Bull Environ Contam Toxicol (2012) 89:557–562
DOI 10.1007/s00128-012-0742-4

Evaluation of Environmental Impacts of Two Common Restoration Methodologies for Pipes that Convey Stormwater Runoff

Dianjun E. Ren · James A. Smith

Received: 8 June 2011 / Accepted: 10 July 2012 / Published online: 22 July 2012

Abstract This study investigated the environmental impact of two commercial stormwater pipe-repair technologies (Ultraliner and Troliner). These technologies use liners believed to contain three plasticizers of potential environmental concern: bisphenol A (BPA), di-(2-ethylhexyl) phthalate (DEHP), and benzyl butyl phthalate (BBP). The release of these two products was investigated both experimentally and mathematically. Kinetic batch experiments were conducted to determine if contaminants were leaching from Ultraliner, Troliner, and the grout (used with Troliner) into water. In all cases for all incubation times up to 48 h, none of the three plasticizers were detected in water in contact with any of the pipe-repair materials. A generic GC-FID scan did not detect any unidentified compounds relative to control samples. In addition, a mathematical model of plasticizer leaching from the pipe-liner material was developed. Under various pipe geometries, simulated aqueous concentrations of the plasticizers were less than regulatory limits.

Keywords Pipe repair · Phthalate · Stormwater · Plasticizer · Release

Many storm-water pipes and culverts have reached the end of their service life or have otherwise become damaged. Consequently, repair or replacement of worn or damaged pipes is a significant maintenance concern. “Trenchless” pipe-repair technologies repair existing underground pipes in place rather than using the conventional method of unearthing and replacing sections of damaged pipe. These less-disruptive and potentially economical trenchless alternatives, however, have not been evaluated for their impact on the environment. Some of these methods use synthetic liners coupled with steam treatment, chemical sealants, or grouting to provide a watertight seal between the liner and the damaged pipe wall. Since storm water conveyed by these pipes is often discharged directly into natural surface waters, it is important to insure that these repair technologies are not releasing contaminants into the environment.

According to a recent study, it is suspected that one common trenchless pipe-repair technology, cured-in-place pipe (CIPP) rehabilitation, has the potential to contaminate downstream water during and after installation, particularly when certain installation variables (e.g., resin and cure-water containment) are not properly controlled (Donaldson 2009). Two other trenchless technologies, Troliner and Ultraliner, have not previously been evaluated for their environmental impacts. The main constituents in these products that are also potential pollutants are three plasticizers: di-(2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), and bisphenol A (BPA). Extensive prior research has pointed out that phthalates have negative effects on the reproductive physiology of fish (Norrgren et al. 1999) and mammals (Catherine et al. 1997; Moore 2000; Kavlock et al. 2002). Since 2000, the Water Frame Directive (DCE 2000/60/CE) in Europe listed DEHP as one of 33 hazardous substances that shall be regulated. The US Environmental Protection Agency (EPA) lists DEHP and BBP as priority pollutants. Considering the existence of these contaminants in products and their potential action as endocrine disruptors, DEHP, BBP, and BPA were selected as the target contaminants for this investigation. It is

D. E. Ren · J. A. Smith (✉)
Department of Civil and Environmental Engineering, University of Virginia, Charlottesville, VA 22904-4742, USA
e-mail: JAS9E@Virginia.edu

hypothesized that these compounds may leach from commercial pipe-repair products into water following installation.

The purpose of this study was to evaluate the impact of pipe rehabilitation on water quality using two products: Troliner and Ultraliner. The focus of the work was to quantify leaching of anthropogenic constituents from the rehabilitation grout or coatings into water discharged from the pipe following restoration through experiments and simulation.

Materials and Methods

All reagents were analytical grade and were used as received. DEHP, BBP, BPA, HPLC-grade acetonitrile, and HPLC-grade water were all provided by Sigma-Aldrich (Milwaukee, WI, USA). Deionized, organic-free water used in batch reactor experiments was obtained directly from a Nanopure Ultrawater system. Syringe filters used in sample processing were 0.45 µm PTFE filters purchased from Fisher Scientific.

The detection of BPA, DEHP, and BBP was performed using an Agilent LC1100 high-performance liquid chromatography coupled with a UV–Vis detector (HPLC UV–Vis). Total organic matter was quantified through a generic gas chromatography scan with a Perkin-Elmer Autosystem gas chromatograph and flame ionization detector (GC-FID). Details of each analytical method are provided in Table 1. The recovery rate for each compound was 99.9 % ± 2.15 %, 93.5 % ± 8.96 % and 94.9 % ± 6.03 % for BPA, DEHP and BBP, respectively.

In setting up batch experiments, 5 g of each liner material (Ultraliner, Troliner, or grout as a binding agent for Troliner) were placed in 12 50-mL (nominal volume) plastic tubes. Deionized, organic free water was added to minimize headspace in each tube. Sample tubes were then placed on a mechanical shaker for complete mixing. At predetermined time points, a water sample was withdrawn from one tube and centrifuged for 30 min at 1,150 g. A total experimental time period of 48 h was chosen as a typical time span in field application. For desorption experiments with grout, an extra filtration step was necessary to separate grout from water. For these cases, the sample was passed through a 0.45 µm PTFE filter. Stock solutions of DEHP and BBP were prepared in methanol: water mixture with a 1:99 (v/v) ratio due to the limited aqueous solubility of these analytes.

Results and Discussion

Figure 1 gives the chromatogram derived from Troliner analysis of aqueous samples in contact with DI water at different incubation times. Aqueous samples in the batch reactors in contact with each liner material were sampled at 0, 6, 12, 24 and 48 h. In Fig. 1, the uppermost chromatogram is a blank sample (e.g. the batch reactor contained water but no liner material). Each chromatogram is essentially the same as the blank-sample chromatogram, indicating that over the 48-h incubation time, none of the target analytes were detected in the aqueous phase in the samples. A few small peaks are present during the first 2 min on the graph. As these peaks are also present in the blank samples, they were probably from the addition of 1 % (v/v) methanol to each sample. Results of batch desorption experiments for Ultraliner and grout also showed no detectable desorption of the plasticizer relative to the blank sample (data not shown).

The three target analytes, BPA, DEHP, and BBP, were chosen based on review of the material safety data sheets of each pipe-liner product. To determine if other organic compounds were leached from the liner materials, a general GC-FID scan was performed for samples collected from the batch reactors at different times. Figure 2 shows the resulting chromatograms for Troliner. The upper chromatogram in the figure is for a blank batch reactor (e.g. water without any pipe-repair product). The remaining chromatograms, from top to bottom, correspond to batch incubation times of 0, 6, 12, 24, and 48 h, as (b) to (f) shown on the graph. Comparison of the blank samples to samples incubated with the Troliner show that there

Table 1 Instrument settings for chromatographic analyses

High performance liquid chromatography		Gas chromatography	
Column	Agilent TC-C18 column (4.6 × 150 mm, 5µm)	Column	Supleco PTE-5 fused silica capillary column, 30 m × 0.32 mm i.d.
Flow rate	0.5 mL/min	Carrier gas	Helium, purity: 99.99 %. Flow pressure: 10 psi
Detection wavelength	227 nm	Injector	1 µL splitless, injection temperature 260°C
Sample	20 µL injection by autosampler	Detector	Flame ionization detector, 320°C
Gradient wash program	Water: Acetonitrile = 50:50 from 0 to 5 min, 5:95 from 5 to 18 min; 50:50 from 18 to 20 min.	Oven temperature program	50°C isothermal for 5 min; increase to 320°C at 5°C/min; 320°C isothermal for 5 min.

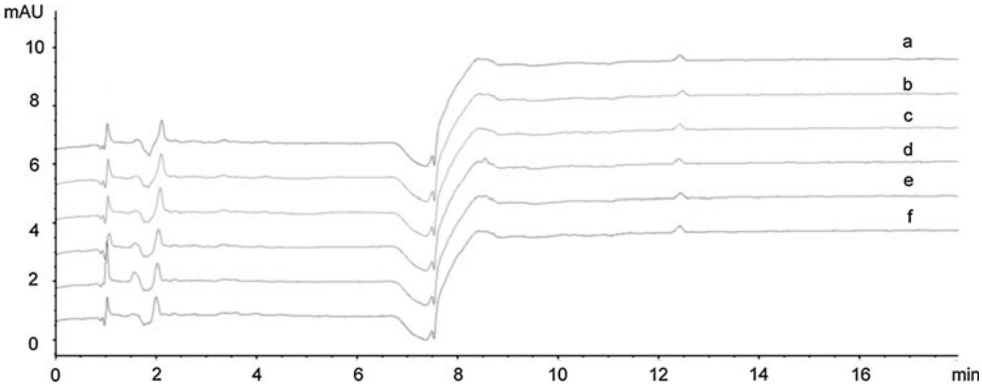

Fig. 1 HPLC chromatograms for aqueous samples equilibrated with Troliner in 50-mL batch reactors for different equilibration times. The uppermost chromatogram is for a blank sample (water with no Troliner present). Chromatograms below the blank sample **a** from top to bottom correspond to equilibration times of 0, 6, 12, 24, and 48 h **b**–**f** respectively

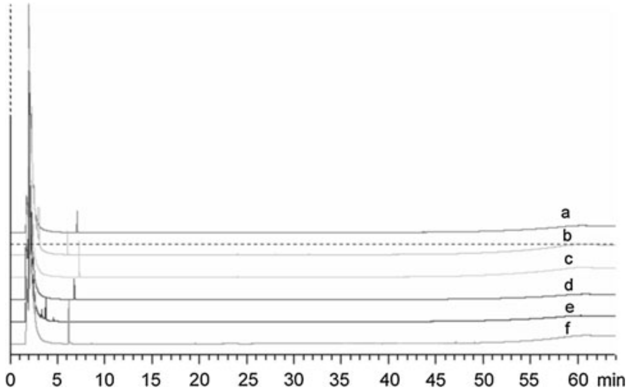

Fig. 2 GC-FID chromatograms for aqueous samples equilibrated with Troliner in 50-mL batch reactors for different equilibration times. The uppermost chromatogram is for a blank sample (water with no Troliner present). Chromatograms below the blank sample **a** from top to bottom correspond to equilibrations times of 0, 6, 12, 24, and 48 h **b**–**f** respectively

were negligible organic solutes released from the products into water during the 48-h incubation period. Similar results were obtained for batch experiments with Ultraliner and grout (data not shown). The flame-ionization detector (FID) is a relatively nonspecific detector capable of responding to a wide range of organic compounds. Therefore, these results further indicate that these pipe-repair materials did not leach significant quantities of trace pollutants into water for incubation times up to 48 h.

The results of the batch desorption experiments described above resulted in no detection of the target analytes and no evidence of other organic solutes leaching from the pipe-liner materials based on the GC-FID scans. However, it is possible that the target analytes were released into water at concentrations below the method detection limit. To better estimate the possible range of released concentrations of contaminants, we developed a mathematical model to simulate the kinetic release of the target analytes from the pipe-liner material. We assumed the worst-case scenario within the context of our batch experimental data. To do this, we assumed that after a 48-h desorption time, the concentrations of the target analytes were exactly equal to our limits of detection. This kinetic desorption rate, combined with estimates of the sorbent surface area per unit volume of water, allowed us to predict aqueous concentrations of the target analytes over time in simulated pipes under active flow conditions and for different pipe diameters. We only modeled the release from Troliner and Ultraliner materials because the grout is a binding agent installed between Ultraliner and the inner surface of the pipe. Therefore, the grout should not have direct contact with the water in the pipe.

To simulate a typical installation scenario in field practice, flowing water through the repaired pipe section continuously after installation was considered. We assume that desorption in our batch reactors obeyed zero-order kinetics over 48 h and the concentrations of analytes at the end of the experiment exactly equaled our analytical detection limit. The release rates of the target analytes from Troliner and Ultraliner were assumed to be proportional to the contact time with water and the surface area of the material in contact. Then, based on different detection limits for each compound, we were able to calculate the release rate (k) for each plasticizer. The rates calculated in this manner from the batch experiments are given in Table 2. Note that since each plasticizer has a different analytical detection limit (0.029 mg/L, 0.191 mg/L, and 0.447 mg/L for BPA, DEHP, and BBP, respectively), the *k* values are different.

In a mathematical model, we considered a circular cross section of a stormwater pipe with diameter d (m), the depth of water as h (m), wetted perimeter P (m), arc angle θ (rad) and cross-sectional area A (m^2).

Table 2 Release rate (*k*) of chemicals from Troliner and Ultraliner per unit surface area

Release rate (μg/m^2/h)	Troliner	Ultraliner
BPA	3.226	14.999
DEHP	21.150	98.339
BBP	49.459	229.958

The relation between θ and the ratio of water depth to pipe diameter (h/d) is

$$\theta = 2\arccos\left(1 - \frac{2h}{d}\right) \tag{1}$$

The wetted perimeter is given by

$$P = \frac{1}{2}\theta d \tag{2}$$

Thus for a section of pipe with length L, the area that water contacts the pipe, M (m^2), can be written as

$$M = \frac{1}{2}\theta dL \tag{3}$$

and the cross-sectional area of water flow is

$$A = \frac{(\theta - \sin\theta)d^2}{8} \tag{4}$$

For our first scenario, we assumed that water is flowing through the stormwater pipe. This is likely to be the scenario that best represents actual field conditions. For each target analyte, i, the governing equation for solute transport in the flowing water can be expressed as

$$\frac{\partial C_i}{\partial t} = D_i\frac{\partial^2 C_i}{\partial x^2} - v\frac{\partial C_i}{\partial x} + \lambda_i \tag{5}$$

where D is the longitudinal dispersion coefficient (m^2/s), t is the elapsed time since the water enters the repaired section (s), v is cross sectional average velocity of water (m/s), C_i is the concentration of analyte i (mg/L), λ_i is the zero-order kinetic solute desorption rate constant (mg/(L s)), with initial condition

$$C(x, 0) = 0 \tag{6}$$

and boundary conditions

$$C(0, t) = 0 \tag{7}$$

$$\frac{\partial C}{\partial x}(L, t) = 0 \tag{8}$$

The zero-order rate coefficient, λ_i, can be calculated using k_i values from Table 2 that were in turn determined from our batch experiments. The relation between λ_i and k_i is as follows for the circular pipe geometry:

$$\lambda_i = \frac{k_i M}{V} = \frac{4k_i\theta}{d(\theta - \sin\theta)} \tag{9}$$

The analytical solution to the advection–dispersion-reaction equation above (and subject to the specified boundary and initial conditions) is given by Genuchten and Alves (1982).

For our simulations, we assumed 0.25-, 0.5-, and 1.0-m-diameter stormwater conveyance pipes and a 10-m-long repair section. Water velocity in the pipe can be quite variable. We chose a relatively low average velocity of 2.5 cm/s, as larger velocities will result in lower plasticizer concentrations. The dispersion coefficient D (2.54 cm^2/s) was selected to be on the same order of magnitude as the advection velocity based on published data from Fischer (1979) and Guo (2003). Matlab® (2010b, Natick, Massachusetts, the MathWorks Inc.) was use to solve the governing Eq. (5). Simulation results reported here show plasticizer concentrations at the effluent end of the renovated pipe section as a function of time for the flow scenario.

Table 3 gives the steady-state effluent concentrations of each plasticizer and for each liner material at different pipe diameters and water-depth-to-diameter ratios. As an example, the concentration profile over time for one combination out of nine is shown in Fig. 3. From the graph, it can be noticed that the concentrations of each plasticizer increases over time until they reach equilibrium at times less than 0.3 h. The equilibrium concentrations differ for each plasticizer because of their different release rates from the materials (which is a function of the different analytical detection limits of each compound and the surface areas

Table 3 Simulated steady-state aqueous concentrations of BPA, DEHP, and BBP at the outlet of stormwater pipes with different geometries for both Troliner and Ultraliner

Diameter (m)	Depth/diameter ratio	Troliner (ng/L)			Ultraliner (ng/L)		
		BPA	DEHP	BBP	BPA	DEHP	BBP
0.25	0.3	7.40	4.87	11.38	34.54	226.50	529.60
	0.5	5.10	3.33	7.78	23.62	154.80	362.00
	0.8	4.20	2.74	6.39	19.41	127.30	297.50
0.5	0.3	3.70	2.45	5.69	17.27	113.20	264.80
	0.5	2.54	1.66	3.89	11.81	77.43	181.00
	0.8	2.10	1.37	3.22	9.71	63.62	148.80
1	0.3	1.90	1.22	0.28	8.64	56.61	132.40
	0.5	1.30	0.83	1.95	5.90	37.81	90.50
	0.8	1.00	0.68	1.60	4.85	31.81	74.38

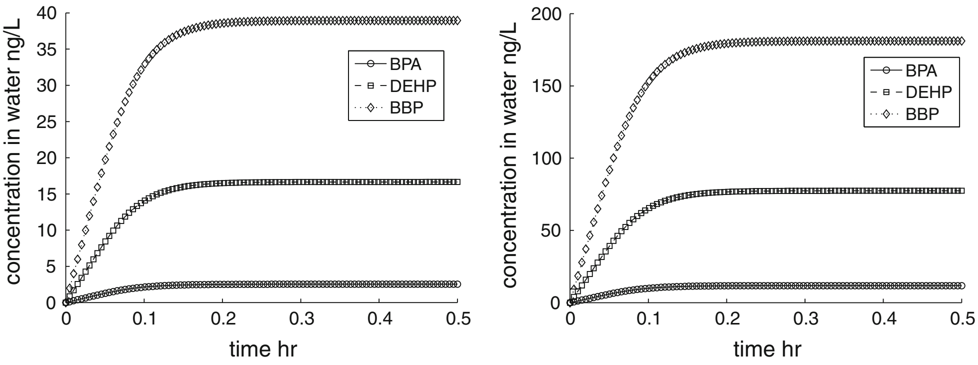

Fig. 3 Simulated concentration profiles of BPA, DEHP and BBP over time at the outlet of a 10 m Troliner-repaired stormwater pipe (*left*) and Ultraliner-repaired pipe (*right*). For this simulation, the inner diameter of the pipe is 0.5 m and the ratio of the depth of water in the pipe to the pipe diameter is 0.5

used in the batch experiments). The steady-state effluent concentrations for Troliner are 2.54, 1.66 and 3.89 ng/L for BPA, DEHP and BBP, respectively. Likewise, a profile for Ultraliner for the same parameters is obtained from the simulation. The equilibrium concentrations of the plasticizers are 11.81, 77.43 and 181 ng/L for BPA, DEHP and BBP, respectively.

From Table 3, it can be seen that the geometric combination with smallest diameter and least depth/diameter ratio would yield the highest concentration profile at steady state for both Troliner and Ultraliner. Overall, Ultraliner produces a higher concentration of each plasticizer compared to Troliner at the same geometry combination owing to higher plasticizer release rate. It should be noted, though, that the release rates are worst-case scenarios calculated from batch experiments using the analytical detection limit of each solute and the surface area of each pipe-liner material. Therefore, these relative concentration differences should not be taken as positive or negative characteristics of either liner material. The data in Table 3 also show that solute concentration varies inversely with both pipe diameter and the water-depth-to-diameter ratio. This result is expected given that they relate to water flows in the pipe. Increased pipe discharge relative to the wetted perimeter would be expected to cause lower solute concentrations.

It is helpful to put the simulated plasticizer concentrations in perspective based on regulatory limits. In the National Primary Drinking Water Regulations, the US Environmental Protection Agency (1995) has set the limit for DEHP in drinking water as 6 μg/L. The National Recommended Water Quality Criteria for BBP is 1.5 mg/L. Although there is some evidence that BPA may have negative environmental impacts, no regulatory limit has been established. The mean concentration of BPA in ambient surface water is reported to be around 0.081 μg/L for North America (Klecka et al. 2009). These concentrations are all higher than the concentrations determined from our simulations as a worst-case scenario (Table 3). All simulated concentrations are less than 1 μg/L. Furthermore, it is worthwhile to note that any plasticizers released from the pipe-liner materials would likely be attenuated once released into the storm water by processes such as sorption, volatilization, and degradation. The convergence of storm water flow into streams or rivers would further facilitate this process.

Despite the encouraging results of this study, we should note that it is possible that extremely low levels of these plasticizers may bioaccumulate in aquatic organisms. The octanol/water partition coefficient, K_{ow}, correlates with the bioconcentration factor (BCF) of aquatic pollutants and is often used to determine the potential of bioaccumulation of organic contaminants in aquatic organisms. Staples et al. (1997) reported that log K_{ow} values for BBP and DEHP are 4.59 and 7.50, respectively. Therefore, these plasticizers can bioconcentrate to appreciable levels in the lipid reservoirs of aquatic organisms. BPA is least likely to bioaccumulate owing to its relatively high water solubility and low log K_{ow} (Staples et al. 1998).

Acknowledgments The authors thank the Virginia Center for Transportation Innovation and Research (VCTIR) for providing support for this research. We also thank Dr. G. Michael Fitch of VCTIR for technical support.

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