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Exposure Assessment Framework for Antimicrobial Copper Use in Urbanized Areas

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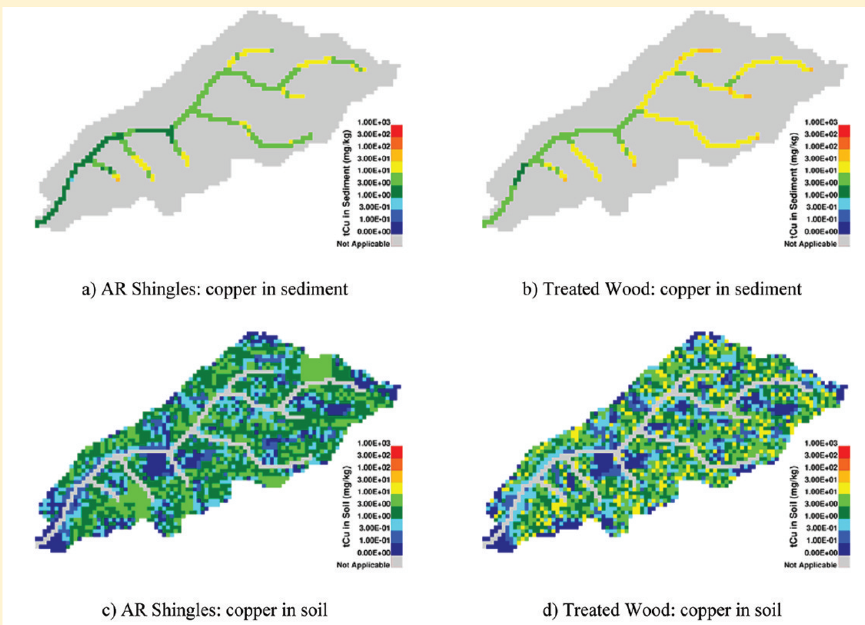
Supporting Information



ABSTRACT: Copper is used as an antimicrobial agent in building materials such as algae-resistant roofing shingles and treated wood products for decks, fences, and utility poles used in urbanized areas. Releases from these materials may pose risks to aquatic and terrestrial organisms. Copper exposures in surface water, sediment, and soil were estimated for a hypothetical urban setting using the TREX watershed model. Drainage and soil characteristics were based on an existing watershed. Urban landscape characteristics were developed from data regarding housing densities and copper use in building materials. This setting provides a spatially distributed, upper-bound assessment scenario. Release rates from algae-resistant shingles and treated wood were defined based on surface area and rainfall. Simulations for the urban landscapes were performed for a 10-year period. Simulation results were used to evaluate exceedences of benchmark concentrations for water, sediment, and soil. For algae-resistant shingles, exposures did not exceed benchmarks in any media. For treated wood, exposures did not exceed sediment and soil benchmarks, and surface water benchmarks were exceeded on 2 days in 10 years. Based on this analysis, copper use as an antimicrobial agent in algae resistant shingles and treated wood is not expected to pose significant adverse environmental risks on an individual use basis.

■ INTRODUCTION

In the United States, copper use as an antimicrobial pesticide is regulated under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The U.S. Environmental Protection

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Agency (USEPA) registers pesticide uses and performs exposure assessments to evaluate risks posed by pesticide uses. Exposure assessments for copper-based pesticides have focused on agricultural settings.[1,2] However, copper use as an antimicrobial pesticide in building materials differs from agricultural uses and requires a spatially detailed assessment approach.

USEPA uses the Pesticide Root Zone Model (PRZM) with the Exposure Analysis Modeling System (EXAMS) to perform exposure assessments.[3] PRZM is a field-scale model that represents the environment as a single spatial compartment and estimates pesticide concentrations in runoff and soil.[4] Similarly, EXAMS is parametrized to represent a constant volume pond as a single compartment and estimate pesticide concentrations in surface water and sediment.[5] Output from PRZM is used as input to EXAMS. USEPA has a series of standard agricultural scenarios to represent different conditions for rainfall, soils, and other factors that affect pesticide transport. These scenarios assume pesticides are uniformly applied over broad areas at a few intervals during the growing season each year.

Copper is also used as an antimicrobial agent in building materials such as algae-resistant (AR) shingles and treated wood. In urbanized areas, these materials are used in roofs, decks, fences, and utility poles and occur in both densely clustered and widely dispersed locations. Antimicrobial copper in these materials is slowly and intermittently released over time from spatially variable sources rather than being uniformly applied and rapidly released at known intervals. USEPA's agricultural models are not well-suited to perform realistic exposure assessments for urban areas where antimicrobial copper is used in building materials because they cannot represent spatially variable, intermittent releases.

To provide a more realistic assessment, estimated exposure concentrations (EECs) of copper released from building materials were determined using the Two-dimensional Runoff, Erosion, and Export (TREX) watershed model[6,7] to perform spatially distributed calculations for a simulated urban landscape. Copper uses as an antimicrobial agent in AR shingles and treated wood were examined. Assessment objectives were to determine whether releases from these specific copper uses are likely to result in concentrations that pose significant, adverse environmental risks in water, sediment, or soil on an individual use basis.

■ MATERIALS AND METHODS

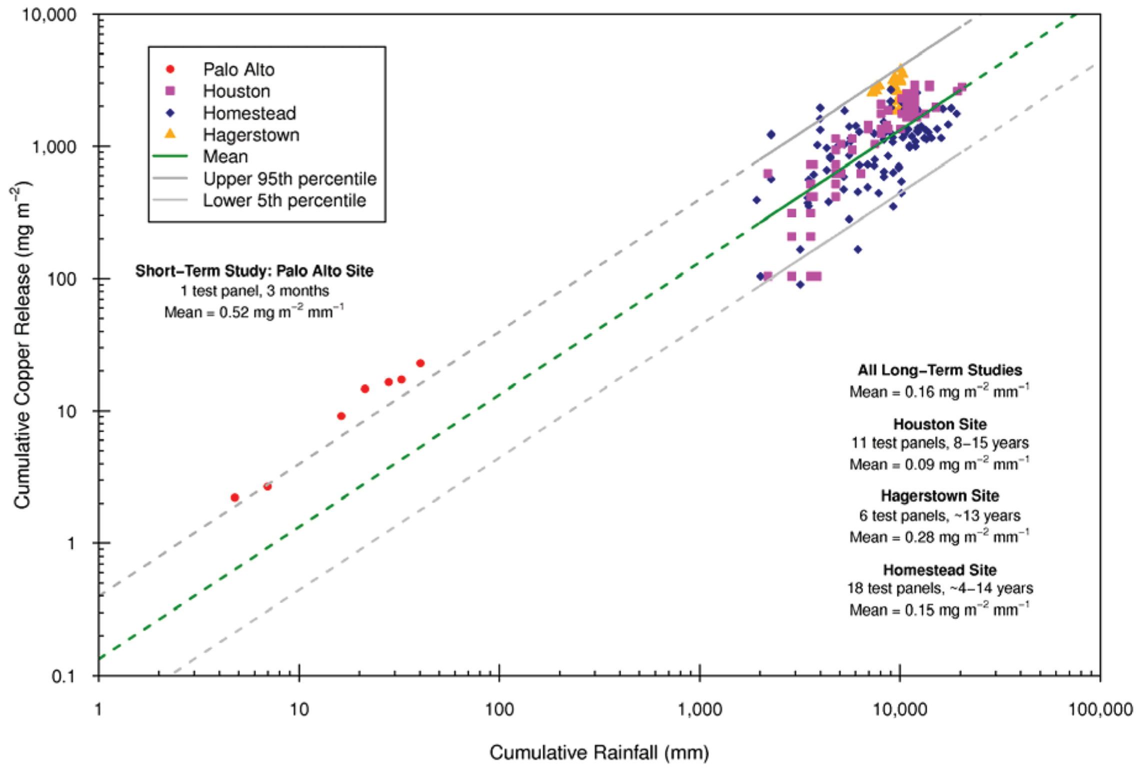
The exposure assessment required: (i) copper release rates from AR shingles and treated wood; (ii) landscape characteristics for copper sources in an urbanized setting; (iii) environmental quality benchmarks for evaluation of EECs; and (iv) watershed model setup and simulation of copper EECs for an urban landscape. Calculated EECs were compared to benchmarks to examine potential for adverse risks in surface water, sediment, and soil on the basis of individual uses. Evaluation of individual pesticide uses is consistent with the approach USEPA uses in its first tier of risk assessment.[1,2]

Copper Release Rates. Copper releases from AR shingles were determined from three independent studies[8,9] (Table 1). One short-term (3 months) study measured copper in runoff from AR shingles during rainfall events for a site near Palo Alto, California.[8] Two long-term (~2 to 15 years) studies measured copper in weathered AR shingles over time for sites near Houston, Texas, and also Homestead, Florida, and Hagerstown, Maryland.[9] Copper losses over time were calculated and normalized to exposed surface area to determine release rates as a function of cumulative rainfall depth (Figure 1). Relationships between copper releases, temperature, and other rainfall characteristics (e.g., intensity, power, kinetic energy, etc.) were explored but did not improve release rate estimates. Although experimental differences precluded complete assessment, short-term release rates were roughly a factor of 3 larger than long-term rates but are not representative of typical conditions. The mass released during the first months of service is small and is roughly equal to the upper 95% of long-term release rates. Also, more than 60% of initial copper remained in shingles after 15 years, so long-term release rates were considered to be a representative upper-bound for rates over the service life of shingles. The AR shingle exposure assessment was performed based on the mean long-term copper release rate of 0.16 mg m^{-2} mm^{-1}. This corresponds to a copper concentration of 160 μg L^{-1} at the shingle surface during rainfall.

Copper releases from intermittently wetted treated wood were determined from field studies[10−15] (Table 1). Most experiments used chromated copper arsenate (CCA) and a smaller number used alkaline copper quaternary (ACQ) or copper azole (CA). Information from manufacturers indicated that these compounds constitute the majority of preservatives used for lumber at the time of this study. Copper losses over time were calculated and normalized to exposed surface area to determine release rates as a function of cumulative rainfall (Figure 2). Rates varied by preservative and wood species.[14,15] Release rates for CCA-treated wood were significantly different than non-CCA-treated wood (ACQ and CA), whereas rates for ACQ and CA were similar. Rate variations with factors such as rainfall intensity and pH[12,13] were less significant than variation by preservative and species. Short-term release rates are a factor of 2−3 larger than long-term rates but are not representative of typical conditions because they only occur during initial months of service.[14,15] Long-term (1−2 year) release rates gradually declined over time and are expected to decline over the service life of wood.[13] Because of these gradual declines, release rates over the first 1−2 years of service are an upper bound for rates for the full service life of treated wood. To further ensure reasonable upper bound conditions, wood in service was assumed to be 80% non-CCA-treated and 20% CCA-treated. The treated wood exposure assessment was performed based on the mean long-term copper release rate of 2.6 mg m^{-2} mm^{-1} for this aggregate mixture of wood. This corresponds to a

Table 1. Summary of Copper Release Rates

application	material	period	release rate	units
roofs	AR shingles	short-term	0.52	mg m^{-2} mm $rain^{-1}$
		long-term	0.16	mg m^{-2} mm $rain^{-1}$
treated wood	CCA-treated wood	short-term	0.36	mg m^{-2} mm $rain^{-1}$
		long-term	0.26	mg m^{-2} mm $rain^{-1}$
	non-CCA-treated wood	short-term	5.7	mg m^{-2} mm $rain^{-1}$
		long-term	3.2	mg m^{-2} mm $rain^{-1}$
	aggregate wood mixture (20% CCA, 80% non-CCA)	short-term	4.6	mg m^{-2} mm $rain^{-1}$
		long-term	2.6	mg m^{-2} mm $rain^{-1}$



Notes: Upper and lower percentiles defined as mean ±1.96 standard deviations of release rates for all long-term sites (Houston, Hagerstown, and Homestead). Extrapolation of mean, upper and lower percentile release rates beyond the range of long-term data are shown as dashed lines. Short-term (Palo Alto) and long-term sites used substantially different sample collection and analytical procedures. Short-term release rates are similar to upper 95th percentile of mean rate for all long-term sites.

Figure 1. Copper release from AR shingles with rain over time.

copper concentration of 2,600 μg L^{-1} at the wood surface during rainfall.

Landscape Characteristics for Copper Sources in an Urbanized Setting. The setting used to simulate antimicrobial copper EECs combines a hypothetical urbanized land use scenario with topographic and soil characteristics of an existent watershed. It was designed to provide a realistic upper-bound scenario for spatial distribution of copper sources in an urbanized area. Use of a hypothetical setting to simulate EECs is analogous to USEPA's approach to evaluate agricultural pesticides.[1,2] The Goodwin Creek watershed (Panola County, Mississippi) was the basis for urbanized setting development (Figure 3). This site was selected because (i) its physical attributes are well-established;[16] (ii) it is in a climatic zone where rainfall and runoff are relatively high;[16,17] and (iii) manufacturer data indicate it is in a region with extensive antimicrobial copper building material use. Land surface elevations and soil characteristics in the setting reflect physical attributes of the existent watershed. Land uses for the setting represent a hypothetical case based on typical housing densities with upper-bounds for copper-treated building material occurrence. A summary of urban setting land use characteristics is presented as Supporting Information (SI) (Table SI-1).

The watershed area is 2066 ha (5104 acres) and includes a network of streams. Land uses for the setting were assigned into residential (1829 ha; 4520 acres), commercial (8.1 ha; 20 acres), government (12.1 ha; 30 acres), educational (9.3 ha; 23 acres), and open space (182.9 ha; 452 acres) categories to mimic development patterns that occur in urban areas. Residential areas included developments at 1, 4, and 8 houses per acre densities as identified by USEPA,[18] yielding 19 583 houses in the setting. Characteristics such as population, size and distribution of open space, and impervious cover, were determined from Census Bureau statistics,[19] urban design guidelines,[20] recreation and park guidelines,[21] and land use ordinances.[22] Impervious surfaces account for approximately 25% of the setting developed area.

Shingled rooftop area per house was estimated as 232.3 m^2 (2500 ft^2) for the 1 and 4 house per acre categories and 176.5 m^2 (1900 ft^2) in the eight house per acre category and were derived from home construction and census statistics.[23,24] In each category, 40% of houses were assumed to have AR shingle roofs based on market share information from manufacturers. Locations of houses with AR shingle roofs were randomly distributed within each residential development and included one 40.5 ha (100 acre) development in each density category where all houses had AR shingle roofs in order to represent reasonable upper bound use conditions. Cumulative rooftop surface area for AR shingles is approximately 1 550 700 m^2 (16 692 000 ft^2).

Exposed areas of wood per deck were assumed to be 17.8 m^2 (192 ft^2) for the 1 and 4 house per acre categories and 11.1 m^2 (120 ft^2) in the eight house per acre category. The average percentage of new homes with decks was 37% in 1992, 25% in 2006, and varied by geographic region.[24] Given this range, and considering homeowners could add a deck after initial construction, 40% of houses were assumed to have a wood deck. Similarly, exposed areas of wood per fence were 292.6 m^2

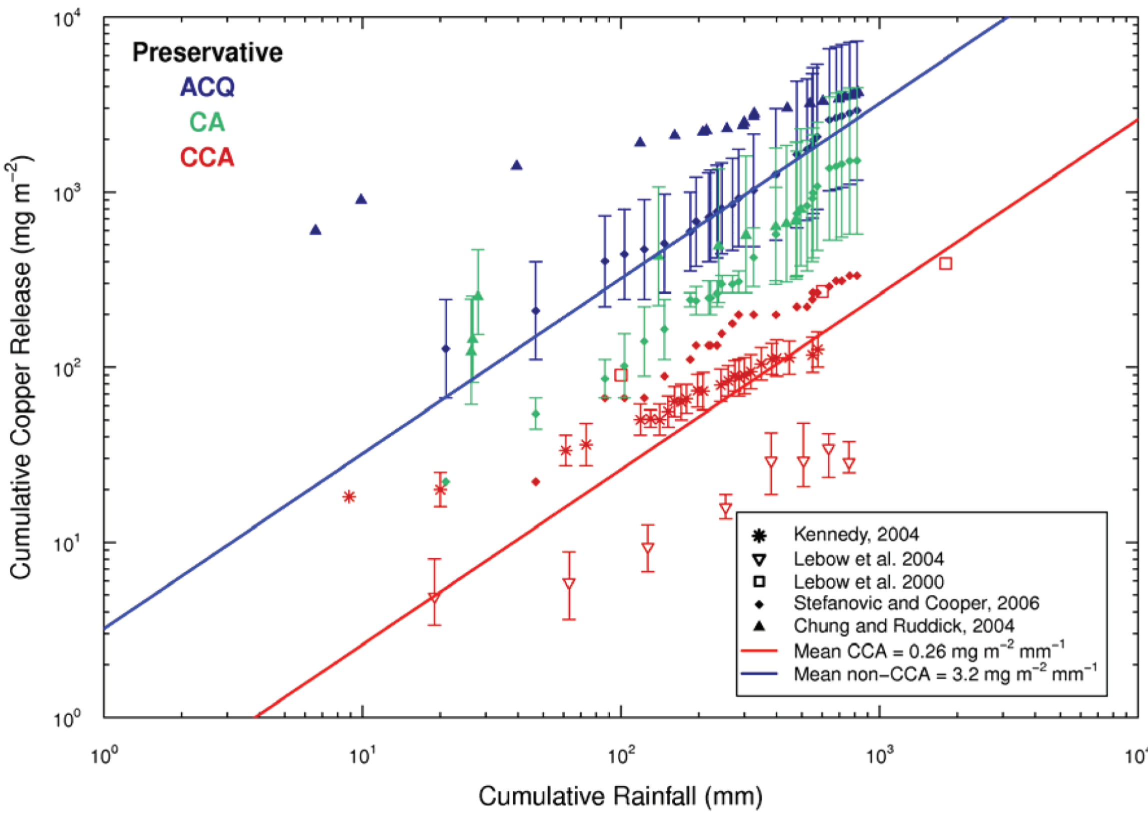


Figure 2. Copper release from treated wood with rain over time (plotted points indicate median values and whiskers indicate the corresponding range).

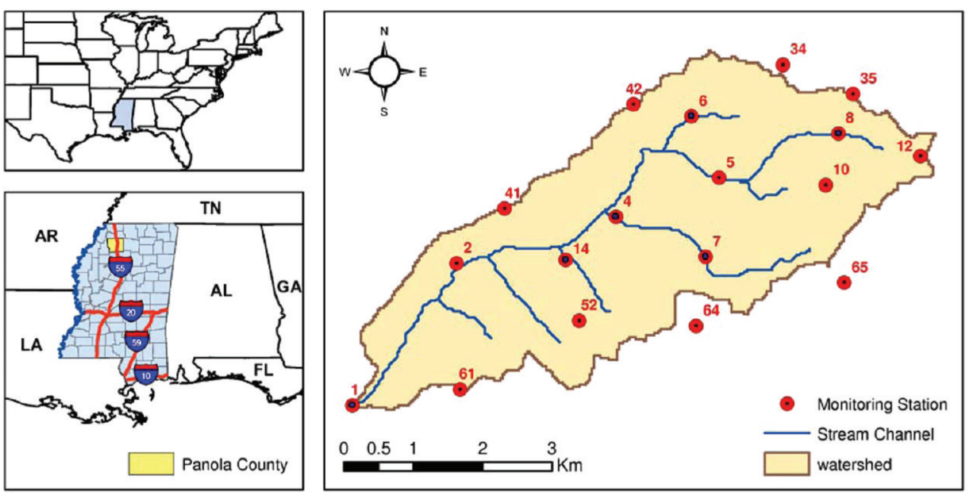


Figure 3. Locations of the State of Mississippi (upper left), Panola County (lower left), and the Goodwin Creek watershed, stream channel network, and monitoring stations.

(3150 ft^2), 146.3 m^2 (1575 ft^2), and 104.5 m^2 (1125 ft^2) for the 1, 4, and 8 house per acre categories, respectively. Statistics regarding houses with fences were not available so the setting assumes 33% of houses have a fence. The U.S. fencing market is 45% wood, 44% metal, 11% other materials.[25] Market share studies indicate that 42% of wood used for fences is copper-treated. Statistics for wood used in decks were not available so the setting assumes all decks are constructed from wood and that 42% of wood used for decks is copper-treated. Combining these factors, 16.8% of houses have a deck constructed of copper-treated wood and 6.3% of houses have a fence constructed of copper-treated wood. Locations of houses with treated wood decks and fences were randomly distributed within each residential development. Cumulative exposed surface areas of houses with copper-treated wood decks or fences are approximately 45 200 m^2 (586 500 ft^2) for decks and 162 700 m^2 (1 750 000 ft^2) for fences.

The exposed area of utility poles was estimated to be 8.76 m^2 (94.2 ft^2) per pole based on dimensions reported in field studies.[26] In urbanized areas with overhead utilities, typical spacing between poles is 30.5−45.7 m (100−150 ft), corresponding to an average of 5.36 poles per ha (2.17 poles

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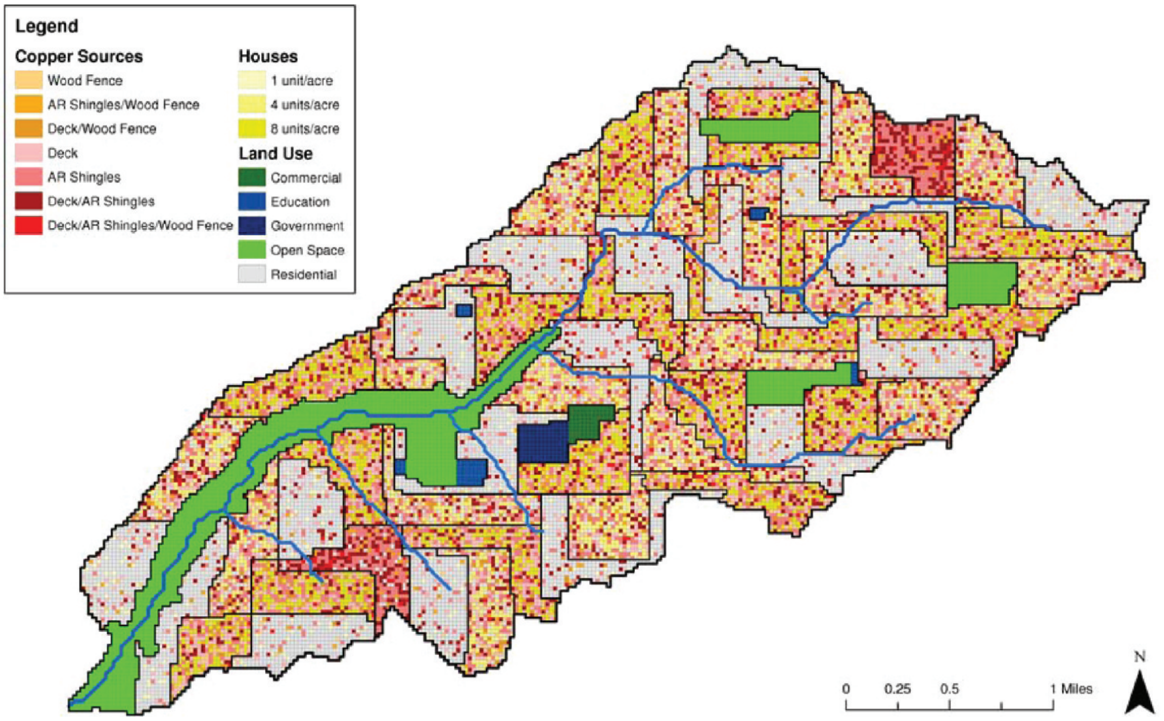


Figure 4. Overall spatial distribution of houses showing combinations of different copper sources: AR shingles, wood decks, and wood fences.

per acre).[26] Utilities in 20−30% of new developments are typically placed underground,[27] reducing the likely number of poles. For simplicity, the setting assumes all poles are wood and are limited to residential areas, with underground utilities in other areas. Information from utilities estimate that 9% of wood utility poles in service were CCA-treated and that 31% of new poles entering service would be CCA-treated.[28] Given this expected shift in preservative use, the setting assumes that 15% of poles are CCA-treated, yielding 1471 CCA-treated utility poles. Locations of CCA-treated utility poles were randomly distributed within each residential development. The cumulative exposed surface area of copper-treated utility poles is approximately 6450 m^2 (69 400 ft^2).

Spatial distributions of antimicrobial copper sources (AR shingle roofs, copper-treated wood deck and fences, and CCA-treated utility poles) in the setting are presented in Figure 4. Different combinations of copper sources occur across the setting. Some houses have every copper source (i.e., roof, deck, fence, and pole), most have one or more sources (e.g., roof and deck, roof and fence, deck only, etc.) and some have no sources. The ability to represent spatial variation is a benefit of this exposure assessment approach. The distribution and density of copper sources for this setting also provides a realistic upper bound for the occurrence of copper-treated building materials in an urbanized area.

Environmental Quality Benchmarks. Benchmarks for water, sediment, and soil were established using bioavailability-based methods. Water quality benchmarks were generated using the biotic ligand model (BLM) for copper[29−31] based on water chemistry data (pH, dissolved organic carbon, calcium, etc.) for six rivers in the region (Tennessee, Arkansas, Mississippi).[32] These rivers span a range of flow conditions and degrees of urbanization (rural to urban). The BLM was used to calculate monthly surface water benchmarks, which ranged from 11 to 34 μg/L. A sediment benchmark was derived using the acid-volatile sulfide (AVS) framework.[33,34] As a conservative estimate, all copper in sediments was assumed to be in excess of AVS (i.e., all copper is bioavailable). Sediments were also assumed to have a 5% organic carbon content, yielding a sediment benchmark of 320 mg/kg. A soil benchmark was estimated from empirical relationships where adverse effects were correlated to soil properties.[35] The most sensitive end point was the 10% effect concentration on barley root elongation and is based on soil cation exchange capacity and organic carbon content. These properties for Goodwin Creek soils were obtained from the Soil Survey Geographic (SSURGO) database,[36] yielding a soil benchmark of 36 mg/kg.

Watershed Model Setup. The TREX watershed model[6,7] was used to perform simulations because of its abilities to simulate chemical transport and represent a diverse landscape with spatially variable inputs. TREX is a physically based, spatially distributed model where runoff and streamflow, solids, and chemicals move between model compartments in response to rainfall based on topography and physical factors such as soil hydraulic conductivity, surface roughness, particle grain size, and chemical partition coefficients. Further detail regarding model formulation is presented as Supporting Information.

The model was operated at a 90 m grid scale and the watershed was simulated with over 2500 compartments ("grid cells") to represent spatially variable landscape conditions. Model setup was performed using a two-step process. The first step was to perform setup for existent (i.e., nonurban) conditions for Goodwin Creek, a densely monitored watershed with a rich database of flow and in-stream solids measurements.[16] Data for this model setup step were obtained from the U.S. Department of Agriculture[16,36] and other literature.[37−39] The model was calibrated to match measured runoff (flow) and suspended solids measurements for three storm events studied by others:[37−39] October 17, 1981; August 28, 1982; and September, 20, 1983. Model results for these three storms are presented as Supporting Information (Figure SI-1). Calibration for existent conditions ensures parameters that control model

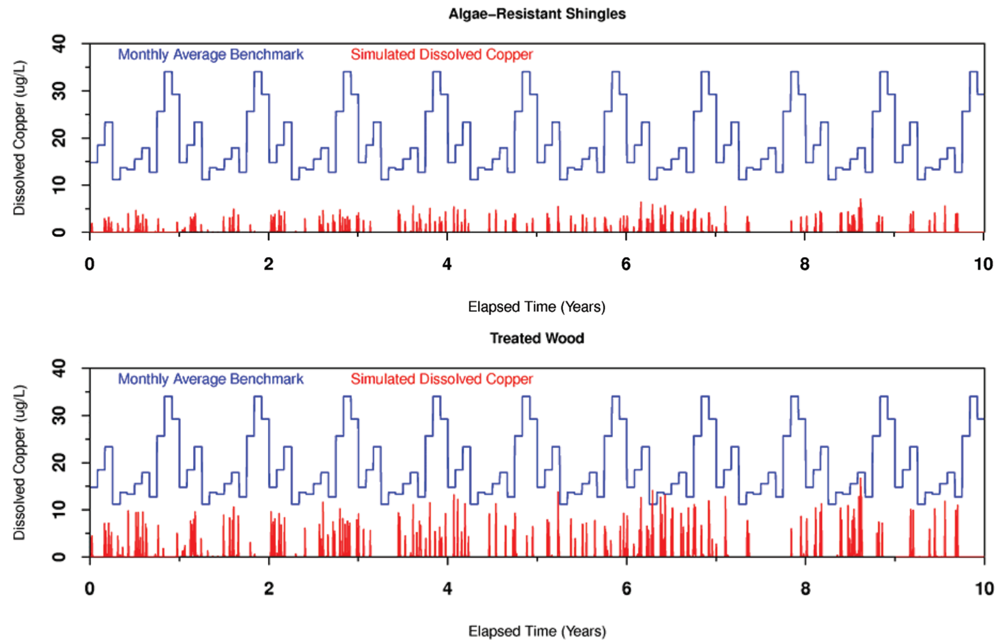


Figure 5. Time series of daily average estimated environmental concentrations of dissolved copper in surface water (μg/L) from algae-resistant shingles (upper panel) and treated wood (lower panel) at the watershed outlet over 10 years of simulation with monthly water quality criteria benchmarks.

Table 2. Summary of Estimated Exposure Concentrations and Benchmark Exceedances for Copper in Surface Water, Sediment, And Soil in the Urbanized Setting[a]

	simulated copper concentration						
media	mean	standard deviation	minimum	maximum	benchmark range	units	benchmark exceedances
AR Shingles							
water	0.25	0.79	0	7.1	11.7−33.7	μg/L	0
sediment	6.7	4.9	1.0	34.5	320	mg/kg	0
soil	1.7	1.5	0	8.8	36	mg/kg	0
Treated Wood							
water	0.58	1.7	0	16.7	11.7−33.7	μg/L	2
sediment	14.1	9.4	2.1	66.8	320	mg/kg	0
soil	3.8	4.9	0	31.8	36	mg/kg	0

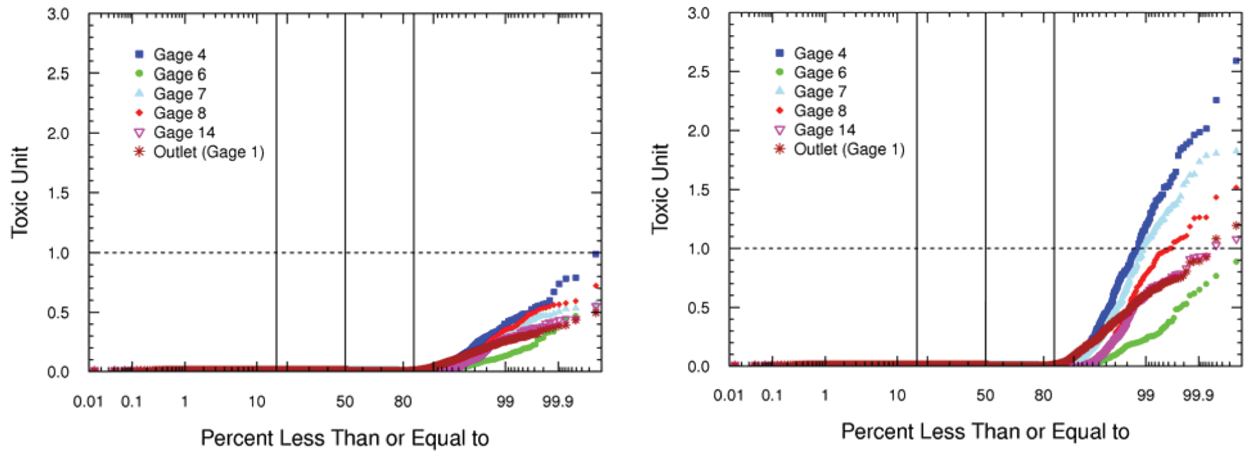
[a]Notes: (1) values for surface water are daily averages over the 10-year simulation period; (2) values for sediment and soil are spatial averages at the end of the 10 year simulation period; (3) exceedances indicates the number of times benchmark concentrations were exceeded; (4) exceedances for water were determined at the watershed outlet.

response are within acceptable ranges and that runoff, erosion, and sediment transport are realistically computed. Parameters calibrated in this manner include terms for infiltration and flow resistance. The second step was to perform setup for hypothetical, urbanized landscape conditions. For this step, the watershed's existent land uses were replaced by spatially variable copper sources and land uses of the urban exposure assessment scenario. Parameters initially determined based on existent watershed conditions were scaled for use with the urbanized landscape according to the fraction of pervious and impervious surface area in each grid cell. As an example of this process, soil infiltration parameters in grid cells without any impervious surfaces retained 100% of their calibrated value while parameters in cells with impervious surfaces were proportionately reduced as impervious area increased.

The watershed model was then used to perform copper transport simulations for the urban setting. Simulated copper concentrations represent exogenous copper from AR shingles and treated wood released by rainfall. A 113-year rainfall record for a weather station near the watershed was reviewed. The 10 year period with the largest annual average rainfall was used for simulations because copper releases are proportional to rainfall. During this period, rainfall averaged 1575 mm/year (62 in./year), well above the long-term average of 1290 mm/year (50.82 in./year). From this period, 772 storms were identified using 15 min rainfall measurements. Simulations for each storm were performed in sequence, with final conditions for the prior storm providing initial concentrations for the next storm in the sequence. Copper EECs in water, sediment, and soil were calculated and compared to environmental quality benchmarks to tabulate exceedances and assess potential for adverse risks on an individual use basis.

■ RESULTS

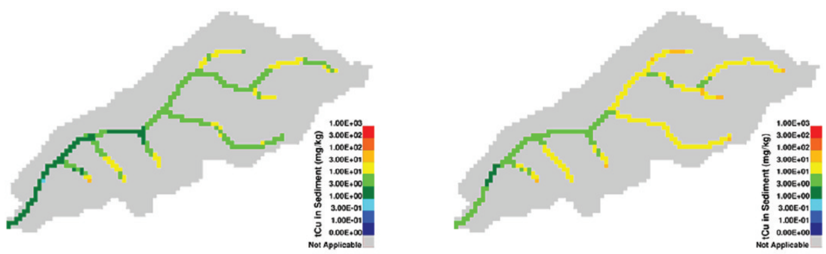
At the watershed outlet, daily averaged surface water EECs for dissolved copper from AR shingles had a mean of 0.25 μg/L, a standard deviation of 0.79 μg/L, and ranged from 0 to 7.06 μg/L. Similarly, daily averaged EECs for dissolved copper from



a) AR Shingles: copper toxic units in surface water

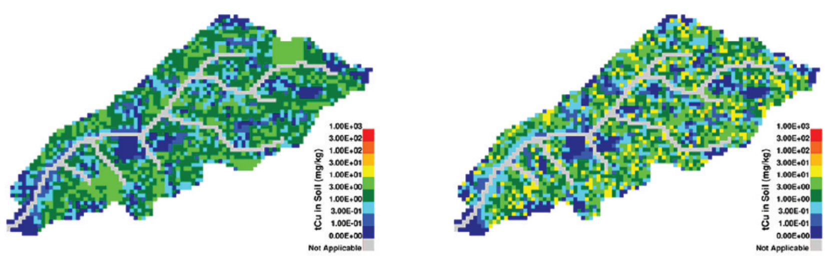
b) Treated Wood: copper toxic units in surface water

Figure 6. Probability distributions of daily average estimated environmental concentrations of dissolved copper in surface water, expressed as toxic units, at the watershed outlet and locations within the stream network. Note: Gage locations are shown in Figure 3.



a) AR Shingles: copper in sediment

b) Treated Wood: copper in sediment



c) AR Shingles: copper in soil

d) Treated Wood: copper in soil

Figure 7. Spatial distributions of estimated environmental concentrations of total copper (tCu) from algae-resistant shingles and treated wood (mg/kg) in surface sediment and soil (0−5 cm) after 10 years of simulation.

treated wood had a mean of 0.58 μg/L, a standard deviation of 1.7 μg/L and ranged from 0 to 16.7 μg/L. Surface water EECs at the watershed outlet and benchmarks used to assess compliance are presented in Figure 5 and summarized in Table 2. EECs for AR shingles did not exceed surface water benchmarks. EECs for treated wood exceeded benchmark values on two days during the 10 year simulation period. Probability distributions of daily averaged surface water EECs at locations throughout the watershed, expressed as toxic units (i.e., concentration divided by its benchmark), are presented in Figure 6. Results for interior locations are generally similar to results for the watershed outlet and typically vary by a factor of ±2 or less.

For the 0−5 cm sediment layer at the end of the 10 year simulation period, EECs for copper from AR shingles averaged 6.7 mg/kg, with a standard deviation of 4.9 mg/kg and a range of 1.0−34.5 mg/kg. Similarly, sediment EECs for copper from treated wood averaged 14.1 mg/kg, with a standard deviation of 9.4 mg/kg and a range of 2.1 to 66.8 mg/kg. Sediment EECs throughout the watershed are presented in Figure 7 (panels a and b) and summarized in Table 2. Spatial variations in sediment EECs reflect differences in proximity to upland copper sources. EECs for AR shingles and treated wood did not exceed sediment benchmark values.

For the 0−5 cm soil layer at the end of the 10-year simulation period, EECs for copper from AR shingles averaged 1.7 mg/kg, with a standard deviation of 1.5 mg/kg and a range of 0−8.8 mg/kg. Similarly, soil EECs for copper from treated wood averaged 3.8 mg/kg, with a standard deviation of 4.9 mg/kg and a range of 0 to 31.8 mg/kg. Soil EECs throughout the watershed are presented in Figure 7 (panels c and d) and summarized in Table 2. Again, spatial variations in soil EECs reflect differences in proximity to copper sources. EECs for AR shingles and treated wood did not exceed soil benchmark values.

■ DISCUSSION

Based on these simulations, copper use as an antimicrobial agent in algae resistant shingles and treated wood is not expected to pose significant environmental risks on an individual use basis. USEPA guidelines[40] indicate that water quality exceedances should not occur more frequently than one day in three years (e.g., 3−4 days in 10 years). Potential risks in surface water were judged to be acceptable on an individual use basis because only two exceedances occurred in 10 years for treated wood and none occurred for AR shingles. Potential risks in sediment and soil were also judged to be acceptable on an individual use basis because no exceedances occurred for either copper use. These inferences regarding potential risks are specific to copper from these individual uses. Higher levels of risk assessment could consider multiple uses (e.g., copper from shingles, wood, and other sources) but would also require more refined exposure assessment.

This urban setting was designed to generate much larger than average EECs because release rates and spatial densities of copper-treated building materials reflect reasonable upper-bound values. Benchmark exceedances were nonetheless rare. Simulated EECs do not exceed benchmarks more frequently because application rates of copper are relatively low. Over the 10-year simulation, copper releases to residential areas were 2980 kg (6570 lbs) for AR shingles and 6590 kg (14 530 lbs) for treated wood. This corresponds to effective application rates of 0.16 kg/ha/year (0.15 lbs/acre/year) for AR shingles and 0.36 kg/ha/year (0.32 lbs/acre/year) for treated wood. In contrast, application rates for agricultural uses of copper-based pesticides range from 1.1 kg/ha/year (1 lb/acre/year) for field crops to 17.9 kg/ha/year (16 lbs/acre/year) for tree fruits and tree nuts.[2] Driven by application rate differences, surface water EECs (0.25 μg/L for AR shingles and 0.58 μg/L for treated wood) should be at the low end of values for agricultural uses (0.4−80 μg/L).[2]

Because the urban setting is a hypothetical construct, simulated EECs were compared to field measurements to evaluate whether model results were reasonable. Dissolved copper at the outlet of a 173 ha (427 acre) agricultural watershed with vineyards regularly treated using copper-based fungicides averaged 40 μg/L and ranged from 10 to 117 μg/L.[41] Effective application rates for that agricultural area were high, 16−24 kg/ha/year (14.3-21.4 lbs/acre/year). Dissolved copper at the outlet of a 46.5 ha (115 acre) urban watershed that received runoff from a sheet copper roof averaged 14 ± 7 μg/L during sixteen storm events[42] and averaged 0.9 μg/L over time (event and nonevent periods) when copper from other sources was excluded. The effective application rate for that urban study was low, 0.19 kg/ha/year (0.17 lb/acre/year). For comparison, surface water EECs calculated using the distributed watershed model averaged 0.25 μg/L and ranged from 0 to 7.1 μg/L for AR shingles and averaged 0.58 μg/L and ranged from 0 to 16.7 μg/L for treated wood. Although comparisons are complicated by differences in copper sources, land use, and other factors, EECs for the urban setting are qualitatively similar to values measured in field studies, with lower concentrations corresponding to smaller copper application rates. This qualitative similarity suggests that simulated surface water EECs are within reasonable bounds.

At broader spatial scales, total copper concentrations in samples from agricultural areas averaged 73 mg/kg (ranging from 18 to 209 mg/kg) in sediment, 31 mg/kg in woodland soils, 30 mg/kg in pasture soils, 139 mg/kg in abandoned vineyards, and 246 mg/kg (ranging from 157 to 434 mg/kg) in active vineyard soils.[41] Although differences in land use, application rates, and other conditions exist, those field measurements are illustrative because they demonstrate spatially variable copper concentration patterns that occur in sediment and soil. The relatively low simulated EECs in sediment (6.7 mg/kg for AR shingles, 14.1 mg/kg for treated wood) and soil (1.7 mg/kg for AR shingles, 3.8 mg/kg for treated wood) of the urban setting are consistent with field measurements, with lower concentrations occurring in the urban setting in rough proportion to differences in copper application rates.

Copper concentrations may also vary over small spatial scales. Total copper in the 0−5 cm soil layer beneath treated wood decks that were in service for 4 months to 15 years averaged 75 mg/kg and decreased to background levels within 15 cm below the soil surface.[43] Similarly, copper in soils near CCA-treated posts that were in service for more than 40 years averaged 225 mg/kg within 2.5 cm of posts, decreased to 30 mg/kg at a distance of 15 cm, and were 1.5 mg/kg at a distance of 30 cm.[44] However, copper accumulation in a wetland downstream of a boardwalk constructed with treated wood did not have measurable biological impacts, consistent with findings that copper mobility is limited under ambient conditions.[45] Sediment and soil EECs calculated using the distributed watershed model are expected to be lower than field values measured at very fine spatial scales because of differences between the scale of measurements (0.1 to 1 m) and the model grid scale (90 m).

Simulations were performed for a 10 year period. It is possible that total copper concentrations in sediment and soil could be larger if a longer period were simulated and copper continued to accumulate. However, even if total copper in sediment and soil were larger, adverse effects may not occur because exchangeable (bioavailable) copper is expected to decrease significantly over time. Copper aging studies demonstrate that exchangeable copper in soils becomes irreversibly bound and decreases by 20% within 30 days, 30% in 6−12 months, and more than 50% after 5−8 years.[46,47] Similarly, only 8% of copper added to soils from vineyards treated with copper fungicides for more than 100 years was desorbable.[48] These studies suggest that 50−90% of total copper in soil or sediment may not be bioavailable.

The approach used for this assessment offers several benefits compared to standard approaches to calculate EECs. TREX can represent spatially variable use patterns for different product types (e.g., shingles, decks, fences, poles) and their temporally variable releases. Structures built from these products can each have a different surface area. Each can be made from a different product and each product can have its own characteristic release rate wherever that product is used and whenever releases occur over time. TREX can also provide exposure estimates for different chemical formulations (e.g., CCA, ACQ, and CA treated wood). This spatially variable approach is useful because it aids development of exposure assessment scenarios that more realistically reflect distributions of chemical sources across the landscape. For conditions simulated, model results suggest that copper use as an antimicrobial agent in AR shingles and treated wood is not expected to pose significant adverse risks on an individual use basis.

■ ASSOCIATED CONTENT

Supporting Information

Information related to urbanized setting development, watershed model operation, calibration results for three storm events under existent conditions, and a tabular summary of urbanized setting land use characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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