PEX.047

PERGAMON

Water Research 37 (2003) 1912–1920

WATER RESEARCH

www.elsevier.com/locate/watres

Volatile organic components migrating from plastic pipes (HDPE, PEX and PVC) into drinking water

Ingun Skjevrak*, Anne Due, Karl Olav Gjerstad, Hallgeir Herikstad

Regional Food Control Authority, Midt-Rogaland, Forusbeen 3, N-4033 Stavanger, Norway

Received 19 February 2002; received in revised form 11 November 2002; accepted 15 November 2002

Abstract

High-density polyethylene pipes (HDPE), crossbonded polyethylene pipes (PEX) and polyvinyl chloride (PVC) pipes for drinking water were tested with respect to migration of volatile organic components (VOC) to water. The odour of water in contact with plastic pipes was assessed according to the quantitative threshold odour number (TON) concept. A major migrating component from HDPE pipes was 2,4-di-tert-butyl-phenol (2,4-DTBP) which is a known degradation product from antioxidants such as Irgafos 168®. In addition, a range of esters, aldehydes, ketones, aromatic hydrocarbons and terpenoids were identified as migration products from HDPE pipes. Water in contact with HDPE pipes was assessed with respect to TON, and values $\geqslant 4$ were determined for five out of seven brands of HDPE pipes. The total amount of VOC released to water during three successive test periods were fairly constant for the HDPE pipes. Corresponding migration tests carried out for PEX pipes showed that VOC migrated in significant amounts into the test water, and TON $\geqslant 5$ of the test water were observed in all tests. Several of the migrated VOC were not identified. Oxygenates predominated the identified VOC in the test water from PEX pipes. Migration tests of PVC pipes revealed few volatile migrants in the test samples and no significant odour of the test water.

Keywords: Plastic pipes; Drinking water; VOC; Migration

1. Introduction

Pipes made of high-density polyethylene (HDPE) and polyvinyl chloride (PVC) have found wide-spread use in the drinking water distribution net. However, the quality of water passing through polyethylene pipes can be affected by migration of components from the plastic material such as additives and degradation products thereof as well as oxidation byproducts of the polymer. Leaching of phenolic compounds related to antioxidants such as BHT and various carbonyl compounds from polyethylene used in HDPE pipes and PE granulate is documented in the literature [1–4]. For PVC pipes, migration of various chlorinated compounds and organotin compounds have been reported [4–7]. Details on VOC migration from crossbonded polyethylene (PEX) pipes, used as a substitute for copper tubings for in-house installations, are not found.

Testing of organoleptic properties of drinking water in contact with plastic pipes was according to the CEN method for organoleptic assessment of water in piping systems.[1] This method prescribes static contact between water and plastic pipe for three successive periods each of 72 h duration. According to a Danish proposal for testing of plastic pipes for drinking water [8] based on the test conditions in the CEN method, no significant taste and odour of water should be observed in the third and final test. In addition, visual changes in the test

*Corresponding author..
E-mail address: skjevrak@nmt-mrog.rl.no (I. Skjevrak).

[1] EN 1420-1: Influence of organic materials on water intended for human consumption. Determination of odour and flavour assessment of water in piping systems. Part 1: Test method. CEN/TC164/WG3, 1999.

0043-1354/03/$ - see front matter
doi:10.1016/S0043-1354(02)00576-6

water should not be observed and the total amount of carbon (TOC) should decline from the first to the third test to a value less than 0.3 mg/l. Literature data describing the individual migrating species under these test conditions are however sparse. On background of the methods and proposals for testing of plastic pipes the present work focus on the identification and quantification of migrating VOC. The odour intensity of water kept in contact with plastic pipes is assessed as well as the relationship between VOC and odour. The total content of organic compounds is also measured. Organic components migrating from plastic pipes may serve as nutrients for micro-organisms, and thus promote microbial growth in pipelines [9–12]. The present work contributes to the knowledge on types and amounts of migrants available for microbial utilization in plastic pipes for drinking water.

2. Materials and methods

2.1. Principle

The quality of water in contact with plastic pipes during three successive test periods is described in terms of threshold odour number (TON), migration of volatile organic components (VOC) and bulk concentrations of organic carbon. Preparation of the test water samples is based on CEN method EN-1420-1 for testing of organoleptic properties of drinking water in contact with plastic pipes.

2.2. Plastic pipes used for testing

Seven brands of HDPE pipes (pressure and dimension classification: PN 10, PE50) were investigated and three 1 m test pieces of each brand were applied for migration testing. The dimension of HDPE pipes was $63 \times 5.8\,mm^2$ with an inner diameter (i.d.) corresponding to 51.4 mm. The ratio between area and volume of the tested pipes was $774.7\,cm^2/1000\,ml$ which corresponds to 0.8:1. Two different brands of PEX pipes were tested. One test piece of 13 m length was tested for each of the brands. The dimension of the tested PEX pipes was $15 \times 2.5\,mm^2$ with i.d. = 12 mm. The surface area to volume ratio of PEX pipes hence corresponds to $4000\,cm^2/1000\,ml = 4{:}1$. With respect to PVC pipes, two different brands were tested. Three test pieces each of 30 cm length were tested of each brand. The dimension of tested PVC pipes (PN 10), $110 \times 5.3\,mm^2$ and i.d. = 99.4 mm, thus corresponds to an area to volume ratio of $402\,cm^2/1000\,ml = 0.4{:}1$.

2.3. Migration tests

Ultrapure Milli-Q water used for migration tests (referred to as Milli-Q water) was obtained by prepurification of tap water using an Elgastat Option 4 equipped with reverse osmosis unit, UV-photo-oxidation and filter unit. Prepurified water was fed to a Milli-Q Gradient equipped with Millipore Q-Gard and Quantum filter units for additional polishing with respect to organic species. Pipe test pieces were flushed and kept in contact with Milli-Q water at stagnant conditions for 24 h according to the procedure described in EN-1420-1 prior to migration tests. After rinse and prewash, test pieces were filled with Milli-Q water, sealed with Al-stoppers and left at room temperature for 72 h. The water in the test pieces, referred to as the test water in the following text, was collected after 72 h and analysed with respect to VOC, TON, TOC and chemical oxygen demand (COD_{Mn}). The test pieces were refilled with Milli-Q water and left for an additional period of 72 h before sampling and analysis of the test water as described above. In total three successive tests each of 72 h duration were performed. An extended migration test of 41 days duration was carried out for HDPE pipe no. 1, and the test water analysed with respect to selected VOC. Migration tests were carried out in triplicate for each of the three successive tests for HDPE pipe no. 5 in order to evaluate the repeatability of VOC quantifications.

Reference samples were prepared by storing Milli-Q water in glass bottles with glass stoppers in parallel with the migration tests carried out for plastic pipes and analysed in correspondence with the test water samples.

2.4. VOC analysis

All glass equipment in contact with the test water samples or reference water samples for VOC determinations was heated to 450°C for 2 h prior to use in order to remove organic contaminants. VOC were concentrated from 1000 ml portions of the test water and reference samples by a purge and trap method based on the open-loop stripping principle [13,14]. Prior to purging two internal standards (1-chloro-octane and 1-chloro-decane, each 50 ng/l) were added to test and reference samples. Ultrapure N_2 (hydrogas 6.0, flow 100 ml/min) was used for purging and VOC were trapped on a Tenax GR adsorbent (60–80 mesh, Alltech). The Tenax adsorbent was kept in stainless-steel tubes supplied with the Perkin Elmer ATD-400 instrument. The water samples were kept at 40°C in a waterbath for 1 h during the purge and trap sequence while the Tenax tubes were kept at 55°C. VOC adsorbed on Tenax tubes were thermally desorbed using Perkin Elmer ATD-400 equipped with a Peltier cryofocusing Tenax GR trap and directly introduced to the column (Chrompack CP Sil 13 CB, 25 m, 0.25 mm i.d., 1.2 μm film thickness) of a HP 6890 GC connected to HP 5973 MSD using 70 eV EI ionization. Identification of VOC mass spectra was based on the Wiley database of mass spectra and confirmed with pure reference compounds in most cases. Calibration curves for quantification of VOC were established correspondingly by analyses of dilution series of reference compounds in Milli-Q water.

2.5. *Threshold odour number (TON)*

The organoleptic properties of water were assessed according to EN 1622 [15] which is based on a quantitative dilution method. Five dilutions of the test water samples were performed, and TON was assessed at a scale from 0 to $\geqslant 5$. Milli-Q water (TON = 0) was used as reference. TON values higher than three were assigned to water samples with significant odour in accordance with Norwegian drinking water regulations. The uncertainty in TON assessment is estimated to ± 1 by repetitive determinations.

2.6. *Bulk parameters for organic content*

Chemical oxygen demand (COD_{Mn}) was determined according to a Norwegian standard method [16], and the limit of detection is 1 mg/l O. TOC was determined according to ISO-8245 [17]. The limit of detection was 0.4 mg/l C.

3. Results

3.1. *VOC in the test water from HDPE pipes*

Table 1 shows VOC identified in the test water samples from HDPE pipe migration experiments. The identified VOC in HDPE pipe test samples were grouped in six compound classes (Table 1). These compound classes comprised of components related to antioxidants, esters, aldehydes, ketones, terpenoids and aromatic hydrocarbons. The same components were quantified in the three successive tests and represent major parts of identified VOC for all HDPE pipes (Table 2). VOC detected but not identified in the test water samples were present in minor amounts.

Control of VOC background level in water used for testing and the applied analytical apparatus is crucial for successful low-level VOC determination. Concentration levels of background VOC in reference water samples showed that the amounts of total VOC (TVOC) in reference samples varied between 80 to 280 ng/l for the same classes of VOC as those determined in the test water (Table 2). These concentrations were low compared to the lowest concentration of TVOC observed in the test water samples (1.3 μg/l, pipe no. 6).

The TVOC in the test water samples varied among the HDPE pipe brands (Fig. 1). The lowest yields of TVOC were observed in the test water from HDPE pipe no. 4 and 6, whereas TVOC yields in the test water from pipe

Table 1
Classification of detected VOC in migration tests with HDPE pipes

Component class	Class no.	Identified VOC	Abbreviation
Components related to antioxidants	1	2,6-Di-tert-butyl-benzoquinone	2,6-DTBQ
		2,4-Di-tert-butyl phenol	2,4-DTBP
		4-Methyl-2,6-di-tert-butyl-phenol	BHT
Esters	2	Butyl acetate	
		Ethyl hexanoate	
		Hexyl acetate	
		Propyl hexanoate	
		Butyl hexanoate	
		Ethyl octanoate	
		Hexamethyl butanoate	
		Isobornyl acetate	
		Hexyl hexanoate	
		Ethyl decadienoate	
		2,2,4-Trimethyl-1,3-pentanediol-diisobutyrate	2,2,4-TPD
Aldehydes	3	Nonanal	
		Decanal	
Ketones	4	2-Decanone	
		2-Undecanone	
		2-Dodecanone	
Terpenoids	5	Alpha pinene	
		Delta carene	
		Limonene	
		Alpha terpinolene	
		Alpha farnesene	
Aromatic	6	Benzene	
		Hydrocarbons	
Toluene			
		Ethyl benzene	
		m- and *p*-xylene	
		o-Xylene	
		Styrene	
		Isopropyl benzene	
		n-Propyl benzene	
		Ethyl methyl benzene	
		1,3,5-Trimethyl benzene	
		1,2,4-Trimethyl benzene	
		p-Isopropyl toluene	
		Naphthalene	

Table 2
Quantitative results for VOC in test water from seven HDPE pipe brands. Migration tests were carried out by three successive tests each of 72 h duration

Pipe brand no.	Test no.	VOC i test water (ng/l)							Testwater TON	VOC in reference water (ng/l)							Reference water TON
		Component class no.								Component class no.							
		1	2	3	4	5	6	Total VOC		1	2	3	4	5	6	Total VOC	
1	1	2220	540	840	210	40	1100	4950	≥5	0	0	70	0	0	30	100	0
	2	1490	430	880	270	50	1200	4320	≥5	0	0	90	0	0	20	110	0
	3	1760	390	780	300	40	1080	4350	≥5	0	0	50	0	0	20	80	0
2	1	780	350	730	60	40	600	2560	4	0	0	70	0	0	30	100	0
	2	450	190	460	50	40	540	1730	4	0	0	100	0	0	20	120	0
	3	400	200	700	60	40	400	1800	4	0	0	50	0	0	30	80	0
3	1	780	20	60	120	20	1270	2270	4	10	0	70	0	0	100	190	0
	2	1130	10	70	120	10	1390	2730	≥5	10	0	100	0	0	120	240	0
	3	750	20	40	90	10	1310	2220	≥5	20	0	60	10	0	40	140	0
4	1	330	110	260	120	50	930	1800	1	10	0	110	20	10	70	220	0
	2	390	140	460	120	40	940	2090	2	10	0	60	10	0	40	120	0
	3	300	110	340	160	30	810	1750	2	10	0	100	10	0	30	160	0
5	1	5180	710	950	300	60	1150	8350	≥5	10	0	50	0	0	20	90	0
	2	5010	610	600	250	70	840	7380	4	20	0	70	10	0	130	230	0
	3	4320	530	690	230	60	660	6490	≥5	10	0	50	0	0	180	250	0
%RSD[a]		10	10	4	12	7	3	7									
6	1	780	30	70	50	30	410	1370	1	10	0	60	10	0	30	120	0
	2	680	100	130	70	20	320	1320	1	10	0	80	10	0	10	100	0
	3	990	90	120	70	30	290	1590	0	10	0	70	10	0	10	100	0
7	1	1670	280	500	80	80	450	3060	≥5	10	0	60	0	0	30	100	0
	2	1990	170	150	60	50	390	2810	4	10	0	80	10	0	180	280	0
	3	2530	140	110	60	50	220	3110	≥5	10	0	70	20	0	30	130	0

Class 1 = components related to antioxidants, class 2 = esters, class 3 = aldehydes, class 4 = ketones, class 5 = terpenoids, class 6 = aromatic hydrocarbons.

[a] %RSD is based on triplicate runs of each test for HDPE pipe no. 5.

no. 2 and 3 were slightly higher. The highest amounts of TVOC were observed in test samples from pipe no.1, 5 and 7 (Table 2).

3.1.1. *Classes of identified VOC*

Components related to antioxidants (class 1, Table 1) predominated most of the test water samples from HDPE pipes, and include 2,4-di-tert-butyl phenol (2,4-DTBP), 2,6-di-tert-butyl benzoquinone (2,6-DTBQ) and in some of the test samples, trace amounts of BHT. 2,4-DTBP is known as a degradation product of, e.g. Irgafos 168® (tris(2,4-di-tert-butyl-phenol)phosphite)[18]. 2,4-DTBP was a major component within the class 1 components in the test water samples from all tested HDPE pipes except pipe nos. 2 and 4 (Table 3). The relative contribution of 2,4-DTBP to the amount of TVOC in successive tests varied from 1% to 4% (pipe no. 4) and 53% to 79% (pipe no. 7). High relative contribution from 2,4-DTBP to TVOC was also found in test samples from pipe no. 5. The highest concentrations of 2,4-DTBP (5 μg/l) was observed in test no. 1 from pipe no. 5.

2,6-DTBQ, a degradation product of the antioxidants Irganox 1010® and Irganox 1076® [19], was present in lower yields than 2,4-DTBP in most test water samples except in test waters from HDPE pipe brands no. 2 and 4. The yield of 2,6-DTBQ varied between 60 and 600 ng/l (data not shown) in the test water samples from the seven HDPE brands. BHT is widely used as an antioxidant in plastics and is frequently encountered as a background contaminant. The amount of BHT in the test samples corresponded to the background (reference) level or slightly above the background level in some of the test samples, and is thus regarded as insignificant in this context.

A number of ester compounds were identified in the test water from HDPE pipes (class 2, Table 1). Butyl hexanoate was a major individual component with maximum concentration around 300 ng/l. Another abundant ester component, 2,2,4-trimethyl-1, 3-pentanediol diisobutyrate (2,2,4-TPD) is known as a plasticizer in surface coatings, moldings and for PVC plastisols and organosols [18]. 2,2,4-TPD has been reported as a plasticizer in HDPE pipes [1]. HDPE pipes investigated in the present work are however unplasticized. 2,2,4-TPD is an abundant background component in our reference water samples, and is therefore also present in the test water samples. Potential migration of 2,2,4-TPD from HDPE pipes was thus considered less likely, and its presence in the test water was ascribed to the high background level. Hence, this component was not included in the total amount of esters (Table 2).

The aldehydes nonanal and decanal (class 3, Table 1) were encountered in amounts well above the reference level in most test water samples except in the test water samples from HDPE pipes no. 3 and 6. The maximum concentrations of these aldehydes in the test water samples were close to 1 μg/l. Aldehydes are known to be thermal degradation products generated during pipe production [2,3]. The background level of nonanal and decanal is mainly due to degradation of the Tenax adsorbent. Ketones (class 4) in the test waters were comprised of 2-decanone, 2-undecanone and 2-dodecanone which probably are high-temperature byproducts as described for aldehydes. Terpenoids (class 5) were also detected in amounts less than 100 ng/l (Table 2). The origin of terpenoids is not known.

Aromatic hydrocarbons (class 6, Table 1) in the test water samples were comprised of benzene, toluene, ethylbenzene, xylenes, styrene and various C3- and C4-alkylated benzenes in addition to naphthalene. The background level of aromatic hydrocarbons is mainly due to toluene in ambient air. The concentration of aromatic hydrocarbons in the test water varied within the range 200–1300 ng/l (Table 2). The amount of benzene varied between blank level or slightly above blank level up to concentrations of 500 ng/l in the test water from pipe no. 4, and 1 μg/l in pipe no. 3.

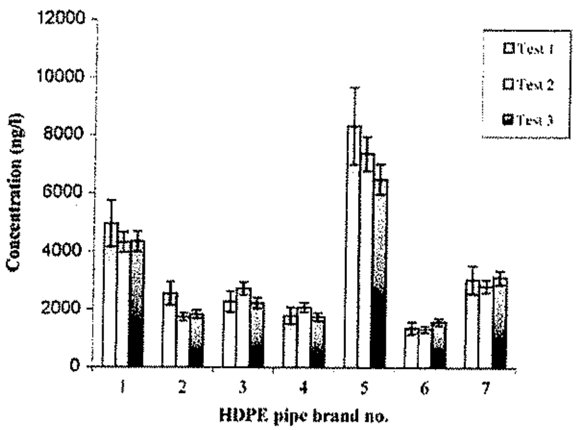

Fig. 1. Concentration of TVOC in the test water samples from HDPE pipes. The analytical uncertainty between successive tests is indicated.

3.1.2. *VOC concentration in successive tests*

Migration tests were carried out in triplicate for each of the successive tests for HDPE pipe no. 5. The analytical deviations based on the repeated migration tests for the various classes of components varied between 3% mRSD and 12% RSD for HDPE pipe no. 5 (Table 2). The difference observed between tests of HDPE pipe no. 5 was investigated by Students *t*-test, and the analytical uncertainty at 95% confidence level corresponds to 2.3 times the standard deviation. At 95% confidence level no significant difference was found between tests 1 and 2 with respect to the amount of TVOC. The difference between tests 1 and 3 with respect to TVOC was however significant. Analytical uncertainties for HDPE pipe no. 5 were considered representative for all HDPE pipes and are indicated in Fig. 1. The analytical deviation for 2,4-DTBP corresponded to 10% RSD (data not shown), and the concentration

Table 3
Migration of 2,4-di-tert-butyl phenol from HDPE pipes to water during three successive tests

Pipe brand no.	Concentration in test water (ng/l)				Concentration in reference water (ng/l)		
	Test 1	Test 2	Test 3	Total	Test 1	Test 2	Test 3
1	1950	1320	1570	4840	0	0	0
2	140	60	40	240	0	0	0
3	630	940	580	2150	10	0	0
4	60	40	20	120	0	0	0
5	5000	4800	4200	14000	10	10	10
6	700	610	910	2220	0	0	0
7	1600	1920	2470	5990	10	10	10

of 2,4-DTBP in the three successive tests for pipe no. 5 (Table 3) was not significantly different.

Inspection of the VOC data in Table 2 reveals that VOC concentrations of individual classes of components as well as TVOC were rather similar in the three successive tests carried out for each HDPE pipe brand (Fig. 1). In most cases, the observed differences between the successive tests were accounted for by analytical uncertainties as indicated in Fig. 1. Significant reduction in TVOC concentration in test 1 compared to test 3 is observed for HDPE pipes nos. 2 and 5 only. The concentration of 2,4-DTBP (Table 3) was significantly reduced from the first through the third test in the test water from pipe nos. 1 and 4. The concentration of 2,4-DTBP in the test water from the other pipes was similar for all tests or significantly higher in the second or third test compared to the first test. Analyses of VOC in water from the 24 h prewash period showed that the concentrations of VOC were slightly higher or similar to those in the following 72 h tests (data not shown).

Since the VOC concentrations in the successive tests were similar, an extended test of 41 days duration was carried out for one of the HDPE pipes (no. 1) in order to investigate the concentration trends for selected VOC beyond the 10 days specified in the standard method. The concentration of major components related to antioxidants (class 1) decreased just slightly during this extended test period, and after 41 days the concentration approached half the value observed at the first 72 h test. A similar concentration trend was observed for major ester components (hexanoates), although a slightly enhanced decline in concentration with time was observed for these components compared to class 1 components. The results shows that migration of these components persisted beyond the 41 days test period (data not shown).

3.2. *VOC in the test water from PEX pipes*

The predominating VOC in the test water from PEX pipes was methyl-tert-butyl ether (MTBE). In test water from PEX pipe no. 1 the MTBE concentration was reduced from 47.6 μg/l in the first test to 33.5 μg/l in the third test (Table 4). In test water from PEX pipe no. 2 the concentrations were considerably lower: 5.8 μg/l in the first test and 5.0 μg/l in the third test (Table 4). Repeated tests were not run for PEX pipes and the contribution of analytical deviations to the observed differences in VOC concentrations between successive tests is not known. Several unidentified compounds, presumably various oxygenates, were encountered in the test water samples along with the identified VOC. Unidentified VOC were not quantified and their contribution to the total amount of organic migrants is not known. Some of the unidentified components appeared in the test waters for both PEX brands, whereas others were specific for individual brands.

3.3. *VOC in the test water from PVC pipes*

VOC detected in the test water from PVC pipes (data not shown) were comprised of hexanal, octanal, nonanal and decanal. Only trace amounts of hexanal and octanal were found in the test water from the three successive tests for both PVC pipes, whereas nonanal and decanal were present in concentrations from 280 ng/l or less (pipe no. 1) and 170 ng/l or less (pipe no. 2). Analyses of wash water from the 24 h prewash carried out prior to migration experiments revealed that concentration of nonanal and decanal were four to eight times higher than observed in the test water from the first 72 h migration test.

Table 4
Results from migration experiments carried out with PEX pipes for three successive 72-h test periods

Parameter	VOC (ng/l) in test water from PEX pipe no. 1			VOC (ng/l) in test water from PEX pipe no. 2		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Methyl tert-butyl ether	47600	37300	33500	5800	5100	5000
Tert-butanol	540	580	510	1130	300	1180
4-Butoxy phenol	nd	nd	nd	2550	550	2250
5-Methyl-2-hexanone	870	770	660	nd	nd	nd
Ionol	+	+	+	nd	nd	nd
Mesityl oxide	nd	nd	nd	400	50	250
Tert-butyl isobutyl ether	nd	nd	nd	100	50	100
Unidentified VOCs	+ +	+ +	+ +	+ +	+ +	+ +
COD_{Mn} (mg/l)	< 1	< 1	1	2	1,5	1,3
TOC (mg/l)	1,6	1,4	1,3	2,1	2,5	2,5
TON	⩾5	⩾5	⩾5	⩾5	⩾5	⩾5

In cases where quantitative data not were established. Relative amounts of VOC are indicated with + or + +.
nd: Not detected.

3.4. Threshold odour number (TON)

The test water samples from five out of seven different brands of HDPE pipes gave TON ≥ 4 (Table 2). The two HDPE pipes nos. 4 and 6 imparted no or insignificant odour (TON ≤ 2) to water, whereas the test waters from pipes nos. 1, 2,3,5 and 7 showed high TON values. The TON values were not reduced from the first to the third test.

TON values ≥ 5 were assigned to all test samples of both PEX pipes (Table 4).

Significant odour was not observed from PVC test samples where TON mainly was assessed to a value of zero and not higher than two in any of the tests (data not shown).

3.5. Bulk parameters for organic carbon content

Measured values for TOC and COD_{Mn} were lower than the detection limits for the respective methods for all reference and test samples from HDPE pipes.

Migation of organic components was significant for the two tested PEX pipes. COD_{Mn} values of the two first tests of PEX pipe no. 1 (Table 4) were less than the detection limit whereas the COD_{Mn} for the third test was equal to 1 mg/l O. TOC values were reduced from 1.6 mg/l in the first test to 1.3 mg/l in the third test for PEX pipe no. 1. For PEX pipe no. 2 COD_{Mn} was reduced from 2 mg/l O in the first test to 1.5 mg/l O and 1.3 mg/l O in the second and third test, respectively. TOC values increased from 2.1 mg/l in the first test to 2.5 mg/l in the two following tests (Table 4). These data do not indicate positive correlations between COD_{Mn} and TOC values in the test waters from PEX pipes.

TOC and COD_{Mn} results for PVC pipes were lower than the detection limits for all test samples (data not shown).

4. Discussion

The presented data show that water quality can be affected by migration of organic components to a varying extent when plastic pipes are in static contact with water. The tests were carried out on unused pipes, prior to potential impacts of use and ageing.

4.1. HDPE pipes

The composition of VOC in the test waters from HDPE pipes is dominated by components related to antioxidants (class 1) where 2,4-DTBP and 2,6-DTBQ are major individual components. Various carbonyl compounds and aromatic hydrocarbons are present as well. The concentration of benzene in water from one of the tested HDPE pipes corresponds to the limit of benzene (1 μg/l) given in EU's drinking water directive [20]. In the test water from the remaining HDPE pipes the concentration of this compound is well below 1 μg/l. Leaching of phenolic antioxidants such as BHT and alkylbenzenes have been associated with odour of water passing through HDPE pipes [1]. Off-flavours from HDPE pellets are ascribed to the presence of carbonyl compounds such as aldehydes, ketones and esters [2,3,21,22]. Some alkylated benzoquinones are known to cause off-flavours to water [19]. Terpenoids were present in very low concentrations and are less likely to affect TON in the present case, even if these compounds are well-known odourants. Literature data thus confirm that VOC identified in the test waters from HDPE pipes (Table 1) have an odour potential, and the results show that TON values ≥ 4 were measured in all tests with five out of seven brands of HDPE pipe. This means that test samples for five HDPE pipes show unacceptable odour deviations and do not comply with Danish test proposals [8].

Individual VOC can vary considerably with respect to their odour threshold values, which means that individual components contribute to a varying extent to the odour of the sample. In the present work, the test water samples with the lowest amounts of TVOC also showed the lowest TON values and hence, insignificant odour of test samples. Test samples with high concentrations of TVOC showed significant odour and gave high TON values. These results indicate a proportionality between TON and TVOC concentrations. However, test samples from the two HDPE pipes no. 2 and 3 with rather low TVOC yields did not support this trend. This suggests that high concentrations of TVOC were associated with high TON, whereas low concentrations of TVOC not necessarily implies low TON values. In cases where high TON values were noted despite relatively low yields of TVOC it is possible that components contributing to odour are not detected by the applied method, or that additional components with particularly low odour threshold values are present. For most of the test samples it is however concluded that the concentration of TVOC and TON values were positively correlated.

A slight although significant reduction in concentration of TVOC from the first to third test was observed only for two of the seven HDPE pipes. For the remaining pipes the differences between the concentrations of TVOC throughout the successive tests were accounted for by analytical uncertainty. This means that the VOC migration yields were not, or very slightly, reduced from the first to the third test. This is not in agreement with requirements for total organic content in the Danish test proposal [8]. Minor or insignificant differences in concentrations of TVOC in the three tests were in accordance with the stable TON values throughout the test period. This indicate that in cases where high TON values and high concentrations of

TVOC are observed in the first 72 h tests, significant release of VOC and unacceptable odour may be expected also beyond the specified 10 days test period.

The stable concentration levels observed throughout the three successive 72 h tests are confirmed by the test results from the 41 days test period, which showed that VOC concentration decreased slowly in the tests carried out beyond the first 10 days. With respect to class I components, which represents degradation products from antioxidants, persistent migration should be expected as the HDPE polymer is protected against degradation during the lifetime of the pipe by degradation of antioxidants.

Measured values of TOC and COD_{Mn} in the test water from HDPE pipes were less than the respective detection limits in all samples, including those with significant odour. Hence, these bulk parameters are not sufficient for evaluating the migration from HDPE pipes with respect to specific components which affect water quality.

4.2. PEX pipes

Formation of oxygenated byproducts from cross-bonding processes based on organic peroxide reactions during PEX pipe production is likely to contribute to VOC in the test water samples. This is in agreement with the abundant oxygenated components identified in the present work. The major individual component identified, MTBE, is known to cause taste and odour episodes and should, according to recommendations issued by US EPA, not exceed 20–40 µg/l [23,24]. MTBE is thus assumed to be one of the major contributors to the high values for TON ($\geqslant 5$) found in all the test water samples from PEX pipe no. 1. Unidentified VOC probably contribute to high TON values as well.

The total amount of VOC migrating from PEX pipes is not known since unidentified VOC were not quantified. High migration levels were however confirmed by organic bulk parameters. Unlike HDPE pipes, PEX pipes generally produced measurable COD_{Mn} and TOC values in the test water. However, the organic content determined by TOC were not in agreement with those determined by COD_{Mn}. The deviation between these two bulk parameters is not unexpected since the sample work-up procedure differs and the COD_{Mn} method is developed for easily oxidized substances. According to the Danish test proposal [8], the TOC content was too high in the final test of both PEX pipes. The presence of odour potent components as well as the considerable proportion of unknown components suggests that the organic bulk parameters are not sufficient for evaluation of migration from PEX pipes. The high content of organic compounds in PEX test water could be due to either the high area to volume ratio for PEX tubes (area:volume ratio 4:1) or the quality of the PEX material itself. High migration levels of organic compounds from PEX pipes used at in-door temperatures may promote bacterial regrowth, and needs further investigation.

4.3. PVC pipes

Particularly high relative concentrations of nonanal and decanal in wash water samples compared to the subsequent migration tests were observed for PVC pipes. These observations were different to the situation for HDPE pipes where the VOC concentration in samples taken from the 24 h wash water was slightly higher or comparable to those of the following test samples. The relatively high concentration of aldehydes in wash water from PVC pipes suggests that major parts of VOC from PVC pipes originate from a surface layer which is readily removed by the initial rinse and wash procedure. Organic bulk parameters and TON values confirm low migration from PVC pipes.

5. Conclusions

- Volatile organic components (VOC) migrating from high-density polyethylene pipes (HDPE) pipes into water were comprised of compounds related to antioxidants in addition to esters, aldehydes, ketones, aromatic hydrocarbons and terpenoids. 2,4-di-tert-butyl phenol was a major individual component.
- The test water from five out of seven brands of HDPE pipes showed threshold odour number (TON) $\geqslant 4$, and thus significant odour. The total amounts of VOC (TVOC) were proportional to TON in the test water from most of the HDPE pipes.
- Values for COD_{Mn} and TOC from HDPE pipe test waters were lower than the detection limits and these parameters are thus not suited for determination of migration with respect to specific components which can affect water quality.
- Several VOC were observed in the test water from PEX pipes, but relatively few were identified. The identified VOC were mainly constituted by oxygenates with MTBE as the major individual VOC.
- MTBE was found in concentrations above the recommended US EPA taste and odour values for MTBE in drinking water in one PEX pipe, and is probably a significant contributor to the high TON values of test water from PEX pipes.
- COD_{Mn} and TOC indicated in most cases leaching of organic material from PEX pipes to water. The high concentrations of organics in test water could be due to the quality of the PEX material as well as high area to volume ratio in these pipes.
- Test water from PVC pipes contained few VOC in low concentrations and TON was mainly zero.

Acknowledgements

The Norwegian Research Council is thanked for financial support of this work. Dr. Gunnar Mosevoll, Skien Kommune, is thanked for reading through the initial project report upon which this manuscript is based. Dr. Dag Hongve, Norwegian Institute of Public Health, is thanked for reviewing the manuscript.

References

[1] Anselme C, N'Guyen K, Bruchet A, Mallevialle J. Can polyethylene pipes impart odors in drinking water ? Environ Technol Lett 1985;6:477–88.

[2] Bravo A, Hotchkiss JH, Acree TE. Identification of odor-active compounds resulting from thermal oxidation of polyethylene. J Agric Food Chem 1992;40:1881–5.

[3] Bravo A, Hotchkiss JH. Identification of volatile compounds resulting from the thermal oxidation of polyethylene. J. Appl Polym Sci 1993;47:1741–8.

[4] Suffet I, Mallevialle J, Kawczynski E (Eds.). Advances in taste and odor. Treatment and control. Cooperative Research Report, American Water Works Association Research Foundation, Lyonnaise des Eaux, 1995. p. 296–306, ISBN 0-89867-744-0.

[5] Mallevialle J, Suffet I. Identification and treatment of tastes and odors in drinking water. Report, American Water Works Association Research Foundation (Denver, Colorado) and Lyonnaise des Eaux, 1987.

[6] Hao O, Phull K, Simmers K. Laboratory evaluation of the leaching of organics from fabric material. Journal of American Water Works Association 1992;84:92–8.

[7] Sadiki A, Williams D, Carrier R, Thomas B. Pilot study on the contamination of drinking water by organotin compounds from PVC-materials. Chemosphere 1996; 32(12):2389–98.

[8] Forslund J. Release of components from materials. Lecture Given at the 1. Nordic Conference on Drinking Water Supply, Norwegian, May 26–28, Kristiansund N, Norway, (Afgivelse av stoffer fra materialer. Forelesning ved den 1.nordiske Vannforsyningskonferansen 26–28. mai, Kristiansund N, Norge), 1998.

[9] Van der Kooij D, Suylen G. Interaction of water with pipes. Water Supply 1991;9(3–4):1–12.

[10] LeChevallier M, Schulz W, Lee R. Bacterial nutrients in drinking water. Appl Env Microbiol 1991;57(3):857–62.

[11] Van der Kooij D, Veenendaal HR. Assessment of the biofilm formtion potential of synthetic materials in contact with drinking water during distribution. Proceedings of the AWWA WQTC, 1993. p. 1395–1407.

[12] Kerr CJ, Osborn KS, Roboson GD, Handley PS. The relationship between pipe material and biofilm formation in a laboratory model system. J Appl Microbiol 1999;85: 29–38.

[13] Skjevrak I. Drinking water off-flavours-can we identify their chemical constituents? Vatten 1998;54:209–12 [Norwegian, English abstract].

[14] Sävenhed R, Boren H, Grimvall A, Tjeder A. Stripping techniques for the analysis of odorous compounds in drinking water. Water Sci Technol 1983;15(6–7): 139–48.

[15] EN 1622 Water analysis. Determination of the threshold odour number (TON) and threshold flavour number (TFN), October 1997.

[16] NS-4759 Water analysis. Determination of chemical oxygen demand COD_{Mn}. in: Oxidation with permanganate, Norwegian standard, 1st ed. November 1981.

[17] ISO-8245-1 Water quality. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC), 1999.

[18] Ash M, Ash I. Plastic and Rubber Additives Electronic Handbook, Gower, England 1995.

[19] Effect of distribution on organic contaminants in potable water. Final Report to the Department of the Environment DoE 2215-M/1, Report No. DW10032, EPA, 1990.

[20] EU Drinking Water Directive, Council Directive 98/93, 3 November, 1998.

[21] Villberg K, Veijanen A, Gustafsson I, Wickstrøm K. Analysis of odour and taste problems in high-density polyethene. J Chromatogr A 1997;791:213–9.

[22] Villberg K, Veijanen A. Identification of off-flavour compounds in high-density polyethylene (HDPE) with different amounts of abscents. Polym Eng Sci 1998; 38(6): 922–5.

[23] Gullick RW, LeChevallier M. Occurrence of MTBE in drinking water sources. Journal of American Water Works Association 2000;92(1):100–13.

[24] Dale MS, Koch B, Losee RF, Crofts EW, Davis MK. MTBE in Southern California water. Journal of American Water Works Association 2000;92(8):42–51.