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Impact of Infrastructure Coating Materials on Storm-Water Quality: Review and Experimental Study

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Abstract: A literature review and 30-day leaching regime were conducted to determine the extent storm-water infrastructure coatings affect water quality. Newly installed polymer-enhanced cement mortar (PECM) and polyurea (PEUU) storm-water pipe coatings were removed from the field and underwent 10 three-day water immersion periods. For both materials, the greatest water quality alterations occurred during the first water contact period, followed by significant reductions in water quality alterations. Mineral release from PECM consistently elevated pH from 7.1 to 10.1–11.8 throughout the entire study. Organic contaminant release [total organic carbon (TOC) and UV_{254}] was also detected for PECM during the first two water contact periods only. Alkalinity increased by 534 mg/L as $CaCO_3$ because of the first contact period and 18–50 mg/L as $CaCO_3$ for each remaining periods. Isocyanate resin from PEUU reacted with water and reduced water pH by 1.0 to 1.2 pH units during the early contact periods and lesser magnitude for the remaining exposure period. Chemical oxygen demand (COD), TOC, and UV_{254} results showed that organic contaminants were released from PEUU. A limited quantity of organic contaminants released by PEUU was biodegradable. Nitrogen compounds were detected only during the first PEUU water contact period. **DOI: 10.1061/(ASCE)EE.1943-7870.0000662.** © *2013 American Society of Civil Engineers.*

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Introduction

Much of the US storm-water infrastructure has or is about to reach the end of its useful life and primarily consists of concrete and metallic structures [Missouri Department of Transportation (MODOT) 2008; Transportation Research Board (TRB) 2002]. These materials are highly susceptible to corrosion and many have deteriorated past the point of rehabilitation and require replacement. For assets that have not structurally failed, trenchless pipeline rehabilitation technologies such as spray–on coatings are being applied [Cooney et al. 2011; Hollingshead and Tullis 2009; Salem and Najafi 2008; Piehl 2005; Ariaratnam 1998; American Water Works Association (AWWA) 2000, 2007a, b, 2008; Conroy et al. 1995; Environmental Protection Agency (EPA) Office of Research, and Development 2009; Kanchwala 2010; Oram 2004; Tullis et al. 2010]. Spray–on coatings are less costly than open–trench asset replacement, can halt material deterioration, sometimes provide structural support, and extend infrastructure service life by 25–75 years (Ellison et al. 2010). Coatings are generally prepared on site by mixing ingredients followed by spray application. Popular coatings include cement mortar (CM), epoxy (EP), polyurethane (PU), polyurea (PEUU), and PU/PEUU blends.

An emerging concern regarding storm-water infrastructure rehabilitation is that rinse waters generated during and shortly after material installation can pose downstream water quality and aquatic toxicity hazards. For example, multiple fish kills, aquatic vertebrate inhibition, and air contamination incidents have been documented at several different cured-in-place pipe (CIPP) installations in the United States, Canada, and Europe (Table 1). Cured-in-place-pipe is a popular rehabilitation technology that involves insertion and curing of a polymer-impregnated fabric into an existing pipe [Brier 2010; Kampbell 2009; Burkhard 2008; Griffin 2008; National Association of Sewer Service Companies (NASSCO) 2008; Hoffstadt 2000; Lee 2008; Snyder 2004]. These field–cured CIPP environmental contamination incidents have resulted in hospital evacuations, emergency response, fish kills, litigation, and moratoriums on technology use (Table 1). Commonly, rinse waters are discharged on site in a drainage ditch, stream bed, or to nearby waterways and sanitary sewers. Like CIPP, coating technologies are polymer based, cured on site, and are rinsed after installation. However, little to no testing has been carried out to quantify the environmental impacts of coating rinse waters.

Waste discharge to waterways can cause impairment and harm aquatic life. Water pH, dissolved oxygen, nutrient, and turbidity levels can help describe waterway health. The largest variety of aquatic animals prefer a water pH range of 6.5 to 8.0, whereas

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outside this range, most organism physiological systems are stressed and reproduction is reduced. Low pH can also facilitate heavy metal dissolution and bioavailability. A great quantity of organic compounds discharged into a waterway [sometimes monitored as total organic carbon (TOC) or chemical oxygen demand (COD) concentration] can also facilitate oxygen depletion as aerobic and facultative microorganisms utilize oxygen to break down organic matter for energy. The amount of oxygen consumed by these organisms is known as the biochemical oxygen demand (BOD). Excess nutrients (e.g., nitrogen/phosphorous) could also promote nuisance levels of algae and other aquatic vegetation (e.g., macrophytes), and indirect dissolved oxygen (DO) consumption through nitrification.

In the present study, a literature review and polymer-enhanced cement mortar (PECM) and PEUU coating leaching experiment were conducted to identify the water quality impacts of storm-water pipe coating materials. Because of unpublished environmental and safety concerns, the California Transportation Agency (CALTRANS) effectively banned the use of coatings that contain isocyanate materials, including PEUU (G. DeCou, personal communication, January 13, 2012). While transportation agencies have begun to assess and respond to water quality impacts resulting from CIPP installations (McLuckie 2011; J. Sicluna, personal communication, November 1, 2010; Donaldson 2009; Donaldson and Baker 2008), no studies were found that documented water quality impacts caused by PECM or PEUU materials. The goal of the present work was to quantify water quality alterations caused by newly installed PECM and PEUU storm-water pipe coatings. Specific objectives included the characterization of inorganic and organic contaminants imparted to water over a 30-day exposure period and identification of actions to minimize environmental impacts.

Literature Review

Most related literature applies to CM (not PECM) and epoxy coatings, few studies were found for PU coatings, and no reports were found for either PEUU or PU/PEUU blend coatings (Table 1). Of these records, almost all pertain to chemical leaching phenomena for approved potable water infrastructure coatings; none pertain to storm-water infrastructure. Moreover, most reports describe testing for which a series of water stagnation contact periods were conducted, not dynamic/flowing water experiments. Although potable water literature is informative, many of those coatings analyzed were previously approved by the National Sanitation Foundation International (NSFI) Standard 61 (ANSI/NSFI 2007). In the United States, NSFI Standard 61 certified products have undergone short-term premarket testing, leading to a determination that they do not cause drinking water to exceed U.S. Environmental Protection Agency maximum contaminant levels and certain NSFI Standard 61 limits for several unregulated contaminants. No certification exists for storm-water coatings. Thus, it is possible that greater quantities of contaminants are released from coatings installed for storm-water infrastructure than similar materials installed in potable infrastructure. A summary of contaminants detected in coating contact waters is provided in Table 2, and coating synthesis reactions are shown in Fig. 1.

Cement Mortar

Cement mortar coatings for potable water contact and bridge repair have been found to increase water pH; alkalinity; total dissolved solids (TDS); hardness; and concentrations of alkali, transition metals, and heavy metals. For example, one drinking-water-approved CM coating significantly increased water pH over an entire 30–day test period from 6.5–8.0 to 10.2–12.5 (Deb et al. 2010). This CM coating also greatly increased alkalinity concentration (>500 mg/L as $CaCO_3$), TDS concentration, and metal levels during the first several days of water contact. As contact water was replaced, gradual reductions in alkalinity and TDS alterations were observed. Other investigators have detected similar CM water quality impacts during laboratory CM potable water pipe leaching studies, within newly CM coated potable water pipelines, and for new concrete used for structural marine purposes (Fitch 2003; Gove et al. 2002; Berend and Trouwborst 1999; Guo et al. 1998; Germaneau et al. 1993; Kanare and West 1993; Colucci et al. 1993; Yuskus 1984; Douglas and Merrill 1991, 1993; Douglas et al. 1996; Guo 1997). Water pH and alkalinity levels are affected because major CM components such as silicates (Ca_3SiO_5, Ca_2SiO_4) and aluminates ($Ca_3Al_2O_6$) are released. Once dissolved in water, $Ca(OH)_2$ forms, which dissociates into Ca^{+2} and OH^- ions (Deb et al. 2010). Heavy and transition metals also have been found to leach from CM pipe rehabilitation coatings into waters (Table 2) for up to two years (Berend and Trouwborst 1999). Metal sources include minerals (i.e., silicates, aluminates) and residue remaining in kilns used to create cement (Guo et al. 1998). Because of ion dissolution, total dissolved solids and water hardness concentrations typically increase because of CM contact.

Epoxy

Although water quality impacts from epoxy coatings were not experimentally evaluated in this study, a literature review of those materials was conducted to better understand contaminant release from coatings. Water quality impacts of epoxy coatings have been documented by many investigators, and in the field, contaminants have been found to be released after epoxy-lined drinking water piping had been in service for five months (Crathorne and Warren 1986), six months (Crathorne et al. 1990), and two years (Jackson et al. 2007). Specific contaminants detected in contact waters included organic compounds, such as carcinogenic and emerging contaminants. Sources were identified as resin, hardener, additives, ingredient degradation products, and solvents used for coating application. Certain solvents were assumed to have evaporated during coating cure but were still detected in contact waters. Like CM coatings, the greatest contaminant release occurred shortly after epoxy installation, and impacts decreased over time. Water quality monitoring of EP coatings in the field and studied in laboratories showed elevated aqueous TOC and COD concentrations (A. Bruchet, personal communication, October 2010; Heim and Dietrich 2007; Jackson et al. 2007; Modayil et al. 2002; Bae et al. 2002; Romero et al. 2002; Rigal and Danjou 1999; Crathorne et al. 1990; Alben et al. 1989; Crathorne and Warren 1986; Satchwill 2002). Notably, Bae et al. (2002) found that organic chemical release from three brands of drinking-water-approved epoxy were not similar. In another study, toluene was detected in contact water and originated from equipment cleaning before use, not the coating itself (Modayil et al. 2002). Extended curing time has been found to reduce contaminant release (Alben et al. 1989), whereas greater water temperature facilitated contaminant release (Bae et al. 2002).

Polyurethane and Polyurea

Only two reports were found that quantified the impact of a PU infrastructure coating on water quality. Both of those studies were conducted in batch, and no reports were found that examined PEUU coatings. In one study, PU produced a consistent 0.2 to 0.7 water pH reduction during the 30-day exposure period at room temperature (Deb et al. 2010). Total organic carbon concentration increased by 0.0010 to 0.0022 $mg/cm^2 \cdot$ day for 1-day exposure

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Table 1. CIPP Related Air, Water, and Soil Contamination Incidents and Reports in the United States, Europe, and Canada

Incident date, location	Media	Styrene level	Description of incident or report	Information lacking that inhibits strategic specification development and inspection
Californi (G. DeCou, personal communication, January 13, 2012; W. Alwan, personal communication, 2012)	—	—	Following new CIPP specifications by VDOT, CALTRANS developed similar specifications. The California Regional Water Quality Control Board has since placed a moratorium on CIPP	A CALTRANS investigation is underway to determine risks
Hamilton, Ottawa, Toronto, Canada (Bauer 2012)	Air and water	Not reported	Odors detected kilometers from worksite and within nearby private residences. Actions implemented: 0.04 ppm sewer discharge limit; GAC curing water treatment; ambient temperature and testing required before discharge; exhaust fans used; nearby building occupants notified	Information was provided in platform presentation file; details of release conditions, curing water or discharge water characteristics, and material properties not described; short-term release only considered
New York (Doran 2012)	Air	Not reported	Odors permeated into nearby residences; residents complained and evacuated their homes	Only perspective of reporter; no quantitative data
Ontario, Canada (Sullo 2012)	Water	Not reported	Treatment processes at two wastewater facilities impacted during low flow periods; odors reported near worksites; subsequent installations involved capture and treatment of excess resin, condensate, and process water; 0.072 ppm allowable discharge concentration to waterways	Details of wastewater treatment facility impacts not reported; 0.058 ppm and 35 ppm styrene concentration reported, but location not described; short-term release only considered
Massachusetts (Dayal 2011)	Air	60 to 70 ppm	Fumes caused daycare center evacuation; headaches reported; emergency responders called to site	Styrene level in water not reported; CIPP characteristics and procedures not examined; short–term release only considered
Ottawa, Canada (Ontario Ministry of Transportation, personal communication, Feb. 5, 2011)	—	—	Ministry of Trans. CIPP moratorium because of a fish kill; investigation ongoing and under litigation	Data not published
Minnesota (Marohn 2011a, b, c)	Soil and air	Not reported	5,678 L (1,500 G) of resin spilled and residual left for five months; state-mandated soil testing and cleanup; odor caused building evacuations; 12.2 m (40 ft) × 30.5 m (100 ft) × 0.32 m (1.25 ft) contaminated area of soil	Detailed test results were not provided, only an event summary
Michigan (Banovic 2011)	Air	Not reported	Hazardous materials response team (HAZMAT) responded; odors from nearby operation entered school ventilation system; building evacuated; children transported to hospital for chemical exposure symptoms	Only perspective of reporter, interviews with emergency responders; no quantitative information provided
Massachusetts (Tempesta 2011)	Air	Not reported	Firefighters ordered evacuation of elementary school because of strong odor; dizzy and light-headed symptoms reported	Only perspective of reporter, interviews with emergency responders; no quantitative information provided
Pennsylvania (Hayes and Biedka 2011)	Air	Not tested	Elementary and high school students were evacuated for fear of gas leak; odors from nearby CIPP operation were the cause	Only perspective of reporter, interviews with sanitation authority; no quantitative information provided
Montana (Banks 2010)	Air	Not reported	Fire department evacuated nearby affected building because of complaints of strong odors, nausea, and headaches	Only perspective of reporter, and interviews with emergency responders; no quantitative information provided
Washington [Washington State Department of Ecology (WSDOE) 2010]	Water	Not reported	Citizens discovered creek had odor, saw an oil sheen, resin, white milky water, and dead crayfish. Water flowed through relined pipe during relining the night before; odor remained for at least 14 days following event; state fined contractor	Detailed test results were not provided, only an event summary
Virginia (ARLnow.com 2010)	Air	Not reported	Nearby installation caused odor; fire department responded	Only perspective of reporter and nearby residents; no quantitative information provided
Virginia (Donaldson 2009)	Water	Up to 77 ppm	Seven storm-water sites monitored after installation over 1 year; contaminants detected above fish toxicity levels	Properties of cured CIPP not examined; short-term release only considered

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Table 1. (*Continued.*)

Incident date, location	Media	Styrene level	Description of incident or report	Information lacking that inhibits strategic specification development and inspection
Nevada (Loendorf and Waters 2009)	Water	60 to 70 ppm	Process water treated by GAC; GAC effluent <2 ppm then discharged into a sanitary sewer	Replicates not provided; properties of cured CIPP not examined; short-term release only considered
Florida (Donaldson 2009)	Water	100 ppm	Fish kill because of uncured resin released into a storm-water drain	Data not published
Pennsylvania (WPXI-TV 2009)	Air	Not reported	Firefighters evacuated nearby apartment buildings; initially suspected cyanide gas, but styrene was ultimately detected	Only perspective of reporter and interviews with emergency responders; no quantitative information provided
New York (M. O'Reilly, New York State Department of Transportation, personal communication, October 28, 2010)	Water	41,110, 120, 130 ppm	Four CIPP installations tested for styrene in curing release water; stricter specifications now required for use at New York State DOT	Data not published
Massachusetts (Moore 2008)	Air	Not tested	Contractor released styrene vapors and discharged to sanitary sewer; utility cease–desist order issued	Air and aqueous levels not monitored; details of installation not described
Virginia (Lee 2008)	Water	Up to 51 ppm	Water sampling of process water during fabric insertion and curing; curing helped reduce styrene aqueous levels	Concentration data not reported; properties of cured CIPP not examined
Bielefeld, Holland (Lee 2008)	Water	Up to 100 ppm	Water sampling during and after curing and flushing; curing helped reduce styrene aqueous levels	Raw data not available; discharged styrene level unknown; concentration variability not reported; cured CIPP not examined
California (Henry 2008)	Water	Not tested	Suspected wastewater treatment facility sludge settling and UV disinfection harmed by process water that was discharged into the sanitary sewer	No water sampling conducted; properties of cured CIPP not examined; short-term release only considered
Unknown location (Lockheed Martin 2007)	Water	100 ppm	An estimated 11.3 L (3 G) to 15.1 L (4 G) of uncured resin released during a CIPP installation into a storm-water drain; Residual uncured resins were carried to a creek, resulting in the death of more than 5,500 fish of various species. Water sampling at a manhole downstream of the spill showed styrene present	Details of release and follow-up were not provided
Somerset, UK (Wills 2007)	Air	Not tested	Foul styrene odor permeated into residence through drain because of nearby installation	Only perspective of reporter and building residents; no air sampling conducted
New York (Lysiak 2007)	Air	Not tested	Foul styrene odor permeated into buildings through drain because of nearby installations	Only perspective of reporter and building residents; no air sampling conducted
British Columbia, Canada (Gerrits 2007)	Water	2 to 85 ppm	Fish kill because of process water discharged into nearby tributary	Only perspective of reporter who investigated the fish kill; little quantitative information provided
Ottawa, Canada (Bauer and McCartney 2004)	Air	Two sites: 20, 115 ppm	Venting determined to be necessary to prevent air backup into nearby residences/ buildings	Styrene level in water not reported; CIPP not examined; short-term release only considered
Virginia (Gowen 2004)	Air	500 ppm	HAZMAT team responded because of styrene vapor backup into nearby buildings; illness symptoms reported	Only perspective of reporter and building residents; little quantitative information provided
Connecticut [Groundwater and Environmental Services, Inc. (GESI) 2004]	Water and soil	0.596 ppm	Estimated 18.1 kg (40 lbs) to 73.0 kg (161 lbs) of process water and resin released to storm-water pipe and retention pond; water able to be captured was discharged to sanitary sewer; after 12 days, 0.0291 ppm concentration detected; remediation required by state	Actual data not provided in letter to state; delay between incident and sampling inhibits complete understanding of the release; soil sampling recommended by consultant but data not reported
Florida (Saewitz 2001)	Air	Not tested	Styrene odor detected; hospital evacuated; HAZMAT team responded	Only perspective of reporter and building residents; little quantitative information provided

and by 0.0001 to 0.0009 $mg/cm^2 \cdot day$ at day 15, when TOC sampling was halted. A chlorinated isocyanate compound was also detected, but its concentration was not quantified. The second PU study pertained to the application of a PU coating onto a vinyl-lined potable water pipe to eliminate tetrachloroethylene (PCE) release from the original vinyl lining (Gove et al. 2003). Although PCE leaching was reduced by the PU coating application, other water quality characteristics were not reported. On the basis of a review

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Table 2. Literature Summary of Contaminants Detected in Coating Contact Waters Not Including Results of the Present Work

Material (number of studies)	Contaminants detected in contact water and their source[a]	Summary
CM (14)	Water pH and alkalinity: hydroxide ions from cement Metals (aluminum, arsenic, barium, beryllium, cadmium, calcium, chromium, iron, lead, manganese, nickel, potassium, selenium, silica, thallium, zinc): minerals and residue from kilns used for cement production Total dissolved solids/hardness: ions from cement	pH, alkalinity, TDS, hardness, and various metals imparted to water
EP (14)	Resins and hardeners: BADGE, BFDGE, bisphenol A, THMD, PTSA Solvents: MEK, MIBK, toluene, benzene, styrene, xylenes Antioxidants, stabilizers, and degradates: benzaldehyde, benzyl alcohol, phthalate, nonylphenol, 4–*tert*–butylphenol	TOC and COD affected by organic compound release; specific VOC and EDC contaminants also released
PU (1)	Water pH: resin reacts with water to form CO_2 2,4–DTBP: antioxidant degradate Chlorophenol isocyanate: resin modifier	The single lab study examined only one PU coating; water pH and TOC were affected
PEUU (0)	No lab or field data available	
PU/PEUU blend (0)	No lab or field data available	

[a]Bisphenol A diglycydyl ether (BADGE); Bisphenol F diglycidyl ether (BFDGE); trimethylhexamethylenediamine (THMD); *p*–toluene sulphonic acid (PTSA), Methyl iso butyl ketone (MIBK); Methyl ethyl ketone (MEK); 2,4–Di–*tert*–butylphenol (DTBP); Total dissolved solids (TDS); Volatile organic compound (VOC); Endocrine disrupting compounds (EDC).

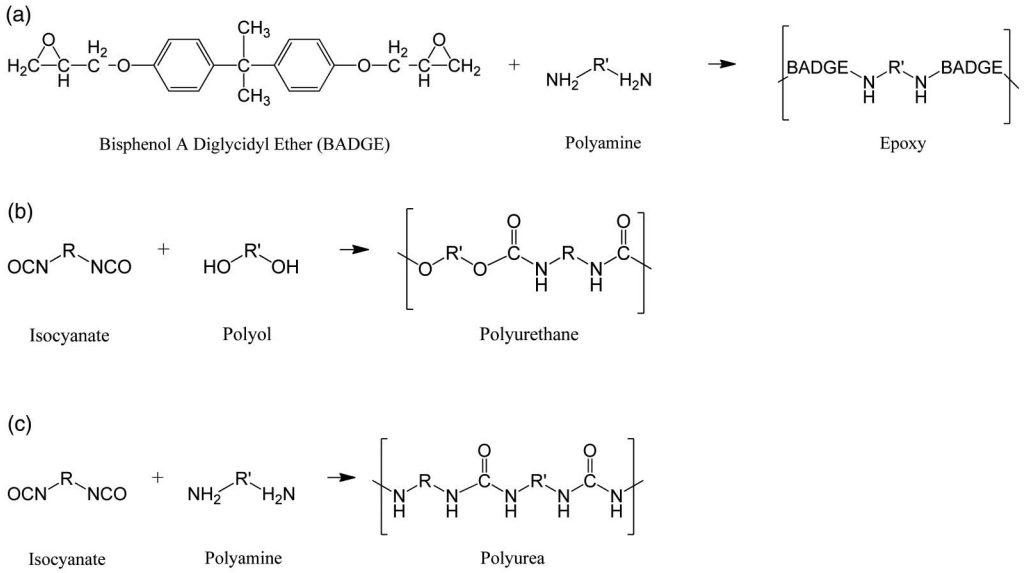

Fig. 1. Synthesis reaction schemes for: (a) epoxy; (b) polyurethane; (c) polyurea coatings

of PU formulation literature (Wicks et al. 2007), organic compounds detected in PU contact water could include resin, hardener (i.e., polyols), binders, and ingredient degradation products. No water contact data were found for PEUU coatings. Like PU, PEUU is also synthesized with isocyanate resin, but the formulation includes polyamine hardener instead of a polyol. Similar water quality impact phenomena are expected for PEUU.

Although not described by published leaching studies, a water pH reduction can be attributed to reaction between isocyanate resin and water (Fig. 2) (Yakabe et al. 1999; Heimbach et al. 1996; Gilbert 1988; Brochhagen and Grieveson 1984; Saunders and Frisch 1962; Shkapenko et al. 1960). Isocyanate resins quickly hydrolyze and form carbamic acid intermediates, which quickly decompose to diamines and evolve CO_2 (Sterner 2010; Hegarty et al. 1975). For example, the half–life of phenyl isocyanate resin in water was approximately 20 seconds (Castro et al. 1985). Heimbach et al. (1996) found that isocyanate resin dosing to artificial ponds caused significant water pH reductions (pH 9 to 6.5) as well as macrophyte and phytoplankton growth for three months and resulted in elevated DO levels. The specific reasons for increased microbiological growth were not explained. Hardened PEUU polymer was also found on top of the sediment and was suspected to be caused by the reaction of isocyanate resin and water (Fig. 2). Because of this hardened PEUU layer, the investigators suspected that certain macrobenthic organism populations were reduced because of "physical obstruction by the PEUU layer, lack of oxygen, and elevated carbon dioxide concentrations" (Heimbach et al. 1996).

Experimental

Specimens

Polymer enhanced cement mortar and PEUU coating samples were removed 24 h after their installation on metallic storm-water pipes in Virginia in the spring of 2012. Because PEUU is known to fully

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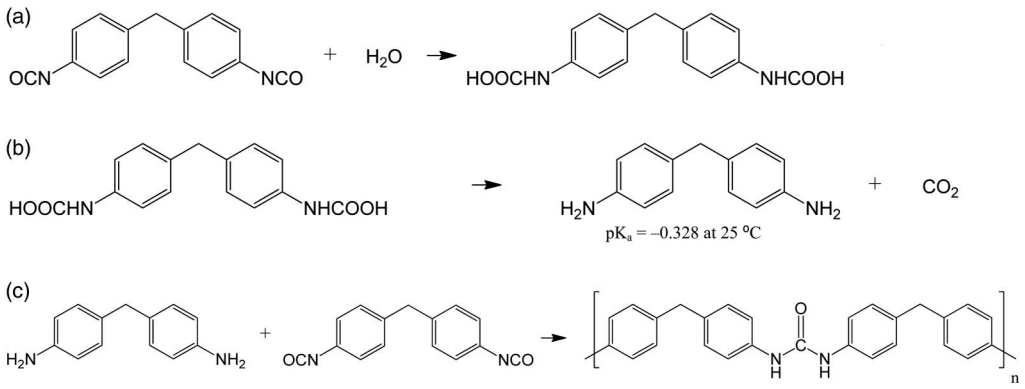

Fig. 2. Reaction schemes for: (a) 4,4′–diphenylmethane diisocyanate and water to form a carbamic acid functionalization; (b) carbamic acid functional group decomposition to form a diamine; (c) diamine reaction with 4,4′–diphenylmethane diisocyanate to form polyurea. The pK_a value was reported by Christensson et al. (1978)

cure within minutes of application, and the PECM manufacturer stated 24 h were required for product curing, specimens exhumed were presumed to be fully cured. These cured materials were not rinsed before or after removal. The nominal specimen surface area was 145.6 cm^2 (PECM) and 920.2 cm^2 (PEUU). Specimens were stored in sealed plastic bags with a damp cloth at 4°C until tested. Samples were damp at the time of testing.

Immersion Testing

Because there is no standardized water quality impact test for stormwater infrastructure rehabilitation materials, and a dynamic approach would introduce many variables (e.g., flow rate, turbulence, surface area), a static closed-system testing procedure was applied. Ten days after specimen removal from the field, samples were immersed in precleaned glass jars, covered with a glass plate (headspace free) that contained synthetic water (pH 7.1) with an alkalinity concentration of 47 mg/L as $CaCO_3$. Immersion testing involved 10 consecutive 3-day static exposure periods (22°C). Contact water was prepared using Type I Millipore water, sodium bicarbonate, and hydrochloric acid. After each 3-day contact period, water was removed and characterized. Triplicate samples were taken and analyzed for each water sampling period. After each 3-day period, newly prepared synthetic water replaced the water in each container. A surface area to water volume ratio (SA/V) of 1.0 cm^2/mL was desired, but the CM sample provided was not in great enough quantity. The SA/V for each test was 0.16 cm^2/mL (PECM), 1.04 cm^2/mL (PEUU), and 0 cm^2/mL (control vessel).

Water Quality Characterization

Analyses were carried out according to approved standard methods (SM) [American Public Health Association (APHA) et al. 2000]. Water pH was analyzed using a research-grade accumet AB15 pH meter (Fisher Scientific; Pittsburgh, Pennsylvania) according to SM 4500 − H^+. Alkalinity concentration was measured by end point titration (pH 4.5) using 0.025 N sulfuric acid according to SM 2320B. Turbidity was quantified using a DR 2000 direct reading HACH spectrophotometer (Loveland, Colorado) (Standard Method 2130). A HACH DR 5000™ UV–VIS spectrophotometer was used to characterize ultraviolet (UV) absorption at 254 nm and total nitrogen (TN) concentration (after sample digestion). Total nitrogen was quantified in 2 mL samples after persulfate digestion at 105°C. Nitrogen standards [Ammonia–*p*–Toluenesulfonate (PTSA), Glycine–PTSA, and Nicotinic–PTSA] demonstrated 98–99% recovery. Standard method 5310A was followed to determine aqueous total organic carbon TOC concentration. Total organic carbon calibration standards (0, 2, 4, and 5 μg/L) resulted in calibration curve correlation coefficients of 0.997–0.999. Chemical oxygen demand was quantified according to the U.S. EPA reactor digestion method using 2 mL aliquots (APHA et al. 2000). A 5-day biochemical oxygen demand (BOD_5) was conducted according to SM 5210B for water from the first 3-day exposure period. Biochemical oxygen demand dilution water was seeded with 24 h stabilized primary influent from a local activated sludge wastewater treatment facility. Biochemical oxygen demand samples were created using approximately 20 mL (PEUU) and 160 mL (PECM) of sample water. Total nitrogen and BOD_5 measurements were conducted to gain insight into possible oxygen consumption downstream from rehabilitated pipe attributable to aerobic and nitrification processes.

Statistical Analyses

Mean and standard deviation values were calculated for each water quality characteristic. Results were statistically analyzed using two approaches. A two way analysis of variance was applied to determine if there was a significant variance between contact waters of PECM, PEUU, and the control. The Tukey–Kramer multiple comparison test was carried out using results of each source. The Type I error applied for all statistics was 0.10 for rejection of the null hypothesis. The alternative hypothesis tested for each sampling period was that contact water quality for each material differed from the control solution after the 3-day exposure.

Results and Discussion

Materials

According to the PECM material safety data sheet (MSDS), the material contained highly alkali cement components (pH 12–14), fly ash, aggregate, and ad components were present. Although the MSDS indicated that the coating was crosslinked after curing, the specific "polymer" was not specified. The literature review showed that the incorporation of a polymer into a CM coating was not common. The PEUU material safety data sheet indicated that PEUU was created using a mixture of 4,4′–diphenylmethane diisocyanate (MDI) and a modified isocyanate. The formulation also contained multiple amine-based hardener compounds (polyoxpropylenediamine, diethyltoluenediamine, and unspecified polyamines). The literature review revealed that PEUU coatings are typically created using 50–60% isocyanate resin and 10–40% polyamine hardener by weight.

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Inorganic and Turbidity Contaminants

Experimental results showed that newly installed PECM and PEUU coatings altered water quality in different ways. As expected, PECM coatings consistently increased pH during the 30-day study from approximately 7.1 to 10.1–11.8. The greatest pH increase occurred during the first exposure period, after which the magnitude of pH change decreased gradually (Fig. 3). Polymer-enhanced cement mortar also significantly elevated alkalinity (534.2 ± 91.6 mg/L as $CaCO_3$) for the first 3-day exposure period. Elevations were typically 18–50 mg/L for each remaining contact period. Alkalinity was equivalent to that of the control solution by day 30.

The PEUU coating significantly reduced water pH during eight of the 10 contact periods, and alkalinity was not affected. The greatest water pH reductions occurred during the first two periods, during which pH decreased from 7.1 to 5.9 and 7.5 to 6.5, respectively. For the other periods, pH reductions were 0.02 to 0.37 pH units. Water pH reductions may have resulted as unreacted isocyanate resin reacted with water to form CO_2. Because the primary source of alkalinity was the carbonate system, total carbonate added to the system was also calculated from pH and alkalinity results. As expected, total carbonate of the contact water was relative to water pH reductions. Turbidity levels were only statistically different for the first exposure period: CM (3.0 ± 0.0 NTU), PEUU (2.0 ± 0.0 NTU), control waters (0.7 ± 0.6 NTU). Although statistically different from one another, turbidity differences in water quality are likely insignificant.

Organic Contaminant Release

A limited quantity of organic contaminant leached from PECM during the first two periods as detected by TOC and UV absorbance measurements. The PEUU, however, released organic contaminants during the entire 30-day exposure period. The PEUU coating significantly altered UV_{254} absorbance, as well as COD, TOC, TN, and BOD_5 concentration: COD concentration (98.3 ± 7.6 mg/L), TOC concentration (19.9 ± 0.3 mg/L), and UV_{254} absorbance (0.087 ± 0.003) were greatest during the first exposure period (Fig. 4). Subsequent water contact periods resulted in gradual reductions of COD and TOC concentrations as well as UV_{254} absorbance. Day 21, 24, and 30 samples of PEUU contact water produced COD levels that were not statistically different than those of the control water. Day 27 results were again statistically different; however, TOC and UV_{254} absorbance results imply organic compounds were imparted to water during the entire experiment. This difference between TOC and COD results can be attributed to inherent variability of the COD quantification method applied and the limit of detection for the TOC method. As expected, correlations were observed among COD and TOC concentrations and UV_{254} absorbance (Fig. 5). Correlation coefficients were 0.947 (TOC versus COD), 0.703 (COD versus UV_{254}), and 0.783 (TOC versus UV_{254}). Both UV_{254} absorbance correlations, however, were strongly influenced by day 3 results. More work is needed to determine the applicability of UV_{254} absorbance as a surrogate for evaluating organic contaminant release from PEUU.

Biological Related Contaminants

The BOD_5 concentration of PECM contact water was statistically indistinguishable from the control water. The BOD_5 concentration of PEUU contact water, however, was significantly greater than the control (9.2 ± 0.5 mg/L). Although a significant quantity of contaminant was apparently released by the PEUU coating, most was

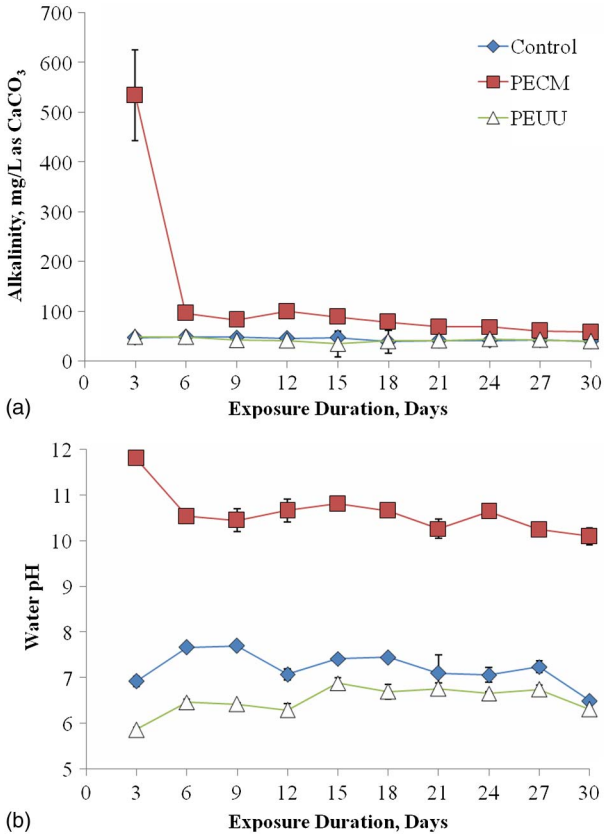

Fig. 3. Impact of polymer-enhanced cement mortar (PECM) and polyurea (PEUU) coatings on: (a) alkalinity concentration; (b) water pH

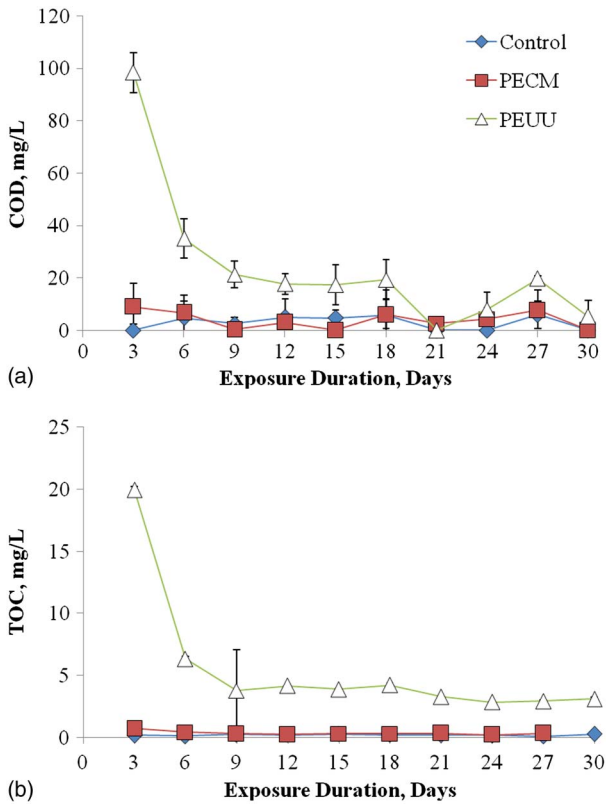

Fig. 4. Influence of polymer-enhanced cement mortar and polyurea coatings on: (a) chemical oxygen demand; (b) total organic carbon concentration

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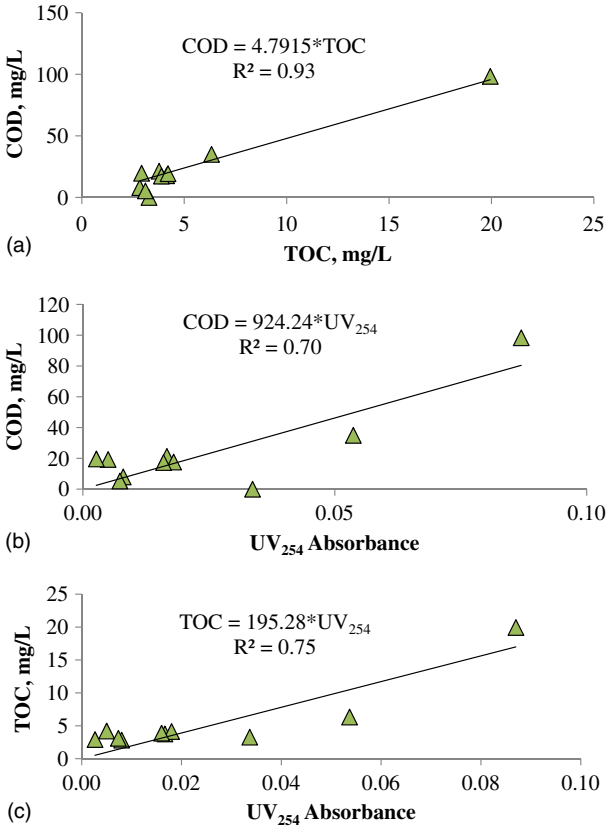

Fig. 5. Relationship between: (a) total organic carbon and chemical oxygen demand; (b) chemical oxygen demand and UV_{254} absorbance; (c) total organic carbon and UV_{254} absorbance characteristics of polyurea coating contact waters

not readily biodegradable, as indicated by the calculated COD/BOD_5 and COD/TOC ratios (COD/BOD_5 = 10.5; COD/TOC = 4.9). The COD/BOD_5 and COD/TOC ratios for municipal wastewater are typically between 1.5 to 4.0 and 2.0 to 3.5, respectively (Henze 2008). Interestingly, Bae et al. (2002) also detected an elevated COD level, and microbial growth in their epoxy coated water tanks was greater than that in their control tank.

The PEUU coating elevated total nitrogen concentration (2.8 ± 0.3 mg/L) for the first exposure period only. PEUU's resin MDI hydrolyzes in water to form compounds such as primary amines and ureas (Yakabe et al. 1999). Because the polyamine hardeners also contained nitrogen, the nitrogen source cannot be identified from the present data. From an environmental fate standpoint however, ureas react with water to form ammonia and bicarbonate ions. Nitrifying organisms utilize ammonia for respiration and consume DO; it is possible that resin hydrolysis will result in low DO events that negatively affect aquatic life. In contrast, polyamines are relatively stable and not readily biodegradable in water.

Contaminant Flux

Results from the present study were converted into contaminant flux (mass/surface area time) values for each exposure period (Table 3). These results were then applied to predict contaminant concentration if 30.5 cm (12 in.) to 91.4 cm (36 in.) interior diameter pipes were coated, filled with water, and exposed for three days (Table 4). Once pipes are installed in the field, new pipes are not typically filled with static water before commissioning. While Table 4 results likely overestimate field contaminant levels, calculated results show that contaminant concentration increased as pipe diameter decreased as a result of the surface area-to-water volume ratio. Therefore, the greatest water-quality impacts would likely be found for small-diameter

Table 3. Contaminant Flux from Polymer-Enhanced Cement Mortar and Polyurea Coatings, 10^{-3} mg/cm^2 · day

	Exposure duration, days[a]									
Water quality characteristic	3	6	9	12	15	18	21	24	27	30
PECM coating										
Alkalinity	983	96.0	70.7	109	85.0	79.1	55.6	55.6	37.0	—
Chemical oxygen demand	—	—	—	—	—	—	—	—	—	—
Total organic carbon	8.6	6.4	—	—	—	—	—	—	—	—
Total nitrogen	—	—	—	—	—	—	—	—	—	—
PEUU coating										
Alkalinity	—	—	—	—	—	—	—	—	—	—
Chemical oxygen demand	94.6	33.7	20.5	17.0	16.7	18.6	—	—	18.9	—
Total organic carbon	6.4	2.0	1.2	1.3	1.3	1.4	1.1	0.9	0.9	1.0
Total nitrogen	2.7	—	—	—	—	—	—	—	—	—

[a]Results were calculated using mean values; dashes indicate that the water quality value was not statistically different from control water.

Table 4. Estimated Aqueous Contaminant Levels for Contact with Newly Installed Polymer-Enhanced Cement Mortar and Polyurea Coated Pipes for a Single Static 3-Day Exposure Period

	Material and contaminant concentration, mg/L[a]				
	Polymer-enhanced cement mortar		Polyurea		
Pipe interior diameter	Total organic carbon	Alkalinity	Chemical oxygen demand	Total organic carbon	Total nitrogen
91.4 cm (36 in.)	621	70,994	6,832	462	195
61.0 cm (24 in.)	860	98,300	9,460	640	270
30.5 cm (12 in.)	1,577	180,217	17,343	1,173	495

[a]Results were calculated by applying experimentally measured data to surface area and water volume calculations for each pipe.

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pipes coated with one of these materials. A dynamic testing protocol that examines coating material water-quality impacts would better estimate contaminant concentrations that occur in the field. Such a protocol could also address standing water scenarios, contaminant dilution away from the pipe wall, and the kinetics of contaminant leaching. Also important is that only one formulation/installation condition for each material was tested in the present study. As Bae et al. (2002) discovered for epoxy drinking water pipe coatings, great differences between contaminant leaching can result from different curing conditions and brands.

Conclusions

Despite incidents of fish kills and environmental contamination caused by CIPP installations, no laboratory or field investigations have documented water quality impacts caused by PECM, EP, PU, PEUU, or PU/PEUU storm-water infrastructure coating materials. Almost all literature reports documented contaminant release from materials that are approved for potable water coatings. Results of the present experimental study appear to be the first documented water quality impacts of storm-water pipe coating materials using a static leaching experiment.

Literature review demonstrates that contaminants released into waters are specific to the ingredients and impurities of each material. Generally, the greatest water quality alterations (e.g., pH, COD, TOC, metals) have been reported for waters that contact new coatings. Those alterations decrease during multiple water contact periods. Cement mortar coatings release inorganic contaminants that increase water pH, alkalinity, hardness, TDS, and metals concentrations. Epoxy and PU coatings primarily release organic contaminants (e.g., COD, TOC, UV_{254}) and include resins, hardeners, additives, and ingredient degradation compounds. The water pH reduction unique to PU is attributable to reaction of its isocyanate resin with water. Prior investigations into the water quality impacts caused by PEUU and PU/PEUU blend coatings were not found in the literature.

Static immersion testing of newly installed PECM and PEUU coatings demonstrated that both materials altered water quality characteristics and that the greatest alterations occurred during the initial exposure period. Polymer-enhanced cement mortar consistently elevated water pH from 7.1 to 10.2–11.8 during all 10 exposure periods. Although PECM also elevated alkalinity concentration during all exposure periods, the greatest increase was detected after the first exposure period (>500 mg/L as $CaCO_3$). Polymer-enhanced cement mortar contained a "polymer" for performance enhancement, and organic contaminants (TOC and UV_{254}) were released during the first two exposure periods only.

During the first two water contact periods, PEUU decreased solution pH by 1.2 and 1.0, respectively, and imparted organic contaminants to the water. Subsequent exposure periods produced similar water quality impacts but of lesser magnitude. Only a fraction of organic contaminants released during the initial exposure period was biodegradable. Nitrogen compounds were released from PEUU during the first exposure period only, but their exact source(s) could not be determined.

This work demonstrates that inorganic and organic contaminants can be released from storm-water infrastructure coatings into waters they contact. Future work is necessary to document water quality alterations caused by materials consisting of different formulations and installation conditions (e.g., curing time, temperature, ingredient mixing ratios). Additional effort should include elucidating short- and long-term aquatic toxicity for rinse waters. Development of a dynamic storm-water coating leaching test would allow infrastructure managers to select low leaching materials and design specifications that limit environmental impacts of rehabilitation operations. For rinse waters suspected to contain elevated levels of contaminants, water collection, testing, and proper disposal is recommended. If water quality testing is considered, knowledge of material ingredients is necessary to effectively select the water quality characteristics to monitor. Results demonstrated that pH, alkalinity, TOC, COD, UV_{254}, BOD_5, and TN analyses were all effective in quantifying contaminant release, but not all characteristics were applicable for both materials.

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