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Metals leaching from common residential and commercial roofing materials across four years of weathering and implications for environmental loading☆

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A B S T R A C T

Urban stormwater is a major source of chemical pollution to receiving waters. Anthropogenic materials in the built environment can be an important source of chemicals to stormwater runoff. Roofing materials can leach significant amounts of metals, which vary over the life of the roof. We report concentrations of three metals (As, Cu, Zn) leaching into runoff from experimental panels of 14 roofing materials over 4.5 years of weathering. Ten roofing materials leached metals. Several leached >10 ppb during one or more study periods. The most common correlate with metal concentration was panel age, followed by precipitation amount. Extrapolating from these observations, we estimated the loading of metals from each roofing material during the first 10 years following installation. Eight materials were predicted to leach metals above background at the end of the 10 years. In combination with information on the prevalence of different roofing materials in the Puget Sound region of the Pacific Northwest, we estimated the relative amount of metals contributed from roofing materials in this basin. Most arsenic and copper was estimated to be contributed by residential roofing; nearly all arsenic from wood shakes manufactured with copper chromated arsenic, and copper contributed mainly from treated wood shakes followed by copper granule-containing asphalt shingles. Most zinc was estimated to be contributed by commercial roofs, including Zincalume and painted metal roofs. Overall our data shows that roofing materials can be an important long-term source of As, Cu, and Zn to stormwater runoff. Compared with atmospheric deposition, roof materials were a significant source, particularly of As and Cu. To get a complete picture of metals sourced from buildings, there is a need to study whole roof systems, including gutters, downspouts, and HVAC systems, as well as metals contributed from homeowner-applied treatments to their roofs.

1. Introduction

Roofing materials are a source of metal contamination to urban runoff (Good, 1993; Hafera, 2006; Lye, 2009). Roofs are made from a wide variety of materials, some of which are known to leach metals (e.g., copper and galvanized steel roofing), and others about which relatively little is known (e.g. PVC, built-up roofing). Numerous factors affect leaching of metals into runoff, including the roofing material, climate (rainwater pH, rain volume, and intensity), and the physical characteristics of the roof (slope, path length, age).

Of the climatic factors influencing metal concentrations in runoff, rainwater pH is the most influential. As rainwater pH decreases, the solubility of metals increases, as do the metals concentrations in the runoff (He et al., 2001; Bielmyer et al., 2011; Wallinder et al., 2004). In fact, Wicke et al. (2014) found that copper and zinc concentrations from metal roofs increased exponentially as rainfall pH decreased.

Researchers have found an inverse correlation between amount of precipitation and metals concentrations in runoff (He et al., 2001; Wallinder and Leygraf, 1997; Chang and Crowley, 1993; Winters et al., 2015). Various researchers have also reported an inverse relationship between rainfall intensity and metals concentrations in runoff from roofs (He et al., 2001; Jungnickel et al., 2008; Winters et al., 2015). The physical characteristics of slope and path length are associated with residence time of rain on the

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roof, with steeper slopes and shorter path lengths associated with lower concentrations (Wallinder et al., 2000; Arnold, 2005; Bielmyer et al., 2011).

Although metal concentrations in runoff from roofs of various ages have been studied, few have reported the effects of weathering *in situ* over the life-time of the roofing material. Copper concentrations in the runoff from copper roofs declined between 8-year old roofs and 37- and 45-year old roofs (Pennington and Webster-Brown, 2008). A similar pattern was reported for copper roofs aged 11 and 72 years (Boulanger and Nikolaidis, 2003). Lindstrom and WallInder (2011) reported that zinc concentrations in the runoff from galvanized steel diminished over the first two years, however, in an extensive study of zinc roofs in Europe that ranged in age from new to 145 years old. Wallinder et al. (1998) reported that loading was similar regardless of age. Results of these studies verified earlier findings that once a patina (corrosive layer) formed on a metal roof, the metal concentrations in the runoff were in steady-state with the metals in the patina (Wallinder and Leygraf, 1997).

In the Pacific Northwest of the U.S.A., concern about contaminant loading to Puget Sound through runoff has become a major issue. Urban runoff contains a complex mixture of contaminants (Du et al., 2017) that can cause acute toxicity to Pacific salmon (Spromberg et al., 2016; Chow et al., 2019) and other aquatic organisms (McIntyre et al., 2014, 2015). Stormwater runoff is considered one of the largest sources of pollution to Puget Sound and as such metals and other contaminants in stormwater discharges are regulated by the National Pollutant Discharge Elimination System (NPDES). Although the contribution of roofing materials to the pollutants entering Puget Sound is unknown, priority metals such as arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) are well-known contaminants of stormwater runoff (Lye, 2009).

A previous study in the Puget Sound region examined the potential for a wide array of roofing materials (14 types) to leach priority metals into rainwater during storm events (Winters et al., 2015). They found that 10 types of newly installed roofing materials leached significant amounts of As, Cu, and Zn during 20 rain events collected over a period of approximately one year. Seven roof types leached high concentrations (>10 μg/L) of at least one metal into runoff. Of these, four showed a significant decrease in the concentration of at least one metal in runoff over the year. For some of the roof types, metal concentration in runoff was also significantly correlated with precipitation parameters including amount of precipitation, peak rain intensity, and duration of antecedent dry period (Winters et al., 2015).

The current study expands on Winters et al. (2015), sampling eight more rain events over a 13-month period following a weathering interval of 842 days (2.3 years). The objectives of this study were to assess changes in measured concentrations of As, Cu, and Zn in runoff across sampling periods, model the combined effect of roof aging and various rain event parameters on the concentrations of metals leaching into runoff, and finally assess the relative contribution of each of the roofing materials to loading of these metals in the Puget Sound basin, based on weathering patterns and roof types in the region.

2. Methods

2.1. Overview

Metal concentrations were measured in runoff from 14 roofing materials plus control panels located at the Washington State University Research and Extension Center between May 2016 and June 2017. Concentrations in runoff were compared with runoff collected from glass and stainless steel panels to assess whether metal concentrations in runoff represented leaching from the roofing materials rather than simply atmospheric deposition. Concentrations from each material that leached metals into runoff were compared with two earlier sampling rounds during 2013–2014. Regression models were built from metal concentrations in sampled runoff using time and rain parameters to explain variability in the data set. These models were then used to estimate the relative contribution of various roofing materials for loading of metals in the Puget Sound basin.

2.2. Panels and study location

We analyzed stormwater runoff from 17 unique roofing panels (each 1.2 m × 2.4 m), including two glass panels to control for bulk (wet + dry) atmospheric deposition and a stainless-steel panel to assess wet weather deposition. The panels were located in Lacey, WA for Round 1 (Feb–Apr 2013) and Round 2 (Oct 2013–Jan 2014) of the study (Winters et al., 2015) but were re-located 40 km to the WSU Research and Extension Center in Puyallup, WA prior to Round 3 (May 2016–Jun 2017). The roofing materials evaluated represent the main types of roofing materials installed in the Puget Sound basin (Table 1). The stainless steel panel (STS) was added for Round 3 of the study rather than another glass panel because small amounts of lead (Pb) leached from the glass panels during Rounds 1 and 2 of the study (Winters et al., 2015).

All panels faced south-southwest to receive prevailing winds and maximize precipitation collection, with steep-slope (residential) panels angled at 26.5° and low-slope (commercial) panels angled at 1.2° from the horizontal. Runoff from each of the eight sampled events was collected in decontaminated stainless-steel containers by way of dedicated Teflon®-lined gutters. Containers were kept on ice during collection and transport to Analytical Resources Incorporated (Tukwila, WA) where they were filtered (0.45 μm), acidified, and analyzed for dissolved arsenic, cadmium, copper, lead, and zinc by EPA method 200.8 (ICP-MS). Cadmium and lead concentrations were rarely above detection limits (0.04 μg/L, 0.06 μg/L, respectively), so the current study reports only the results for arsenic, copper, and zinc. Non-detected values are reported as a concentration of one half the method detection limit (MDL). Field parameters collected included rain gauge data, pH, specific conductance, temperature, and volume of runoff collected.

This analysis defines leaching from a roofing panel as a metal concentration in runoff that was significantly higher than that from the glass control. Atmospheric deposition on the glass control panels did not differ significantly between Round 2 conducted in Lacey, Washington and Round 3 conducted in Puyallup, Washington. All statistical analyses were conducted using the software program SPSS v. 25 (IBM Corp).

2.3. Atmospheric deposition

Linear regression was used to test whether slope affected atmospheric deposition of metals that became dissolved in runoff. For the eight events in Round 3, metal concentrations ($\log_{10}$) in runoff from the steep-slope glass panel (GST) were regressed against those measured in runoff from the low-slope glass panel (GLO). Pairs where both values were less than the MDL were excluded from the analysis. The metals concentrations in the runoff from the two glass panels were highly correlated ($r = 0.953$, $p < 0.001$, $n = 25$) with a slope ($m = 0.902$) and intercept ($b = -0.047$) not significantly different from that of a 1:1 relationship (respectively $t_{m=0} = 15.167$, $p < 0.001$; $t_{b=0} = -0.75$, $p = 0.461$, $F = 230.038$, $p < 0.001$). Therefore, slope of the glass panels did not affect atmospheric deposition of metals.

Table 1
Roofing materials used in the study.

Roof Slope	Abbreviation	Description
Steep (residential)	AAR	Asphalt shingle with algae resistant granules of copper
	ASA	Asphalt shingle without granules
	CPR	Copper
	CTI	Concrete tile
	PAZ	Painted galvanized steel
	TWO	Treated wood shake (chromated copper arsenate)
	WOS	Wood shingle (untreated)
	GST	Frosted glass (atmospheric deposition control)
	STS	Stainless steel (wet deposition control)
Low (commercial)	BUR	Built-up roof with oxidized asphalt granulated cap sheet
	BUA	BUR with atactic polypropylene granulated cap sheet
	BUS	BUR with styrene butadiene styrene granulated cap sheet
	EPD	Ethylene propylene diene terpolymer (EPDM)
	PVC	Polyvinyl chloride
	TPO	Thermoplastic polyolefin
	ZIN	Zincalume® (a trade name for Galvalume)
	GLO	Frosted glass (atmospheric deposition control)

Runoff concentrations ($\log_{10}$) from the two glass panels (steep slope, low slope) were averaged for each event. These averages were then regressed on concentrations in runoff from the stainless-steel panel in order to compare total atmospheric deposition to wet-only deposition (as measured in the runoff from the stainless-steel panel). Pairs where both values were less than the MDL were excluded from the analysis. The two parameters were again highly correlated ($r = 0.918$, $p < 0.001$, $n = 25$), and not different from a 1:1 relationship ($m = 0.876$, $t_{m=0} = 11.133$, $p < 0.001$; $b = -0.077$, $t_{b=0} = -0.875$, $p = 0.391$, $F = 123.944$, $p < 0.001$). Therefore, dry deposition did not appear to contribute additional metals to runoff above wet-only deposition in the runoff collections in Round 3.

2.4. *Comparing metals in runoff across study rounds*

Total metals were measured during Rounds 1 and 2, but dissolved metals were measured during Round 3. To compare metal concentrations in runoff across Rounds, we had to estimate dissolved metals concentrations for Rounds 1 and 2. During Round 1, dissolved and total metals were measured for three of the 10 sampled rain events (Appendix D in Winters et al., 2014). Average ratios of dissolved to total metals ranged from 0.74 to 1 (Table S1). Coefficients of variation (COV) were 1% to 13%, with a median of 4% (Fig. S1), supporting that the ratios were acceptably consistent across events. A one-way Z-test tested the null hypothesis that the ratios of dissolved to total metal concentration were equal to 1. Average ratios were significantly <1 for three of the 10 metal-roof combinations (Table S1). For the remaining roofs, a ratio of 1 was used (Table S1).

Differences in metals concentrations among the three rounds were assessed for each of the 10 roof-metal combinations using a Kruskall-Wallis non-parametric test for multiple independent samples. Correction of the critical p-value for multiple comparisons was conducted by a modified false discovery rate method (Narum, 2006). For combinations with a significant difference among rounds, post-hoc testing was conducted to determine if differences were between Round 1 and 2, Round 2 and 3, or both. Post-hoc testing used a Mann-Whitney test, again with critical p-value correction for multiple comparisons.

2.5. *Weathering analysis*

Multiple linear regression was used to explore the relative importance of roof panel age and rainfall event parameters on leaching of metals. The dependent variable for each regression was $\log_{10}$ (metal concentration) across all rounds of the study. Parameters tested for inclusion in the model were the natural log of panel age (years since first collection event in Round 1), rainfall amount (RA) in mm, duration of rain (h), rainfall intensity (RI; mm/h when raining), rainfall amount in the 6 h preceding sampling, antecedent dry period (ADP; in days), and average air temperature during runoff collection (T; in °C). Despite the importance of pH to metal leaching, pH of rainfall was not included in the model due to its low variability (coefficient of variability; COV = 8%) relative to the tested parameters (COV = 36−121%). A stepwise selection method was used for parameter inclusion. Because this selection method can inflate the significance level of the associated R^2 value by more than an order of magnitude (Wilkinson and Dallal, 1981), significance for each regression was set at $\alpha = 0.005$ rather than $\alpha = 0.05$. Using the regression models for which age was a significant negative predictor of metal concentration (Table 2), we input median values for other predictor variables from Round 3 (RA = 9.65 mm; ADP = 0.875 d; RI = 1.61 mm/h; T = 7.9 °C; Duration = 15.6 h) to predict the number of years until sampled runoff would no longer leach each metal (i.e. concentration reached median of runoff from the glass panels).

2.6. *Contribution of metals from roofing materials installed in the Puget Sound basin*

Using results from regression modeling and Round 3 sampling, we modeled the mass of metal that would leach from each panel across 10 years under average conditions in the Puget Sound basin. Prevalence in the Puget Sound basin of each of the roofing materials assessed in this study was estimated from a survey of roof types in the Puget Sound basin (Ecology, 2011). Categories comprised of more than one roofing material used in this study were assumed to be comprised equally of the different materials. For example, asphalt shingle comprised 71% of roof area in the Puget Sound basin (Ecology, 2011). We assumed that 50% of asphalt shingle roofs were AAR and 50% were ASA (Table 3).

For each metal-roof combination that leached metals during any round of the study, an average annual concentration of metal in leachate was estimated across 10 years from the time of installation. For 'high leaching' materials (>10 ppb in any round of the study) the average concentration was integrated and averaged from the linear regressions described above. For regressions of high leaching materials that reached background concentrations within 10 years, integration and averaging was for the period of time with values predicted to be greater than background. For 'low' leaching

Table 2
Multiple linear regression statistics and parameters for dissolved metal concentration (log_{10}) in runoff as a function of multiple independent variables for 28 runoff collection events over the 4.5-year study period.

Regression Coefficients											
Roof Panel	Metal	R^2_{adj}	F	p	LnAge	RA	ADP	RI	T	Dur	Intercept
PVC	As	0.950	102.72	<0.001	−0.701[a]	−0.048			0.066	0.018	0.118
EPD	Zn	0.843	49.474	<0.001	−0.446[a]	−0.029	0.088				2.226
TWO	Cu	0.752	28.333	<0.001	−0.293[a]	−0.063				0.023	2.864
TWO	As	0.589	20.363	<0.001	−0.210[a]	−0.034					3.255
AAR	Zn	0.589	38.191	0.001	−0.201[a]						0.670
TWO	Zn	0.428	11.101	<0.001	−0.126[a]	−0.018	0.046				1.018
ZIN	Zn	0.572	13.016	<0.001		−0.072[a]		0.205		0.025	2.090
AAR	Cu	0.282	10.840	0.003		−0.041[a]					1.706
CPR	Cu	0.760	22.418	<0.001		−0.015	0.029	−0.125[a]		0.008	3.475
PAZ	Zn	0.672	19.420	<0.001	0.133[a]	−0.030[a]		−0.088			2.226

LnAge = Natural log of years since first runoff collection.
RA = Rainfall amount during collection (mm).
ADP = antecedent dry period (days).
RI = Rainfall intensity during collection (mm/h).
T = Temperature (°C).
Dur = Duration of runoff collection (h).
[a] Greatest absolute value standardized beta coefficient.

Table 3
Distribution of roof types in Puget Sound watershed and estimated contribution of each roofing material to loading of arsenic, copper, and zinc from roof materials. Bold study roofing material – metal combinations are those that leached >10 ppb during a round of the study. Missing values (–) did not significantly leach the listed metal.

Roof Type	% in Puget Sound[a]	Study Roofing Material	Leached over 10 Years (g)			Estimated % in Puget Sound	% Contribution		
			As	Cu	Zn		As	Cu	Zn
Asphalt shingle	71								
		AAR	0.001	**0.399**	**0.016**	35.5	0.1	24.9	2.9
		ASA	–	0.003	–	35.5	–	0.2	–
Built-up	13								
		BUA	–	–	–	4.3	–	–	–
		BUR	–	–	–	4.3	–	–	–
		BUS	–	–	–	4.3	–	–	–
Wood shingle	6.5								
		TWO	**21.121**	**10.149**	**0.069**	3.25	99.9	57.8	1.1
		WOS	<0.001	0.003	–	3.25	<0.1	<0.1	–
Metal	5.3								
		ZIN	–	–	**5.451**	2.65	–	–	73.7
		PAZ	–	–	**1.625**	2.65	–	–	22.0
Concrete tile	2.9	CTI	0.004	0.001	–	2.9	<0.1	<0.1	–
Copper	<1	**CPR**	–	**29.927**	–	<1	–	17.1	–
Clay tile	<1	n.a.	n.a.	n.a.	n.a.	<1	n.a.	n.a.	n.a.
Masonite	<1	n.a.	n.a.	n.a.	n.a.	<1	n.a.	n.a.	n.a.
Other	<1								
		EPD	–	–	**0.448**	0.08	–	–	0.2
		PVC	**0.011**	–	–	0.08	<0.1	–	–
		TPO	–	–	–	0.08	–	–	–

[a] Data from WA Ecology, 2011. Publication No. 11-03-024.

materials (<10 ppb), the average concentration of each metal was simply the median concentration across Round 3 of the study. Average annual metal concentrations from 'low' leaching roofing types were corrected for aerial deposition by subtracting the median concentration on the glass panel (Table S2). The average annual concentration was then multiplied by the volume of rainfall from a panel (accounting for the differences in slope for 'residential' vs 'commercial' roofing materials), in order to estimate the mass of metal released from each roofing type across a 10-year period.

Finally, the estimated mass was weighted by the prevalence of that roofing material in use in the Puget Sound basin to arrive at a % contribution of each roofing type to the metal leaching from roofing materials. For example, the AAR roofing panel leached a median of 0.06 μg/L As during Round 3 (Table S2). Receiving 2619 L of runoff per year, the AAR panel was estimated to release 0.002 g of arsenic across 10 years. Comprising 35.5% of all roofs, AAR was estimated to contribute 0.1% of the arsenic leaching from all roofing materials in the Puget Sound basin (Table 3). We assumed that average annual precipitation was 40 inches (Puyallup, WA; www.usclimatedata.com).

In addition to the equal-weighted distribution for categories containing multiple roofing types, two additional distribution scenarios were explored; a worst-case scenario in which the higher leaching material in the category predominated (90%) and a best-case scenario in which the lower leaching material predominated (10%). Results from these additional scenarios are presented in Table S4. Finally, the basin-wide estimates of the relative amount of As, Cu, and Zn leaching from the roofing materials under each distribution scenario were compared with the amount of each metal expected to run-off from atmospheric deposition alone across the 10-year model period based on the median concentrations on the glass panels during study Round 3.

3. Results

3.1. Round 3 metal concentrations in runoff

The results of the current study round (Round 3) were similar to those of the previous two rounds published in Winters et al. (2015). Ten of the 14 roof materials leached at least one of the three metals into runoff (Table S2), but only five leached metals at a median concentration > 10 ppb (Table S2). These were copper from the AAR and CPR panels, arsenic and copper from the TWO panel, and zinc from the PAZ and ZIN panels. As with the previous rounds, four of the low slope (commercial) roofing panels did not significantly leach metals: the three built-up roofs (BUR, BUA, BUS), and the thermoplastic olefin roof (TPO). More details on the complete results of Round 3 can be accessed via the Washington Stormwater Center's website: http://www.wastormwatercenter.org/(Winters et al., 2018).

3.2. Changes in metals released between study rounds

Changes in metal concentrations in runoff across the 4.5-year study were assessed for roof-metal combinations with a median metal concentration >10 ppb in any of the three study rounds. For the seven roofing materials that met this criterion, 10 roof-metal combinations were identified: arsenic from TWO and PVC, copper from AAR, CPR, and TWO, and zinc from AAR, TWO, EPD, PAZ, and ZIN. Seven of these combinations showed a significant change in concentration between study rounds (Table S3). Post-hoc pairwise comparisons further indicated that metal concentration in runoff decreased between each round of the study only for arsenic from PVC, copper from TWO, and zinc from EPD (Table S3). The remaining roof-metal combinations showed a decrease in concentration between only one of the rounds or showed no change in concentration across rounds (Fig. 1).

3.3. Effects of panel age and rain event parameters on metal concentrations in runoff

Multiple linear regressions were conducted on the 10 metal-roof combinations that leached >10 ppb during a round of the study. Regressions were statistically significant for all of the 10 metal-roof combinations ($p \leq 0.003$; Table 2). Up to five of the evaluated parameters explained 28%–95% of the variability in metal concentrations across the three rounds of the study (Table 2). Roofing panel age and rainfall amount were the most common predictors of metal concentration in runoff; both were included in six of the ten regression models. Less common predictors were antecedent dry period (three models), rain intensity (three models), rain duration (four models), and temperature (arsenic from PVC).

Standardized β coefficients (not shown) allowed us to compare the relative importance of parameters within a model. Age was the most important predictor of metal concentration for the seven models that incorporated age and was the only predictor of zinc in runoff from AAR (Table 2). For most of the models, age was negatively associated with metal concentration, however age was positively associated with Zn in runoff from PAZ. Among the three models that did not incorporate age, the amount of rain that fell during runoff collection was the only significant predictor explaining variability in copper from AAR and was the most important of four predictor variables for zinc in runoff from ZIN. Rain intensity was the most important of four predictor variables for copper from CPR (Table 2).

Of the six regression models for which age was a significant negative predictor of metal concentration, only one metal-roof combination was predicted to stop leaching within the 4.5-year study period (Fig. 2); the model for zinc from AAR predicted that zinc would reach background levels 1.6 years after installation. This was supported by Round 3 results, for which Zn runoff from AAR was not significantly different from background (Table S2). Three of the regression models predicted reaching background in a total of 5.9, 8.2, and 15.0 years, respectively; zinc from EPD, zinc from TWO, and arsenic from PVC. Round 3 sampling concurred with this prediction for zinc from EPD and arsenic from PVC (i.e., median concentrations had not reached background). In contrast, the median concentration of zinc from TWO during Round 3 (5.0 μg/L) was not significantly different than background (3.1 μg/L). The discrepancy between this observation and the regression prediction likely reflects the positive skewing of the data in Round 3 (average = 5.9 μg/L), and also that this regression had the lowest R^2 among the regressions including age and the weakest relationship between age and metal concentration (Table 2). The above regressions predicted reductions to background within- or near-lifetime for those products. In contrast, at the rate of loss observed across the 4.5-year study, regressions for arsenic and copper from TWO predicted that concentrations would remain well above background for >1000 years, well beyond the product lifespan.

3.4. Metals leaching from roofing materials in Puget Sound basin

Across a 10-year period under average conditions, we predicted that 21.121 g of arsenic would leach from the TWO panel and 0.011 g from the PVC panel, with much smaller amounts from the AAR, CTI, and WOS panels (Table 3). The largest amount of copper was predicted to leach from the CPR panel (29.93 g), followed by the TWO panel (10.15 g), and the AAR panel (0.40 g), with again only small amounts (<0.01 g) from the ASA, CTI, and WOS panels. Zinc was predicted to leach 5.5 g from the ZIN panel and 1.6 g from the PAZ panel followed by 0.5 g from the EPD panel and smaller amounts (<0.1 g) from other panels (Table 3).

The amount of metal leaching from the panels did not translate directly into predictions of relative importance of loading in the Puget Sound basin due to differential use of these roofing materials in the region (Table 3). Assuming an equal distribution of roof types in a category, we estimated that nearly 100% of the arsenic (99.9%) leaching from roofing materials in the Puget Sound basin originates from treated wood shingles (TWO). We estimated that copper leaching from roofing materials in Puget Sound is almost entirely (99.9%) from three roofing materials; treated wood shingles (TWO; 57.8%), algae-resistant asphalt shingles (AAR; 24.9%), and copper (CPR; 17.1%). Finally, we estimated that zinc leaching from roofing materials in Puget Sound is almost entirely (95.7%) from two roofing materials; galvanized metal roofing (ZIN; 73.7%) and painted galvanized metal roofing (PAZ; 22.0%), with much smaller contributions from algae-resistant asphalt shingles (AAR; 2.9%) and treated wood shingles (TWO; 1.1%). Compared with atmospheric deposition of metals, roofs were predicted to be a 661-fold higher source of As and a 50-fold higher source of Cu. In contrast, Zn leaching from roofing materials was only 2-fold the amount contributed from atmospheric deposition.

Alternative worst-case or best-case scenarios for distribution of roof types within a category tended to make very little difference in these conclusions (Table S4). In all three scenarios >99% of As leaching from roofing materials was expected to come from the AAR type of asphalt shingles. In the worst-case scenario (90% of asphalt shingles were AAR, 90% of wood shingles were TWO and 90% of metal roofs were ZIN), the only appreciable change was that nearly all of Zn was predicted to be from the ZIN type of metal roof (92%). Under the best-case scenario (10% of asphalt shingles were AAR, 10% of wood shingles were TWO, 10% of metal roofs were ZIN), there was a shift towards Cu leaching predominantly from copper

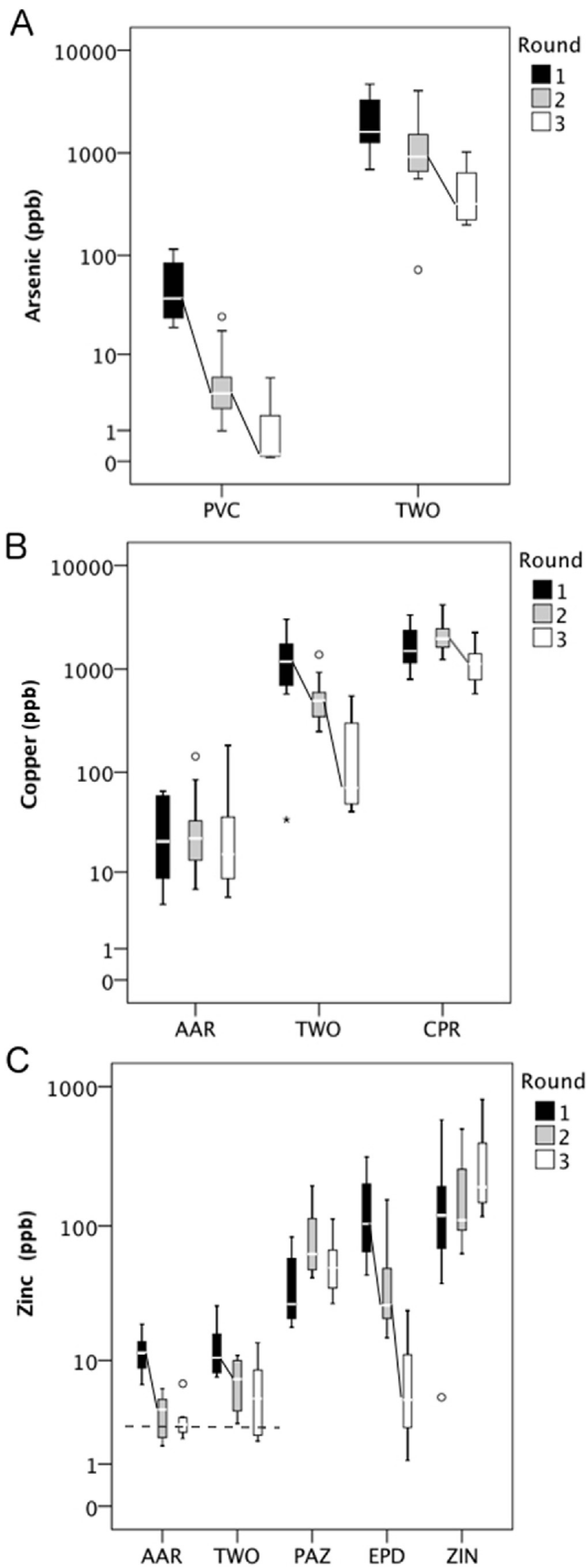

Fig. 1. Metal concentrations for roofs leaching a minimum median concentration of 10 ppb A) arsenic, B) copper, C) zinc during the three rounds of the study. Plots show median (horizontal white bar), 25th and 75th percentile, and range (whiskers). Significant changes between Rounds are indicated by a solid line connecting median values. Dashed horizontal lines cross data for Rounds where data were not significantly different than background. Circles and asterisks represent outliers beyond 1.5 times and 3 times the interquartile range, respectively.

roofs (CPR; from 17% to 50%) instead of from wood or asphalt roofs. Leaching of Zn predicted to be contributed from the two types of metal roofs was strongly affected by the distribution scenario, but the contribution from other roof types changed at most only a few percentage points across the scenarios (Table S4).

Distribution scenario had a strong impact on the relative importance of leaching from roofs compared with atmospheric deposition for As and Cu. The contribution of As from roofs ranged from 132-fold higher than atmospheric deposition under the 'best-case' scenario to 1190-fold under the 'worst-case' scenario. For Cu, contribution from roofs ranged from 17-fold to 83-fold higher than background for best- and worst-case scenarios, respectively. For Zn, the distribution scenario did not have as strong an impact, ranging from 1-fold to 3-fold for the best- and worst-case scenarios, respectively.

4. Discussion

After 4.5 years of *in situ* weathering, ten of the 14 roofing materials in the study still leached at least one metal. These were the same that leached when the materials were new (Winters et al., 2015). Some of the materials that leached zinc at the beginning of the study (AAR, TWO, WOS, PVC) were no longer doing so by the end of Round 3. Other materials leached significantly less over time; including arsenic from PVC and TWO, copper from TWO and CPR, and zinc from AAR, TWO, and EPD. Despite these reductions in leaching, five of the roofing materials (CPR, TWO, ZIN, PAZ, AAR) continued to leach at least one metal at concentrations >10 ppb.

Roofing materials leach metals for different reasons. For roofing materials that are made of (e.g., CPR) or coated in metal (e.g., ZIN), rainwater slowly dissolves metal directly from the material surface. In the current study, concentrations of metals leaching from metal roofing materials into runoff were more or less constant over time. These findings agree with Wallinder and Leygraf (1997) and Lindstrom and Wallinder (2011) who found that once a corrosion layer of oxidized metal (patina) had formed on a metal roof, metal concentrations in runoff remained approximately stable over time.

Metal roofing that is painted leaches less metal than uncoated metal roofing (Clark et al., 2008; Robert-Sainte et al., 2009; Heijerick et al., 2002). This was observed for painted galvanized steel (PAZ) in the current study, which leached Zn (50 ppb) at a much lower concentration than the Zincalume® (ZIN; 193 ppb). However, as the paint or coating is degraded, metal may leach directly from the underlying galvanized surface at a higher concentration. The concentration of zinc in runoff from PAZ was predicted to increase slightly but significantly over time, presumably due to the slow degradation of the painted surface (Fig. 2). A recent field study by the Washington State Department of Ecology similarly measured higher concentrations of dissolved zinc in runoff from older (>10 years) painted metal roofs compared with younger roofs (<5 years) (Ecology, 2019).

Metals are included in some roofing materials as a preservative. For example, algae-resistant asphalt shingles (AAR) incorporate time-release, copper-containing granules to resist the growth of algae that can discolor roofs. The granules are designed by the manufacturer to be slowly dissolved over the life of the product (Jacobs and Thakur, 1997). In fact, we found no reduction in copper concentration in runoff from AAR over the 4.5-year study period, suggesting that the granules were releasing copper at a more or less

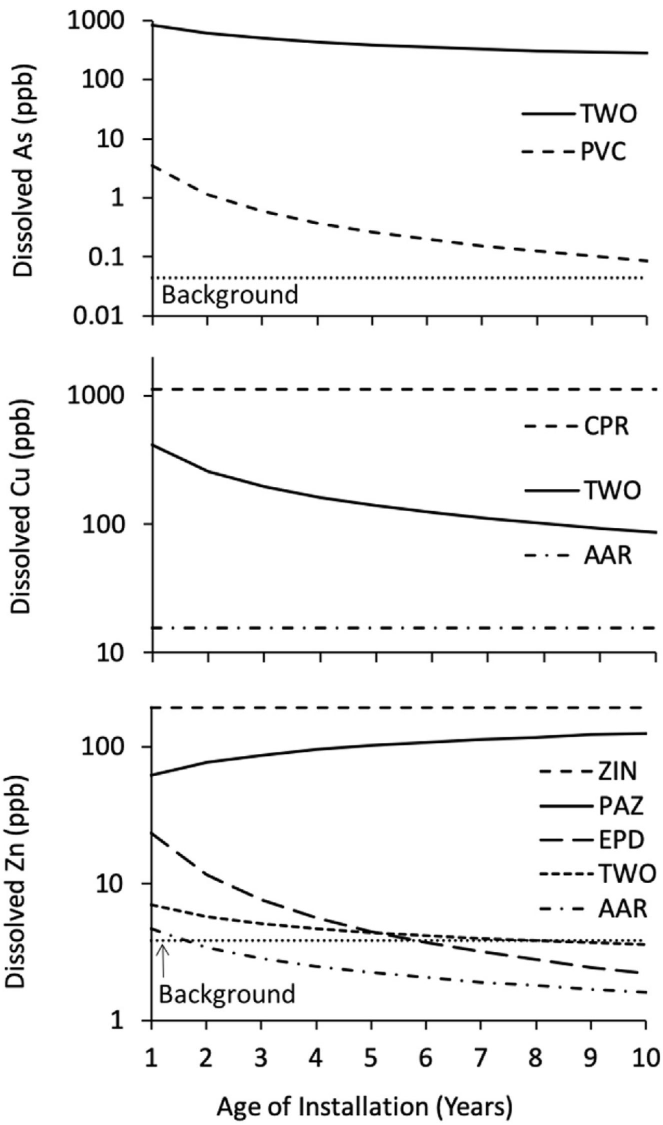

Fig. 2. Average expected concentration of A) arsenic, B) copper, C) zinc in runoff from each roofing material during the first ten years following installation. Background is the median concentration in runoff from glass panels during Round 3 (Table S2). For copper, background was 0.43 ppb.

constant rate, as designed. In contrast, a recent field study surveying AAR roofs of different ages measured a median dissolved copper concentration of 134 ppb in runoff from AAR roofs <5 years old and a median concentration of 6 ppb for AAR roofs more than 10 years old (Ecology, 2019).

Another roofing material in this study with metals incorporated as a preservative was TWO; wood shingles treated with chromated copper arsenate (CCA). Manufacturers voluntarily canceled production of CCA-treated wood for most residential uses in 2003 (US EPA, 2019); however, this may not have extended to materials used on roofs, such as TWO. Although we did find a reduction in both As and Cu released from TWO into runoff over time, the concentration of both arsenic and copper in leachate from TWO was very high (333 ppb and 74 ppb, respectively, during Round 3) and the rate of decline relatively low (Fig. 2). As a result, TWO was expected to continue to leach As and Cu at a high rate for longer (>1000 years) than the likely useful life of the product.

Finally, some roofing materials leach metals unintentionally. This may be due to the use of metals during the manufacture of the material itself, or the metal may be an unexplained contaminant. For example, many synthetic rubber materials leach zinc due to its use as a catalyst during production. Also, PVC may leach arsenic as a result of its presence in 10, 10′-oxybisphenoxyarsine (OBPA) added to PVC as an antimicrobial biostabiliser (Zweifel, 2001). In contrast, zinc leaching from AAR, TWO, PVC, and WOS is not associated with known manufacturing needs. In these unexplained cases, zinc tended to leach at lower concentrations and for shorter durations. For example, the median zinc concentrations (6–11 ppb) leaching from AAR, TWO, WOS, and PVC at the beginning of the study (Winters et al., 2015) had declined to background levels by the end of the current study. In contrast, zinc leaching from EPD and arsenic leaching from PVC had not reached background levels by the end of the current study and were expected to continue leaching for several more years.

4.1. *Recommendations for Puget Sound and beyond*

Based on the relative contributions of the various roofing materials to arsenic, copper, and zinc loading, the current study findings could inform policy changes for the Puget Sound region. In terms of metals released by roofing panels, reduction efforts should focus on limiting the use of metal roofs (especially copper, but also galvanized and zinc alloys) and treated wood shakes. Currently, metal roofing is considered a pollution-generating impervious surface requiring controls under the NPDES, but only on new construction >5000 ft^2. Jurisdictions may consider prohibiting the installation of such roofing materials in order to limit loading of copper and zinc to Puget Sound.

However, these roofing materials are not commonly used in the Puget Sound basin (Ecology, 2011). Asphalt shingles are overwhelmingly the most popular roofing material in the region (approximately 71% by area). Despite releasing an order of magnitude lower copper concentration than treated wood shakes (TWO), algae-resistant asphalt shingles containing copper granules (AAR) are responsible for a substantial release of copper, even under a best-case scenario in which regular asphalt shingles are more prevalent. State regulators may consider working with manufacturers of shingle products such as AAR and TWO to reduce the amount of copper and arsenic included in these materials.

Alternatively, stormwater utilities could consider requiring downspout treatment of runoff from high-leaching roofs prior to discharge to a storm drain. This requirement could be especially considered for new installations of copper roofs, unpainted galvanized metal or zinc alloy metal, and treated wood roofing materials. Stormwater utilities could consider a phased-in approach addressing first those buildings with runoff discharging directly to water bodies. Green infrastructure techniques involving bioretention can significantly reduce the amount of metals in stormwater runoff. For example, dissolved copper in runoff (median = 892 ppb) from a copper roof in Towson, MD was reduced by 94% and 98% by treating the runoff through bioswales and planter boxes, respectively (LaBarre et al., 2016). These stormwater control measures also prevented most acute mortality that otherwise occurred (100%) in tests with aquatic invertebrates (LaBarre et al., 2017).

Results from the current study can be used in fate and transport analyses to understand the contribution of different anthropogenic structures and activities to environmental metals loadings. Monitoring metals in runoff generated by roofing panels in the current study should continue as the panels age in order to optimize modeling the temporal dynamics of metal-generating roofing materials for use in loading studies. This is especially true for loading from TWO which showed no decline in concentrations over the 4.5-

year study period. Further model improvement that could be useful to regulators is incorporation of spatial variability in rainfall and roof type. Results from a spatially-explicit model could be used to focus public education campaigns.

The amount of metal leaching from different roofing materials and the relative importance of those materials to metal loading in a specific basin will depend on the distribution of roofing materials in the basin as well as the climate. Rain intensity and rain amount were important predictors of metal leaching for many materials, particularly metal roofs. Metals would leach more rapidly from those materials in climates with larger annual and more intense precipitation, shifting the relative importance of those materials in a whole-basin analysis of metal pollution.

To better assess metal loading from the built environment, research is needed to understand the amount of metals contributed from entire roofing systems. In addition to the roofing materials themselves, roofs on buildings may contribute metals from flashing, gutters, ventilation and HVAC systems. Such an effort was recently initiated by Ecology (2019). Finally, homeowner applications of metal-containing products for moss reduction to roofing materials such as asphalt and wood shingles need to be considered when assessing the amount of metals leaching from entire roofing systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113262.

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