that DEHP has reproductive toxicity, therefore, work is underway to search for substances with similar properties, but so far this substance has not been banned from use (Ma et al., 2020).

After exploitation of PVC products, they end up massively at industrial and household waste landfills, where they are affected by environmental factors, including rain and melted snow water. There is gradual mechanical fragmentation, and slow photo and thermo-oxidative degradation (Facciola et al., 2021). As a result, secondary microplastics (MPs) are formed, as well as leaching and migration of harmful substances from the polymer into water, soil and air (Hahladakis et al., 2018). This process is dangerous for both humans (Prata et al., 2020) and representatives of the biota (Ulker OC and Ulker O 2019).

The aim of this work was to study toxicological properties of water after contact with three PVC materials at different temperatures and to determine the principle of drawing up the safest composition using components classic for PVC materials.

MATERIAL AND METHODS

For the study samples of plasticized polyvinyl chloride prepared according to different technological recipes were taken.

Samples were prepared by stage-by-stage mixing of seven components (Table 1) in a production laboratory on the dissolving tank (a mixing device). At the same time the following parameters were controlled: the order of introducing the components, the humidity of the working area, the temperature of the mixture, the mixing time, and the relative viscosity of the resulting paste.

As a result, the studied PVC materials were fundamentally different from the PVC-polymer base and in the amount of the plasticizer di(2-ethylhexyl) phthalate (DEHP), from the proportion of which the elasticity of the products depends on. From highly plasticized samples (HPL) soft products are made, from medium plasticized sample (MPL) - medium-hard, from low-plasticized oneы (LPL) - semi-hard.

To determine the degree of toxicity of the prepared samples, they were crushed and water extracts were prepared. The particle size of PVC materials was 0.5×0.5 cm. The ratio of solid and liquid phases was 1:10, which is recommended by the bioassay protocols for the study of solid waste. The contact time of water and PVC samples was 2.5 hours. Simultaneously, the effect of cold (20 °C) and hot (70 °C) water was simulated. Further bioassay was carried out at 20 °C. Drinking water was used as a control, as well as an extracting liquid; the source was an artesian well.

The toxicity of extracts from crushed samples was determined by mortality and changes in fertility of the lower crustaceans *Daphnia magna* Straus (Federal Register FR 1.39.2007.03222 2007) and *Ceriodaphnia affinis* Lilljeborg (Federal Register FR 1.39.2007.03221 2007), as well as by express methods for the chemotactic reaction of protozoa *Paramecium caudatum* Ehrenber (Federal Register FR 1.39.2015.19242 2015) and bioluminescence of bacteria *Escherichia coli* M-17 (Environmental Regulatory Document PND FT 14.1: 2: 3: 4.11-04. T.16.1: 2: 3: 3.8-04. 2010).

The sensitivity of the test organisms used to standard toxicants was previously established in accordance with the requirements of the bioassay protocols.

The experiments were carried out in 3 replicates in accordance with the requirements of the relevant methods. The results were processed statistically and presented as mean values and their standard deviations (x ± δ). The significance of the differences was assessed at the significance level of $p \leq 0.05$.

RESULTS

Acute toxicity

In express bioassays, all PVC samples showed the maximum toxic effect. In the bioassay for *P. caudatum*, the toxicity indices varied from 0.95 to 0.98, which corresponded to the

Table 1. Composition of samples of PVC materials

Component name	Class of hazard	The proportion of the component in the sample, %		
		LPL	MPL	HPL
PVC-polymer emulsion pasting, K = 70*	3	-	62	55
PVC-polymer microsuspension pasting, K = 70*	3	57	-	-
PVC polymer suspension extender	3	10	-	-
The plasticizer di(2-ethylhexyl) phthalate (DEHP)	2	27	34	39
Viscosity regulator (mixture of unsaturated hydrocarbons)	3	2.5	2.5	1.6
Epoxidized vegetable oil	-	1.5	1.2	2.8
Combined lubricant (mixture of ester compounds)	-	1	0.5	0.7
Mg-Zn heat stabilizer	-	0.8	0.5	0.6
Inorganic iron oxide pigments, titanium dioxide, cromophthales	2	0.2	0.3	0.3

Note: * K – Finkentcher's constant characterizing the molecular weight of the polymer; LPL – low plasticized sample, MPL – medium plasticized sample, HPL – highly plasticized sample.

toxicity group III "high toxicity" (Federal Register FR 1.39.2015.19242 2015). *E. coli* bioluminescence was inhibited by 95% compared to the control, which, according to the classification of the method used, means "the sample is highly toxic" (Environmental Regulatory Document PND FT 14.1: 2: 3: 4.11-04. T.16.1: 2: 3: 3.8-04. 2010). It should be noted that during express bioassay (30 min exposure), we assessed not the lethal effect of the samples, but their effect on functional parameters – chemotaxis and bioluminescence. In our previous works, these bioassay methods were also distinguished by high sensitivity to the tested contamination of both mineral and organic nature (Olkova and Berezin 2021; Olkova and Zimonina 2021).

However, further bioassay using *C. affinis* showed that all aqueous extracts from PVC materials are also acutely toxic in terms of crustacean mortality. *C. affinis* died in the studied water extracts on the first day of the experiment. The crustaceans *D. magna* turned out to be more resistant; death occurred later, some survived. As a result, the 96-hour bioassay for the mortality of *D. magna* showed that extracts from low- and medium-plasticized samples are acutely toxic, and the extract from highly plasticized PVC sample does not have an acute toxic effect on *D. magna.*

Chronic toxicity

We determined the chronic toxicity of aqueous extracts from the three studied PVC materials in terms of fertility and mortality of *D. magna* over 24 days of exposure. If we observed the acute toxicity of the aqueous extract, then we diluted it with a control medium and then carried out the determination of chronic toxicity. In this case, the tested solutions were changed every 5 days of the experiment. Table 2 shows the main results of chronic experiments.

A highly plasticized sample of PVC material turned out to be the safest. The water extract from this sample, prepared both by the "cold" and "hot" methods, did not require additional dilution, since in a short-term experiment (96 hours) it did not have an acute toxic effect on daphnia. However, in a long-term experiment, the sample had a chronic toxic effect. The permissible level of mortality of crustaceans (20%) was exceeded in both "cold" and "hot" extracts. Interestingly, the contact of the HPL sample with cold water did not lead to a decrease in the fertility of crustaceans, and with hot water, it significantly reduced the indicator by almost 3 times.

When testing low- and medium-plasticized samples, their acute toxicity was established. Only when the original extracts were diluted (100%) by the factor 2–4, daphnia survived within 96 hours. The upward trend in toxicity when PVC materials are exposed to hot water continued. For example, in the water extract (50%) from the MPL sample prepared by the hot method, *D. magna* could not leave offspring, and after the "cold" contact the ability to reproduce was preserved, but it was significantly suppressed in comparison with pure water ($p < 0, 05$).

We compared the dynamics of *D. magna* mortality in water extracts from samples that turned out to be the most dangerous and require dilution

Table 2. Indicators of chronic toxicity of PVC materials for *D. magna*

Sample / Dilution rate of the water extract		Acute toxicity (mortality within 96 hours)		Fertility within 24 days		Mortality of adult specimen on the 24th day**, %	
		20 °C	70 °C	20 °C	70 °C	20 °C	70 °C
Control		-		13.6±1.6		0	
LPL	100	+	+	0	0	-	-
	50	+	-	0	6.0±3.2	-	100
	25	-	-	3.5±1.1*	2.5±0.8*	100	36.7
	10	-	-	9.9±4.0	2.7±1.2*	23.3	10
MPL	100	+	+	0	0	-	-
	50	-	+	9.0±0.4*	0	20	-
	25	-	-	7.4±2.5*	5.3±2.1*	3.3	40
	10	-	-	6.8±1.1*	3.8±2.1*	0	16.7
HPL	100	-	-	16.6±3.0	4.9±1.2*	40	90

Note: Names of samples as in Table 1; * the differences are reliable in comparison with the control; ** inaccuracy within the metrological characteristics of the procedure (Federal Register FR 1.39.2007.03222 2007).

to level the acute toxicity for daphnia (Fig. 1). The analysis of the process within 24 days showed that the LPL sample is the most dangerous, since all crustaceans died in the "cold" extract even when it was diluted by 4 times; when diluted by 10 times, the mortality also exceeded the permissible criterion. In the "hot" extract, dilution of the sample by the factor of 10 allowed the majority of daphnia to survive, but their fertility decreased by 4.7 times compared with the control ($p < 0.05$). The graphs also show that exposure of PVC samples to hot water leads to the fact that the death of test organisms in such extracts occurs at an accelerated rate.

In this work, we focused on the contact of polymers with hot water, which is very common in everyday life. At the same time, many polymers are not recommended for use with hot products and liquids, as indicated by the manufacturer. The results of the experiment showed that the high temperature of the aquatic environment can be a factor of increasing its toxicity after contact with the polymer. This is probably due to an increase in the rate of physicochemical processes (dissociation, dissolution) when increasing temperature and, as a consequence, the migration of some components into the solution. It is shown in (Kataeva 2013) that hot water enhances the migration of lead-based stabilizers from PVC pipelines.

Next, we solved the problem of determining the substances that caused the toxicity of water after contact with PVC materials.

Chromatomass-spectrometry

The method of chromatomass-spectrometry was used to determine the substances present in aqueous extracts from PVC materials that could cause toxicity. The analysis was carried out on the DSQ gas chromatograph-mass spectrometer (USA). The spectra were decoded using the mass spectrometric spectra library of the National Institute of Standards and Technology (NIST) (Mass Spectral Library – NIST 2020).

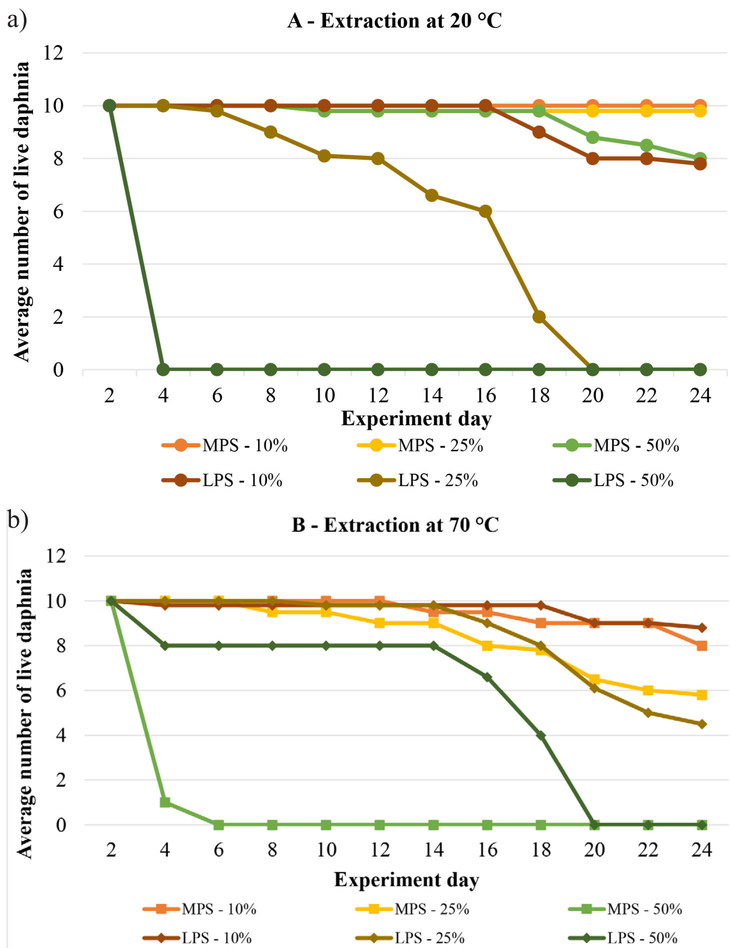

Figure 1. Dynamics of mortality of *D. magna* in aqueous extracts of plastic compounds.

Note: «MPL-10%» and suchlike mean the type of sample and the degree of dilution of the aqueous extract, %

We analyzed all the peaks in the chromatograms. Most of them characterized the phase inside the column (Mc Lafferty 1993). When analyzing the extracts prepared at 70°C, there were peaks different from the phase. An example of such a peak for a medium plasticized sample is shown in Figure 2, the exit time is 15.3 minutes.

This peak belongs to the phthalate class. The NIST library matches 95.6% (synonyms: Phthalic acid, Diisobutyl ester, Diisobutylester kyseliny ftalove). The plasticizer di(2-ethylhexyl) phthalate (DEHP) was most likely the source of this substance in the composition for the preparation of the studied PVC. It belongs to the 2nd class of hazardous substances (highly hazardous substances). The LD50 (peroral) of such substances is 15-150 mg/kg. At lower concentrations such substances inhibit various functions of living organisms (Svarc-Gajic 2009). Scientists proved the reproductive toxicity of such plasticizers, including for humans (Salazar et al., 2004; Latini, De Felice and Verrotti 2004). Prolonged presence of phthalates in water leads to the destruction of the endocrine system of hydrobionts, which can manifest itself long after exposure (Daiem et al., 2012).

For other samples similar results were obtained. At the same time, phthalates were found in trace amounts in extracts prepared at the temperature of 20 °C.

The data obtained are consistent with the work (Kida and Koszelnik 2021), which showed that phthalic acid esters and polycyclic aromatic hydrocarbons are primarily leached from plastics of different compositions. There is also evidence that plasticizers can migrate during the use of PVC products to their surface, carrying along with them other ingredients of the composition, for example, heat stabilizers (Sheftel ‘and Kataeva 1978; Group 1996).

Thus, methods of mass spectrometry showed that not all components of PVC compositions after the polymerization reaction are subject to migration into the aqueous medium. We observed the extraction of the DEHP plasticizer, since this component does not undergo chemical bonding with polymer molecules during polymerization, but it is retained inside the plastic compound formed by van der Waals electrostatic forces.

DISCUSSION

The paradoxical fact was experimentally found: compositions with a high content of plasticizer are less toxic, despite the potential danger of DEHP. This is probably due to the fact that highly plasticized PVC polymers are more thermally stable than low plasticized samples. The decomposition products formed as a result of thermal destruction can be temporarily retained in the matrix of low plasticized PVC, and then migrate into the aquatic environment,

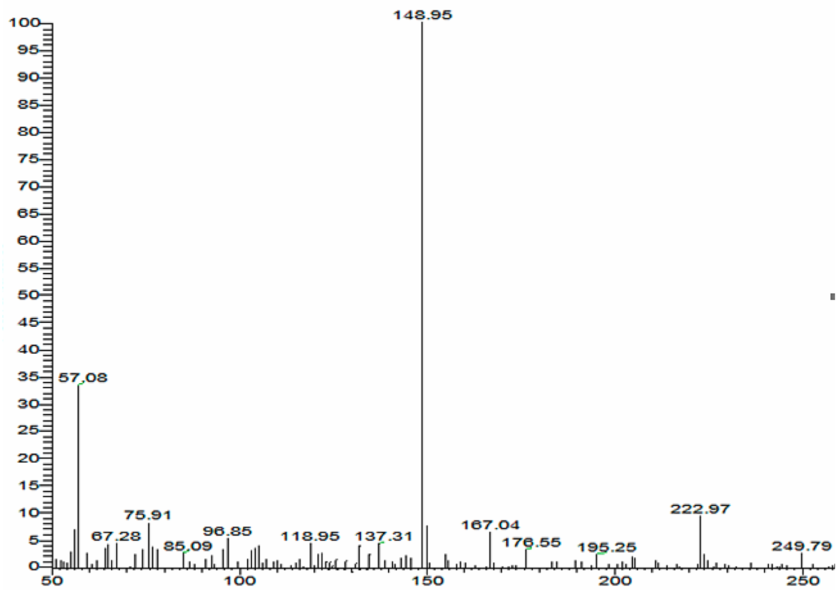

Figure 2. The spectrum of the isolated peak, got when analysing the aqueous extract from the medium plasticized PVC material (extraction at 70 °C). X-axis: the ratio of the mass of the ion to its charge. Y-axis: the relative amount of ions of the given species

exerting a toxic effect. Among the parameters affecting the extraction of hazardous substances from polymers, scientists name the composition content and the structure of the final polymer matrix, the properties of the extracting liquid, the extraction time, the temperature and size of the plastic particles (Kida and Koszelnik 2021).

We simulated the primary physical destruction of PVC material and secondary destruction in contact with hot water (70 °C). It is known that under the conditions of mechanical destruction of plastic and its physicochemical destruction, the risk of microparticle absorption by organisms (<50 μm in diameter) increases, which is typical for filtering organisms and organisms that feed on phagocytosis (Feng et al., 2021). This explains the acute toxicity of aqueous extracts from three types of PVC materials for ciliates *P. caudatum*, bacteria *E. coli*, and lower crustaceans *C. affinis*. A further mechanism of intracellular toxic action can be associated with leaching of phthalates from PVC materials, which is shown in this study by the mass spectrometry method. For example, in human cell cultures, exposure to phthalates at concentrations of 1.0 and 10 μM caused clear mutagenic effects and DNA damage (Duarte et al., 2021).

Of course, the search for substances and materials that can be used instead of phthalate derivatives for plasticizing PVC is an urgent scientific and practical task (Ma et al., 2020; Fernandes et al., 2021). Different authors propose various compounds as alternatives to phthalates: novel saturated polyesters (Fernandes et al., 2021), epoxidized dicarboxylic acid dimethyl ester (Li et al., 2017). However, in this work it was shown that the toxicity of PVC materials and aqueous media after contact with them depends not only on the concentration of the DEHP plasticizer in the PVC polymer, but also on the degree of its stability. Therefore, until the most successful replacement for DEHP that satisfies ecologists, doctors and manufacturers of PVC products is found, it is necessary to select the optimal composition of PVC compositions with an orientation towards the minimum toxicity of the product.

CONCLUSIONS

The toxicity of water after contact with PVC materials was expressed in epy inhibition of *P. caudatum* chemotaxis, a decrease in *E. coli* bioluminescence, mortality of *C. affinis* and *D. magna* in short-term bioassays, as well as a decrease in the fertility of *D. magna* in tests for chronic toxicity. An increase in temperature led to enhanced extraction of toxic substances from plastic compounds. Water extracts prepared under heating conditions up to 70 °C were significantly more toxic than those prepared at 20 °C.

The studies carried out confirmed that the migration of hazardous substances into the environment from polyvinyl chloride materials, primarily the DEHP plasticizer, is possible. However, with the optimal ratio of PVC-polymer, plasticizer and heat stabilizer, a reduction in toxicity can be achieved. In our experiment, the highly plasticized sample turned out to be the safest, which contained 39% DEHP in the original composition, which is, on average, 10% more than other samples.

REFERENCES

1. Daiem M.M.A., Rivera-Utrilla, J., Ocampo-Perez, R., Mendez-Diaz, J.D., Sanchez-Polo, M. 2012. Environmental impact of phthalic acid esters and their removal from water and sediments by different technologies — A review. Journal of environmental management, 109, 164-178. DOI: 10.1016/j.jenvman.2012.05.014
2. Duarte N.D.A., de Lima L.E., Maraslis F.T., Kundi M., Nunes EA., Barcelos G.R.M. 2021. Acute Toxicity and DNA Instability Induced by Exposure to Low Doses of Triclosan and Phthalate DEHP, and Their Combinations, in vitro. Frontiers in genetics, 12, 649845. DOI: 10.3389/fgene.2021.649845
3. Environmental Regulatory Document PND F T 14.1:2:3:4.11-04. T.16.1:2:3:3.8-04. 2010. Method for determining the integrated toxicity of surface waters, including marine, ground, drinking, waste waters, water extracts from soils, waste, sewage sludge by changes in bacterial bioluminescence using the «Ecolum test-system». Moscow: Nera-S, 30 p.
4. Facciola A., Visalli G., Ciarello M.P., Di Pietro A. 2021. Newly Emerging Airborne Pollutants: Current Knowledge of Health Impact of Micro and Nanoplastics. International journal of environmental research and public health, 18(6), 2997. DOI: 10.3390/ijerph18062997
5. Federal Register FR 1.39.2007.03221. 2007. Methodology for determining the toxicity of water and water extracts from soils, sewage sludge, and waste by mortality and changes in fertility of ceriodaphnias. Moscow: Akvaros, 51 p.
6. Federal Register FR 1.39.2007.03222. 2007. Methodology for determining the toxicity of water and

water extracts from soils, sewage sludge, and waste by mortality and changes in fertility of daphnias. Moscow: Akvaros, 51 p.

7. Federal Register FR 1.39.2015.19242. 2015. Environmental Regulatory Document PND F T 16.2:2.2-98. Methodology for determining the toxicity of samples of natural, drinking, domestic and drinking, household waste, treated sewage, waste, thawed, technological water by the express method using the Biotester device. St. Petersburg: SPEKTR-M, 21 p.
8. Feng J.X., Zhao H.S., Gong X.Y., Xia M.C., Cai L.S., Yao H., Zhao X., Yan Z.H., Li Z.P., Nie H.G., Ma X.X., Zhang S.C. 2021. In Situ Identification and Spatial Mapping of Microplastic Standards in Paramecia by Secondary-Ion Mass Spectrometry Imaging. Analytical chemistry, 93(13), 5521-5528. DOI: 10.1021/acs.analchem.0c05383
9. Fernandes, M.C.S., Pereira, V.A., Fonseca, A.C., Ramalho, A., Coelho, J.F.J., Barros, R., Pereira, P., Pereira, J., Serra, A.C. 2021. Synthesis and characterization of biobased polyester PVC plasticizers to industrial manufacturing of tubes. Journal of applied polymer science, e50941. DOI: 10.1002/app.50941
10. Group E. 1996. Environmental fate and aquatic toxicology studies on phthalate esters. Environmental Health Perspectives, 65, 337.
11. Hahladakis J.N., Velis C.A., Webe R., Iacovidou, E., Purnell P. 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. Journal of hazardous materials, 344, 179-199. DOI: 10.1016/j.jhazmat.2017.10.014
12. Kataeva S.E. 2013. The kinetics of the migration of stabilizers containing lead, out of polyvinylchloride pipes. Vodoochistka. Vodopodgotovka. Vodosnabzhenie, 3(63), 24-28.
13. Kida, M., Koszelnik, P. 2021. Investigation of the Presence and Possible Migration from Microplastics of Phthalic Acid Esters and Polycyclic Aromatic Hydrocarbons. Journal of Polymers and the Environment, 29(2), 599-611. DOI: 10.1007/s10924-020-01899-1
14. Latini G., De Felice C., Verrotti A. 2004. Plasticizers, infant nutrition and reproductive health review. Reproductive Toxicology, 19(1), 27–33.
15. Li M., Li S.H., Xia J.L., Ding C.X., Wang M., Xu L.N., Yang X.H., Huang K. 2017. Tung oil based plasticizer and auxiliary stabilizer for poly(vinyl chloride). Materials & Design, 122, 366-375. DOI: 10.1016/j.matdes.2017.03.025
16. Ma Y.F., Liao S.L., Li Q.G., Guan Q., Jia P.Y., Zhou Y.H. 2020. Physical and chemical modifications of poly(vinyl chloride) materials to prevent plasticizer migration – Still on the run. Reactive & Functional polymers, 147, 104458. DOI: 10.1016/j.reactfunctpolym.2019.104458
17. Mass Spectral Library – NIST. 2020. Gaithersburg: National Institute of Standards and Technology.
18. Mc Lafferty, F.W. 1993. Interpretation of mass spectra. Mill Valley: University Science, 371 p.
19. Olkova A., Berezin G. 2021. “Battery of Bioassays” for Diagnostics of Toxicity of Natural Water when Pollution with Aluminum Compounds. Journal of Ecological Engineering, 22(2), 195–199. https://doi.org/10.12911/22998993/131029
20. Olkova A.S, Zimonina N.M. 2021. Transformation of Urbanozems in the Areas of Gas Stations. Ecological Engineering & Environmental Technology, 22(3), 51–58. https://doi.org/10.12912/27197050/135448
21. Pham L.Q., Uspenskaya M.V., Olekhnovich R.O., Bernal R.A.O. 2021. A Review on Electrospun PVC Nanofibers: Fabrication, Properties, and Application. FIBERS, 9(2), 12. DOI: 10.3390/fib9020012
22. Pompili E., Fabrizi C., Fumagalli L., Fornai F. 2020. Autophagy in trimethyltin-induced neurodegeneration. Journal of neural transmission, 127(7), 987-998. DOI: 10.1007/s00702-020-02210-1
23. Prata J.C., da Costa J.P., Lopes I., Duarte A.C., Rocha-Santos T. 2020. Environmental exposure to microplastics: An overview on possible human health effects. Science of the total environment, 702, 134455. DOI: 10.1016/j.scitotenv.2019.134455
24. Salazar V., Castillo C., Ariznavarreta C., Campron R., Tresguerres J.A.F. 2004. Effect of oral intake of dibutyl phthalate on reproductive parameters of Long Evans rats and prepubertal development of their offspring. Toxicology. 205(2), 131–137.
25. Sheftel’ V.O., Kataeva S.E. 1978. The migration of hazardous chemicals from polymeric materials. M.: Khimiya, 168 p.
26. Svarc-Gajic J. 2009. General Toxicology. NY, USA: Nova Science Publishers, 287 p.
27. Ulker O.C., Ulker O. 2019. Toxicity of Formaldehyde, Polybrominated Diphenyl Ethers (PBDEs) and Phthalates in Engineered Wood Products (EWPs) from the Perspective of the Green Approach to Materials: A Review. Bioresources, 14(3). DOI: 10.15376/biores.14.3.Ulker
28. Wypych G. 2020. PVC degradation and stabilization. In: Health & Safety and environmental impact, 4th Edition, Toronto Scarborough, Canada: Chemtec Publishing, p. 431-458, DOI: 10.3390/fib9020012