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Long-term study of migration of volatile organic compounds from cross-linked polyethylene (PEX) pipes and effects on drinking water quality

Vidar Lund, Mary Anderson-Glenna, Ingun Skjevrak and Inger-Lise Steffensen

ABSTRACT

The objectives of this study were to investigate migration of volatile organic compounds (VOCs) from cross-linked polyethylene (PEX) pipes used for drinking water produced by different production methods, and to evaluate their potential risk for human health and/or influence on aesthetic drinking water quality. The migration tests were carried out in accordance with EN-1420-1, and VOCs were analysed by gas chromatography-mass spectrometry. The levels of VOC migrating from new PEX pipes were generally low, and decreasing with time of pipe use. No association was found between production method of PEX pipes and concentration of migration products. 2,4-di-tert-butyl phenol and methyl tert-butyl ether (MTBE) were two of the major individual components detected. In three new PEX pipes, MTBE was detected in concentrations above the recommended US EPA taste and odour value for drinking water, but decreased below this value after 5 months in service. However, the threshold odour number (TON) values for two pipes were similar to new pipes even after 1 year in use. For seven chemicals for which conclusions on potential health risk could be drawn, this was considered of no or very low concern. However, odour from some of these pipes could negatively affect drinking water for up to 1 year.

Key words | drinking water quality deterioration, migration of VOC, PEX pipes, risk assessment

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ABBREVIATIONS

ADI	acceptable daily intake
CEN	European Committee for Standardization
1,3-DTBB	1,3-di-tert-butylbenzene
2,4-DTBP	2,4-di-tert-butylphenol
2,6-DTBP	2,6-di-tert-butylphenol
2,6-DTBQ	2,6-di-tert-butyl-p-benzoquinone
DOC	dissolved organic carbon
ETBE	2-ethoxy-2-methylpropane
GC-MS	gas chromatography-mass spectrometry
NOAEL	no observed adverse effect level
NVOC	non-volatile organic compounds
MTBE	methyl tert-butyl ether
PB	polybutene
PE	polyethylene
PEX	cross-linked polyethylene
RSD	relative standard deviation
TDI	tolerable daily intake
TM	tolerable migration
TON	threshold odour number
TVOC	total volatile organic compounds
UF	uncertainty factor
US EPA	United States Environmental Protection Agency
VOC	volatile organic compounds
WHO	World Health Organization

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INTRODUCTION

In recent years, plastic pipe-in-pipe systems have replaced copper pipes for the distribution of water within buildings. Often the flexible pipe contained within this system is cross-linked polyethylene (PEX). Information regarding the possible health effects of using plastic drinking water pipes is limited. However, as more and more old copper pipe systems are being replaced and virtually all new installations are based on plastic, it is necessary to be aware of any health risks that such synthetic materials may pose.

Thermoplastics, such as PEX, have the potential to leak additives, for example antioxidants, stabilizers, adhesives and breakdown products thereof into water in contact with their surface (Gätcher & Müller 1990; Brocca *et al.* 2000, 2002; Denberg *et al.* 2007, 2009). The identity of chemicals leaking from PEX pipes is linked to their manufacturing method. Cross-linking of polyethylene in PEX pipes is achieved by three main processes: using peroxide (PEX-a), using the 'Silane' method (PEX-b) or using irradiation (PEX-c).

Previous investigations have demonstrated that PEX pipes leak organic matter which can support biofilm formation and give rise to taste and odour problems in drinking water (Anselme *et al.* 1986; Hem & Skjevrak 2002; Skjevrak *et al.* 2003, 2005). These investigations have shown that significant quantities of organic matter leak out of PEX pipes under stagnant conditions (Mørkebjerg Nielsen *et al.* 2007). Only a minor part of the leakage products have been identified. International studies indicate that organic components from PEX pipes could be carcinogenic and that opportunistic human bacterial pathogens such as *Legionella* and *Aeromonas* could grow in biofilms in PEX pipes, but not to the same extent in biofilm on copper pipes (Rogers *et al.* 1994; Kerr *et al.* 1999; van der Kooij *et al.* 2003).

The first objective of this study was to identify and quantify volatile organic compounds (VOCs) as primary migrants from PEX pipes used for drinking water produced by different production methods. We did not intend to investigate reaction products between water constituents (including disinfection by-products) and PEX pipe migrants. The second objective was to evaluate the potential risk of the identified VOCs for human health and/or influence on aesthetic drinking water quality.

The quality of water in contact with eight different brands of PEX pipes and one polybutene (PB) pipe, during three successive test periods, is described in terms of migration of VOCs, threshold odour number (TON) and dissolved organic carbon (DOC). Preparation of the test water samples was based on CEN method EN-1420-1 for testing of organoleptic properties of drinking water in contact with plastic pipes (EN 1420-1 1999). This method prescribes static contact between water and plastic pipe for three successive periods each of 72 h duration. According to this standard no significant taste and odour of water should be observed in the third 72 h test period.

Representatives from all three manufacturing processes of PEX pipes were included in this investigation. Leakage tests were carried out in the laboratory according to the European standard 12873-1 (EN 12873-1 2003) on new PEX pipes as well as pipes that had been in operation for 5 months. The work includes migration tests of organic constituents from all PEX pipes on the Nordic market and a risk assessment of the potential health effects related to consumption of drinking water from these PEX pipes.

MATERIAL AND METHODS

Plastic pipes tested

Eight different brands of PEX pipe were tested. Additionally, a smaller dimension of one brand of PEX pipe was included, to test the influence of volume to surface area on migration of VOC from the pipes (Table 1). PEX pipes were grouped according to production method in three different groups. Five representatives of PEX-a, two of PEX-b and three of PEX-c were included in the investigation. Description of the different types of PEX pipe tested is given in Table 1. One brand of polybutene pipe (PB) was tested for comparison because this pipe material is suggested as a replacement for PEX pipes in some applications. All the different pipes were included in the construction of a pilot plant test system. The test plant alternated between stagnant periods and flow periods to simulate normal household use.

Table 1 | Description of the different types of PEX pipes tested

Pipe ID	PEX type	Dimension (mm)	Inner diam. (mm)	O_2 barrier	Surface area to volume ratio	Application
PEX 1	PEX-b	16 × 2.2	11.6	Yes	3.4:1	Hot and cold water
PEX 2	PEX-c	16 × 2.0	12.0	No	3.4:1	Drinking water
PEX 3	PEX-a	18 × 2.5	13.0	No	3:1	Drinking water
PEX 4	PEX-b	20 × 2.5	15.0	Yes	2.7:1	Hot and cold water
PEX 5	PEX-c	15 × 2.5	10.0	No	4:1	Drinking water
PEX 6	PEX-a	16 × 2.2	11.6	Yes	3.4:1	Drinking water
PEX 7	PEX-a	16 × 2.2	11.6	No	3.4:1	Drinking water
PEX 8	PEX-a	16 × 2.2	11.6	No	3.4:1	Hot and cold water
PEX 9	PEX-c	16 × 2.2	11.6	Yes	3.4:1	Hot and cold water
PEX 10	PEX-a	16 × 2.2	11.6	No	3.4:1	Drinking water
PEX 11	PEX-a	12 × 1.8	8.4	No	4.8:1	Drinking water[a]
PB	PB[b]	20 × 1.9	16.2	No	2.5:1	Drinking water

Dimension is external pipe diameter (D_e) x wall thickness.
Glass and copper were used as negative control materials.
[a]Not approved for drinking water in the Nordic countries.
[b]Polybutene pipe.

Magnetic valves were opened three times a day for 15 min periods to allow flow through of water.

Migration tests

Ultrapure water used for the migration tests was obtained by prepurification of tap water using ELGA Purelab Prima with particle filter, pretreatment cartridge and reverse osmosis unit. The water passes through an ELGA Purelab Ultra genetic unit with ion exchange in two steps, separated by UV irradiation at 254 and 185 nm for photo-oxidation and an ultrafilter at the end (ELGA, brand name of Veolia water systems and USFilter). Pipe test pieces were flushed for 1 h and kept in contact with ultrapure 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 ultrapure water, sealed at both ends with glass stoppers (preheated to 450 °C for 2 h to remove organic contaminants) and kept at room temperature for 72 h. The water in the test pieces, at room temperature, referred to as the test water in the following text, was collected after 72 h and analysed with respect to VOC, TON and DOC. The test pipes were refilled with ultrapure water and left for 72 h at room temperature before they were emptied and the water from the second extraction period was used for odour analyses (TON). Water from the third test period of a total of three successive test periods each of 72 h duration, was also analysed for the same parameters as for the first 72 h test period, described above. Reference samples were prepared by storing ultrapure water in glass bottles with glass stoppers in parallel with the migration tests and analysed in correspondence with the test water samples.

Leaching of VOC was analysed on new pipes as well as after 5 months in use of the same pipes. DOC, a measure for total migration from the pipes, and odour, as the threshold odour number (TON), were determined in samples from the same pipes when they were new, after 5 months of use and after 1 year of use. The intention was to perform this migration test on new PEX pipes, after 5 months, and after 1 year in use. However, because the commercial test laboratory used closed down its VOC testing before the pipes had been in service for 1 year, it was only possible to do VOC analysis for new pipes and after 5 months in service.

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. VOCs were concentrated from 1,000 ml portions of the test water and reference samples by a purge and trap method based on the open-loop stripping principle (Skjevrak 1998). 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 VOCs 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 water bath 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 for quantified compounds. Other migration substances were tentatively identified by library match only.

Calibration curves for quantification of VOCs were established correspondingly by analyses of dilution series of reference compounds in ultrapure water. The RT parameter shown in brackets in Table 2 for the individual reference compounds corresponds to the gas chromatographic retention time.

Table 2 | Reference compounds used for quantification of migrated compounds

Reference compound	CAS number (GC retention time)
2-methylpropene	CAS 115-11-7 (RT 0.95)
2-methyl-2-propanol	CAS 75-65-0 (RT 1.44)
Methyl tert-butyl ether (MTBE)	CAS 1634-04-4 (RT 1.63)
2-ethoxy-2-methyl-propane (ETBE)	CAS 637-92-3 (RT 2.11)
Di-tert-butyl peroxide	CAS 110-05-4 (RT 4.63)
5-metyl-2-hexanone	CAS 110-12-3 (RT 8.95)
1,3-di-tert-butyl benzene (1,3-DTBB)	CAS 1014-60-4 (RT 22.12)
2,6-di-tert-butyl phenol (2,6-DTBP)	CAS 128-39-2 (RT 27.96)
2,6-di-tert-butyl-p-benzoquinone (2,6-DTBQ)	CAS 719-22-2 (RT 28.66)
2,4-di-tert-butyl phenol (2,4-DTBP)	CAS 96-76-4 (RT 29.66)

Control of VOC background level in the ultrapure water used for testing and the applied analytical apparatus is crucial for successful low-level VOC determination. Concentration level of background VOC in reference water samples showed that the amounts of total VOC (TVOC) in reference samples was lower than the detection limit (0.05 μg/l) for the same classes of VOC as those determined in the test water (Skjevrak *et al.* 2003).

The analytical deviation for the VOC method was previously assessed (Skjevrak *et al.* 2003) by repeated migration tests for HDPE pipes. The analytical deviations for various chemical compound classes varied between 3 and 12% RSD.

TON analysis

The organoleptic properties of water were assessed according to EN 1622 (EN 1622 1997), which is based on a quantitative dilution method. Five dilutions of the test water samples from the second 72 h extraction period were performed, and TON was assessed at a scale from 0 to ≥5. Ultrapure water (TON = 0) was used as reference. TON values higher than 3 were assigned to water samples with significant odour in accordance with Norwegian drinking water regulations. The uncertainty in TON assessment is estimated at ±1 by repetitive determinations.

Bulk parameter for organic content

DOC was determined according to NS-EN 1484, 1. ed., Nov 1997: Vannundersøkelse. Retningslinjer for bestemmelse av totalt organisk karbon (TOC) og løst organisk karbon (DOC) (in Norwegian) and Skalar Methods, catnr:311–411 issue 123098/MH/98205613.

Risk assessment

The highest value for leached VOC over a 72 h period, independent of which of the three successive 72 h periods it was from, was used in the risk assessments of individual chemicals.

In these assessments of potential health risks from intake of drinking water containing chemicals leached from the

pipes, restrictions, i.e., limit values for the chemicals in drinking water determined by the World Health Organization (WHO 2008) or United States Environmental Protection Agency (US EPA 1997), were used if found. National positive lists for materials and chemicals in contact with drinking water in Germany (Umweltbundesamt, Germany 2009) and the Netherlands (Ministerial Regulation, The Netherlands 2007) were also checked, and the few limit values listed there were included. However, in most cases, no limit values for these chemicals in drinking water were found. Then the positive list for plastic food contact materials in the EU (European Commission 2002) was checked for limit values of these chemicals, as well as the Synoptic Document, listing such substances (European Commission 2005). For substances where no limit values could be found, available repeated dose toxicity data was used to calculate a provisional value for tolerable migration (TM) of these chemicals into drinking water for use in the risk assessments.

Values for ADI (acceptable daily intake) or TDI (tolerable daily intake, used for chemical contaminants that do not have an intended function in the drinking water) are generally calculated by dividing the value for the no observed adverse effect level (NOAEL) (i.e. the highest dose found not to cause an adverse effect in a preferably long-term animal study) by an uncertainty factor (UF). This UF is meant to cover uncertainties caused by interspecies variation when extrapolating from animal experiments to humans, inter-individual variation in humans, and variations in data quality. The default UF value is 100. However, if the data was from a study of shorter duration than life-time exposure (2 years), such as a 90-day or a 28-day study, then an UF of 1,000 was used.

From an ADI or a TDI value calculated from a NOAEL value divided by a UF, a TM value was calculated. The ADI and TDI values are meant to cover all sources of exposure to a certain chemical. A default value of 10% of an ADI or a TDI value was allocated to exposure via drinking water, unless specific data indicated that other values should be used. Further calculations were based on a daily intake of 2 l of water, a body weight of children (8 years) of 25 kg and of adults of 60 kg. The TM value was then compared with the highest value of migration from the pipes for the individual chemical, to assess potential health risks from the exposure.

DOC and TON values measured in the leachate, indicating general level of migration from the pipes, were also taken into consideration in the risk assessment.

RESULTS AND DISCUSSION

VOC in the test water from PEX pipes

Table 3(a) shows quantifiable VOCs identified in the test water samples from PEX pipe migration experiments with new pipes. The quantified VOCs were grouped in three compound classes according to their likely origin (Table 4). The components were quantified in the first and the third migration test periods and represent the major part of the identified VOCs for all PEX pipes tested. Concentration units (μg/l) of migrants are used in the following text, whereas migration quantified in terms of weight/area (μg/m^2) is shown in the tables.

Large numbers of VOCs tentatively identified by mass spectra library search were observed in the PEX pipe migration test waters. These compounds made up a relatively small fraction of the chromatographically detected migration substances. The components which are not identified by reference compounds comprise saturated and unsaturated short-chain aliphatic alcohols, ketones, esters, aldehydes and ethoxylated alkanes (data not shown).

Water from the second migration test period was used for taste and odour tests. Non-identifiable VOCs detected in the test water samples were present in minor amounts. Examples of chromatograms of VOCs from representative pipes of PEX-a, PEX-b and PEX-c and the PB pipe are displayed in Figure 1.

Tests of new PEX pipes

One of the compounds detected in leakage from all new PEX pipes tested was 2,6-di-tert-butyl-p-benzoquinone (2,6-DTBQ), in concentrations between 0.1 and 3.0 μg/l from the third 72 h extraction period (Table 3(a)). This is somewhat lower than the results from a Danish study by Mørkebjerg Nielsen *et al.* (2007), who found concentrations between 0.5 and 12 μg/l for 2,6-DTBQ in leakage from five new PEX pipes, tested according to the same standard,

Table 3(a) | Quantified leakage products from GC-MS analyses of new PEX pipes, given as weight/pipe surface area (μg/m^2)

Pipe ID	2-methyl propene	2-methyl-2-propanol	Methyl tert-butyl ether	Ethoxy-2-methylpropane	Di-tert-butyl peroxide	5-methyl-2-hexanone	1,3-di-tert-butyl benzene	2,6-di-tert-butyl phenol	2,6-di-tert-butyl benzoquinone	2,4-di-tert-butyl phenol
Pex 1	<0.1	0.1	3.4	27.0	1.1	nd	nd	nd	<0.1	4.9
Pex 2	<0.2	nd	nd	0.4	nd	0.2	1.3	nd	10.5	8.7
Pex 3	<0.2	nd	nd	nd	0.2	nd	nd	nd	0.6	nd
Pex 4	nd	nd	nd	7.9	nd	nd	nd	nd	1.7	8.2
Pex 5	<0.1	nd	nd	0.6	nd	0.2	nd	0.4	8.0	0.2
Pex 6	<0.1	0.2	0.8	nd	nd	nd	nd	nd	0.6	0.2
Pex 7	nd	nd	0.3	nd	nd	nd	nd	nd	0.4	nd
Pex 8	<0.1	1.8	420.3	nd	0.3	2.4	nd	nd	1.6	1.8
Pex 9	<0.1	nd	nd	0.4	nd	0.02	nd	0.4	8.4	0.2
PB	nd	nd	nd	nd	nd	nd	nd	<0.2	<0.2	1,396.8
Pex 10	1.1	0.5/1.0	518.8	nd	463.8	63.8	nd	nd	1.5	nd
Pex 11	0.5	0.3	447.5	nd	4.0	4.8	nd	nd	0.5	nd

Quantification is based on the 3rd 72 h extraction period and pure reference compounds.
Reference water (ultrapure water): below the detection limit (0.05 μg/l) for all leakage products.
nd = not detected.

Table 3(b) | Leakage products from GC-MS analyses of PEX pipes used for 5 months, given as concentration/pipe surface area (μg/m^2)

Pipe ID	2-methyl propene	2-methyl-2-propanol	Methyl tert-butyl ether	Ethoxy-2-methylpropane	Di-tert-butyl peroxide	5-methyl-2-hexanone	1,3-di-tert-butyl benzene	2,6-di-tert-butyl phenol	2,6-di-tert-butyl-*p*-benzoquinone	2,4-di-tert-butyl phenol
Pex 1				7.6						
Pex 2							0.7		3.7	1.1
Pex 3										
Pex 4										1.0
Pex 5									3.3	
Pex 6										
Pex 7										
Pex 8		0.2	31.6							
Pex 9								<0.1	3.4	
Pex 10	<0.1		3.7		8.0					

Blank means below the detection limit.

and analyzed by a similar GC-MS method. For the PB pipe tested in our study, the leakage of 2,6-DTBQ was below the detection limit (<0.05 μg/l). Another identified compound, 2,4-di-tert-butylphenol (2,4-DTBP) was found in the leachate from eight out of thirteen tested pipes in concentrations between 0.08 and 2.2 μg/l. This is in the same range as reported for two PEX pipes tested by Mørkebjerg Nielsen *et al.* (2007). However, a concentration of about 1.4 mg/m^2 pipe surface was found in the leakage water from the tested PB pipe, corresponding to a flux of 4.7 μg/dm^2/day.

Another leakage compound from new PEX pipes, identified in high concentrations, was metyl-tert-butyl ether (MTBE), found in leakage water from six pipes, in

Table 4 | Likely origin of quantified VOCs in migration tests with PEX pipes

Component class according to origin	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
		2,6-di-tert-butyl phenol	
		1,3-di-tert-butyl benzene	
		2-methyl propene	
Component related to cross-binding process	2	Methyl tert-butyl ether	MTBE
		2-methyl-2-propanol (Tert-butanol)	
		2-ethoxy, 2-methyl propane	ETBE
		Di-tert-butyl peroxide	
PE degradation products	3	5-methyl-2-hexanone	

concentrations between 0.2 and 213 μg/l. The concentrations of MTBE from the third 72 h extraction period varied between 0.1 in PEX 7 and 179 μg/l in PEX 10. For PEX 11, which had the highest concentrations of MTBE after the first 72 h extraction period, the concentration was reduced from 213 in the first 72 h extraction period to 83 μg/l in the third extraction period. Results from leakage tests after 5 months in use showed that generally the concentrations of MTBE were reduced, but for PEX 8 the concentration was still as high as 11 μg/l, which is higher than the drinking water criteria for MTBE of 5 μg/l. However, the leakage of MTBE from PEX 10, which had high concentration for new pipe, was reduced to 1.3 μg/l after 5 months. The observed MTBE concentrations is high compared to the Danish study mentioned before, which also carried out lab tests on PEX pipes available in the Nordic market, which for six out of seven pipes detected MTBE concentrations between 0.04 and 0.4 μg/l. The only exception was one PEX pipe with a MTBE concentration of 47 μg/l in the first extraction decreasing to 12 μg/l in the third 72 h extraction period. The field investigation with analysis of leakage from pipes which have been in use for at least 6 months demonstrated concentrations in two out of six sites of 0.02 to 0.33 μg/l, and in all field measurements the concentration was below the drinking water criteria for MTBE of 5 μg/l (Mørkebjerg Nielsen *et al.* 2007). Skjevrak *et al.* (2003) found that for two PEX pipes examined, using the same extraction protocol and GC-MS method, that MTBE was the dominant leakage chemical from these pipes, with 33.5 and 5.0 μg/l, respectively.

We also detected 5-metyl-2-hexanone, a water soluble compound from the cross-binding process, from six out of 13 PEX pipes tested. The highest concentrations were found in leakage waters from PEX 8, 10 and 11. Concentrations decreased from the first to third extraction period as follows, 9.0–7.8 μg/l, 20–16 μg/l, and 16–10 μg/l, respectively. This is about ten times higher than what was found by Mørkebjerg Nielsen *et al.* (2007) and Skjevrak *et al.* (2003). In the other pipes, the concentrations were close to or below the detection limit (0.05 μg/l). Additionally, Skjevrak *et al.* (2003) also identified tert-butanol (2-metyl-2-propanol) and 4-butoxy phenol, in concentrations up to 2.2 μg/l. 2-methyl-2-propanol was also detected in five of our tested PEX pipes, in concentrations of 0.1 to 1.8 μg/l (Table 3(a)). However, 4-butoxy-phenol was not detected in leakage water from our tested pipes. 3,5-di-tert-butyl-4-hydroxybenzaldehyde and 3,5-di-tert-butyl-4-hydroxy acetophenone, two breakdown products of antioxidants, were identified as the most abundant organic compounds in water which had been in contact with PEX pipes by Brocca *et al.* (2002) and Mørkebjerg Nielsen *et al.* (2007). These compounds were not identified with certainty from our leakage tests with PEX pipes, but we observed low concentrations of a compound tentatively identified as 2,6-di-tert-butyl-4 hydroxy benzaldehyde, possibly corresponding to the 3,5-di-tert-butyl-4-hydroxy acetophenone, since no certain identification beyond library matching is done in our case.

PEX 4 is an alupex pipe built up by multiple layers, with one aluminium layer surrounded by two PEX layers, intended for both drinking water and waterborne floor heating. As a result of the aluminium layer, this pipe has a thinner PEX layer in contact with the water, and therefore we would expect lower concentrations of leakage products from this pipe. On the other hand PEX 4 is manufactured using the PEX-b process, where cross-binding is carried out by the addition of multiple chemicals, and therefore it would be expected that the number of VOC migrants

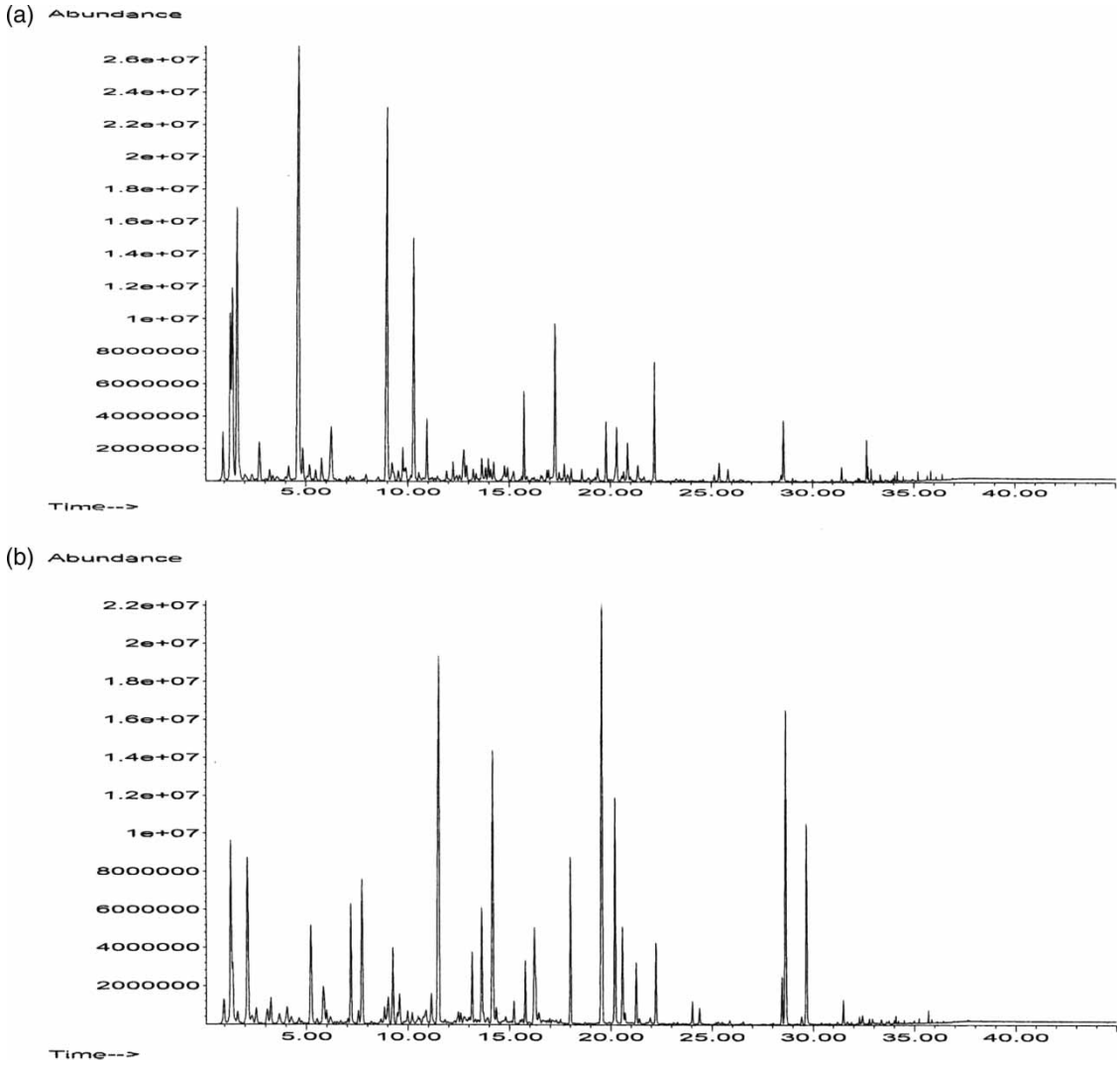

Figure 1 | Typical chromatograms of leakage products from (a) PEX-a, (b) PEX-b, (c) PEX-c and (d) PB pipes tested, showing abundance vs. time.

would be higher than for PEX-a and PEX-c. The results in Table 3(a) illustrate that only a few of the quantifiable migrants were detected from this pipe, except for the values for 2-etoxy-2-methylpropane (ETBE), 2,4-di-tert-butyl-phenol and 2,6-di-tert-butyl-benzoquinone, which had quite high values, compared with most of the other tested PEX pipes. However, except for ETBE, which is a compound related to the cross-binding process, the other two are breakdown products of antioxidants. Similar results were also found by Mørkebjerg Nielsen *et al.* (2007).

Results from long-term testing of PEX pipes are shown in Table 3(b). The migration of MTBE ($\mu g/m^2$) from the new PEX 8 and PEX 10 is maintained at a relatively high level also after 5 months. MTBE migration in the new pipes (>400 $\mu g/m^2$, Table 3(a)) is reduced after 5 months to 1–10% of the initial values (Table 3(b)). PEX 2 also shows persistent migration of 1,3-di-tert-butylbenzene where the migration level after 5 months use is reduced to around 50% of the initial value. The PEX 2, 4, 5 and 9, which have the highest initial migration level of 2,4-DTBP and 2,6-di-tert-butyl-benzoquinone (8–10 $\mu g/m^2$) still release 10–50% of the initial values after 5 months in use. Hence, high migration values from tests of new PEX pipes indicate that migration stays relatively high after 5 months in use.

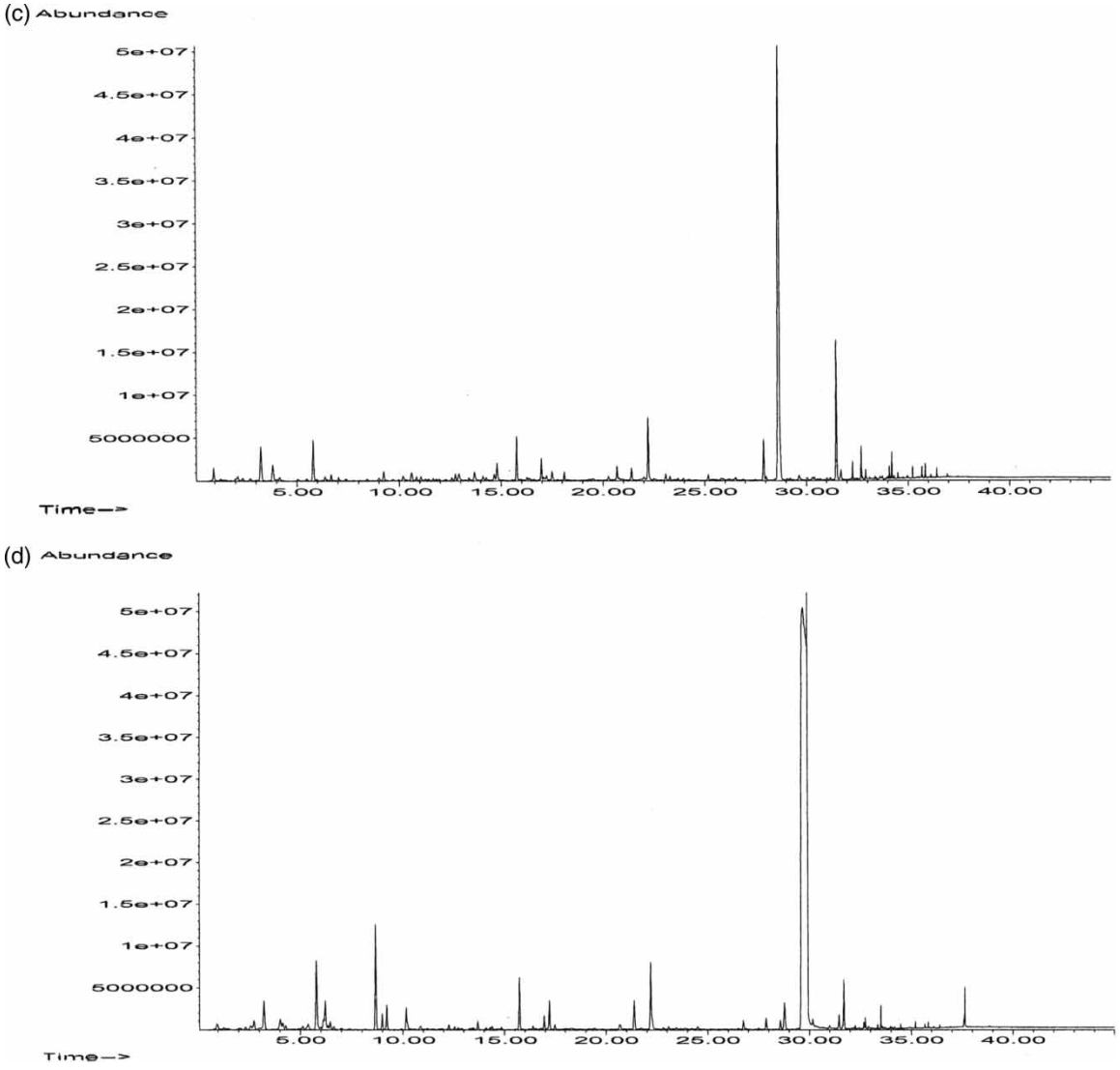

Figure 1 | Continued.

Pipe surface area vs. volume ratio

All the leakage tests were, according to the test protocol, performed with three successive extraction periods, each of 3 days extraction (1st to 3rd extraction). Based on this it is possible to calculate the flux in ng/dm^2/day, which is a measurement of the amount of leakage per inner surface area for the pipes and the contact time between the pipe surface and the test water. This makes it possible to do a direct comparison between extractions from pipes of different diameters. The results are given in Table 5. PEX 10 and 11 are manufactured according to the same specifications and only vary in dimensions. Therefore in principle they should be equal. Despite the larger surface area to volume ratio for PEX 11 compared with PEX 10, our results show that, of all the quantified leakage products, PEX 10 displayed the highest values of migrants.

Migration to ultrapure water vs. to tap water

Water quality parameters, such as high chlorine concentrations, which under special occasions may be present in distributed drinking water, may influence the pipe material and the leakage from the PEX pipes. According

Table 5 | Flux (ng/dm^2/day) for new pipes (216 h, 3rd extraction period)

Pipe ID	2-methyl propene	2-methyl-2-propanol	Methyl tert-butyl ether	Ethoxy-2-methylpropane	Di-tert-butyl peroxide	5-methyl-2-hexanone	1,3-di-tert-butyl benzene	2,6-di-tert-butyl phenol	2,6-di-tert-butyl benzoquinone	2,4-di-tert-butyl phenol
Pex 1	<0.5	0.5	11.3	90	3.7	nd	nd	nd	<0.3	16.3
Pex 2	<0.5	nd	nd	1.5	nd	0.5	4.3	nd	35	29
Pex 3	<0.5	nd	nd	nd	0.5	nd	nd	nd	1.8	nd
Pex 4	nd	nd	nd	26.2	nd	nd	nd	nd	5.6	31.3
Pex 5	<0.4	nd	nd	2.1	nd	0.6	nd	1.2	26.7	0.7
Pex 6	<0.5	0.7	2.7	nd	nd	nd	nd	nd	2.1	0.7
Pex 7	nd	nd	0.9	nd	nd	nd	nd	nd	1.4	nd
Pex 8	<0.5	6	1,401	nd	1.1	0.8	nd	nd	5.4	6
Pex 9	<0.5	nd	nd	1.3	nd	0.07	nd	1.3	28	0.7
PB	nd	nd	nd	nd	nd	nd	nd	<0.7	<0.7	4,656
Pex 10	3.7	1.5/3.2	1,729	nd	1,546	213	nd	nd	4.8	nd
Pex 11	1.7	1.1	1,492	nd	13.3	15.9	nd	nd	1.5	nd

to representatives from the PEX industry high concentrations of chlorine dioxide have an even more pronounced detrimental effect on plastic pipes than sodium hypochlorite. Because of this sensitivity to oxidative disinfectants, the manufacturers of PEX pipes do not recommend that the pipes are used for transporting water with higher chlorine concentrations than 0.3 mg/l Cl_2 (Marcel Lüscher, Georg Fischer JRG AG, pers.com, September 2010). Water in distribution systems does normally have even lower chlorine concentrations, and therefore chlorine probably will have only a minor impact on migration from PEX pipes. A Danish investigation (Mørkebjerg Nielsen *et al.* 2007) compares the flux of PEX pipe migrants in tap water based on field observations and laboratory tests with ultrapure water. The flux (ng/dm^2/day) of PEX migrants observed in the field tests was generally lower than observed in their laboratory tests, as well as in our laboratory experiments, using new PEX pipes (Table 5). This indicates that risk assessments based on concentrations of migrants detected in laboratory tests may overestimate the health risk from exposure to these migrants in drinking water at the tap. Furthermore, pH in distributed drinking water, which could possibly affect migration, normally does not differ much from pH in ultrapure water. Based on these considerations, risk assessment based on our results of migration from PEX pipes to ultrapure water is relevant for risk assessment of drinking water at the tap.

Unidentified migrants

Unidentified VOC migrants, presumably various oxygenates, were detected in test waters from all the different PEX pipes along with the identified VOCs. However, the concentrations of the unidentified migrants compared with the known components were low. The number of unidentified compounds varied from at least one in most of the tested PEX pipes, up to nine in PEX 1. The number of unidentified migrants detected from PEX 1 corresponds to 33% of the total number of migrants. Half of the detected components in leakage water from PEX 6 were unidentified. Unidentified VOC migrants along with substances not detected by GC-MS (non-volatile organic compounds (NVOC)) challenge our knowledge on the composition of the total migrate from the PEX pipes. Non-identified and non-detected substances represent an uncharacterized contribution to the exposure of leakage products from PEX pipes on the consumers of the water, not included in the risk assessment, and on the biofilm formation in drinking water PEX pipes. This has also been addressed by Skjevrak *et al.* (2003). Mørkebjerg Nielsen *et al.* (2007) studied the migration of NVOCs in addition to VOCs in a laboratory and a field study of five PEX pipes

from the Nordic market, probably some of the same brands of PEX included in our study. During the laboratory test, they found that two of the tested PEX pipes exceeded 0.3 mg/l in the third extraction in the leakage test, which is the maximum acceptance level for NVOC in the third extraction given in the Danish approval standard for plastic pipes, owing to the risk of microbial growth in the pipes (Danish Standard 2004). In the field study, however, for two of six tested sites, the NVOC concentration in water samples taken from consumers' taps was slightly higher than in water entering the properties. It was not clear if the difference in NVOC content was due to contamination from the PEX pipes or variation in the quality of the water from the water works.

Potential health risks based on migrating levels of VOC

The levels of volatile organic compounds found to migrate from new PEX pipes were generally low. The highest values found for individual chemicals ranged from 0.15 μg/l of 2,6-DTBP to 213 μg/l of MTBE. For the only PB-pipe tested, the highest value of migrating chemicals was 345 μg/l of 2,4-DTBP.

Regarding potential chronic effects, for seven of the ten migrants there were available limit values and/or sufficient data from repeated dose toxicity studies to reach a provisional conclusion on potential health risks from the levels of chemicals found to migrate from the pipes. For five of these seven chemicals (2-methylpropene, 2-methyl-2-propanol, 5-methyl-2-hexanone, 2,6-DTBP and 2,6-DTBQ), the highest levels were well below the limit values set and/or levels set on the basis of the toxicological studies, and therefore, they are not considered to constitute any significant health risk for either children or adults. For two of these seven chemicals (MTBE and 2,4-DTBP (from PB pipes only)), however, the highest levels leached were above the calculated tolerable migration (TM) both for children and adults. For MTBE, the values decreased over time, and were below the calculated TM values after 5 months. The weight of evidence is that MTBE is not genotoxic, and there is no clear evidence of carcinogenicity relevant to humans. For 2,4-DTBP from PB pipes, unfortunately, no further analysis was done on this pipe after 5 months so it is not known whether the level decreased over time or not. The available data does not indicate clear genotoxic effects. An ADI or a TDI value should, in principle, not be exceeded. It is widely agreed that a slight excess of the intake of a compound above its ADI or TDI for a short period (in relation to the duration of onset of the critical effect) would not be of health concern provided that the ADI or TDI is not exceeded on a long-term basis (ILSI Europe 1999).

For three of the chemicals, ethoxy-2-methylpropane, DTBP-peroxide and 1,3-DTBB, no repeated toxicity data was found. The available data for ethoxy-2-methylpropane (i.e. some *in vitro* and *in vivo* genotoxicity data, all negative, and absence of structural determinants indicating genotoxicity or carcinogenicity) indicate that this substance is not genotoxic or carcinogenic. The levels leached were low (maximum 9.3 μg/l) from new PEX pipes, and decreased over time. For DTBP-peroxide, the available mutagenicity/genotoxicity tests were negative or ambiguous, and an old carcinogenicity study reported only equivocal tumorigenic effects in mice with a dose of 585 mg/kg bw or above. The levels leached decreased over time. Any adverse effects of these two substances would therefore be expected to have thresholds, and the low levels found to migrate would not be expected to cause any health risks. No toxicological data at all was found for 1,3-DTBB, which was found in migration waters at a very low concentration (maximum 0.43 μg/l from new pipes).

For all of these chemicals, the highest levels were found to leach from new pipes. When migration from the pipes was analysed after 5 months of use, the levels of leached chemicals were considerably lower than from new pipes. Therefore, the human exposure levels will decrease over time from the levels detected in new pipes, and will most likely not be present for a significant part of a lifetime. In reality, the exposure levels will also be lower than the values found by these analyses, since these chemicals are more or less volatile and will partly be lost from the drinking water before consumption.

No acute toxic effects would be expected from any of the chemicals migrating from pipes at the levels detected.

Bulk parameters for organic content: dissolved organic carbon (DOC)

Measured values of DOC varied from <0.2 to 9.5 mg/l for new PEX pipes, <0.2–0.5 mg/l after 5 months and 1 year,

Table 6 | DOC values for leakage water from PEX and PB pipes

	New pipes		After 5 months		After 1 year	
Pipe ID	DOC, max value, mg/l	DOC, mg/m²/day	DOC, max value, mg/l	DOC mg/m²/day	DOC, max value, mg/l	DOC mg/m²/day
Glass	–	–	–	–	–	–
Cu	–	–	–	–	–	–
PEX 1	9.0	8.7	0.2	0.2	0.2	0.2
PEX 2	<0.2	<0.2	<0.2	<0.2	0.4	0.4
PEX 3	1.8	1.9	<0.2	<0.2	0.2	0.2
PEX 4	0.8	1.0	0.5	0.6	1.1	1.4
PEX 5	0.4	0.3	<0.2	<0.2	<0.2	<0.2
PEX 6	0.4	0.4	0.2	0.2	<0.2	<0.2
PEX 7	2.2	2.1	<0.2	<0.2	<0.2	<0.2
PEX 8	1.7	1.6	0.5	0.5	0.2	0.2
PEX 9	0.3	0.3	<0.2	<0.2	0.5	0.5
PB	1.5	2.0	nt	nt	nt	nt
PEX 10	9.5	9.2	0.2	0.2	<0.2	<0.2
PEX 11	4.8	3.4	nt	nt	nt	nt

Glass and copper were used as negative control materials.
Glass: Di = 8.2 mm; De = 10.0 mm.
Copper: Di = 11.8 mm; De = 15.0 mm.
e = external, i = inner.
nt = not tested.

corresponding to a flux varying from <0.2 to 9.2 mg/m^2/day in new pipes, to <0.2–1.4 mg/m^2/day (Table 6). The highest values of DOC were in migration water from PEX 1 and PEX 10, corresponding to the high concentrations of isolated VOCs, particularly from PEX 10.

Values of DOC (in mg/l), as a general parameter of migration of dissolved organic chemicals from the pipes, were lower from pipes used for 5 months than from new pipes, and in most cases even lower after 1 year of use. This indicates that migration of non-volatile chemicals (NVOC), not measured in this study, is also generally decreasing over time. This is actually demonstrated in a recent laboratory and field study with seven different PEX pipes, performed by the Danish Environmental Protection Agency (Mørkebjerg Nielsen *et al.* 2007).

The Norwegian regulations for approval of materials in contact with drinking water, which are based on the German regulations, were used. The limit value for total organic carbon (TOC) for pipes, which shall be measured with a surface area:volume ratio of 1:1, is 2.5 mg/m^2/day. When the DOC values determined in this study was recalculated as mg/m^2/day, using a surface area:volume ratio of 1:1 and assuming DOC = TOC, only the new pipes PEX 1, PEX 10 and PEX 11 had DOC values above the German limit value (3.5, 3.7 and 1.4 times, respectively). The highest values were 8.7, 9.2 and 3.4 mg/m^2/day, respectively, for PEX 1, PEX 10 and PEX 11. For all three pipes, the DOC values were below the limit value after use for 5 months and for 1 year.

Odour

Samples of water in contact with the pipes were also checked for organoleptic quality; that is, by measuring odour. For some pipes, the odour decreased over time, but for a few pipes similar TON values were reported after use for 5 months as for new pipes (Table 7). For one pipe (PEX 9), a higher TON value was reported after use for 1 year than for 5 months, and one pipe (PEX 8) had the maximum TON value even after 1 year in service. The odour from these pipes was characterized as solvent-like or plastic-like. So, for some of these pipes, the potential for odour to negatively affect drinking water is quite long-lasting.

Data on thresholds for taste and odour were found only for MTBE. In four studies, the taste and odour responses

Table 7 | Results from odour tests (TON values) for different PEX pipes, for new pipes, after 5 months and 1 year in use

Pipe ID	New pipe	After 5 months	After 1 year
PEX 1	5	4	2
PEX 2	5 and 4 and 3[a]	–	1
PEX 3	5	–	0
PEX 4	5	–	0
PEX 5	5	–	0
PEX 6	5	–	1
PEX 7	5	–	1
PEX 8	5 and 5	–	5
PEX 9	4	2	4
PEX 10	5	5	0
PEX 11	5	–	–
PB	2	–	–
Reference water	0	0	0

The TON values are based on five dilution steps.
Odour description in the table above: solvent-like (PEX 5 and PEX 11), solvent-like/plastic-like (PEX 9, 10), plastic-like (PEX 8).
[a]TON = 3 and 4 are done with a scale with four dilution steps.

varied from 24 to 135 μg/l and 15 to 180 μg/l, respectively, indicating wide variability in individual responses (WHO 2005). In another large study based on 57 subjects, the geometric mean detection threshold and the recommended odour threshold of MTBE was 15 μg/l (WHO 2005). Since the level of MTBE was up to 213 μg/l in new pipes, this chemical could give a chemical taste or odour to the drinking water. However, these effects should be temporary since the highest level after 5 months of use was 10.9 μg/l, i.e., below the apparent thresholds. However, for two of the pipes where high concentrations of MTBE migration were detected (PEX 8 and PEX 10), the TON value was similar for new pipes as for after 5 months or even after 1 year, indicating that chemicals other than MTBE may also contribute to odour in the drinking water after contact with these pipes. The same must be true for PEX 9 which still had high a TON value (Table 7) after 1 year, even though MTBE was not detected in leakage water from this pipe (Table 3(a)). Skjevrak *et al.* (2005) identified a whole range of volatile compounds in biofilm from polyethylene pipes, including compounds frequently associated with cyanobacteria, algae, bacteria and fungi. Bacterial degradation of organic material is known to produce odorous organic sulfides (Zechman *et al.* 1986; Gibson *et al.* 1997) as well as volatile amines (Larsson *et al.* 1978; Klochenko 1996). Therefore, it is possible that chemicals produced by biofilm in PEX pipes can contribute to the high TON value observed in some PEX pipes, even after 1 year in service.

CONCLUSIONS

VOCs migrating from the tested PEX pipes into the water comprised compounds related to antioxidants, components related to the cross-binding process and PE degradation products. All pipes analysed leach different chemical compounds into the test water which has been demonstrated by GC-MS analysis and indicated to a certain degree also by TON analysis. The number of identified leakage products differed from quite high numbers (27 chemicals) to very low (two chemicals). No association was found between production method of the PEX pipes and concentration of migration products. 2,4-DTBP and MTBE were two of the major individual components detected.

In three of the tested PEX pipes, MTBE was detected in concentrations above the recommended US EPA taste and odour values for MTBE in drinking water, and is probably a significant contributor to the high TON values of test water from new pipes. However, after 5 months in service, the MTBE concentrations for all the tested pipes were below the recommended value. Despite this, the TON value for two of the pipes was similar to that for new pipes, even after 1 year, indicating that chemicals other than MTBE may also contribute to odour in drinking water from these pipes. The same must be true for another pipe brand, which still had a high TON value after 1 year, even though MTBE was not detected in leakage water from this pipe. A possible explanation for this might be that the biofilm microorganisms formed on the inner surface of the PEX pipes after months in service have produced chemicals contributing to the high TON values observed. However, high TON values due to unidentified or undetected PEX pipe migrants cannot be ruled out. For some of the PEX pipes the potential for odour to negatively affect the drinking water is quite long-lasting. Care should be taken by the producers to assure that any migration from the pipes is as low as possible.

The levels of VOCs found to migrate from new PEX pipes were generally low, and decreasing with time of use of the pipes. For those seven chemicals where limit values and/or sufficient toxicological data were found to draw at least provisional conclusions on potential health risk, this was considered of no or very low concern for chronic effects, and of no concern for acute effects. For three of the chemicals, little toxicological data was available. For these chemicals, the potential for chronic health risks was considered small, because the available data did not indicate genotoxic effects, and/or the levels were low and decreasing over time. Unidentified VOC migrants, presumably various oxygenates, were detected in test waters from all the different PEX pipes. Even though the concentrations of the unidentified migrants compared with the known components were low, they constituted up to 50% of the total number of migrants in some pipes. Therefore, unidentified and undetected substances represent an uncharacterized contribution to the exposure of leakage products from PEX pipes to the consumers of the water, not included in the risk assessment.

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