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Fate and Effects of the Triazinone Herbicide Metribuzin in Experimental Pond Mesocosms

J. F. Fairchild, L. C. Sappington

U.S. Geological Survey, Columbia Environmental Research Center, 4200 New Haven Rd., Columbia, Missouri 65201, USA

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Abstract. Metribuzin is a triazinone herbicide that is widely used for the control of grasses and broad-leaved weeds in soybeans, sugarcane, and numerous other crops. Metribuzin is highly toxic to freshwater macrophytes and algae under laboratory conditions (median plant EC_{50} = 31 μg/L; n = 11 species) but has not been studied under controlled outdoor conditions. We conducted a 6-week study to examine the aquatic fate and effects of metribuzin in 0.1-ha outdoor aquatic mesocosms. Mesocosms (n = 2 per treatment) were treated with metribuzin at one of five concentrations: 0, 9, 19, 38, or 75 μg/L. Concentrations were selected to bracket known laboratory effect concentrations and to reflect calculated edge-of-field concentrations. The dissipation half-life of metribuzin in water was 5 days. Metribuzin had no statistically significant effects on water quality, periphyton biomass, macrophyte biomass, macrophyte species composition, fish survival, or fish growth at treatment levels ranging up to and including 75 μg/L. Although metribuzin is highly toxic to freshwater macrophytes and algae under laboratory conditions, it poses little risk to nontarget aquatic plants due to the short aqueous dissipation half-life. The findings also demonstrate that current herbicide risk assessment procedures used in the registration process could benefit from empirical assessments of the fate of chemicals under realistic environmental conditions.

Metribuzin is a triazinone herbicide that is widely used in the United States and Canada for control of a variety of broadleaves and grasses. Soybeans account for the greatest total use of metribuzin; lesser amounts are applied in wheat, potatoes, and sugarcane (Pauli *et al.* 1990). Metribuzin ranked 17th on a list of herbicides applied to major field crops in the United States in 1995 when approximately 700,000 kg were applied to nearly 2.4 million ha of cropland (Anderson and Magelby 1997).

Metribuzin, like other triazine and triazinone herbicides, is prone to runoff into surface waters due to its physical and chemical characteristics: water solubility = 1,220 mg/L; K_{oc} = 41; vapor pressure < 1.3 mPa; and soil half-life = 30 days (Pauli *et al.* 1990; Wauchope *et al.* 1992). Modeling efforts have indicated that metribuzin can reach concentrations as high as 390 μg/L in surface water runoff (Pauli *et al.* 1990; US EPA 1998). However, actual measured environmental concentrations of metribuzin in water are typically less than 25 μg/L (Richards and Baker 1993; Battaglin *et al.* 2001). The discrepancies between predicted and measured environmental levels of metribuzin are difficult to interpret due to gaps in the environmental fate databases.

Metribuzin is relatively nontoxic to fish and invertebrates and exhibits toxicity values that exceed 10,000 μg/L (EC_{50}) (Mayer and Ellersieck 1986; Buhl *et al.* 1989; Ort *et al.* 1994). However, Fairchild *et al.* (1998) determined that metribuzin was extremely toxic to 10 species of nontarget algae and macrophytes at aqueous concentrations ranging from 14 to 152 μg/L; the median toxicity of metribuzin to aquatic plants was 31 μg/L (4-day to 14-day EC_{50}s). Furthermore, metribuzin was more toxic to aquatic plants than were atrazine, alachlor, or metolachlor.

The United States does not establish specific aquatic life criteria for pesticides such as metribuzin. However, Canada has established an Interim Water Quality Guideline of 2 μg/L metribuzin for protection of aquatic life that was calculated by dividing the response level of the most sensitive aquatic plant species by 10 (Pauli *et al.* 1990). This value may be extremely conservative because it is based upon a fraction of the response of the most sensitive species and does not account for anticipated environmental dissipation due to abiotic and biotic degradation processes that might mitigate the exposure of aquatic organisms to the chemical. Furthermore, this guideline may be difficult or impossible to achieve based on current desktop risk assessment approaches that are predicting edge-of-field exposures that greatly exceed the guideline (Pauli *et al.* 1990; US EPA 1998).

To date, there have been no published outdoor studies of the fate and effects of metribuzin to determine the actual environmental risk of metribuzin to nontarget aquatic species. The objective of this study was to examine the fate and effects of metribuzin in outdoor experimental aquatic mesocosms under realistic environmental conditions. We use these data to demonstrate the conservative nature of existing desktop risk assessments used in the United States and Canada. We further argue

Correspondence to: J. F. Fairchild; *email:* james_fairchild@usgs.gov

that empirical determination of the true aquatic fate of chemicals in the pesticide registration process is a major data gap that should be addressed.

Materials and Methods

A series of 10 0.1-ha mesocosms (maximum depth 2.0 m; volume 750 m^3) at the Columbia Environmental Research Center (Columbia, MO) were used in this study. The physical, chemical, and biological characteristics of these systems have been previously described in Fairchild *et al.* (1992, 1994). Ten mesocosms were randomly assigned to one of five metribuzin treatments (0, 9, 19, 38, or 75 μg/L; n = 2 replicates). Levels of metribuzin were chosen based on the single species laboratory assessments of Fairchild *et al.* (1998) that demonstrated that metribuzin decreased biomass of *Najas guadalupensis* (the dominant macrophyte in these test systems) at 19 μg/L (14-day EC_{50}). Thus, chosen treatment levels effectively bracketed the demonstrated laboratory toxicity response of the species.

Juvenile bluegill (*Lepomis macrochirus*) (3 cm length, mean weight 0.5 g) were obtained from Hartley Fish Farms (Lenexa, KS) on May 1. On May 2 fish were stocked into the mesocosms at a biomass of 0.45 g/m^3, which corresponded to a range of 600–750 fish per mesocosm depending on volume. At study termination (June 25) the ponds were drained, and all fish were collected, counted, measured (± 0.1 cm) and weighed (± 0.01 g).

Ponds were treated on May 22 with technical-grade metribuzin (4-amino-6-[1,1-dimethyl-ethyl]-3-[methylthio]-1,2,4-triazin-5[4H]-one; CAS 21087-64-9; 95% AI). Metribuzin was dissolved in acetone (posttreatment concentration of 0.01 ml acetone/L pond water). Metribuzin solutions were injected beneath the water surface at 0.5 m depth behind a motor-driven boat. Metribuzin was injected over a 10-min time interval followed by an additional 5-min mixing interval (15 min total mixing time).

Treatment concentrations were measured in each pond on day 0 from duplicate composite samples. Each composite was obtained by combining 12 randomly collected 1-L depth-integrated subsamples taken at 0.25 h posttreatment. Additional duplicate samples were taken in one high-treatment pond over an extended time series (*e.g.*, days 1, 2, 7, 14, 28, and 56) to determine the dissipation curve (*i.e.*, combined aqueous losses due to photolysis, hydrolysis, sorption, volatilization, and biodegradation) for the chemical. Water samples were analyzed according to EPA method #633 (US EPA 1982). The method had a detection limit of 0.46 μg/L. Analytical recovery of six 5.2-μg/L spiked samples averaged 98.2 ± 2.7%.

Temperature, pH, conductivity, and dissolved oxygen were measured hourly in each mesocosm using a fixed-station Hydrolab Surveyor Instrument (Hydrolab, Austin, TX). Chlorophyll *a*, ammonia, nitrate-nitrite, soluble reactive phosphorus, total nitrogen, and total phosphorus were measured weekly as previously described by Fairchild *et al.* (1992).

Periphyton samples were taken from glass microscope slides attached to Styrofoam floats anchored just beneath the water surface. Slides were incubated for 28 days posttreatment. Two slides were retrieved from each pond at 7-day intervals and extracted and analyzed for chlorophyll *a* as an indicator of periphyton biomass (expressed as μg chlorophyll *a*/cm^2).

Macrophytes were sampled on three dates: −7, 20, and 30 days posttreatment. A total of 10 samples were taken from each mesocosm along two parallel transects using a 0.1 m^2 stovepipe sampler. Macrophytes were isolated using the sampler and then removed using a rake. Samples were then washed on a 1-mm mesh screen using well water, spun in a mesh bag to remove water, and then weighed (± 0.1 g) to determine wet weight biomass. Percentage species composition (either *N. guadalupensis* or *Chara* sp.) was estimated by visual assessment based on the substantial morphological and color differences between the two species as described in Fairchild *et al.* (1994).

Data were analyzed using the Statistical Analysis System (SAS 2000). Percent data (*e.g.*, fish survival and percentage composition of macrophytes) were normalized using the arcsin square root transformation (Snedecor and Cochran 1969). Data were analyzed using two-way analysis of variance with the date and treatment as main effects. Differences were measured at the $p \leq 0.05$ level of significance.

Results

Metribuzin had no effects on periphyton biomass, macrophyte biomass, macrophyte species composition, fish survival, or fish growth at concentrations up to 75 μg/L in water. Grand means (± 1 SE) of water-quality variables across all times and treatments were as follows: temperature = 19 ± 4°C (n = 885); dissolved oxygen = 6.4 ± 5.3 mg/L (n = 885); pH = 8.1 ± 1.2 (n = 885); alkalinity = 83 ± 13 mg/L as $CaCO_3$ (n = 80); conductivity = 243 ± 77 μmhos (n = 885); turbidity = 4.2 ± 2.6 NTUs (n = 100); phytoplankton chlorophyll *a* = 6.3 ± 9.0 μg/L (n = 199); soluble reactive phosphorus = 19 ± 35 μg/L (n = 80); nitrate-nitrite = 5.5 ± 8.6 μg/L (n = 80); ammonia = 149 ± 110 μg/L (n = 80); total phosphorus = 31 ± 16 μg/L (n = 80); and total nitrogen = 508 ± 166 μg/L (n = 80).

Metribuzin concentrations in mesocosm water measured 15 min after chemical application averaged ± 10% of nominal target values (Figure 1). Time-zero treatment concentrations in the various treatments were 0, 10 ± 1, 23 ± 1, 37 ± 2, and 79 ± 7 μg/L (mean ± 1 SE; n = 2) in the control, 9, 19, 38, and 75 μg/L treatments, respectively. Metribuzin concentrations dissipated to near background levels in the mesocosms within 15 days posttreatment. The calculated half-life of dissipation of metribuzin in water was 5 days (Figure 1).

Metribuzin treatment had no effects on macrophyte biomass development (p = 0.104) or species composition (p = 0.270) (Table 1). Date, however, was a significant main effect as both macrophyte biomass (p = 0.001) and percentage composition of *Najas* (p = 0.036) significantly increased over time as observed in previous studies within these systems (Fairchild *et al.* 1994). There was no significant interaction between treatment and date (p = 0.676) and macrophyte composition and date (p = 0.824). Macrophyte biomass (range 34–55 g/sample) and dominant species composition (range 71–84% *Najas*) were similar across treatments prior to chemical application. Macrophyte biomass increased 140% from an average of 46 g/sample to 110 g/sample in the controls over the 6-week interval of the study. The proportion of *Najas* likewise increased in controls from an average of 84% (7 days pretreatment) to an average of 94% (30 days posttreatment). Percentage of the macroalgae *Chara* sp. declined over time from an average of 16% to 6% composition in control treatments. Thus, metribuzin had no significant effects on either macrophyte biomass or species composition over a range of 0–75 μg/L nominal treatment concentrations.

Periphyton biomass accrual increased from 0 to approximately 30 μg/cm^2 in the control mesocosms over the 28-day posttreatment monitoring period (Table 2). However, there were no significant treatment effects due to metribuzin (p = 0.825). Date, however, was a significant main effect (p =

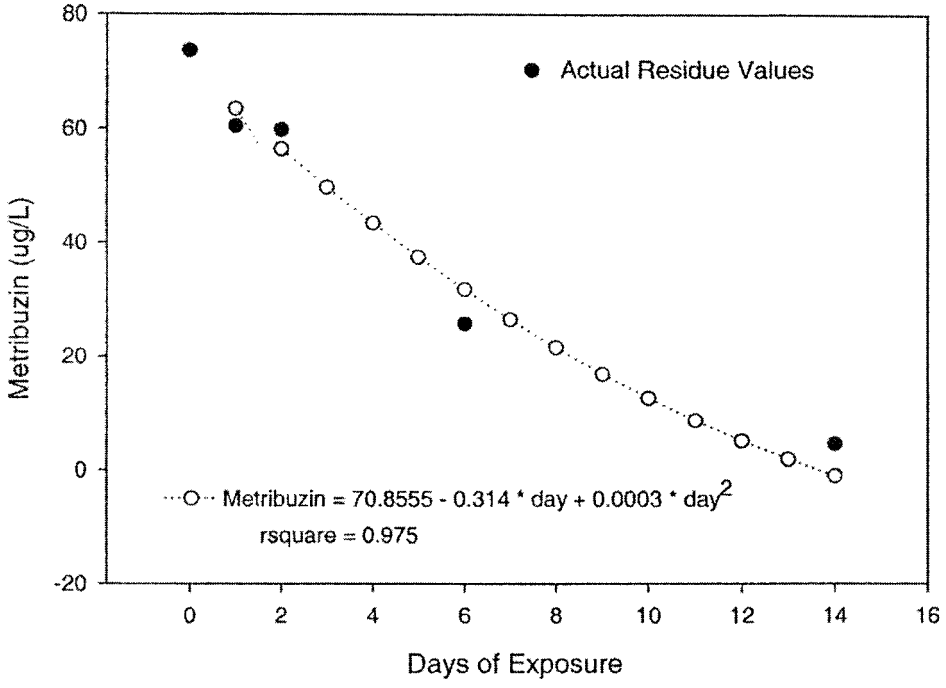

Fig. 1. Aquatic dissipation of metribuzin over time in experimental mesocosms. Dark circles represent actual measured values. Open circles indicate concentrations calculated for each date from the regression equation

Table 1. Comparison of macrophyte biomass and species composition in mesocosms treated with metribuzin

Days Posttreatment	Nominal Treatment (μg/L)	Macrophyte Biomass (g/m^2)	*Najas* Composition (%)	*Chara* Composition (%)
−7	0	46.4 ± 6.0	84.5 ± 3.5	15.5 ± 3.5
	9	54.6 ± 6.9	80.5 ± 0.5	19.5 ± 0.5
	19	34.3 ± 11.8	81.0 ± 6.0	19.0 ± 6.0
	38	39.9 ± 2.1	71.0 ± 6.0	29.0 ± 6.0
	75	45.8 ± 5.8	74.5 ± 2.5	25.5 ± 2.5
20	0	71.6 ± 6.5	89.6 ± 1.6	10.4 ± 1.6
	9	62.9 ± 10.5	80.2 ± 3.2	19.8 ± 3.2
	19	49.1 ± 2.2	77.0 ± 5.9	22.9 ± 5.9
	38	46.2 ± 4.8	66.0 ± 13.0	34.0 ± 13.0
	75	67.2 ± 6.0	86.6 ± 6.2	13.3 ± 4.4
30	0	109.9 ± 0.4	94.4 ± 0.6	5.5 ± 0.6
	9	121.8 ± 7.4	87.4 ± 9.4	12.6 ± 9.4
	19	86.6 ± 6.3	88.6 ± 2.6	11.4 ± 2.6
	38	108.1 ± 10.5	78.8 ± 5.7	21.2 ± 5.7
	75	117.1 ± 1.4	93.4 ± 0.4	6.5 ± 0.4

Days presented span the period before and after the May 22 treatment date. Numbers denote mean (± 1 SE) of n = 2 mesocosms. Each mesososm value was determined as a mean of 10 samples.

Table 2. Comparison of chlorophyll *a* (biomass) of periphyton on glass slides incubated in mesocosms treated with metribuzin

Days Posttreatment	Metribuzin (μg/L)	Chlorophyll *a* ($\mu g/cm^2$)
7	0	8 ± 0.9
	9	5.8 ± 0.7
	19	8.2 ± 4.7
	38	5.4 ± 1.7
	75	5.4 ± 3.4
14	0	16.2 ± 2.0
	9	9.7 ± 5.0
	19	41.4 ± 28.6
	38	8.7 ± 2.6
	75	10.9 ± 0.5
21	0	30.6 ± 6.4
	9	68.3 ± 55.9
	19	42.0 ± 25.0
	38	55.2 ± 6.3
	75	11.0 ± 1.9
28	0	28.0 ± 15.1
	9	78.4 ± 57.7
	19	53.2 ± 28.3
	38	71.0 ± 9.2
	75	36.8 ± 0.3

Days posttreatment represent the cumulative number of days slides were exposed following the May 22 treatment date. Numbers denote mean (± 1 SE) of n = 2 mesocosms. Each mesocosm value was determined as a mean of two slides.

0.001) as periphyton continued to increase throughout the study. Likewise, there was a significant metribuzin × date interaction ($p = 0.006$). This interaction, in the absence of a metribuzin main effect, complicates the interpretation of the data to some degree. However, the data indicate that date had a stronger effect on periphyton biomass than metribuzin. Periphyton biomass in the 75 μg/L treatment was lower than the control value on three of four dates and increased to a level higher than the control on the 28-days posttreatment date (Table 2). In contrast, periphyton biomass measured at intermediate levels of metribuzin exposure was frequently higher than control values. A comparison of least squared means between the control and 75 μg/L treatments on each posttreatment date (corrected for the date × metribuzin interaction within the Proc Mixed Procedure) showed no significant inter-treatment difference (range $p = 0.167$ to $p = 0.339$).

Metribuzin had no significant effects on fish survival or growth during the study (Table 3). Survival of fish ranged from 48–63% across treatments. No dead or stressed fish were observed during the study. Loss of fish was likely due to low morning dissolved oxygen levels (frequently 0 mg/L) measured within dense macrophyte beds during the latter part of the study. Such low dissolved oxygen levels are common in both experimental and natural systems due to the high nighttime respiration rates of macrophytes. In many cases bluegill can survive these conditions by finding refugia containing sufficient dissolved oxygen. Evidently, conditions were severe enough to cause some mortality in this study, but this was not related to metribuzin concentration. Bluegill grew rapidly in the study from an initial average size of 0.50 g/fish to approximately 10 g/fish over the 56-day study duration for an average growth rate of 0.17 g/fish/day. There were no growth trends in fish attributable to metribuzin.

Table 3. Bluegill survival and growth in mesocosms treated with metribuzin

Nominal Treatment (μg/L)	Survival (%)	Mean Length (cm)	Mean Weight (g)
0	48 ± 1	7.71 ± 0.12	10.02 ± 0.45
9	52 ± 5	7.88 ± 0.08	10.28 ± 0.73
19	56 ± 8	7.81 ± 0.23	10.20 ± 0.88
38	63 ± 1	7.94 ± 0.09	10.68 ± 0.60
75	61 ± 10	7.67 ± 0.03	9.60 ± 0.18

Bluegills were retrieved and measured 4 weeks following the May 22 treatment date. Numbers represent mean ± SE of n = 2 mesocosms. Each mesocosm value for lengths and weights were a mean of n = 100 fish.

Discussion

Fairchild *et al.* (1998) determined that metribuzin was toxic to *Najas* sp. in the laboratory at 19 μg/L (16–23 μg/L 95% CI; 14-day EC_{50}) and was toxic to eight other species of aquatic plants at concentrations below 44 μg/L. However, in the present study we observed no statistically significant direct effects (*e.g.*, changes in biomass or species composition) or indirect effects (*e.g.*, changes in survival or growth of juvenile bluegills) of metribuzin in outdoor aquatic mesocosms at concentrations up to 75 μg/L.

Metribuzin, a triazinone herbicide, disrupts the photosynthetic processes of a wide variety of plants due to inhibition of Photosystem II of the Hill Reaction (Pauli *et al.* 1990); therefore, it is anticipated to be toxic to nearly all species of plants. The lack of toxicity of metribuzin under field conditions was most likely due to the rapid dissipation rate of metribuzin (5-day half-life) that minimized exposure and effects to aquatic plants. Furthermore, both fish and invertebrates are insensitive to metribuzin at concentrations up to 7,100 μg/L (EC_{50} range 7, 100–100,000 μg/L metribuzin; Ort *et al.* 1994). Thus, we observed no direct or indirect food-chain responses in this study.

This is the first published evaluation of the fate of metribuzin under realistic outdoor exposure conditions. Existing literature is limited to controlled laboratory studies of photolysis and hydrolysis of the chemical (US EPA 1998). Metribuzin is stable to hydrolysis in sterile aqueous conditions at pH 5, 7, and 9; however, it undergoes rapid photolysis (half-life 4.3 h) under natural sunlight at pH 6.6 (US EPA 1998). Aquatic biodegradation studies have not been conducted; however, soil studies have indicated that biodegradation half-lives exceed 100 days under both aerobic and anaerobic conditions (US EPA 1998). Thus, photolysis is considered the primary degradation pathway for metribuzin and appears to be the major cause for rapid dissipation in our mesocosms.

The U.S. EPA (1998) modeled the fate of metribuzin under various use scenarios using the Generic Expected Environmental Concentration Program (GENEEC). The GENEEC program predicts the expected environmental concentration (EEC) in edge-of-field farm ponds based on assumptions of application rate, soil sorption, soil degradation, hydrolysis, and photolysis. The model predicted worst-case EECs of 390, 240, and 120 μg/L at days 0, 21, and 56, respectively, in ponds at the edges of sugarcane fields where metribuzin was aerially applied at 6.7 kg/ha concentrations. The GENEEC model predicted aquatic exposures of 24, 15, and 8 μg/L at days 0, 21, and 56, respectively, for ground-incorporated applications of metribuzin at 0.56 kg/ha. These modeled calculations were used to predict a risk quotient of 45 (*i.e.*, risk = EEC/EC_{50}) for the most sensitive diatom species under the cited worst-case sugarcane example (US EPA 1998). Our measured environmental dissipation data clearly indicates that the GENEEC model overestimates aquatic exposures to metribuzin at 21 and 56 days because of inadequate fate predictions. Our study, which evaluates the dissipation rate of metribuzin under realistic environmental conditions, indicates that the risk of metribuzin to aquatic plants is far less than that predicted from the GENEEC model.

This conclusion is supported by environmental data that indicates that aquatic concentrations of metribuzin are typically less than 5 μg/L and only rarely exceed the most sensitive plant EC_{50} value of 14 μg/L (*Ceratophyllum* sp.; Fairchild *et al.* 1998). Richards and Baker (1993) examined herbicide concentrations (3,802 total observations) in seven Lake Erie Basin tributaries in Ohio over an 8-year period from 1983–91. These tributaries and sampling stations were located in drainage basins ranging from 88–16,000 km^2 with land use ranging from 67–83% cropland. Metribuzin ranked 5th in total herbicide use in Ohio in 1986. The maximum concentrations of metribuzin observed in these seven tributaries ranged from 2–25 μg/L, whereas the 95th (0.37–1.83 μg/L) and 50th (0.00–0.01 μg/L) percentiles where dramatically lower. Battaglin *et al.* (2001) sampled 71 Midwestern streams for metribuzin (total of 134 stream samples) during peak runoff periods of May, June, and July. Metribuzin was detected in 66% of samples but never exceeded 2 μg/L during the study: maximum = 1.76 μg/L; 25th percentile ≤ 0.01 μg/L; 50th percentile = 0.02 μg/L; 75th percentile = 0.10 μg/L; and 95th percentile = 0.33 μg/L metribuzin (Battaglin *et al.* 2001). Thus, environmental concentrations rarely reach the level known to be toxic to even the most sensitive aquatic plant species and indicates that the true risk quotient for metribuzin and aquatic plants is far less than 1.

In summary, our data suggest that metribuzin poses rela-

tively little aquatic risk in natural environments. Although highly toxic to aquatic plants in the laboratory, metribuzin dissipates quite rapidly (half-life of 5 days) in aquatic environments. Thus, no direct effects on plants or indirect effects on fish were observed at concentrations up to 75 μg/L, which greatly exceeds measured environmental concentrations in streams and rivers of intensive agricultural areas of the Midwestern United States. Our data also demonstrate the value of conducting fate and exposure assessments in mesocosms under realistic environmental conditions. Currently, aquatic dissipation studies of herbicides are only requested on a case-by-case basis in the United States. This is questionable given the frequency of application and amounts of herbicides that are applied to the environment. Such data should be required in pesticide registration to provide a sound scientific dataset for conducting ecological risk assessments for chemicals. This need is dramatically illustrated in the case of metribuzin, where the proposed guideline for protection of aquatic life in Canada is 2 μg/L (Pauli *et al.* 1990). Our data indicate that this value is extremely conservative due to the rapid dissipation rate of the chemical in natural environments. Empirical determination of the fate of herbicides under realistic environmental conditions could greatly improve the accuracy of nontarget aquatic risk assessments.

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