Drinking water contaminants from epoxy resin-coated pipes: A field study

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ABSTRACT

Rehabilitation of aged drinking water pipes is an extensive renovation and increasingly topical in many European cities. Spray-on-lining of drinking water pipes is an alternative cost-effective rehabilitation technology in which the insides of pipes are relined with organic polymer. A commonly used polymer is epoxy resin consisting of monomer bisphenol A (BPA). Leaching of BPA from epoxy lining to drinking water has been a concern among public and authorities. Currently epoxy lining is not recommended in some countries. BPA leaching has been demonstrated in laboratory studies but the behavior and ageing process of epoxy lining in situ is not well known. In this study 6 locations with different age epoxy linings of drinking water pipes done using two distinct technologies were studied. While bisphenol F, 4-n-nonylphenol, and 4-t-octylphenol were rarely found and in trace concentrations, BPA was detected in majority of samples. Pipes lined with the older technology (LSE) leached more BPA than those with more recent technology (DonPro): maxima in cold water were 0.25 μg/L and 10 ng/L, respectively. Incubation of water in pipes 8—10 h prior to sampling increased BPA concentration in cold water 1.1—43-fold. Hot water temperature caused even more BPA leaching - at maximum 23.5 μg/L. The influence of ageing of epoxy lining on BPA leaching on could be shown in case of LSE technology: locations with 8—9 years old lining leached 4—20-fold more BPA compared to a location with 2-year-old lining. Analysis of metals showed that epoxy lining can reduce especially iron concentration in water. No significant burden to water could be shown by the analyzed 72 volatile organic compounds, including epichlorhydrin, precursor used in epoxy resin. Estrogenicity was detected in water samples with the highest BPA loads. Comparable responses of two yeast bioreporters (estrogen receptor α and BPA-targeted) indicated that bisphenol-like compounds were the main cause of estrogenicity. Compared to the estimated average daily BPA exposure, additional BPA load via cold drinking water in the studied locations was low, maximum 8.7%. However, hot water should also be considered as exposure source due to higher BPA concentrations. Epoxy lined locations should be monitored in future in order to evaluate ageing process and control increasing leaching of potentially harmful chemicals.

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1. Introduction

Access to pure drinking water is one of the most important issues for human population. Drinking water distribution system plays a key role in delivering this resource to consumers. In addition to pathogenic microbes which are the major threat to drinking water quality in the world, chemical safety is another emerging challenge (WHO, 2011). Chemical contaminants can enter to drinking water in several stages: they can originate from source water, purification process, and distribution system components, or via backflow, breakdowns, leakage, or vandalism.

Drinking water is exposed to many different pipe materials in distribution system. Water can reside in the pipes for several days during which corrosion and leaching of compounds from the pipes can affect water quality (Kekki et al., 2007). Small pipes in households, however, can have potentially greater impact on water compared to large main pipes in the distribution system where the quality of water remains more stable due to larger pipes and more

constant flow (Kekki et al., 2007).

Rehabilitation of old drinking water pipes is an increasingly topical issue in many European countries. Majority of apartment houses have been built in the decades after the Second World War (Meijer et al., 2009), and their water pipes are coming to the end of their life time. Old drinking water pipes suffer from corrosions, blockages, biofilm formation, and they have been shown to leach metals such as iron, zinc, copper, and lead to the drinking water (Kekki et al., 2007).

Pipe rehabilitation is an extensive renovation, and consequently expensive and time-consuming. Usually the apartments are uninhabitable during the time of pipe replacements which may take up to several months. For these reasons alternative pipe rehabilitation methods are attractive. Relining of the inside surface of pipes has been used as such a method. The so-called spray-on-lining is the oldest used technology to restore the functioning of the pipe and stop internal corrosion (Ellison et al., 2010). Organic polymers such as epoxy resins and polyurethane are most commonly used lining materials. Epoxy resins have good thermal stability, tight attachment to metal and ceramic surfaces, and they can span over small holes in the pipe (Ellison et al., 2010; Kekki et al., 2007). Spray-on epoxy lining is suitable also for narrow pipes because the used thickness is only about 0.3—4 mm (Ellison et al., 2010; Pekkinen, 2011).

The epoxy-based spray-on-lining procedure typically includes several steps such as drying the pipes, cleaning with pressure and sand blasting, application of the epoxy mass with pressure, and drying. After the lining procedure the pipes are ready to be flushed and used within 12—24 h (Ellison et al., 2010; Pekkinen, 2011). Due to the non-invasive nature of this technology and no need for renovation of other surfaces, the costs are generally about half of the traditional pipe replacement renovation (Pekkinen, 2011). For this reason there is still growing interest towards this technology, was commonly used in 1980's and 1990's in Europe and in the USA (Ellison et al., 2010).

Spray-on-lining has several challenges. The most important issues include proper cleaning of the pipe inner surface, efficient spreading of the lining material, correct formula and sufficient curing time of the epoxy resin (Ellison et al., 2010; Pelto-Huikko and Kaunisto, 2011). All of these factors affect the attachment of the resin to the pipe and consequently leaching of contaminant into drinking water. Detected errors in lining include drainage of the resin in branches and turns, weak cleaning and resin attachment, and breakage of the lining due to errors in subsequent couplings (Ellison et al., 2010).

Epoxy resins used for pipe lining commonly comprise of two main components: bisphenol A (BPA) and epichlorhydrin. These two react to different polymer length, consisting of pre-polymer unit bisphenol A diglycigyl ether (BADGE). As BPA is a well-characterized endocrine-disrupting compound (e.g. reviewed by Flint et al., 2012, and Rubin, 2011), the safety of epoxy resin-based lining technology has caused concern among consumers and authorities. It has been shown that epoxy coating can leach BPA, BADGE, and other related organic compounds (Bruchet et al., 2014; Kosaka et al., 2012; Umweltbundesamt, 2010). Currently, epoxy-based lining is not allowed in Germany, and not recommended in Sweden (Pelto-Huikko and Kaunisto, 2011). The information on the use of epoxy lining in other regions is limited and it follows highly variable country-specific regulations and procedures. In addition, insurance companies have varying policies, and many do not insure renovations based on spray-on-lining (Pelto-Huikko and Kaunisto, 2011).

In this study the impact of epoxy lining on drinking water quality was studied using the field research in 8 houses with different age rehabilitations in Helsinki, Finland. The effects of age, used lining technology, temperature, and incubation time on the occurrence and burden of chemical compounds (i.e. metals, volatile compounds and organic chemicals - including BPA) were evaluated. In addition, total estogenic potential of water extracts were measured using bioassays and compared to concentrations of BPA in order to evaluate the proportion of estrogenicity caused by BPA. Finally, risk assessment based on highest detected BPA concentrations was done.

2. Methods and materials

2.1. Samples

Samples were collected in 6 apartment houses with epoxy lined drinking water pipes in Helsinki capital area, Finland, during July-—April in 2015 (Table 1). Additional samples were taken from two other locations. Location TR (for Traditional Renovation) had been renovated using traditional pipe-replacement technology. This location was in a close distance from location D, and it was both built and its pipes rehabilitated at the same time as in location D. Location NR (for Non-Renovated) was built in 1960's and had original non-renovated drinking water pipes. TR and NR locations were sampled in December 2015. Finally, a drinking water treatment plant (DWTP) in Helsinki was sampled for treated drinking water in both summer 2015 and December 2015 to assess original chemical burden of water before entering the distribution system.

The epoxy lining of drinking water pipes at locations A-F were done during years 2006—2013 using two spray-on lining technologies LSE and DonPro (Table 1). LSE technology was developed by a Swiss engineering LSE-SYSTEM AG in 1987. Since then it has been often used in Europe, and adopted in Finland in 2005, being the first used spray-on-lining technology for drinking water pipes (Markelin-Rantala and Rautiainen, 2007). DonPro technology was further developed from LSE by Donauer & Probst GmbH & Co in 1994. The main difference between the two technologies is pipe cleaning where LSE method uses sandblasting with over-pressure while DonPro uses a more pipe-friendly under-pressure cleaning (personal communication with contractor II). No specific formula of the epoxy resin materials is available. LSE epoxy material is marketed under the name LSE-001 NA (tested according to ANSI/NSF standard 61), while in DonPro the Tubeprotect-coating is used (Table 1). Service life expectancy of the coating work is generally 30—50 years with guarantee of 2—5 years.

All locations were sampled twice on different days in order to have an idea of daily variation. In all sampling places the residents were asked not to use water in the whole apartment for about 8—10 h before sampling. This was done in order to assess the leaching of chemicals from pipes during incubation of water in pipes. Location D was an exception because the apartment was uninhabited, and incubation times for the two samplings were about 1 month and 1 week, respectively. Kitchen tap was sampled for pipe-incubated water from both cold and hot water lines, and water from both lines after 2 min flowing on full pressure. One more sample was taken from a water tap as close to the plot pipe as possible (usually ground floor/basement tap) to represent water coming to the house from communal distribution system. This sample was collected after 2 min flowing from the cold water line. In total 5 samples were studied at each location - (i) incoming water, (ii) cold water incubated, (iii) cold water flowed, (iv) hot water incubated, and (v) hot water flowed.

2.2. Sample handling

All samples were collected in amber glass bottles which were cleaned by rinsing with acetone and distilled water, and baked in

Table 1
Epoxy coated sampling locations, and epoxy lining technology characteristics.

Sampling location	Building time	Pipe renovation characteristics			
		Year	Contractor	Coating technology	Epoxy coating material
A	1960's	2013	II	DonPro (Donauer & Probst GmbH & Co)	Tubeprotect
B	1950's	2013	I	LSE (LSE-SYSTEM AG)	LSE-001 NA
C	1950's	2012	II	DonPro (Donauer & Probst GmbH & Co)	Tubeprotect
D	1950's	2007	I	LSE (LSE-SYSTEM AG)	LSE-001 NA
E	1910's	2006	I	LSE (LSE-SYSTEM AG)	LSE-001 NA
F	1930's	2013	II	DonPro (Donauer & Probst GmbH & Co)	Tubeprotect
NR	1960's	—	Non-renovated location		
TR	1950's	2007	Renovated by traditional pipe replacement		

50 °C until dry. Water was carefully drained along the side of bottle to avoid excess loss of volatile compounds. Sample volume was 0.93—1.29 L, except for drinking water treatment plant, where 2 L sample was taken. Based on pipe charts of one of the locations, 1 L volume was calculated to be roughly the volume of water pipes of a particular apartment, and thus a good sampling volume for pipe-incubated water. One extra 1 L sample was taken at each sampling location and spiked with 1 μg of BPA and 0.5 μg of bisphenol F (BPF), 4-n-nonylphenol (4-n-NP), and 4-t-octylphenol (4-t-OP)) to test primarily for stability and yield of chemicals after sample handling and processing. This sample was co-extracted and analyzed with other samples. The measured concentrations were compared to a non-extracted reference sample to calculate yield, and then used to correct the measured concentrations of other samples accordingly.

Samples were stored for maximum 20 h in 4 °C before extraction.

Sub-samples for analyses of volatile compounds were taken immediately after sampling to two 40 mL vials (or to one 500 mL bottle during March 2016 additional sampling for dedicated analyses of epichlorhydrin). The vessels were filled head-space-free and stored in 4 °C until analysis.

For metal analysis, 25 mL aliquot was taken to acid-cleaned LDPE bottles and acidified 1% v/v with nitric acid. Samples were stored in 4 °C until analyzed.

Rest of the water sample was extracted by solid phase extraction (SPE) using Oasis HLB 200 mg glass cartridges (Waters Corporation, USA), and slightly modified method published by Baugros et al. (2008). Shortly, cartridges were conditioned with 10 mL MeOH, 10 mL 50% MeOH, and 10 mL LC-MS Ultra Chromasolv water (Sigma-Aldrich, Germany), then loaded with sample water at flow rate of approximately 10 mL/min. Analytes were eluted from columns with 10 mL acetone and 10 mL ethyl acetate. The elute was evaporated to smaller volume, divided in two parts, then evaporated to dryness and each aliquot was reconstituted to 100 μL acetonitrile for alkylphenol analysis or DMSO for bioassays.

2.3. Alkyl phenol analysis and volatile organic compounds

Alkyl phenols were analyzed from 50 μL volume of the acetonitrile extracts using dansyl chloride derivatization and LC—ESI—MS/MS described by Pernica et al. (2015).Extracts were analyzed for BPA, BPF, 4-t-OP, and mixture of nonyl phenols (iso-NP), 4-n-NP. Injection volume was 10 μL and instrumental detection limit was 0.83 pg/injection for all analytes.

Volatile organic compounds were analyzed in contracted accredited laboratory ALS Global in Brno, Czech Republic. The analytes were in total 71 and are listed in Certificate of Accreditation No. 819/2015 of 30/11/2015 (http://alsglobal.cz/website/var/assets/media-general/certificates-2015/819_2015_eng_whole_cai_pdf.pdf), and they were analyzed using US EPA 8260 (GC-MS) method. In addition, epichlorhydrin was analyzed in extra collected samples in March 2016 by ALS Global using a GC-MS method with detection limit of 100 μg/L.

2.4. Metal analysis

Inductively Coupled Plasma — Mass Spectrometry (Agilent 7700x ICP-MS, Agilent Technologies, Japan) was used for determination of metals (iron, copper, zinc and lead) in the acidified water samples. Elements were measured in He collision mode using Octopole Reaction System for reduction of polyatomic interferences coming from sample matrix. 200 ppb solution of internal standards (Ge and Bi) was used for correction of matrix effects and drift.

2.5. Bioreporter assays

The DMSO extracts were tested for total estrogenicity and bisphenol A-equivalent activity using yeast bioreporters with human estrogen receptor α (Leskinen et al., 2005) and bisphenol A-targeted receptor (Rajasärkkä and Virta, 2013). The BPA-targeted receptor (BPA-R) is insensitive to estradiols at least up to 190 μg/L, and has about 4-fold greater potency towards BPA than ERα (Rajasärkkä and Virta, 2013; Rajasärkkä et al., 2011). The BPA-R has also at least 15 times higher potency towards BPA than bisphenols F or S, whereas ERα has similar potency towards BPA and BPF (Rajasärkkä et al., 2014).

The yeast assays were done as described by Leskinen et al. (2005).Briefly, yeast cells were grown overnight in 5 mL of minimal SD medium (containing Yeast Nitrogen Base Without Amino Acids (Sigma-Aldrich, Germany), 2% glucose and supplemented with adenine, histidine and leucine) at 30 °C with 250 rpm shaking, and diluted in the morning in fresh SD medium to OD600 of 0.4. The culture was further grown for approximately 2 h until OD600 reached 0.6—0.7. Assays were performed in white 96-well plates (Nunc, ThermoFischer Scientific) by first pipetting 2 μL of sample extracts (diluted 1:1 in DMSO), standard chemical solutions, or blank solvent (100% DMSO) in the wells. Then 98 μL of yeast culture was added, and the plates were incubated for 2.5 h at 30 °C after which 100 μL 1 mM D-luciferin stock solution in 0.2 M sodium citrate buffer (pH 5) was added to the wells and immediately measured for luminescence using BioTek Synergy 4 microplate reader. Data was analyzed as described in Rajasärkkä and Virta (2013). Fold luminescence signals of samples were compared to the BPA standard dose-response curve, and BPA equivalent concentrations (BPAeq) were calculated.

3. Results and discussion

3.1. Metals

The European Drinking Water Regulations 2014 (European

Union, 2014) set standards for 48 microbiological, chemical and indicator parameters which should be monitored regularrly to assure good water quality. The parameters also include maximum limits for metals, such as copper (2 mg/L), iron (200 μg/L) and lead (10 μg/L).

Galvanized steel was the most common material installed in household cold water lines between 1900 and 1970 in Finland (Kekki et al., 2007), and it was expected that iron and zinc would be good indicators of pipe ageing in the studied houses.

Indeed, iron concentrations in the non-renovated location NR were high in cold water samples (Fig. 1). Even in flowed cold water iron concentration exceeded the maximum limit during one of the two repeated samplings. Also zinc concentrations were high at site NR (>280 μg/L) in incubated and incoming water samples (Table S1 in supplemetrary material).

In majority of epoxy lined locations (A-F) iron and zinc concentrations in cold water were clearly lower compared to location NR (Fig. 1 and Table S1) which indicates that epoxy lining can lower the levels of iron and zinc in drinking water, but metal concetrations should have been measured before renovations for conclusive confirmation. Locations B and C, however, still had relatively high concentrations of iron (Fig. 1). In location D the incubated samples had high iron concentrations most likely due to very long incubation times (1 month and 1 week, respectively) but for all other samples collected at the location the concentrations were below 50 μg/L, i.e. at about the same level with the close-by location TR which had traditional pipe rehabilitation (Fig. 1 and Table S1).

Pipes made of copper have been commonly used in household hot water pipes, but since mid 1970's they have been applied to cold lines as well (Kekki et al., 2007). In the present study copper concentrations were generally higher in hot water samples with an average of 157 μg/L, whereas cold water had only on average 31 μg/L. None of the samples exceeded the EU quality limit 2 mg/L, and epoxy lining seems to have no effect on copper concentration in water (Table S1).

Lead has not been used extensively in water pipes in Finland (Kekki et al., 2007), and lead concentrations in all studied samples were below the recommended quality level of 10 μg/L (Fig. 2). Similar to profiles of iron and zinc, incubated samples in location D and the traditional renovated location (TR) had relatively high concentrations of lead. Possible sources can be connectors or sealings.

Metal concentrations measured at the DWTP in Helsinki in this study were in good agreement with the results obtained by the DWTP in August 2015: 20.4/21.6 μg/L vs. 31 μg/L for iron, and 5.2/4.8 μg/L vs. 5 μg/L for copper. Measured concentrations for zinc and

lead by the DWTP were below LOD, while 0.7 and 0.03 μg/L were measured in this study (Table S1).

The incoming water samples had great varation in metal concentrations between different locations, although they were generally lower than those in corresponding cold flowed water samples (Fig. 1). Communal distribution system can be the source, however, in Finland it comprises on average 61% of plastic pipe materials, and only 36% steel or iron pipes, much less than in Europe and the USA (Gonzalez et al., 2013; Kekki et al., 2007). Possibly plot pipes, i.e. pipes branching from communal system to houses, can be made of old steel pipes contributing to observed variability.

3.2. Volatile organic chemicals

Of the 71 volatile compounds analyzed the chlorination by-product chloroform was detected in all samples at levels 0.1–0.99 μg/L with an average of 0.21 μg/L (Table S2 supplementary data). Another chlorination by-product bromo-dichloromethane was occasionally detected in DWTP and few other samples at concentrations 0.10–0.16 μg/L (Table S2). In the incubated samples at location D methyl-tertbutylether (MTBE) and tert-butylalcohol (TBA) were detected in concentrations 1.45–11.7 μg/L and 47–535 μg/L, respectively. MTBE and TBA have been associated with polyethylene water pipes as cross-linking reagent by-product (Whelton and Nguyen, 2013). Detectable concentrations in incubated samples from location D can likely be associated with very long incubation times, possibly originating from plastic couplings or sealings.

No epichlorhydrin was detected in any of the samples (detection limit 100 ng/L) upon resampling campaign in March 2016. Epichlorhydrin is a potential carcinogen according to the US EPA (Group B2), and WHO classifies it as "probably carcinogenic to humans (IARC Group 2A). A maximal limit of 100 ng/L has been set in The European Drinking Water Regulations (2014) (European Union, 2014). The compound is very reactive and probably not detectable even if small amounts would be leaching from the resin.

3.3. Alkylphenols

For alkylphenol analysis the water samples were extracted by solid phase extraction. Based on yield controls, the yields for studied compounds were on average 83% for BPF, 82% for BPA, 120% for 4-t-octylphenol, and 58% for 4-n-nonylphenol. Yield-corrected detection limits (LOD) for concentration in water samples were 0.43 ng/L for BPF and BPA, 0.04 ng/L for 4-t-octylphenol, and
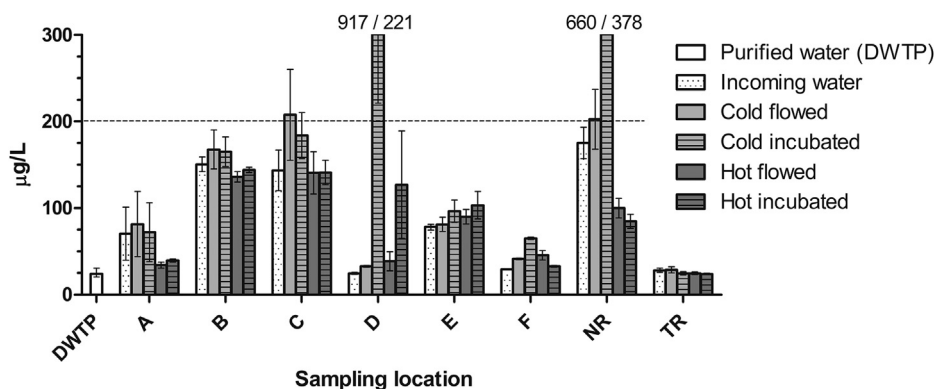

Fig. 1. Iron concentrations in tap water samples. Average with range of the two sampling time points are shown. The two actually measured concentrations in two repeated samplings are also shown for bars exceeding the scale of Y-axis. DWTP = drinking water treatment plant, NR = non-renovated location, TR = traditional renovated location (pipe replacement). Horizontal dashed line: recommended maximal limit for iron (200 μg/L).
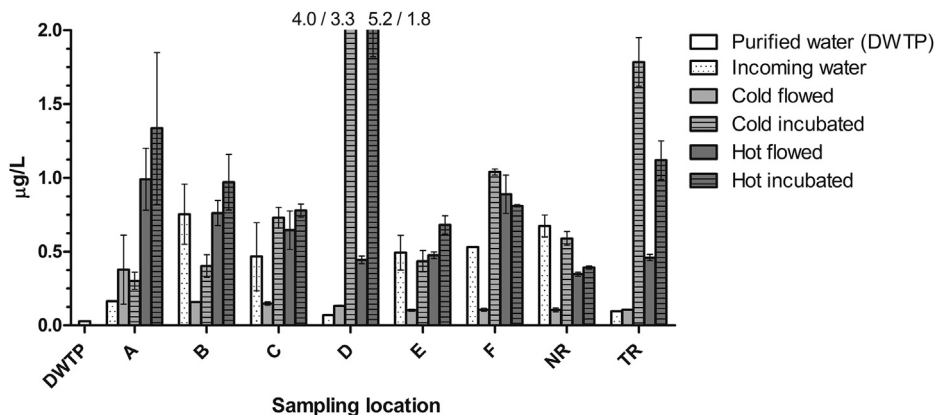
Fig. 2. Lead concentrations in tap water samples. Average with range of the two sampling time points are shown. The two actually measured concentrations in two repeated samplings are also shown for bars exceeding the scale of Y-axis. DWTP = drinking water treatment plant, NR = non-renovated location, TR = traditional renovated location (pipe replacement).

0.16 ng/L for 4-n-nonylphenol.

BPF was detected only in the long-incubated water samples at location D, and the concentrations were generally low, 8–24 ng/L (Table S3, supplementary material) indicating that the resin may contain residues of BPF. Interestingly, in another study with epoxy lined pipes BPF concentrations were clearly higher, 25–1050 ng/L even without long incubation time (Bruchet et al., 2014). Occurrence of BPF in water thus probably depends on the resin formulation.

Minimal occurrence and low concentrations were observed for 4-n-nonylphenol (two samples 1.6 ng/L and 13 ng/L) while concentrations of iso-NP mixture exceeded those of blanks (max 32.5 ng/L) on only two occasions in hot incubated water in location E (69 ng/L) and in hot flowed water in location F (66 ng/L) (Table S3). 4-t-octylphenol was detected in low concentrations in 8 samples of the epoxy lined locations (0.7–22 ng/L), in all three DWTP samples (0.5–1.2 ng/L) and in relatively high frequency at locations NR (non-renovated) and TR (traditional renovation), in 14 samples of total 20 samples (0.9–33.5 ng/L, see Table S3). Concentrations of 4-t-octylphenol were highest in location TR in the incubated samples, probably due to new plastic pipe or coupling materials.

BPA and BPF were not detected in DWTP samples nor at location NR (Table S3). At location TR BPF and BPA was detected only once in incubated cold water sample at low concentrations of 4 and 5 ng/L,

respectively.

BPA was detected in majority of the samples from locations with epoxy resin lining. The frequency of detection was lowest in the incoming water samples (Fig. 3 and Table 2), of which BPA was detected only in locations B, C, and D. Probably in these locations there was a stretch of epoxy lined pipe upstream of the sampled tap. It is also possible that the sampled taps (sauna at the basement, laundry room in ground floor, and water/heat supply room for B, C, and D, respectively) were less frequently used, and remainders of contaminants were still detectable even after 2 min of water flowing.

In cold flowed water BPA concentrations were low, maxima 10–11 ng/L at locations A-C and F, while locations D and E maxima were 148–252 ng/L (Table 2). Flowing water for 2 min before its use is not, however, a common practice for residents. To simulate water standing in the pipes e.g. overnight or during working day, the residents were asked not to use water in the apartment for 8–10 h before sampling. Incubation did increase the concentration of BPA in all locations 1.1–43-fold, up to maximum of 505 ng/L at location E (Table 2), indicating that incubation increases the BPA-burden of water.

Similar BPA concentrations in cold water have been observed in other studies. In laboratory scale experiments pipes lined with epoxy resin were shown to leach BPA in concentrations of few nanograms to 250 ng/L (Bruchet et al., 2014; Kosaka et al., 2012). Examination of houses with epoxy lined pipes in France showed BPA levels of 18–421 ng/L (Bruchet et al., 2014). According to German Umweltbundesamt (Umweltbundesamt, 2010), BPA concentrations in studied renovated locations in Germany were below 1 μg/L.

In this study hot water samples were also studied and clearly higher BPA concentrations were compared to cold water were observed with maximum of about 23 μg/L in locations D and E (Fig. 3, Table 2.). Hot temperature has been shown previously to increase BPA leaching from epoxy resin in laboratory experiments (Bae et al., 2002). Umweltbundesamt (Umweltbundesamt, 2010) has also reported that hot water samples from houses with epoxy lined pipes had BPA concentrations above 30 μg/L of BPA, and even up to 280 μg/L in one location with poorly assembled lining. In the present study incubation of water increased BPA concentration in hot water lines by maximum 2-fold in location E, whereas in other location it had no or low effect (Fig. 3 and Table 2). It is possible that in warm temperature BPA reacts with other compounds or may undergo degradation. In location E the pipes were not insulated and hot pipes are probably cooled down faster.
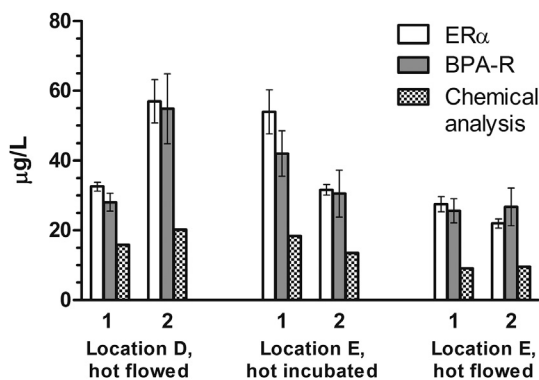

Fig. 3. Bisphenol A equivalent concentrations in the hot water samples from locations D and E measured by yeast ERα and BPA-R bioreporters compared to BPA concentrations measured by chemical analysis. The bioassay results are given as average ± standard deviation of two independent analyses, each with 3 parallels.

Table 2
Bisphenol A concentrations in sampling locations A-F, NR (non-renovated), TR (traditional renovation), and DWTP (drinking water treatment plant). Concentrations of both sampling time points are shown.

Sampling location	Bisphenol A concentration in water (ng/L)									
	Incoming		Cold flowed		Cold incubated		Hot incubated		Hot flowed	
A	<LOQ		10	<LOQ	410	<LOQ[a]	593	422[a]	713	349
B	52	<LOQ	11	<LOQ	40	20	1264	2183	2536	1567
C	200	82	10	<LOQ	51	<LOQ	660	347	640	383
D	10	9	148	175	416	290	2134	397	18 460	23 504
E	<LOQ		252	236	505	269	23 174	17 058	11 512	12 102
F	nd	<LOQ	<LOQ		34	29	716	613	517	424
NR	<LOQ									
TR	<LOQ		<LOQ		<LOQ	5	<LOQ		< LOQ	
DWTP	<LOQ									

nd: not determined. <LOQ: below the limit of quantification.
[a] Sample was not incubated as requested.

In addition to temperature, pipe lining technology had a great influence on BPA concentration in water. The highest BPA concentrations were observed in locations B, D, and E rehabilitated using the LSE technology, while locations A, C, and F (DonPro technology) had low concentrations (Fig. 3, Table 2). This was especially clear in hot water samples in which DonPro-renovated locations had at maximum 0.72 µg/L of BPA, while LSE locations had 1.57—23.5 µg/L. In cold water, LSE-locations D and E had 15—25 fold higher BPA concentrations than locations with DonPro lining. Although LSE lining in location B was of similar age with DonPro lining locations A, C, and F, BPA concentrations were clearly higher in hot water (Tables 1 and 2, Fig. 3).

Ageing of LSE lining was also reflected in water BPA-burden. Compared to older LSE locations D and E, location B still had about 4—20-fold lower concentrations of BPA in water (Fig. 3, Table 2), and it may be expected that BPA concentrations in this location will increase during the following years. Increasing concentrations of BPA in water can thus be a sign of accelerating degradation of the resin, and BPA concentration in water should be monitored regularly also in hot water in which degradation of the resin is potentially faster.

Attachment of the resin to the inner surface of water pipe is an important factor for the expected life time for the lining. For example, in location D the resin was visibly crumbling from the pipes and blocking filters in taps after only about 8 years (personal communication with local service). Without structural inspection of pipe samples it is difficult to estimate life time of the lining work. Such inspection was done by Swiss authority EMPA (EMPA, 2004) by studying a sample of a 16-old LSE epoxy lined pipe. The pipe was reported to have slightly impaired attachment of the lining but it still fulfilled its purpose as corrosion inhibition. EMPA estimated that the lining would fulfill its purpose for another 5—10 years, resulting in total life time of 21—26 years.

The results of this study indicate that LSE technology is less favorable spray-on-lining technology than DonPro in respect of BPA leaching. This is possibly due to better attachment of the resin to the pipes (following more efficient pipe cleaning used in DonPro) or different resin composition. It should be pointed, however, that all studied DonPro locations were of about same age, and no conclusions about changes during time in these locations can be done.

3.4. Yeast bioreporter assays

In addition to analyses of individual chemicals, integrative effect-based monitoring approaches are currently highlighted as a viable water quality assessment tool for detection of biological effects of unidentified compounds and mixtures (Escher et al., 2014; Wernersson et al., 2015), of which estrogenicity is of main concern (Jarosova et al., 2014).

As yeast LODs for BPA were relatively high, 601 ± 122 µg/L for ERα bioreporter and 145 ± 38 µg/L for BPA-R bioreporter (average ± standard deviation, given as total concentration in mixture with yeast cells), only those water sample extracts with highest BPA concentrations induced the yeast bioreporters. These were the flowed hot water samples from location D, and both flowed and incubated hot water samples from location E, while none of the other samples from other locations elicited significant potency above bioassay LOD. The bioassay-based BPAeq concentrations in positive samples were similar with both bioreporters in all samples, indicating that bisphenol-like compounds were the main cause of estrogenic activity in the studied samples (Fig. 3).

The yeast bioreporter results were in line with chemical analysis results: BPAeq concentrations were highest in hot flowed sample no. 2 from location D and hot incubated sample no. 1 from location E, which also had the highest measured BPA concentrations in LC-MS analysis (Fig. 3). However, all bioassay-derived BPAeq concentrations were about 2—3-fold higher than concentrations measured by HPLC, and it is thus possible that samples could contain other bisphenol-like and estrogenic compounds that have potency in the yeast assay were not instrumentally analyzed.

For example, chlorinated bisphenols can be formed in pipes when chlorine used for disinfection reacts with epoxy resin components. It has been shown that when chlorinated water was exposed to epoxy-coated pipes, chlorinated bisphenol A derivatives and degradation product 2,4,6-trichlorophenol (a probable human carcinogen) could be detected at concentrations 8—96 ng/L and 50—16 000 ng/L, respectively (Bruchet et al., 2014; Kosaka et al., 2012). It was also noted in both studies that the epoxy resin is able to accumulate the compounds on its surface. Interestingly, chlorinated bisphenol A derivatives have been shown to have greater estrogenic potential than non-chlorinated BPA (Hu et al., 2002), and thus presence of chlorinated bisphenol A derivatives could be responsible for higher detected estrogenicity than would be expected by BPA alone.

3.5. Exposure and risk assessment

Analyses of VOCs, metals as well as majority fo alkylphenols in the present study indicate negligible health risks of the investigated epoxy linings. Only rare occurrences and very low concentrations of VOCs (no epichlorhydrin) as well as alkylphenols (BPF, 4-n-NP and 4-t-OP) were observed. Metal concentrations were - with few exceptions - generally below the limits set by the European Drinking Water Regulations 2014 (European Union, 2014) being 2 mg/L for copper, 200 µg/L for iron, and 10 µg/L for lead.

With regard to BPA, there is no generally accepted regulatory

limit in drinking water. A few countries have set their limit values. For example, in France a reference value of 100 ng/L for BPA is recommended (Bruchet et al., 2014), whereas in Germany the limit value is 30 µg/L (Umweltbundesamt, 2010) and in Japan 100 µg/L (Kosaka et al., 2012). In addition, the US ANSI/NSF-61 standard suggests total allowable concentration of 200 µg/L of BPA permitted in drinking water. Compared to these limits, maximum detected BPA concentrations in cold flowed drinking water samples in the present study were well below the French limit of 100 ng/L - except for locations D and E where up to 252 ng/L were detected.

BPA exposure of residents was assessed according to the estimated 2 L/day consumption of drinking water for adults by U. S. EPA (U.S. EPA, 2000). Assuming a 70 kg person uses 2 L of water per day for drinking and cooking, then BPA exposure with the abovementioned national limits would be 0.003 µg/kg, 0.86 µg/kg, and 2.86 µg/kg per day for France, Germany, and Japan, respectively. None exceeds the current tolerable daily intake of 4 µg/kg for BPA set by the European Food Safety Authority (EFSA, 2015).

However, EFSA has estimated that average daily dietary BPA intake is 0.132 µg/kg for adult women, 0.126 µg/kg for men, and 0.375 µg/kg for children. Using water with BPA concentration at the German limit would cause over 6-fold increase in average adult BPA intake, while with the French limit the increase would be about 2%. Thus, the French limit should be more applicable for regulatory purposes, especially if target is to ensure only minor increase in overall BPA exposure.

Intake rates of BPA for adults via cold water in the studied locations with epoxy lining was neligible: 0.27—7.2 ng/kg/day for adults and 0.58—15.3 ng/kg/day for small children, estimated with the average intake rates by the US EPA (Table 3). These correspond to a 0.2—5.7% increase in the average daily BPA intake via food (EFSA, 2015).

Hot water, which is not generally considered to be drinking water, contained from 45 to over 200-fold more BPA than cold water in the studied locations. For this reason unintentional exposure via hot water can potentially cause increase in daily intake of BPA. Direct consumption of hot water could happen due to improper flowing in water, as well as accidental ingestion or water aerosol aspiration in shower or bath. Unintended ingestion of water during swimming has been evaluated by the U. S. EPA (U.S. EPA, 2011). According to the estimated ingestion rate during swimming (21 mL/h for adults and 49 mL/h for children) and average showering and bathing time of 17.1 min/day, BPA exposure was found low, 0.04—2 ng/kg/day for adults, and 0.66—21.9 ng/kg/day for children (Table 3).

Summarized alltogether, the highest BPA exposures were 8.2 ng/kg/day and 32.5 ng/kg/day for adults and children, respectively, corresponding to 6.5% and 8.7% increase in average intake of BPA.

Another exposure route can be dermal absorption in shower and bathing, however, currently there are no recommended methods for dermal exposure via this route.

4. Conclusions

BPA concentrations were higher in locations with epoxy lining done using LSE lining technology than those using DonPro technology. Higher leaching of BPA can be due to less efficient cleaning of pipes and consequently less tight attachment of the resin to the pipes. Also differences in resin compositions can effect leaching.

Locations D and E with 8—9 years old LSE coating leached more BPA compared to 2 years old location B. Thus ageing of the resin was seen as increased BPA leaching to water. No conclusions about ageing effect concerning locations with DonPro technology could be done due to the same age of these locations.

In all samples hot water contained more BPA than cold water. Life expectancy of epoxy lining can be shorter in hot water lines than in cold water lines, and should be taken into account when estimating working life for the lining work. More studies concerning ageing should be done, especially with hot water lines.

Intake of BPA via water in the studied locations is low and correspond maximum of 8.7% increase in average BPA intake via other sources.

Formation of chlorinated bisphenols is possible in epoxy coated water pipes with chlorinated water. This should be further studied and taken into account in risk assessment due to higher biological potency of chlorinated BPAs.

Drinking water pipe lining can be a reasonable option for pipe renovation if.

- an efficient pipe cleaning and thus good resin attachment can be ensured,
- harmful amounts of metals, especially iron and lead, occur in drinking water
- a non-invasive renovation is strongly preferred due to, for example, recent renovation of other surfaces,
- it is acceptable that rehabilitation by lining might not have as long life time as conventional rehabilitation by pipe replacement.

Author contributions

J.R. and L.B. designed research; J.R., M.P, J.K., J.L., and Z.S. performed research and analyzed data; J.R. wrote the paper; J.R., Z.S. and L.B. contributed to the financial support of the research. All the authors contributed to the interpretation of the data and paper finalization.

Conflict of interest

The authors declare no conflict of interest.

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Table 3
Calculated BPA exposure levels via cold drinking water and ingestion via hot water in shower or bath for adults (>18 years, 70 kg) and children (toddlers 2—3 years, 15 kg). Highest measured concentration in each location was used.

Location	Adult (ng/kg/day)			Child (ng/kg/day)		
	Cold water[a]	Hot water[b]	Sum	Cold water[a]	Hot water[b]	Sum
A	0.27	0.06	0.33	0.58	0.66	1.24
B	0.32	0.22	0.53	0.67	2.36	3.03
C	0.28	0.05	0.33	0.59	0.60	1.19
D	4.99	2.01	7.00	10.62	21.88	32.50
E	7.20	1.03	8.23	15.31	11.27	26.58
F	–	0.04	0.04	–	0.48	0.48

[a] Daily consumption for adults 2 L and for child (2—3 years) 0.912 L (U. S. EPA, 2000 and 2011).
[b] Intake rate 21 mL/h for adults and 49 mL/h for children, time 17.1 min/event (U.S. EPA, 2011).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.07.027.

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