Protective Disposable Face Masks Used During the COVID-19 Pandemic as a Source of Pollutants in the Aquatic Environment – A Study of Short-Term Effects

Valentyna Loboichenko[1*], Nataliia Leonova[2,3], Olga Shevchenko[4],
Oleg Blyashenko[5], Alexander Soshinskiy[6], Vasyl Servatyuk[7],
Nataliia Tregub[8], Ihor Khmyrov[6], Oleksandr Burmenko[9]

1 Department of Civil Security, Lutsk National Technical University, Lvivska Str., 75, 43018, Lutsk, Ukraine

2 Water Research Institute, Nábr. arm. gen. L. Svobodu, 5, 81249, Bratislava, Slovakia

3 Chemical Metrology Department, V.N. Karazin Kharkiv National University, Svobody Sq., 4, 61022, Kharkiv, Ukraine

4 Department of Automatic Safety Systems and Information Technologies, National University of Civil Defence of Ukraine, Chernyshevska Str., 94, 61023, Kharkiv, Ukraine

5 Ministry of Defence of Ukraine, Povitroflotskyi Av., 6, 03168, Kyiv, Ukraine

6 Scientific Department on Problems of Civil Defense and Technogenic and Ecological Safety, National University of Civil Defence of Ukraine, Chernyshevskaya Str., 94, 61023, Kharkiv, Ukraine

7 The National Defence University of Ukraine named after Ivan Cherniakhovskyi, Povitroflotskyi Av., 28, 03049, Kyiv, Ukraine

8 Kharkiv State Academy of Design and Arts, Mystetstv Str., 8, 61002, Kharkiv, Ukraine

9 Department of Service and Training, National University of Civil Defence of Ukraine, Chernyshevska Str., 94, 61023, Kharkiv, Ukraine

* Corresponding author's e-mail: vloboichm@gmail.com,

ABSTRACT

The paper examines the impact of protective equipment used during the COVID-19 pandemic on the environment. The impact of protective face masks on the aquatic environment was analyzed in more detailed way. The amount of protective face masks penetrated into the environment as a result of the COVID-19 pandemic and their role in the increase of plastic and microplastic things in the environment was noted. The aim of the work was to study the migration of a number of metals from disposable protective masks into the aquatic environment in the short term. Using the method of atomic absorption spectroscopy, the value of Cu, Pb, Mn, Zn, Fe in the investigated model systems containing protective disposable face masks was obtained by varying the pH of the aqueous medium. It was found that for manganese, lead and iron there is a permanent (Mn) or temporary (Pb, Fe) excess of these metals in the aquatic environment according to national and European standards. The probable possibility of sorption effects and the need for further research in this direction were noted.

Keywords: disposable protective face mask, pollution, atomic adsorption spectroscopy, aqueous environment, heavy metal.

INTRODUCTION

The up-to-date world is the result of a complex interaction of natural and anthropogenic factors, where constant changes in the surrounding natural environment cause disturbances in man-made space and vice versa. Thus, it is possible to note significant climatic changes that

affect the yield of agro-industrial crops [Rosegrant et. al., 2021] and the population [Sesana, et. al., 2021; Dickerson et. al., 2022]. At the same time, anthropogenic activity is currently the main driving force that changes the natural world as in its individual elements [Popovych V. et. al., 2021; Mali et. al., 2023], and in general [Han et. al., 2023]. Negative anthropogenic actions on the environment can also include the effects of certain types of emergency situations, in particular, hostilities [Weir, 2020], terrorist acts [Divizinyuk et. al., 2019], fires and their consequences [Strelets et. al., 2021; Abramov et. al., 2019]. At the same time, pollution of the environment and of water bodies, in particular, may occur in the point and diffuse sources of pollution [Loboichenko et. al., 2021; Horta Ribeiro Antunes et. al., 2021].

Another challenge to humanity and the planet as a whole was the pandemic which was named COVID-19. Significant human casualties, negative consequences for the health of sick persons, revision of the work of national and international medical, service and transport services are only part of the consequences caused by this disease. The environment has also suffered additional impacts due to the huge amount of medical waste that have started to enter the environment since the beginning of the pandemic, and it primarily concerns personal protective equipment (PPE) [Yang et. al., 2022]. PPE, including protective face masks, have become a problem in many cities [Ammendolia et. al., 2021; Tesfaldet Y et. al., 2022], cluttering city streets and further entering the environment. Thus, the share of medical waste from PPE in urban garbage has grown significantly since the pandemic; the largest, 80-fold increase is noted for disposable protective face masks [Norris, 2021]. Only in the first year of the pandemic the waste was generated containing almost 4 million metric tons of masks [Patrício Silva et. al., 2021a]. So, at the present, the total annual volume of the waste from 36 countries reaches 1.5 million tons of protective face masks [Shukla et. al., 2022].

Among the ways to reduce their number in the environment, in addition to rational waste management [Alieva et. al., 2021], limited reuse of disposable protective masks is also considered [Alcaraz et. al., 2022], their production using biodegradable materials [Babaahmadi et. al., 2021], green technologies [Du et. al., 2022] and stricter approaches to raw materials [Chen et. al., 2022].

The massive use of rubber gloves, disposable suits, and protective face masks additionally caused up to 400,000 tons of waste to enter the marine environment [Patrício Silva et. al., 2022] that cause short-term and long-term, direct and indirect effects on biota.

In many studies the negative effects of plastic and microplastics from PPE on the environment are noted. First of all, the role of disposable protective face masks in polluting the environment with plastic is noted, due to the mass of their use and the fibrous structure of the material [Pizarro-Ortega et. al., 2022]. It is noted that both disposable and reusable protective masks made of polymer and cotton materials are a source of microfibers entering the environment [De Felice et. al., 2022], Moreover, the number of microfibers from used disposable masks is 6-7 times higher than from new ones [Chen et. al., 2021].

It is also noted that in addition to the significant amount of plastic and microplastics entering the aquatic environment from PPE, the leaching of organic compounds that may be a component of the PPE production process [Uddin et. al., 2022] or provide antimicrobial, protective, cleansing properties, for example, of protective face masks [Patrício Silva et. al., 2021b]. Additional polluting components used in the production of protective masks can also be metal nanoparticles, extracts of vegetable oils, etc. [Chen et. al., 2022]

Many studies have noted the negative impact of disposable protective face masks on aquatic ecosystems [Akhbarizadeh et. al., 2021; Wu et. al., 2022]. It is indicated that most of such masks are made of petroleum-based non-renewable polymers that are non-biodegradable and hazardous to the environment [Dharmaraj et. al., 2021]. Considerable attention is paid to the kinetics leaching microplastic and fiber sizes. Thus, [Liang et. al., 2022] it is noted that the rate of the washing out does not depend on the type of the investigated masks, and the size of microplastic fibers is less than 500 μm. It is noted that directly protective masks can act as vehicles for transferring other sorbed pollutants to them in the water environment [Wang et. al., 2022].

The impact of physical factors, in particular, ultraviolet and mechanical impact of shoreline sand on the waste of protective masks and their contribution to the formation of microplastic is noted [Wang et. al., 2021]. The increase in the extraction of microfibers from PPE and protective masks under the influence of the sea water and the current is indicated [Rathinamoorthy et. al., 2022]. This microplastic and compounds washed

into the water environment from protective masks can be adsorbed on algae, included in trophic chains [Ma et. al., 2021] and cause toxicogenomic effects on living beings [Sendra et. al., 2022]. Cross-contamination of different types of masks with microplastic of different origins can also occur, which makes it difficult to assess the individual effects of these masks [Torre et. al., 2022].

At the same time, the chemical effects on the environment from protective masks have been studied relatively less. Thus, a significant experiment conducted [Bussan et. al., 2022] for 24 surgical and KN95 face masks showed the direct presence of lead, copper, zinc, and antimony in some of them which can be washed away. The authors [Leonova et. al., 2022] indicate the excess of zinc and lead in the soil in the presence of protective disposable face masks and emphasize the need for further research. In the paper [Sullivan et. al., 2021] a daily study of a number of disposable masks showed the leaching of trace amounts of lead, cadmium, antimony and various organic substances from them. In the paper [Kutralam-Muniasamy et. al., 2022] the authors emphasize the lack of regulation of chemical compounds in protective masks and PPE, although heavy metals and organic pollutants enter the water environment from them. The need for further research into the features of chemical degradation of PPE is noted. The research by the authors [Liu et. al., 2022] showed that leaching of heavy metals from surgical disposable masks is easier than from respirators, and in the filtrates during a 15-day study of a number of samples, Co, Cu, Ni, Sr, Ti, Zn were detected, and in some masks – also Cd, Cr, Mn and Pb. The leaching of microplastics and organic compounds is also shown acetophenone, 2,4-Di-tert-butylphenol, benzothiazole, bisphenol-A, phthalide and environmentally persistent free radicals.

Thus, it can be noted that the specifics of the chemical effects of protective face masks on the aquatic environment are not sufficiently studied today. Considering the above, the aim of the work is to study the migration of a number of metals from disposable protective masks into the aquatic environment in the short term.

MATERIALS AND METHODS

The following reagents, materials and equipment were used in the research process:

- hydrochloric acid, sodium hydroxide, standard samples of the composition of solutions 0.1 g/l Me (Cu, Zn, Mn, Pb, Fe) (Ukraine), distilled water. The qualifications of all reagents were "pure for analysis" and higher;
- laboratory scales AS 220.R2; pH meter PH-150MI (pH error = ±0.02); atomic adsorption spectrophotometer C 115 M1; measuring laboratory equipment (flasks, glasses, pipettes, funnels), laboratory scales TVE-0.21-0.001-a.

The solutions necessary for the work were prepared by diluting from more concentrated solutions or by weighing the required mass of appropriate reagents with their subsequent dissolution. The study used three-layer ("spunbond + meltblown + spunbond" materials) protective disposable masks manufactured by Abifarm (Herbal fresh) - Mask (I) and Meddins - Mask (II). 10 masks from each manufacturer were completely immersed in closed containers with distilled water (250 cm^3), which were stirred 3 times a day. To study the effects of pH, aliquots of 0.1 M NaOH or HCl were added to a number of containers on the 5th, 15th, 25th and 35th day of the study.

The study was conducted by measuring indicators on the 5th, 15th, 25th, and 35th day of the study. A total of 4 measurements were made. Determination of pH of aqueous solutions – place an aliquot of the test solution in a beaker with a capacity of 50 cm^3 and measure its pH according to the instructions for the device.

Preparation of calibration solutions for atomic absorption analysis of the content of heavy metals

Standard solutions are prepared from solutions containing 0.1 g/l of metal (Cu, Zn, Mn, Pb, Fe) by diluting aliquots of HNO$_3$ (ω = 1.5%). Solutions with a lower concentration are prepared by diluting the original solution.

Atomic absorption study of the content of heavy metals

The device is prepared for operation according to the instructions. Next, a lamp with a hollow metal (Cu, Zn, Mn, Pb, Fe) cathode is connected to the monochromator of the device, and the analytical line of the corresponding metal is

derived. Next, the light absorption of the calibration solutions or the studied aliquot of the solution is measured. Next, they construct calibration dependence for each metal and determine its content in the studied samples. Standard mathematical approaches are used for data processing.

RESULTS AND DISCUSSION

In the work, 4 aliquots of aqueous solutions containing masks were taken, respectively, on the 5th, 15th, 25th and 35th day of the study. First, data of changes in the pH of the water environments in which the investigated masks were located during the experiment were obtained. The dependence of the change in the pH of aqueous solutions in the absence and with the addition of appropriate amounts of hydrochloric acid or sodium hydroxide in the container with the investigated masks is shown in Figure 1. As it can be seen from the obtained values, for both types of masks, similar dependence of the pH change on the time of the

study is observed, except point 3 for Mask (II) in hydrochloric acid, which can be considered a fluctuation deviation, which is leveled at point 4.

During the study, the pH of the medium changes by 1 pH both in the direction of increasing acidity (6.2) and in the direction of decreasing acidity (8.2) compared to the original, neutral medium. Fig. 2–6 represent the dependence of the content of heavy metals (Mn, Cu, Zn, Pb, Fe) on the time of the study for Mask (I) and Mask (II) taking into account the pH of the medium. As it can be seen from the obtained data (Fig. 2), the main leaching of manganese occurs on the first days of the mask entering the water for both Mask (I) and Mask (II). For Mask (I) with a slight decrease in the pH of the medium, and for Mask (II) – with an increase in the pH of the medium relative to its neutral state. Under the conditions of a neutral medium, we can tell about a more gradual (within 25 days) leaching of manganese compounds into the solution. A decrease in the manganese content in an acidified or alkaline environment may indicate the possible sorption of
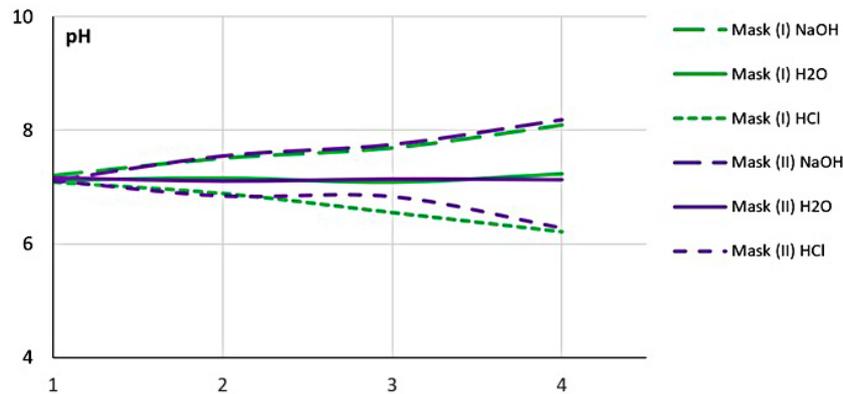

Fig. 1. pH values of aqueous solutions containing Mask (I) and Mask (II) in an acidified (HCl), neutral (H_2O) and alkaline (NaOH) medium on the 5th (1), 15th (2), 25th (3) and 35th (4) day of the research
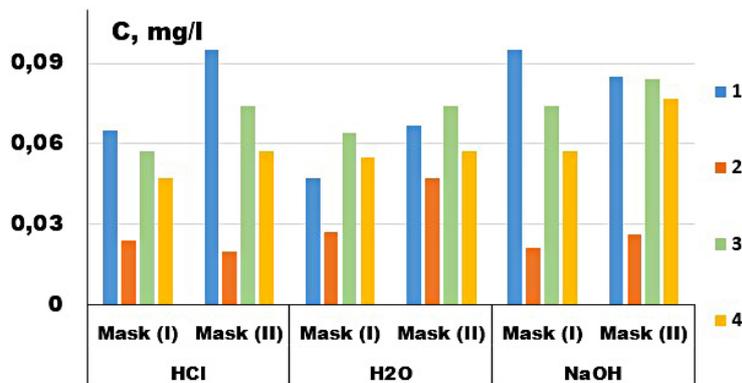

Fig. 2. Manganese content in the solution containing Mask (I) and Mask (II) in an acidified (HCl), neutral (H_2O) and alkaline (NaOH) aqueous environment on the 5th (1), 15th (2), 25th (3) and 35th (4) day of the study

its compounds by the mask material during the study period. For copper (Fig. 3), a similar situation is observed as for manganese, for both types of masks, although for Mask (II) its content is slightly higher in a neutral, acidified and alkaline environment, and leaching occurs more slowly (on the 15th day of the study, the highest values for both types of masks) and in the future, sorption or binding of its compounds into poorly soluble forms also takes place.

For zinc (Fig. 4), it is possible to note the similarity of the values of its content in aqueous neutral and alkaline environments for Mask (I) and Mask (II). The highest values of zinc content in both cases are observed on the 25th day of research. In an acidified environment, zinc is washed out more slowly (higher values are characteristic of the 35th day of the study) and slightly

higher values of its content are characteristic of Mask (II). Lead is characterized by more active leaching on the 15th day of the study in all environments for Mask (I) and Mask (II). Possible sorption effects or transfer to a slightly soluble state are also characteristic in this case. Mask (II) is characterized by higher values of lead content in all types of studied aqueous environments compared to Mask (I).

For iron, a more gradual leaching is observed on the 25th–35th day of the studies for Mask (I) and Mask (II), which practically does not depend on the pH of the investigated aqueous environment in both cases. The obtained values of the content of metals in the water environment were also compared with the normative values (Table 1) [DSanPiN 2.2.4–171–10, 2010; Directive (EU) 2020/2184, 2020; WHO, 2022].
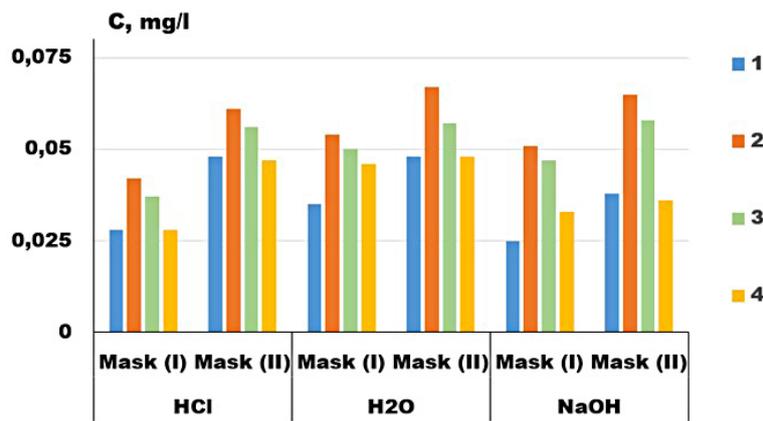

Fig. 3. Copper content in the solution containing Mask (l) and Mask (ll) in an acidified (HCl), neutral (H$_2$O) and alkaline (NaOH) aqueous environment on the 5th (1), 15th (2), 25th (3) and 35th (4) day of the study

Fig. 4. Zinc content in the solution containing Mask (I) and Mask (II) in an acidified (HCl), neutral (H$_2$O) and alkaline (NaOH) aqueous environment on the 5th (1), 15th (2), 25th (3) and 35th (4) day of the study
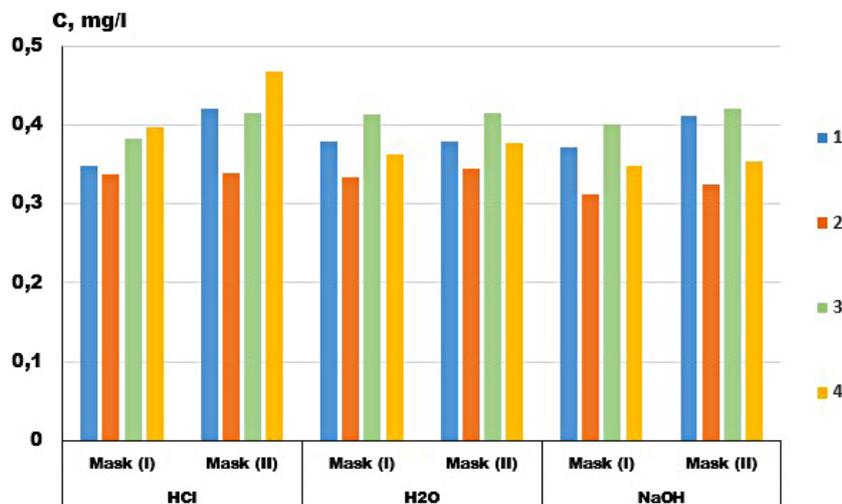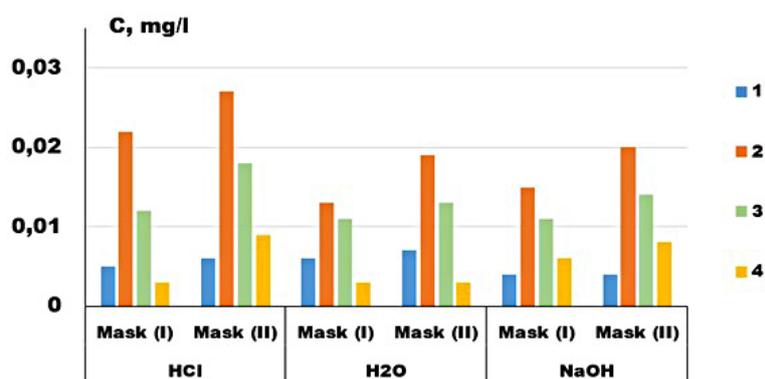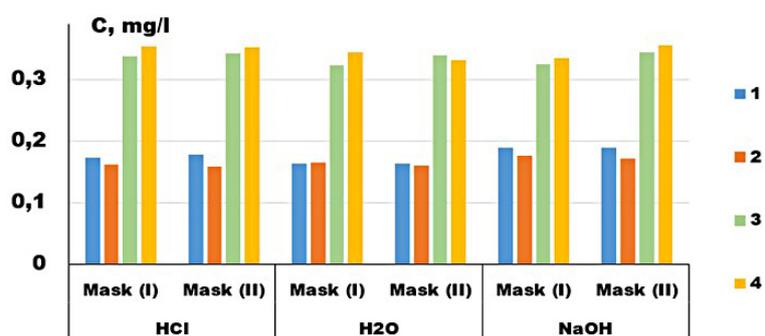
Fig. 5. Lead content in the solution containing Mask (I) and Mask (II) in an acidified (HCl), neutral (H$_2$O) and alkaline (NaOH) aqueous environment on the 5th (1), 15th (2), 25th (3) and 35th (4) day of the study

Fig. 6. Iron content in the solution containing Mask (I) and Mask (II) in an acidified (HCl), neutral (H$_2$O) and alkaline (NaOH) aqueous environment on 5th (1), 15th (2), 25th (3) and 35th (4) day of the study

Table 1. The value of the maximum content of metals being determined in drinking water according to various regulatory documents

Metal	DSanPiN 2.2.4–171–10, mg/l	Directive (EU) 2020/2184, mg/l	WHO, mg/l
Manganese	0.05	0.05	0.08
Copper	1.0	2.0	2.0
Zinc	1.0	-	-
Lead	0.01	0.01	0.01
Iron	0.2	0.2	-

As it can be seen (Figs. 2–6), for manganese there is an excess for both types of masks according to European and Ukrainian standards for drinking water, and an excess according to WHO standards in the first days of the study. For copper and zinc, there is no excess of their content, and for lead and iron there is a temporary excess, respectively, on the 15th and 25th (for lead) and 25th and 35th (for iron) day of the research according to all permissible standards. Accordingly, the obtained results indicate the ambiguity of the short-term impact of disposable protective face masks on the state of the aqueous environment, both neutral and alkaline to 8.2 pH or acidified to 6.2 pH. Thus, during the studied period, multi directional changes in the content of heavy metals Mn, Cu, Zn, Pb in the aqueous environment may be associated with sorption effects or features of the transition to other forms, which requires further study.

CONCLUSIONS

Thus, it is possible to note a significant increase in the interest of scientists all over the world in the issue of finding an additional amount of plastic waste from COVID-19 in the

environment. It is noted that essential amount of PPE, in particular, disposable protective face masks enter the aquatic environment. At the same time, both plastic and microplastic, as well as chemical compounds of various nature, enter the environment. The emphasis is on the difficulties of identifying individual sources of pollution, which are represented by masks of various types, and the inadequacy of studying the effects of the chemical component of masks on the aquatic environment.

The short-term effect of two types of protective face masks on the aquatic environment under the conditions of its neutral, acidified and alkalized state was analyzed by the content of Mn, Cu, Zn, Pb and Fe. The multi directionality of the dynamics of fluctuations in the content of various heavy metals in the aqueous environment for both types of masks was noted, depending on the period of the study, which is probably related to sorption effects or the binding of metals into poorly soluble compounds. At the same time, there is a similarity in the dynamics of heavy metal content fluctuations for Mask (I) and Mask (II) under the same research conditions. For manganese, lead and iron, there is a permanent (Mn) or temporary (Pb, Fe) excess of these metals in the aqueous environment according to national and European standards. It is possible to note the insufficiency of data to unambiguously determine the short-term effects of disposable protective face masks on the state of the aquatic environment, which indicates the need for further research in this direction.

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