

Release of organic contaminants migrating from polyvinyl chloride polymeric into drinking water under three successive stagnant periods of time

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ABSTRACT

Drinking water is found contaminated with various volatile organic compounds (VOCs) at supply end. Chlorinated polyvinyl chloride (CPVC) and polyvinyl chloride (PVC) pipes used to supply drinking water may be the possible source of the contamination. In this study, leaching ability of VOCs from CPVC and PVC was tested under controlled experimental conditions and correlated with real water samples. For experimental design, nine polymeric plastics in Saudi Arabia were purchased locally and incubated with pure water for leaching study. A total of 58 tap water samples were collected from buildings and villas within the city of Madinah Al-Munawwarah and analyzed for the targeted compounds including benzene, 2-butanone, 1,1,1-trichloroethane, pyridine, 1,2-dichloropropane, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane, phenol, benzyl chloride, 2-nitrophenol, 2,4-dichloropropane, and 2,4,6-trichlorophenol. Analytical results show that volatile and phenolic contaminants released by tested pipes increased significantly over incubation time. The quantification of the targeted compounds in Milli-Q water samples incubated in pipes in laboratory-scale experiment conformed that these contaminants are more likely to be migrated from PVC plastic pipes comprising tap water. The levels of some contaminants were above the limits stated by World Health Organization, while others were within the allowable levels. Their accumulation during longer contact time can potentially increase the exposure to harmful constituents in water and causes health problems. The results also indicated a correlation between the source of contamination and level of pollutants.

Keywords: Organic contamination; Water quality; VOCs; Phenols; Plastic pipes; Kingdom of Saudi Arabia

1. Introduction

Plastic pipes made of polyvinyl chloride (PVC) are used widely in the drinking water supply systems compared with the old metallic pipes due to the resistivity toward corrosion, long durability, cost effective, etc. [1]. However, plastic materials are important and have been applied in various

applications in recent years [2]. The quality of water flows in these polymeric plastic pipes can be affected by contamination of components from the plastic materials. Leaching of phenolic contaminants related to antioxidants used in the manufacturing from various types of plastic pipes made of PVC, polyethylene (PE), cross-linked polyethylene (PEX), polypropylene (PPR), and high-density PE is affecting potable water distribution networks in many countries in the world [3]. Previous studies on volatile leached compounds during

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processing and thermal degradation of polymers have been carried out intensively [4]. The United States Environmental Protection Agency (EPA) spent about \$20–\$22 billion USDs over the next 20 y for maintaining and replacing its existing infrastructure in water distribution system. In the 10th five-year plan, China employed plastic pipes with particular pipe diameter below 400 mm in urban water networks which accounts for 80% of Materials Committee 2000. Currently, approximately 69% of the polymeric pipes used in the drinking water network system are from synthetic materials [5]. Studies concerning the migration of organic contaminants from synthesized polymeric pipes into water have revealed that many volatile organic compounds (VOCs) were found in the water running through the polybutylene, PVC, PPR, PE, and chlorinated polyvinyl chloride (CPVC) pipes [6]. PE and PVC fulfilled 33.35% and 62% of the demand, respectively.

There are many evidences from recent researches that the synthetic materials like plastic pipes used in water distribution systems are capable of leaching various VOCs and phenolic organic compounds [7]. These contaminants, which are mainly released from the additive agents to the polymer materials during synthesis, can change the quality of drinking water, thus diminishing water quality and impairing human health [8]. Measure of migration of organic contaminants from pipe materials varies depending on the temperature, structure of polymer, and the antioxidant additives [9]. The organisms that grow on pipe surface, lining materials, and water chemistry also play significant roles on the leaching process. Polystyrene is able to release residual styrene monomer and other VOCs including benzene, toluene, pentane, ethyl benzene, xylene, isomers, *n*-propyl benzene, 1,2,3-trimethylbenzene, methyl styrene, benzyl aldehyde, benzyl chloride, alcohol, and acetophenone at room temperature [10,11]. These products are formed by the polymerization of styrene monomer in the presence of blowing agent such as pentane [11]. These compounds are classified among the hazardous environmental pollutants that harm human health [8] by inducing negative effects on the mucous membranes of the eyes, skin, nose, face, throat, neck, and hands [12]. International Agency for Research on Cancer (IARC) considered styrene is the main compound released from expended polystyrene products that affects human health inducing risk of cancer (Group 2B) [13]. When inhaled, styrene causes tissue irritation and neurological impairment

[14]. Our previous work has demonstrated that PE pipes, PEX, can be a potential source for contamination of tap water with significant levels of organic pollutants, e.g., VOCs [15]. Analysis on 5,083 samples from a total of 473 sampling points was conducted in Malaysia. Out of 473 sampling points monitored, 278 (59%) were classified as clean, 161 (34%) were slightly polluted, and 34 (7%) were considered polluted [16].

The present study aimed on identifying targeted trace organics, e.g., phenols and volatile halogenated hydrocarbons leaching from polymeric pipes used in domestic water supply under different incubation time periods. This study was extended further to identify the compounds released in field conditions, where water samples from old and new houses and newly installed pipes in a distribution network were collected. Thus, the objective of this research was to screen tap water samples for the presence of volatile and phenolic compounds and correlate them to the PVC plastic pipes used in the present study.

2. Materials and methods

2.1. Materials, chemicals, and instrumentation

Different types of polymeric pipes were purchased from local market and used to perform the migration test for organic contaminants leached from plastic pipes into test water conducted in the laboratory of three successive incubation cycles (Table 1). Table 1 describes the nine different types of polymeric pipes (PVC, CPVC, un-plasticized polyvinyl chloride (UPVC), PPR, and PEX-a) that were used for the migration study in the laboratory. The nine plastic pipes represent pipe materials commonly used in drinking water distribution network. The length of pipes is 2 m with the following internal diameters: *A*, 33.4–104 mm; *B*, 33.4–50 mm; *C*, 40 mm; *D*, 40 mm; and *E*, 104 mm. Pipes *A* and *B* consist of PVC and CPVC, respectively, whereas pipe *C* consists of UPVC, pipe *D* consists of PPR, and pipe *E* consists of PEX.

All pipes used in the present study were obtained directly from the local market and packed in aluminum foil and stored in paper bags prior to analysis. Solid-phase extraction (SPE) cartridges HLB 6 cc/200 mg absorbent per cartridge were purchased from Oasis, Product number WAT 106202, China. This cartridge is a universal polymeric

Table 1
Description of the different types of polyvinylchloride (PVC) plastic pipes tested

Pipe ID	Pipe type	Size (mm)	Manufacturer	Application	Country made
PVC	CPVC	33.4	Nepro plastic	Water ASTM	KSA
PVC	PVC	33.4	Gepco plastic	Water ASTM	USA
PVC	CPVC	32.0	QSU plastic	Water ASTM	Jordan
PVC	CPVC	34.4	Gepco plastic	Water ASTM	KSA
PPR	Type III	40.0	Gepco plastic	Water ASTM	KSA
PVC	UPVC	40.0	Nepro plastic	Water ASTM	KSA
PVC	CPVC	50.0	Nepro plastic	Water ASTM	KSA
PVC	PVC	104.0	BSC plastic	Water ASTM	Bahrain
PEX	PEX-a	104.0	Gepco plastic	Water ASTM	KSA

reverse-phase sorbent that was developed for extraction of neutral, acidic, and basic compounds from various matrices using a generic protocol. Similarly, pure chemicals were purchased from Sigma-Aldrich Bayouny Trading Co. Ltd., Saudi Arabia. Standards of Phenols Calibration Mix (11 components-31029) and Standard of Volatiles Organic Mega Mix (76 components-30633) were purchased from Restek representative (US) Ashban chemicals (Jeddah, KSA) for the determination and quantification of phenols and volatile organic contaminants. Thermo Fisher Scientific (Mexico, USA) Model 1300 gas chromatography (GC) coupled with flame ionization detector (GC-FID) with column specification of RTX 30 m × 0.25 mm, internal diameter (ID) 1.40 μm was used for the analysis. GC-FID was calibrated before analysis for identification of phenols and volatile identification individually.

2.2. Migration experiment protocol

An experimental protocol procedure was constructed to investigate migration of organic pollutants from polymeric plumbing pipes. Nine 6-m pipes were examined, each of three (2 m) segments were used to accommodate the required sample volume for analysis. The inner surface of the pipe was brought into contact with the test water for three-cycle incubation periods (24 h) at ambient temperature. Prior to test, the pipes were flushed 3 times with purified water for 5 min. The pipes were then filled with test water, and the two ends were closed using brass stoppers and left for incubation cycle 1 (24 h). The incubated water samples were stored in fridge until subsequent preparation and analysis. Same procedure was followed for incubation cycles 2 (48 h) and 3 (72 h). Between incubation cycles, the pipes were flushed with purified water for 5 min to minimize cross-contamination from previous incubated water. Each polymeric pipe was tested in triplicate. Blank samples were produced by incubating water in glass tubes resembling plastic pipes with brass stoppers inside glass tubes. Then, the test water was removed, and subsequently, the migrated organic compounds were extracted using SPE. The extract was analyzed, and the determination of volatile compounds was conducted by GC-FID [17]. Each polymeric pipe was analyzed in triplicate. Blank

controlled samples for the tests of migration and extraction were also performed.

2.3. Sample preparation

Method adapted from the official EPA method 8270D (EPA 2007) has been utilized for the extraction of the leached organic compounds from incubated water. In this procedure, water samples were divided into two portions. The first portion was acidified to pH 2, and the other part was adjusted to pH 12. The two portions were pretreated in the following sequences. First, SPE cartridges were preconditioned with 5 mL of 0.045 M HCL, and then 100 mL of water sample was loaded to HBL 6 cc/200 mg cartridge at 5 mL/min, with standard ASE-12 head manifold Auto Science (EPA following the official EPA method 8270D). After extractions, cartridges were dried for 5–10 min on a positive pressure with nitrogen, and then trapped volatile contaminants were eluted with 2 mL of dichloromethane with oven dried sodium sulfate, LiChrolut EN resins [18].

2.4. Characterization of GC-FID

The determination of the organic compounds extracted from the leached water was obtained from a GC-FID-1300 Thermo. Hydrogen gas was used as a carrier gas at a constant flow of 5 mL/min. Two microliters of extracted solution was injected in the split-split mode into injection port at initial temperature of 280°C. Employing a capillary column of RTX 30 m × 0.25 mm, ID 0.25 mm film thickness, the oven temperature was held at 45°C for 4 min, raised by 10°C/min to 200°C, and then held for 5 min at 280°C for 15°C/min. Part of identification of the extracted components was made using the calibration results which was performed of three-point calibration as presented in Table 2.

2.5. Quality control

Three-point calibration curves in triplicates were made for different chemicals ranging from 1 to 8.0 mg/L. The calibration curves were made using standards containing all parameters generated by GC-FID. Values were calculated

Table 2
Calibration parameters for analyzed organic compounds at the gas chromatography operating conditions (GC-FID)

Compounds	R_i (min)	Molecular weight (g/mol)	Calibration equation	R^2
1,1,1-Trichloroethane	2.34	133.4	$Y = 0.0705X - 0.2$	0.9990
2-Butanone	2.43	72	$Y = 31.992X + 6.6794$	0.9982
Benzene	2.46	78	$Y = 38.751X - 34.535$	0.9981
1,2-Dichloropropane	3.96	113	$Y = 0.0213X - 0.0224$	0.9999
Pyridine	4.71	79.1	$Y = 0.1520X - 0.0632$	1.0000
1,1,2,2-Tetrachloroethane	11.58	167.85	$Y = 0.0186X - 0.0083$	0.9992
1,2,3-Trichloropropane	11.85	147.4	$Y = 0.0210X + 0.0001$	0.9932
Benzyl chloride	14.96	126.6	$Y = 15.16X + 1.0821$	0.9945
2,4,6-Trichlorophenol	17.54	197.5	$Y = 0.001X - 0.30$	0.9970
2-Nitrophenol	8.85	139.11	$Y = 0.001X - 0.50$	0.9960
2,4-Dichloropropane	9.92	163	$Y = 0.006X - 0.20$	1.0000
Phenol	7.03	94.1	$Y = 0.0013X - 0.10$	1.0000

from the correlation coefficients, while accuracies were calculated as the measured concentrations determined from the calibration curve. Table 2 describes calibration of each parameter for analyzed organic compounds at the GC-FID operating conditions as shown in Table 3.

3. Results and discussion

3.1. Concentration of organic contamination leached from PVC pipes

The migration of VOCs in water sources as investigated in many reports [19,20] shows that more than 15 VOCs have been identified in drinking water samples. Many chlorinated by-products, chlorinated solvents, and different levels of oxygenated methyl ethyl ketone (MEK) also have been detected in water samples from residential homes [21].

In the present work, nine different brands of polymeric pipes were tested under developed continuous procedure and analyzed for twelve targeted volatile and phenolic contaminants using capillary GC. The targeted contaminants detected in this study were benzene, 1,1,1-trichloroethane, 2-butanone, 1,2-dichloropropane, pyridine, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane (TCP), benzyl chloride, phenol, 2-nitrophenol, 2,4-dichloropropane (DCP) and 2,4,6-trichlorophenol that exist in the migration experiment conducted in laboratory at three successive periods of time. Similarly, Tables 4 and 5 show the concentrations of the

migrated compounds in the test water samples as well as the minimum, maximum, mean standard deviations, and World Health Organization (WHO) limits in drinking water from tested pipes. Table 6 shows concentrations of organic contaminants with minimum, maximum, mean, standard deviation, and percentage of water samples above the guideline values stated by WHO recorded in tap water samples.

One of the components is 1,1,1-trichloroethane which is being leached from all the examined pipes in the concentration between 0.05 and 11.46 $\mu\text{g/L}$ with mean value of 3.79 $\mu\text{g/L}$ and standard deviation of 4.85. Obviously, 1,1,1-trichloroethane leached during all of the incubation periods, but the highest amount seems to be leached in the second period. Pipes number 5, 6, and 8 leached more VOCs as compared with other pipes used in migration experiments. These compounds are widely used as cleaning solvents and for coatings of polymeric plastic pipes. The concentrations in drinking water in USA ranged from 0.02 to 0.6 $\mu\text{g/L}$ [22]. A concentration of 0.37 $\mu\text{g/L}$ was found in drinking water sample from Italy [21]. The occurrence of 1,1,1-trichloroethane in drinking water could cause many serious health impairments including vomiting and diarrhea in humans [18], and its allowable limit set by WHO is 200 $\mu\text{g/L}$.

Another identified component 2-butanone (MEK) was found leached from all nine brands of PVC pipes tested with concentrations between 4.97 and 26.79 $\mu\text{g/L}$, mean value of 14.24 $\mu\text{g/L}$, and standard deviation of 7.36. The primary use of this component as a 2-butanone was found in drinking water

Table 3
Optimization of gas chromatography with flame ionized detector

Operation condition of GC-FID	
Injection volume	2 μL
Carrier gas	Hydrogen
Column type	RTX 30 m \times 0.25 mm \times 0.25 μm
Column oven	Initial 45°C, hold 4 min, ramp 10°C/min to 200°C, hold 5 min, ramp 280°C, 15°C/min
SSL injector	250°C: Carrier gas hydrogen in split mode with split ratio of 100
Column flow	1.2 mL/min
Detection limit	Less than 1 $\mu\text{g/L}$ or ppb

Table 4
Quantified leaching components from GC-FID analysis of plastic pipes ($\mu\text{g/L}$) from the three incubation cycles

PVC	TCE	Butanone	Benzene	DCP	Pyridine	TCE	TCP	BC	TCP	2NP	DCP	Phenol
RT	2.34	2.36	2.37	3.96	4.71	11.58	11.85	14.96	7.03	8.85	9.92	17.54
PVC1	0.47	4.97	1.89	8.81	2.75	0.55	0.20	0.30	0.50	11.38	0.20	3.49
PVC2	0.05	10.99	1.89	8.93	7.08	0.50	0.30	0.63	0.20	12.40	7.47	5.10
PVC3	0.13	7.60	1.89	8.95	4.23	1.64	0.10	0.70	23.55	5.67	5.09	15.48
PVC4	0.05	13.86	5.52	18.14	2.58	1.59	0.56	1.53	0.20	18.80	3.56	2.79
PVC5	6.65	26.79	9.41	19.24	3.94	1.92	1.78	1.04	4.53	13.54	12.21	10.90
PVC6	11.45	14.28	13.24	2.68	2.11	1.49d	1.79	0.45	5.55	21.49	16.24	12.57
PVC7	0.40	15.11	9.39	18.03	2.44	4.64	0.50	1.40	4.91	20.28	23.52	7.13
PVC8	11.36	24.94	8.30	19.93	4.90	3.24	3.91	1.96	4.81	15.6	6–4	6.23
PEX-a	3.46	9.66	9.12	16.22	5.35	3.24	2.20	2.91	4.41	14.05	3.12	12.7

Table 5
Concentration of compounds with minimum, maximum, mean, and standard deviation of VOCs leached from PVC pipes ($\mu\text{g/L}$)

Compound	Minimum	Maximum	Mean	Standard deviation	WHO limits
1,1,1-Trichloroethane	0.05	11.45	3.78	4.85	200
2-Butanone	4.97	26.79	14.24	7.37	–
Benzene	1.89	13.24	6.74	4.13	5
1,2-Dichloropropane	2.68	19.93	13.44	6.17	30
Pyridine	2.11	7.08	3.93	1.65	–
1,1,2,2-Tetrachloroethane	0.29	4.64	1.76	1.41	40
1,2,3-Trichloropropane	0.10	3.91	1.26	1.27	70
Benzyl chloride	0.30	2.91	1.21	0.84	20
2,4,6-Trichlorophenol	0.20	23.55	5.41	7.16	10
2-Nitrophenol	5.67	21.49	14.80	4.93	40
2,4-Dichloropropane	0.20	23.52	8.61	7.42	40
Phenol	2.79	15.48	8.49	4.54	40

Table 6
Concentration compounds with minimum, maximum, mean, standard deviation, and percentage of analytes in drinking water sample ($\mu\text{g/L}$)

Compound	Minimum	Maximum	Mean	Standard deviation	% Analytes
1,1,1-Trichloroethane	0.02	10.23	1.21	2.45	74
2-Butanone	0.03	14.49	3.38	2.89	81
Benzene	0.90	11.34	2.03	2.42	81
1,2-Dichloropropane	1.02	12.07	4.97	4.60	25
Pyridine	0.29	19.98	2.55	3.41	77
1,1,2,2-Tetrachloroethane	0.57	2.99	0.46	0.76	36
1,2,3-Trichloropropane	0.07	0.95	0.11	0.22	35
Benzyl chloride	0.29	11.01	1.07	2.10	43
2,4,6-Trichlorophenol	4.43	7.10	0.47	2.34	7
2-Nitrophenol	6.19	20.02	2.38	4.84	24
2,4-Dichloropropane	5.50	13.57	0.69	2.67	8
Phenol	2.19	26.38	2.03	4.99	22

at several sites [23]. No information on the carcinogenicity of 2-butanone and MEK by the oral or inhalation routes in humans was identified. Based on the dermal carcinogenicity study, exposure to MEK does not relate to skin tumor [24].

Benzene is another migrating component leached from new PVC pipes, identified in high concentration from six pipes out of nine plastic pipes used in migration tests which had the highest concentration of benzene after 72 h incubation cycles. The concentrations were found between 1.89 and 13.24 $\mu\text{g/L}$ with mean value of 6.73 $\mu\text{g/L}$ and standard deviation of 4.13 (Tables 4 and 5). Benzene compound is often used as solvent during the manufacture of plastic pipes. Similar observation was also reported in a previous study conducted and designed to identify and quantify VOC such as benzene leached into drinking water samples [6]. Federal drinking water surveys in the United States of America estimated that approximately 1.3% of water systems contained benzene at concentrations greater than 0.5 $\mu\text{g/L}$, with the highest level reported at 80 $\mu\text{g/L}$ [23]. The guideline value of benzene stated by WHO is, however, at 5 $\mu\text{g/L}$.

1,2-Dichloropropane was also detected from all pipes used in migration experiment, in the concentration range between 2.68 and 19.93 $\mu\text{g/L}$, with mean value of 13.437 $\mu\text{g/L}$ and standard deviation of 6.168. 1,2-DCP usually serves as an intermediate in the perchloroethylene production and other chlorinated products [6]. Previous study found that 1,2-DCP concentration in water was high at 51 $\mu\text{g/L}$ [23]. In 1989, a study that was conducted in Japan found that 1,2-DCP was detected in 20 out of 78 water samples with concentrations ranging from 0.000 01 to 0.14 $\mu\text{g/L}$ [21]. Concentrations of 1,2-DCP from potable water samples collected in 1990 in eight homes in three communities in USA ranged from 0.7 to 19.0 $\mu\text{g/L}$ [25]. The levels of 1,2-dichloropropane in leaching process are below the allowable limits of WHO (30 $\mu\text{g/L}$).

Similar to benzene, pyridine molecule was detected from all pipes with recorded concentration ranging from 2.11 to 7.08 $\mu\text{g/L}$, with mean of 3.93 $\mu\text{g/L}$ and standard deviation of 1.648 (Tables 4 and 5). Fifty percent of pipes included in the present study released more concentrations. Pyridine derivatives are added as intermediate substances during the

manufacturing of active gradients in the synthesis process of plastic pipes to strengthen the composites. Previous study on the leaching of organic compounds from plastic piping indicated that pyridine was found to be released from polymeric plastic pipes [26]. Although there are many concerns about its detrimental health effects including liver damage, neurological disorders, renal disease, and irritation, there is no guideline value stated by any regulating agency for pyridine.

1,1,2,2-Tetrachloroethane is another contaminant leached from new PVC pipes used for migration experiments and the concentration ranged between 0.29 and 4.64 $\mu\text{g/L}$, with an average value of 1.762 $\mu\text{g/L}$ and standard deviation of 1.407 (Tables 4 and 5). 1,1,2,2-Tetrachloroethane is among the possible carcinogenic agents for human EPA 2008. The concentration of this compound is below the maximum contamination limits stated by WHO (40 $\mu\text{g/L}$). Exposure to 1,1,2,2-tetrachloroethane in drinking water at level above 0.4 $\mu\text{g/L}$ for several years could lead to damage to some of liver cells [27]. However, there are no reports of this chemical causing cancer.

The component 1,2,3-TCP was detected leached from all PVC pipes used in migration tests. The concentration ranged between 0.10 and 3.91 $\mu\text{g/L}$, with mean value of 1.26 $\mu\text{g/L}$ and standard deviation of 1.271 (Tables 4 and 5). 1,2,3-TCP is a regulated chemical with an established State Maximum Contaminant Level (MCL) in drinking water of 5 $\mu\text{g/L}$. The maximum allowable limits of 1,2,3-TCP is 70 $\mu\text{g/L}$ stated by WHO. Common source of TCP in water is discharges of solvent.

Benzyl chloride contaminants leached from all PVC pipes used in migration experiments, in the concentration value between 0.30 and 2.91 $\mu\text{g/L}$, with mean value of 1.21 $\mu\text{g/L}$ and standard deviation of 0.838. Benzyl chloride monomers undergo chemical process to form larger molecules and are used in the manufacturing of numerous products including plastic pipes. The concentration of this compound is under the allowable maximum contamination level of WHO (20 $\mu\text{g/L}$) [7].

2,4,6-Trichlorophenol was detected leached from all PVC pipes used in migration experiments, in concentrations ranging between 0.20 and 23.55 $\mu\text{g/L}$. The mean value is 5.407 $\mu\text{g/L}$ with standard deviation of 7.158 (Tables 4 and 5). The concentration of this component in pipe number 3 exceeded the concentration limits considerably may be due to manufacturing problem. Phenolic compounds are usually by-products used as additives and as antioxidants in the manufacturing of plastic materials. The allowable limit of this contaminants regulated in 1987 by EPA in drinking water is 10 $\mu\text{g/L}$. Chlorophenols are observed in drinking water supply from the phenol chlorination during disinfection process as biocides and as by-products from the reaction of hypochlorite with phenolic acids or as degradation products of phenoxy herbicides. Chlorophenols were found in Finnish tap water at a level of one order of magnitude higher than study done in Germany [28].

2-Nitrophenols were recorded in 72 h migration periods conducted in laboratory experiment, in concentrations ranging between 5.67 and 21.49 $\mu\text{g/L}$, with mean value of 14.80 $\mu\text{g/L}$ and standard deviation of 4.929 (Tables 4 and 5). All the leaching values are under the guideline value stated by EPA (40 $\mu\text{g/L}$). There is considerably concern about the

adverse health effects of these chemicals on wildlife and human [29]. 2,4-DCP was also recorded in all PVC pipes used in migration experiments conducted in laboratory. The migration concentrations leached from plastic pipes were between 0.20 and 23.52 $\mu\text{g/L}$ with mean concentration value of 8.606 $\mu\text{g/L}$ and standard deviation of 7.417. Similar to chlorophenols, 1,2-dichlorophenols were found in drinking water due to the phenol chlorination during disinfection process as biocides and as by-products from the reaction of hypochlorite with phenolic acids or as degradation products of phenoxy herbicides. Chlorination increased the concentration of 2,4-DCP at 0.07 $\mu\text{g/L}$. No health-based guideline value has been derived because of the limitation of database for the toxicity of 2,4-DCP.

Phenol is another organic contaminant detected from migration tests leached from PVC pipes, in concentrations ranging between 2.79 and 15.84 $\mu\text{g/L}$, with mean value of 8.488 $\mu\text{g/L}$ and standard deviation of 4.541 (Tables 4 and 5). In 2010, a study conducted in Europe has identified two antioxidant degradation products detected in the migration experiments with PEX pipes A and B using the solid phase micro extraction [30].

3.2. VOCs in tap water samples

Fifty-eight tap water samples used for drinking and potable purposes were randomly collected from buildings and villas at different ages from Medina city. Thirteen targeted VOCs were analyzed in tap water samples. 1,1,1-Trichloroethane was detected in 74% of tap water samples between the range of 0.02–10.23 $\mu\text{g/L}$ with average of 1.2 $\mu\text{g/L}$ and standard deviation of 2.45 (Table 6). The levels of this contaminant were generally low as allowable limit of WHO (40 $\mu\text{g/L}$) and no concern for chronic effects and potential risk to health. This compound is chlorinated hydrocarbon characterized with their high chemical stability [31].

2-Butanone and benzene contaminants were recorded in 81% of water samples out of 58, in the concentration range between 0.26 and 14.49 $\mu\text{g/L}$ and 0.90 and 11.34 $\mu\text{g/L}$, respectively. The average means of 2-butanone and benzene are 3.78 and 2.02 $\mu\text{g/L}$ with standard deviations of 2.89 and 2.41, respectively. The concentration of 2-butanone was under the allowable limit of WHO (10 $\mu\text{g/L}$) but the level of benzene among them is about 14% exceeding the maximum contamination level of WHO (5 $\mu\text{g/L}$). The other contaminants 1,2-dichloropropane recorded 60% of tap water samples in concentration range from 1.02 to 12.07 $\mu\text{g/L}$, with an average of 4.97 $\mu\text{g/L}$; the levels of 1,2-dichloropropane in all samples were below the EPA allowable limits (40 $\mu\text{g/L}$).

Similarly, pyridine was identified in 77.5% of samples with concentrations from 1.13 to 19.98 $\mu\text{g/L}$, with average of 2.54 $\mu\text{g/L}$ and standard deviations of 3.41. The allowable limits in drinking water were not stated by WHO or other organizations, although it is believed to damage liver and there is other health concern for humans including neurological and renal effects, also irritation of the skin and eye. It is not certain whether these contaminants can cause cancer and birth defects [32,7].

Other contaminants 1,1,2,2-tetrachloroethane and 1,2,3-TCP were quantified in 36% and 35% of tap water samples

out of 58 and recorded concentrations from 0.57 to 2.99 $\mu\text{g/L}$ and 0.07 to 0.95 $\mu\text{g/L}$ with average values of 0.46 and 0.11 $\mu\text{g/L}$ and standard deviations of 0.76 and 0.22 (Table 6). The concentrations of both contaminants are within the permissible limits stated by WHO (40 and 70 $\mu\text{g/L}$). Both contaminants are among the possible carcinogen agents for human beings. The results published demonstrated the plastic pipe leakage of organic compounds to drinking water [33].

Benzyl chloride detected in 43% out of 58 tap water samples collected which is used for drinking purpose. The recorded concentration varied from 0.29 to 11.01 $\mu\text{g/L}$, with an average of 1.07 $\mu\text{g/L}$ and standard deviation of 2.10 (Table 6). All the values of this contaminant are lower than the allowable limit of WHO (20 $\mu\text{g/L}$). EPA classified this compound as Group 2B; this is probably a human carcinogen agent when found in water at levels above the MCL (20 $\mu\text{g/L}$).

Phenols and 2-nitrophenols were recorded in 22.41% and 24.13% of tap water samples out of 58 samples. The concentration varied between 2.18 and 26.38 $\mu\text{g/L}$ and 6.19 and

20.02 $\mu\text{g/L}$, with averages of 2.03 and 2.38 $\mu\text{g/L}$ and standard deviations of 4.99 and 4.84, respectively. The concentrations of these compounds were less than the guideline values recommended by the WHO (40 $\mu\text{g/L}$). Both compounds have significant health risks due to high carcinogenicity and listed as priority pollutants due to toxicity [19].

Other phenolic contaminants 2,4-DCP and 2,4,6-trichlorophenol were recorded in 8% and 7% of tap water samples out of 58, collected from Madinah Al-Munawwarah city. The recorded concentration values varied from 5.5 to 13.57 $\mu\text{g/L}$ and 4.43 to 7.1 $\mu\text{g/L}$, with averages of 0.68 and 0.47 $\mu\text{g/L}$ and standard deviations of 2.67 and 2.32 (Table 6). Both contaminants were under the maximum allowable limits stated by WHO (40 $\mu\text{g/L}$). These compounds have significant health risks due to toxicity [34,26]. The same analytical methods of the present study were previously shown to be capable of detecting phenolic compounds by others [21,28].

Figs. 1–3 show the chromatograms of VOCs and phenols leached from PVC pipes during incubation periods of time and VOCs detected in tap water samples. Figs. 4 and 5

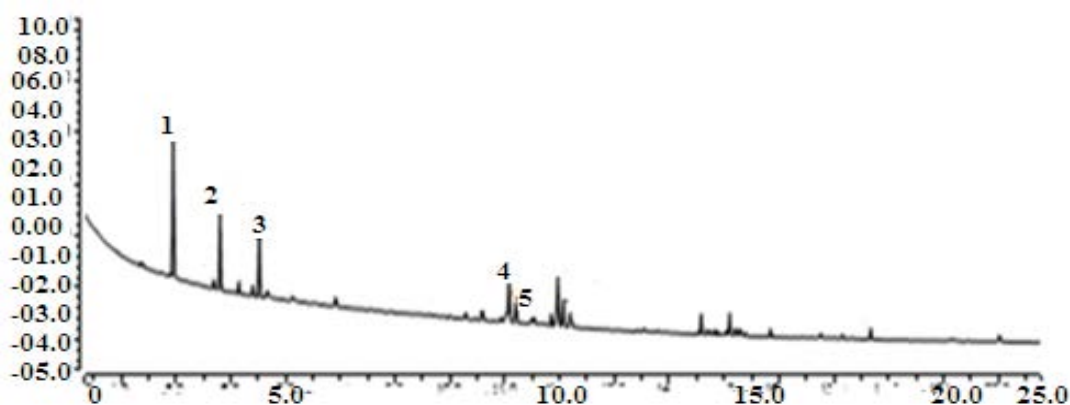


Fig. 1. Chromatogram graph shows the separation resolution of the migrated volatile organic compounds ($\mu\text{g/L}$) from tap water samples after 72 h of incubation period. (1) 1,1,1-Trichloroethane, (2) 2-butanone, (3) pyridine, (4) 1,1,2,2-tetrachloroethane, and (5) 1,2,3-trichloropropane.

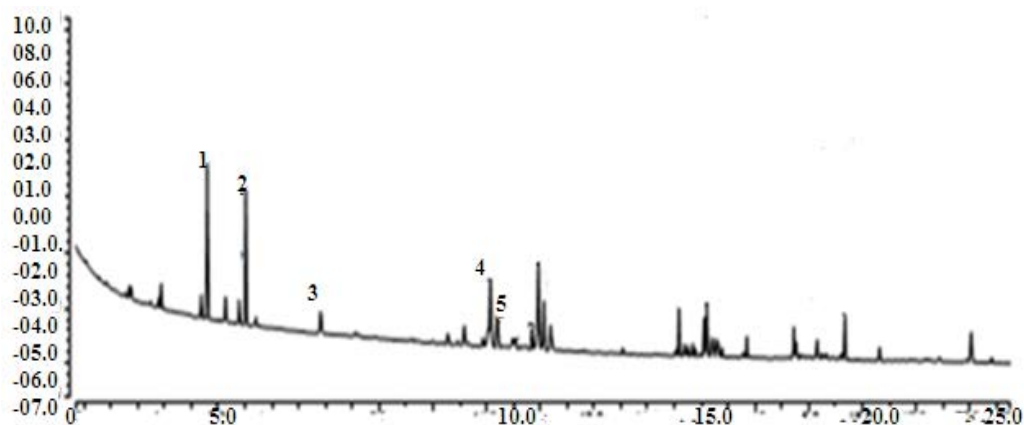


Fig. 2. Chromatogram graph shows the separation resolution of the migrated volatile organic compounds ($\mu\text{g/L}$) from PVC after 72 h of incubation period. (1) 1,1,1-Trichloroethane, (2) 2-butanone, (3) pyridine, (4) 1,1,2,2-tetrachloroethane, and (5) 1,2,3-trichloropropane.

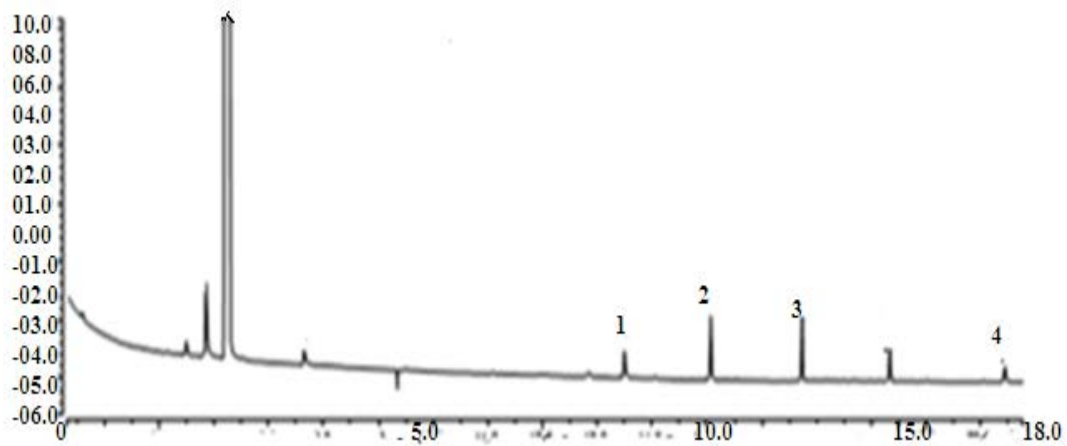


Fig. 3. Chromatogram graph shows the separation resolution of the migrated phenolic compounds ($\mu\text{g/L}$) leached from PVC after 72 h of incubation period. (1) 2,4,6-Trichloro phenol, (2) 2-nitrophenol, (3) 2,4-dichlorophenol, and (4) phenol.

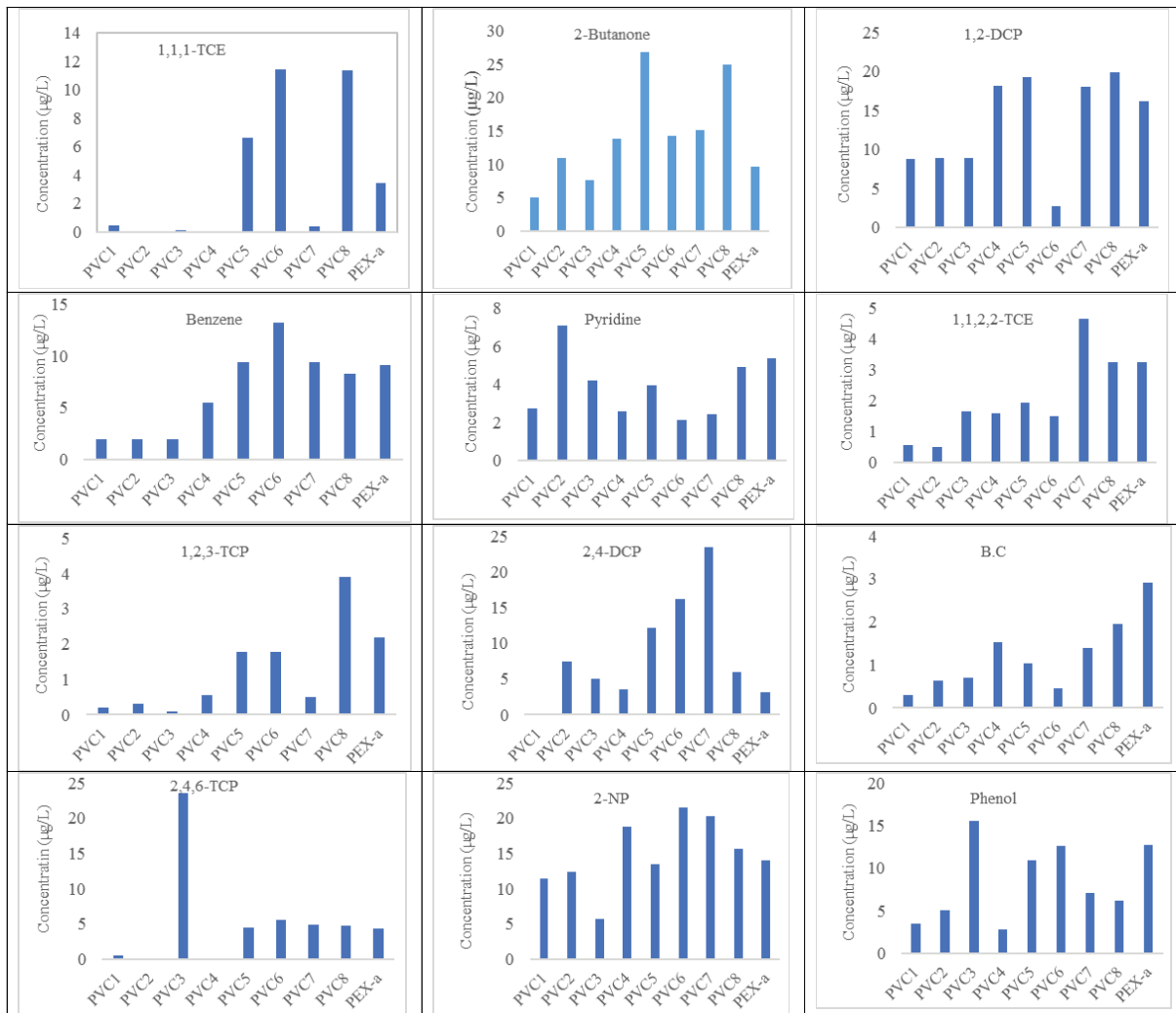


Fig. 4. Bar graph shows the total concentration of organic compounds desorbed from plastic pipes in three incubation periods. (1) 1,1,1-Trichloroethane, (2) 2-butanone, (3) 1,2-dichloropropane, (4) benzene, (5) pyridine, (6) 1,1,2,2-tetrachloroethane, (7) 1,2,3-trichloropropane, (8) 2,4-dichlorophenol, (9) benzyl chloride, (10) 2,4,6-trichlorophenol, (11) 2-nitrophenol, and (12) phenol.

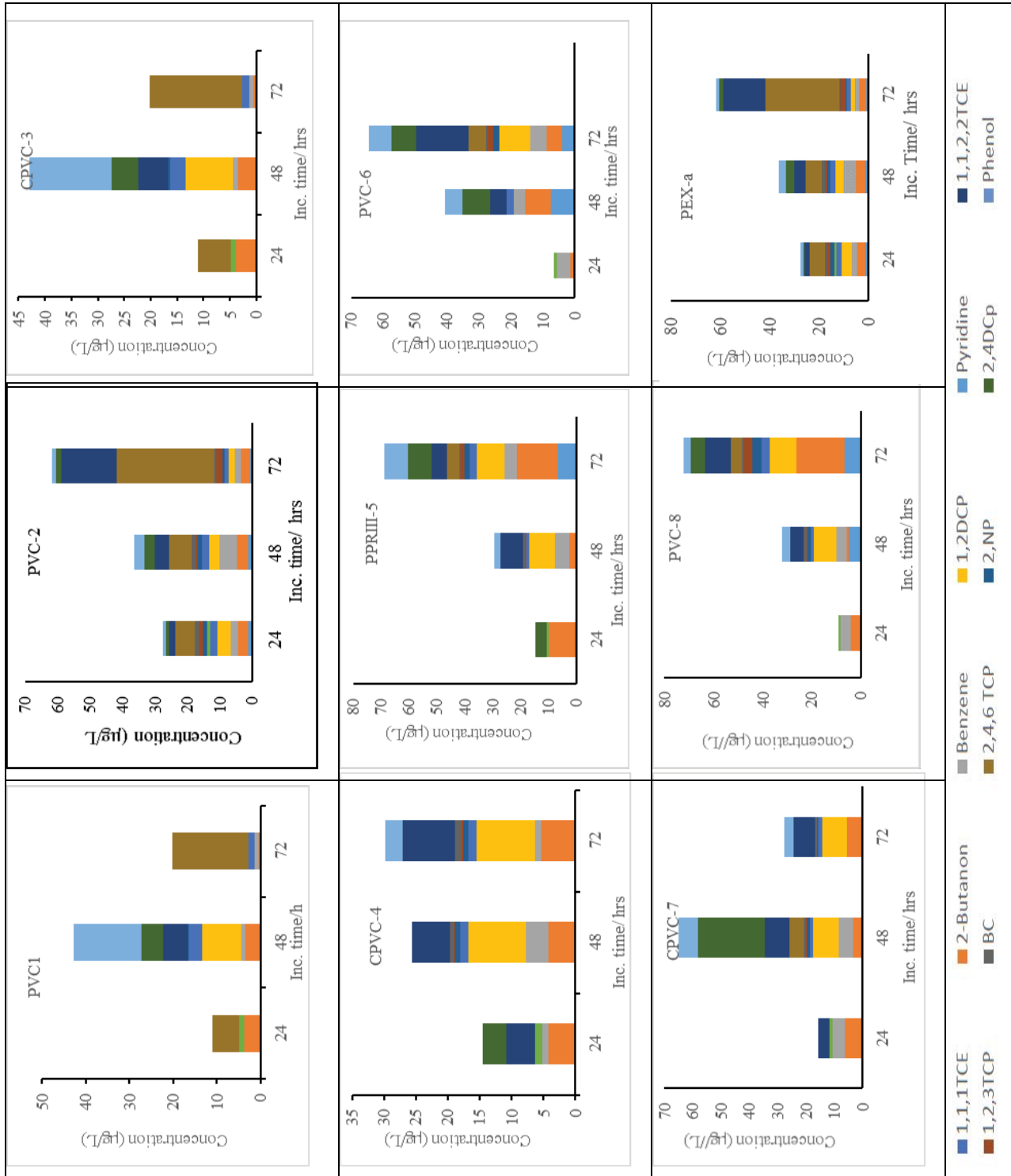


Fig. 5. Bar graph shows effects of incubation time on leaching of volatile organic compounds from PVC plastic pipes into test water samples.

Table 7
Pearson correlation matrix (*r*) for VOCs and phenols leached from PVC pipes for 24, 48, and 72 h

Compounds	1,1,1-TCE	2-Butanone	Benzene	1,2-DCP	Pyridine	1,1,2,2-TCE	1,2,3-TCP	BC	2,4,6-TCP	2NP	2,4-DCP	Phenol
1,1,1-TCE	1											
2-Butanone	0.645	1										
Benzene	0.724	0.555	1									
1,2-DCP	-0.009	0.601	0.171	1								
Pyridine	-0.092	0.019	-0.371	0.081	1							
1,1,2,2-TCE	0.687	0.564	0.584	0.521	0.118	1						
1,2,3-TCP	0.849	0.679	0.606	0.395	0.173	0.944	1					
BC	0.124	0.239	0.348	0.684	0.263	0.750	0.568	1				
2,4,6-TCP	-0.054	-0.164	-0.163	-0.213	0.004	-0.204	-0.134	-0.117	1			
2NP	0.388	0.343	0.747	0.146	-0.497	0.380	0.277	0.180	-0.558	1		
2,4-DCP	0.224	0.373	0.617	0.031	-0.350	-0.019	0.003	-0.128	0.017	0.594	1	
Phenol	0.280	-0.004	0.330	-0.263	0.057	0.021	0.148	0.093	0.750	-0.277	0.194	1

Table 8
Pearson correlation matrix (*r*) for VOCs and phenols detected in tap water samples

Compounds	1,1,1-TCE	2-Butanone	Benzene	1,2-DC	Pyridine	1,1,2,2-TCE	1,2,3-TCP	BC	2,4,6-TCP	2NP	2,4-DCP	Phenol
1,1,1-TCE	1											
2-Butanone	0.449	1										
Benzene	0.401	0.118	1									
1,2-DCP	0.112	0.461	0.168	1								
Pyridine	0.013	0.153	0.409	0.081	1							
1,1,2,2-TCE	0.231	0.148	0.243	0.162	0.284	1						
1,2,3-TCP	0.317	0.280	0.384	0.137	0.378	0.944	1					
BC	0.362	0.172	0.325	0.153	0.328	0.517	0.691	1				
2,4,6-TCP	0.290	0.410	0.322	0.443	0.294	0.163	0.219	0.192	1			
2NP	-0.045	-0.213	0.095	-0.014	0.135	0.018	0.248	0.203	0.137	1		
2,4-DCP	0.070	-0.181	0.032	-0.018	-0.058	0.024	0.194	-0.025	0.156	0.405	1	
Phenol	0.156	-0.010	0.193	-0.072	0.057	0.222	0.438	0.136	0.506	0.429	0.217	1

describe the bar graph of total VOCs and phenols in three successive incubation periods of time.

The values of Pearson correlation matrix in Tables 7 and 8 show strong correlations between the concentrations of most of the analyzed components. This implies that migrated contaminants originated from the same source. It is worth to note that the concentration of leachable volatile and phenolic compounds increases with extended incubation time. Although the levels of the VOCs and phenols monitored in the controlled migration study and in some of the real samples are below the allowable limit, their accumulation over lengthy consumption of contaminated water escalates the risk on human health.

In previous studies that were conducted in Malaysia for water quality, they found many organic and trace metals originated from the biofilm deposited in water supply network and caused changes in the test and odor of drinking water [34–37]. They collected river water used for drinking purpose and analyzed in the field and laboratory tests for identification and source of contamination. Most of water were contaminated in trace levels, and some of the samples showed that the contamination levels were above the limits of environmental protection and human health concern.

4. Conclusion

This work describes a study of the migration of 12 volatile organic components from nine different brands of PVC used as adhesive and antioxidants in the manufacture of plastic pipes as sanitary pipes into tap water. The compounds identified by GC-FID analysis include benzene, 1,1,1-trichloroethane, 2-butanone, pyridine, 1,2-dichloropropane, 1,1,2,2-tetrachloroethane, 1,2,3-TCP, phenol, benzyl chloride, 2-nitrophenol, 2,4-DCP, and 2,4,6-trichlorophenols. The substantial variation in the concentrations of the pollutants was due to the difference in the migrating rate of these compounds from each polymeric type. It is possible to classify the migration as strong, moderate, and weak based on the amount of the leached compounds. The levels of these organic contaminants have been demonstrated to increase over stagnant periods of time although most of the values obtained in this research are below the MCL produced by EPA. There is clear association (correlation) between analytes found in migration test and that obtained in tap water samples collected from residential buildings (villas and apartments) from Medina city. These preliminary findings provide indication pertaining to water contamination due to leaching from plastic piping and plumbing materials in residential water network in selected study areas located in Medina Al-Munawwarah. This may raise awareness to work on a strategy involving change of the manufacturing process using less organic additives to improve the quality of polymeric pipes when in contact with drinking water. However, this aspect needs further detailed investigation and analysis because this issue is perilous in relation to public health.

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