



Suleyman Demirel University Journal of Health Sciences Volume 15, Issue 2, 226 - 235, 2024

Determination of Major Heavy Metal Levels in Pepper Gas Used as Chemical Agents in CBRN Field

KBRN Alanında Kimyasal Ajan Olarak Kullanılan Biber Gazlarında Başlıca Ağır Metal Düzeylerinin Belirlenmesi

Eda ARICI ¹, Mümin POLAT ²

¹ Antalya Bilim University, Health Services Vocational School, First and Emergency Aid Department, Antalya, Türkiye ² Burdur Mehmet Akif University, Faculty of Health Sciences, Emergency Aid and Disaster Management Department, Burdur, Türkiye



ABSTRACT

Introduction: The pepper gases used in the study are in the group of riot control agents. In this study; It was aimed to determine the main heavy metal levels of pepper gases obtained from capsaicin, the active ingredient of peppers grown in soil that we think may contain heavy metals.

Material and Method: The presence of a total of 7 heavy metals, including iron, chromium, cobalt, copper, cadmium, lead and nickel, was investigated. The pepper gas sprays were subjected to sample preparation with a microwave combustion device. Then, heavy metal analyzes of the prepared samples were carried out with the ICP OES device.

Results: According to this; As a result of the measurements, Chromium (Cr), Nickel (Ni), Cadmium (Cd) and Cobalt (Co) elements were not found in any of the samples. The amount of Lead (Pb) was determined as 0.653±0.064 mg/kg, and the amount of Iron (Fe) was 5.246±0.000 mg/kg. Finally, the Copper (Cu) element detected in a single sample was measured as 0.815 mg/kg.

Discussion and Conclusion: We also think that the necessary sensitivity should be shown in laboratory and clinical studies to examine the content of pepper spray and to determine the optimum ratios of its active ingredients. We foresee that preparing promotional brochures, informative public service ads on topics such as what pepper gas is in what situations pepper gas should be used, and informing the public about the health problems it may cause will increase the conscious use of pepper gas.

Keywords: heavy metal; pepper gas; CBRN, inhalation, public health

Alınış / Received: 15.05.2024 Kabul / Accepted: 11.08.2024 Online Yayınlanma / Published Online: 28.08.2024



ÖΖ

Giriş: Araştırmada kullanılan biber gazları kargaşa kontrol ajanları grubunda yer almaktadır. Bu çalışmada; ağır metal içerebileceğini düşündüğümüz topraklarda yetiştirilen biberlerin etken maddesi olan kapsaisin'den elde edilen biber gazlarının başlıca ağır metal düzeylerinin belirlenmesi amaçlanmıştır.

Materyal ve Metot: Demir, krom, kobalt, bakır, kadmiyum, kurşun ve nikel olmak üzere toplam 7 ağır metalin varlığı araştırıldı. Biber gazı spreyleri mikrodalga yakma cihazı ile numune hazırlamaya tabi tutuldu. Daha sonra hazırlanan numunelerin ICP OES cihazı ile ağır metal analizleri yapıldı.

Bulgular: Buna göre; yapılan ölçümler sonucunda numunelerin hiçbirinde Krom (Cr), Nikel (Ni), Kadmiyum (Cd) ve Kobalt (Co) elementlerine rastlanmadı. Kurşun (Pb) miktarı 0,653±0,064 mg/kg, Demir (Fe) miktarı ise 5,246±0,000 mg/kg olarak belirlendi. Son olarak tek bir numunede tespit edilen Bakır (Cu) elementi 0,815 mg/kg olarak ölçülmüştür.

Tartışma ve Sonuç: Biber gazının içeriğinin incelenmesi ve etken maddelerinin optimum oranlarının belirlenmesi konusunda laboratuvar ve klinik çalışmalarda da gerekli hassasiyetin gösterilmesi gerektiğini düşünmekteyiz. Biber gazının olası etkilerinin ne olduğu, hangi durumlarda kullanılması gerektiği gibi konularda tanıtım broşürleri hazırlanması, bilgilendirici kamu spotları hazırlanması, yol açabileceği sağlık sorunları konusunda kamuoyunun bilgilendirilmesinin biber gazının bilinçli kullanımını artıracağını öngörmekteyiz.

Anahtar Kelimeler: Ağır Metal; Biber Gazı; KBRN, İnhalasyon, Halk Sağlığı.



1. Introduction

CBRN; It consists of the initials of the words Chemical, Biological, Radiological and Nuclear. These substances, which constitute the content of CBRN, also express the possible danger situations that may occur. The dangerous substances it contains can be used deliberately in terrorist incidents or pose a risk to society by creating dangerous situations in the areas of use of developing technology. Events caused by these dangerous substances; It is examined in two cases: human and natural origin. Human-caused events can occur intentionally or accidentally. Events such as major industrial accidents, human errors during the storage or transportation of hazardous materials, wars and terrorist attacks can be given as examples of events that occur as a result of intent. Natural events occur when these hazardous substances are damaged as a result of natural disasters in the areas where they are produced, processed and stored (1). Considering today's rapidly developing war technology, industrialization and advances in industry, CBRN risk factors increase in parallel with this development. Reasons such as lack of knowledge in the field of CBRN, irregular or non-performing inspections, and intentional use of dangerous substances pose a risk to society. As a result of terrorist incidents and accidents, large masses are negatively affected (2). Throughout history, advancements in technology and chemistry have played a leading role in synthesizing many new compounds. It has been realized that some of these compounds can be used as chemical warfare agents. It is seen that in the 20th and 21st centuries, chemical warfare agents were used in world and national wars for many reasons such as killing, maiming, neutralizing the opposing side during war and reducing capacity. Chemical warfare agents are examined in 6 classes. These are grouped as nerve gases, corrosive gases, lung irritants, blood poisons, capacity disruptors and riot control agents (3).

Riot control agents; They are generally known as tear-inducing, disabling agents and are used by security forces to suppress mass events or keep groups demonstrating without permission under control. In addition to being tear-inducing, they pose an inhalation hazard since they are used in aerosol form. Aerosol properties such as morphology, particle size and charge significantly affect deposition in the respiratory tract, which can lead to unexpected effects on health (4). Tear-inducing

agents began to be produced for the first time in 1871. The use of tear gas in the form of sprays and bombs dates back to the 1990s. With the decision taken in the Geneva Protocol in 1969, gas bombs were included among the banned chemicals. Considering the existing danger potential, it has been stated that its use should not be allowed under any circumstances. On the other hand, gas bombs continue to be used in countries such as the United States, England, Ireland, Vietnam, Philippines, Chile, Panama, South Korea, Gaza, Israel, Iraq, Turkey and Egypt (5). Common ingredients used as turmoil control agents include Oleoresin capsicum (OC), o chlorobenzlidene malononitrile (CS), dibenzoxazepine (CR), and chloroacetophenone (CN). It is relatively cheaper than other riot control agents, and there is no need for a license, certificate or training for its purchase and use (6),(7). In this context, it is of great importance to examine the contents of these compounds used, to supervise their purchase and sale, and to obtain various training and certificates for their use.

The term "heavy metal", which we have heard frequently in recent years and has an important place in the literature, is a widely used term. They are called metals or semi-metals, which are often associated with contamination and potential toxicity or eco-toxicity. The definition of heavy metal is used to refer to metals with a density greater than 5 g/cm3 (8). In this study, the widely used compound Oleoresin capsicum (OC), popularly known as pepper gas, was chosen. It was aimed to detect possible heavy metal content in pepper sprays purchased from 4 different brands in total. Pepper spray is an oil obtained as a result of the extraction of red pepper called Chile pepper or hot Cayenne pepper obtained from Capsicum annum or Capsicum frutescens from the Solancea family. It is insoluble in water but soluble in organic solvents such as alcohol, ether and chloroform. This solvent is then evaporated and the remaining wax-like substance is called "Oleoresin Capsicum". This extract contains many different natural compounds in varying concentrations. It is the most abundant substance called Capsaicin (which makes hot peppers hot). Concentration or caustic value of the pepper spray used: The percentage OC value written on the product (7%, 10%, etc.) shows how much OC is in the box compared to other contents such as spraying agent and paint. In a study conducted in the United States, it was shown that the concentration of OC in pepper sprays varied between 1-10%, while the rates of Capsaicin alkaloids were much less (5).

2. Material and Method

In this study, pepper sprays purchased from 4 different brands were used. 3 of the pepper sprays purchased were ordered online, and 1 was purchased directly from the store selling the product. Information about the purchased pepper gas samples is given in Table 1. Purchased pepper sprays were randomly coded. Experimental studies were carried out at Burdur Mehmet Akif Ersoy University Scientific and Technology Application and Research Center Laboratory. The wavelengths, correlation coefficient (R²), limit of detection (LOD) values determined for the heavy metals included in the study are given in table 2.

Sample Code	Weight (ml)	Expiration Date (year)	Date the sample was used (year)	Production place (country)
Jx-1	40 ml	2025	2023	Turkey
Nt-2	40 ml	2027	2023	Germany
Jt-4	40 ml	2026	2023	Turkey
Bg-3	40 ml	2026	2023	Germany

Table 1. Some information about the pepper spray samples purchased in the study

Element	LOD (ppb) (mg/kg)	R ²	Wavelength (nm)
Cd	5	0,993	228,8
Fe	5	0,999	259,9
Cu	5	0,999	324,7
Co	5	0,999	228,6
Cr	5	0,999	205,5
Pb	10	0,999	220,3
Ni	5	0,998	231,6

Table 2. Wavelengths, correlation coefficient (R²), limit of detection (LOD) values determined for the heavy metals included in the study

Sample preparation of the 4 pepper sprays used in the study was carried out as follows; For each sample, 9 ml of nitric acid and 3 ml of hydrochloric acid were added to Teflon containers. The weight of the Teflon container, lid and acids was zeroed on a precision scale. Then, pepper gas was added to the Teflon containers by spraying them in a fume hood. Following this process, the weight of pepper spray was determined by measuring again on a sensitive scale. Table 3 gives the weights of pepper gas used in the study. The pepper gas samples, whose net weight was determined, were placed in the microwave incineration unit for incineration. The operating stages of the microwave unit used are listed in table 4.

Table 3. Net weights of pepper gas samples used in the study

Sample Code	Net weight (g)		
Jx-1	0,83		
Nt-2	2,26		
Bg-3	2,80		
Jt-4	1,15		

Table 4. Stages and temperature of the microwave device

Time	Temperature		
15 min	110°C (15 min 110°C turns out)		
15 min	110°C (15 min 110°C staying)		

The samples, whose burning process was completed, were removed from the microwave device. Then, the samples taken from the Teflon containers were poured into capped plastic tubes and made up to 50 mL by adding ultrapure water. Heavy metal analyzes of the samples, whose combustion process was completed, were carried out on the ICP OES device. Cd, Fe, Cu, Co, Cr, Pb, Ni were measured in each of the 4 samples. Also all procedures performed in the study are expressed in figure 1.



Figure 1. All processing steps performed in the study

3. Results

In this section, data regarding 7 heavy metal analysis of 4 pepper sprays used in the study are presented. In the research, the amount of Cadmium in pepper gas samples purchased from different brands was examined and according to the results of the heavy metal analysis, Cadmium could not be detected in any of the samples. In the analysis performed for the amount of iron, Fe could not be detected in the Nt-2 sample. When we consider the iron content of the remaining samples, our lower and upper limit values were determined as 0.000-5.246 mg/kg. In our study, Cu could not be detected in Nt-2, Bg-3 and Jt-4 samples when determining the copper content of pepper spray samples. In the Jx-1 sample, the amount of Cu was found to be 0.815 mg/kg. Cobalt was not detected in any of the pepper gas samples obtained. In the study, neither Cadmium nor Chromium was detected in any of the pepper gas samples.

According to heavy metal analysis data for the amount of lead; The Lead content of Jx-1, Nt-2 and Bg-3 samples is below the LOD (limit of detection) value. The LOD value is also the smallest concentration that can be distinguished from the blank sample with 95% probability. In other words, it is the amount by which an analytical process can be detected. Here, the compound can be detected, but this amount is not sufficient for quantitative analysis. In our last sample, Jt-4, the amount of lead was determined to be 0.653 mg/kg. Nickel, the last metal we examined in our study, could not be detected in any of our pepper gas samples. The heavy metal analysis results of the 4 selected pepper gas samples determined by the ICP-OES device are shown in Table 5. As a result of the analysis, the lower and upper limits of heavy metals determined in pepper gas samples and the limit values determined by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) are expressed in Table 6.

Sample	Cr	Pb	Cd	Ni	Со	Fe	Cu
Jx-1	-	0,527	-	-	-	5,246	0,815
Nt-2	-	0,125	-	-	-	-	-
Bg-3	-	0,064	-	-	-	0,246	-
Jt-4	-	0,653	-	-	-	1,770	-

Table 5. Heavy metal analysis results of pepper gas samples (mg/kg)

-; Could not be detected. Dark colored results are below the LOD value.

Table 6. Lower and upper limits of heavy metal amounts of pepper gas samples (mg/kg) and limit values determined by WHO-FAO (μ g g-1) (9).

Cr	Pb	Cd	Ni	Со	Fe	Cu
0,000±0,000	0,064±0,653	0,000±0,000	0,000±0,000	0,000±0,000	0,246±5,246	0,000±0,815
5	0,30	0,2	67	-	450	40

4. Discussion and Conclusion

Capsaicin, a compound found in the pepper sprays we examined in our study, is obtained from Albanian or Chilean peppers grown in soil. In this context, 7 heavy metal elements that we can encounter in pepper gas and are most abundant in soil were selected to be examined in our study. In our study, iron, copper, lead, cobalt, nickel, cadmium and chromium were investigated in 4 pepper spray samples purchased from brands sold under different trade names.

In their study, Polat and Öğüt (2018) investigated the heavy metal concentrations in 6 different unpackaged herbal teas sold in herbalists. They investigated the presence of heavy metals Fe, As, Cd, Cr, Cu, Hg, Ni, Pb and Al in herbal teas obtained from green tea, linden, St. John's wort, chamomile, sage and thyme. Accordingly, significant amounts of heavy metal residues were found in these herbal teas. While Fe (302 mg/kg) was found in the highest concentration, heavy metals Cd and Cr were not found in any of the herbal tea samples in question. Among the herbal tea samples, the highest amount of heavy metal residues were found in thyme. The lowest heavy metal concentration was found in Linden tea samples. It has been reported by researchers that these unpackaged herbal teas, which are frequently preferred by the public and obtained from herbalists, may pose significant risks in terms of heavy metal contamination, but these risks can be reduced by taking precautions during both the production and commercialization stages (10). As is known, capsaicin, the active ingredient of pepper sprays whose heavy metal concentration was investigated in this study, is obtained from Albanian and Chilean peppers. It is obvious that heavy metal contamination may occur in the soil where these peppers are produced, especially during the harvesting process and the subsequent addition of pepper gas. It is known that heavy metal contamination can be observed directly in the soil or in products during the production stages, and it is thought that this risk can be minimized by taking the necessary precautions.

Adepoju et al. (2023), in their study in Sierra Leone, investigated possible heavy metal contamination in some vegetables, some of which are indigenous to the region and preferred by the public. Among the plants they researched is pepper (Capsicum annuum), from which Capsaicin, the main active ingredient of the pepper sprays used in this study, is obtained. Researchers have revealed the concentrations of heavy metals Cr, Cu, Fe, Zn and Pb in the vegetable and plant samples they selected. They measured heavy metal concentrations with an x-ray fluorescent device and checked whether they were above the limits set by the World Health Organization. Accordingly, Zn, Cr, Fe, Cu and Pb heavy metal levels were measured in plant samples and respectively; 4.70 - 5.69%; 3.46 - 4.58%; 4.00 - 4.52%; It was found to be 2.87 - 3.42%, 0.5 - 1.2%. According to these results, it was

reported that the heavy metal levels obtained were not within the range recommended by the World Health Organization and it was stated that the vegetables in question should not be consumed in the safe food category. When looking at the heavy metal concentration of the pepper plant, researchers; It has been stated that it is above the specified limits and this may be due to the fact that these plants are grown on roadsides (11). We observe that it is similar to the values in this study, especially when the active ingredient of pepper spray is considered. The cultivation of plants on the roadside makes them susceptible to contamination with many heavy metals, especially the exhaust gas released from vehicles. It is clearly seen that it is not surprising to see such high heavy metal concentrations.

In the study conducted by Grace et al. in 2020, they examined the heavy metal concentration of pepper samples sold in large markets in Osogbo city, Osun State, Nigeria. A total of 72 pepper samples were used in this research conducted in Nigeria, Africa's largest pepper producer. It was aimed to detect the presence of lead, cadmium, mercury, arsenic and nickel in the peppers used using the atomic absorption spectrometry method (AAS). According to the research results; It was determined that all pepper samples contained high levels of lead and cadmium. It has been reported that the lead heavy metal detected in the research may have negative effects on the nervous system, kidneys and blood cells, and cadmium heavy metal may cause kidney damage, osteoporosis and cancer (12). It is obvious that the pepper plant that constitutes the pepper gas samples we used in our research is contaminated with heavy metals. In this context, the negative effects of lead heavy metal, which we detected in our study, on human health are reported by Grace et al. (2020) states, it can cause serious health problems in the kidneys, blood cells and bones. For this reason, it is of great importance to investigate and monitor both the pepper gases, is obtained, in terms of heavy metal contamination.

In a study conducted by Young and Tarawou (2014), they carried out heavy metal analysis (zinc, copper, chromium, iron, manganese and cobalt) of Capsicum annum, Capsicum chinens and Capsicum frutescens pepper samples collected from the abandoned garbage dump in Gbarantoru city of Bayalse State. After the pepper samples were dried and powdered, they were made ready for analysis with a mixture of sulfuric acid, perchloric acid and nitric acid. Then, analysis was performed using atomic absorption spectrophotometry (AAS). According to the research results of Young and Tarawou; Capsicum annuum (Zn = 40.28 mg/kg, Cu = 4.17 mg/kg, Cr = 3.32 mg/kg, Fe = 105.23 mg/kg, Mn = 0.54 mg/kg, Co = 0.69 mg/kg), Capsicum chinens (Zn = 54.48 mg/kg, Cu = 4.22 mg/kg, Cr = 2.81 mg/kg, Fe = 158.33 mg/kg, Mn = 0.66 mg/kg, Co = 0.73 mg/kg), Capsicum frutescens (Zn = 47.45 mg/kg, Cu = 4.36 mg/kg, Cr = 3.20 mg/kg, Fe = 63 .13 mg/kg, Mn = 0.59 mg/kg, Co = 0.77 mg/kg) (13). When we examine the heavy metals we investigated in pepper gas samples and the common heavy metals in the research conducted by Young and Tarawou; Each of the heavy metals this may be due to the type of soil where the pepper gas samples. The reason of this; It is thought that this may be due to the type of soil where the pepper gar samples.

Uğulu et al. (2021) grew Capsicum annuum L. (red hot pepper) using farm manure, poultry waste and press sludge (dewatered sludge) and conducted a pot experiment. The research was carried out in the Department of Botany, Pakisan Sargodha University, to examine the growth performance and heavy metal accumulation of Capsicum annuum. In the research, they analyzed the heavy metal accumulation in Capsicum annuum plants grown in both soil and pots using the AAS method. 12 soil and 12 pepper samples were randomly taken from the pots where the plants were grown. Four groups were created: control group, farm manure, poultry waste and press sludge, and the amount of heavy metals Cd, Cr, Co, Cu, Pb, Fe, Mn, Zn were measured in both the soil of each group and the peppers grown in these soils. When we examined the results of the research, as a result of the application of farm manure, poultry waste and press sludge, Zn, Fe, Cu, Co showed higher concentrations, and Cr, Cd, Mn, Pb showed lower concentrations. As a result of the application, it was seen that heavy metal accumulation in the soil was not prominent in any fertilizer type, but different applications caused different heavy metal accumulation. When we examined the pepper samples, no significant difference was found in terms of average heavy metal accumulation in pepper samples grown in soil containing farm manure, press sludge and poultry waste, as in soil samples. In this research conducted by Uğulu et al., soil samples were detected below the limits declared by USEPA (United States Environmental Protection Agency). In addition, heavy metal accumulation in pepper samples was detected below the maximum limits determined by the World Health Organization (14). In this context, we can clearly state that the use of natural fertilizers (farm manure, press sludge and poultry waste) used in the study by Uğulu et al. instead of chemical fertilizers in the cultivation of Capsicum annuum peppers used in the production of pepper gas can reduce the amount of heavy metals we detected in pepper gas samples.

In his thesis study, Özyürek (2016) measured the accumulation of heavy metals in soil, water and vegetables collected from lands irrigated with different water sources in the Nevşehir region. In the research, 4 different plant species grown agriculturally in Nevsehir, Lycopersicon esculentum (tomato), Capsicum annuum (pepper), Allium cepa (onion), Phaseolus vulgaris (bean), and the soil where these plants were grown and the available water used in the study area (well, river, canal, stream) the amount of Cu, Zn, Fe, Cr, Cd, Pb, Ni was examined. In the thesis study, heavy metal levels were determined using the ICP-OES device. According to the research results; The amount of heavy metals in the examined plants was compared with the amount determined by WHO and it was determined that the plant samples did not exceed these limit values, except for Ni. It has been stated that the heavy metal accumulation in plant samples is highest in the root, then in the stem and leaf, and finally in the fruit. The soil samples collected in the research were evaluated according to the soil control regulation, and it was stated that the heavy metal limit values were not exceeded, but the amount of Fe was found to be very close to the limit value. And finally, the amount of heavy metals in the irrigation water was reported to be below the irrigation water limit values according to the water pollution control regulation (15). Ni heavy metal, which was detected in the plant samples examined in this regional study and exceeded the limit value, could not be detected in our study. However, as in Özyürek's study of the Capsicum annuum plant, which is one of the structures that make up the content of pepper sprays, it is important to examine the accumulation of heavy metals both in the irrigation water of the plant and in the soil where it grows and in various parts of the plant (root, stem, leaf, fruit). At this stage, this will help determine whether the risk is high.

The effects of heavy metals on human health vary depending on various parameters. These; Heavy metals can be listed as solubility value, chemical structure, way of entry into the body and frequency of presence in the environment (8). According to the literature, heavy metal accumulation in soil, water and plants varies in many studies. The heavy metal accumulation in the pepper gas sprays we used in our study was examined based on the Capsaicin substance obtained from Albanian or Chilean pepper. In this context, it has been determined that parallel results were obtained with some of the studies we discussed, and different results were obtained in others. In addition to heavy metal studies in the literature, there are also various clinical studies to examine the effects of pepper spray on human health.

In Tulga's thesis study in 2011, the histopathological effect of pepper spray application on the airway was examined and 42 Sprague-Dawley rats were used in the study. The 42 rats used were divided into 3 groups. While the first group consisted of 6 rats, only physiological saline was applied. The second group consisted of 18 rats and a single dose of pepper gas was applied. In the last group, 3 doses of pepper gas were applied to the remaining 18 rats. The pepper gas used was 5% OC 100 ml sprays applied by the law enforcement forces. As a result of the study, inflammation and degeneration (deterioration of the normal structure of tissues) in the nose were detected and a significant difference was noted between the groups. Edema was observed in only 2 rats in the 3rd group. When the data were compared in terms of edema, no significant difference was found between the groups. When the larynx was examined in groups 2 and 3, degeneration was observed. When the groups were evaluated in terms of inflammation in the trachea, significant inflammation was observed in all groups except the control group (16). It is clearly seen that the histopathological effects on the airways seen in rats in Tulga's study may occur in individuals to whom pepper gas is applied, and that pepper gases can seriously affect vital functions such as respiration.

In the thesis study conducted by Seyhan (2010), the effect of pepper spray on some biochemical parameters in rats was examined. 35 rats were used in the study; Rats were divided into 4 groups. The first group consisted of 6 rats and the control group, the second group consisted of 9 rats and pepper spray was applied for 4 seconds, the third group was applied to 10 rats and pepper gas was applied for 8 seconds, and the last and 4th group was applied to 10 rats and pepper gas was applied for 2 seconds. At the end of OC applications, the animals were sedated by a short preanesthetic procedure with ether and blood samples were taken. In the blood samples taken; Blood gases and Na, K, Cl, Ca and glucose levels were measured. As a result of the study, it was stated that the Ph value decreased in the rats administered OC for 4, 8 and 12 seconds, and no significant difference was detected for the normal value in blood gas analysis, but a difference was compared with the values of the

other three groups, significance was found only in the third group. No statistical significance was observed in the changes in Na and Ca values. Serum K levels of controls were found to be lower than the average values of the experimental groups. A significant increase was detected when the averages of the 2nd and 3rd groups were compared with the controls (17). In this study conducted by Seyhan, the effect of pepper gas applied for different periods of time was revealed. In all applications, it was emphasized that pepper spray lowered blood pH and the importance of the difference between groups in pepper sprays applied for different periods of time was emphasized. In this context, it is obvious how important the application time is for individuals who are subjected to pepper gas.

Another study examined the effects of pepper spray on the eyes. They retrospectively examined the files and found that there was corneal abrasion in 7 out of 100 cases admitted to the emergency room due to pepper gas exposure. In this study, they reported that all pepper gases in use at that time were at 10% concentration (18). Dursun et al. (2015), 6 of 2534 forensic cases who applied to Gazi University Faculty of Medicine Gazi Hospital Pediatric Emergency Department were exposed to pepper gas. In these 6 cases exposed to pepper gas, the symptoms seen in people were stated as shortness of breath, vomiting, dizziness and burning in the eyes. It was stated that the average age of the people in these 6 cases examined was 11.3 years and they were discharged after receiving symptomatic treatment for symptoms after exposure (19). Considering the evaluated facts, it is seen that there is no age limit for the purchase or use of pepper spray and that children use pepper spray for joking purposes. In this sense, it is noteworthy that serious precautions must be taken in the sale of pepper gas.

In conclusion; Chromium, cadmium, nickel and cobalt could not be detected in any of the pepper sprays in this study. Lead heavy metal was below the LOD value in samples Jx-1, Nt-2 and Bg-3, and was found above the LOD value in sample Jt-4. In this context, there was lead in all 4 samples, but the amount determined for the samples below the LOD value was not found sufficient for quantitative analysis. When we examined the amount of iron in the study, it could not be detected in the Nt-2 sample. However, the highest amount detected among other samples was 5,246 mg/kg. The last heavy metal we looked at, copper, was detected in a single sample and measured as 0.815 mg/kg.

Since there are no legal restrictions on the purchase and use of pepper gas in Turkey, anyone who wants can easily access these products. It is clearly stated that there are great debates all over the world about the use of pepper gas being clearly not compatible with human rights. Again, the content of pepper spray, its active ingredient rate, method of use and dosage are among the ongoing debates. CBRN substances, whose use has increased with the developing technology today, pose a risk to societies. It is of great importance to control the use of pepper gas, which is also considered a chemical warfare agents.

We see age restrictions for the purchase of pepper sprays, the requirement for training or certification, and in some cases their acceptance as chemical warfare agents, among the main precautions that should be taken. We also think that the necessary sensitivity should be shown in examining the content of pepper gas and conducting the necessary laboratory and clinical studies to determine the proportional amount of the active ingredient. In addition to all these steps, we believe that it is of great importance to prepare promotional brochures, informative public service spots, and inform people about the health problems it may cause, in order to raise awareness in order to prevent the unconscious use of pepper gas, both in the world and in our country. In this study, some possible heavy metals were detected in the pepper gases used as chemical warfare agents in the CBRN field. We believe that our study can reveal current ideas and actions regarding pepper gas and make significant contributions to the literature.

Etik Beyanı

In this study, we undertake that all the rules required to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" are complied with, and that none of the actions stated under the heading "Actions Against Scientific Research and Publication Ethics" are not carried out.

References

- 1. Doğan G 2019. Study to determine the information, training and exercise needs of institutions against CBRN incidents: the example of Gümüşhane and Trabzon provinces. Gümüşhane University, Social Sciences Institute, Master's thesis, Gümüşhane / Turkey.
- Kızılkaya M 2021. Determination of the preparedness perceptions and knowledge levels of Çanakkale Onsekiz Mart University emergency aid and disaster management department students against CBRN events. Çanakkale Onsekiz Mart University, Institute of Educational Sciences, Master's thesis, Çanakkale / Turkey.
- 3. Erkekoğlu P, Koçer GB 2018. Chemical Warfare Agents: Their History, Toxicity, Detection, and Preparedness. HU J. Pharm. 38:24-38.
- 4. de Bruin-Hoegée M, Alkema DPW, Busker RW, Joosen MJA, van Wuijckhuijse, AL 2023. Real-time characterization of chemical threat agent aerosols for improvement of inhalation studies. Inhalation Toxicology, 35:254-265. https://doi.org/10.1080/08958378.2023.2254323
- 5. Turkish Medical Association 2011. Chemical weapons demonstration control agents. 1st Edition, Ankara: TTB Publishing. 7-8. ISBN 978-605-5867-49-2
- 6. Gören İE, Dağlıoğlu N, Efeoğlu P, Gülmen MK 2014. Forensic Toxicological Analysis of Chemical Warfare Agents and Metabolites in Biological Samples. J. For. Med. 28:154-163. doi: 10.5505/adlitip.2014.52196
- 7. Sezigen S, Karayılanoğlu T 2006. Effects of Chemical Warfare Agents on the Respiratory System and Treatment Approaches. Turkish Hij Den Bio J. 63:129-134. https://dergipark.org.tr/tr/pub/thdbd/issue/63977/968188.
- 8. Özbolat G, Tuli A 2016. Effects of heavy metal toxicity on human health. Arch. Med. Rev. J.25:502-521. doi:10.17827/aktd.253562
- 9. Sönmez O, Kılıç FN 2021. Heavy Metal Pollution in Soil and Removal Methods. TURKAGER, 2:493-507. https://doi.org/10.46592/turkager.2021.v02i02.020
- 10. Polat M, Ogut S 2018. Heavy metals in some medicinal plants sold in herbal shops. Fresenius Environ Bull. 27:1999-2002.
- 11. Adepoju A, Jalloh A, Femi-Adepoju A 2023. Heavy Metal Contaminants in Popularly-consumed Vegetables of Freetown, Sierra Leone. European j. nutr. food saf. 15:12-21. doi: 10.9734/EJNFS/2023/v15i31297
- Grace FA, Adewale OO, Olawale AI, Keji BB 2020. Assessment of Heavy Metals in Peppers Sold in Major Markets in Osogbo, Osun State, Southwest, Nigeria. Int. j. adv. res. chem. sci 7:01-08. doi: https:// doi.org/10.20431/2349-0403.0709001
- 13. Young E, Tarawou T 2014. Determination of metals in pepper by flame atomic absorption spectroscopy. Int. j. biol. chem. sci. s. 8:2891-2895. doi:10.4314/ijbcs.v8i6.45.
- 14. Ugulu I, Akhter P, Khan ZI, Akhtar M, Ahmad K 2021. Trace metal accumulation in pepper (Capsicum annuum L.) grown using organic fertilizers and health risk assessment from consumption. Food Res. Int. 140:109992. doi:10.1016/j.foodres.2020.109992.
- 15. Özyürek F 2016. Heavy metal (Cd, Cr, Cu, Fe, Ni, Pb, Zn) accumulation in vegetables irrigated with different water sources in Nevşehir. Nevşehir Hacı Bektaş Veli University, Institute of Science and Technology, Master's thesis. Nevşehir/Turkey.
- Tulga T. 2011. Experimental Investigation of the Histopathological Effect of Pepper Spray Application on the Airway. Ondokuz Mayıs University, Faculty of Medicine, Department of Otorhinolaryngology, Specialization Thesis. Samsun/Turkey.
- 17. Seyhan E. 2010. Effect of Pepper Spray on Some Biochemical Parameters in Rats.Yüzüncüyıl University, Institute of Health Sciences, Department of Biochemistry, Doctoral Thesis. Van/Turkey.
- 18. Brown L, Takeuchi D, Challoner K 2000. Corneal abrasions associated with pepper spray exposure. Am. J. Emerg. Med. 18: 271–272. doi: 10.1016/s0735-6757(00)90120-7
- Dursun AZ, Sarı S, Özkök A, Derinöz O, Akar T, Demirel B 2015. Evaluation of Cases Exposed to Pepper Spray Who Admitted to Gazi University Faculty of Medicine Gazi Hospital Pediatric Emergency Department. Gazi Med. J., 26: 110. doi:http://dx.doi.org/10.12996/gmj.2015.33