

Herbicide Runoff along Highways.

1. Field Observations

XINJIANG HUANG, THERESA PEDERSEN,
MICHAEL FISCHER,
RICHARD WHITE, AND
THOMAS M. YOUNG*

*Department of Civil and Environmental Engineering,
University of California—Davis, One Shields Avenue,
Davis, California 95616*

Herbicides are widely applied along highways to control roadside vegetation, and surface water is frequently nearby. To determine whether herbicide runoff along highways threatens water quality, a field study was conducted at two sites in northern California for three rainy seasons. The herbicides oryzalin, isoxaben, diuron, glyphosate, and clopyralid were selected for study to include compounds with significant variation in physical/chemical properties. Concentrations of herbicides in runoff were monitored for up to 11 storms following herbicide application, and 24 samples were collected per storm, providing unprecedented temporal detail. Flow-weighted event mean concentrations were calculated for each herbicide in each storm and ranged from below detection limits to 43.13 $\mu\text{g/L}$ for oryzalin. The least soluble compounds, isoxaben and oryzalin, were detected in all storms monitored while the more soluble compounds, diuron and clopyralid, declined to levels below detection limits before monitoring was concluded. Very small amounts of glyphosate were mobilized, but its transformation product aminomethylphosphonic acid was detected at higher concentrations, in more storm events, and at greater depth in the soil profile. A first-order model successfully described the declining herbicide concentrations in spray zone soil and in surface runoff for all sites and herbicides. Fitted first-order coefficients were always higher for runoff than for soil, indicating that the herbicide that persists in the source zone becomes less available for runoff as the time since application increases. The percentage of the applied herbicide that was detected in surface runoff over a season ranged from 0.05% to 43.5%, and the most critical variables in controlling the variation were the solubility of the herbicide and the runoff volume. For a given herbicide and site, the most critical factors in determining seasonal herbicide loss to surface water were the timing and intensity of the first storm following application, affecting total seasonal runoff by up to 2 orders of magnitude. Minimizing runoff of herbicides along highways will thus require careful attention to the intrinsic mobility of the compound and the timing of its application.

Introduction

Highway-related environmental problems have been studied for nearly three decades (1–3). Highway contaminants

typically come from two sources: road materials and traffic. Contaminants from road materials result from the chemicals used for construction and maintenance (e.g., soil stabilizers, silicones, rubber, paints and glass beads, plastic tapes and reflectors, de-icing compounds, and herbicides) and from pavement wear (the breakdown of asphalt and/or concrete surfaces). Traffic-derived pollutants include brake linings, tire and steel parts attrition, leakage of oil and lubricants, catalytic converters, vehicle exhaust, and wear of bearings and bushings.

Highway contaminants are transported into the environment through runoff water and air, and the controlling processes have been widely investigated (3–10). Constituents that may be found at elevated levels in highway runoff and nearby air include cations/metals (Fe, Ni, Pt, Pd, Pb, Cu, Mg, Mn, Cr, Zn, Cd, Na, Ca, and Al), inorganic anions (Cl^- , HS^- , and CN^-), nutrients (N, P, and K), gases (NO_x , CO, and hydrocarbons), semivolatile and particle-phase organic compounds (e.g., polycyclic aromatic hydrocarbons), solids, bulk organics (e.g., oil and grease), biological material, and litter.

Although traffic-related environmental problems have been extensively studied, herbicides applied along roadsides have not been the focus of significant research. Herbicide application is used by many highway agencies to control vegetation growth along roadsides to improve visibility for drivers, reduce fire risk, and prevent physical damage to the road surface. This practice has been reported to be at least 40% more cost-effective than mowing or other alternatives (11). However, nonpoint sources of pollution such as highway runoff have emerged as one of the leading causes of the degradation of receiving water quality in the United States (12), and environmental regulatory agencies have consequently focused increased attention on them. Herbicide-contaminated runoff has been identified as an agent of toxicity in several studies (13–15), but the role of highway inputs as contributors to such events has not been explored.

Previous studies regarding herbicide runoff from agricultural operations are a valuable source of information in predicting runoff along highways and indicate that the concentration and mass load of herbicides in runoff are controlled by rainfall characteristics (intensity and duration), herbicide properties (solubility, octanol–water partition coefficient), soil conditions (texture, antecedent moisture, ground cover), site topography, crop practices and herbicide use patterns (application time, mode, and rate), and distance of transport (16). Herbicide concentrations in runoff typically decline with time after application either because the concentration in the source zone soil declines (17–19) (e.g., biotic or abiotic transformations, leaching during previous events, or infiltration to groundwater) or because the herbicide becomes less available (e.g., because of desorption rate limitations) (20, 21). The relative importance of these varied causes of the decline in runoff concentrations has not been the subject of systematic investigation in previous research.

The runoff potential of herbicides applied along highways may differ from those applied to agricultural plots because (i) the application zone is frequently a low organic carbon, coarse material such as gravel that would not be expected to retain herbicides as effectively as agricultural soils; (ii) many highway sites feature relatively steep slopes; and (iii) nearly all of the rain falling on the adjacent pavement becomes surface runoff.

This project was designed to determine (i) the concentrations and mass loads of herbicide leaving highway rights-

* Corresponding author phone: (530)754-9399; e-mail tyoun@ucdavis.edu.

TABLE 1. Sampling Site Characteristics

sampling site	width of road surface (m)	length of road surface (m)	road drainage area (m ²)	slope parallel to road	average slope width (m)	slope perpendicular to road	slope drainage area (m ²)
Tolay Creek site	10.37	140.82	1460.61	1.60°	5.76 ^a 3.61 ^b	4.08–6.16° ^a 3.23–10.66° ^b	811.11 ^a 508.35 ^b
Eel River site	13.87	104.44	1256.04	1.02°	9.23	1.5–21.5°	967.93

^a Vegetated slope 1. ^b Vegetated slope 2.

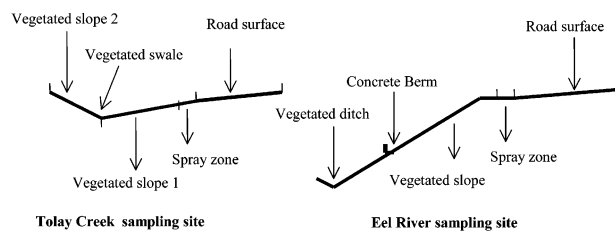


FIGURE 1. Sampling site cross sections.

of-way during the first storm events following application; (ii) the extent to which herbicide concentrations and mass loads attenuate with time following application; and (iii) the influence of rainfall and runoff characteristics, topography, and herbicide properties on initial and subsequent herbicide runoff. A companion paper (22) focuses on the role of sorption and desorption rates and equilibria in controlling this process. The data set presented here is unique in its detail: it spans 3 yr of application at two sites, considers five herbicides with widely differing properties, and features detailed temporal resolution. These features are critical to the ability to answer the research questions posed above.

Experimental Section

Site Descriptions. Two sites were selected for study to provide differences in slope, precipitation, and soil characteristics, each of which was viewed as potentially significant in controlling runoff water quality (Figure 1 and Table 1). The first site (Eel River) was a 104-m strip along the west side of U.S. highway 101 at the north end of the Eel River Bridge, Rio Dell, CA; U.S. 101 is a controlled access divided highway with two lanes in each direction. The sampling site has a slope that varies from approximately 1.5–21.5° perpendicular to the highway. An earthen drainage ditch at the base feeds into a culvert that discharges directly into the Eel River. The second site (Tolay Creek) selected for testing was a 141-m strip located on the north bank of California highway 37 in Sonoma County. The site slope (vegetated slope 1) is approximately 5° perpendicular to the highway with an earthen drainage ditch at the base. The ditch also receives flow from an adjacent property not subject to application of the target herbicides along vegetated slope 2; characteristics of this slope are also included in Table 1. A drainage channel at the west end of the sampling site directs the stormwater into Tolay Creek, a tidally influenced stream that discharges to San Pablo Bay. An automated sampling system collected all of the runoff leaving the herbicide application zone, the designated segment of the road surface, and the vegetated slope. Stormwater that had traveled down the embankment was conveyed to the monitoring point by either (i) a concrete berm built along the middle of the slope at the Eel River site or (ii) a vegetated ditch at the Tolay Creek site. At both sites vegetation cover was sparse in the spray zone because of the annual herbicide applications, but the roadside slopes were fully covered with grasses that were ~5 cm high at application and grew to ~20 cm during the monitoring season. Characteristics of the site soils are described in a companion paper (22).

Herbicide Application. Five herbicides with a range of physical/chemical properties were selected from among the 33 herbicides used by the California Department of Transportation (Caltrans) at the time the study was initiated. The properties of the five herbicides isoxaben (*N*-(3-(1-ethyl-1-methylpropyl)-5-isoxazolyl)-2,6-dimethoxybenzamide), oryzalin (4-(dipropylamino)-3,5-dinitrobenzenesulfonamide), glyphosate (*N*-phosphomethylglycine), clopyralid (3,6-dichloro-2-pyridinecarboxylic acid), and diuron (1,1-dimethyl-3-(3,4-dichlorophenyl)urea) are shown in Table 2 (23). Glyphosate and diuron are among the top 10 herbicides used in California, and nearly half of the diuron is used along highway rights-of-way. Caltrans personnel applied the herbicides to a 1.23 or 1.83 m wide strip along the highway shoulder using a truck sprayer. Application typically occurred after the first fall storm, and the application rates and dates are shown in Table S1 in Supporting Information. Exact application rates were determined by analyzing herbicides recovered from deposit collection plates (100 cm²) constructed of glass fiber sample pad (CEM Corporation, Matthews, NC) on corrugated cardboard that were located within the spray zone during herbicide application (24). Three sampling locations were selected within the spray zone (33-m intervals at the Eel River site and 45-m intervals at the Tolay Creek site), and three deposit collectors were placed at each location on the bare spray zone surface. Measured application rates were in close agreement with target application rates chosen by Caltrans (Table S1 in Supporting Information). Collection plates were also placed along the roadside slope outside the spray zone during the first two sampling seasons, but these collectors never contained detectable amounts of herbicide, and the practice was discontinued for the third field season.

Sampling. At the monitoring location runoff flow rates were determined using a flume (ISCO 0.75 feet H) and an automatic sampling station (ISCO 6700), which included a rain gauge (ISCO 674) and a bubbler flow module (ISCO 730), began taking samples when 0.01 mm of rain fell in 30 min and the flow level exceeded 3.0 mm. Each sampling event included up to 24 samples collected at intervals of between 20 and 120 min. Sampling times, rainfall volumes, and runoff flow rates were recorded by the automatic sampling system and were downloaded from the sampler to a laptop computer using an ISCO 581 rapid transfer device. Data were exported to a spreadsheet (Microsoft Excel) using ISCO Flowlink software. Upon completion of a sampling event, the automated samplers were reset, and clean sample bottles were installed. The first 6–11 major storm events following herbicide application were monitored. A composite soil sample was collected from the spray zone after every other storm event. All samples (deposit collectors, runoff water, and soil) were stored in coolers on dry ice during transport to the laboratory. Deposit collectors and soil samples were stored in a –20 °C freezer until analysis. Water samples were split into two parts: a 10-mL aliquot from each sample was frozen (–20 °C) until analysis for glyphosate, aminomethylphosphonic acid (AMPA), and clopyralid. The remainder of each water sample was stored at 4 °C (≤72 h) until the extraction of oryzalin, isoxaben, and diuron was completed.

TABLE 2. Herbicide Chemical and Physical Properties (23)

properties	oryzalin	isoxaben	diuron	clopyralid	glyphosate
molecular formula	C ₁₂ H ₁₈ N ₄ O ₆ S	C ₁₈ H ₂₄ N ₂ O ₄	C ₉ H ₁₀ Cl ₂ N ₂ O	C ₆ H ₃ Cl ₂ NO ₂	C ₃ H ₈ NO ₅ P
molecular weight	346.4	332.4	233.1	192.0	169.1
melting point (°C)	141–142	176–179	158–159	151–152	189.5
vapor pressure (mPa)	1.3 × 10 ⁻³	5.5 × 10 ⁻⁵	1.1 × 10 ⁻³	1.33	negligible
log(<i>K</i> _{ow})	3.73	2.60	2.85	-1.81 (pH 5)	-4.1
p <i>K</i> _a	9.4	nonionized	nonionized	2.3	2.3, 5.6, 10.9
biological activity	pre-emergence (germination)	pre-emergence (germination)	post-emergence (root)	post-emergence (leaves and root)	post-emergence (foliage)
water solubility (25 °C; mg/L)	2.6	1.42	42	143000	11600

Extraction. Deposit collection plates were extracted via sonication (60 min) with a methanol/water mixture (50/50 v/v) for isoxaben and oryzalin, acetone for diuron, deionized (Nanopure) water for clopyralid, and a 0.25 M NH₄OH and 0.1 M KH₂PO₄ aqueous solution for glyphosate. Extracts were then centrifuged for 30 min at 3500 rpm.

A 300-mL sample of runoff water containing oryzalin, isoxaben, and/or diuron was extracted using C₁₈ solid-phase extraction cartridges (SPE: Mega Bond Elut, Varian) pre-conditioned with acetonitrile, methanol, and Nanopure water. The cartridges were eluted with 5 mL of acetone, and extracts were concentrated under N₂ to dryness. The residues were dissolved in 1 mL of methanol for oryzalin and isoxaben or in 1 mL of acetone for diuron. Both glyphosate and clopyralid were analyzed directly from the runoff water samples (25).

Glyphosate and AMPA were extracted from homogenized soil samples (5 g) with a 20-mL aqueous solution containing 0.25 M NH₄OH and 0.1 M KH₂PO₄. Samples were sonicated for 60 min and centrifuged for 30 min at 3500 rpm. Oryzalin and isoxaben soil extractions from soil (10 g) involved refluxing with 20 mL of a methanol/water mixture (75/25 v/v) at a gentle boil for 90 min on a hot plate followed by centrifugation for 30 min at 3500 rpm. A 125-mL separatory funnel containing 1 mL of the supernatant, 10 mL of Nanopure water, and 2.5 mL of methylene chloride was shaken vigorously for (2 min) and allowed to separate, and the methylene chloride phase was collected. The extraction was repeated, and the combined methylene chloride was evaporated to dryness under N₂. The residues were dissolved in 1 mL of methanol for further analysis. Diuron extraction followed the same procedures except that an acetone/water mixture (75/25 v/v) was used for refluxing and 1 mL of acetone was used to dissolve the residues. Clopyralid was extracted from homogenized soil samples (10 g) with 20 mL of 0.005 M CaCl₂ solution in a 45-mL Teflon centrifuge tube. Samples were tumbled end-over-end for 24 h and centrifuged for 30 min at 3500 rpm.

Analysis. Glyphosate and AMPA were quantified using GC–MS analysis of derivatized samples (25). The derivatizing mixture (1.5 mL of heptafluorobutanol and trifluoroacetic anhydride; 1:2 v/v) was placed in an aluminum heating block and cooled to -60 °C with dry ice, 50 µL of sample was added, and the vial contents were mixed using the disposable tip of the transfer pipet. Vials were heated for 1 h at 92–97 °C in an identical heating block seated in a sand bath to complete the derivatization. After being cooled, the solutions were evaporated for 30 min past apparent dryness with N₂. Derivatized samples were brought to a volume of 500 µL with ethyl acetate containing 0.1% citral.

Glyphosate and AMPA were determined by GC–MS (model 6890 GC, 5973 mass selective detector, 7683 series automated injector; Hewlett-Packard Co., Wilmington, DE). Derivatized samples (2 µL) were separated using an Agilent DB-5 MS column (30 m × 0.25 mm, 0.25 µm film; J & W Scientific, Folsom, CA) with He carrier gas. The injection temperature was 270 °C, and the detector temperature was

250 °C. The initial oven temperature (90 °C held for 2 min) was ramped to a final temperature of 290 °C (30 °C/min) and held for 1 min. Selective ion monitoring mode was employed to quantify the glyphosate (*m/z* 611 and 584) and AMPA (*m/z* 446 and 372) derivatives.

Oryzalin, isoxaben, diuron, and clopyralid were analyzed using a high-performance liquid chromatograph (Hewlett-Packard 1100 series HPLC, Wilmington, DE) with diode array detector (HP G1315A) (26–28). Separation of analytes was performed using the following Phenomenex (Torrance, CA) reverse-phase columns: for diuron (Prodigy, 100 mm × 2.00 mm, 5 µm ODS (3) 100Å), for isoxaben and oryzalin (Luna, 250 mm × 3.00 mm, 5 µm C₁₈ (2)), and for clopyralid (Luna, 150 mm × 3.00 mm, 5 µm C₁₈ (2)). The initial mobile phase was acetonitrile/water (60/40 v/v) for isoxaben and oryzalin, water/acetonitrile (70/30 v/v) for diuron, and water/acetonitrile/acetic acid (91.5/5/3.5 v/v/v) for clopyralid. During the 30-min run (1 mL min⁻¹), the ratio of solvents was changed with a linear gradient to acetonitrile/water (90/10 v/v) for isoxaben, oryzalin, and diuron. Detection was accomplished at the maximum absorbance measured for each compound: diuron (252 nm), isoxaben (236 nm), oryzalin (236 nm), and clopyralid (285 nm).

Herbicide recoveries ranged from 80 to 105% during analytical method development. Matrix spikes were included in the analysis batch for each storm event, and recoveries from these samples were always similar to the results of the recovery study. All herbicide concentrations were therefore corrected using average recovery rates for each compound. All runoff water samples were filtered, solids recovered on the filters were extracted in the same manner as soil samples, and extracts were analyzed for herbicide content. Herbicide concentrations in the suspended solids were always below the method quantitation limit (MQL). Even if herbicide concentrations on the suspended solids had been equal to the MQL, suspended solid-bound herbicides would still have not been an important contributor to total herbicide loading. Herbicides in the suspended solids are thus not included in the reported runoff concentrations.

Results and Discussion

Overview of Herbicide Concentrations at the Field Sites.

Herbicide runoff was monitored for up to 11 storm events following herbicide application (~2 months). The Tolay Creek site was operated for three seasons: 1999–2000 (T1), 2000–2001 (T2), and 2001–2002 (T3); and the Eel River site was operated in the first two years (E1 and E2). Depending on the duration of the storm, up to 24 runoff samples were collected in each storm event. The mass of herbicide leaving the site with surface runoff, referred to as an event mean load (EML), was determined by summing the product of measured concentrations and flow volumes in each time interval over an entire event. An event mean concentration (EMC) was calculated as the EML divided by the total runoff volume. The variation in isoxaben concentration over time during a typical storm event at the Tolay Creek site is shown in Figure 2, and variation in isoxaben EMCs during season

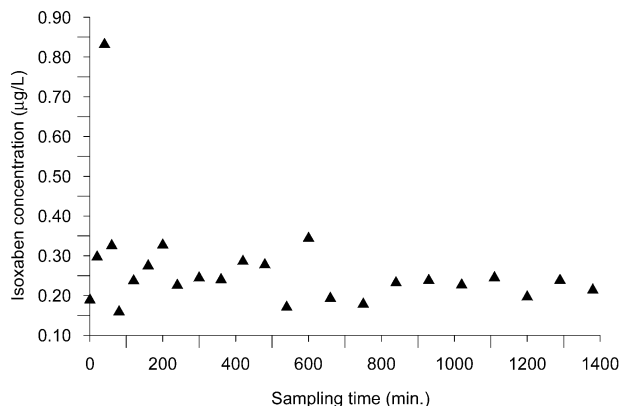


FIGURE 2. Isoxaben concentration change over time during a typical sampling event at the Tolay Creek site (1/27/2002).

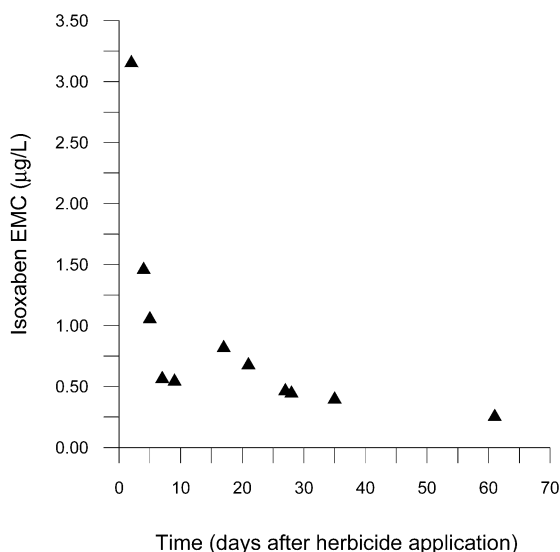


FIGURE 3. Variation of isoxaben event mean concentrations among sampling events at the Tolay Creek site during 2001–2002 (T3).

T3 are shown in Figure 3. Isoxaben concentrations were relatively constant within one sampling event, although they were often highest in the initial samples, while the EMCs decreased with time following application in an exponential manner.

A summary of herbicide runoff concentrations and the fraction of the applied mass leaving the site via surface runoff (load %) is presented in Table 3. The first storm was not sampled at either site during 1999–2000 because the flow and rainfall thresholds that initiate sampling were set too high. Diuron and clopyralid were below our MQL for the last 7 and 9 storms, respectively, during T3; and glyphosate was below the MQL for all but the first four events during E2. Table 3 includes a seasonal mean concentration ($\Sigma\text{EML}/\text{total seasonal runoff volume}$) and a range of EMC values (maximum–minimum) for each herbicide in each season. Some of the applied herbicides were found in runoff from all sampling seasons, and EMC values declined as the time and number of storms following application increased, similar to the pattern shown in Figure 3. Seasonal mean concentrations of a particular herbicide varied more between sites than they did across sampling seasons at the same site, even though application rates were nearly the same at the two sites (Table S1 in Supporting Information). Maximum EMC values occurred during the first sampling event except during 1999–2000 when the first events were missed and for glyphosate during 2000–2001. Significant differences were observed between sites and across herbicides in the per-

centage of applied herbicide leaving the site in surface runoff, with a range from 0.05 to 43.53%. Individual herbicides exhibited load percentages that varied by 2 orders of magnitude. The remainder of this paper is devoted to examining the factors responsible for the observed differences in concentration and loading.

Effect of Differences in Rainfall, Runoff, and Site Configuration. Herbicide runoff along highways is unique in several respects and differs significantly from an agricultural field where runoff and infiltration usually occur over a relatively homogeneous soil surface. In many highway situations, including the sites we studied, runoff occurs from the road surface, the application zone, and the adjacent vegetated slope. Nearly all of the rain falling on the impervious highway surface becomes surface runoff, and if berms are absent, this runoff can pass directly over the application zone (Figure 1) magnifying the herbicide leaching potential of a particular storm. For example, the two sites in our study had road surface areas 8–10 times larger than those of the respective spray zones. Sheet flow from the highway may thus serve as a major force for mobilizing herbicides from the spray zone. Another important difference between highway and agricultural sites is that runoff along highways often passes over relatively steep vegetated slopes while agricultural fields are more typically level and feature substantial amounts of exposed soil surface.

A hot, dry summer and rainy, cooler winter characterize the climate at the study sites. Rainfall and runoff quantities varied significantly between the two sites and across sampling seasons (Table S2 in Supporting Information). Runoff coefficients for each event were calculated by dividing the event runoff volume by the product of the rainfall amount and the total drainage area at the site (Table 1). The largest and smallest seasonal precipitation totals were recorded at the Tolay Creek site, while the Eel River site had more consistent rainfall. The highest runoff volumes were usually recorded during long storms such as the one that lasted from December 27, 2001, to January 2, 2002, at the Tolay Creek site. The large increase in the runoff coefficient at the Tolay Creek site each year was probably caused by different rainfall patterns. During sampling periods of nearly the same duration, the number of rainy days was 8, 15, and 28; and the total rainfall amounts were 43.9, 129.8, and 280.9 mm for seasons 1–3, respectively.

The average seasonal runoff coefficients (33–172%) from the Tolay Creek site were much higher than those (1.1–7.1%) from the Eel River site, a difference that can be explained by differences in site configuration and runoff collection design and by differences in timing of sampling events between the different monitoring years (Figure 1 and Table 1). Since the impervious portion of the drainage area will have runoff coefficients of approximately 100%, locations with higher ratios of road area to total drainage area will have higher runoff coefficients. Road surface covered 64.3% of the drainage area at the Tolay Creek site but was 56.5% of the area at the Eel River site. Runoff coefficients above 100% were routinely recorded at the Tolay Creek site and probably resulted from subsurface flow originating outside the drainage area and discharging to the ditch (Figure 1). A final factor contributing to the difference in runoff coefficients arose from the way water was directed to the sampling sites. At the Tolay Creek site, a natural vegetated swale at the bottom of the slope conveyed water to the sampling location while the runoff channel at the Eel River site was built on the surface at the middle of the slope. The Tolay Creek sampling site consequently received both overland flow and interflow or subsurface flow, but the concrete channel at the Eel River site would only catch overland flow. The relative timing of precipitation and runoff during a typical event supports the idea that subsurface flow was an important contributor to the collected runoff at the Tolay Creek site but not at the Eel

TABLE 3. Summary of Herbicide Mass Loading and Runoff Concentration

		Tolay Creek site			Eel River site	
		12/9/99–1/23/00 (T1) ^a	11/21/00–1/27/01 (T2) ^a	11/27/01–1/27/02 (T3) ^a	11/16/99–12/13/99 (E1) ^a	11/29/00–1/26/01 (E2) ^a
oryzalin	load (%)	0.05		5.43	0.05	0.50
	mean concn ^b	0.87		2.23	11.76	11.41
	(max–min)	(1.13–0.26)		(6.03–0.52)	(14.16–10.48)	(43.13–9.40)
	events >MQL	5		11	6	7
isoxaben	load (%)	0.26		15.02	0.12	1.32
	mean concn	1.23		0.85	6.81	3.82
	(max–min)	(1.60–0.42)		(3.15–0.25)	(9.09–5.76)	(14.43–2.85)
	events >MQL	5		11	6	7
diuron	load (%)		0.57	4.44		
	mean concn		1.34	0.82		
	(max–min)		(10.78–0.30)	(2.46–0.08)		
	events >MQL		8	4		
clopyralid	load (%)			43.53		
	mean concn			6.00		
	(max–min)			(7.11–3.03)		
	events >MQL			2		
glyphosate	load (%)	na ^c			na ^c	0.11
	mean concn	<0.1 ^d			<0.1 ^d	2.69
	(max–min)					(9.44–1.36)
	events >MQL					4

^a Sampling period is the first and the last sampling date. ^b Mean concn, mean concentration ($\mu\text{g/L}$) is the ratio of the total mass to total runoff volume for the entire season; max–min is the range of EMC ($\mu\text{g/L}$) values observed during the sampling season. ^c na, not available. ^d Glyphosate was detectable but did not occur at concentrations above the method quantitation level (MQL).

River site (Figure 4). At the Tolay Creek site, runoff typically continued well beyond the cessation of precipitation while at the Eel River site the runoff stopped even before the rainfall stopped. The time required for surface water to flow from the most remote point to the collection point at the Tolay Creek site should be less than 4 min, strongly suggesting that the runoff came from subsurface flow.

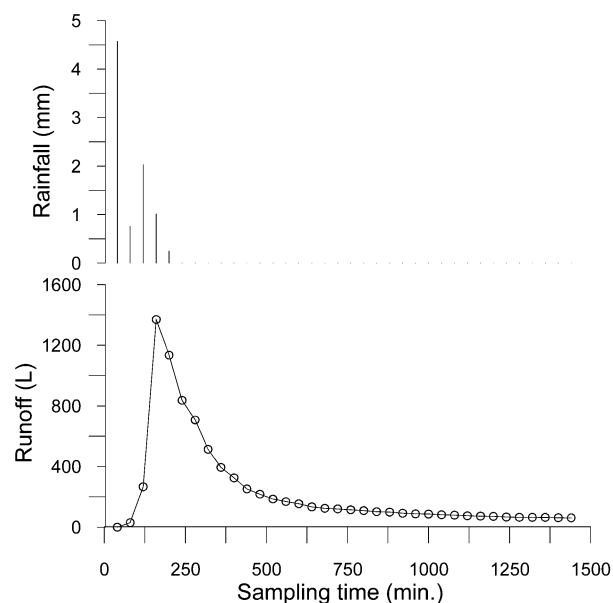
The diluting effects of flow from vegetated slope 2 and the subsurface flow are presumably the major reasons for the lower EMC values observed at the Tolay Creek site. Each of these sources is presumed to contribute little to the herbicide mass recovered at the sampling point: the former because there is no reason to expect that the selected herbicides would have been present, and the latter because of the more significant sorptive retardation that occurs during subsurface transport. Water moving down slope within the soil should be purged of most of the herbicide that it picked up in the spray zone. In contrast, overland flow should retain higher concentrations of surface-applied chemicals (29). Since the concrete berm at the Eel River site only caught the surface runoff and the runoff in the swale at the Tolay Creek site included both surface and subsurface flow, higher EMCs resulted at the Eel River site despite similar herbicide application rates.

Comparing Tables 3 and S2 in Supporting Information reveals that higher runoff volumes were correlated with higher mass loading of herbicide. At the Eel River site during 2000–2001 (E2), for example, the loading percentages for oryzalin and isoxaben carried by a total of 19 270 L runoff were approximately 10 times higher than those from the previous season carried by a runoff volume of 3150 L. Much higher loading percentages were also recorded at the Tolay Creek site during 2001–2002 (T3) accompanying a higher runoff volume than in 1999–2000 (T1). It is interesting to note that the loading percentages for isoxaben and oryzalin at both sites were nearly the same during the first year despite the large difference in runoff totals between the sites. For example, the runoff volume at the Tolay Creek site was nearly 9 times higher than that from the Eel River site, but this was offset by seasonal mean concentrations of isoxaben and oryzalin that were between 5 and 14 times lower.

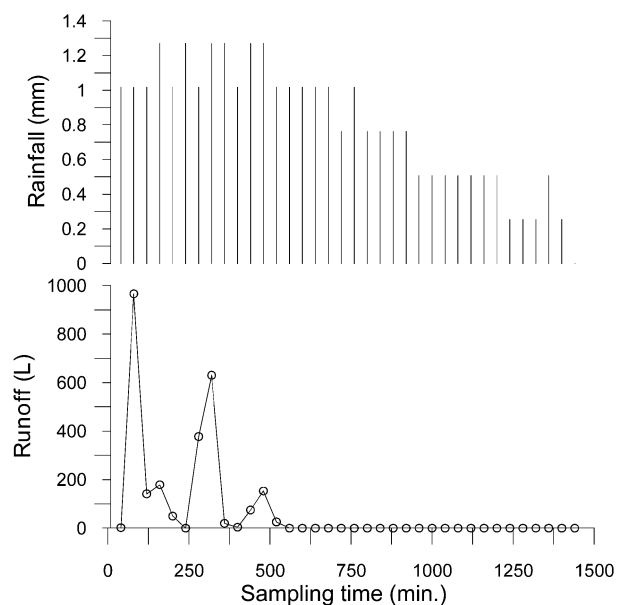
Cumulative Loading and Runoff Analysis. The concentration of herbicide in runoff is expected to decline over time as surface runoff, infiltration, and biotic/abiotic degradation deplete herbicide mass from the source zone and as the compounds become less available for desorption. Rapid, often exponential, declines in runoff concentration during a storm, referred to as a “first flush”, have been previously reported for a variety of contaminants in highway runoff (30–32). One way to visualize the extent of this decline is to plot the cumulative mass of herbicide released during a storm against the cumulative runoff that has passed over the site (17). Klaine et al. (17) found almost 90% of the atrazine was discharged during the first 65% of the runoff. Briggs et al. (33) reported that 70–100% of chlorpyrifos, thiophanate-methyl, and trifluralin losses happened in the first 20–40% of total runoff.

The high temporal resolution of our herbicide runoff data within each storm allows the presence of a first flush to be precisely tested. Plots of cumulative mass load as a function of cumulative runoff for each storm event are all nearly identical, with slopes of approximately unity. Consequently, all data for a given herbicide, site, and season can be displayed on one graph (Figure S1 in Supporting Information). For example, Figure S1 (in Supporting Information; T1, oryzalin) summarizes oryzalin runoff results for six storm events at the Tolay Creek site during 1999–2000. Most of the data points are distributed near the unity line, which indicates that herbicide losses were approximately proportional to flow throughout each runoff event. A first flush effect was not apparent. Although herbicide concentrations at the beginning of an event were often higher than at the end (e.g., Figure 2), the higher concentrations were limited to a short period and stabilized for the duration of the event. The relatively constant loading–runoff relationship indicates that the herbicide source did not change significantly during each storm event and suggests the importance of sorption processes in determining the herbicide mobilization. This topic is explored in more detail in a companion paper (22).

The preceding discussion focused on temporal trends in herbicide mass loading within a single event. The same approach was used to evaluate the proportionality of mass



(a)



(b)

FIGURE 4. Comparison of typical rainfall and runoff from the two sampling sites. (a) Tolay Creek site during January 26–27, 2002, and (b) Eel River site during January 10–11, 2001.

loading and cumulative runoff over an entire sampling season (Figure 5). A slope of unity on such a plot indicates that each liter of runoff carries approximately the same herbicide mass over the entire season while initial slopes significantly above unity indicate that mass losses are more pronounced in early season storm events. Two types of curve were observed: data points above the unity line (2000–2002 seasons) and slope near unity (1999–2000 season). When the slope for a given herbicide in a particular year is above unity, losses were most significant during early storm events, with a range of 54.6–78.2% of isoxaben, oryzalin, diuron, clopyralid, and glyphosate being discharged during first 40% of the runoff during the latter two seasons (Table 4). However, when slopes are nearly unity, 40% or less of the mass losses occurred in the

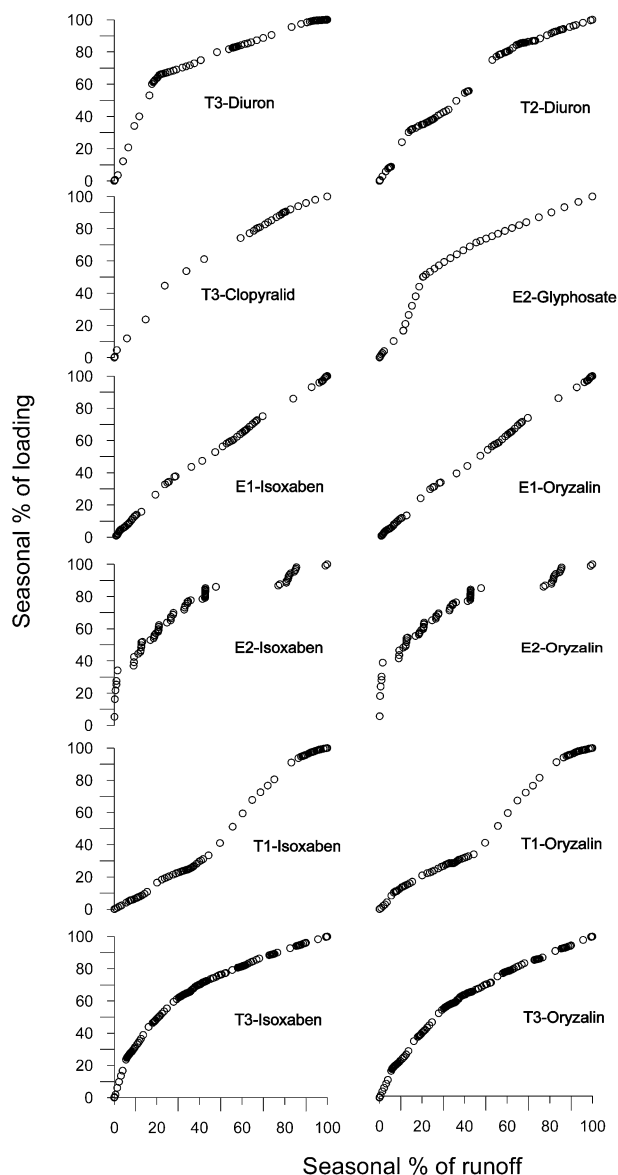


FIGURE 5. Percentage of the total seasonal herbicide mass leaving the field sites in a particular cumulative percentage of total runoff volume.

TABLE 4. Percentages of Seasonal Herbicide Mass Loads Leaving the Site in the First 40% of Total Runoff

	Tolay Creek site			Eel River site	
	1999–2000	2000–2001	2001–2002	1999–2000	2000–2001
oryzalin	32.0		63.9	43.1	77.0
isoxaben	29.8		70.2	46.6	78.2
diuron		54.6	74.5		
clopyralid			59.3		
glyphosate					64.6

first 40% of total runoff, presumably because the first storm event of 1999–2000 was not sampled.

To demonstrate the sensitivity of the mass loading pattern to missing an initial storm, the 2000–2002 data were reanalyzed after omitting the data from the first event. In all cases the revised analysis shows a significant decrease in the fraction of the total load discharged in the remaining early events. For the Eel River site, for example, less than 50% (dropping from over 70%) of the isoxaben and oryzalin were

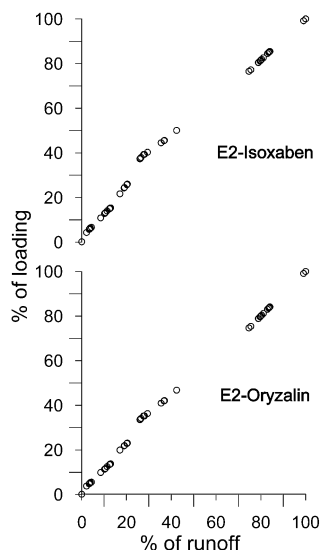


FIGURE 6. Cumulative herbicide loading plotted as a function of cumulative runoff. Data in this figure are re-graphed from Figure 5 (E2, isoxaben; E2, oryzalin) assuming that the first event was missed.

discharged during the first 40% of the runoff, a nearly identical pattern to that observed in 1999–2000 (Figure 6).

It is important to note that the herbicide loading is a function of herbicide concentration and runoff flow rate and therefore is not confined to the first storm, especially if the runoff volume of that storm is small (34). For example, although the EMC of the first event at the Tolay Creek site during 2000–2001 was much higher than during the rest of the season, the runoff volume was only 45 L, accounting for about 0.02% of the total seasonal runoff. For this case, the percentage of the total herbicide mass load leaving the site in the first 40% of cumulative runoff decreases from 54.65% to 54.61% if the first event is not considered.

The critical role of the first few storms in mobilizing herbicide makes the timing and size of these storms the single most important determinant of the total seasonal mass loss of herbicide to surface water. The first storm of 2001–2002 at the Tolay Creek site provides nearly a worst-case example of herbicide mobilization. The storm started within 24 h of herbicide application, was relatively large (34.29 mm), and generated 99 445 L of runoff. Almost 3% of the applied diuron was measured in runoff from this event, accounting for 65% of the total seasonal mass loading, and exceeded by nearly 6 times the mass lost during the entire T2 season. The importance of large runoff events occurring shortly after herbicide application in establishing off-site transport risk has been widely reported previously (17, 35–38).

Effect of Herbicide Properties. One goal of the experimental design was to study herbicides with physical and chemical characteristics representative of all herbicides currently used by Caltrans so that the findings could be extended to herbicides that were not tested. As expected, mobility generally increased with herbicide solubility and decreased with increasing octanol–water partition coefficient (Tables 2 and 3). The one exception to this trend is glyphosate for reasons that are discussed below and in a companion paper (22).

To illustrate the effect of physical and chemical properties in controlling mobilization, the herbicide mass reaching the sampling site (as a percentage of the applied mass) is plotted against the cumulative runoff volume for the first storm event at the Tolay Creek site in 2001–2002 (Figure 7). The mass loading increased proportionally with runoff for all four herbicides but at very different rates. Nearly 40% of the

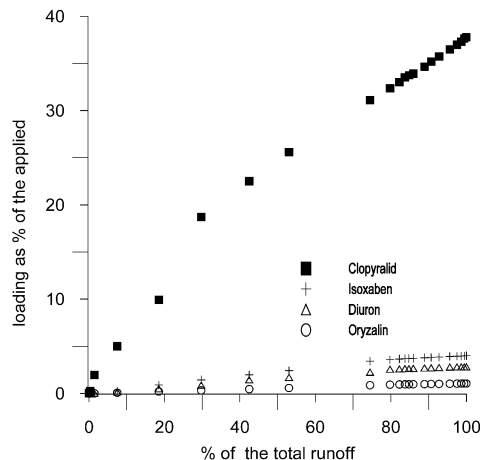


FIGURE 7. Herbicide loading as a percentage of the applied mass vs runoff from the first sampling event at the Tolay Creek site during 2001–2002 (T3).

applied clopyralid was transported to the sampling site in the first storm, while less than 4% of the other three herbicides was mobilized during the same storm. The percentage of the applied clopyralid transported in a single event was almost three times higher than the total percentage transported for any of the other herbicides for the whole season (Table 3). Clopyralid was not applied during the other two monitoring seasons at either site so its mobility under less extreme initial storm conditions is unknown. Clopyralid has a solubility of 143 000 mg/L while the other three herbicides applied at the same time (isoxaben, oryzalin, and diuron) have solubilities of 42 mg/L or less, which is the primary factor controlling the differential mobility of clopyralid. The magnitude of the difference in mass loads between clopyralid and the other three herbicides was also significantly higher than differences caused by site- and weather-related factors such as topography and rainfall. No previous reports related to surface runoff of clopyralid were identified in a literature survey. For the less polar and less soluble of the herbicides tested (isoxaben and oryzalin), the differences in the total percentage of the applied mass reaching the sampling site was better explained by K_{ow} than by aqueous solubility. Isoxaben loading percentages were always nearly two times higher than those for oryzalin at the same site and same season no matter how different were other factors such as application rates, rainfall, and runoff characteristics (Table 3).

The persistence of herbicide in spray zone soil following an initial storm event was hypothesized to be a key factor controlling the decline in herbicide runoff concentrations. Since the main loss processes for herbicides are solubilization (washoff) and degradation (abiotic or biotic), the natural independent variables for such an analysis are rainfall/runoff volume (39) or time since application (40), respectively. Substantial covariance among these parameters makes an unambiguous selection impossible, however. For example, models of the exponential decline in runoff EMC for oryzalin and isoxaben (T3) could be successfully described ($R^2 > 0.75$) using any one of the three independent variables (cumulative rainfall, cumulative runoff, or elapsed time). Time since application provided the best fit for all of the runoff EMC and spray zone soil dissipation for all herbicides, study sites, and seasons where sufficient data were available; this approach is used in all subsequent analysis. Representative data and the fitted exponential decay functions are shown in Figure 8, and the corresponding fitting parameters are summarized in Table 5. This analysis was not performed for data from 1999 to 2000 because the first event was missed at both sites. Also, clopyralid, diuron, and glyphosate were detectable only in the early storms, so insufficient EMC data

TABLE 5. First-Order Dissipation Coefficients (k), Pre-exponential Factors (a), and Fitting Criteria (R^2) Estimated from Runoff Event Mean Concentration and Herbicide Concentrations in Soil^a

season	medium	oryzalin			isoxaben			diuron		
		a ($\mu\text{g/L}$ or $\mu\text{g/kg}$)	k (d^{-1})	R^2	a ($\mu\text{g/L}$ or $\mu\text{g/kg}$)	k (d^{-1})	R^2	a ($\mu\text{g/L}$ or $\mu\text{g/kg}$)	k (d^{-1})	R^2
Tolay Creek Site										
2001–2002	runoff	4.6	0.038	0.91	1.8	0.039	0.80			
2000–2001	soil	4997.5	0.017	0.98	635.8	0.030	0.98	513.3	0.020	0.93
	runoff							8.6	0.038	0.79
	soil							5339.6	0.023	0.98
Eel River Site										
2000–2001	runoff	39.6	0.019	0.76	14.8	0.022	0.81			
	soil	6007.8	0.007	1.00	1045.3	0.005	0.92			
^a $y = ae^{-kt}$.										

$$^a y = ae^{-kt}$$

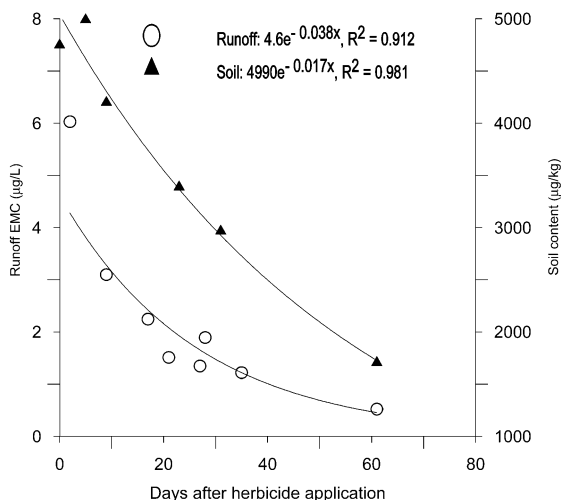


FIGURE 8. First-order equation fitting for runoff event mean concentration and soil dissipation of oryzalin at the Tolay Creek site during 2001–2002 (T3).

were available for the exponential fit to be meaningful for these compounds.

The first-order equation produced good fits for soil herbicide dissipation and runoff EMC changes in seven cases ($R^2 > 0.90$), while more scatter was observed around the regression line in the other four cases ($R^2 > 0.75$). In all cases the best-fit value of the first-order rate coefficient for runoff concentration was higher than that for soil dissipation. Lennartz et al. (40) had previously reported that first-order loss coefficients for diuron and simazine concentrations in runoff were twice as large as the corresponding soil decay coefficients. One possible explanation for this phenomenon is that the herbicide in the spray zone soil becomes more resistant to desorption with increasing contact time (21) causing runoff concentrations to decline faster than soil concentrations. Another possible reason is that the herbicide in the spray zone soil may become less available to be extracted by rainwater with increasing depth below the surface (20). These explanations are tested further in a companion paper (22).

The successful application of the first-order model to describe soil dissipation of three herbicides at two field sites in this study is consistent with previous findings. Dissipation of dicamba, nicosulfuron, and rimsulfuron in surface soil followed a first-order model (41, 42). Laboratory monitoring demonstrated that a first-order model provided the best description of data on the degradation of pesticides in soils (43–46). Dissipation of atrazine was well-described by a first-order model, and alachlor behavior in the soil could be described by first-order dissipation for the 2 months following

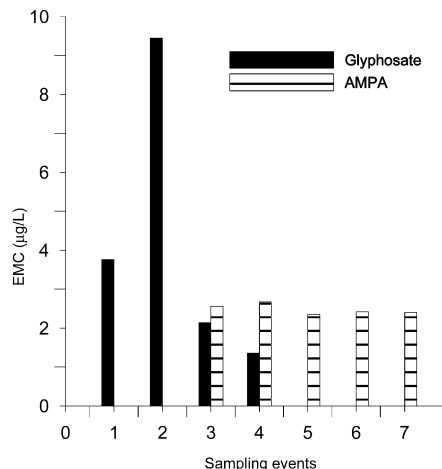


FIGURE 9. Event mean concentrations for glyphosate and AMPA at the Eel River site during 2000–2001 (E2).

application and zero-order dissipation after (47). In contrast, several investigators (48, 49) have suggested that a dual exponential model provides a superior description of agrochemical dissipation in some soils. It is possible that the success of the single-exponential model in our case resulted from the somewhat shorter (<2.5 month) data record as compared with some previous studies.

Tracking the fate of parent compounds is only one portion of understanding herbicide fate and transport. Products of abiotic or biotic degradation of herbicides may have substantially different properties than the parent material, and thus their fate and transport may differ considerably. One example of this is provided by our results for AMPA, a major degradation product of glyphosate (50). The off-site migration of glyphosate was limited despite its high aqueous solubility. This herbicide was above our method detection limit but below our MQL in runoff during 1999–2000 even though glyphosate application rates were close to those for isoxaben and oryzalin (Table S1 in Supporting Information), which have far lower solubility. A higher glyphosate application rate was implemented for 2000–2001 at the Eel River sampling site to improve the ability to detect the compound in runoff, and the EMC results for glyphosate and AMPA are shown in Figure 9. Glyphosate was so readily transformed to AMPA that only AMPA was found above the method detection limit during the last three storm events.

The factors governing herbicide infiltration are similar to those controlling runoff so that mobile species such as AMPA are expected to infiltrate more readily than more strongly sorbing compounds. To demonstrate this effect, soil core samples were collected at the end of the 2000–2001 season from the spray zone at the Eel River site and herbicide

concentrations were determined. Isoxaben and oryzalin were above the detection limit only in the top soil layer (0–12 cm), glyphosate was found in the 25–36 cm layer, and AMPA was detectable at depths of 37–50 cm (Figure S2 in Supporting Information). Herbicide transformation needs to be carefully considered when designing a monitoring program because the largest mobility and greatest toxicity may be associated with degradation products (51–53).

The field monitoring results reported here clearly indicate that as leaching and time proceed, herbicides in application zone soil decline and the residual material becomes less available to runoff. The exponential decrease in event mean concentrations is closely tied to these phenomena; desorption rate limitations and movement to deeper soil layers may each explain these findings. A companion paper (22) explores the role of sorption processes in the mechanistic control of herbicide runoff concentrations.

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Supporting Information Available

Tables giving herbicide application rates and rainfall and runoff comparison at the two sampling sites and figures showing event first-flush analysis and vertical distribution of glyphosate and AMPA content within soil. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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