Field leaching of alkaline copper quaternary-treated red pine lumber over 3 years: long-term dynamics

Wendong Tao

ABSTRACT

Alkaline copper quaternary (ACQ), a wood preservative, consists of copper oxide and quaternary ammonium compounds. Three red pine piles were monitored over 3 years to evaluate the dynamics of contaminant leaching from ACQ-treated and untreated lumber. There were small temporal changes in the volumetric leachate/rain ratio with the ACQ-treated lumber, while the volumetric ratio decreased across the 3 years with the untreated lumber, most likely due to considerable weathering that increased the capacity of the untreated lumber to absorb rain water. The average copper (Cu) concentration in leachate from the ACQ-treated lumber (4,033 μg/L) was much higher than that in leachate from the untreated lumber (87 μg/L) and rain (48 μg/L) in the first leaching year. Cu concentration in leachate from the ACQ-treated lumber in the second and third years decreased to 46–51% of that in the first year. There were significant seasonal decreases of Cu concentration in leachate from the ACQ-treated lumber, which were correlated to exposure time and meteorological parameters. ACQ-treatment did not affect leachate pH and concentrations of quaternary ammonium compounds and chemical oxygen demand. There were insignificant temporal changes of leachate pH and concentrations of chemical oxygen demand and total dissolved solids in leachate from both ACQ-treated and untreated lumber piles.

Key words | alkaline copper quaternary, leachate, lumber, wood leaching, wood preservative

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INTRODUCTION

Lumber for outdoor use is usually pressure treated with preservatives to retard wood decay. Alkaline copper quaternary (ACQ) has replaced chromated copper arsenate as the major preservative for residential use since 2004 in the USA, partly due to concerns about the environmental hazards of arsenic and chromium leaching out of wood that was treated with chromated copper arsenate. The most common formula of ACQ (type D) consists of 66.7% copper oxide and 33.3% quaternary ammonium compounds (quat) as didecyldimethylammonium chloride (US EPA 2012). Copper (Cu) is the primary biocide of ACQ. Quat allows copper oxide to penetrate into difficult-to-treat species, and provides additional fungicide and insect resistance properties (US EPA 2012). However, recent studies (Hasan *et al.* 2010; Tao *et al.* 2013) have found substantial leaching of Cu by rainfall out of ACQ-treated lumber in outdoor storage, still posing risks to aquatic ecosystems and water use.

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Leachate generation and metal leaching from preservative-treated lumber is influenced by weather conditions, water absorption by wood, and weathering (Taylor & Cooper 2005; Hasan *et al.* 2010; Mercer & Frostick 2012; Tao *et al.* 2013). Tao *et al.* (2013) investigated the relationships of meteorological parameters with leachate generation and contaminant leaching from ACQ-treated lumber. However, Hasan *et al.* (2010) and Tao *et al.* (2013) only reported field leaching of newly ACQ-treated lumber during a leaching period of less than a year, whereas treated wood could be stored and used outdoors for many years. Furthermore, out of service treated wood may be disposed of in open storage sites. There is are no reports on the leaching dynamics of treated wood across longer periods. The objective of this study was to investigate the dynamics of leachate generation and contaminant leaching from ACQ-treated red pine lumber under field conditions over 3 years. This paper provides the timber products sector and environmental authorities with basic information to manage wood leachate and contaminated stormwater.

MATERIALS AND METHODS

Setup of wood leaching piles

Four wood leaching piles were set up on March 6, 2010 in an open area located in Syracuse, New York, USA (Tao *et al.* 2013). Each pile was stacked with new red pine lumber (51 cm long) to 92 cm tall in a rectangular polypropylene tank with interior floor dimensions of 32 cm by 53 cm. The four piles included 12 pieces of large (15 cm × 15 cm) ACQ-treated lumber (L-ACQ), 48 pieces of small (7.6 cm × 7.6 cm) ACQ-treated lumber, 12 pieces of large untreated lumber, and 48 pieces of small untreated lumber, respectively. Starting from March 20, 2011, the present study combined the two sizes of untreated lumber into one (UW), which consisted of six large and twenty four small pieces of untreated lumber as shown in Figure 1. The ACQ-treated red pine lumber was produced for above ground use, which had a preservative retention level of 2.4 kg Cu/m^3 as specified by the Book of Standards (2008). Each pile had a total lumber volume of 0.14 m^3 and a top surface area of 0.16 m^2. When leachate was generated during rainfall events, it was drained freely by gravity into acid-washed polypropylene bottles. An analog rain gauge was set up beside the leaching piles to record rainfall depth and collect rain samples for individual rainfall events. Daily air temperatures recorded at the nearby SUNY ESF Station (NOAA 2013) were collected for the study period.

Leachate sampling and laboratory analysis

During the field experiments from March 6, 2010 to December 5, 2012, there were 75 rainfall events that generated leachate in all the wood piles. Rainfall and leachate volume were measured at the end of each leachate-generating event. Rainfall and leachate samples were collected in 51 events for water quality analysis; the other leachate-generating events were not sampled because of logistical reasons. Concentrations of Cu and quat were measured with a DR 2800 spectrophotometer (Hach Company, Loveland, CO, USA), following US Environmental Protection Agency approved bicinchoninate and direct binary complex methods, respectively (Hach Company 2005). The method detection limit for Cu was 0.01 mg/L, which was reported for undetected samples. Chemical oxygen demand (COD) was determined colorimetrically with the spectrophotometer, following Standard Method 5220-D (*Standard Methods* 1998). Total dissolved solids (TDS) concentration was measured using an HQ40d meter with a CDC401 conductivity probe (Hach Company, Loveland, CO, USA). The pH was measured with a portable pH meter (pH 6 model, Oakton Instruments, Vernon Hills, IL, USA).

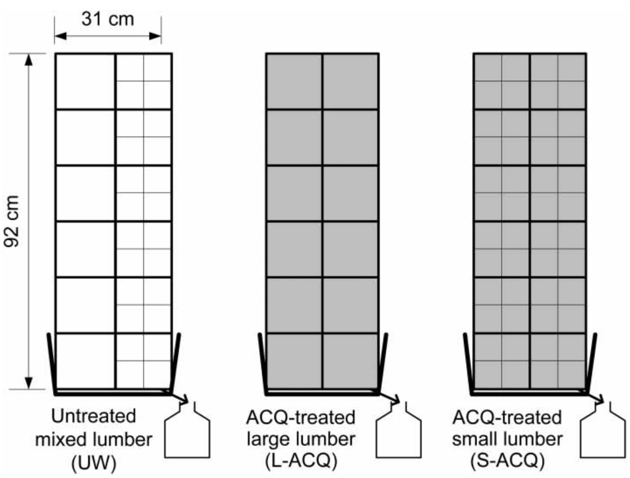

Figure 1 | Field setup of lumber leaching piles.

Data analysis

The results from the large and small untreated lumber piles in 2010 were averaged and treated as the mixed-size UW pile. One-way analysis of variance (ANOVA) was performed to compare the three leaching piles in terms of leachate volume, pH and contaminant concentrations. One-way ANOVA was also used to test the differences between rain and leachate from the untreated lumber pile. Least significant difference (LSD) was calculated to identify the significant differences (Townend 2002). Pearson correlation analysis and multiple linear regression was performed with a forward addition approach to determine whether there were significant changes in leachate volume and contaminant concentrations over time. The significance level (p value) was set at 0.05 for all statistical analyses. There was a strong correlation when a coefficient of determination (R^2) was greater than 0.81.

RESULTS AND DISCUSSION

Syracuse has a humid continental climate, with cold, snowy winters and relatively cool summers. The average temperature during the study period was 12.7 °C in 2010, 15.0 °C in 2011, and 17.0 °C in 2012, with a maximum daily temperature of 35.3 °C and a minimum temperature of −7.5 °C. Leachate is generated when the volume of rain that falls on a pile of wood is in excess of the volume that the wood can absorb

(Tao *et al.* 2013). The leachate-generating events had rainfall depth in the range of 6.1–140.4 mm. Rain water in the lighter rainfall events was completely absorbed into the lumber.

Temporal variation of leachate generation

Figure 2 shows the variations of rainfall depth and leachate volume during the study period. Exposure time (number of days since the setup of the leaching piles) was insignificantly correlated to leachate volume for the ACQ-treated lumber piles ($p = 0.06$–0.65), and significantly correlated to leachate volume for the untreated lumber pile ($p = 0.003$). Leachate volume could be predicted with Equations (1) and (2). The square root transformation of leachate volume produced the greatest R^2 value compared with the other common types of data transformation (Townend 2002). The untreated lumber might have been subjected to considerable weathering and the capacity to absorb rain water increased over time (Tao *et al.* 2005; Aydin & Colakoglu 2007). Consequently, the volumetric ratio of leachate/rain decreased across the 3 years with the untreated lumber pile, while there was little change across the years with the ACQ-treated lumber piles (Figure 3)

$$\sqrt{V} = 0.031D - 0.012T - 0.0003t + 0.82 \text{ for untreated lumber } (p < 0.001, R^2 = 0.88) \quad (1)$$

$$\sqrt{V} = 0.028D - 0.016T + 0.79 \text{ for ACQ-treated lumber } (p < 0.001, R^2 = 0.83) \quad (2)$$

where V is the leachate volume generated during a rainfall event (L); D is the rainfall depth in a leachate-generating event (mm); T is the average air temperature between two consecutive leachate-generating events (°C); and t is the exposure time (d).

The volumetric ratio of leachate/rain was significantly lower with the small ACQ-treated lumber than the large ACQ-treated lumber ($p = 0.001$–0.002, LSD $= 0.10$–0.13) due to the larger surface area of small lumber to absorb rain water (Figure 3). This was consistent with that reported by Tao *et al.* (2013) for 2010.

Temporal variations of contaminant leaching

Lumber size did not make a significant difference in leachate Cu concentration over the study period ($p = 0.28$–0.67). The average Cu concentrations of leachate from the ACQ-treated lumber piles decreased in 2011 and 2012 to 46–51% of that in 2010 (Table 1). Cu concentration in rain and leachate from the untreated lumber pile was constantly low over the study period. It demonstrated a combination of yearly and seasonal changes for leachate from the ACQ-treated lumber piles (Figure 4). The yearly and seasonal decreases in leachate Cu concentration did not always have strong correlations

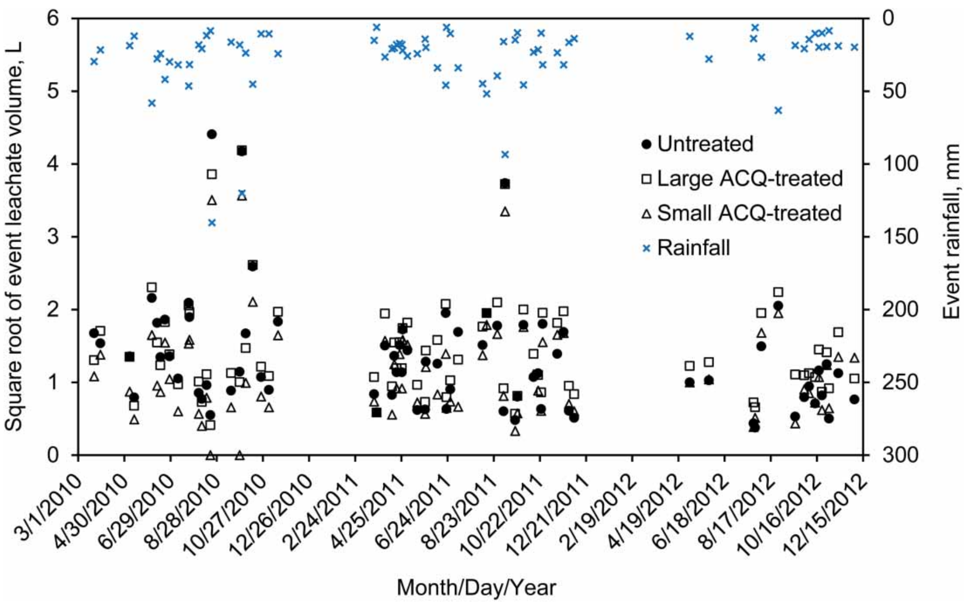

Figure 2 | Temporal variations of rainfall and leachate volume generated in ACQ-treated and untreated red pine lumber piles during individual rainfall events.

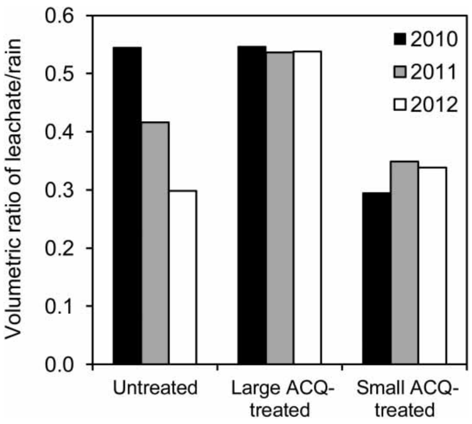

Figure 3 | Yearly variation in volumetric ratio of leachate to rain for ACQ-treated lumber in comparison to untreated lumber.

with exposure time alone ($r = -0.58$ to -0.83). However, the Cu concentrations in leachate from the ACQ-treated lumber piles were strongly correlated with rainfall intensity, the number of days between two consecutive leachate-generating events, rain Cu concentration and pH, and exposure time in 2011 ($p < 0.001$, $R^2 = 0.86$) and 2012 ($p = 0.001$, $R^2 = 0.85$). The seasonal decreases in leachate Cu concentration could be attributed to the rapid leaching of Cu bound to the surface of the treated wood (Jambeck *et al.* 2006) after each snowy season, when little leachate was generated. Copper tends to bind weakly to labile wood cellulose and can be washed out of wood surfaces with fiber and due to UV breakdown of lignin (Lebow *et al.* 2003; Mercer & Frostick 2012).

The quat concentrations were similar in rain (0.83–0.97 mg/L), leachate from the untreated lumber pile (0.82–0.96 mg/L), and leachate from the ACQ-treated lumber piles (0.91–1.19 mg/L) ($p = 0.80$–0.96), indicating little impact of ACQ treatment and exposure time on quat leaching. This was attributed to the recalcitrance of quat and its high affinity to biomass-based materials (Hong *et al.* 2013).

Lumber size did not make significant differences in pH, COD and TDS of leachate from the two ACQ-treated lumber piles ($p = 0.12$–0.82). Leachate from the ACQ-treated lumber piles and the untreated lumber pile had similar pH values, COD concentrations, and TDS concentrations except for a significant TDS difference in 2010. Compared with leachate, rain had significantly lower pH values ($p < 0.001$, LSD = 0.3–0.4), COD concentrations ($p < 0.01$, LSD = 28–91), and TDS concentrations ($p < 0.01$, LSD = 7–8) over the study period (Table 1).

There were slight changes of leachate pH over the 3 years. Leachate COD concentration appeared to decrease over time, especially in the first year, as shown in Figure 5. TDS concentration in leachate from the ACQ-treated lumber piles appeared to be higher in year 2010 in comparison to 2011 and 2012 as shown in Figure 6. The significantly higher TDS concentration in leachate from the ACQ-treated lumber piles in 2010 ($p < 0.001$, LSD = 13) indicated that ACQ treatment not only increased Cu leaching, but leaching of other unidentified constituents from newly

Table 1 | Yearly variations of leachate and rain quality (mean ± standard deviation)

	2010 ($n = 17$)	2011 ($n = 18$)	2012 ($n = 16$)
ACQ-treated lumber			
Cu concentration, μg/L	4,033 ± 1,646	2,039 ± 944	1,838 ± 798
TDS concentration, mg/L	53.8 ± 23.0	39.0 ± 12.3	42.0 ± 11.1
COD concentration, mg/L	310 ± 147	196 ± 69	208 ± 44
pH	5.81 ± 0.62	5.81 ± 0.32	5.85 ± 0.49
Untreated lumber			
Cu concentration, μg/L	87 ± 56	23 ± 36	37 ± 33
TDS concentration, mg/L	34.7 ± 11.2	32.8 ± 14.0	36.8 ± 8.5
COD concentration, mg/L	257 ± 109	185 ± 62	217 ± 47
pH	5.71 ± 0.34	5.71 ± 0.46	5.74 ± 0.55
Rain			
Cu concentration, μg/L	48 ± 52	10 ± 10	37 ± 23
TDS concentration, mg/L	18.3 ± 17.1	13.5 ± 8.4	18.0 ± 8.9
COD concentration, mg/L	131 ± 112	101 ± 83	61 ± 19
pH	5.21 ± 0.98	4.79 ± 0.49	5.00 ± 0.45

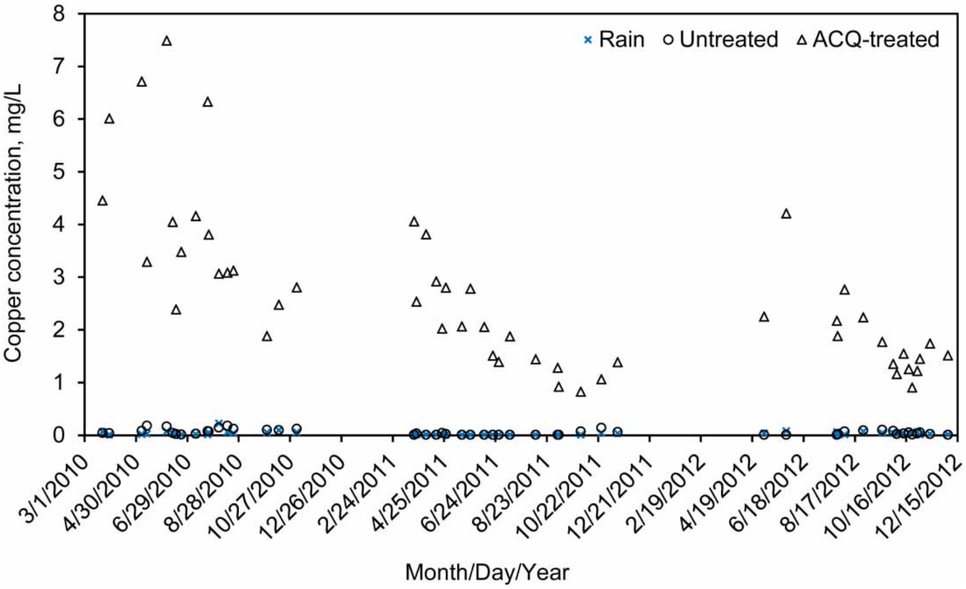

Figure 4 | Dynamics of Cu concentration in leachate and rain.

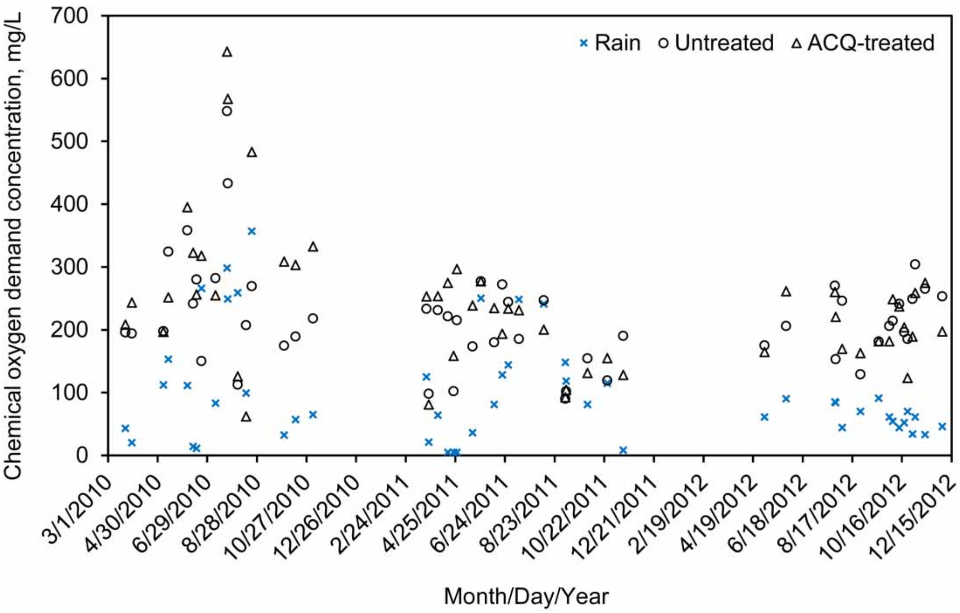

Figure 5 | Dynamics of chemical oxygen demand concentration in leachate from ACQ-treated and untreated red pine lumber piles.

treated lumber (Tao *et al.* 2013). However, there were weak correlations of exposure time with TDS and COD concentrations in leachate from ACQ-treated and untreated lumber piles ($r = -0.67$ to 0.41). The higher TDS and COD concentrations in 2010 were likely due to the wash-out of original surface residues (Tao *et al.* 2013).

Significance of copper leaching from ACQ-treated lumber

The New York State Multi-Sector General Permit Associated with Industrial Activity sets the benchmark monitoring cutoff for wood leachate and contaminated

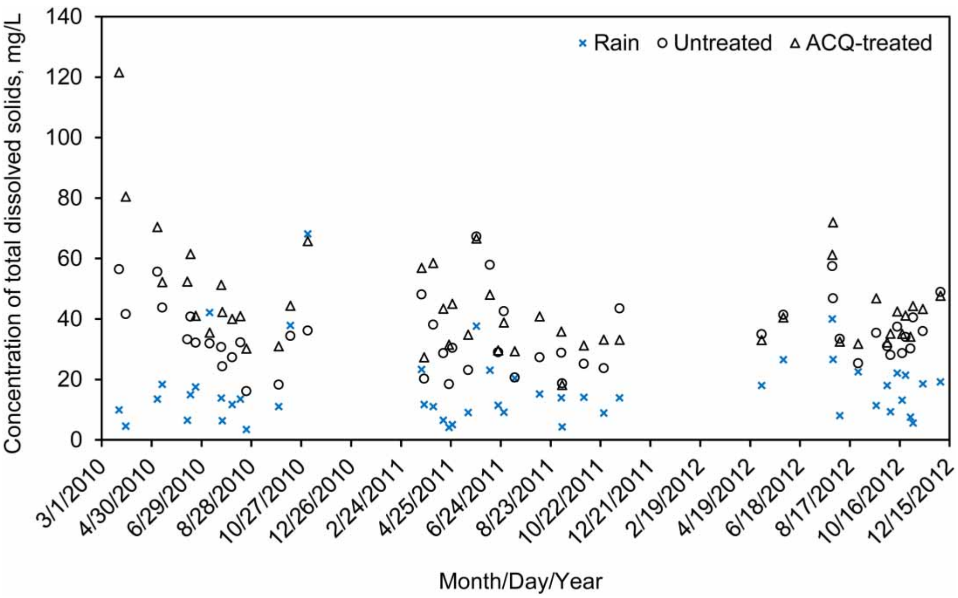

Figure 6 | Dynamics of total dissolved solids concentration in leachate from ACQ-treated and untreated red pine lumber piles.

stormwater associated with the timber products sector at 12 μg/L acid recoverable Cu, 120 mg/L COD, and pH 6–9 (NYSDEC 2012). Leachate from both the ACQ-treated and untreated lumber exceeded all of these cutoffs, indicating the necessity of on-site leachate treatment. In particular, substantial removal of Cu from the leachate generated in ACQ-treated lumber piles is needed for discharge-permit compliance. Based on the leachate volume measurements in all the 75 leachate-generating events and leachate Cu concentrations determined, it was estimated that leaching of ACQ-treated red pine lumber by rainfall generates 2.33 mg Cu per mm rain from 1 m^3 lumber in the first year and 1.02 mg Cu/mm/m^3 in subsequent years. Nevertheless, the New York State benchmark monitoring cutoff was lowered from 64 μg Cu/L in the preceding permit to 12 μg Cu/L in the current permit for years 2012–2017, which is often lower than Cu concentration in the local rainfall (Table 1). This raised a question about the appropriateness of the monitoring cutoff.

CONCLUSIONS

- Untreated red pine lumber could absorb more rain and produce less leachate as it is exposed to weathering over time. In contrast, leachate generation from ACQ-treated lumber is not affected by cumulative exposure time.
- The average Cu concentration in leachate from the ACQ-treated lumber was 4,033 μg/L in the first leaching season, being much higher than that in the leachate from the untreated lumber (87 μg/L) and rain (48 μg/L), and 336 times the benchmark monitoring cutoff (12 μg/L) for the timber products sector in New York State.
- Cu concentration in leachate from ACQ-treated lumber decreased by 49–54% after 1 year of field leaching. Moreover, Cu concentration decreased with increasing exposure time during each leaching season and was correlated to meteorological parameters.
- There were no significant temporal changes in leachate pH and concentrations of COD, TDS, and quat.

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