



Research article

Migration of pentachlorophenol and copper from a preservative treated bridge



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ABSTRACT

The potential for migration of pentachlorophenol (PCP) and copper naphthenate (CuNaph) from Douglas-fir was assessed in a bridge over a stream located in Western Oregon in the United States. All rainfall runoff was collected from a portion of the bridge on 15 occasions over a 27 month period and analyzed for pentachlorophenol or copper. PCP and copper were detected at every time point. PCP concentrations ranged from 0.296 to 6.183 $\mu\text{g}/\text{mL}$, while those for copper ranged from 0.37 to 7.80 $\mu\text{g}/\text{mL}$. These data were then used to estimate PCP and Cu inputs in runoff from the entire bridge. Stream flow data were then used to predict the concentrations that would develop in the receiving stream. The results showed that runoff from the bridge would result in PCP and copper concentrations that were 500–1000 times lower than the reported levels of effect for each component. The results are discussed in the context of this location as well as other sites with lower stream flow conditions.

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1. Introduction

Wood is one of the most important renewable structural materials and is used in a variety of applications. One negative wood attribute is a propensity to deteriorate when used in exterior exposures. While the heartwoods of some species have exceptional resistance to deterioration, most woods are susceptible to biodegradation (Zabel and Morrell, 1992). Deterioration can be arrested through impregnation with preservatives; combinations of vacuum and pressure force chemical into wood to create a barrier of protection. Effective wood preservatives have been available since the mid 1800's and there are thousands of facilities globally that treat wood to extend its useful life; reducing pressure to harvest additional trees.

At the same time, all wood preservatives are inherently toxic and virtually all have some degree of water solubility (Lebow, 1996). Water solubility is essential; chemical must be available in water within wood cells for it to be absorbed and kill or inhibit growth of degrading organisms. Solubility also results in migration of preservative into the surrounding environment. For decades

preservative migration from wood was viewed positively because it provided an added area of protection in surrounding soil. Growing concerns about uncontrolled chemical releases into the environment and the risks these chemicals might pose to non-target organisms have fostered a shift in attitudes.

Increased regulations and restrictions on treated wood use, especially in aquatic applications in the U.S. Pacific Northwest (PNW); home to many threatened and endangered salmon species, encouraged the development of models to predict the risk of chemical migration combined with Best Management Practices (BMP's) to reduce the potential for chemical migration (WWPI). These tools allow users and regulators of treated wood to make more informed decisions concerning the use of these materials (Lebow and Tipple, 2001; WWPI, 2012; 2014). While the models draw from results of previous studies, there are relatively few field assessments of chemical migration from preservative treated wood in service and even fewer studies investigating the ability of the BMP's to reduce preservative migration. These data could be used to assess the validity of the models and to more carefully define loss rates for various treatments.

The purpose of this research was to investigate preservative migration from a Douglas-fir bridge in the foothills of the Cascade Mountains in Oregon and to use these data in combination with reported stream flow data to predict the levels of preservative migration into a receiving stream.

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2. Materials and methods

The House Rock Bridge is located on the South Santiam River east of Sweet Home Oregon in the Willamette National Forest. The nearest town (Sweet Home, Oregon) receives an average of 1.375 m of rainfall per year, mostly falling between October and May. The climate is Mediterranean, with mild winters and warm, dry summers. The bridge was constructed with Douglas-fir (*Pseudotsuga menziesii*) decking treated with pentachlorophenol (PCP) to a retention of 9.6 kg/m³ in a petroleum solvent and supported by laminated beams pressure treated with copper naphthenate (CuNaph) in diesel oil to a retention of 1.2 kg/m³ (as Cu). While PCP is not widely used elsewhere in the world, it remains an important industrial preservative in the United States. CuNaph is less commonly used, but has been proposed as a PCP replacement. The materials were treated following the standards of the American Wood Protection Association following recommendations for Best Management Practices (AWPA, 2016; WWPI, 2012). The bridge had already been in place for several months prior to the start of the test, preventing any initial background surveys. However, the construction took place during the drier summer months and the wood was only subjected to a few light rainfalls before monitoring began.

The bridge was too big to sample completely. Instead, a temporary collection system was built below a section of the bridge representing 7.1% of the total surface area. Plastic tarps were attached below the bridge super-structure so that they could capture all rainwater runoff from the desired portion of the bridge. Runoff was funneled into a tared collection container and the total amount was determined by weight gain. This system was easily assembled each time a collection was made. The collected runoff was agitated, then three 300 mL sub-samples were removed for analysis.

Samples for PCP analysis were processed immediately to minimize the risk of sample degradation (Simonsen et al., 2008). Two hundred mL of each sub-sample were transferred to a tared 250 mL glass volumetric flask and weighed to the nearest 0.01 g.

Samples were causticized by adding 2.5 mL of 1 N NaOH to each flask. A Teflon™ stir bar was added and the flasks were stirred for 1 min and allowed to stand for 30 min. This procedure converted PCP to sodium pentachlorophenate. Next 2.5 mL of iso-octane was added and the flasks were stirred for 1 min. The solvent layer was removed from the top and discarded. This step was repeated with another 2.5 mL of iso-octane. The process removed residual oils and other organics from the sample.

Sodium pentachlorophenate was converted back to PCP by adding 3.0 mL 1 N H₂SO₄, stirring for 1 min and allowing the mixture to stand for 30 min. 2.5 mL of iso-octane was added to the flask and stirred for 1 min. The iso-octane layer was removed and transferred to a 20 mL glass vial. The extraction was repeated with an additional 2.5 mL of iso-octane and the two extracts were combined.

PCP was quantified with high resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS). Analysis was carried out by injecting 1 µL of sample into a Shimadzu HRGC-LRMS system class 5000 equipped with an RXI-5ms column (0.25 mm inner diameter by 30-mm long) at a flow rate of 1.0 mL/min. The carrier gas was helium (grade 5) and the system was operated in splitless mode. The injector and detector temperature were 250 and 280 °C, respectively. The oven was programmed to hold for 2 min at 40 °C, ramp to 80 °C at 40 °C/min, then ramp to 260 °C at 25 °C/min. The system was flushed with iso-octane between injections to minimize the risk of carryover.

PCP was scanned and identified using the National Institute of Science and Technology (NIST) Mass Spectral Library #107

software. The retention time was 9.70 min and the selected ion for quantitation was m/z = 266, with reference ions of 264 and 268. HRGC-LRMS auto tuning was performed with perfluorotributylamine (PTFB). An 8 point calibration curve was employed for PCP quantitation. Standard concentrations were 5, 10, 25, 50, 100, 150, 200, and 250 µg/mL. The limit of detection (LOD) of this method was estimated to be 0.025 ng/mL as defined in the Federal Register Part 136, Appendix B, procedure (b), as three times the standard deviation of replicate analyses of the analyte.

Ten mL of the remaining runoff sub-samples were acidified with 0.5 mL of 1 N nitric acid and analyzed for copper (Cu) by ion coupled plasma spectroscopy. These results were used to determine the amount of CuNaph (as Cu) leached.

Migration was assessed 15 times over a 3 year period. Total amounts of PCP and Cu migrating from the bridge to the stream were estimated by measuring the surface area of all bridge components and the surface area from which runoff was collected. Results were extrapolated for the entire structure. The area surrounding the bridge was extremely rocky and this, in combination with the fast water flow, precluded sediment collection beneath or downstream from the structure.

Potential impacts of PCP and/or Cu runoff from the bridge on the receiving river were determined by comparing total runoff from a given precipitation event with nearby stream flow gauges for the same time period. In addition, stream flow data were examined to identify typical low and high flow conditions. Low stream flow conditions were of more interest since they had the greatest potential to result in elevated downstream chemical concentrations. Gauge data were obtained from the closest USGS gauge located about 10 miles downstream (<https://waterwatch.usgs.gov/?m=real&r=or>, accessed 3/27/2017). These data were used to determine the concentration of PCP and/or Cu that could develop downstream and these levels were compared with either regulatory limits or minimum effects levels.

3. Results and discussion

Amounts of water collected varied widely over the 15 collections from a low of 970 mL to over 44,840 mL (Table 1). The bridge is located in the foothills of the Cascade Mountain Range and rainfall is normally steady, but light. Typical total daily precipitation might

Table 1
Concentrations of Cu and pentachlorophenol (PCP) in rain water runoff collected at various times from the House Rock Bridge near Upper Soda, Oregon.

Date collected	Total runoff (L)	Runoff concentration (µg/mL) ^a	
		PCP	Cu
1/9/2014	40.07	6.183 (3.494)	4.27 (0.32)
1/10/2014	20.35	3.264 (0.206)	4.90 (0.26)
3/26/2014	40.6	1.165 (0.004)	3.03 (0.81)
3/27/2014	30.48	1.506 (0.051)	2.00 (0.00)
3/28/2014	36.49	1.362 (0.025)	2.03 (0.06)
11/20/2014	21.62	0.506 (0.009)	2.67 (0.58)
11/21/2014	0.97	0.608 (0.020)	7.80 (0.35)
12/10/2015	40.2	^b	1.40 (0.00)
12/11/2015	40.66	8.728 (0.143)	1.40 (0.00)
12/23/2015	12.09	5.717 (0.036)	0.73 (0.02)
12/8/2016	39.68	0.432 (0.026)	0.37 (0.06)
2/16/2017	44.84	0.296 (0.022)	0.83 (0.06)
3/22/2017	12.58	0.669 (0.001)	0.91 (0.09)
3/23/2017	10.42	0.672 (0.004)	0.97 (0.04)
3/24/2017	39.58	0.681 (0.100)	0.53 (0.03)

^a Values represent means of 3 replicates per time point. Figures in parentheses represent one standard deviation.

^b Samples lost.

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