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Volatile organic pollutants in bottled water from saudi arabia: occurrence, method development, and analysis using GC-MS and SPE

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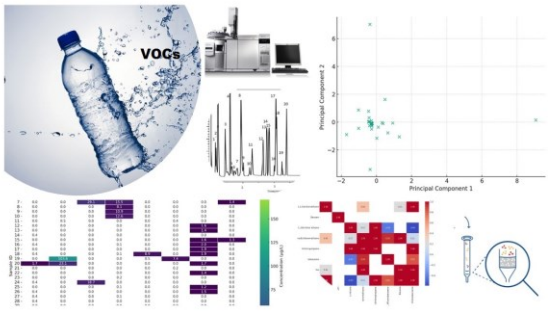
Graphical abstract



Abstract

Bottled water is considered a safe water source and extensively consumed worldwide. However, increased health concerns about its contamination by organic pollutants and polymeric micro/nonfibrous particulates have arisen in the last few years. Therefore, this work is designed to screen the bottled water marketed in Saudi Arabia for the existence of volatile organic compounds (VOCs). For this purpose, 40 samples of bottled water from Madinah city's markets were collected and analyzed to verify their containment of VOCs. The samples were preconcentrated using solid-phase extraction (SPE) and analyzed by gas chromatography techniques calibrated with an environmental standard mixture containing 26 VOCs.

The results confirmed the presence of several volatile organic pollutants in some samples. These pollutants include: 1,1-dichloroethane (1,1DCE), Benzene (B), 1,2-dichloroethane (1,2DCE), Bromodichloromethane (BDCM), 1,2-dichloropropane (1,2DCP), 1,4-difluorobenzene (1,4FB), Toluene (T), and 1,4-dichlorobenzene (1,4DCB). Bromodichloromethane is one of the most common compounds found in bottled drinking water, detected in approximately 40% of the samples, followed by Toluene in 35% of the samples. The least frequently detected component in bottled drinking water was 1,2-dichloropropane, which was found in only 7.5% of the samples.

Keywords: organic pollutants; bottled water; gc; gc-ms; saudi market

1. Introduction

The consumption of bottled water has grown extensively worldwide as it is advertised/marketed as a safe and healthy water source. However, over the last few years, many apprehensions have been raised about the quality and the negative impacts of the bottled water industry on the environment, including the generation of massive amounts of waste and the expenditure of valuable nonrenewable energy resources. Among the emerged potential issues, the occurrence of organic pollutants in bottled water attracted significant attention of many researchers from broad spectrum of scientific disciplines (D'Altrui 2017). Volatile Organic Compounds (VOCs) in bottled water can arise from various sources. Contaminated source water is a primary contributor, where VOCs from industrial activities, agricultural runoff, or natural sources can contaminate underground aquifers. Packaging materials (Khalili Sadrabad *et al.* 2023) used in bottling, such as plastic bottles and caps, may emit VOCs that can migrate into the water over time. During water treatment processes, disinfection by-products resulting from the reaction of disinfectants with organic matter can also contribute to VOC presence (Alshehri *et al.* 2022). The hot weather and the current storage and transportation practices may trigger the leaching of organic residues from polymeric containers to water and sun light exposure and temperature of storing cause changes in all physicochemical properties of water in the plastic bottle (Muhamad *et al.* 2011; Diduch *et al.* 2013).

Numerous published research studies have provided compelling evidence that bottled water can harbor substantial concentrations of organic compound residues, encompassing volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), phthalates, styrene

molecules, and various other pollutants (Leivadara *et al.* 2008; Al-Mudhaf *et al.* 2009; Ikem 2010; Ghanem *et al.* 2013). Some examples of previous published research dedicated to the monitoring of organic compounds in bottled water from different countries worldwide are highlighted in the following paragraphs.

Significant levels of toluene, ethylbenzene, total xylenes, naphthalene, styrene, (1,2-dichloropropane), (1,2,4-trimethylbenzene), and trihalomethanes in bottled water distributed in the Kuwaiti market (Al-Mudhaf *et al.* 2009) . It was proven that an increased concentration of VOCs are found in ozonated water that had come into contact with PP, EVA, and HDPE polymers, but not in water that had come into contact with PET (Al-Mudhaf *et al.* 2009).

In a similar study in Greece, researchers investigated the presence of organic compounds, including trihalomethanes, chloral hydrate, trichloropropanone, dichloropropanone,dichloroacetonitrile,monochloroaceto nitrile, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, dibromoacetic acid, and bromo-dichloroacetic acid in bottled water available in the Greek market A noteworthy variations in the concentrations of the analyzed pollutants were observed in the different bottled water brands, but no significant variation was found between samples stored in adjustable temperature conditions (Leivadara *et al*. 2008).

Another investigation analyzed the presence of trihalomethanes in bottled and tap water in the USA. The study found varying amounts of VOCs and THMs in different brands of bottled water purchased from major supermarket stores in Jefferson City. However, tap water had higher concentrations of analytes such as chloromethane, chloroform, bromodichloromethane, dibromochloromethane, and bromoform compared to both bottled and source waters. All the analyzed bottled and source waters had concentrations of trihalomethanes below the regulatory limits recommended for drinking water (Ikem 2010).

In an analytical study on bottled water from Spanish market, researchers identified the presence of dimethyl selenide and dimethyl sulphide compounds, which are added to cause off-flavors in bottled mineral waters. These volatile-alkylated S and Se species were detected in 56% of the samples (Guadayol *et al.* 2016).

While the production and consumption of bottled water are relatively high in Saudi Arabia, only two reports regarding the occurrence of organic pollutants in this water have been published so far. One of these studies investigated the quality of bottled and tap water in the industrial city of Yanbu, Saudi Arabia, and found no significant difference in quality between the two water sources. However, Trihalomethanes (THMs) screening confirms the presence of trace levels of disinfection by products (DBPs) e.g., $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ $CHBr_3$ in both tap and bottled water samples (Ahmad & Bajahlan 2009).

The same researchers also examined the levels of leached styrene and other aromatic compounds (benzene, toluene, and ethylbenzene) in three brands of polystyrene (PS) bottled water marketed in Yanbu. The study found significant levels of styrene and other aromatic compounds in the water samples, with styrene being the most prominent compound (Ahmad & Bajahlan 2007).

In Japan, a study identified 42 types of compounds listed as Positive Hazardous pollutants including atrazine, lindane, trans chlordane, aldrin, dieldrin, trans-chlordane, cis-chlordane, in bottled water samples (Jin *et al.* 2010).

In similar work in Jordan, trace levels of six phthalate compounds were identified and quantified in seven brands of commercial bottled mineral water. The samples were extracted using a mixture of ether methyl chloride - petroleum and then analyzed using GC-MS and HPLC equipped with ultraviolet detection. The results indicated contamination of the bottled water samples with dibutyl-, di-2-ethylhexyl-, and din-octyl-phthalate, with total phthalate concentrations ranging from 8.1 to 19.8 µg/L. The storage temperature of the bottled water was found to influence the leached phthalate content (Zaater *et al.* 2013).

A comprehensive study in Lebanon aimed to assess the quality of PET-bottled waters compared to polycarbonate-bottled and tap waters. The study optimized and validated both HS-SPME-GC/FID and SPE-GC/FID methods for the determination of volatile organic compounds (VOCs) in the water samples. The analysis showed that the analyzed bottled water samples were not contaminated with benzene, chlorobenzene, styrene, and benzaldehyde. When other VOCs were detected, their concentrations were very low, below the limit of quantification (LOQ). Therefore, the safety of Lebanese drinking water in terms of VOC analysis was confirmed (Ghanem *et al.* 2013).

Finally, a study conducted in Italy investigated VOCs as contaminants and additives in PET bottles used for packaging mineral waters. The most abundant compounds identified included acetic aldehyde (AA), 1,3-dioxolane, octanal, 5-hepten-2-one, nonanal, and decanal, with ESBO identified as a potential source of VOCs likely introduced during PET bottle manufacturing. Additionally, the study proposed poly(m-xylene adipamide) (MXD6) as an efficient aldehyde scavenger, offering potential solutions to mitigate VOC presence in PET-bottled beverages (Dattilo *et al.* 2022).

The objective of this paper was to investigate and quantify the presence of volatile organic compounds (VOCs), specifically major trihalomethanes (THMs) and benzene, in bottled waters from the Saudi market, utilizing gas chromatography with flame ionization detection (GC-MS) as the analytical technique. In order to enhance the sensitivity and achieve quantification levels suitable for GC-MS analysis, solid-phase extraction (SPE) was employed as the sample preparation method for preconcentrating the targeted analytes.

2. Materials and methods

2.1. Reagents and materials

Dichloromethane (DCM), methanol, 0.05N HCl, 6N HCl, sodium thiosulfate (Na_2SO_4), benzene and toluene

purchased from from Loba Chemicals (Mumbai, India). The SPE cartridge C18 40-60 µm,120Å 500mg/6ml obtained from Auto Science (Shanghai, China).

2.2. Standards and calibration

Standard 8270 Mega Mix (26 components) of volatile compounds (Restek Corporation, Bevlfon, Pennsylvania, U.S.) used for calibration. All reagents and chemicals were of analytical grade and used without further purification.

2.3. Instrumentation and measurement

The SPE manifold used for sample preparation was comprised of the ASE 12-head manifold, AP-9950 (Auto Science Shanghai, China) operated by Welch® Gardner Denver vacuum pump, (Thomas GmbH, Fürstenfeldbruck, Germany). The targeted analytes were determined using GC model 1300 gas chromatography (Thermo Fisher Scientific, Santa Clara, California, U.S) equipped with Rtx column (30m x 0.25mm x 0.25µm) and flam ionized detector. The GC used at recommended operating conditions for the analysis of targeted organic compounds.

2.4. Samples collection

Bottled Water samples were collected from local supermarkets. The samples were collected from different brands of different sizes. The type of packaging used was Polyethylene Terephthalate, High Density Polyethylene and Polyvinyl Chloride.

2.5. Sample preparation

Sample preparation was performed by solid phase extraction (SPE) manifold using C18 40-60 µm,120Å 500mg/6ml cartridges following a method adapted from that reported in literatures (Jin *et al.* 2010; Ghanem *et al.* 2013) and the official EPA method 8270D (Epa 2007). Briefly, the SPE cartridges were cleaned three time with 2 ml dichloromethane (DCM), 2 ml acetone, dried with nitrogen and conditioned with 1:1 water: methanol. 250 ml sample (acidified to pH 2 with HCl) was loaded to the cartridge at pressure 20 psi. Cartridge was dried with nitrogen, then the trapped VOCs were eluted into 5ml of dichloromethane, and a precleaned portion of oven dry sodium sulphate was added to remove any water residue. Similarly, another 250 ml water sample (its pH to 12 adjusted with NaOH) was loaded to SPE cartridge following same procedure. Both elutes were mixed and analyzed by GC-MS.

3. Results and discussion

3.1. GC-MS calibration

The GC-MS was calibrated with a certified mixture of 26 VOCs diluted in DCM. The chromatogram presented in **Figure 1** illustrates that the components were well separated, exhibiting good resolution.

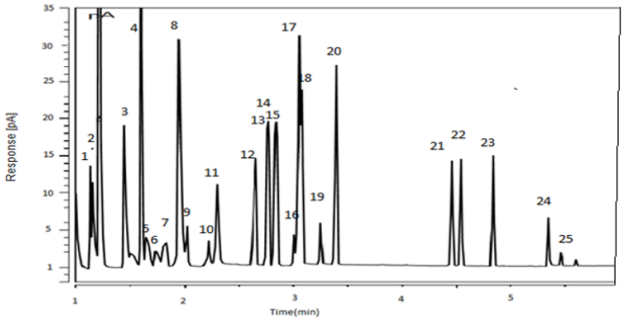


Figure 1. Chromatogram example of VOCs certified standard reference material (5 µg/L). The figure represents: 1 (Dichloromethane), 2 (Vinyl Chloride), 3 (Bromo methane) , 4 (Allyl Chloride), 5 (Methylene Chloride), 6 (1,1-Dichloroethane), 7 (Acrylonitrile), 8 (1,1Dichloroethene), 9 (Vinyl Acetate), 10 (Bromo chloromethane), 11 (Chloroform), 12 (Carbon tetrachloride), 13 (Propargy lAlcohal), 14 (1,1,1Trichloroethane), 15 (2Butanone), 16 (Benzene), 17 (Dichloromethe), 18 (Methacrylonitril), 19 (1,2-Dichloroethane), 20 (Trichloroethane), 21 (1,4-difluorobenzene), 22 (Dibromomethane), 23 (Bromodichloromethane), 24 (1,2-dichloropropane), 25 (Toluene), 26 (1,4-Dichlorobenzene)

Eight VOCs were selected for analysis in bottled water. The VOC analytes, eluted from the SPE procedure, were analyzed using GC-MS. Their retention times (Rt), molecular weights, and coefficients of regression equations are depicted in **Table 1**.

Table 1. VOCs analyzed, ordered by retention time (Rt), molecular weight, calibration equation and coefficient of regression.

Compounds	Chemical formula	Boiling point (°C)	M.W(g·mol^{-1})	R_t (min)	R^2
1,1, Dichloroethane	$C_2H_4Cl_2$	57.2	98.96	1.75	0.9996
Benzene	C_6H_6	80.1	78.11	3.347	0.9981
1,2-Dichloroethane	$C_2H_4Cl_2$	84	98.95	3.32	1.0000
1,4-Difluorobenzene	$C_6H_4F_2$	97	114	4.43	1.0000
Bromodichloromethane	$CHBrCl_2$	90	163.8	4.73	0.9998
1,2-Dichloropropane	$C_3H_6Cl_2$	95	112.98	5.34	1.0000
Toluene	C_7H_8	111	92.14	5.41	0.9992
1,4-Dichlorobenzene	$C_6H_4Cl_2$	174	147	5.26	0.9924

The chromatogram presented below (**Figure 2**) exemplifies the analysis of a sample following its extraction process.

3.1.1. Response and repeatability of GC –MS system

The analytical method development experiments have been conducted using a mixture of benzene and toluene. The two compounds used to validate the repeatability of GC –MS system and the feasibility of SPE for extraction of the volatile molecules from water samples.

The response and repeatability of GC–MS system was validated by the injection (3 times) of benzene and toluene mixture (2 µg/L) in dichloromethane (**Figure 3**).

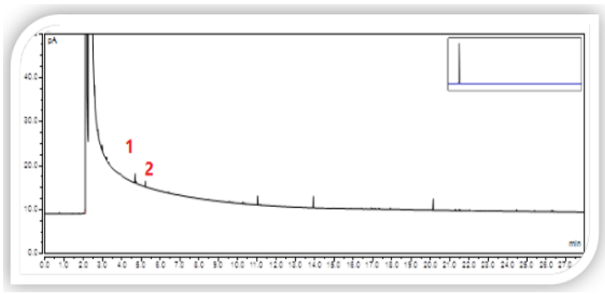


Figure 2. Chromatogram example of a sample analysis after extraction. 1(1,4-difluorobenzene), 2 (Toluen)

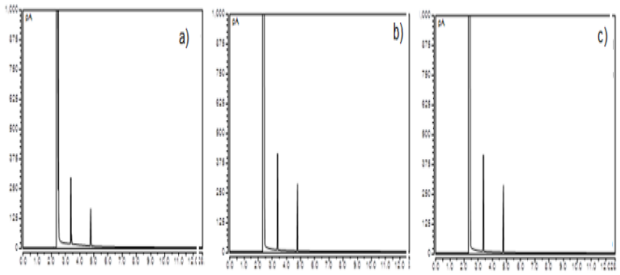


Figure 3. Chromatogram benzene and toluene in DCM (direct injection of 2 µg/L) injected three times a, b and c

The chromatograms of the three injections presented in **Figure 3** indicated that the benzene and toluene peaks are well resolved with adequate repeatability so that the GC-MS system anticipated to work well with the targeted analytes.

3.2. Validation of the SPE method

The solid-phase extraction (SPE) process has been proposed for the extraction of analytes from water samples. To verify the validity of the SPE method for this purpose, a standard solution comprising toluene and benzene was prepared/spiked at a concentration of 1 µg/L in 100 ml distilled water. The solution was processed using the SPE protocol and then analyzed by GC-MS. The results of three replicates are shown in **Figure 4**. The satisfactory resolution of the chromatographic peaks with adequate reproducibility demonstrates the appropriateness of the SPE method for the extraction of the analyzed compounds.

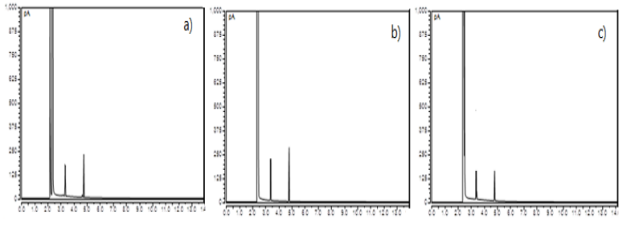


Figure 4. Chromatogram benzene and toluene in distilled water after SPE with C18 cartridge (100 ml, 1µg /L) Repeated three times a, b and c

3.3. Comparison of SPE and LLE

LLE method is a common procedure to extract organic compounds from water samples. To compare the performance of SPE to the LLE a mixture of toluene and benzene (2µg /L in 100 ml distilled water) was processed using LLE protocol and then analyzed by GC-MS. The results of three samples are shown in **Figure 5**.

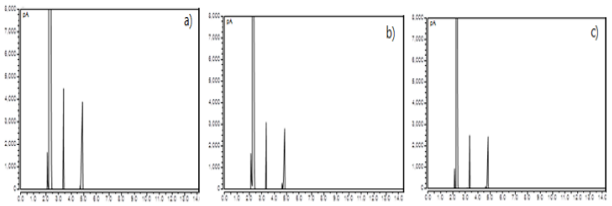


Figure 5. Chromatogram benzene and toluene in distilled water after using LLE (2 µg/L) Repeated three times a, b and c

As can be seen from the **Figures (4 & 5)** there was no significant difference between the two methods but the SPE method is favored as an ecofriendly method. So, the SPE was proposed in this work to be suitable method for sample preparation.

3.4. Volatile organic compounds in bottled water samples

The existence of organic compounds in bottled water could be ascribed to the migration of organic fragments from plastic bottles, especially upon storage in hot place or during transportation. Water contact with plastic pipes and plastic filter during production/bottling is also expected to be an indispensable source for the occurrence of organic in bottled water (Alshehri *et al.*, 2022; Khalili Sadrabad *et al.*, 2023).

In this study, the screening and analyzed organic pollutants found in bottled water, forty bottled water samples from the popular brands distributed in Almadinah AlMunawrah local market, have been analyzed for eight organic compounds. **Figure 6** shows the heatmap for VOCs concentrations across 40 samples (40 brand names). The key observation can be summarized in the following:

1,1-Dichloroethane is detected in a few samples with relatively low concentrations, except for sample 4 which shows a higher concentration of 5.39 µg/L.

Benzene concentrations vary, with a notable peak of 103.61 µg/L in sample 19, indicating significant contamination in this particular sample.

1,2-Dichloroethane shows fluctuating levels across the samples where it is detected, with sample 1 having the highest concentration at 27.01 µg/L.

Bromodichloromethane is more consistently found across samples, with concentrations ranging from low to moderate levels, peaking at 77.605 µg/L in sample 3.

1,2-Dichloropropane is notably detected only in two samples in which sample 18 contained the highest concentration of 8.9001 µg/L.

1,4-Fluorobenzene and **Toluene** show sporadic detection across samples. Toluene, in particular, shows a very high concentration of 200.21 µg/L in sample 4.

1,4-Dichlorobenzene is detected in a few samples, with the highest concentration being 2.25 µg/L in sample 40.

Also, as shown in **Table 2** and their concentration disparity represented in **Figure 7**, Bromodichloromethane (BDCM) and Toluene (T) were the most common organic

pollutants detected in the analyzed samples. The bromodichloromethane was detected in 16 samples included trace concentration (40%) while toluene was found in 14 samples (35%). The average bromodichloromethane content was 13.998 µg/L, and its concentration in the contaminated samples ranged from 0.0753 to 73.56 µg/L. However, its concentration in most of samples was less than the WHO recommended level of 60 µg/L (except in two samples (5%) where it was found to exceed the WHO recommended level (see **Figure 7a**).

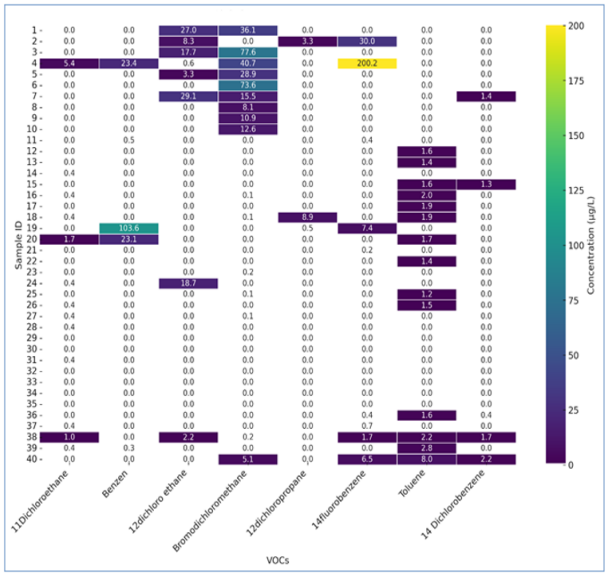


Figure 6. Heatmap of VOC concentration across samples

The presence of bromodichloromethane (BDCM) in approximately 40% of the bottled water samples could be indicative of disinfection by-products (DBPs) resulting from exposure to chlorinated water or chloramine-based disinfection processes. Studies have documented similar levels of BDCM in bottled waters sourced from chlorinated municipal supplies or treated with chlorine for microbial safety (Al-Mudhaf *et al*. 2009; Ikem 2010). The detection of other trihalomethanes (THMs), such as chloroform, bromoform, or dibromochloromethane, could help clarify the contamination profile, as these compounds often co-occur in chlorinated waters (Leivadara *et al*. 2008). While most BDCM concentrations in this study remained below WHO-recommended limits (60 µg/L), two samples exceeded these guidelines, warranting further examination of the source water quality and potential disinfection practices.

Former screening on bottled water samples from Kuwait market declared an average concentration of 0.83 µg/L of bromodichloromethane (Al-Mudhaf *et al.* 2009). An average concentration of 1.24 µg/L of this pollutant also detected in bottled water sample from USA market (Ikem 2010). The average Toluene content was 2.2003 µg/L, and its concentration ranged from 1.2295 to 8.0134 µg/L (see **Figure 7b**). Providentially, the concentration of Toluene in the analyzed samples was less than the WHO recommended level of 700 µg/L. In a previous study in Kuwait an average concentration of 0.46 µg/L of Toluene was found in Bottled water (Al-Mudhaf *et al.* 2009). Higher concentration was found in bottled water samples produced in USA (average concentration of 24 µg/L) (Ikem 2010). Moreover, larger amounts (average 52 µg/L) was found in bottled water samples distributed in Lebanon (Ghanem *et al.* 2013).

Benzene was less frequent pollutant in the studied bottled water. It was present in 6 samples (15%) with an average content of 25.1470 µg/L and its minimum and maximum concentration ranged from 0.0452 to 103.61 µg/L. The concentration of benzene in three samples (7.5%) was higher than the WHO recommended level of 10 µg/L, as shown in **Figure 7c**. Benzene was detected in previous study carried out on Bottled water from Kuwait market, where its average concentration was 0.78 µg/L (Al-Mudhaf *et al.* 2009).

A former study on bottled water sample from Yanbu shops, Saudi Arabia also reported an average concentration of 0.16µg/L (Ahmad & Bajahlan 2007). Furthermore, a higher concentration of benzene (49 µg/L) was found in bottled water samples sold in Lebanon market. Exposure to elevated concentrations of benzene affects the central nervous system and could also cause leukemia (Ghanem *et al.* 2013).

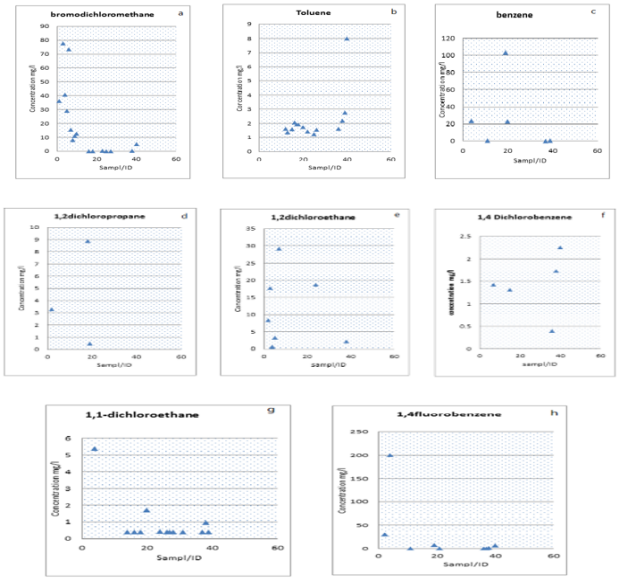


Figure 7. Disparity of organic compounds concentrations (µg/L) in bottled water samples

This investigation has indicated that 1, 2dichloroethane (1,2DCE) exists in eight samples (20%). Its average concentration was 10.780 µg/L, with range from 0.64 to 29.11 µg/L (see **Figure 7e**). However, the concentrations of 1,2DCE in all samples were within the WHO recommended level of 50 µg/L.

Similarly, 1,2dichloropropane (1,2DCP) was found in three samples (7.5%). However, the concentration was less than the WHO recommended level of 40 µg/L. The average of 1,2DCP content was 4.680 µg/L, with range from 0.4616 to 8.900 µg/L. However, the concentration was within the WHO recommended level of 40 µg/L. The variation of 1,2DCP concentration depicted in **Figure 7d**.

In a previous study conducted in Kuwait the average concentration of 1,2DCP in bottled water was 0.46 µg/L (Al-Mudhaf *et al.* 2009). The compound, 1,4

Dichlorobenzene (1,4DCB) monitored in five samples (12.5%) with high disparity as seen in (**Figure 7f**), nonetheless the concentration of 1,4DCB in all samples was less than the WHO recommended level of 300 µg/L.

Additionally, the compounds; 1,1-dichloroethane (1,1DCE) and 1,4-difluorobenzene (1,4FB) were detected in 13 samples (30%) and 9 samples (22.5%) respectively with perceived variations in concentration (see **Figure 7g & 7h**). However, none of these compounds were investigated in former studies. **Figure 7** shows an example of disparity in the analysis of a bottled water sample using GC-MS.

Table 2. Concentration of the studied organic compounds in bottled water sample (µg/L)

Samples	Compounds /concentration (µg/L)							
	1,1DCE	**B**	**1,2DCE**	**BDCM**	**1,2DCP**	**1,4FB**	**T**	**1,4DCB**
Min	0.3982	0.0452	0.64	0.0753	0.4616	0.1798	1.2295	0.398
Max	5.39	103.61	29.11	73.56	8.9001	200.21	8.0134	2.25
Mean	0.92	25.1470	10.780	13.998	4.680	27.184	2.2003	1.394
SD	1.3931	40.04	10.66	25.61	4.293	65.45	1.71	0.523
SUM	12.075	150.882	53.904	195.985	9.361	217.477	30.80	7.11
% Analytes in samples	30	15	20	40	7.5	22.5	35	12.5
WHO limit µg/L	-	10	50	60	40	-	700	300
% of samples above the limit	-	7.5	0	5	0	-	0	0

Table 3. Comparison between the concentration of organic compounds and previous studies µg/L.

Location	benzene	bromodichloromethane	1,2dichloropropane	Toluene	Ref.
This Study	25.14	10.7	13.9	2.84	This study
Kuwait	0.78	0.83	0.46	0.46	(Al-Mudhaf *et al.* 2009)
USA	___	1.24	___	___	(Ikem 2010)
Lebanon	49	___	___	52.5	(Ghanem *et al.* 2013)
Yanbu, KSA	0.73	___	___	1.24	(Ahmad & Bajahlan 2009)

3.5. Comparison of the concentration of volatile organic compounds in bottled water samples with other studies

Some of the VOCs pollutants of concern in this study have been reported in former investigations by other researchers as shown in **Table 3**. The most frequent VOCs that seems to be common in bottled water samples are benzene, toluene, bromodichloromethane and 1, 2-dichloropropane. The data presented in Table 3 demonstrate that the concentration of benzene in this work were higher than that reported in samples from Yanbu and Kuwait but lower than the average concentration found in samples from Lebanon market. Similar observation also can be seen for toluene. On the other hand, the average concentrations of bromodichloromethane and 1,2dichloropropane obtained in this work were significantly greater than that reported in samples from Kuwait and Yanbu shops.

3.6. Correlation of the concentration of volatile organic compounds in bottled water samples

Figure 8 shows the correlation between the organic compounds in the bottled water samples. Correlation coefficients range from -1 to 1, where 1 means a perfect positive linear relationship, -1 means a perfect negative linear relationship, and 0 implies no linear correlation.

The correlation matrix suggests that some compounds have strong positive correlations with each other, indicated by the darker red squares (e.g., the pair Benzene and 1,4-Dichlorobenzene). This might imply that these compounds tend to increase or decrease together in concentration, potentially due to common sources or similar environmental behavior. Conversely, dark blue squares (e.g., between 1,1-Dichloroethane and 1,4-Dichlorobenzene) suggest a negative correlation, where one compound's concentration increases as the other decreases. White or light-colored squares indicate a lack of significant correlation.

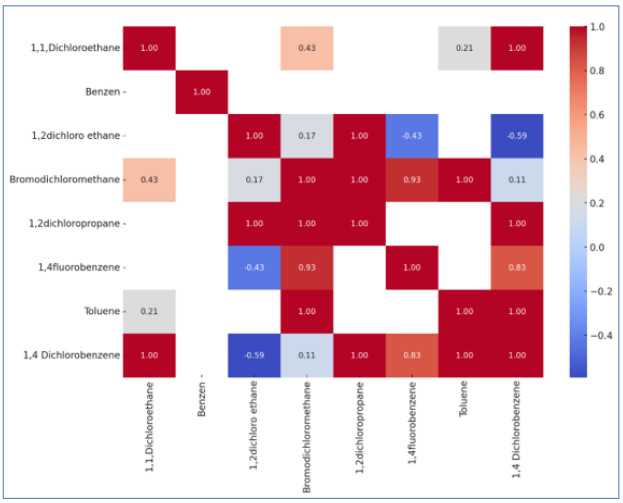


Figure 8. Correlation Matrix Compound Concentrations

3.7. Dimensionality Reduction of VOCs Dataset Using PCA accompanied by hierarchical clustering Analysis

The PCA of VOCs dataset resulted in a 2-dimensional representation, as visualized in the scatter plot (**Figure 9**). This plot provides insights into the data's underlying structure, revealing patterns, clusters, or outliers that may exist within the dataset. The first principal component explains approximately 27.9% of the variance in the dataset, while the second principal component accounts

for about 20.8%. Together, these two components explain roughly 48.7% of the total variance.

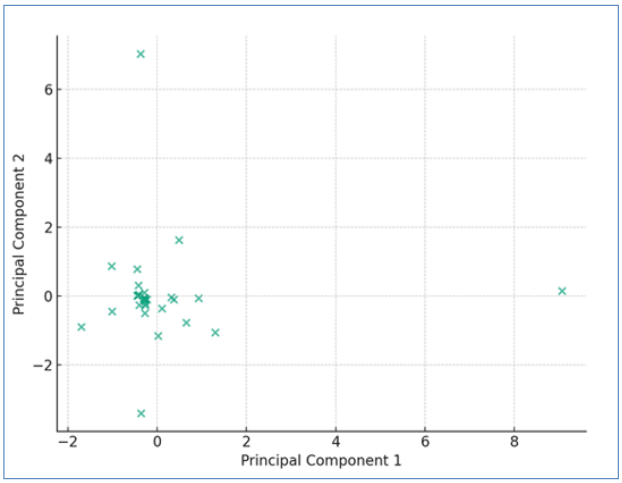


Figure 9. PCA of VOCs Dataset

The component loadings (**Figure 10**) indicate the contribution of each original variable (feature) to the principal components. Here are some observations from the first two principal components:

PC1 is significantly influenced by "1,1, Dichloroethane" with a loading of 0.636, suggesting that variations in this compound contribute considerably to the variance captured by PC1. The PC2 shows more balanced contributions from different compounds, though no single compound dominates this component significantly, indicating that PC2 captures a more diverse aspect of the dataset's variance.

The cumulative in **Figure 10** explained variance plot helps in determining the number of components needed to capture a significant portion of the total variance in the dataset. The first component explains about 27.9% of the variance. The first two components together explain approximately 48.7% of the variance. To capture over 80% of the variance, we need four components. To capture over 90% of the variance, six components are required. With all eight components, 100% of the variance is captured, as expected.

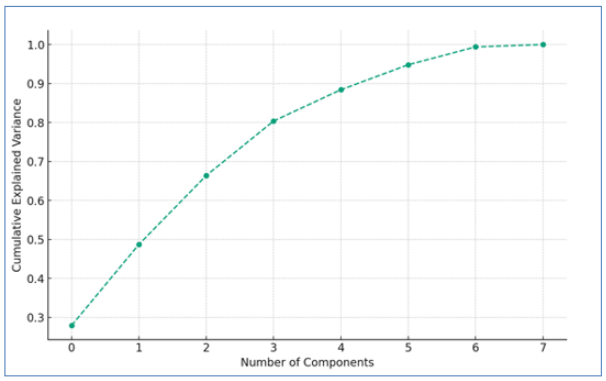


Figure 10. Cumulative Explained Variance by PCA components

Figure 11 presents the PCA-reduced data with K-means clustering, where we chose to segment the data into three clusters (a choice based on visual inspection and simplicity, but this can be refined with techniques like the elbow method or silhouette analysis for optimal cluster number determination). It presents the PCA-reduced data with K-means clustering, where we chose to segment the data into three clusters (a choice based on visual inspection and simplicity, but this can be refined with techniques like the elbow method or silhouette analysis for optimal cluster number determination).

Clusters: Each point represents a sample, colored according to the cluster it belongs to. The clustering suggests natural groupings within the data based on the first two principal components.

Cluster Centers: Marked with red 'X', these indicate the centroids of the clusters, representing the "average" location of each cluster in the PCA-reduced space.

The dendrogram (**Figure 12**) depicts the results of a hierarchical cluster analysis of 40 water samples based on 8 VOCs. Samples are grouped by similarity, with the y-axis indicating the distance or dissimilarity between clusters. Shorter vertical lines show similar samples, and the structure suggests possible natural groupings within the data. A chosen cut-off distance across the dendrogram defines the number of distinct clusters.

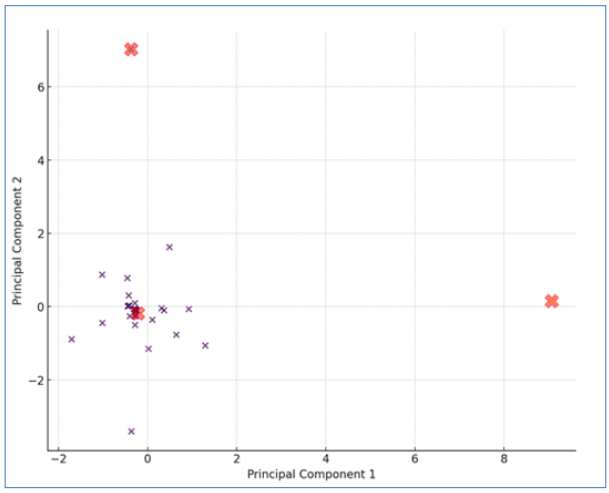


Figure 11. PCA-reduced Data with K-means Clustering

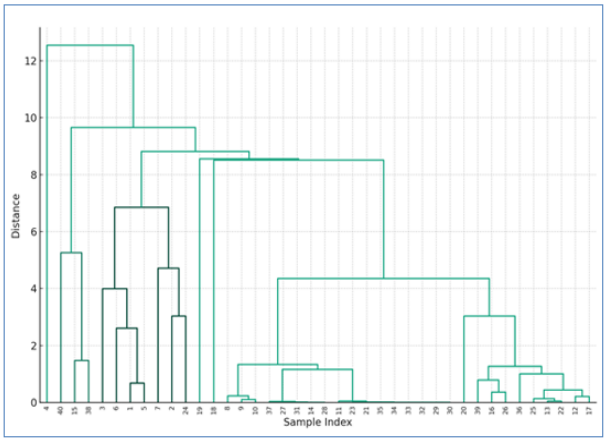


Figure 12. Hierarchical Clustering Dendrogram

4. Conclusions

This preliminarily screening confirms that bottled water could contain significant levels of VOCS. Forty bottled water samples from the popular brands distributed in Almadinah AlMunawrah local market have been analyzed

for eight organic compounds (1,1, Dichloroethane (1,1DCE), Benzen (B), 1,2dichloroethane (1,2DCE), Bromodichloromethane (BDCM), 1,2dichloropropane (1,2DCP), 1,4-difluorobenzene (1,4FB), Toluene (T), 1,4 Dichlorobenzene (1,4DCB). Bromodichloromethane was one of the most common compounds in bottled drinking water, identified in about 40% of the samples. Toluene followed in 35% of the samples, and 1,2-dichloropropane was the least common component, found in 7.5% of the samples. However more detailed study using large number of samples must be undertaken to draw clear conclusion on the occurrence of VOCs and other organic contaminants in bottled water. Further work will be accomplished for the analysis of VOCs and other organic molecules in bottled water. Particularly, the findings indicate that bottled water may contain DBPs such as bromodichloromethane, likely arising from chlorination or disinfection practices associated with the water source. Further investigation, including the analysis of other DBPs (e.g., chloroform, dibromochloromethane, bromoform), could provide a more comprehensive understanding of VOC contamination and its sources in bottled waters. Other sample preparation methods such as headspace, purge and trap, as well as highly sophisticated analytical methods like gas chromatography-tandem mass spectrometry (GC-MS/MS), are recommended.

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References

Ahmad M. and Bajahlan A.S. (2007). Leaching of styrene and other aromatic compounds in drinking water from PS bottles, *Journal of Environmental Sciences*, **19**, 421–426.

Ahmad M. and Bajahlan A.S. (2009). Quality comparison of tap water vs. bottled water in the industrial city of Yanbu (Saudi Arabia), *Environmental Monitoring and Assessment*, **159**, 1–14.

Al-Mudhaf H.F., Alsharifi F.A. and Abu-Shady A.-S.I. (2009). A survey of organic contaminants in household and bottled drinking waters in Kuwait, *Science of The Total Environment*, **407**, 1658–1668.

Alshehri M.M., Ouladsmane M.A., Aouak T.A., ALOthman Z.A. and Badjah Hadj Ahmed A.Y. (2022). Determination of phthalates in bottled waters using solid-phase microextraction and gas chromatography tandem mass spectrometry, *Chemosphere*, **304**, 135214.

D'Altrui E.M. (2017). Bottle Water Bans: How can we curb the thirst for bottled water? *Elements*, **13**.

Dattilo S., Gugliuzzo C., Mirabella E.F., Puglisi C., Scamporrino A.A., Zampino D.C. and Samperi F. (2022). Characterization of VOCs and additives in Italian PET bottles and studies on potential functional aldehydes scavengers, *European Food Research and Technology*, **248**, 1407–1420.

Diduch M., Polkowska Ż. and Namieśnik J. (2013), Factors affecting the quality of bottled water, *Journal of Exposure Science & Environmental Epidemiology*, **23**, 111–119.

Epa (2007). Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), *US Environmental Protection Agency*, 1–72.

Ghanem A., Maalouly J., Saad R.A., Salameh D. and Saliba C.O. (2013), Safety of Lebanese Bottled Waters: VOCs Analysis and Migration Studies, *American Journal of Analytical Chemistry*, **04**, 176–189.

Guadayol, M., Cortina, M., Guadayol, J.M., & Caixach, J. (2016), Determination of dimethyl selenide and dimethyl sulphide compounds causing off-flavours in bottled mineral waters, *Water Research*, **92**, 149–155.

Ikem A. (2010). Measurement of volatile organic compounds in bottled and tap waters by purge and trap GC–MS: Are drinking water types different? *Journal of Food Composition and Analysis*, **23**, 70–77.

Jin B.H., Xiao F., Chen B., Chen P.J. and Xie L.Q. (2010). Simultaneous determination of 42 organic chemicals in bottled water by combining C18 extraction disk with GC-MS and LC/MS/MS technique, *Journal of Water and Health*, **8**, 116–125.

Khalili Sadrabad E., Hashemi S.A., Nadjarzadeh A., Askari E., Akrami Mohajeri F. and Ramroudi F. (2023). Bisphenol A release from food and beverage containers – A review, *Food Science & Nutrition*, **11**, 3718–3728.

Leivadara S.V., Nikolaou A.D. and Lekkas T.D. (2008). Determination of organic compounds in bottled waters, *Food Chemistry*, **108**, 277–286.

Muhamad S., Esmail L. and Hasan S. (2011). Effect of storage temperature and sunlight exposure on the physicochemical properties of bottled water in Kurdistan region-Iraq, *Journal of Applied Sciences and Environmental Management*, **15**.

Zaater M.F., Tahboub Y.R. and Al Sayyed A.N. (2013). Determination of Phthalates in Jordanian Bottled Water using GC–MS and HPLC–UV: Environmental Study, *Journal of Chromatographic Science*, **52**, 447–452.