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Migration of Volatile Organic Compounds from Different PVC Pipes into Drinking Water at Extended Retention Times

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ABSTRACT

A study of the diffusion of organic additives from polyvinyl chloride, Chlorinated polyvinyl chloride, Un-plasticized polyvinyl chloride (PVC, CPVC, and UPVC) pipes for drinking water was tested with respect to migration of volatile organic components (VOC). Various structures of organic chemicals were identified in the water extracts by means of gas chromatography-mass spectrometry analysis. Plastic piping made of polyvinyl chloride (PVC), Unplasticized PVC and chlorinated PVC (CPVC), is being increasingly used for drinking water distribution lines. Given the formulation of the material from vinyl chloride (VC), there has been concern that the VC (a confirmed human carcinogen) can leach from the plastic piping into drinking water. PVC/CPVC and UPVC pipes in the laboratory and drinking water samples collected from consumer's homes and another sample is from double distilled water revealed vinyl chloride accumulation in the tens of ng/L range after 25 days. Preliminary evidence suggests that VC may accumulate not only via chemical leaching from the plastic piping but also as disinfection by-product (DBP) via a chloride-dependent reaction. Most of them presented a basic common structure characterized by a phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring. The structures attributed to some of the chemicals have been confirmed using commercial or purposely synthesized standards. Unprocessed granules of raw PVC, CPVC and UPVC were also analyzed, in order to investigate the origin of the chemicals detected in the water samples. Consequently, the presence of some of the compounds was attributed to impurities or by-products of typical phenolic additives used as antioxidants in pipeline production.

1. INTRODUCTION

Old pipes used to supply drinking water are often being replaced with pipes manufactured from polymer materials. Various types of polyethylene (PE) and polyvinyl chloride (PVC) are used presently, although the trend is to select PE materials rather than PVC materials (Trew *et al*. 1995). The polymer materials contain a variety of organic and inorganic additives in order to improve the material's durability, the manufacturing, and handling during installation, as well as to modify the color. The additives used include the following: antioxidants and other stabilizers, lubricants, softeners and coloring agents (Gatcher and Muller, 1990). Since the pipes are expected to last over 100 years on the ground, stringent quality requirements regarding mechanical strength must be fulfilled by the manufacturers. While good mechanical properties of the pipes are fundamental, the possibility that toxic organic compounds from the pipes may leach into the drinking water, resulting in contamination must be considered as well. Such leaching could occur directly, by diffusion of chemicals into the water, or indirectly, for example, metabolites from biological growth in a biofilm on the interior surface of the pipes being released into the water. Thus, a situation could arise where high-quality water leaving water works is contaminated before reaching the consumer. Polyvinyl chloride (PVC) piping is popular due to its relatively low cost, Structural strength, ease of installation and corrosion-resistant properties (Al-Malack and Sheikheldin, 2001). It is currently estimated that 69% of the piping used in the main drinking water distribution system is plastic, and the majority of the plastic pipe is PVC (Burn, 2005; Vang *et al*. 2014; Ryssel *et al*. 2015).

During the manufacturing of PVC, chlorine and ethylene are combined to create ethylene dichloride, which is converted into vinyl chloride (VC) monomers through a cracking process before polymerization to PVC (Saeki and Emura, 2002). Additionally, chlorinated PVC (CPVC), which is PVC that has been chlorinated via a free radical chlorination reaction and the application of heat, is commonly found in hot water drinking systems and residential homes (ATSDR, 2004). 1.2. Vinyl chloride monomer in PVC pipe there has been reports that residual VC monomer in the pipe matrix of the PVC/CPVC piping can be released into air or drinking water (Sano *et al*. 2001). VC is a known human carcinogen and is regulated by the Environmental Protection Agency (EPA) with a maximum contaminant level (MCL) of 2.0 mg/L and an MCL-goal (MCLG) of 0 mg/L in water for potable water (Flournoy and Monroe 1999). Vinyl chloride concentrations well above the EPA's MCL were reported in stagnant

PVC pipelines in Kansas, Missouri, Texas, and Arkansas (MDNS, 2006). Additional studies have detected VC levels above the EPA's MCL at 14 mg/L in PVC pipe manufactured before 1977, The Vinyl Institute and Uni-Bell PVC Pipe Association, (1994). While modifications to the manufacturing process in 1977 drastically reduced the VC monomer residual in US-manufactured pipe, little work exists that examines the leaching of VC into the water from modern US PVC/CPVC pipes e particularly as the pipe ages.

Recent work in Saudi Arabia has been performed indicating that static unplasticized PVC (UPVC) accumulates 2.3 mg/L of VC over 14 days when exposed to ultraviolet radiation (Al-Malack, 2004), 2.5 mg/L of VC over 30 days when exposed to temperatures of 45°C (Al-Malack *et al*. 1999), 2.0e 2.1 mg/L of VC in both raw groundwater and chlorinated drinking water and 2.5 mg/L of VC over 30 days when exposed to direct solar radiation. However, all of these analyses used locally manufactured pipes from Saudi Arabia. Another study with Japanese pipe (unknown manufacturer and production date) found that static PVC pipes filled with deionized water or phosphate buffer did not accumulate detectable VC over a three day period (detection limit in mg/L range), but that segments sealed in serum vials did produce detectable VC at more than 50 mg/L (Ando and Sayato, 1984). Finally, an Italian study looking at the migration of VC into drinking water bottled in locally obtained plasticized PVC found that VC accumulated at a rate of 1ng/L/day (Benfenati *et al*. 1991). Organic components migrating from plastic pipes may serve as nutrients for microorganisms and thus promote microbial growth in pipelines (Vander Kooij and Suylen, 1991; LeChevallier *et al*.1991; Vander Kooij and Veenendaal, 1993; Kerr *et al*. 1999).

The present work contributes to the knowledge on types and amounts of migrants available for microbial utilization in plastic pipes for drinking water. It has been commonly noticed that long retention time could result in water quality problem in the water distribution system, an especially low concentration of chlorine residual. Past literature have reported the investigation on the impact of stagnation time on the migration of some specific substances from water pipes (Lasheen *et al*. 2008; Lund *et al*. 2011; Lytle and Schock, 2000; Walter *et al*. 2011). However, few studies researched the influence of various long retention times related to the stagnant conditions in real distribution system on water quality from the perspective of contaminant migration of different plastic pipes.

An extraction and identification of the organic chemicals migrating from a PVC, CPVC and UPVC pipeline into the water were undertaken. Three different PVC pipe materials available

on the market were tested. Furthermore, the presence of some of the identified chemicals was investigated under field conditions, i.e. in water samples from newly installed pipes in a distribution system. Finally, in order to understand the origin of the degraded additives detected in water, as well as the chemistry of these additives. This paper will present the details of the diffusion test, the liquid-liquid extraction, and the gas chromatography -mass spectrometry (GC–MS) analysis and chlorine estimation. The results of the identification study will also be presented furthermore, a comparison of the laboratory results (Distilled water) and results obtained from in situ drinking water samples will be reported.

2. MATERIALS AND MEASUREMENTS METHODS

2.1. Samples

Three different PVC material pipes (PVC, UPVC, and CPVC) were employed as samples during the laboratory study. Sample A consisted of Polyvinyl chloride (PVC), Samples B consisted of Unplasticized Polyvinyl chloride (UPVC), and Samples C consisted of Chlorinated Polyvinyl chloride (CPVC). The three sample types are representative of pipe materials commonly used in drinking water distribution systems. Pipe pieces had lengths of 1m, and the following internal diameters: A, 10mm; B, 28mm; C, 31mm. All samples used in this study were obtained directly from the manufacturers and prior to analysis were packed in aluminum foil and stored in paper bags.

2.2. Additive migration test

During the migration test, the inner surface of a sample was brought into contact with test water (MilliQ water) for 7 days at a temperature of 35±2°C. The pipe surface area with water volume ranged from 13 to 43dm^{-1}. Prior to the migration test, the pipe samples were filled with test water for 24 h, flushed with tap water for 60 min and finally rinsed with test water for 2 min. Immediately after this pre-treatment, the pipes were filled with fresh test water and capped with brass stoppers at both ends. At the end of the test period 25 days, the test water was removed and subsequently extracted with an organic solvent. The organic extracts were analyzed by GC. Each polymeric material was tested in triplicate. Blank migration and extraction tests were also performed. Blank samples were created by placing brass stoppers in glass bottles, immersing the stoppers in test water and sealing the bottles with Teflon caps.

2.3. Liquid-liquid extraction method

Prior to the extraction of leached water, 100 mL of an internal standard (IS) solution (2-naphthol, 50ppm in pentane) was spiked into the water. The resulting water solution was shaken for approximately 1min. The leached water was then transferred to a separating funnel and 15mL of chloroform (SupraSolv Merck) was added. The resulting solution was shaken manually for approximately 3 min. The organic phase was stored in a glass flask and the water phase was re-extracted with 15mL of fresh chloroform. The two organic fractions were unified. The volume of the organic solution was reduced to approximately 100mL under a gentle nitrogen stream (approximately 50min). The concentrated extracts were stored in a refrigerator at -14°C until analysis.

2.4. Characterization of Gas chromatography-Mass spectroscopy for Volatile organic compounds analysis

The identification of the organic compounds extracted from the leached water was performed by GC coupled with a mass spectrometry detector (GC–MS). Electron impact (EI) spectra were obtained on a Hewlett-Packard 6890 GC coupled with a Hewlett-Packard 5973 MS. The carrier gas was helium at a constant flow of 1.2mLmin^{-1}. One micro liter of solution was injected in the split-split less mode (the split was opened after 30 s) into the injection port at a temperature of 280°C. The MS scan range was from 20m/z to 650m/z (full scan) 3.6 times every second under an electron impact condition of 70 eV. Employing a capillary column (Hewlett- Packard, HP-MS5 30 m, 0.25mm i.d., 0.25mm film thickness) the oven temperature was held at 45°C for 1 min, raised by 5°Cmin^{-1} to 300°C, and then held at 300°C for 10 min. Part of the identification of the extracted compounds was made using the reference spectra held in the library NBS 75K (NIST HS Chem Station Library.)

2.5. Chlorine tests

For the chlorine tests, the total chlorine was measured by HACH pocket colorimeter TM II analysis systems. Using appropriate powder pillows based on the DPD method ((N, N-diethyl-p-phenylenediamine), concentrations of total chorine were determined either within low range (0.02-2.00 mg/L Cl_2) or within high range (0.1-0.8 mg/L Cl_2). Notably, total chlorine tests were conducted before and after the test water was stored in pipe segments and negative controls. Chlorine consumption in mg/L was calculated by subtracting negative control values from those obtained in the corresponding migration waters. Moreover, chlorine

consumption rate in mg/ (Ld) was obtained by dividing chlorine consumption values by the duration of migration time in days (d).

3. RESULTS AND DISCUSSION

Typical total ion chromatogram (TIC) of the water extracts the extraction and the analysis condition was appropriate for a good peak resolution and internal standards (IS) recovery. A variable number of peaks (between 26 and 50) of different intensities were detected, during the GC–MS analysis of the water samples which were in contact with the three PVC pipe samples (PVC, CPVC, and UPVC). Some peaks, however, were both present and dominant in all three samples. The compounds are enumerated in order of chromatographic elution. Once a more precise theory regarding the chemistry of the ‘‘unknown" compounds was formulated, the structure attributed to a particular chemical was confirmed by recording chromatograms and the MS spectra of standards. Thus, the structure attributed to a detected compound was considered to be a positive identification whenever both the GC retention time and the mass spectra of pure standards matched with the two corresponding parameters of the unknown compound. Some of the standards were commercially available those, which were not were synthesized.

Fig. 1 shows a typical total ion chromatogram (TIC) of the water extract. The extraction and the analysis conditions were appropriate for a good peak resolution and are recovery. A variable number of peaks (between 35 and 60) of different intensities were detected, during the GC–MS analysis of the water samples which were in contact with the three PVC pipe samples (PVC, CPVC, and UPVC). Some peaks, however, were both present and dominant in all three samples. The following results concern only eight of these peaks, i.e. eight compounds. The compounds are enumerated in order of chromatographic elution. During the mass spectra interpretation, the structural identification of ‘‘unknown’’ chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library or by interpreting the fragmentation pattern of the mass spectra. Once a more precise theory regarding the chemistry of the ‘‘unknown’’ compounds was formulated, the structure attributed to a particular chemical was confirmed by recording chromatograms and the MS spectra of standards. Thus, the structure attributed to a detected compound was considered to be a positive identification whenever both the GC retention time and the mass spectra of pure standards matched with the two corresponding parameters of the unknown compound. Some of the standards were commercially available: those, which were not, were

synthesized. To date, not all of the eight compounds in Table 1 have been positively identified here in this Table 1 show the Volatile organic compounds migration from PVC pipe to double distilled water the compounds like

Acetamide, 2-(adamantan-1-yl)-N-(1-adamantan-1-ylethyl)-

2-(4, 5-Dihydro-methyl-6-oxo-1-phenyl-4-pyrazolyl)-nitrobenzoic acid

Spirost-8-en-11-one,3-hydroxy(3.beta.,5.alpha.,14.beta.,20.beta.,22.beta.,25R)-

Androstane-11,17-dione,3{(trimethylsilyl)oxy},17-{O(phenylmethyl)oxime},(3.alpha.,5.alpha.)-

9, 12, 15-Octadecatrienoicacid, 2-[(trimethylsilyl) oxy]-1-[[(trimethylsilyl) oxy]methyl]ethyl ester,(Z,Z,Z)- were detected.

Fig. 2 variable numbers of peaks (between 25 and 40) of different intensities were detected. The following results concern only fourteen of these peaks, i.e. fourteen compounds. The compounds are enumerated in order of chromatographic elution. During the mass spectra interpretation, the structural identification of ‘‘unknown" chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library or by interpreting the fragmentation pattern of the mass spectra. Here in this Table 2 show the Volatile organic compounds migration from CPVC pipe to double distilled water the compounds like 1, 2-Cyclopentanediol, trans-, n-Hexadecanoic acid, 6-Methyl-1,7 diazabicyclo [4.1.0]heptanes, 1(-p-Cumenyl) adamantine, 4-(Prop-2-benzyloxy) tetradecane, n-Butyl myristate, Biphenyl-4-carboxylic acid, 4'-(1,1-dimethylethyl)-, 3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol, 5-(Prop- 2- enoyloxy) pentadecane, Di-n-octyl phthalate were detected.

Fig. 3a variable numbers of peaks (between 35 and 50) of different intensities were detected. The following results concern only fourteen of these peaks, i.e. fourteen compounds. The compounds are enumerated in order of chromatographic elution. During the mass spectra interpretation, the structural identification of ‘‘unknown" chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library or by interpreting the fragmentation pattern of the mass spectra. Here in this Table 3 shows the Volatile organic compounds migration from UPVC pipe to double distilled water

the compounds like Ethene-1,1-diamine,2,2-dinitro-, 3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol, 5- (Prop- 2- enoyloxy) pentadecane, Di-n-octyl phthalate, Spirost-8-en-11-one, 3-hydroxy-,(3.beta.,5.alpha., 14.beta.,20.beta., 22.beta.,25R)- were detected.

Fig. 4 a variable numbers of peaks (between 20 and 52) of different intensities was detected. The following results concern only fourteen of these peaks, i.e. fourteen compounds. The compounds are enumerated in order of chromatographic elution. During the mass spectra interpretation, the structural identification of ‘‘unknown’’ chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library, or by interpreting the fragmentation pattern of the mass spectra. Here in this Table 4 shows the Volatile organic compounds migration from PVC pipe to test drinking water the compounds like N-Isopropyl-3-phenylpropanamide, 4-Isopropyl-1,3-cyclohexanedione, s-Triazole, 3- acetamido-, n-Hexadecanoic acid, n-Butyl myristate, Hexadecen-1-ol,trans-9-,3-Methoxy-D-homoestra-2,5(10)-dien-17beta ol,1Phenanthrenecarboxylicacid,1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-,[1R(1.alpha.,4a.beta.,10a.alpha.)]-,2-[3-(1-Hydroxy-1-methyl-ethyl)- 6a,10b-dimethyl-7-methylene- dodecahydro-benzo[f] chromen-8-yl]-1-phenyl-ethanone, Spirost-8-en-11-one, 3-hydroxy-, (3.beta.,5.alpha.,14.beta.,20.beta.,22.beta.,25R)-, 18,22,22-Trimethyl-17,27,29,30--tetranor-c-homoolean-14-ene-3beta,21alpha-diol, Hexadecanoic acid, 2-pentadecyl-1,3-dioxan-5-yl ester, cis- were detected.

Fig. 5 a variable numbers of peaks (between 20 and 52) of different intensities was detected. The following results concern only fourteen of these peaks, i.e. fourteen compounds. The compounds are enumerated in order of chromatographic elution. During the mass spectra interpretation, the structural identification of ‘‘unknown’’ chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library, or by interpreting the fragmentation pattern of the mass spectra. Here in this Table 5 shows the Volatile organic compounds migration from CPVC pipe to test drinking water the compounds like s-Triazole,3-acetamido-, N-Isopropyl-3-phenylpropanamide, 4-Isopropyl-1,3-cyclohexanedione, n-Hexadecanoic acid, n-Butyl myristate, Hexadecen-1-ol,trans-9-, 5-(Prop-2- enoyloxy) Pentadecane, 1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1, 4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-, 5-(Prop- 2- enoyloxy) pentadecane, 3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol, 1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1, 4a-

dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-, 2-[3-(1-Hydroxy-1-methyl-ethyl)-6a, 10b-dimethyl-7-methylene-dodecahydro-benzo[f]chromen-8-yl]-1-phenyl-ethanone, Spirost-8-en-11-one, 3-hydroxy-,(3.beta.,5.alpha.,14.beta.,20.beta., 22.beta.,25R)-, Androstane-11,17-dione, 3--{(trimethylsilyl)oxy}, 17-{O-(phenylmethyl)oxime}, (3.alpha.,5.alpha.)-, Hexadecanoic acid, 2- pentadecyl-1, 3-dioxan-5-yl ester, cis- were detected.

Fig. 6 variable numbers of peaks (between 25 and 55) of different intensities was detected. The following results concern only fourteen of these peaks, i.e. fourteen compounds. The compounds are enumerated in order of chromatographic elution. During the mass spectra interpretation, the structural identification of ‘‘unknown’’ chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library, or by interpreting the fragmentation pattern of the mass spectra. Here in this Table 6 shows the Volatile organic compounds migration from UPVC pipe to test drinking water the compounds like s- Triazole, 3- acetamido-, 4-(Prop-2-enoyloxy)tetradecane, n-Hexadecanoic acid, Hexahydropyridine, 1-methyl-4-[4,5-dihydroxyphenyl]-, n-Butyl myristate, 3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol, n-Butyl myristate, Hexadecen-1-ol,trans-9-, 1-Phenanthrene carboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1- methyl ethyl)-, [1R-(1.alpha.,4a.beta., 10a.alpha.)]-, 3-Methoxy-D-Homestar-2, 5(10)-dien-17beta-ol, Akuammilan-17-ol, 10-methoxy-, 1, 3- Benzenedicarboxylic acid, bis (2-ethylhexyl) ester were detected. In control system Fig. 7 (double distilled water) there are no peaks related to PVC, CPVC and UPVC were detected.

3.1. Residual chlorine over time

Total chlorine was measured before and after the migration tests both in migration waters and negative controls. Based on those measured total chlorine concentrations, the amounts of chlorine consumption and the chlorine consumption rates were calculated. Thus, the observed variability of total chlorine concentrations before and after migration tests for each pipe material may be attributed to the chemical reaction between chlorine and contaminants leached from PVC, CPVC and UPVC pipes into drinking water. The chlorine consumption data collected during continuous migration tests were shown in Fig. 8, 9 and 10, the amount of chlorine consumption of all polymers presented a significant increase over stagnant time. Notably, the highest amount of chlorine consumption was consumed in the migration waters from CPVC pipes. By 25 days of stagnation, total chlorine consumed in migration water from

PVC pipe was about 2.9 mg/L, total chlorine consumed in migration water from UPVC pipe was about 1.9 mg/L. total chlorine consumed in migration water from CPVC pipe was about 3.2 mg/L This implicated that under long stagnation conditions chlorine consumption would be enhanced resulting in insufficient residual chlorine in the piping water, finally causing a microbial problem in drinking water.

Analyses of VOC in water from the test drinking water showed that the concentrations of VOC were slightly higher when compared to double distilled water. Since the VOC concentrations in the successive tests were similar, an extended test of 25 days duration was carried out for three of the PVC pipes in order to investigate the concentration trends for selected VOC beyond the 25 days specified in the standard method. The concentration of major components related to antioxidants decreased just slightly during this extended test period and after 25 days. A similar concentration trend was observed for major benzene, ester components (hexanoates, decanes, octanes), although a slightly enhanced decline in concentration with time was observed for these components. The results show that migration of these components persisted in 25 days test period. Several unidentified compounds, presumably various oxygenates, were encountered in the test water samples along with the identified VOC (Whelton and Nguyen, 2013). Unidentified VOC was not quantified and their contribution to the total amount of organic migrants is not known. Some of the unidentified components appeared in the test drinking water and double distilled water for PVC, UPVC and CPVC brands. Only trace amounts of hexanal decanal, Hexadecane, Spirost, and octanal were found in the test and distilled water from the three successive PVC, UPVC and CPVC pipes the other compounds like methyl, butyl, biphenyl and octyl were seen.

The organic compounds released from the PVC pipe in to the test water were belong to the class amides, aromatic hydrocarbons, steroid compounds and compounds with hydroxyl as functional group. The organic compounds that were leached from amides group(Acetamide, 2-(adamantan-1-yl)-N-(1-adamantan-1-ylethyl)-, 9, 12, 15-Octadecatrienoicacid,2-[(trimethylsilyl)oxy]-1-[[(trimethylsilyl)oxy]methyl]ethyl ester,(Z,Z,Z)-), benzene group (2-(4,5-Dihydro-methyl-6-oxo-1-phenyl-4-pyrazolyl)-nitro benzoic acid), hydroxyl group (Spirost-8-en-11-one,3-hydroxy(3.beta.,5.alpha.,14.beta.,20.beta.,22.beta.,25R)-), steroid group (Androstane-11,17 dione,3{(trimethylsilyl)oxy},17-{O(phenylmethyl)oxime},(3.alpha.,5.alpha.), might have been used in the manufacture of PVC material.

The organic compounds that were released from CPVC pipes included esters (n-Butyl myristate, Di-n-octyl phthalate), aromatic compounds (1, 2-Cyclopentanediol,trans-, 5-(Prop- 2- enoyloxy)pentadecane), methyl group and compounds with amino methyl phenyl as functional groups (n-Hexadecanoic acid, 6-Methyl-1,7 diazabicyclo[4.1.0]heptanes, 1(-p-Cumenyl) adamantine, 4-(Prop-2-enoyloxy) tetradecane, Biphenyl-4-carboxylic acid, 4'-(1,1-dimethylethyl)-, 3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol).

The organic compounds which were released from UPVC pipes included ethane group (Ethene-1,1-diamine,2,2-dinitro-), esters group (Di-n-octyl phthalate), aromatic compound (5- (Prop- 2- enoyloxy) pentadecane), compounds with methyl and hydroxyl groups as functional groups 3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol,Spirost-8-en-11-one,3-hydroxy (3.beta.,5.alpha.,14.beta.,20.beta.,22.beta., 25R).

Di-n-octyl phthalate was released from both CPVC and UPVC pipes as well this compound is an ester which is colorless, odor less, oil liquid, non-volatile, synthetic substance used to produce soft and flexible polymeric pipes.

In general, considering the amount of chlorine consumption and chlorine consumption rates observed during each time of exposure, an order of materials tested in this research was obtained: PVC>UPVC>CPVC. This suggested that the disinfectant consumption can likely be attributed to the interaction with organics migrating from polymers. This chemical relationship might be linked with the production of disinfection by-products (DBPs), but they were not investigated in this research. The relatively high concentration of aldehydes in wash water from PVC pipes suggests that major parts of VOC from PVC, CPVC, and UPVC pipes originate from a surface layer which is readily removed by the initial rinse and wash procedure.

The migration test conducted to evaluate the leaching of organic compounds from various plastic pipes revealed that water stagnation in the polymeric pipes for considerable period enhances the contamination of synthetic compounds that have been used as additives in the manufacture of plastic pipes. These results might alert industry to change the manufacturing process with less use of organic additives and thereby improving the quality of plastic pipes. On the other hand, the organic compounds that were released might also play a role in biofilm formation and eventually the formation of scales in the water pipes.

4. CONCLUSIONS

✓ The continuous migration tests of this study indirectly investigated the characteristics of VOC migrating from three types of commonly used PVC, CPVC and UPVC under the conditions of long retention times (25days) and also showed the potential relationship between organics migration and water quality change like chlorine consumption.

✓ The migration test conducted in this study has shown that the three PVC pipe samples tested are capable of releasing Volatile organic compounds into drinking water. All the structures were positively confirmed by means of commercial or purposely synthesized standards.

✓ Most of the compounds present a basic common structure characterized by a phenolic and benzene rings typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring, Hexanol, Decanol, Octanol were observed in minimum amounts.

✓ To our knowledge, few of the identified structures have previously been reported in the literature as being present in drinking water. Some of the compounds were likely impurities or by-products of typical phenolic additives employed as antioxidants and vinyl in the pipeline production.

✓ This VOC compounds also play a major role in Biofilm formation in drinking water distribution systems which leads to scaling formation and blocking of pipelines.

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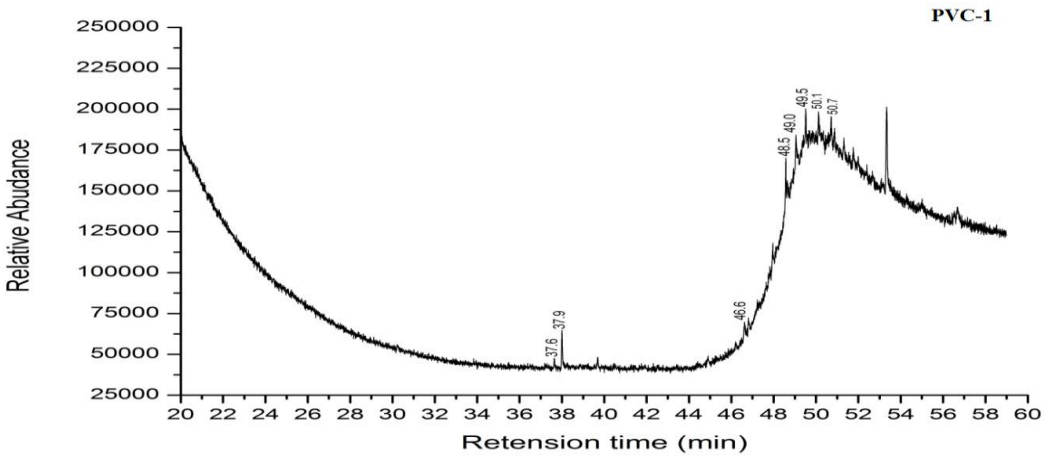


Fig. 1 Typical GC-MS chromatogram of Volatile organic compounds transfer from PVC pipe to double distilled water

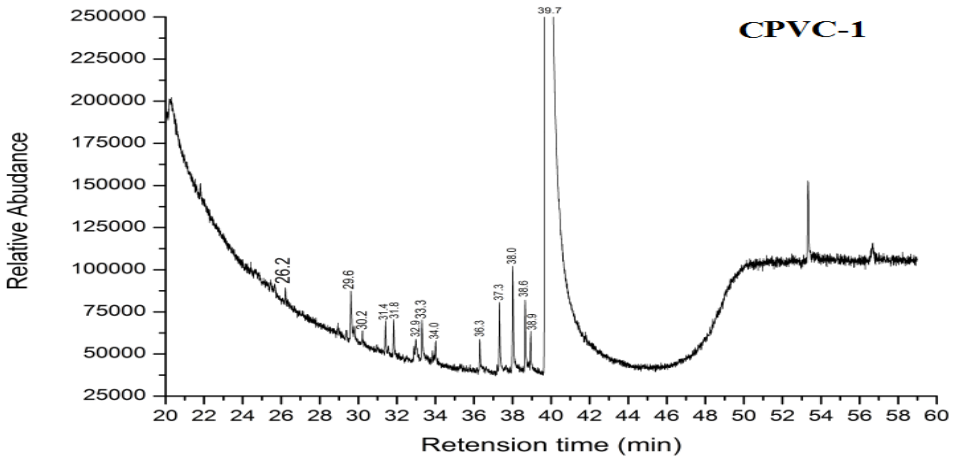


Fig. 2 Typical GC-MS chromatogram of Volatile organic compounds transfer from CPVC pipe to double distilled water

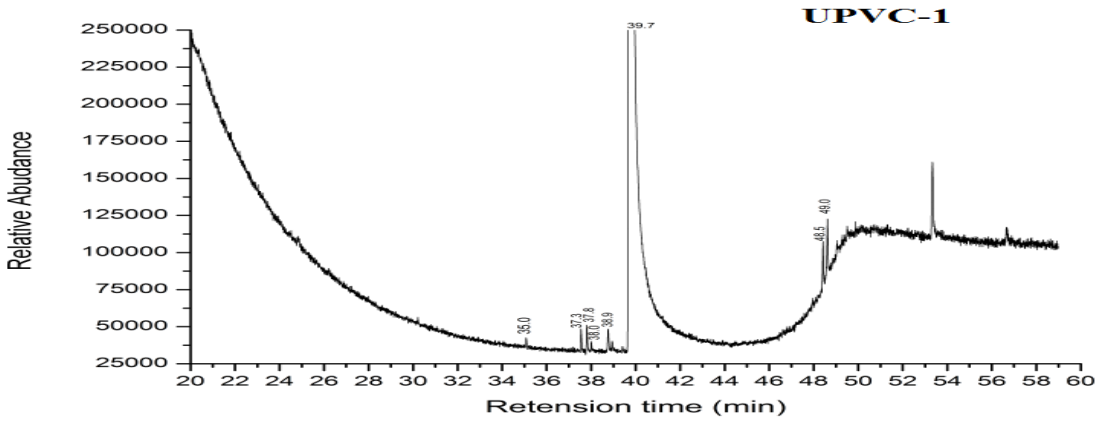


Fig. 3 Typical GC-MS chromatogram of Volatile organic compounds transfer from UPVC pipe to double distilled water

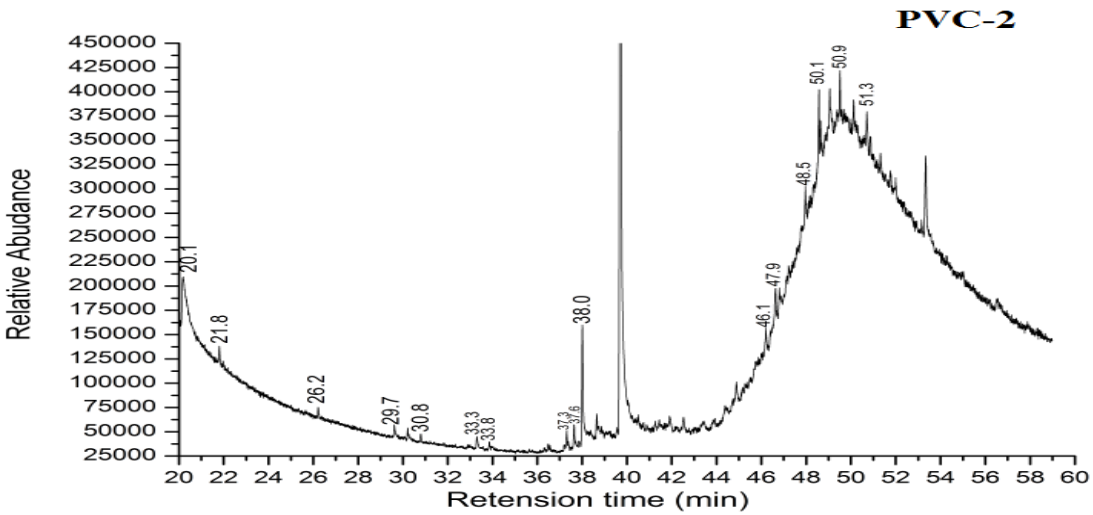


Fig. 4 Typical GC-MS chromatogram of Volatile organic compounds transfer from PVC pipe to test drinking water

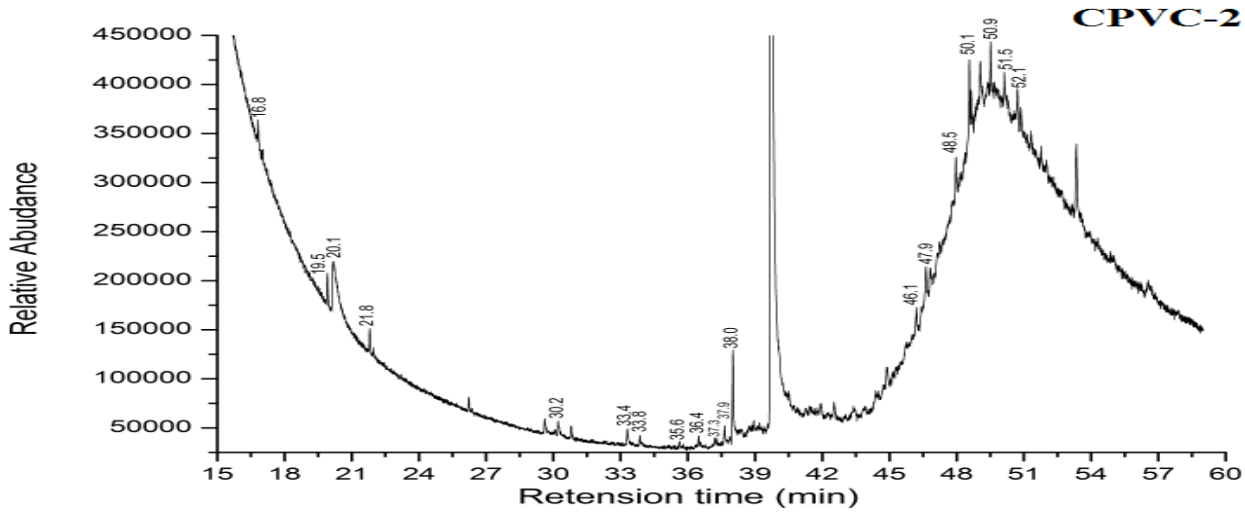


Fig. 5 Typical GC-MS chromatogram of Volatile organic compounds transfer from CPVC pipe to test drinking water

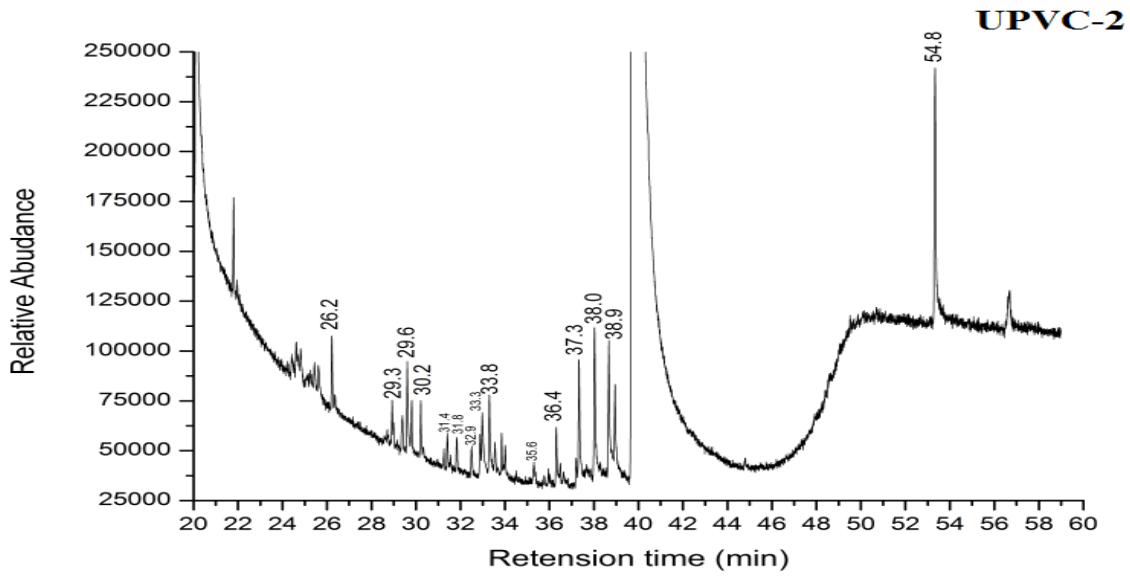


Fig. 6 Typical GC-MS chromatogram of a Volatile organic compounds transfer from UPVC pipe to test drinking water

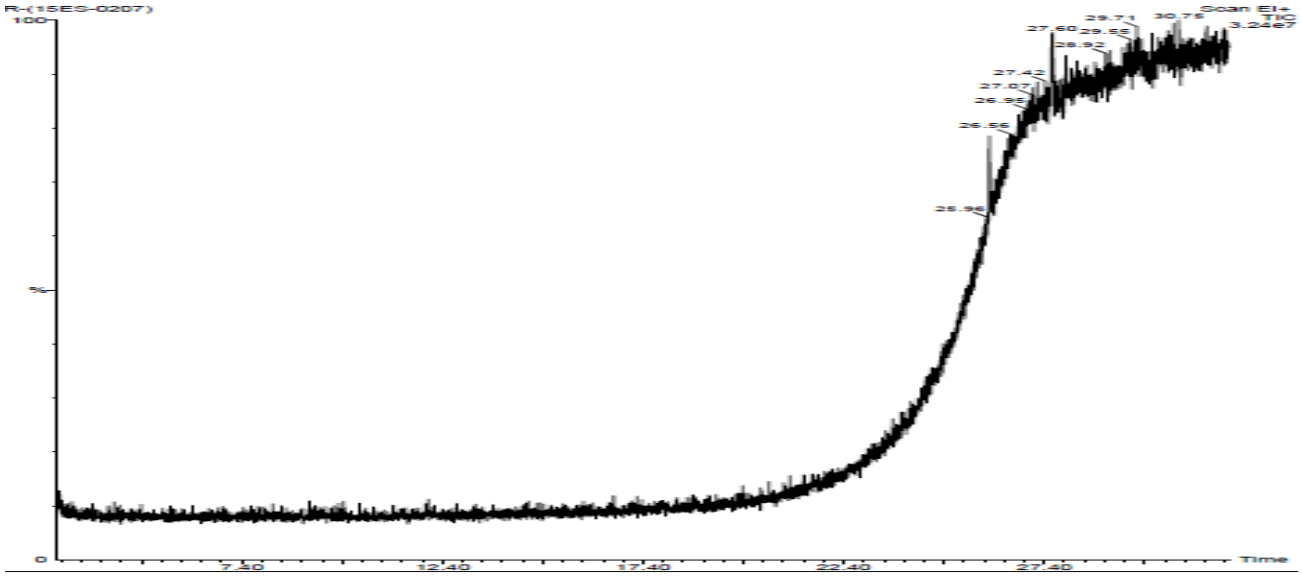


Fig. 7 Typical GC-MS chromatogram of Volatile organic compounds present in control system (double distilled water)

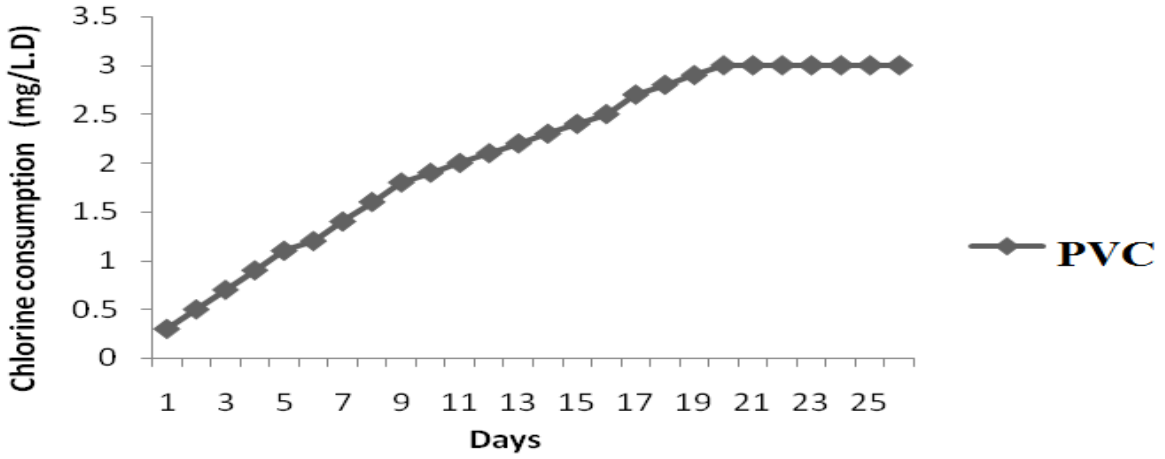


Fig. 8 Chlorine consumption rates (mg/ (L.d)) obtained during continuous migration test from PVC pipe at the end of 25th days

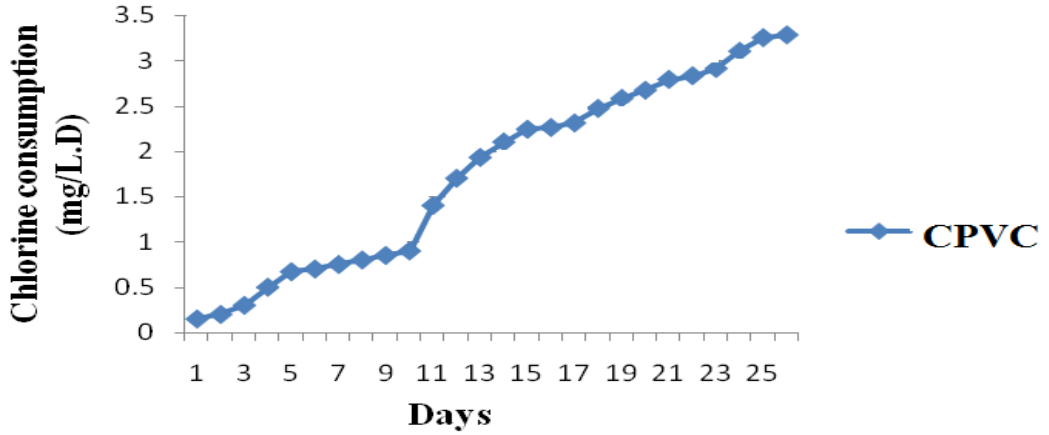


Fig. 9 Chlorine consumption rates (mg/ (L.d)) obtained during continuous migration test from CPVC pipe at the end of 25th days

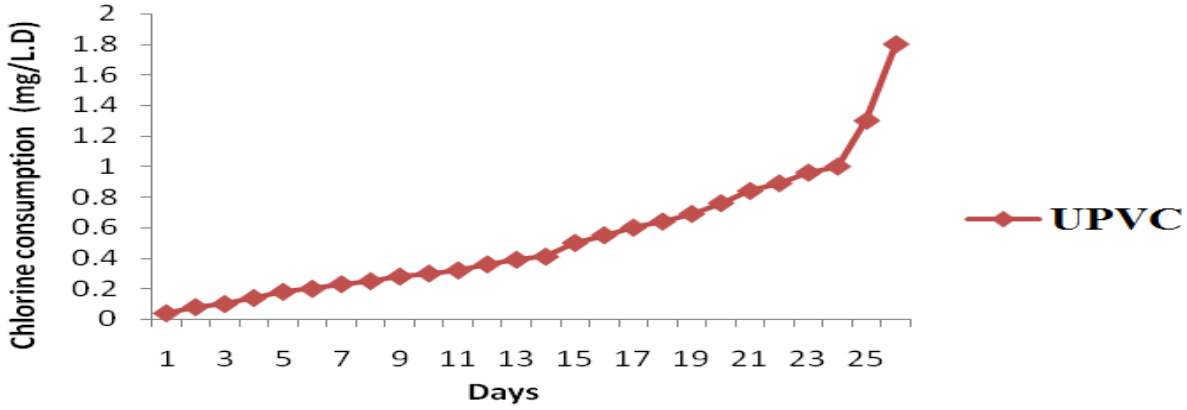


Fig. 10 Chlorine consumption rates (mg/ (L.d)) obtained during continuous migration test from UPVC pipe at the end of 25th days

Table 1 Classification of detected Volatile organic compounds migration from PVC pipe to double distilled water

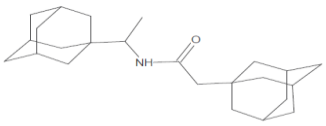
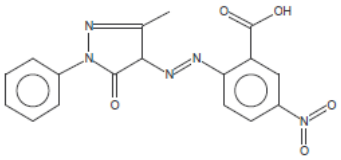
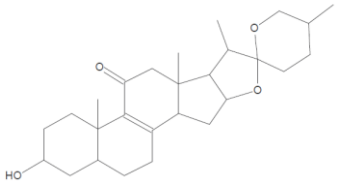
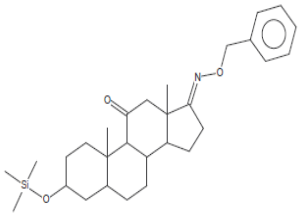
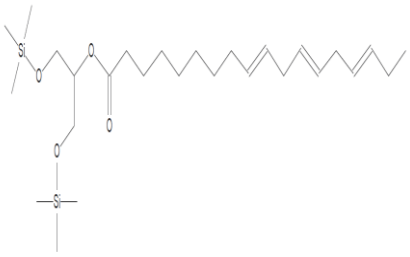
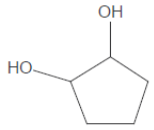
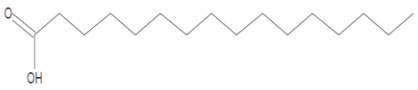
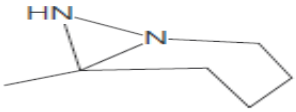
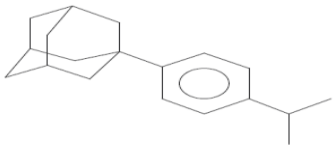
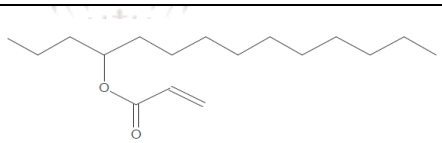
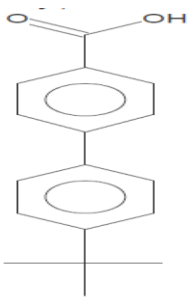
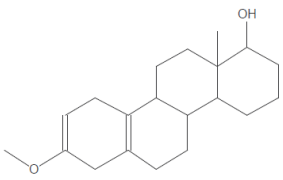
S. no	Retention time	Compounds	Structure	Molecular formula	Molecular weight
1.	37.6, 37.9	Acetamide, 2-(adamantan-1-yl)-N-(1-adamantan-1-ylethyl)-		$C_{24}H_{37}NO$	355
2.	46.6	2-(4,5-Dihydro-methyl-6-oxo-1-phenyl-4-pyrazolyl)-nitrobenzoic acid		$C_{17}H_{13}N_2O_5$	367
3.	48.5, 49.0,49.5	Spirost-8-en-11-one, 3-hydroxy-,(3.beta.,5.alpha., 14.beta.,20.beta., 22.beta.,25R)-		$C_{27}H_{40}O_4$	428
4.	50.1	Androstane-11,17-dione, 3-{(trimethylsilyl) oxy},17-{O-(phenylmethyl)oxime},(3.alpha.,5.alpha.)-		$C_{29}H_{43}NO_3Si$	481
5.	50.7	9,12,15-Octadecatrienoic acid, 2-[(trimethylsilyl)oxy]-1-[[(trimethylsilyl) oxy]methyl]ethyl ester,(Z,Z,Z)-		$C_{27}H_{52}O_4Si_2$	496

Table 2 Classification of detected Volatile organic compounds migration from CPVC pipe to double distilled water

S.no	Retention time	Compounds	Structure	Molecular formula	Molecular weight
1.	26.2	1, 2-Cyclopentanediol,trans-		$C_5H_{10}O_2$	102
2.	29.6	n-Hexadecanoic acid		$C_{16}H_{32}O_2$	256
3.	30.2	6-Methyl-1,7-diazabicyclo[4.1.0]heptanes		$C_6H_{12}N_2$	112
4.	31.4	1(-p-Cumenyl) adamantine		$C_{19}H_{26}$	254
5.	31.8, 32.9	4-(Prop-2-enoyloxy) tetradecane		$C_{17}H_{32}O_2$	268
6.	33.3	n-Butyl myristate		$C_{18}H_{36}O_2$	284
7.	34.0	Biphenyl-4-carboxylic acid, 4'-(1,1-dimethylethyl)-		$C_{17}H_{18}O_2$	254
8.	36.3, 37.3, 38.0, 38.6	3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol		$C_{20}H_{30}O_2$	302

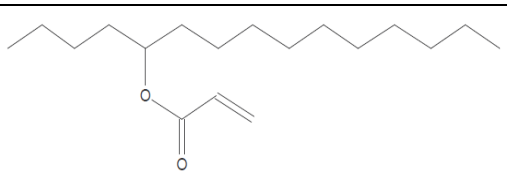
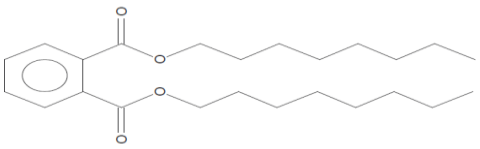
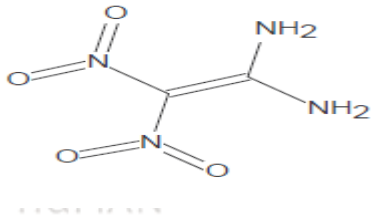
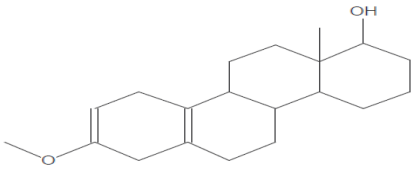
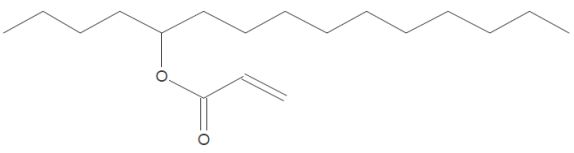
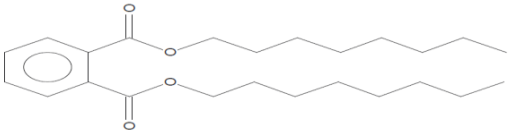
9.	38.9	5-(Prop- 2- enoyloxy) pentadecane		$C_{18}H_{34}O_2$	282
10.	39.7	Di-n-octyl phthalate		$C_{24}H_{38}O_4$	390

Table 3 Classification of detected Volatile organic compounds migration from UPVC pipe to double distilled water

S.no	Retention time	Compounds	Structure	Molecular formula	Molecular weight
1.	35.0	Ethene-1,1-diamine,2,2-dinitro-		$C_2H_4N_4O_4$	148
2.	37.3, 37.8	3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol		$C_{20}H_{30}O_2$	302
3.	38.9	5- (Prop- 2-enoyloxy) pentadecane		$C_{18}H_{34}O_2$	282
4.	39.7	Di-n-octyl phthalate		$C_{24}H_{38}O_4$	390

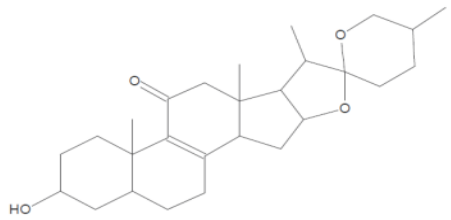
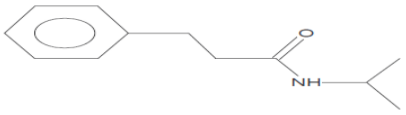
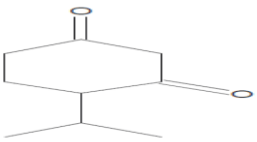
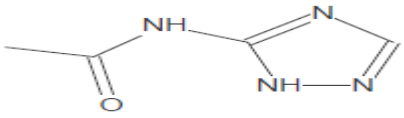
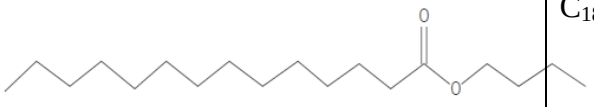
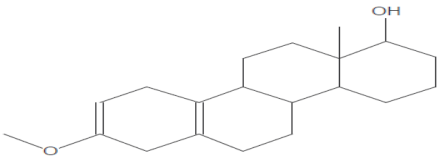
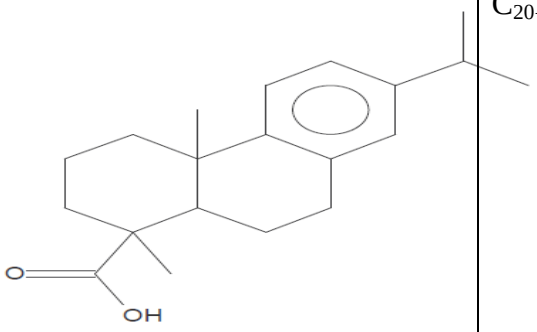
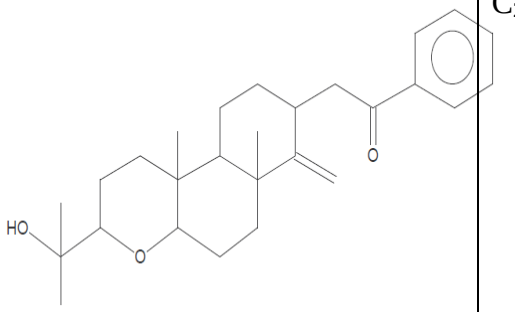
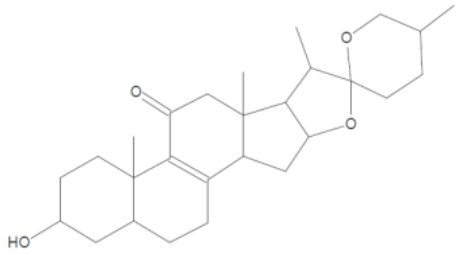
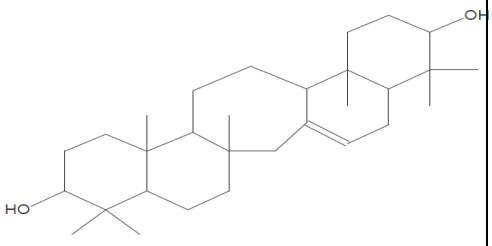
5.	48.5, 49.0	Spirost-8-en-11-one, 3-hydroxy-,(3.beta.,5.alpha., 14.beta.,20.beta., 22.beta.,25R)-		$C_{27}H_{40}O_4$	428

Table 4 Classification of detected Volatile organic compounds migration from PVC pipe to test drinking water

S.no	Retention time	Compounds	Structure	Molecular formula	Molecular weight
1.	20.1	N-Isopropyl-3-phenylpropanamide		$C_{12}H_{17}NO$	191
2.	21.8	4-Isopropyl-1,3-cyclohexanedione		$C_9H_{14}O_2$	154
3.	26.2	s- Triazole, 3-acetamido-		$C_4H_6N_4O$	126
4.	29.7, 30.8	n-Hexadecanoic acid		$C_{16}H_{32}O_2$	256
5.	33.3	n-Butyl myristate		$C_{18}H_{36}O_2$	284
6.	33.8	Hexadecen-1-ol,trans-9-		$C_{16}H_{32}O$	240

7.	37.3, 37.6	3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol		$C_{20}H_{30}O_2$	302
8.	38.0	1Phenanthrene carboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1, 4a-dimethyl-7-(1-methylethyl)-, [1R(1.alpha.,4a.beta., 10a.alpha.)]-		$C_{20}H_{28}O_2$	300
9.	46.1	2-[3-(1-Hydroxy-1-methyl-ethyl)-6a,10b-dimethyl-7-methylene-dodecahydro-benzo[f] chromen-8-yl]-1-phenyl-ethanone		$C_{27}H_{38}O_3$	410
10.	47.9	Spirost-8-en-11-one, 3-hydroxy-, (3.beta.,5.alpha., 14.beta.,20. beta.,22.beta.,25R)-		$C_{27}H_{40}O_4$	428
11.	48.5	18,22,22- Trimethyl-17,27,29,30--tetranor-c-homoolean-14-ene-3beta,21alpha-diol		$C_{30}H_{50}O_2$	442

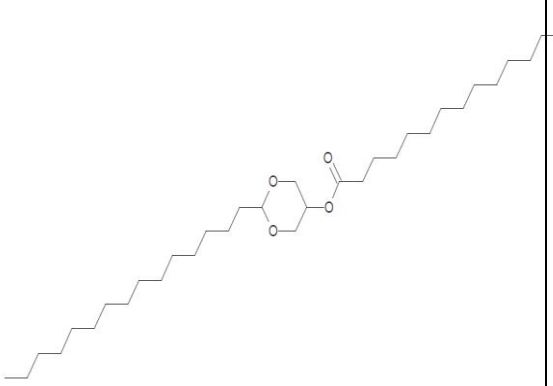
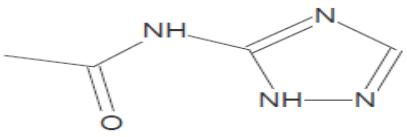
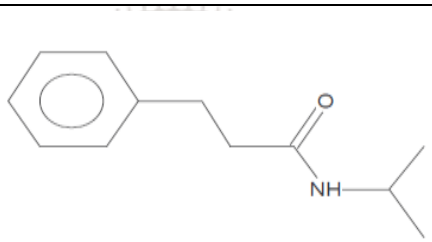
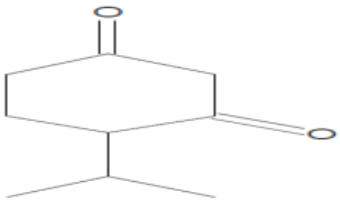
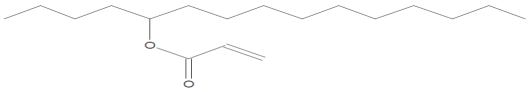
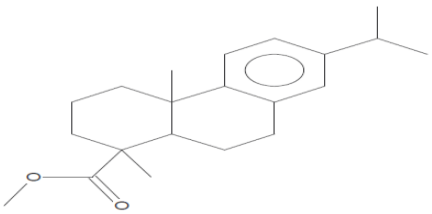
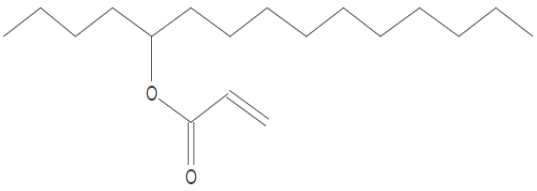
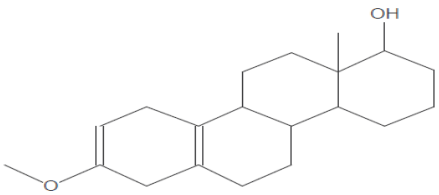
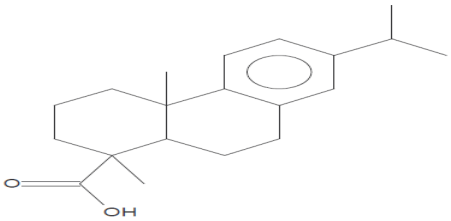
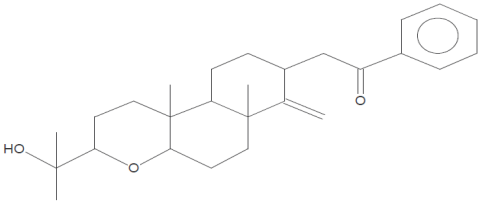
12.	50.1, 50.9, 51.3	Hexadecanoic acid, 2- pentadecyl-1,3-dioxan-5-yl ester,cis-		$C_{35}H_{68}O_4$	552

Table 5 Classification of detected Volatile organic compounds migration from CPVC pipe to test drinking water

S. no	Retention time	Compounds	Structure	Molecular formula	Molecular weight
1.	16.8	s-Triazole,3-acetamido-		$C_4H_6N_4O$	126
2.	19.5, 20.1	N-Isopropyl-3-phenylpropanamide		$C_{12}H_{17}NO$	191
3.	21.8	4-Isopropyl-1,3-cyclohexanedione		$C_9H_{14}O_2$	154
4.	30.2	n-Hexadecanoic acid		$C_{16}H_{32}O_2$	256
5.	33.4	n-Butyl myristate		$C_{18}H_{36}O_2$	284

6.	33.8	Hexadecen-1-ol,trans-9-		$C_{16}H_{32}O$	240

.	35.6	5-(Prop-2- enoyloxy) pentadecane		$C_{18}H_{34}O_2$	282
8.	36.4	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1, 4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-		$C_{21}H_{30}O_2$	314
9.	37.3	5-(Prop- 2- enoyloxy) pentadecane		$C_{18}H_{34}O_2$	282
10.	37.9	3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol		$C_{20}H_{30}O_2$	302
11.	38.0	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1, 4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-		$C_{20}H_{28}O_2$	300
12.	46.1	2-[3-(1-Hydroxy-1-methyl-ethyl)-6a, 10b-dimethyl-7-methylene-dodecahydro-benzo[f]chromen-8-yl]-1-phenyl-ethanone		$C_{27}H_{38}O_3$	410

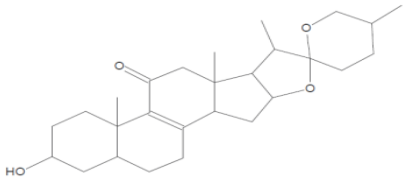
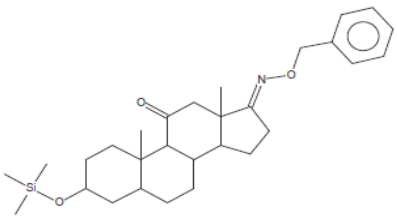
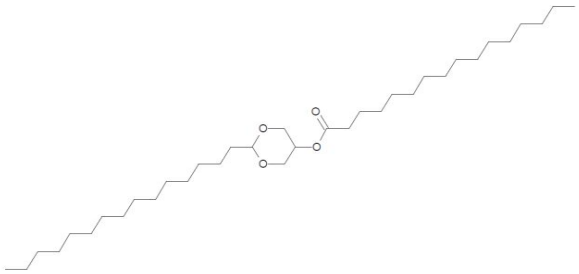
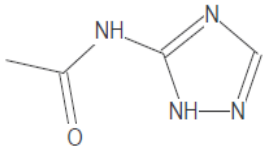
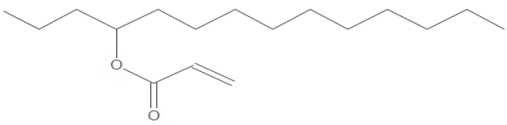
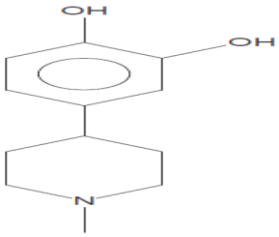
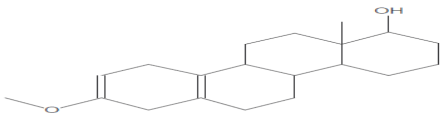
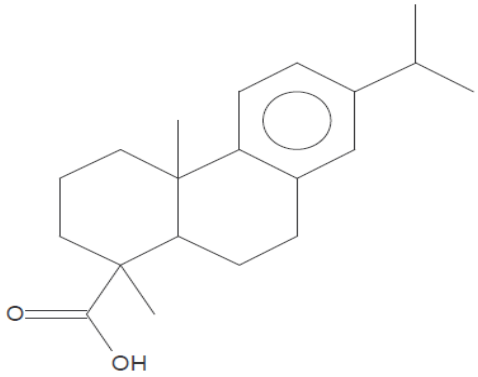
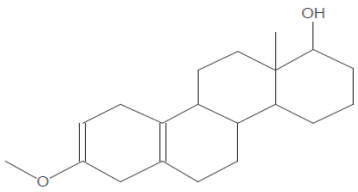
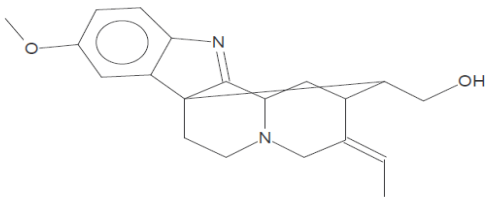
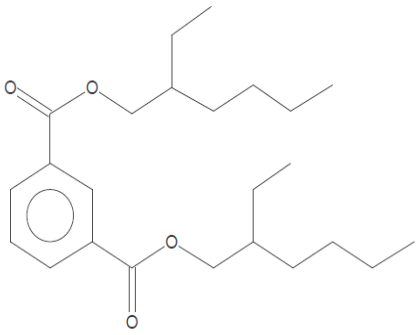
13.	47.9	Spirost-8-en-11-one, 3-hydroxy-,(3.beta.,5.alpha., 14.beta.,20.beta., 22.beta.,25R)-		$C_{27}H_{40}O_4$	428
14.	48.5	Androstane-11,17-dione, 3--{(trimethylsilyl)oxy}, 17-{O-(phenylmethyl)oxime}, (3.alpha.,5.alpha.)-		$C_{29}H_{43}NO_3Si$	481
15.	50.1, 50.9, 51.5, 52.1	Hexadecanoic acid, 2-pentadecyl-1,3-dioxan-5-yl ester,cis-		$C_{35}H_{68}O_4$	552

Table 6 Classification of detected Volatile organic compounds migration from UPVC pipe to test drinking water

S. no	Retention time	Compounds	Structure	Molecular formula	Molecular weight
1.	26.2	s- Triazole, 3-acetamido-		$C_4H_6N_4O$	126
2.	29.3	4-(Prop-2-enoyloxy)tetradecane		$C_{17}H_{32}O_2$	268

3.	29.6	n-Hexadecanoic acid		$C_{16}H_{32}O_2$	256
4.	30.2, 31.8	Hexahydropyridine, 1-methyl-4-[4,5-dihydroxyphenyl]-		$C_{12}H_{17}NO_2$	207
5.	31.4	n-Butyl myristate		$C_{18}H_{36}O_2$	284
6.	32.9	3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol		$C_{20}H_{30}O_2$	302
7.	33.3	n-Butyl myristate		$C_{18}H_{36}O_2$	284
8.	33.8	Hexadecen-1-ol,trans-9-		$C_{16}H_{32}O$	240

9.	35.6, 38.0	1-Phenanthrene carboxylicacid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta., 10a.alpha.)]-		$C_{20}H_{28}O_2$	300
10.	36.5, 37.3	3-Methoxy-D-homoestra-2,5(10)-dien-17beta-ol		$C_{20}H_{30}O_2$	302
11.	38.9	Akuammilan-17-ol, 10-methoxy-		$C_{20}H_{24}N_2O_2$	324
12.	54.8	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester		$C_{24}H_{38}O_4$	390